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EFFECTS AND METHODS OF CONTROL OF THERMAL DISCHARGES

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REPORT TO THE CONGRESS BY THE
ENVIRONMENTAL PROTECTION AGENCY IN
ACCORDANCE WITH SECTION 104(t) OF THE
FEDERAL WATER POLLUTION CONTROL
ACT AMENDMENTS OF 1972

PART 2

IMPACT OF THERMAL DISCHARGES ON AIR QUALITY
EFFECTS OF THERMAL DISCHARGES ON LAND USES
METHODS OF CONTROL OF THERMAL DISCHARGES
TEMPERATURE DISTRIBUTION ANALYSIS
THERMAL ASPECTS OF AQUATIC CHEMISTRY

NOVEMBER 1973

SERIAL NO. 93–14

Printed for the use of the Senate Committee on Public Works

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CONTENTS

	Page
Impact of Thermal Discharges on Air Quality	570A
Effects of Thermal Discharges on Land Uses	615
Methods of Control of Thermal Discharges	639
Temperature Distribution Analysis	769
Thermal Aspects of Aquatic Chemistry	847

LETTER OF TRANSMITTAL

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY,
Washington, D.C., July 13, 1973.

Honorable SPIRO T. AGNEW,
President of the Senate,
Washington, D.C.

DEAR MR. PRESIDENT: The Environmental Protection Agency is pleased to provide you with the enclosed thermal discharge report, which we have prepared in accordance with Section 104(t) of the Federal Water Pollution Control Act Amendments of 1972.

The report contains 10 volumes. These include a summary and 9 individual reports on various aspects of thermal pollution, specifically: control and abatement, beneficial uses, thermal behavior of freshwater and marine biota and ecosystems, impact on water and air quality of heated discharges, relationships between temperature and aquatic chemistry, and the problems of temperature and its possible interactions with toxi-chemicals in the aquatic environment.

An 11th volume dealing with the problems of land use associated with thermal discharges is not included in this report. It is essentially complete and will be transmitted to the Congress shortly.

Sincerely yours,

ROBERT W. FRI,
Acting Administrator.

[Enclosure.]

Impact of Thermal Discharges on Air Quality

Contents

		Page
I.	Introduction	1
II.	Small Scale Effects	2
	A. Cooling Towers	3
	1. Mechanical Draft Towers	5
	2. Natural Draft Towers	7
	3. Dry Cooling Towers	17
	B. Cooling Ponds and Lakes	18
III.	Urban Scale	23
IV.	Regional Scale	27
V.	Global Scale	30
VI.	References	33

IMPACT OF THERMAL DISCHARGES ON AIR QUALITY

BY

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NATIONAL ENVIRONMENTAL RESEARCH CENTER
ENVIRONMENTAL PROTECTION AGENCY

*On assignment from the National Oceanic and Atmospheric Administration, U.S. Department of Commerce.

I. Introduction

Production or use of energy is involved in practically all man's activities, including electrical generation, home heating, transportation, industrial processes, etc. The heat produced as a result of this activity is eventually transferred to the oceans and atmosphere where, in sufficient quantity, it can alter natural weather and climate processes. This chapter will discuss the impact of these thermal and related moisture discharges on air quality. It is restricted to atmospheric effects and such related topics as the synergistic interactions between heat emissions and atmospheric pollutants are not covered herein. Information on many of the topics discussed in this section is expanding rapidly, mainly in response to environmental impact statements. Many technical reports have been prepared by private research groups, and several have been included in the references.

The intensity of heat emissions is strongly related to the area over which they occur. On the smallest scale the most significant heat and moisture releases result from electrical power generation. Various methods have been used to "dispose" of the large amount of waste heat generated during the production of power. First, by the once-through cooling method, water is directly returned to its source, such as a river or lake. Second, wet cooling towers, either mechanical or natural draft, cool water for recirculation back to the plant; however, vast quantities of heat and

moisture are emitted from the towers during the cooling process. Third, cooling ponds, which disperse the heated water over a large area and dilute emissions to the atmosphere, also allow the cooled water to be recirculated. Fourth, by dry cooling towers heat is exchanged by conduction and the cooling water is contained in a closed system. Such towers are not used widely in the United States because of their expense.

The next larger horizontal scale where thermal emissions are significant relative to natural (solar) energy processes is the urban scale. Over large metropolitan areas, man's use of energy and subsequent release of heat during winter months even exceeds that absorbed from sunlight. The resulting warmer urban atmosphere in turn affects other meteorological elements.

The impact of waste heat on a regional scale may become climatically important in the near future. As urban areas expand and merge, thermal emissions may reach several percent of the natural energy received over areas of hundreds of thousands of square kilometers. The subsequent effect on weather patterns is being studied by several institutions. On a global scale, current heat emissions are insignificant in comparison to absorbed solar radiation. However, if current energy growth rates continue, global climatic effects could result in about 100 years.

II. Small Scale Effects

Man has concentrated his liberation of heat over certain rather

small areas of the earth. This energy concentration occurs mainly in conjunction with the generation of electrical power and the thermal inefficiencies associated with that generation. For example, fossil fuel electric power plants being built today are about 40% efficient; i.e., 40% of the heat from burning fuel is converted to electricity. Another 15% is directly lost through the chimney to the atmosphere whereas the remaining 45% is transferred to cooling water and subsequently to the atmosphere by waterways, cooling towers, ponds, or lakes (72). Nuclear facilities are even less efficient than fossil units, but advanced reactors now being developed are expected to have efficiencies similar to those of modern fossil fuel plants. Cooling towers, especially the large natural draft units liberate vast quantities of heat and moisture into the atmosphere. Alternate means for distributing waste heat include cooling ponds and lakes which release waste heat more slowly and over a larger area than do cooling towers. The atmospheric consequences of these various small scale energy emissions will be discussed in this section.

A. Cooling Towers

Besides once-through cooling, waste heat may be disposed of by cooling towers of three main varieties: mechanical and natural draft wet types and dry types. The first two kinds rely mainly on evaporation for heat transfer and consequently emit both heat and moisture into the atmosphere. The third type relies solely on conductive heat transfer and thus emits only heat. Dry towers

currently are used in Europe and other countries, but have not been introduced widely in the U.S.A.

Hewson (4) has recently itemized the possible meteorological problems that may result from water vapor and heat releases from cooling towers and ponds. However, he states that further research is necessary before the magnitude of the effects listed below can be determined. Fogs formed from moisture condensation may drift downwind and affect visibility. As the height of the tower increases, the probability of ground-level visibility reductions decreases. Moisture from tower plumes may fall out as precipitation. Wetting or icing of the surface may occur from moisture precipitated from a plume. Incident solar radiation will be decreased with any increase in fog or clouds. Air temperature will be affected by direct heat emissions or by local energy changes resulting from interaction between clouds and fog and radiation. If air temperature is altered for several days because of fogging, wind speed may be affected. Pollutants in the atmosphere provide added condensation nuclei and thereby increase the density and persistence of fog. Uneven terrain may cause additional problems. For instance, the plume from cooling towers in valleys can strike the valley sides and cause fogging when none would exist in flat terrain.

One of the problems encountered in cooling tower design is that of drift, or the flow of water droplets out of the tower. Without the use of drift eliminators, which now efficiently limit

drift to less than 0.01% of the circulating water volume, significant mist or drizzle can occur immediately downwind of a tower (31, 33). It has been generally assumed in the following discussion that drift eliminators are standard wet cooling tower equipment.

1. Mechanical Draft Towers

Wet cooling units, in which the air flow is caused by mechanically driven fans, are used extensively by many sectors of industry. Smaller units commonly are situated singly on building roofs and typically serve central air conditioning systems. The larger units--those of most environmental concern--can be designed to serve 1000 megawatt electric generating facilities. As such they are constructed in multiple-unit banks. A typical size for seven units is approximately 60 feet high, 75 feet wide at the top and 55 feet at the base, and 325 feet long. A 28-foot fan provides the air flow through each unit (1). The power industry has recently constructed more natural draft than mechanical draft towers at its large generating sites.

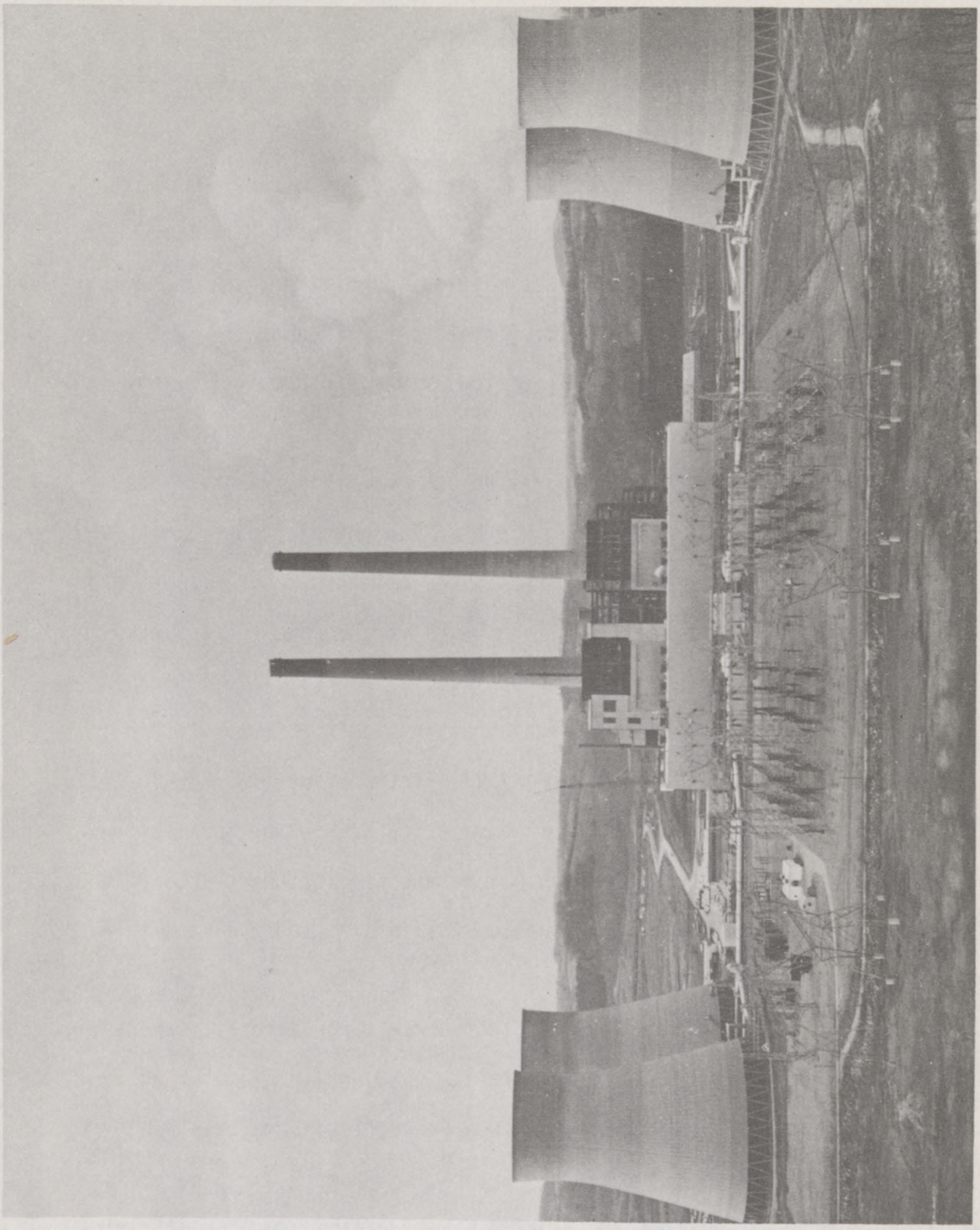
The most common environmental effect of mechanical units is an increase in the frequency of occurrence and the amount of fog in the vicinity of the towers (2). When the atmosphere is relatively humid, calm and cooler than the tower emissions, fog or icing results. In contrast, tower emissions into a dry, warm and windy atmosphere generally will not cause local fog (3). Because the effluent is emitted at a relatively low height, the moisture

plumes occasionally diffuse to ground level where practical problems can result, for example, when towers are located near busy highways (8, 9). When the ambient temperature is below freezing, ice may form on objects upon which the water droplets impinge. Light snowfall has been reported on at least two occasions (65, 66). During one such event, 1/8 inch fell out to one mile from the power station and lesser amounts were observed for two to three miles downwind.

Only a few programs have been organized to systematically observe plume behavior and thereby determine frequencies of occurrence of ground fogging for various meteorological circumstances (5, 20). Consequently, most quantitative estimates of ground fogging have come from mathematical model* calculations of the dispersion of moist plumes. However, since the fogging potential for any given facility strongly depends on the climate of that locality and especially on the natural occurrence of fog, specific calculations have limited general applicability. Kaylor et al. (6, 10) calculated that adjacent to one cooling facility ground fogging would occur more than 1000 hours per year. The frequency rapidly decreases with increasing distance from the plant. McVehil's (15)evaluation of potential effects near lake Michigan showed that fog would occur

---

*In general, mathematical models are used to simulate physical processes with the aid of high speed computers, which can rapidly perform immense numbers of calculations. Thus, once the governing equations of a certain process are formulated and programmed for computer solution, the complex interaction of many variables can be readily studied in quantitative terms.

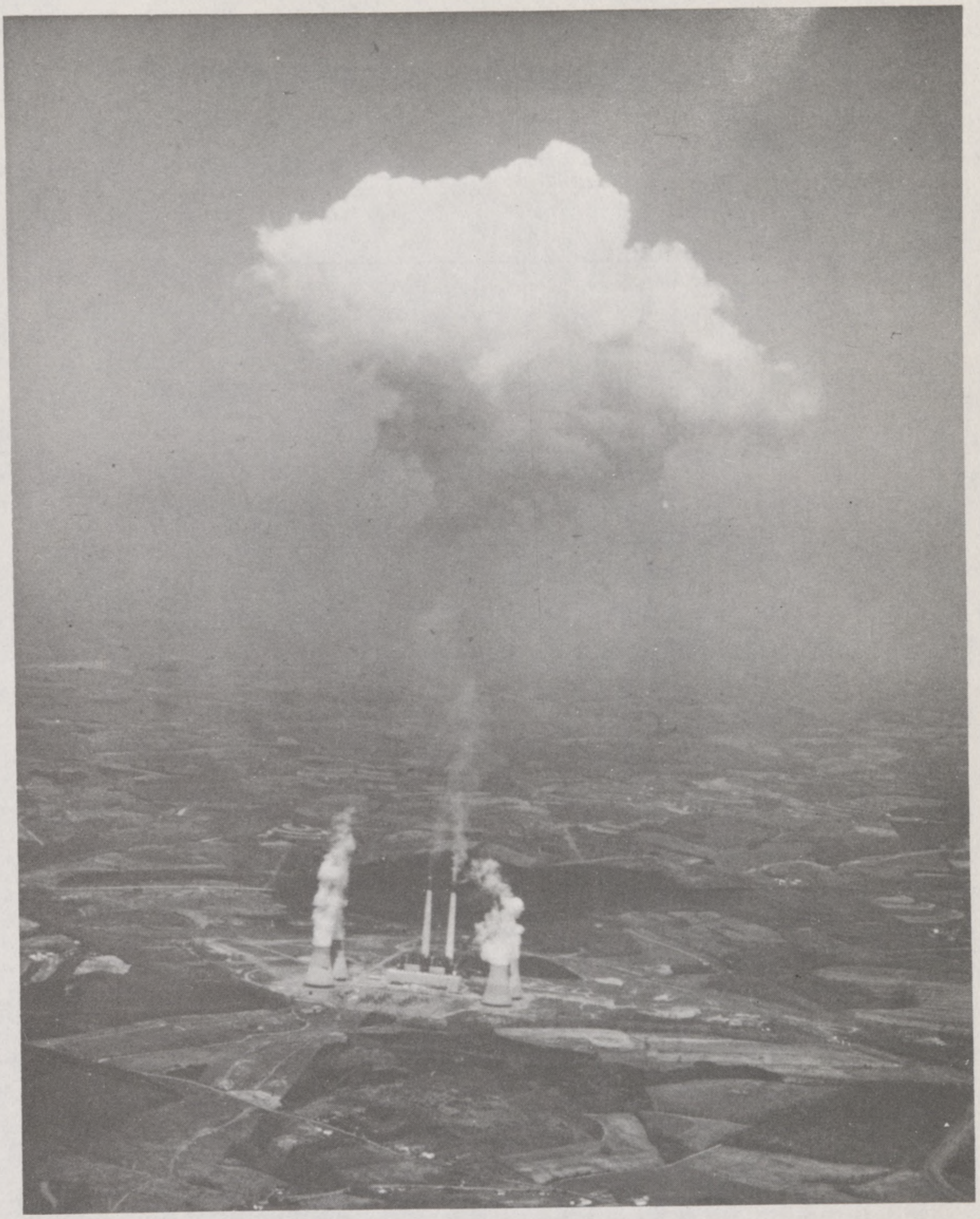


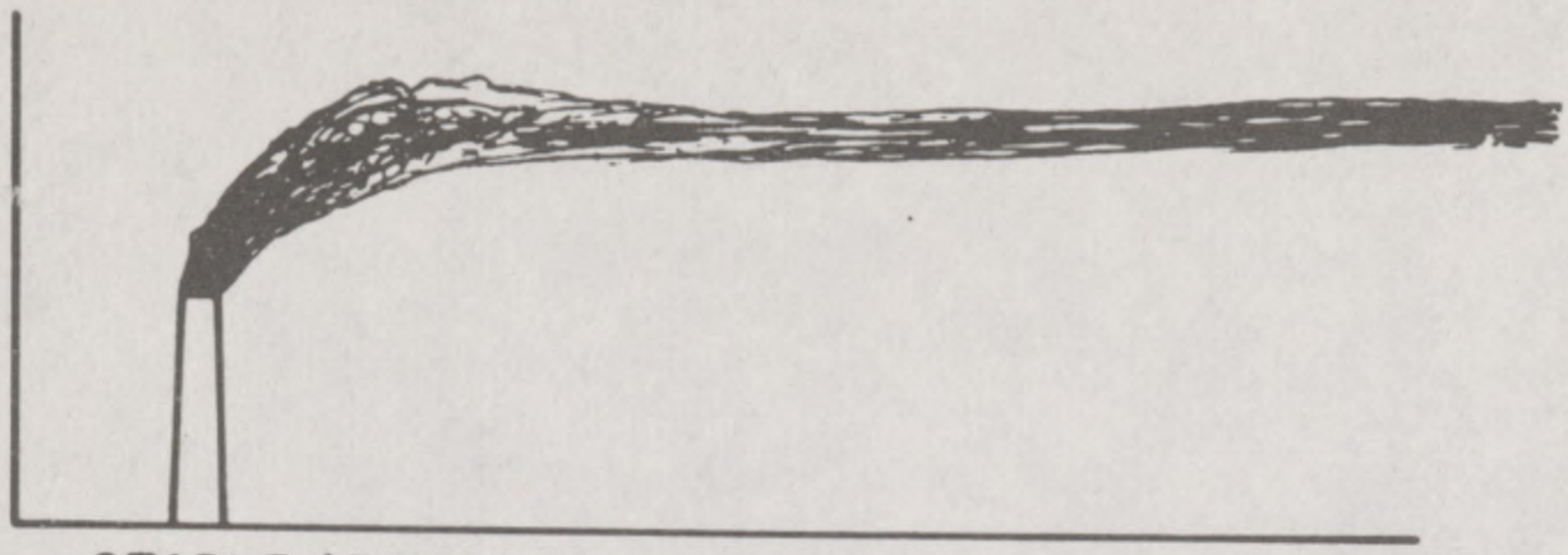
more than 600 hours per year (7.4% of the time). At any single location, however, mechanical towers would cause fog a maximum of about 1% of the time for Milwaukee mean climate and about 0.6% of the time for Chicago meteorological statistics. In contrast, Altomare (11) modelled a hypothetical mechanical draft unit at Pittsburgh, Pa., for one year of actual meteorological conditions. He found that induced fog increased only about 5 hours per year above the 750 hours of naturally occurring fog. His calculations did not include direct visible plume effects, which could occur when the plume is affected by turbulent mixing in the tower's wake. Additional research has concentrated on estimating the length of mechanical tower plumes (12, 13).

2. Natural Draft Towers

Natural draft cooling towers have become increasingly popular alternatives to once-through cooling methods. In 1966 only one such tower was in operation at an electric power station in the United States. By the end of 1971, 51 towers were either installed or planned at 32 power plants. The majority are in the Appalachian region, especially Pennsylvania, but others are scattered around the country in such places as Sacramento, California, and the Pacific Northwest.

Natural draft towers that serve large electric generating stations are typically 325 feet tall, 225 feet in diameter at the base and 150 feet at the top (see Figure 1). Some have been constructed as high as 500 feet. Thus, they often are a significant feature on the landscape and have been subject to aethestic criticism.

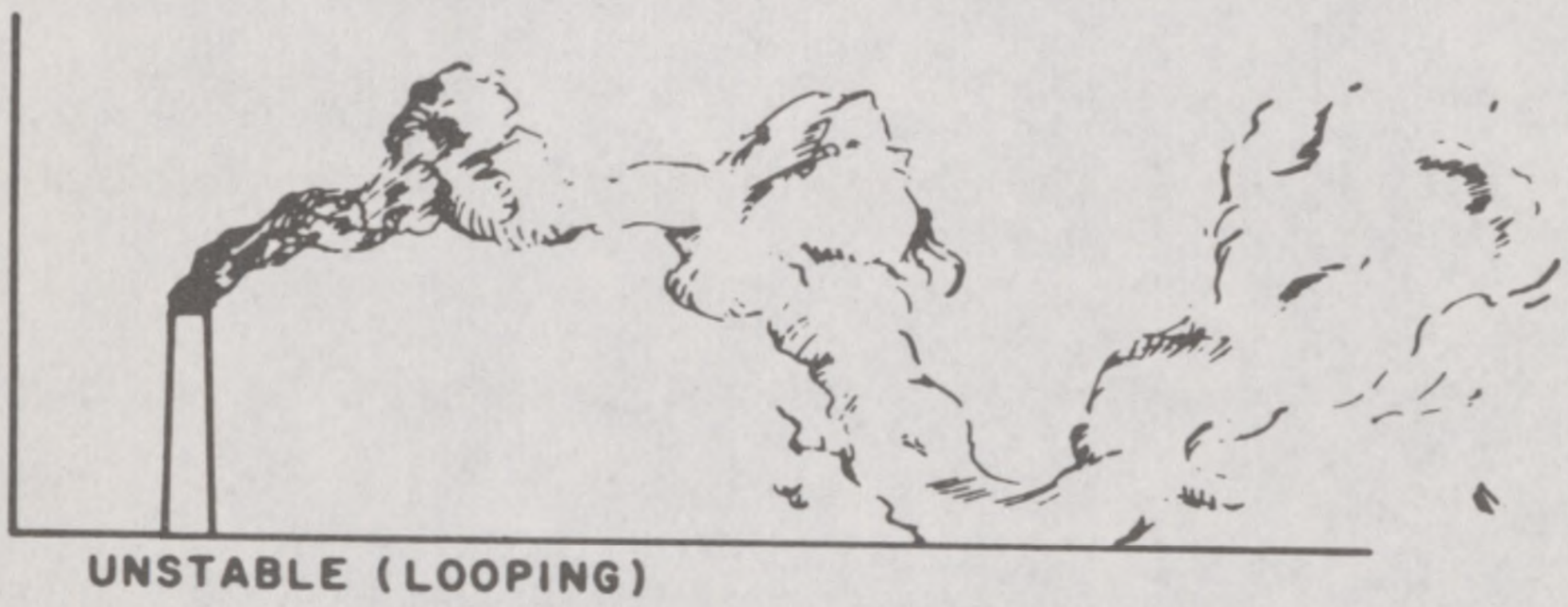




STABLE (FANNING)



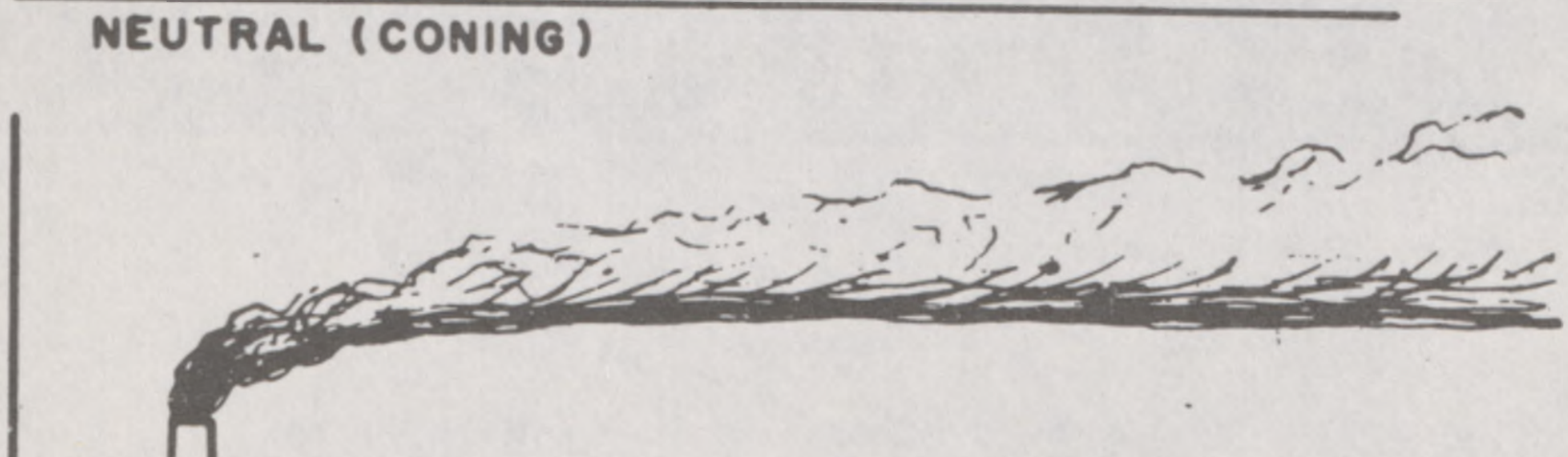
NEUTRAL BELOW, STABLE ABOVE (FUMIGATION)



UNSTABLE (LOOPING)



NEUTRAL (CONING)



STABLE BELOW, NEUTRAL ALOFT (LOFTING)

However, because of their height their emissions reach ground level far less frequently than do those of shorter mechanical units, and fogging frequency is correspondingly reduced. At times, the heat and moisture emissions will cause increased cloudiness in the vicinity of power plants. Figure 2 shows a small cumulus cloud which has formed directly over the Keystone plant in Western Pennsylvania (73). Only on a few occasions have clouds actually been observed to extend many miles downwind of the source (21). Two to four natural draft towers usually are employed at power generation facilities greater than 500 megawatts. For example, four natural units provide cooling at the 1600 megawatt Keystone electric station in western Pennsylvania, and during average summer conditions they emit 5 to 10 million gallons of water per day into the atmosphere (1). The temperature of the exit air may be about 20°C warmer than ambient air. Because of these high emission rates, natural draft units are suspected of influencing cumulus cloud development and growth. By 1990, 5000 megawatt stations are expected to be built. When operating at full capacity, water losses from associated cooling towers will approximate 50 million gallons per day (71).

The behavior of a moisture plume from a cooling tower is not unlike that of a smoke plume from a stack. The rise or subsidence of the plume largely depends on the plume-ambient air temperature difference, the change in ambient temperature with height, wind speed and atmospheric turbulence. Examples of several different plume types are shown in Figure 3. If the atmosphere is

very stable ambient temperature increases with height (temperature inversion) and very little spreading of the plume occurs. This is indicated by the fanning plume in the uppermost example in Figure 3. In the other extreme, when air temperature decreases rapidly with height the atmosphere is very unstable and a looping plume may result with the plume reaching the ground (middle example in Figure 3). Other intermediate situations are also shown. As the height of emission of the plume is increased through the use of taller cooling towers, the likelihood of the plume reaching the ground decreases. However, when the plume does reach ground level fogging can result.

Huff et al. (2) have compiled a useful report on cooling tower effluents in response to the controversy over the use of Lake Michigan as a depository for waste heat. The summary of their literature review is included verbatim below.

> Basically, the literature search revealed a discouraging lack of information on how effluents from large cooling towers, such as those which would be required at Zion, affect atmospheric conditions in their vicinity. Research with respect to this problem has been hampered by the lack of well-organized and properly conducted field studies to collect the meteorological data necessary to promote and accelerate needed research. In turn, the lack of data collection can be attributed partly to the short operational history of large cooling towers in the United States.
>
> Fog and Icing
>
> In the literature, more attention has been given to fog and icing associated with plumes from evaporative

cooling towers than to any other weather effects. A primary reason for this is that such effects are readily observable and immediately troublesome. However, there still has been too little done to define these effects accurately. The majority opinion appears to be that fog and icing are usually minor problems with natural-draft towers employing evaporative cooling, since these towers usually extend to heights of 350 feet or more into the atmosphere so that the plume seldom, if ever, sinks to ground level. Mechanical-type towers release their effluent at a much lower level (50-75 feet) and in a much more turbulent condition due to fan-forced ejection, so that there appears to be a high probability of tower-induced fog and icing at or near the ground on occasions. However, the frequency of such occurrences cannot be assessed accurately with existing observational data.

Clouds and Precipitation

Quantitative data on the effects of cooling tower plumes on clouds and precipitation were found to be extremely meager in the published literature. Occasional observations of light drizzle or snow attributed to tower effluents have been reported. Also, there have been several reports of tower plumes contributing to cloud formation downwind; apparently, these are usually stratus-type clouds and observations of cumulus developments have been rare. A few mathematical calculations have been made to determine the cloud and precipitation producing potential of cooling tower plumes, but no meteorologically acceptable analyses have been made to assess quantitatively the possibility that these plumes augment precipitation and cloud systems associated with naturally occurring storms.

Severe Weather

A search was made for any observed and/or calculated effects of tower plumes on severe weather events, such as thunderstorms, hail, tornadoes, and heavy rainstorms. Very little was found and this was of a highly speculative nature. However, from consideration of atmospheric physics and dynamics, one would expect that any severe weather event resulting from cooling tower effluents would be attained only through a triggering or stimulation effect. That is, the additional heat and/or moisture fed into a developing storm cloud could conceivably produce an imbalance that would result in intensification into a severe weather state. However, the severe weather effect, if any, must be strictly conjectural at this time.

In general, we conclude from available information in the literature that a very distinct void exists in our knowledge of the effects of cooling tower plumes on clouds and precipitation with regard to both initiation and stimulation of these weather events. From climatological observations and cloud physics research it is known that cumulus clouds and rain showers or thunderstorms can be triggered by small inputs of energy. Consequently, it is extremely important that research be initiated to combine existing knowledge of plume and cloud properties into mathematical models that will provide reliable quantitative estimates of the plume effect on downwind clouds and rainfall.

Comparison of Cooling Tower Types

Most of the information in the recent literature relating to meteorological effects associated with cooling tower effluents concerns the natural-draft type employing evaporative cooling. The engineering profession apparently considers these to be the best alternative to waste heat discharge into water courses. To date, no large dry cooling towers have been constructed in the United States. Consequently, dry cooling towers present an environmental problem about which little is known. Qualitatively, the large quantities of heat released to the atmosphere from dry cooling towers could produce increases in convection and turbulence and likely initiate or stimulate the development of cumulus clouds. However, the literature provides no information, and knowledge is not adequate to define in quantitative terms the meteorological significance of the tower heat release. Therefore, no further attempt has been made in this report to present a comparative evaluation of tower-induced atmospheric effects between wet and dry towers.

Similarly, actual quantitative measurements of the differential effects of natural-draft and mechanical-draft tower effluents on atmospheric conditions apparently have not been made. Except for one study by McVehil (1970), only qualitative comparisons were found. Qualitatively, there appears to be general agreement that the mechanical type is more likely to produce fog and icing problems. With their higher level discharge, the natural-draft type would be expected to become involved more readily in cloud and precipitation producing processes in the atmosphere.

Huff's (2) opinion that large natural draft units infrequently cause ground fogging is generally shared by others (7, 17, 18,

19) and is supported by observation (21, 22). As Carson (20) states, these units have the potential to cause ground-level fog but they rarely do.

The likelihood of increased fog occurrence from cooling towers (both natural and mechanical draft) depends strongly on the natural climate, and especially on the natural occurrences of fog and low-level inversions. An analysis of the U.S. geographic potential for cooling tower fog production (16) has shown two large areas of highest potential (heavy fog naturally occurs more than 45 days per year): a band along the Appalachian Mountains from Georgia to Maine and the northwest corner of the country, including all of Washington and parts of Idaho, Montana, Oregon and the California coast as far south as Los Angeles. Moderate potential (heavy fog between 20 and 45 days per year) exists throughout the Great Lakes and the Atlantic and Gulf Coast regions and in a band from western South Dakota to the Texas Panhandle. Slight potential exists elsewhere.

As in the case of mechanical draft towers, a number of mathematical models have been developed to study environmental effects of heat and water vapor emissions. The models have focused generally on the behavior of moist plumes (16, 21, 23, 24, 27, 30) and specifically on ground fogging (11, 15, 26) and cloudiness and precipitation (2, 17, 25, 28). Although observations indicate minimal environmental effects, some of the mathematical models

suggest occasional ground fogging and precipitation. For example, McVehil (15) calculated that a 350 foot natural draft tower at Zion, Illinois, would cause 15 to 75 hours of ground fog per year, about 35% of which would coincide with measureable natural fog. Overcamp and Hoult (25) calculated that when a plume interacts with the tower wake and strikes the ground 0.1 centimeter per hour of precipitation can result at air temperatures of -10°C.

Several scientists have speculated on the possibility of cooling tower effluents affecting cloudiness, precipitation, severe storms and other weather elements beyond the immediate vicinity of the tower. Table 1, from Hanna (28), shows the energy production for various atmospheric processes. It was pointed out above that the amount of heat used to generate power for fossil fuel facilities is about the same as the amount transferred to cooling water. Thus, about 10^9 watts* (1000 megawatts) of heat energy is released to the atmosphere from the wet cooling towers of a 1000 megawatt generating station. Initially (area $10^3 m^2$) the tower energy flux would be about 10^6 watts/m^2 over a small area. However, when the plume has diffused over a thunderstorm-sized area ($10^8 m^2$) the energy flux of 10 watts/m^2 is about 10% of the kinetic energy production of a thunderstorm. Hanna concludes that on this scale "...the artificial energy input may significantly affect the natural process." Hosler

---

*For comparison purposes the heat emissions from a city like Cincinnati, Ohio, average about 9×10^9 watts (45).

(21) also discussed this problem and has concluded:

> On days when cumulus clouds form naturally, there will be a tendency for clouds to favor development in the larger moist plumes. Cloud streets can and do form downwind of larger installations. We cannot rule out the possibility of shower formation in the cloud street downwind. The variability of wind direction and speed will tend to spread this effect over a wide area.

Table 1. Energy Production of Some Atmospheric Processes

Area	Natural Process	Energy Production	Production per Unit Area
$10^4 m^2$	Tornado kinetic energy (K.E.) production.	10^8 watts	10^4 watts/m^2
$10^8 m^2$	Thunderstorm K. E. production	10^{10} watts	100 watts/m^2
	Latent heat release (1 cm rain in 30 min.)	5×10^{11} watts	5000 watts/m^2
$10^{10} m^2$	Great lakes snowsquall latent heat release (4 cm snow in hr.)	10^{13} watts	1000 watts/m^2
$10^{12} m^2$	Cyclone latent heat release (1 cm rain per day)	2×10^{14} watts	200 watts/m^2
$5 \times 10^{14} m^2$	Solar energy flux	1.75×10^{17} watts	350 watts/m^2

These <u>possible</u> cooling tower effects on weather systems are poorly understood and little quantitative data has been gathered on the subject. Hanna and Swisher (17) state that "no analysis has been made of the possibility of these plumes augmenting rainfall from naturally occurring rainstorms." Another opinion of the situation has been given by Carson (20):

The state of the art is such that meteorologists are not able to predict quantitatively how the atmosphere will react to the large amounts of heat energy and water vapor that it will be forced to absorb as the result of the disposal of waste heat from power plants. Conceivably, critical heat release rates may exist for particularly sensitive sites which, when exceeded, may lead to significant meteorological effects, such as the generation of thunderstorms in convectively unstable, subtropical conditions.

Because of the importance of this problem and current lack of understanding, this area obviously is in need of further research.

Cooling towers near coastal areas have the additional environmental problem of salt drift. If sea water, or brackish water, is used as the cooling medium, any drift of water droplets from the tower adds to the salt burden of the atmosphere. If the droplets reach the ground, ecological problems from salt contamination may result. Thus efficient drift eliminators are essential equipment within the towers. Most recently, cooling tower manufacturers guarantee that drift will not exceed 0.002% of the circulating water in the towers, a value about 100 times lower than that reported a few years ago. In practice, however, wide variations (more than 100%) occur about this mean value depending on manufacturer, type of eliminator, air flow rate, etc. (31). Actual tower measurements in 1971 determined a drift percentage of 0.005% to be representative for several contemporary units (33). With a 0.1% drift eliminator, an estimated 10 tons of salt per day would be deposited downwind of a 1000 megawatt nuclear unit (29). Numerical models of cooling tower salt drift (31, 32) generally indicate that because of their size the water drops from a tower readily fall to the ground within about 10 km of the source and

the amount of salt deposition rapidly decreases with distance downwind of the tower. Hosler et al. (67) have developed a series of nomograms to aid the calculation of salt deposition. Wistrom and Ovard (32) summarize their opinion as follows:

> In summary, it can be generally concluded that cooling tower drift effects on the environment are localized and that beyond some reasonable distance that is usually within the plant site boundary, drift does not significantly effect the environment. All field experience during the last 20 years where salt or brackish water has been used in cooling towers supports this general conclusion.

At least two current field studies focus on the salt drift problem: one at Turkey Point, Florida, primarily funded by the U.S. Environmental Protection Agency and Florida Power and Light Company, and the other at the Potomac Electric Power Company's plant at Chalk Point, Maryland. The principal investigator for the former program is Environmental Systems Corp., Knoxville, Tennessee. Various groups, including the State of Maryland, are undertaking environmental studies at Chalk Point.

The Illinois Institute of Technology Research Institute under contract to EPA studied the interaction between cooling tower and stack plumes (69). They noted that when the water plume merged with the SO_2 and particulate matter emitted from the stack that low pH, or acid, droplets resulted. If such drops reach the ground, vegetation damage is possible. The potential problems from this effect have not been fully studied and will require thorough knowledge of both stack and tower plume rise.

3. Dry Cooling Towers

Future projections of electrical power generation indicate that the consumption of water for cooling purposes will increase by about a factor of seven from 1965 to 2000 (34). One answer to such enormous water needs is dry cooling towers which operate on the same principle as the automobile radiator and dissipate heat by conduction rather than evaporation. The cooling water is maintained in a closed cycle and thus the only continuous demand for water is from plant losses, which are quite small. Since only heat is emitted from dry towers no visible plume of water droplets or ground fogging result (35). Because of their independence from sources of cooling water, power plants using dry towers would have much greater siting flexibility than do current facilities. Thus, a vigorous program of dry cooling tower research and development might pay great dividends to the nation (70). The main drawback to dry towers is that they are more expensive to operate than wet towers. Although they have been successfully employed in Europe at power plants of up to 200 megawatt capacity, only one small unit (20 megawatt) is operating at an electrical generating station in the United States; that is located at Wyodak, Wyoming (75).

A thorough engineering-economic appraisal of dry towers has been published by Rossie and Cecil (36). A brief report is also available (37). Boyack and Kearney have prepared a comprehensive report on potential environmental effects (75).

They (75) have also compiled a long list of references on potential effects of dry cooling towers and associated plume behavior. Atmospheric effects from dry towers include possible enhancement of cumulus cloud development and associated precipitation. The related discussion above on potential effects from wet natural draft units on weather systems is also applicable here. Rossie and Cecil (36) conclude:

> It is our general conclusion that the release of heat into the atmosphere from a dry-type cooling tower will be much less harmful to the environment than the combined release of heat and water vapor associated with other cooling methods.
>
> While it is our opinion that a dry-type cooling tower will not produce a measurable effect on a region's climatology, the worldwide buildup of thermal releases and the resultant climatological effects remain important considerations. Thus, on either a local or global scale the subject of the meteorological effects of releasing large amounts of heat into the atmosphere raises many unanswered questions and should be investigated extensively in the next few decades.

Boyack and Kearney (75) also concluded that dry cooling towers are "unlikely" to produce adverse environmental effects. However, they cautioned that the heat emitted from several large power stations closely situated does have the potential to influence mesoscale weather phenomena. Currently, adequate techniques are not available to thoroughly assess this potential influence.

B. Cooling Ponds and Lakes

Other alternatives to once-through cooling and direct introduction of heated water into rivers are cooling ponds and lakes.

Today many utilities are damming rivers to form cooling lakes and ponds for the purpose of receiving heated water. Because the hot effluent gradually diffuses through the lake, heat energy enters the atmosphere over a large area and intense heat and moisture sources (such as cooling towers) are avoided. A rough guide to the necessary size of cooling lakes is that one to two acres of water are needed for each megawatt of generating capacity. Cooling lakes and ponds are most efficient and economical where humidity is low and land is inexpensive. Thus, they are more widely used in the southwestern U.S. than in the more densely populated northeast (29). If the lakes are also used for recreational purposes, they contribute more to the total environment than other alternatives to once-through cooling (40).

As in the case of cooling towers, cooling ponds and lakes add an extra amount of heat and water vapor into the ambient atmosphere. When conditions are right (the environment is humid, calm and cool) fog will form because of these emissions (3). Routine observations or quantitative calculations of hours of fog near cooling ponds are not currently available. Induced fog frequency depends on regional climate and natural fog occurrence, but is generally thought to be restricted to the downwind vicinity of the pond or lake itself. To predict the rate at which heat and moisture are transferred from a water body to the atmosphere, various mathematical models of heated water plumes and pond temperature have been developed (38, 39). Jaske and Drew (41) have compared the evaporation from a 2500 acre

cooling lake to that from a natural draft wet tower. Although their results showed a strong dependence on size of the cooling lake and regional climate, the evaporation resulting from a given thermal addition to a lake is generally less than 50 percent of the evaporation that would result from similar thermal loading of a cooling tower. Part of the total heat transfer from a lake occurs by thermal radiation and conduction to the atmosphere.

A thorough investigation of lake effects from heated wastes has been reported by Carson (20). Although his specific concern is large electric generating installations on Lake Michigan, his ideas are generally applicable to ponds and lakes. Carson states that two scales of weather changes are possible from thermal pollution into the lake. Increased heat and moisture fluxes over the plume can lead to local effects whereas the accumulation of heat in the main water body may cause large-scale modifications. Carson reports that many observations have been made of "thin fog and/or light freezing fog" near cooling ponds, but that these steam fogs tend to dissipate quickly. He found no published examples of such fogs affecting traffic or visibility at nearby land areas. The most observable effect of heated discharges into large water bodies was an increase in the hours and amount of steam fog over the immediate heated plume area.

In the area of potential modification of large scale climate, no documented reports could be found of observations of significant temperature change or precipitation associated with once-through

24-642 O - 73 - pt. 2 - 3

cooling on a large body of water. However, if certain weather phenomena were observed in the vicinity of a lake of several thousand acres or more in size that was being subjected to heated water discharges, it would be difficult to determine whether the cause of the phenomena was natural or man-induced. Since water has a high heat capacity, large lakes are able to store great quantities of heat with little change in water temperature. For example, if the waste heat from a several thousand megawatt generating facility were uniformly mixed throughout any of the Great Lakes the water temperature would increase by only a fraction of a degree per year. However, such complete mixing would not be the rule and during short periods of a few weeks or so the heated water would likely concentrate over small areas in the upper few meters of the lake. The impact of such occurrences on local meteorological conditions has not been fully determined.

The problem of determining the meteorological effects from heated ponds and lakes is similar to that of studying atmospheric characteristics peculiar to metropolitan areas. The air over cities is warmer than that of the nearby countryside; this phenomenon is referred to as the urban heat island (to be discussed below). The influence of these warmer temperatures and the changes of the surface from vegetation to aslphalt and concrete on urban wind flow patterns and other atmospheric features has been studied via numerical models (76, 77). The horizontal scale of cooling lakes is similar to that of cities and it is likely that the

models developed for urban areas can and will be applied to cooling lake environmental problems.

To summarize fogging potential from various types of cooling systems described previously, Table 2 has been constructed using Decker's paper (7), and gives a relative picture of fogging potential.

Table 2. Description of visibility obstruction from several types of cooling systems in increasing order of probability

Type of Cooling System	Descriptive Probability of Obstructing Visibility
Tall, natural-draft towers standing alone, fully equipped with drift eliminators	Extremely low, virtually zero
Tall, natural-draft towers alone but without drift eliminators	Low, but likely to occur with high humidity and stagnation
Tall, natural-draft towers, close to fossil-fuel smokestacks emitting acid-producing stack gases	Low to substantial, depends on prevalence of wind, direction, and spacing of stack and tower(s)
Mechanical-draft towers emitting at low level	Substantial, but highly variable, depending on wind and orientation or grouping of units
Slack water, ponds, and spray ponds	Low to substantial, depending on the stagnation of the atmosphere and confinement of humidified air

While the table is qualitative, it does suggest that other effects and fogging can be minimized by proper site

selection for new power facilities. Among the primary meteorological factors to be considered are the prevailing (most probable) wind direction and any peculiar wind flow patterns due to local topographic features. In addition, variations of the vertical temperature change, including temperature inversion frequency, must be known, since they largely affect the plume rise and vertical dispersion of tower and pond effluent.

De Harpporte (78) recommends that prior to site selection for a new power plant, a two-phase meteorological study be made of local weather and climate. The first phase would use existing meteorological data to study the diffusion and path of potential heat and moisture emissions. These general results would be applied to rank several possible sites by probability of deleterious atmospheric effects. Once a tentative site had been selected De Harpporte suggests that a continuous one-year measurement program be conducted at the site of wind, temperature and humidity at several levels on a high tower. These data would then serve as input to predictive equations of fogging potential, for example, from cooling towers versus a cooling pond. The predictive methods used must be acceptable to both industry and governmental regulatory agencies so that agreement can be reached on the implications of the results. Finally, these meteorological features must be considered along with economics, availability of water, other environmental factors, etc., in determining final site selection.

III. Urban Scale

The climate of cities is notably different from that of nearby

rural areas. Urban climate has been studied for many years and is becoming increasingly well documented as evidenced by a rapidly growing list of publications on the topic (47, 48, 49, 50). Urban-rural climatic differences are largely due to the intense human activity and use of energy in cities along with the replacement of natural vegetation by building materials (42). Building materials more readily absorb and store heat from the sun during daytime than does vegetation. After sunset, while rural areas are cooling, the building materials gradually release their stored heat to the urban atmosphere, tending to keep it warm. An extreme example of urban waste heat emissions is that reported for Manhattan, New York City, where anthropogenic heat is estimated to be 2-1/2 times and 1/6 of that naturally received from the sun during winter and summer, respectively (44). The heat emissions from many large cities annually exceed 10% of the natural solar energy receipt (45).

The most evident feature of city climate is its excess warmth, which is commonly referred to as the urban heat island. Urban-rural temperature differences occasionally reach 10°C, but average about 1.0 to 2.0°C. Heat islands are most intense at night, especially during weather dominated by high pressure with clear skies and low winds. Detailed space-scale measurements of urban air temperature show much fine structure to the heat island with cool pockets associated with "green" areas such as parks and cemeteries (43). Heat islands can be measured in cities of all sizes, during a variety of meteorological conditions, and in all parts of a city, from the center to the outlying suburbs (46, 47).

An advantage of urban heat emissions is that they decrease the likelihood of surface-based air temperature inversions*, and increase the height of the mixed-layer near the surface. Inversions strongly inhibit vertical air motions which can diffuse and dilute pollutants. Heat emissions at the city surface cause a decrease in temperature with height and tend to limit the formation of inversions and their accompanying high pollutant concentrations. Many observations of urban and rural temperature-height profiles have shown the effect of thermal emissions. Ewing (68) estimates that several of the largest U.S. cities currently avoid all inversions during winter, the season of greatest heat use. Moreover, by the year 2000 New York City will have sufficient waste heat to avoid inversions year round.

Other major features of urban climate that are related to energy use include: (1) a longer frost-free growing season which, in Washington, D.C., for example, exceeds that of nearby rural areas by more than a month; (2) less snowfall because it melts while falling through the warmer urban atmosphere; (3) lower relative humidity; (4) decreased occurrence and density of fog because of the lower relative humidity, a feature which may be offset by more particulate matter which serves as condensation nuclei; (5) a slight component of the wind directed toward the city center as a result of the horizontal temperature contrast; and (6) about 5 to 10% more precipitation downwind of cities, a phenomenon partially due to increased convection (vertical motion) (42, 51, 52). The assessment

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*A temperature inversion is an increase in temperature with height.

of the urban influence on precipitation is currently the subject of a major field-laboratory research program (METROMEX) involving several groups with multi-agency funding (53, 54). This program, which focuses on the St. Louis urban-industrial complex, is designed to study the specific causes of certain urban-induced meteorological features.

The most important non-meteorological effect of heat islands is the personal discomfort to those living in urban centers, especially during humid, summer evenings. After sunset, the city does not cool as rapidly as the outlying areas. In mid- and tropical-latitudes, the excess heat can critically increase the thermal burden on the populace. During prolonged hot weather lasting several days or more, urban mortality rates exceed those of the nearby countryside (55). Several studies have linked these excess urban heat deaths to heat island intensities (43, 56, 57, 58). Thus, a reduction in the heat island could result in fewer urban heat deaths. From the viewpoint of energy conservation, the urban heat island is generally beneficial during winter since it reduces the amount of space heating necessary for comfort. In contrast, during summer the heat island adds to energy consumption for air conditioning purposes.

In summary, waste heat has climatic and health effects which are mainly confined to the metropolitan area. An exception is the downwind urban effect on precipitation which has been observed some 40 to 50 kilometers from the city center. The effects of waste heat are currently tolerated, but increasing numbers of people will

be affected and the magnitude of thermal emissions will increase as population centers grow in size and number. Unless the residents become acclamated, their personal discomfort will be aggravated. Despite prolific discussion of urban and regional planning, the design of only a few new developments has included climatic influences. The planned community of Columbia, Maryland is a notable example. As Landsberg (48) has pointed out, the meteorological insight into heat islands is now available for comprehensive town design and if employed would greatly reduce thermal stress on the populace. Such design involves preservation of trees, inclusion of as much surface as possible covered by vegetation, and spacing of buildings.

IV. Regional Scale

In between the intense energy use on a local scale and the current insignificant use on a global basis (to be discussed below) is the intermediate or regional scale where, in the near future, manmade heat generation may become climatically important as urban areas expand and merge. The magnitude of various energy processes must be examined to appreciate the potential climatic problems beyond the urban scale. When averaged over the entire globe the absorption of solar energy by the earth equals about 200 watts/meter^2 (W/m^2), but this obviously changes markedly from north to south. Rates of energy use by man for several geographical areas are shown in Table 3. These vary from the intense energy use in Manhattan, New York City, to that for the world, which is insignificant in comparison to the natural energy balance. On an intermediate

scale, in Los Angeles County with an area of 10,000 km^2 the consumption of energy is already several percent of that naturally received from the sun.

TABLE 3. Energy Consumption Density (ECD), W/m^2, for selected areas of the World, for the late 1960's. From Inadvertent Climate Modification (45).

	Area (km^2)	ECD (W/m^2)
Manhattan, New York City	59	630.
Moscow	880	127.
West Berlin	234[a]	21.3
Los Angeles	3,500[a]	21.0
Northrhein-Westphalia (industrial area)	10,300	10.2
Los Angeles County	10,000	7.5
Northrhein-Westphalia	34,000	4.2
Benelux	73,000	1.66
United Kingdom	242,000	1.21
14 Eastern U.S. States	932,000	1.11
Central Western Europe	1,665,000	0.74
World	510,000,000	0.012

[a]Building area only.

Both forecasts of energy use or extrapolations of past trends indicate a world-wide energy growth rate in the neighborhood of 5% per year to 2000 (45). Thus, from 1970 to 2000 global energy use can be expected to increase by roughly four times, with some countries and regions exceeding this rate and others falling short of it. Based on current energy consumption and expected future use (Table 3), by 2000 the waste heat use of several geographic areas of 100,000 to about a million km^2 will be several percent of the energy naturally received from the sun (59).

Today meteorologists do not know all the specific climatic consequences of such an energy use density. Better mathematical models of the atmosphere must be developed which can describe weather and climate patterns. However, some steps using extreme waste heat inputs have been made toward solution of this problem.

Sellers (60) at the University of Arizona and Washington (61) at the National Center for Atmospheric Research (NCAR) in Boulder, Colorado, have used mathematical models of global climate to study the effect of waste heat. The NCAR model is more sophisticated and detailed, but both have simulated actual climate well. Both investigators applied about 1000 times more waste heat than is currently being used on a global scale (a very extreme amount of energy use). The models showed that the average surface temperature of the earth would increase by 5 to 15°C with such waste heat levels. Washington (62) reran his model for a more realistic, but still extreme, example, He applied about 40 times more thermal energy than is currently being used on a global basis, distributed in the same proportion as the present population. The results suggested that little large-scale climatic change would result. However, the model may not have been sensitive enough to accurately handle the experiment.

These results are representative of the few examples of quantitative work yet to be published on this problem. However, some qualitative arguments also suggest that the waste heat will have climatic importance on a regional scale. For example, various climatic models

(63, 79) show that when an anomaly of one percent of the absorbed solar energy occurs, significant alterations of climate result. For example, on a global scale, a one percent increase in solar input or decrease of surface albedo (reflectivity) will lead to about a 1°C increase in mean surface temperature.

The work of Sellers and Washington suggests that extreme waste heat inputs (i.e., ones which are very unlikely to be reached in the foreseeable future) will probably result in extreme climatic changes. What is now needed is more refinement and further application of such models. In the United States, research on climatic change using very large and fast computers is being pursued by Washington and others at NCAR, Smagorinski's group at NOAA's facility at Princeton, N.J., and by Mintz and colleagues at UCLA.

V. Global Scale

On a local scale the climatic effects of energy use are significant and well documented. On a regional scale they may become important by the turn of the century. However, on the global scale, climatic effects today and for the near future are insignificant. In 1970, world-wide energy consumption was estimated at about 7 to 8×10^{12} watts. Averaged over the entire globe the higher estimate equals 0.016 W/m^2. Distributed over the continental areas only, it yields an energy use density of 0.054 W/m^2. The natural global solar radiation absorption by the earth averages about 200 W/m^2.

Past and projected future global energy use is shown in Table 4. The steadily increasing consumption of energy since 1925 is evident from the figures. From 1960 to 1968, for example, the

world-wide use of energy increased at an average rate of about 5-1/2 percent. The future projections used expected economic growth in all parts of the world as the basis for annual energy growth rates of 5.1 percent to 1980 and 4.5 percent from 1980 to 2000. The result is an approximate fourfold increase from 1970 to 2000. The projected 2000 energy use figure, however, would still be less than 0.1 percent of the natural absorption of solar energy.

TABLE 4. Past and predicted future total energy use for the world, 10^{15} Btu/yr. From Darmstadter (64).

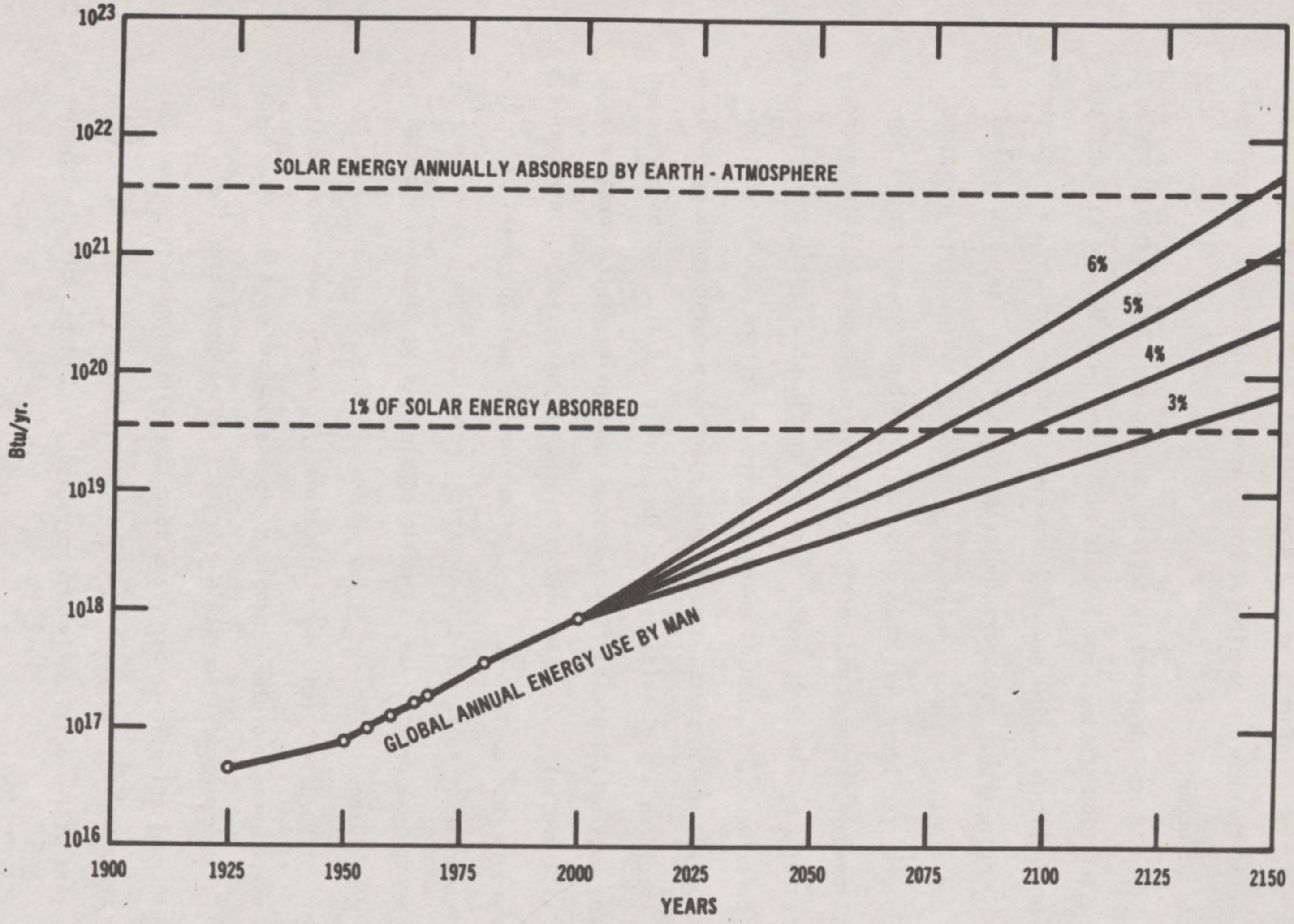
Year	World Energy Consumption, 10^{15} Btu/yr
1925	44
1950	77
1955	100
1960	124
1965	161
1968	190
1980	345
2000	831

The extrapolation of energy use statistics beyond the year 2000 is a very tenuous exercise and little reliability can be placed on such figures. Population, fuel supplies and economic trends, as well as individual and community attitudes, may change markedly by the next century. However, if the energy growth rate remains constant (each year x percent more energy is used than the year before) man's energy use eventually will reach enormous proportions.

Thus, it is informative to ask what the climatic consequences might be of continued expansion of energy use and when those consequences might occur.

Figure 4 graphically depicts man's global annual energy use as a function of time from 1925 to 2150. The past data to 1968 and the projections to 1980 and 2000 are also shown in Table 4 (64). Several possible growth rates are indicated thereafter. The upper dashed line represents the annual solar energy absorbed by the earth and atmosphere; the lower dashed line is one percent of the upper. As mentioned in the previous section a one percent change in solar energy receipt by the earth could lead to significant climatic changes. In other words, if such an energy use growth pattern should continue for 100 to 150 years, a noticeable climatic warming would probably result on a world-wide basis. This conclusion also has been reached by Budyko (74) who cautioned that a substantial air temperature rise will probably take place within a hundred years if the present energy growth rate continues. Thus, if during the next 100 years or so no economic or political considerations force the reduction of the energy use growth rate, climatic considerations might well become compelling.

The development and application of climatic models to the type of regional and global problems discussed above is a pressing need. For example, if large scale climatic consequences are likely from thermal pollution, many years lead time will be necessary for adjustments in regional planning. Therefore, the level of waste heat input that will significantly affect regional and global climate must be determined.


10^{23}
10^{22}
10^{21}
10^{20}
10^{19}
10^{18}
10^{17}
10^{16}
Btu/yr.
SOLAR ENERGY ANNUALLY ABSORBED BY EARTH - ATMOSPHERE
1% OF SOLAR ENERGY ABSORBED
6%
5%
4%
3%
GLOBAL ANNUAL ENERGY USE BY MAN
1900
1925
1950
1975
2000
2025
2050
2075
2100
2125
2150
YEARS

609

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24-642 O - 73 - pt. 2 - 4

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LAND USE CONSIDERATIONS IN THE CONTROL OF THERMAL DISCHARGES

TABLE OF CONTENTS

SECTION		PAGE
I.	Introduction	1
II.	Regulations of Thermal Discharges Under the Federal Water Pollution Control Act Amendments of 1972.....	3
III.	Relationship of Site Use for Cooling With Adjacent and Regional Uses.....	5
IV,	Decision-making Arrangements for Site Selection and Minimization of Adverse Impacts.....	19

SECTION I.

INTRODUCTION

The term "land use" has a broad range of implications, depending on the context in which the term is used. Land use may be viewed as the actual utilization of a piece of land, inter-relationships between uses of land, a major consideration in decision-making processes, a means of controlling development, or a means of controlling environmental quality.

Section 104 (t) of the Federal Water Pollution Control Act Amendments of 1972 (P.L. 92-500) requires consideration of the total environmental impact, including the land use impacts, in the evaluation of alternative methods of controlling thermal discharges.

Land use is therefore defined for the purpose of discussing the impacts of thermal cooling alternatives as related to siting of dischargers of thermal effluents. Three areas of land use are of concern here:

(1) The capacity of a particular waterbody to dissipate waste heat without compromising the protection and propagation of a balanced, indigenous population of fish, shellfish, and wildlife is a major factor which affects thermal pollution abatement requirements-- and thus the range of relevant site alternatives for a thermal discharge facility. The provisions in the FWPCAA (P.L. 92-500, herein abbreviated) under which thermal pollution abatement requirements will be determined are discussed in detail in Section II.

(2) Section III discusses the use of a site for a thermal facility and the associated cooling technology and their relationships to regional land use. Three areas of concern are: (a) the compatibility of the facility with existing and potential land uses in the area; (b) the alternative uses of the site itself, and the relative costs and benefits associated with each use and; (c) the possible multiple uses of the site, compatible with the proposed use, which might serve to reduce the social cost of the proposed use of the site.

(3) Objectives of the State power plant siting arrangements and the relationship of power plant siting to statewide institutional arrangements, for land use planning are discussed in Section IV.

This chapter focuses for the most part on the thermal effluents of steam electric power plants. However, the material generally applies to other thermal effluent sources.

SECTION II

REGULATION OF THERMAL DISCHARGES UNDER THE FWPCAA

There are three significant provisions of the FWPCAA, under which limitations on thermal discharges are established. The capacity of a receiving waterbody to dissipate the thermal component of the discharge and the protection and propagation of fish and wildlife determine which provision applies. These provisions will apply to steam-electric power plants as well as to certain categories of manufacturers using cooling water for in-house power production or manufacturing processes. However, steam electric power plants account for about 80 percent of all water withdrawn for cooling purposes and therefore the use most impacted by these provisions.

Sections 301 and 306 of the FWPCAA require establishment of technology based effluent limitations for existing and new point sources of thermal discharges. Such effluent limitations will provide the basic thermal pollution control requirements to be met by dischargers, unless more stringent requirements are established pursuent to Section 303, or less stringent requirements are permitted under Section 316.

Under Section 303 (d) the State has the responsibility to identify waters within its boundaries for which standards established under Section 301 "are not stringent enough to

assure the protection and propagation of a balanced, indigenous population of shellfish, fish, and wildlife." The State must estimate for such waters the maximum total daily thermal load adequate for protection and propagation of shellfish, fish and wildlife, and must establish effluent limitations for thermal discharges from point sources which are at least as stringent as those established under Sections 301 and 306, in order to meet total daily thermal load requirements and water quality standards.

Section 316 applies to point sources otherwise regulated under Sections 301 and 306. If those effluent limitations are demonstrated by the operator to be "more stringent than necessary to assure the protection (sic) and propagation of a balanced, indigenous population of shellfish, fish and wildlife in and on the body of water into which the discharge is made," a new thermal effluent limitation may be imposed, adequate to ensure protection.

The effluent limitations established pursuent to these provisions will determine the range of thermal abatement technology available to satisfy the limitations. Other factors, such as capital and operating costs, power penalities, etc., and the total environmental impacts of the cooling options-- including land use impacts-- will determine the selection of the particular thermal abatement technology to be employed. These effluent limitations and other factors, in turn, will strongly influence the ultimate location of thermal discharge facilities.

SECTION III

RELATIONSHIP OF SITE USE FOR COOLING WITH ADJACENT AND REGIONAL USES

Any large facility which employs some type of effluent cooling is likely to have certain impacts on existing or potential land use in the region. Two types of impact are of particular concern in the siting of the facility. These are: (a) environmental and aesthetic compatibility with adjacent and nearby existing and potential land uses, and; (b) alternative uses of the site which are precluded by the intended use. Once the site of the facility has been determined, it may be possible to design the facility to provide on-site multiple uses, or beneficial use of the heat otherwise emitted to the atmosphere, which will serve to increase the regional benefits.

Compatibility

A major consideration in siting thermal facilities, particularly power plants, is the environmental and aesthetic compatibility with adjacent land uses. Often thermal facilities are located on rivers, bays, or estuaries, which are in demand for recreational, residential, or conservation uses. While thermal cooling safeguards water quality, cooling technology has certain secondary impacts which make thermal facilities incompatible with other land uses. Among these secondary impacts are air quality, weather modification, operational noise, water use and aesthetics.

Air Quality Impact

The use of cooling towers produces air pollutants in the form of small droplets which ahve the same composition as the cooling water. These water treatment chemicals and dissolve solids-- referred to as "drift" -- add a pollutant load to the atmosphere and surrounding terrain that can affect land use options.

The amount of drift from any cooling tower is primarily a function of tower design, and of the drift eliminators in particular. Total losses to drift are normally expressed as a percentage of flow through the tower. A number of tests, summarized in a report for the Environmental Protection Agency by the Argonne National Laboratory, showed that the drift rate from mechanical-draft towers averaged one-half of one percent of the water flow, while drift from natural-draft towers averaged half of that.

The use of brackish or marine waters in cooling towers aggravates the drift problem because of the concentration of salt in the water. Proper location of the tower with respect to the plant buildings and switchyards can prevent some of the problems encountered with highly saline drift. Whether or not the salt will impact vegetation and ground water, salinity will depend on the increase over the natural deposition of salt on the surrounding terrain.

Fossil-fueled plants have special problems. The stack gases of these plants contain varying amounts of sulfur oxides, depending on the sulfur content of the fuel and the SO_x removal technology present. If the stack gases and the cooling tower fog plume intermix, the fog will pick up sulfur dioxide, forming sulfurous and sulfuric acids. Sice these are corrosive acids, settlement on the surrounding buildings will accelerate deterioration. Vegetation is also affected by this acid fog.

Weather Modification Impact

One of the most noticeable side effects of evaporative cooling towers, spray ponds, and cooling lakes, is fogging. Fog is produced when the warm nearly saturated air from the cooling facility mixes with cooler ambient air. The creation of fog by cooling devices depends primarily on local climatic conditions.

The fog plume from a mechanical draft tower is emitted close to the ground and can drop to the grounder certain conditions. When this happens the fog can create a serious hazard on nearby highways.

The use of natural-draft cooling towers in high potential fog areas seems to be common practice. Since the plumes from the towers are emitted at altitudes of 90 to 150 meters (300 to 500 ft), the plume is normal dispersed before it can reach the ground. Location of 70 percent of the natural draft towers

expected to be constructed through 1977 wukk be in areas of high fog potential. [2]

There are two possible problems with the natural draft tower which are likely to become serious. Although plumes are normally localized, aircraft operation may be impaired due to fogging. Another problem is that the fog may turn to ice upon contacting freezing surfaces, such as highways. This could create a driving hazard.

Although the effects of large thermal releases to the atmosphere cannot be evaluated quantitatively, a number of meteorologists indicate that thermal emissions to the atmosphere could have a significant effect on mesoscale weather phenomena. Some of the artificially produced energy rates are equal in magnitude to those of concentrated natural production rates. [3] It is possible that these thermal discharges may have a "triggering" effect on much larger phenomena, such as thunderstorms or general cloud development and precipitation. With larger and larger stations being build, which will also reject more heat to the atmosphere, weather modification may become a major problem, resulting in anything from mild inconvenience to safety hazards for regional land users.

24-642 O - 73 - pt. 2 - 5

Noise

All cooling towers and powered spray modules produce some noise. Noise from powered spray modules and natural draft cooling towers is primarily from the falling water. In the mechanical draft tower, there is fan noise, and possible noise from high velocity flow of water through the cooling equipment.

Powered spray modules in spray canals are normally located in the banks of the canal, to direct the sound upward with bank surfaces absorbing part of the sound. This cooling system does not present any serious noise problems.

The noise level of cooling towers is of the same order of magnitude as that in the rest of the station. Noise can be a problem in noise-senitive areas. The problem can be alleviated by locating cooling towers away from potential sources of complaints.

Noise problems due to the operation of various types of cooling systems, may prove an irritant to nearby users, if activities associated with the land use are of types disrupted by noise (e.g. homes, camping, picknicking, etc.). However, this problem can be alleviated by site design and incorporation of acoustical features into cooling equipment.

Water Use

Evaporative heat rejections systems depend on availability of water. Consumption of some of the water used occurs through

evaporation and drift. Even the once through system is responsible for consumptive use of water by evaporation during the transfer of heat from the receiving water to the atmosphere.

Consumptive use rates for a 1000 megawatt unit with a closed system varies from 1.3 to 2.1 times that of a river or lake depending on the type of closed system used. Representative consumptive use rates are shown below.[4]

EVAPORATION RATES FOR COOLING SYSTEMS

Cooling System	Evaporation[1] m^3/sec	cfs	MGD	Acre-ft./Year
Cooling Pond (2 acres/MW)	.566	20.0	12.9	14,480
Cooling Pond (L acre/MW)	.453	16.0	10.3	11,584
Mechanical Draft Tower	.368	13.0	8.4	9,412
Spray Pond	.360	12.7	8.2	8,845
Natural Draft Tower	.340	12.0	7.8	8,688
Natural Lake or River	.266	9.4	6.1	6,805

1 For a 1000 MWe fossil-fueled plant at 82 percent capacity factor average annual evaporation (assume constant meteorological condition).

The amount of water consumed depends to some extent on the climatic conditions existing at the site.[5] The use of cooling ponds results in the highest consumptive use since the total consumptive loss is equal to the sum, of the natural evaporation plus that due to heat rejection to the cooling pond. The consumptive use of water in a natural lake or river is low, since the natural losses are not charged against the power station and a significant part of the heat.

There are at present no dry cooling towers at any major U.S. powerplants. Because dry towers do not cause evaporation, such towers may be required in extremely arid regions at some time in the future.

Where water is a scarce resource, consumptive use for cooling may preclude beneficial water uses by industry and agriculture. Excess consumption during period of low streamflow may adversely impact water quality objectives and may increase pressure for phreatophyle control, which may in turn cause fish and wildlife habitat destruction.

Aesthetic Impact

Increased environmental awareness has resulted in concern particularly among the residents of neighboring areas, over the aesthetic appearance of proposed projects. Although natural draft cooling towers cannot be hidden due to their height, they have the merits of low-drift, no fog hazards and dispersal of the heat well above the immediate terrain. Mechanical draft towers will more easily fit into the surrounding area. Landscaping can hide or blend the towers into the terrain. Cooling ponds and spray canals require landscaping but, being at ground level, normally blend into the terrain. Spray canals can be aesthetically pleasing if properly designed. Appropriate landscaping can hide the canal banks and power distribution systems. The sprays themselves can have aesthetic value if arranged in a symmetrical pattern.

Siting of a thermal facility, selection of cooling technology, and site design all must take into account regional impacts of the facility. To do so requires a detailed regional analysis of existing and potential land uses and the susceptibility of these uses to negative impacts due to the operation of the facility.

Alternative Uses

When siting a facility requiring thermal cooling technology, the possible alternative uses of the site and the relative social benefits of each should be considered. Special consideration should be given to this question when rare or valuable historic, natural or recreational resources are involved. In some cases, it may be of more value to society to save such resources for future use or enjoyment than to locate a facility on the site which will prove to be an irretrievable consumptive use of the land. Though this may be a major consideration in the location of many types of permanent facilities, in the case of thermal facilities the problem is exacerbated by the large land requirements of the cooling equipment as well as the environmental and aesthetic impacts of cooling equipment operation.

The land area needed for the installation of cooling systems varies widely. Cooling ponds require large areas, and are usually considered where large quantities of land are economically available. Cooling tower systems also require significant amounts of land but less than cooling ponds.

The mechanical draft tower cell for medium size plants is on the order of 21x12 meters (70x40 ft.). Cells are placed side by side to make up the tower, which can be as much as 180 m. (600 ft.) long, depending on capacity required. For a single tower installation, a circular area with a radius of from 30 to 60 meters (100 to 200 feet) is required around the tower to avoid interference by surrounding structures with tower performance. As a result, 3 to 6 times the area occupied by the tower is required. When two or more towers are necessary, the separation between towers must be 120 to 180 meters (400 to 600 feet) to avoid interference between towers. Total area required for two towers would then be 4 to 7 times the area occupied by towers.[6]

Natural draft towers, which vary in diameter from 108 to 168 meters (350 to 550 ft.), require clear areas with radial distances of 30 m. (100 feet) around tower perimeters. This results in a land area twice the area occupied by the tower. For nuclear units, the tower must be located at a distance equal to its height away from the reactor buildings. The area surrounding the tower become part of the land requirements for the "clear" zone around the reactor. Without restrictions in available land, a 300 megawatt unit using mechanical draft towers might require 3.7 acres. A 600 megawatt unit might require 13.6 acres for mechanical draft towers and 13 acres for two natural draft towers. If land space is restricted there are methods for reducing the acreage used. Surface cooling systems such as the use of pond or canal requires one to two acres per megawatt of capacity depending on climatic conditions. The use of spray modules reduces this land requirement by a factor of about ten.

Projections on the extent of land consumption required by cooling systems varies widely. Teknekron has made projections comparing acreage required for a 1000 MW(e0 plant depending on whether it is nuclear or coal-fired:[8]

	Coal-Fired	Nuclear Plant
Wet Cooling Tower	4-5 acres	6-8 acres
Dry Cooling Tower	9 "	16 "
Cooling Pond	1190 "	2000 "

Certain steps may be undertaken to ameliorate the irretrievable commitment of resources to the facility. For instance, when siting of a power plant on the shoreline will prohibit access to the water for recreational purposes, and will mar the scenic value of the shore for water users, or from vantage points on the opposite shore, it is sometimes possible to set the plant back from the shore, and screen the plant from shore and water view. With adequate steps taken to reduce the intrusive qualities of the plant, it is possible in many cases to provide for several sites uses.

Multiple Use of Sites and Waste Heat

Under certain circumstances, it is possible to redeem a portion of the land resource committed to thermal cooling, through site and facility design providing for multiple use. These beneficial uses fall into two categories: (1) Secondary use of heat otherwise emitted to the atmosphere, and;
(2) multiple use of the site itself.

Waste heat is currently being considered for use in food production. Cooling water used for irrigation can serve to extend the growing season, and cause early seed germination. It can be used in greenhouse heating for year round food production. Ponds and cooling channels may be used to grow commercially valuable fish and shellfish. Currently studies are being conducted to determine the feasibility of increasing Maine Lobster production using waste heat. Cooling ponds or channels may also be used as fish hatcheries.

When power plants are sited near urban areas, particularly new towns designed to utilize waste heat, many beneficial uses may be found. Refrigeration, air conditioning and space heating systems may incorporate waste heat use. In some cases, it could be used to heat pavement for ice and snow removal. Certain industrial processes requiring heat input might also use waste heat. Other possible uses of waste heat include desalinization, sewage sludge drying, and improvement of the biological efficiency of sewage treatment plants.

Multiple uses of sites employing cooling ponds, channels or lakes have already been successfully developed. The variety of uses, obviously depends to a large extent on the size of the impoundment as well as its design.

The discharge basin at the Long Island Lighting Company's Northport plant is being used for production of oysters and hard-shelled clams. The TVA Gallatin steam-electric plant incorporates a facility for testing improved catfish production.

Cooling ponds and lakes have been developed as recreation sites in several regions. Commonwealth Edison of Illinois maintains a 2600 acre lake to provide cooling water for its 1200-megawatt Kincaid generating station. The lake is being developed by the State for fishing, boating, camping and picnicking. As plant and cooling pond sites increase, more varied uses of the water and adjacent shoreline will be possible.

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Section IV. Decision-Making Arrangements for Site Selection and Minimization of Adverse Impacts

The proceeding material in this chapter has covered the thermal effluent provisions of the FWPCA, the specific impacts of thermal control alternatives on land resources, and the relationship of such impacts with adjacent or related land uses, including compatibility, alternative land uses, and multiple use of sites. This section discusses the decision-making arrangements for minimizing adverse land-use impacts relative to location and control technology selection for thermal discharge facilities.

State Power Plant Siting Institutions

In recognition of the important relationship of siting to the dual objectives of providing adequate and reliable electric power while minimizing adverse environmental impacts, several States have taken the initiative to develop a statewide mechanism for siting of power plants. While differing greatly in detail most of those authorities have in common several features including:

1. Adequate consideration of all relevant points of view and background information in decision-making
2. Public participation
3. Bargaining between participants to achieve a viable decision
4. Means of achieving efficient results
5. Timely and judicious decision-making
6. Effectiveness of decision-making in achieving goals

These mechanisms provide an open forum for weighing the costs and benefits of use of a specific site for a power plant. By creating means for public participation it is likely that these new schemes have caused land use questions to become major consideration is future siting decisions.

Utility facility siting is a major land use decision, regardless of who the decision-maker is. As was pointed out in the previous section, the presence of a power plant may preclude some users, or encourage others. Thus, the choice of the site may have wide ramifications for future regional land use.

Relationship Between Powerplant Siting and Statewide Land Use Planning

Utility facility siting is a major land use decision, regardless of who the decision-maker is. As was pointed out the previous section, the presence of a powerplant may preclude some uses, or encourage others. Thus, the choice of the site, may have wide ramifications.

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While currently few States have formal land use planning on a statewide basis, the number is expected to increase, especially if Federal legislation currently being considered is made law. It will therefore be imperative in the future, to either incorporate utility siting into the process of land use planning, or to ensure compatibility between land use planning and utility siting. Otherwise, the overall goal of national use of land resources and protection of the environment will be difficult, if not impossible to achieve.

METHODS OF CONTROL OF THERMAL DISCHARGES

BY

HITTMAN ASSOCIATES, INC.

EPA Review Notice

This report has been reviewed by the Environmental Protection Agency and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

Editor's Preface:

The enclosed report, developed under contract to the Environmental Protection Agency, is by design, a brief overview. Other sections of P.L. 92-500, specifically those dealing with Effluent Guidelines and Problems of Backfitting Power Plants, also have reports being produced which deal with engineering and economic aspects of the control of thermal discharges. These reports, because of their immediate use in setting Effluent Guidelines, are of necessity far more comprehensive. When they are available, they should be used as correlative documents.

Further, it should be appreciated, that under certain conditions, and at certain unique sites, satisfactory water temperature control (in contrast to heat removal) may be attained by once-through systems that involve submerged diffusers or surface jet discharges carefully designed to promote rapid mixing in a minimum volume of receiving water. (Such sites exist in a number of cases alon the Pacific Coast, where deep cold receiving water can be reached in a short economically feasible distance from the shore.) Because such sites are the exception rather than the rule, the technically complex subject of jet plume dispersion prediction and control is not presented in this paper.

24-642 O - 73 - pt. 2 - 6

ABSTRACT

With increasing environmental concern over thermal discharges into our waterways, utilities and industries have been utilizing various methods by which such discharges can be controlled. This report describes thermal pollution control technology as it exists today. The demonstrated technology is described along with on-going research, development, and demonstration efforts. Specific topics addressed in this report include: engineering problems associated with waste heat dissipation; evaporative losses with once-through cooling systems; the characteristics of natural and mechanical draft wet towers, spray ponds and powered spray systems, cooling ponds, natural and mechanical draft dry towers, and hybrid or combined cooling systems; cooling water treatment problems; the beneficial uses of thermally enhanced water; and the technology of power plant intake structures.

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CONTENTS

Section		Page
I	Engineering Problems of Dissipating Heat	1
II	Cooling Methods	23
III	Cooling Water Treatment Problems	55
IV	Problems of Cooling System Backfit	83
V	Beneficial Uses of Waste Heat	89
VI	Technology of Intake Structures	107
VII	Acknowledgments	119
VIII	References	121
IX	Nomenclature	127

FIGURES

Number		Page
1	Rankine Power Conversion Cycle	2
2	Temperature-Entropy Diagram for Rankine Conversion Cycles	4
3	Condenser Cooling Water Requirements	10
4	Heat Transfer Mechanisms of Water Bodies	14
5	Average Annual Lake Evaporation	16
6	Average Annual Runoff	16
7	Types of Natural Draft Wet Towers	24
8	Crossflow Induced Draft Tower	28
9	Types of Heat Rejection System Operation	30
10	Spray Pond	32
11	Cooling Pond Systems	36
12	Indirect, Dry-Type Heat Rejection System with Natural Draft Tower	40
13	Indirect, Dry-Type Heat Rejection System with Mechanical Draft Tower	41
14	Parallel Path Wet-Dry Tower	47
15	Stability Diagram for Calcium Carbonate for Different Alkalinities	59
16	Conventional and Dual-Purpose Steam Turbine Performance	104
17	The Placement and Design of Fish Guidance Systems	108
18	Vertical Travelling Screen	111
19	Plan View of Test Flume Showing Bypass Design With Louver Frame at 20 Degrees to Flow	115

TABLES

Number		Page
1	Magnitude of Thermal Discharge	8
2	Average Daily Natural Evaporative Losses	17
3	Evaporation Rates	20
4	Design Conditions for Natural Draft Wet Towers at Existing Plants	26
5	Plants Over 120 Mw With Dry Cooling Towers	43
6	Comparison Between Characteristics of Wet and Dry Towers	45
7	Economics of Alternative Cooling Methods	50
8	Average Makeup Water Components for Cooling Systems at a Fossil-Fueled Power Plant	70
9	Typical Consumptive Usage in Cooling Water Systems for a Fossil-Fueled Power Station	73
10	Typical Evaporative and Drift Losses in Cooling Systems for 1000 Mwe Fossil-Fueled Power Stations	79
11	Natural Runoff and Projected Consumptive Use of Fresh Water for Steam-Electric Power Generation, 1965-2020	81
12	Energy Use Estimate	90
13	Total Annual Cost Per .4 Hectares (Acre) for Three Crop Protection and Irrigation Systems	92
14	Effects of Soil Heating and Subirrigation on Vegetable Production, Muscle Shoals, Alabama, 1971	93
15	A Comparison of Marketable Crop Yields	95

SECTION I

ENGINEERING PROBLEMS OF DISSIPATING HEAT

Most of the large electrical power generation plants use the Rankine steam-electric power conversion cycle. With the Rankine cycle, high pressure steam is produced in boilers. The high pressure steam is then expanded through turbines in which the thermal energy is converted to mechanical energy. The turbines drive generators which convert the mechanical energy to electrical energy which is distributed to transmission lines for consumer use. Figure 1 is a simplified flow diagram for a typical power plant using the Rankine energy conversion cycle. The thermal discharges from power plants are principally those associated with the steam-electric generation, and the source of this energy is the heat that must be removed in the condenser as discussed later.

The Rankine steam-electric power generation cycle is used with both nuclear and fossil-fired plants. The other types of power plants in use today are primarily diesel plants and gas turbine plants. Diesel plants are generally relatively low capacity and the waste heat from diesel plants is discharged primarily to the air. Gas turbine plants are generally used to meet peak loads, and like diesel plants, heat is rejected primarily to the air. Although water cooling is sometimes used with diesel and gas turbine plants, the thermal discharges from these types of plants are a very small fraction of the energy released to water from Rankine cycle power plants.

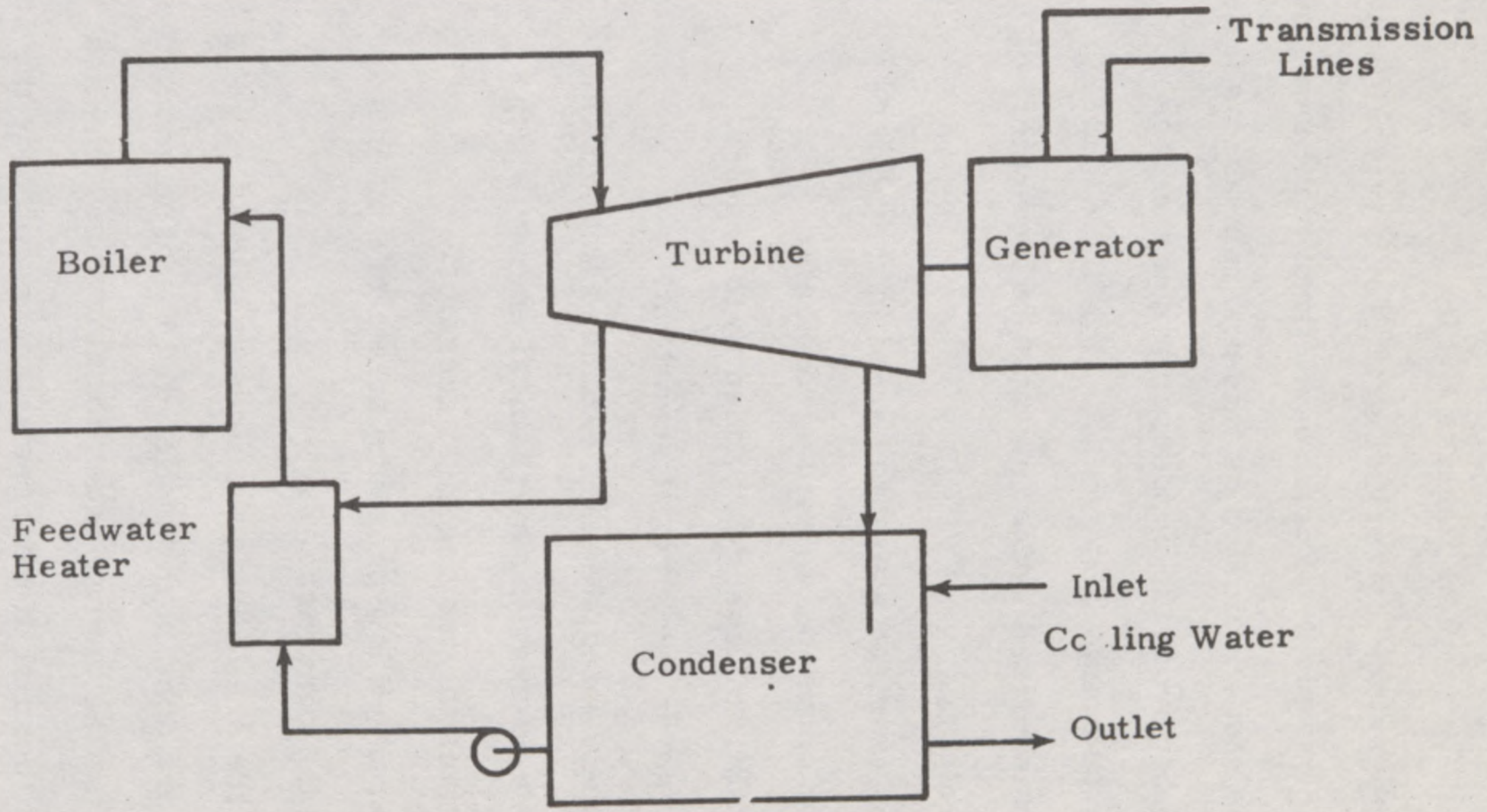


Figure 1. Rankine Power Conversion Cycle

The Rankine Cycle

Figure 2 is a temperature-entropy diagram for a typical Rankine steam-electric power plant. For a fossil-fired plant using superheated steam, the steps indicated by this diagram are as follows:

a to b: Water from the condenser is pressurized by pumping.

b to c': Pressurized water is heated in feedwater heaters.

c' to d': Pressurized water is heated in the boiler and converted to saturated steam.

d' to e': Additional energy is added to the saturated steam in the form of superheat.

e' to f': Superheated steam is expanded through the turbine creating mechanical energy which drives the turbine and generator.

f' to a: Expanded low pressure steam is condensed in the condenser.

In this diagram, the area inside the lines "a-b-c'-d'-e'-f'-a" represents the work done in the cycle, and the area under the lines "a-b-c'-d'-e'-f'" is the energy added to the cycle. The heat rejected and the source of thermal discharges is represented by the area under the line "f'-a." The efficiency of the cycle is the ratio of the work done to the energy added in the cycle.

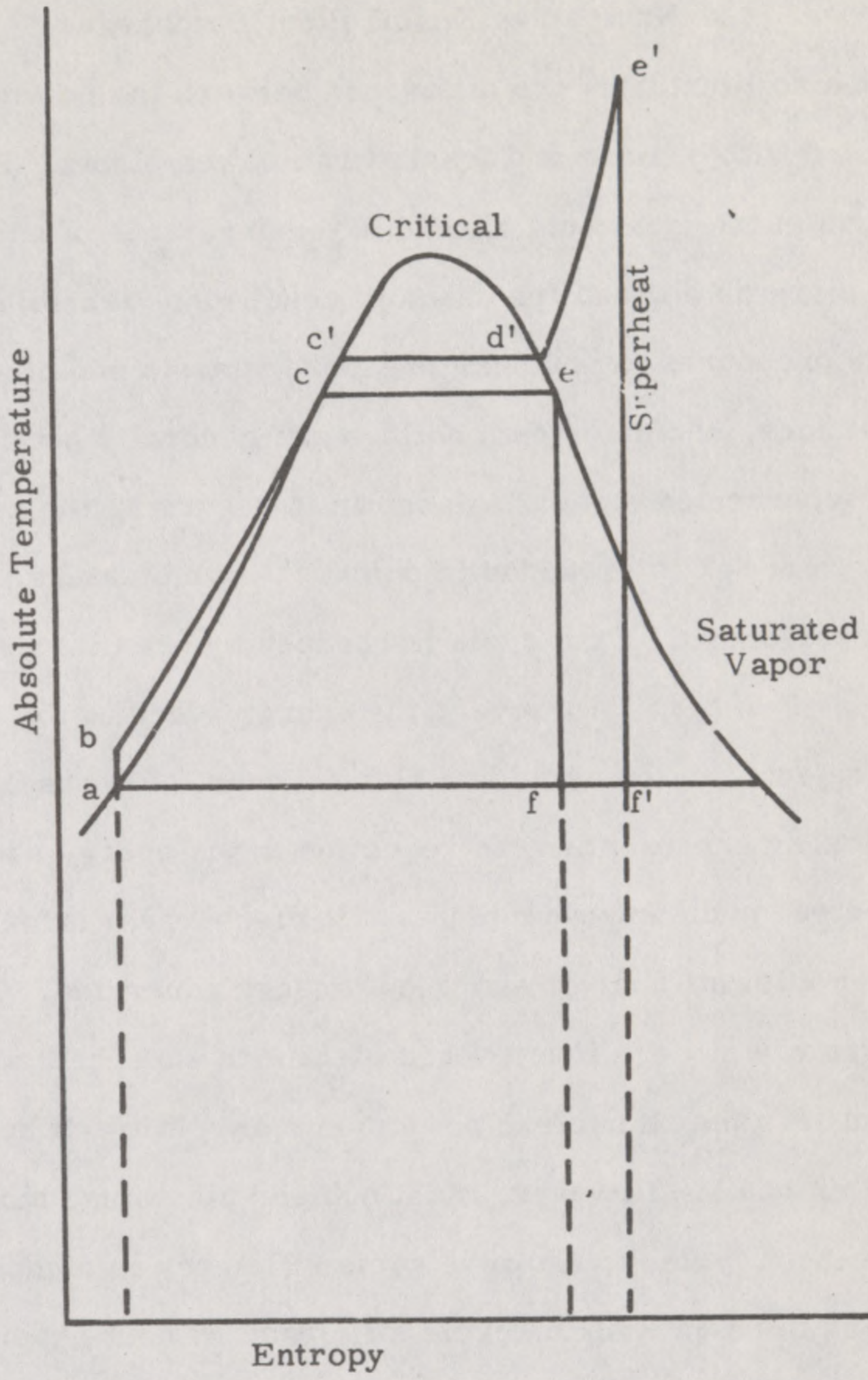


Figure 2. Temperature-Entropy Diagram
for Rankine Conversion Cycles

Nuclear vs Fossil Plant Discharges

Figure 2 also illustrates the difference between the power conversion cycles used with nuclear and fossil-fired power plants. Because of limitations in the maximum allowable temperatures of nuclear fuel, thermal margins allowed for casualty conditions, feasible sizes and allowable pressures for nuclear pressure vessels and other design considerations, nuclear steam boilers are generally not designed to produce superheated steam. As shown in Figure 2, the saturated steam at point "e" is expanded to point "f" in the turbine. As a result, the work performed by the cycle is reduced by area inside lines "c-c'-d'-e'-f'-f-e-c." However, the energy added to the cycle and the heat rejected in the cycle are also reduced. Because the amount of work lost is greater than the reduction in the energy added and the heat rejected, nuclear power plants will discharge a large amount of energy per kilowatt hour of electrical energy generated. Thermal discharges from a modern fossil-fired plant with superheat will be 30 to 50 percent less than a nuclear power plant on a kilowatt hour of electrical output basis. However, most nuclear plants use moisture separation and reheat cycles to improve cycle efficiency to compensate in part for the loss in basic Rankine cycle efficiency without superheat.

Estimating Thermal Discharges

Several terms used in the power generation industry can be used to quantify the magnitude of the thermal discharges from a given power generation plant. These are plant efficiency, cycle efficiency, boiler efficiency, in-plant electrical use, and plant heat rate. The thermal

energy discharged by the plant will be roughly equal to:

Thermal energy discharged = (total energy input) -

(thermal energy loss) - (electrical energy produced) (1)

The total energy input is the heat value of the fuel times the quantity of fuel in the case of fossil-fired plants and is generally expressed as a plant heat rate in kcal or Btu per kilowatt hour. Values are typically 2270 to 2780 kcal (9,000 to 11,000 Btu) per Kw-hr for modern steam power plants. The principal thermal energy other than the energy rejected by the condensers will be the losses from the stack. The amount of this loss is a fraction of the boiler efficiency and, typically 10 to 15 percent of the total energy might be lost in this manner. One Kw-hr of electrical energy is the equivalent of 861 kcal (3413 Btu). For a fossil-fueled plant with a 2400 kcal (~9500 Btu) per Kw-hr heat rate and an 85 percent boiler efficiency, the magnitude of the thermal discharge would be:

2400 - 2400 (1-0.85) - 861 = 1180 kcal (4680 Btu)/Kw-hr(e)

where the electrical energy includes net plant output and inplant electrical use.

The amount of thermal discharge can also be estimated using either the cycle efficiency or plant efficiency with the thermal discharge expressed as:

$$\text{Thermal energy discharged} = [\text{net electrical output} + \text{inplant use}] \times \left(\frac{1}{\text{cycle efficiency}} - 1\right) \quad (2)$$

or:

$$\text{Thermal energy discharged} = \left(\frac{\text{net electrical output}}{\text{overall plant efficiency}}\right) \times$$

(Boiler Efficiency) - (net electrical output + inplant use) (3)

For example, a fossil plant with a 500 Mw(e) net electrical output, an overall plant efficiency of 35 percent, a boiler efficiency of 85 percent, and in-plant electrical uses of 10 percent of net output or 50 Mw(e) will have a thermal energy discharge of:

$$\left(\frac{500}{0.35}\right)(0.85) - (500 + 50) = 665 \text{ Mw(t)}.$$

This thermal energy discharge is equivalent to:

1145 kcal (4540 Btu)/Kw-hr(e).

The methods used with nuclear plants are essentially the same except that nuclear plants do not have thermal losses through stacks. Therefore, this factor is eliminated and the magnitude of the thermal discharges based on input energy is increased accordingly.

Using the methods described above, the quantities of thermal discharge can be estimated for various types of plants. Table I shows the magnitude of the thermal discharge as a function of type of plant, size of plant, and efficiency.

Quantity of Cooling Water

Shell and tube condensers are used with practically all thermal power plants. Cooling water flows inside the tubes and condenses the low pressure expanded steam entering the condenser from the turbine. The steam entering the condenser will have been expanded below saturated conditions. Therefore, a portion will be in the form of moisture and the amount of cooling required to condense the steam will be less than for dry saturated steam. In general, about 555 cal

TABLE 1. MAGNITUDE OF THERMAL DISCHARGE
10^9 kcal/hr (10^9 Btu/hr)

Size (Mwe)	Plant Efficiency 30%	35%	40%	45%
		Fossil		
200	0.33 (1.3)	0.25 (1.0)	0.20 (0.8)	0.15 (0.6)
500	0.82 (3.25)	0.63 (2.5)	0.50 (2.0)	0.38 (1.5)
800	1.31 (5.2)	1.01 (4.0)	0.81 (3.2)	0.61 (2.4)
1000	1.64 (6.5)	1.26 (5.0)	1.01 (4.0)	0.76 (3.0)
		Nuclear		
800	1.51 (6.0)	1.21 (4.8)	0.96 (3.8)	
1000	1.89 (7.5)	1.51 (6.0)	1.21 (4.8)	
1200	2.27 (9.0)	1.82 (7.2)	1.46 (5.)	

Boiler efficiency = 90 percent

In-plant use 10 percent of net electrical output

per gm (1000 Btu per pound) is required to condense the steam and sub-cool it enough to permit the condensate to be pumped from the condenser.

The quantity of water required to condense the steam will be inversely proportional to the temperature rise allowed in the condenser. In this temperature range, one gm of water will remove one cal of energy by being heated one degree centigrade. If a 10 degree temperature rise is allowed, 100 gm of water will be required to condense one gm of steam or remove 1000 cal of thermal energy. The quantity of cooling water required in 800 Mw fossil and nuclear fueled plants as a function of plant efficiency and allowed temperature rise is plotted on Figure 3.

Design Considerations and Constraints

Historically, most steam-electric power generation plants used once-through cooling systems. Cooling water withdrawn from a lake, river, stream, or other body of water was passed through the condenser to remove the energy which must be rejected in the conversion cycle. The heated water was then discharged back into the body of water. With plants of limited capacity, the amount of energy and the quantities of water involved were relatively limited. By limiting the temperature rise, the discharge temperatures could be controlled to limit adverse environmental effects and the temperature could be dissipated from the lake, river, or stream.

With the advent of large power plants, the problems associated with rejection of heat became much more demanding. As shown in Table I, the amount of heat that must be removed is increased significantly.

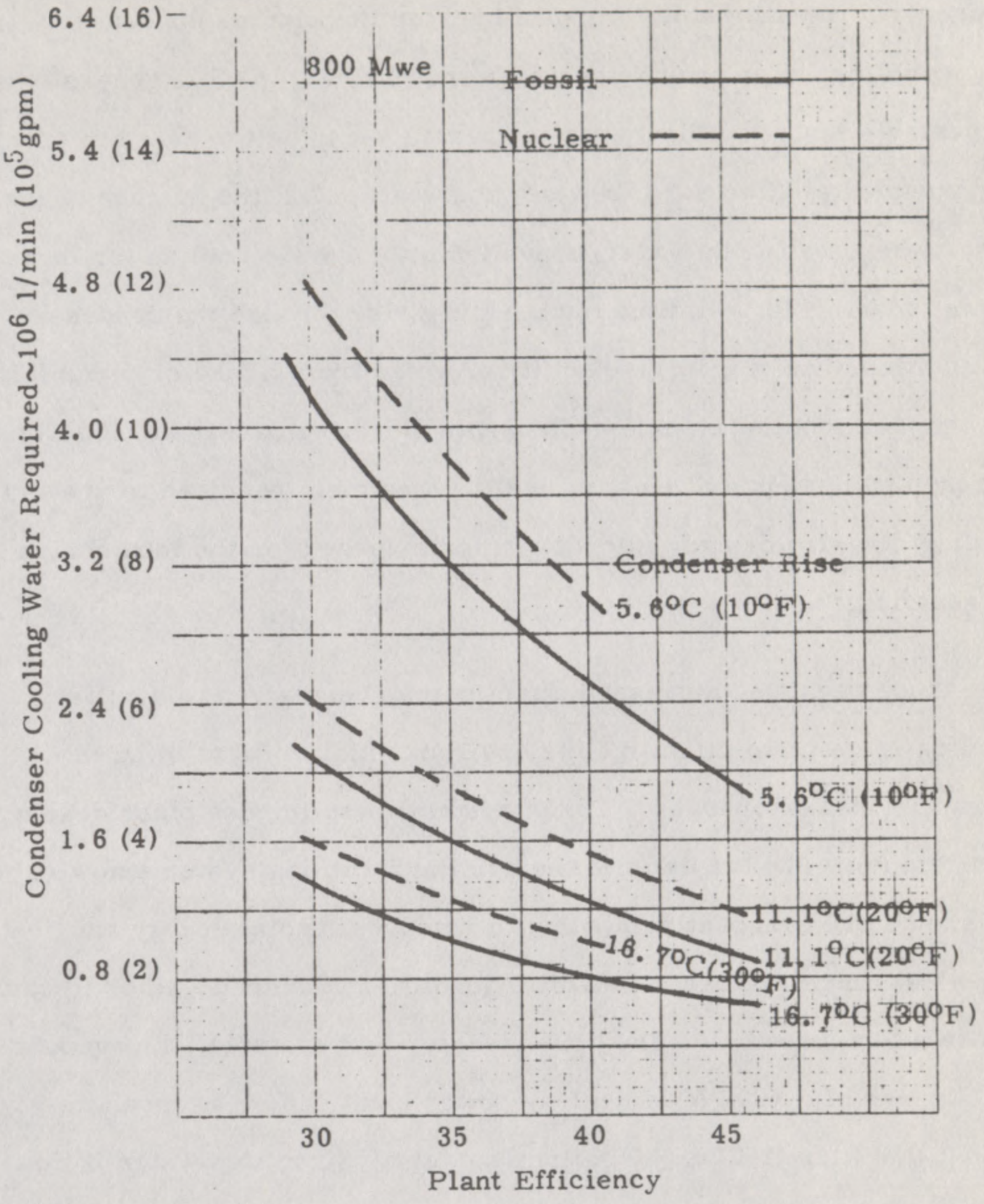


Figure 3. Condenser Cooling Water Requirements

Increasing the allowable temperature rise through the condenser to reduce cooling water requirements as shown in Figure 3 is generally not acceptable since the discharge temperature can be the cause of adverse environmental effects. Likewise, there are a limited number of locations where sufficient water is available to provide cooling for large power plants with a limited temperature rise through the condenser. In addition, use of a large quantity of water from a lake or river for power plant cooling is also undesirable since the passage of the water through pumps and condensers and the treatmert required to prevent fouling can also destroy microorganisms needed for the food chains of aquatic life.

For these reasons, increased attention has been given to auxiliary cooling systems to minimize the environmental impacts of power plant thermal discharges. These systems also impose other design constraints. The majority of the auxiliary cooling systems now in existence use evaporative cooling to remove thermal energy and heat. These systems require substantial quantities of makeup water to compensate for evaporative and drift losses. For example, the evaporative losses of a 1000 Mwe nuclear power plant can be as much as 8,300,000 liter (2,200,000 gallons) per day. Since this water is consumptively used, it is not available for downstream uses. In addition, evaporation removes primarily pure water from the auxiliary cooling system. As a result, the contaminants in the remaining water are concentrated. To inhibit corrosion and fouling, chemicals must be added and the system must be "blown down" periodically to limit the

concentration of contaminants and chemicals. The blowdown can also be a source of water pollution and treatment must be provided before it is discharged.

Auxiliary cooling systems also impose a number of constraints on power plant design and operation. Most cooling systems are "closed cycle" and water is recycled through the cooling system back to the condensers. Because the temperature of cooling towers are limited by wet bulb temperatures and cooling ponds by size, the temperature of the water returning to the condensers is generally higher than with once-through cooling systems. The high temperature of the cooling water causes the condensation temperature and pressure on the steam side of the condenser to be high. In turn, the back pressure on the turbine is increased. As a result, the work done by the cycle and the efficiency are reduced. With the loss of efficiency, more thermal energy must be supplied to produce the same amount of electrical output and the heat removal capacity must also be increased.

In addition to the loss of thermal efficiency, cooling systems also increase the in-plant use of electrical energy. Power is required for the pumps and fans in cooling towers and to circulate the water for cooling and spray ponds. This results in increases in the electrical output, thermal input to the plant, and the amount of thermal energy discharged. A quantitative assessment of the magnitude of some of these effects is included in Section II.

24-642 O - 73 - pt. 2 - 7

Heat Budget

In order to fully appreciate the engineering problems associated with thermal discharges, it is necessary to understand how energy is transferred in natural systems. This is best illustrated by a heat budget or energy balance for a natural water system. Figure 4 shows the source of energy inputs and losses from bodies of water. The net rate of heat transfer, ΔQ, across any water surface can be expressed as:

$$\Delta Q = Q_s - Q_{sr} + Q_a - Q_{ar} - Q_{br} - Q_e - Q_c \qquad (4)$$

Of these terms, Q_s, Q_{sr}, Q_a, and Q_{ar} depend upon solar and atmospheric conditions whereas, Q_{br}, Q_e, and Q_c are temperature dependent terms. When the temperature of the water increases, heat transfer will be increased until an equilibrium condition exists. Under equilibrium conditions, the rate of heat transferred is equal to zero and the water surface temperature remains uniform. This does not mean that no evaporation or conductive losses are taking place at equilibrium conditions. Energy losses can occur under equilibrium conditions which balance the energy inputs from other sources. It is also noted that heat transfer is primarily a surface temperature phenomenon. Because warmer water is less dense, it tends to stratify above colder water unless mixing is present. Accordingly, heat transfer can occur with relatively small changes in the stored energy of the entire body water.

Evaporative Losses of Natural Systems

Evaporation of water occurs nearly continuously in natural areas from both land and bodies of water independent of whether they are used for

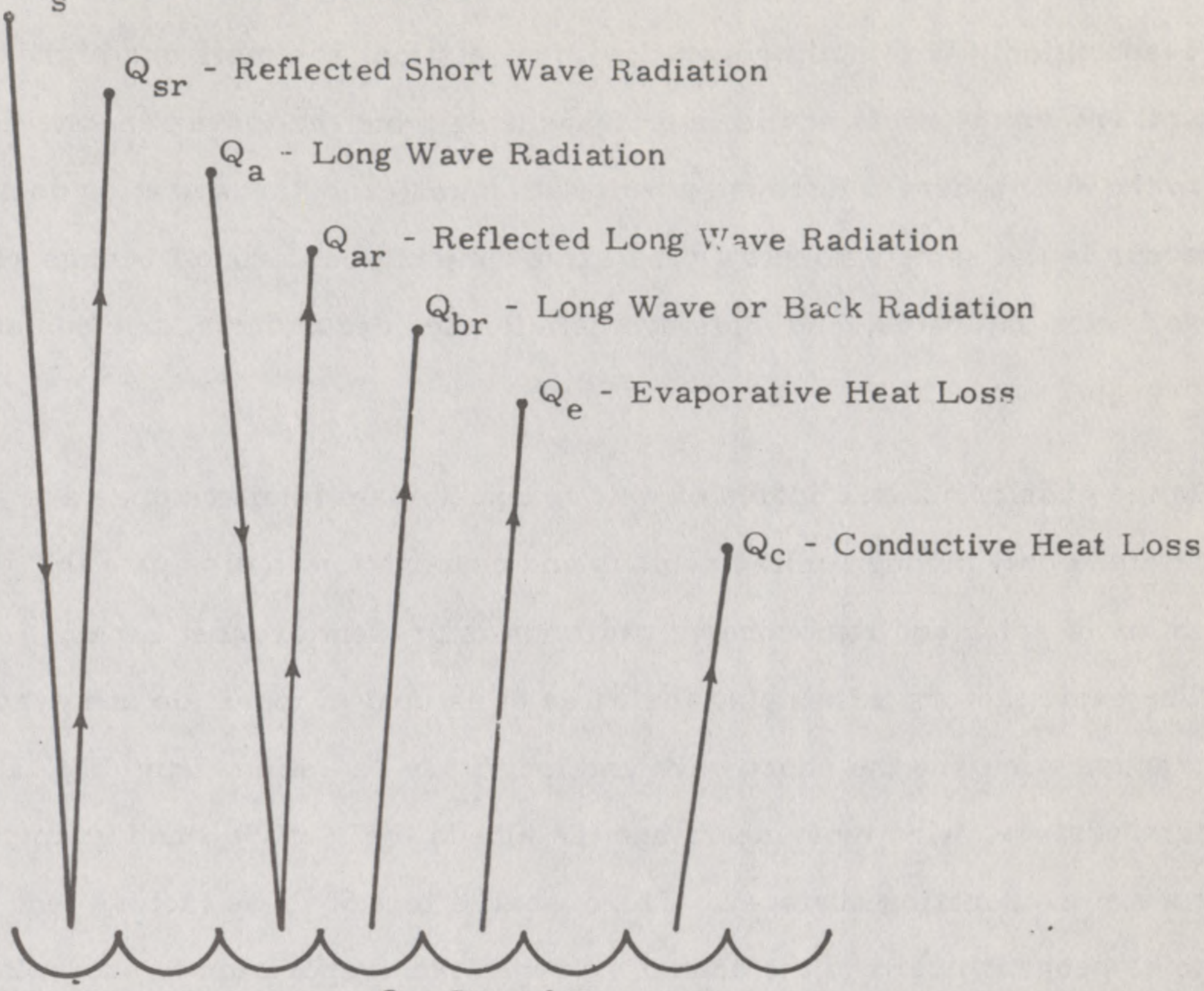


Figure 4. Heat Transfer Mechanisms of Water Bodies

cooling. Solar and atmospheric radiation warms the soil causing evaporation. With soils covered with vegetation, the moisture in the soil enters the roots and is later transpired from the leaves and stems to the atmosphere. Because precipitation and evapotranspiration do not occur in the same amounts or the same time of year, runoff occurs when soils are saturated, and moisture deficiencies occur during periods of drought.

In the case of natural bodies of water, equilibrium temperatures are attained only during limited periods and evaporation to dissipate the influx of solar and atmospheric radiation is present at most times. The basic factors influencing the rates of natural evaporation and evapotranspiration are the short wave and long wave radiation, humidity, air temperature, wind movement, and the albedo (reflectivity) and temperature of evaporating surfaces. The overall effect of these factors tend to be geographical and the annual average lake evaporation is shown in Figure 5, from Reference 1.

To illustrate the magnitude of natural evaporation losses for comparison with the use of once-through cooling and auxiliary cooling systems with power plants, a typical case is assumed. As shown on Figure 5, annual lake evaporation rates of 100 to 125 cm (40 to 50 inches) per year are typical of the midwest and mid Atlantic regions. Cooling ponds for a power plant generally range in size from 0.4 to 0.8 hectares (one to two acres) per Mw of output. If once-through cooling is used, the surface area of the natural body of water associated with the power plant would generally be 1.2 hectares (three acres) per Mw or larger. The

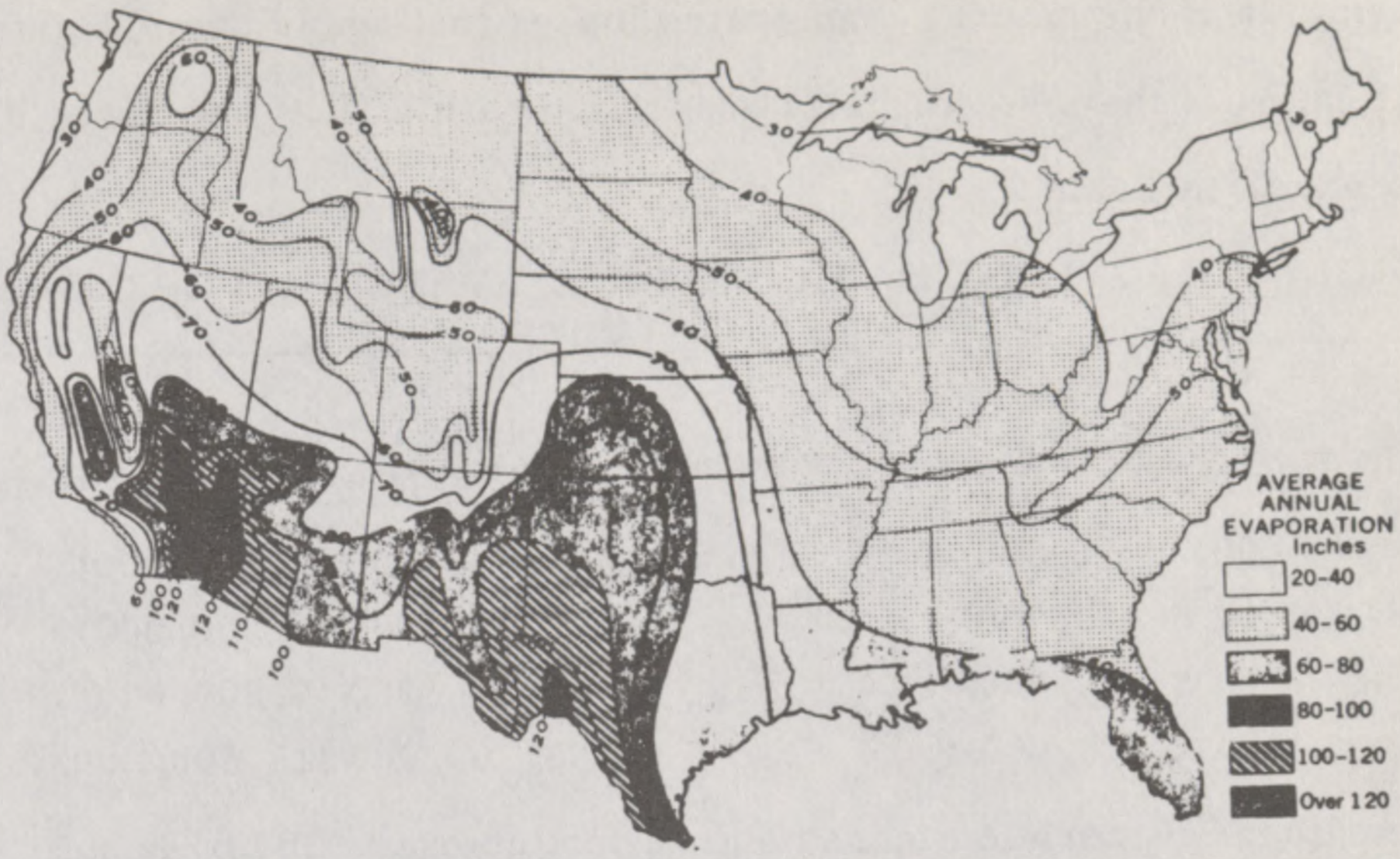


Figure 5. Average Annual Lake Evaporation (Ref. 1)

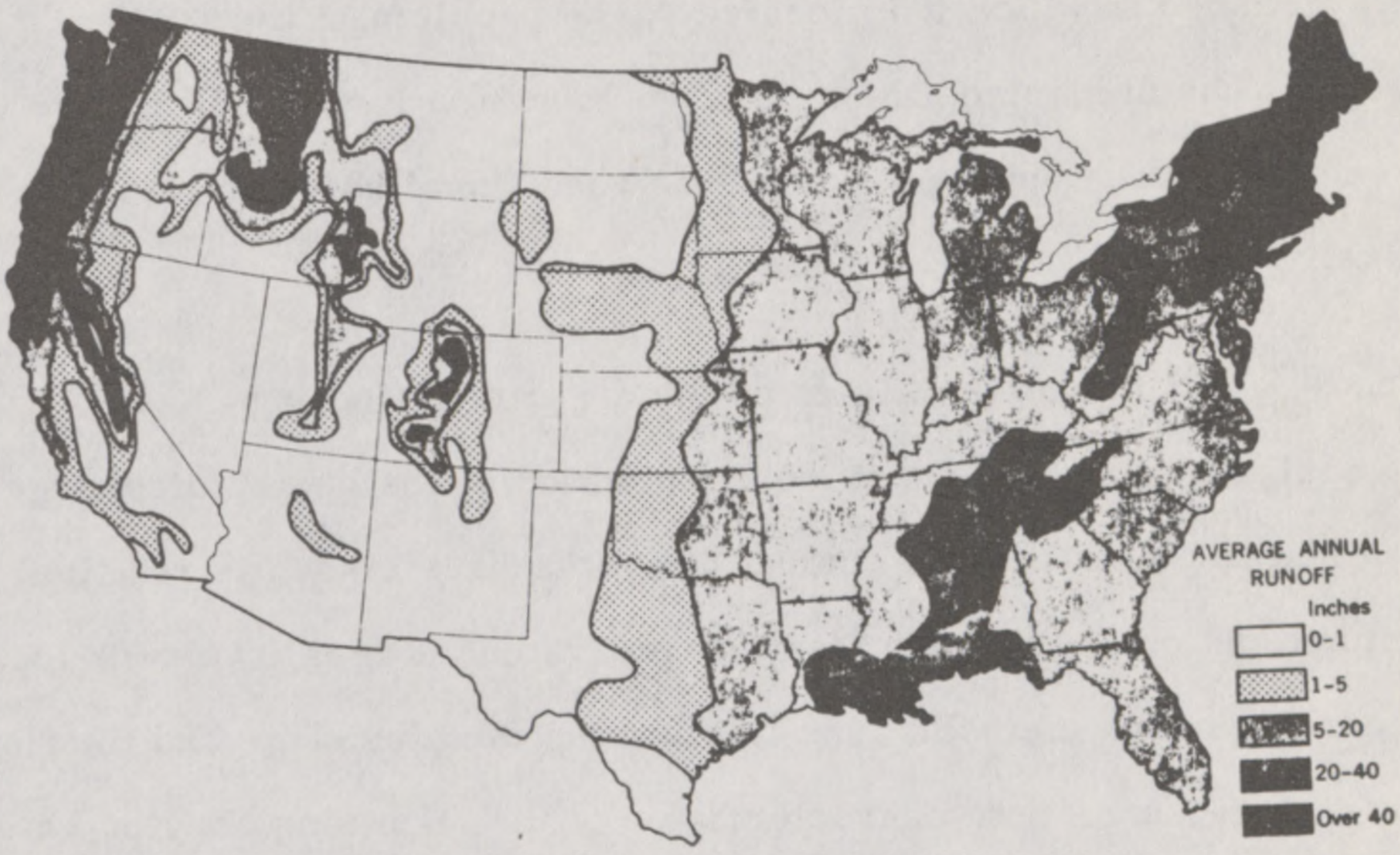


Figure 6. Average Annual Runoff (Ref. 1)

magnitude of the natural evaporative losses that would be associated with lakes of the size normally associated with a 1000 Mw power plant are shown in Table 2.

TABLE 2. AVERAGE DAILY NATURAL EVAPORATIVE LOSSES
100 cm (50 inches) per year)

Lake Area Hectares (Acres)		Natural Evaporation Liter/Day (Gal/Day)
400	(1,000)	11,740,000 (3,100,000)
810	(2,000)	23,500,000 (6,200,000)
1210	(3,000)	35,200,000 (9,300,000)
2020	(5,000)	58,700,000 (15,500,000)

The natural evaporation losses are in part compensated by runoff resulting from precipitation. Figure 6, is a map showing the average annual runoff for various sections of the United States (Ref. 1). It is not possible to relate evaporative loss with the runoff, since the resupply to a specific lake or reservoir will be a function of the size of the watershed in which it is located. The problem in the Southwest region is obvious, since the natural evaporation losses will be two to three times those noted above and the runoff available for resupply is virtually zero.

Evaporative Effects of Once Through Cooling

The analysis of the temperature distribution of the heated discharges from power plants and the amount of evaporative losses is relatively complex and must consider specific geographical area involved, local meteorology, the methods used to disperse the discharge and the flow, temperature, and other characteristics of the receiving body of water. In brief, the accepted analytical methods now in use involve the use of analytical models, physical models, and/or on-site studies to define the

dispersion patterns of the surface and bulk water temperatures. Equilibrium temperatures are calculated based on energy balances along with the lag times required for surface water temperatures to approach equilibrium conditions.

The magnitude of evaporative losses with once-through cooling systems can be illustrated from studies of the water requirements of various types of cooling systems (Ref. 2) and studies made of specific power plant locations. In Reference 2, the evaporative losses of once-through cooling systems are compared for cooling ponds, mechanical draft wet towers, spray ponds, and natural draft wet towers for the following design conditions:

Wet bulb temperature	21°C (70°F)
Relative humidity	60%
Cloud cover	7/10
Wind speed	3.6 m/sec (8 mph)
Cooling range	11°C (20°F)

Based on these specific conditions the water consumptions for the various cooling systems were calculated as follows:

	Liter/Net Kw-hr (Gal/Net Kw-hr)
Cooling ponds (0.8 hectares or 2 acres/Mw)	4.35 (1.15)
Cooling ponds (0.4 hectares or 1 acre/Mw)	3.30 (0.87)
Mechanical draft tower	2.73 (0.72)
Spray ponds	2.58 (0.68)
Natural draft tower	2.42 (0.64)
Once-through cooling	1.89 (0.50)

Average Annual Water Losses

The overall water usage in actual plant applications will generally be much less than those calculated for design conditions for several reasons. Design conditions are generally selected to permit the plant to produce full power 90 to 100 percent of the time during the year. During the majority of the year, conditions will be more favorable than the design conditions. This can be illustrated by considering a study of a 1000 Mwe fossil-fuel power plant made for an actual site (Ref. 3). In this case, the basic design conditions discussed above were used for a plant to be located on Lake Michigan and the following adjustments were made to compute overall water usage on an annual basis.

1. An 82 percent plant capacity factor was assumed.
2. Evaporative losses for wet towers and spray ponds were reduced 20 percent to account for more favorable conditions over the year.
3. Evaporative losses from cooling ponds were reduced to account for the annual average incoming short wave radiation of 4350 kcal per square meter per day (1600 Btu per square foot per day) compared to a design value of about 7600 kcal per square meter per day (2800 Btu per square foot per day) with the difference being equivalent to 285 l/sec (10 cfs) per 405 hectares (1000 acres) pond surface averaged over the year when adjusted for reflective losses.

A comparison of the calculated average annual design evaporative rates averaged for the seven cases is contained in Table 3. In addition to the adjustments noted above, the natural evapotranspiration losses should also be considered in the case of cooling ponds. For this

geographical area, the annual average natural evapotranspiration rate is about 50 cm (20 inches) per year. This equates to 100 1/sec (3.5 cfs) for 600 hectares (1500 acre) ponds and 130 1/sec (4.6 cfs) for 800 hectare (2000 acre) ponds.

Based on these results, it can be concluded that the once-through cooling system will have lower evaporative losses than other cooling systems. However, the difference is not significantly less. Compared to towers and spray channels the difference is only 70 1/sec (2.4 cfs) or 22.5 percent. Where natural evapotranspiration of cooling ponds is considered, once-through cooling is 20 to 30 percent less.

TABLE 3. EVAPORATION RATES
1/sec (cfs)

	Design Condition		Average Annual	
Mechanical draft tower	456	(16.1)	300	(10.6)
Natural draft tower	456	(16.1)	300	(10.6)
Cooling ponds	1050	(37.1)	430	(15.2)
Spray cooling canal	456	(16.1)	300	(10.6)
Once-through cooling	--	--	232	(8.2)

Streams, Rivers, Estuaries, and Oceans

The preceding example considered a power plant sited on a lake. However, the situation would not be appreciably different for streams or rivers. Again, the conditions for the specific site would have to be considered. The evaporative losses with once-through cooling systems would have to consider the quantity of the heated discharge compared to flow of the stream or river, the method of dispersion, amount of stratification or other factors which would influence surface temperatures

and the approach to equilibrium conditions downstream. In this case, the advected energy of the water coming from upstream would be a factor which could reduce the temperatures and the associated evaporative losses.

Estuaries represent a special type of cooling problem in that tidal action can cause flow reversals. This can result in heated discharges being transported to power plant inlets causing losses in efficiency and additional heat loads. Because of the large quantities of water available and natural mixing action in the case of ocean discharges, once-through cooling does not generally present a problem from a temperature or water loss standpoint. The problem is generally one of designing intake and outfall structures to convey the cooling water and discharges to a point sufficiently off shore.

SECTION II

COOLING METHODS

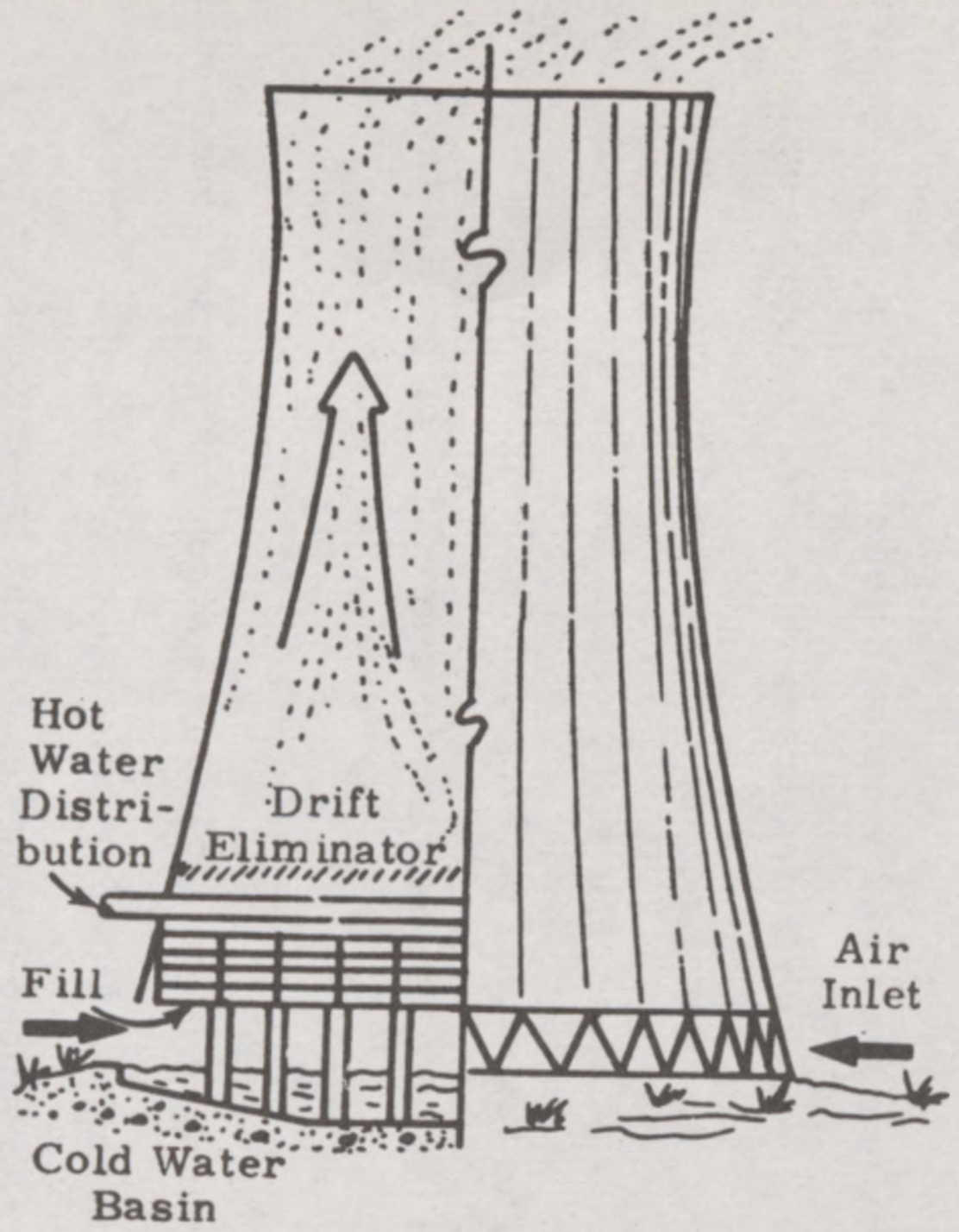
The available cooling methods for removing waste heat from discharged waters are described in this section. Some costs of the alternate cooling methods are presented. There follows a discussion of the makeup water components for the cooling methods.

Natural Draft Wet Towers

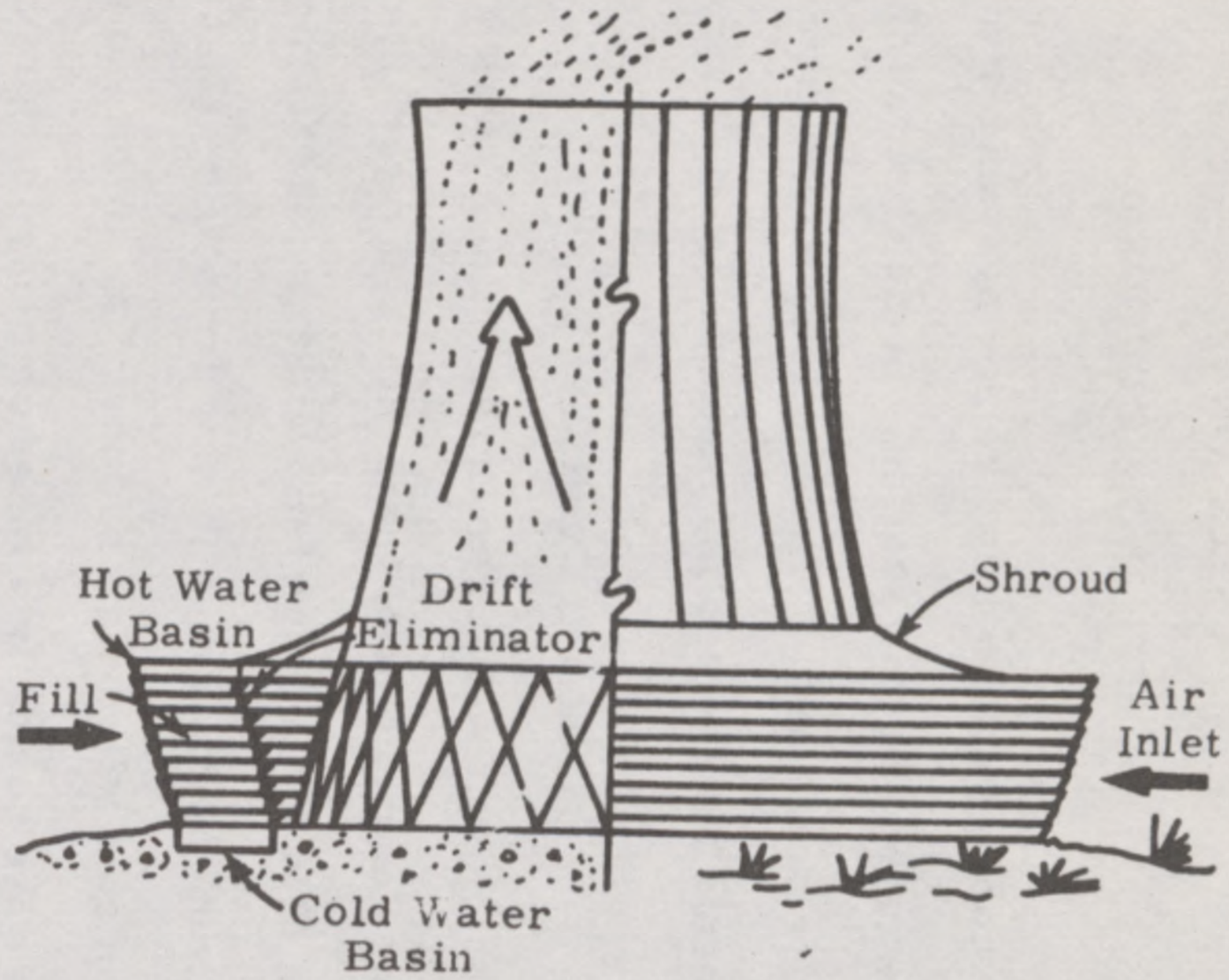
The first natural draft wet tower in the United States was built in late 1962 at the Big Sandy Plant of the Kentucky Power Company. The tower is 74 m (244 ft) in diameter and 98 m (322 ft) high. Currently natural draft wet towers range in size from 76 m (250 ft) to 122 m (400 ft) in diameter with heights from 96 m (320 ft) to nearly 152 m (500 ft). They are basically a large chimney that provides a draft to pull air over a large surface of water.

Natural draft towers are usually constructed from reinforced concrete. The hyperbolic shape distributed across the great height is optimum for aerodynamic and structural reasons rather than thermodynamic. The basic components of counterflow and crossflow tower types are shown in Figure 7. The tower and packing can be designed to operate with air flowing upward through the packing (counterflow) or horizontally across the packing (crossflow).

Among the advantages of natural draft wet towers are long term maintenance free operation, smaller amounts of ground space required for multiple towers, reduced piping costs when towers can be located



Counterflow



Crossflow

Figure 7. Types of Natural Draft Wet Towers

adjacent to plant, no electricity required for operating fans, fewer electrical controls and less mechanical equipment. Disadvantages include a decreased ability to design as precisely as for mechanical draft towers and inability to control outlet temperatures as well as with mechanical draft towers. Also, because of their large size natural draft towers tend to dominate the landscape.

Natural draft wet towers are planned in sizeable numbers (Ref. 4). For nuclear plants, the Atomic Energy Commission (AEC) reports plans for 29 plants with hyperbolic towers. Five of these plants are under construction with none yet in operation. For fossil plants, there were seven hyperbolic towers in use in 1971. The total number of natural draft wet towers including all stages of development is approximately 50.

The design operating conditions for natural draft wet towers at existing power plants are presented in Table 4. The range is the water temperature decrease in the tower. Ranges from 13°C (24°F) to 21°C (38°F) cover those for existing towers. Approach is the difference between the cold water temperature (CWT) out of the tower and the wet bulb temperature (WBT). The WBT, dry bulb temperature (DBT) and the relative humidity are interrelated and are presented on a psychrometric chart. Knowing any two of the parameters, one can determine the third from the chart.

TABLE 4. DESIGN CONDITIONS FOR NATURAL DRAFT WET TOWERS AT EXISTING PLANTS

Plant	Tower Height m (Ft)	Tower Base Diameter m (Ft)	Total Flow Rate 10^6 l/min(10^6 gpm)	Tower Design Basis					
				Range °C(°F)	Approach °C(°F)	WBT °C(°F)	DBT °C(°F)	Relative Humidity %	CWT °C(°F)
Big Sandy No. 1	98(322)	74(244)	0.45(0.12)	13(23)	8(15)	22(72)	26(79.5)	70	31(87)
Keystone Nos. 1&2	99(325)	75(247)	2.12(0.56)	16(28)	10(18)	22(72)	30(86.5)	50	32(90)
Ft. Martin Nos. 1&2	113(371)	115(377)	1.89(0.50)	13(24)	10(18)	22(72)	30(86.5)	50	32(90)
Paradise Nos. 1, 2, &3	133(436)	98(320)	0.98(0.26)	15(27.5)	13(22.6)	23(72.6)	26(78)	78	35(95.2)
Muskingum River	113(371)	120(394)	0.83(0.22)	13(24)	9(16)	21(70)	25(77)	71	30(86)
Big Sandy No. 2	113(371)	121(397)	0.95(0.25)	16(28.7)	9(16)	21(70)	25(77)	71	30(86)
Conemaugh No. 1	113(371)	88(288)	1.06(0.28)	16(28)	10(18)	22(72)	30(86.5)	50	32(90)

670

Mechanical Draft Wet Towers

Mechanical draft wet towers are divided into two categories, forced air flow and induced air flow. Induced draft towers are further subdivided into counterflow and crossflow towers. Induced draft towers are favored over forced draft towers (Ref. 5). Crossflow induced draft towers have advantages over counterflow induced draft towers and are most commonly used. Figure 8 shows the basic arrangement of a crossflow induced draft tower.

Crossflow induced draft towers can usually attain better thermal performance than counterflow towers, i.e., heavier water loadings, longer ranges and closer approaches. For a specified applied horsepower, a greater airflow is possible to crossflow towers because of lower static losses, and thus they are more efficient. Other advantages of the crossflow induced draft tower include low pumping head, convenient arrangement of the distribution system, the fill height approximately equal to the tower height, more airflow per fan horsepower, and the ability to use fans of larger diameter so that fewer cells are required for a given capacity. Disadvantages are an insufficient pressure head on the distribution pans to keep the orifices from becoming clogged and the entire water feed exposed to the air which favors growth of algae. Also a substantial crossflow correction factor needs to be applied to the driving force, particularly where long range and close approach performance are required.

In Reference 4, a table was presented showing a breakdown of the cooling methods planned for turbine generators at power plants 300 Mw and

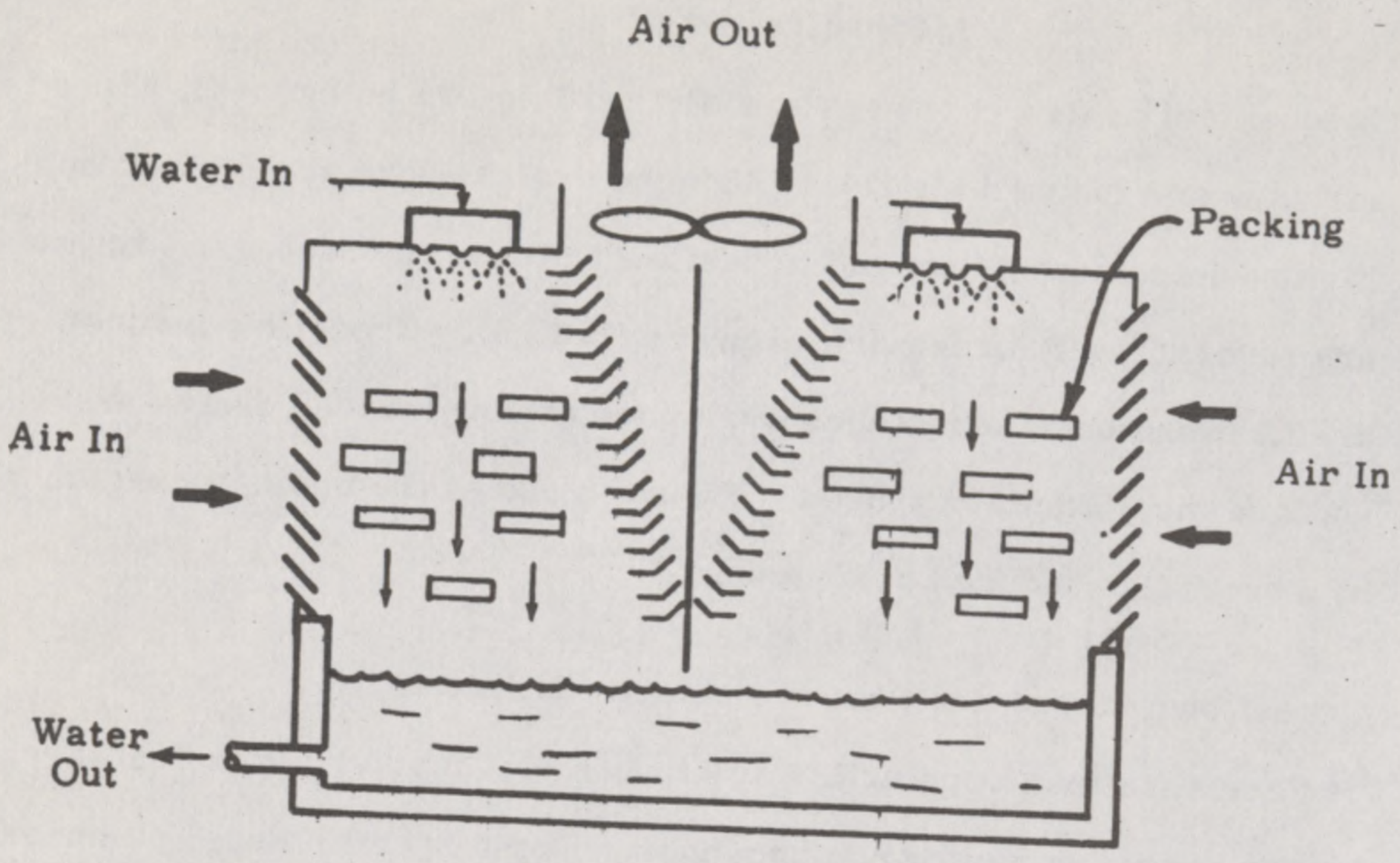


Figure 8. Crossflow Induced Draft Tower

larger on which construction has started or will start within two years. Approximately 115 wet cooling towers are planned. The majority of these would be mechanical draft wet towers.

It was assumed in Reference 6 that wet natural draft towers utilize only the closed cycle mode of operation. However, mechanical draft wet towers, spray ponds, and cooling ponds utilize the closed cycle and open cycle modes of operation. The types of operation for a heat rejection system or cooling method are defined with the aid of Figure 9. Under closed cycle operation the condenser rise is equal to the range of the heat rejection system (wet tower or pond). In the figure, the closed cycle case shows an example where both the range and condenser rise are equal to 14°C (25°F). With evaporative systems, the so called "closed system" is not totally closed since makeup water is required to replace evaporative, drift and blowdown losses.

Open cycle cooling is also illustrated by an example in Figure 9. Hot water from the condenser is passed through a supplementary heat rejection system (wet tower or pond) for cooling prior to discharge into a natural receiving body (stream, river, bay or ocean). An allowable temperature difference is defined as being the temperature of the hot water discharged from the heat rejection system into the stream minus the temperature of the water available from the stream. This allowable temperature difference usually ranges from 0°C (0°F) to 3°C (5°F) maximum and depends upon local state water quality standards. In the example, the discharged water temperature to the stream, 24°C (75°F), minus the available water temperature from the stream, 21°C (70°F), is equal to 3°C (5°F).

24-642 O - 73 - pt. 2 - 8

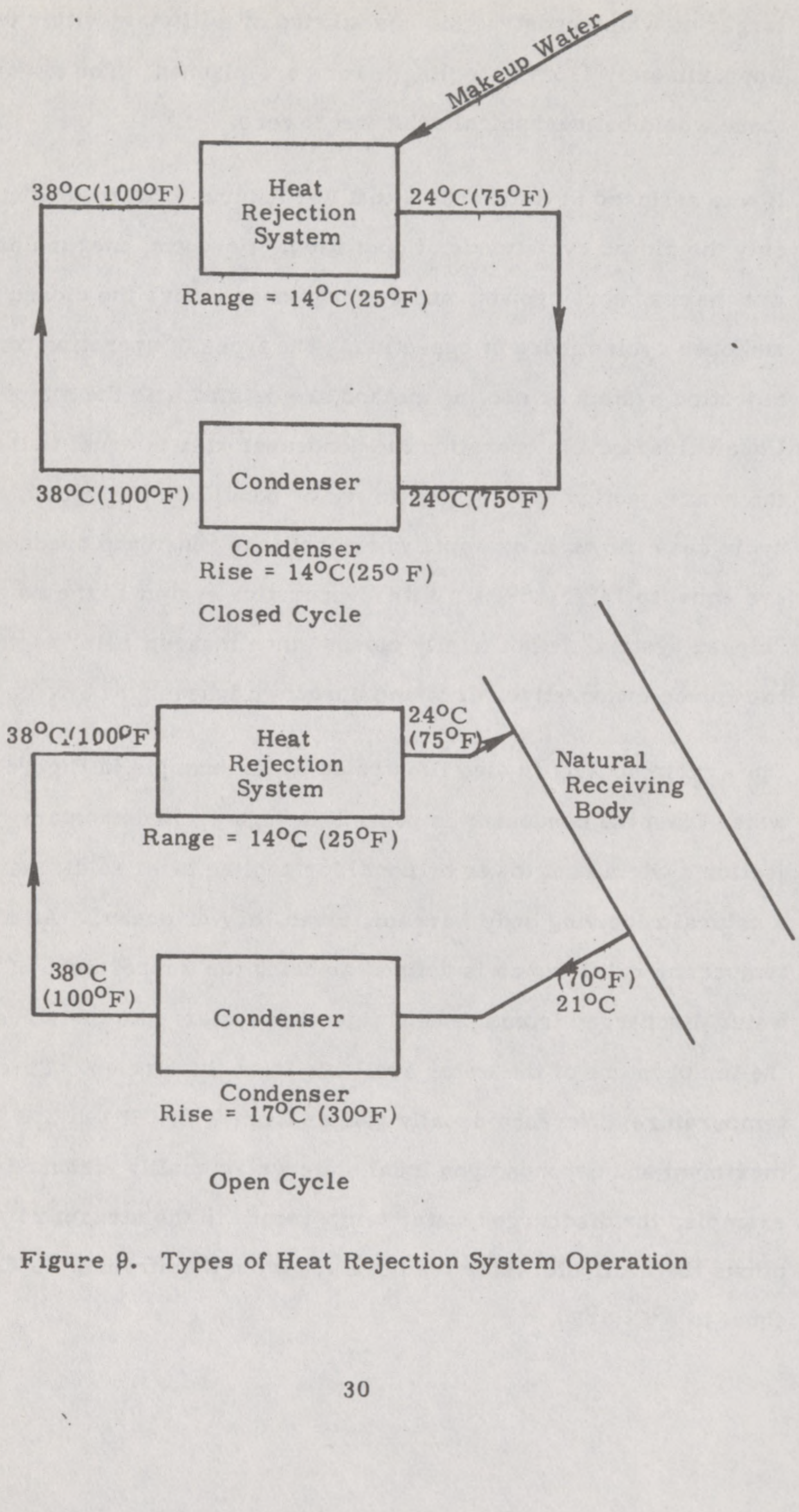


Figure 9. Types of Heat Rejection System Operation

Open cycle cooling has its limitations caused by changing meteorological conditions. It may not work year round. For example, if the wet bulb temperature is 24°C (75°F) and the approach is 5°C (10°F), then the discharge temperature from the heat rejection system would be 29°C (85°F). Water at this temperature would not be allowed to be discharged into the stream if the available water temperature from the stream was 25°C (77°F).

Some power plants can utilize a combination closed cycle and open cycle system. The plant would try to maximize the time during the year where open cycle cooling would take place. However, under adverse meteorological conditions, it would need to close the open cycle loop (utilize the heat rejection system only in Figure 9) when the discharge temperature exceeded that allowed under local water quality standards. Restriction to closed cycle operation might mean that the plant would have to cut back on output (partial load operation to reduce heat rejection).

Once-through cooling is defined as the system wherein cooling water is taken from a natural receiving body, passed through the condenser and finally discharged downstream from the plant. No cooling tower or pond is employed as a heat rejection system. It is estimated in Reference 4 that 113 once-through cooling systems are planned for power plants 300 Mw and larger, on which construction has started or will start within two years. However, the chances are that some of these will be switched to cooling towers by the time all licensing and hearings are concluded.

Spray Ponds and Powered Spray Systems

Spray ponds for utility sites currently are available in two different configurations, conventional spray ponds and powered spray systems, including those produced by Ceramic Cooling Tower Company, Richards of Rockford, and Ashbrook. Also, a spinning disk spray system is being developed by Cherne. In conventional spray ponds, warm water is pumped through pipes from the condenser and then out of the spray nozzles. The nozzles atomize the warm water into fine droplets in the neighborhood of 0.48 cm (3/16 in.) diameter. The power spray systems employ quantities of floating spray modules, with one or more sprays, independently deployed in the warm water discharge canal or reservoir. The modules require mooring and electrical connections to shore.

The basic arrangement of a conventional spray pond is shown in Figure 10. The spray nozzles are usually located 1.5 to 3.0 m (five to 10 ft) above the surface of the pond. Height of the sprays is approximately 2 m (seven ft). The drops move irregularly relative to the air medium and a are more or less deformed, while circulation occurs within the droplets. Heat transfer between the droplets and the medium occurs by the three mechanisms of conduction, convection and radiation.

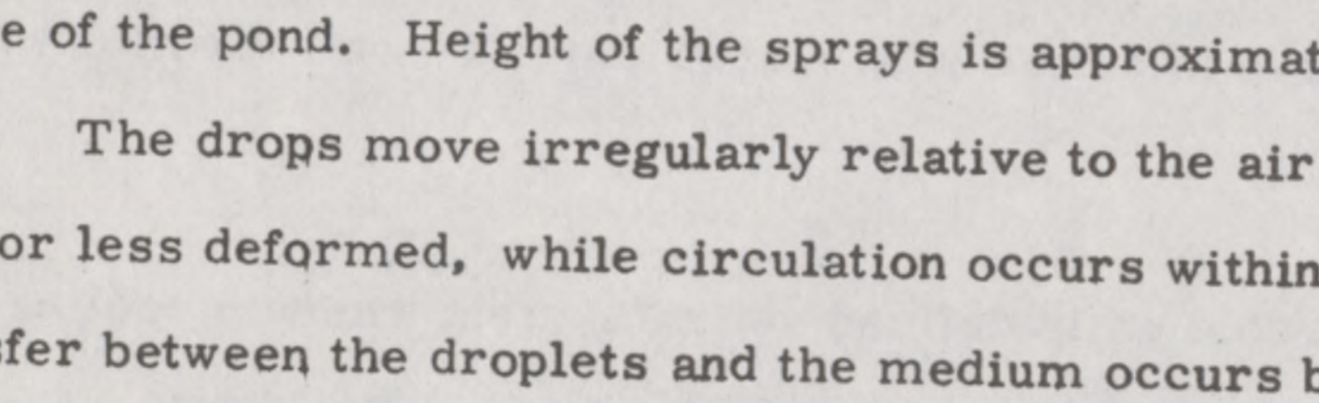


Figure 10. Spray Pond

Performance of the spray pond is a strong function of the design of the nozzles. Poor designs require high pressure and power, do not mix the air and water efficiently, and have excessive water losses. However, water losses can be decreased with the use of louvered fences. Performance is limited by the relatively short contact time between the air and water spray.

An advantage of spray ponds is the requirement for very little maintenance other than occasional cleaning of the pipes and nozzles and routine maintenance on the pumps. However, impurities can easily enter the open water area and be carried into the condenser, increasing maintenance requirements. The disadvantages of the danger of freezing and/or poor heat transfer due to climatic conditions may also occur.

A 4 ha (ten-acre) conventional spray pond is in operation at the Canadys Station of South Carolina Electric and Gas Company (Ref. 7). Condenser cooling water to the 490 Mw plant comes from the Edisto River. The heated discharge water is pumped to the pond where it is spray cooled. The pond can cool 682,000 l/min (180,000 gpm) of water from 38°C (101°F) to 31°C (88°F) with an ambient WBT of 26°C (78°F). This spray pond was built into the once-through cooling system in 1968.

The Powered Spray Module (PSM) system produced by Ceramic Cooling Tower Company (Ref. 8) consists of individual units, each containing four spray nozzles. Various quantities of these units are deployed

depending upon the heat rejection load. PSM systems spray water droplets approximately the size of large marbles and thus minimize drift losses. PSM systems are installed at the following power plant stations in order to cool the plant discharge water:

- Merrimack Station of the Public Service Company of New Hampshire
- Chesterfield Station of the Virginia Electric and Power Company

At Commonwealth Edison Company, a PSM system temporarily served Dresden Units No. 2 and 3 for discharge water cooling while a 556 ha (1375 acre) cooling lake was being constructed. The PSM system will be optimized into the ultimate cooling system by operating in conjunction with the lake.

The basic thermal rotor module developed by Cherne Industrial, Inc. (Ref. 9), consists of round, smooth disks (61 cm or 24 in. diameter) spinning at low speed (600 rpm). Hot water flows by gravity through spouts onto the sides of the spinning disks and is sprayed into the air. As the thermal rotor disks spin, they spread water in one direction thereby inducing significant air currents which bring a continuous stream of cool dry air to the water droplets at all times. A thermal rotor system is made up of any number of modules or units, each 18 m (60 ft) in length, having 150 disks spinning on a common shaft, and driven by a single 37 Kw (50 hp) motor. A production prototype of the system consisting of nine floating units is in operation at the 550 Mw Allen S. King power station of Northern States Power Company. A nine-month demonstration

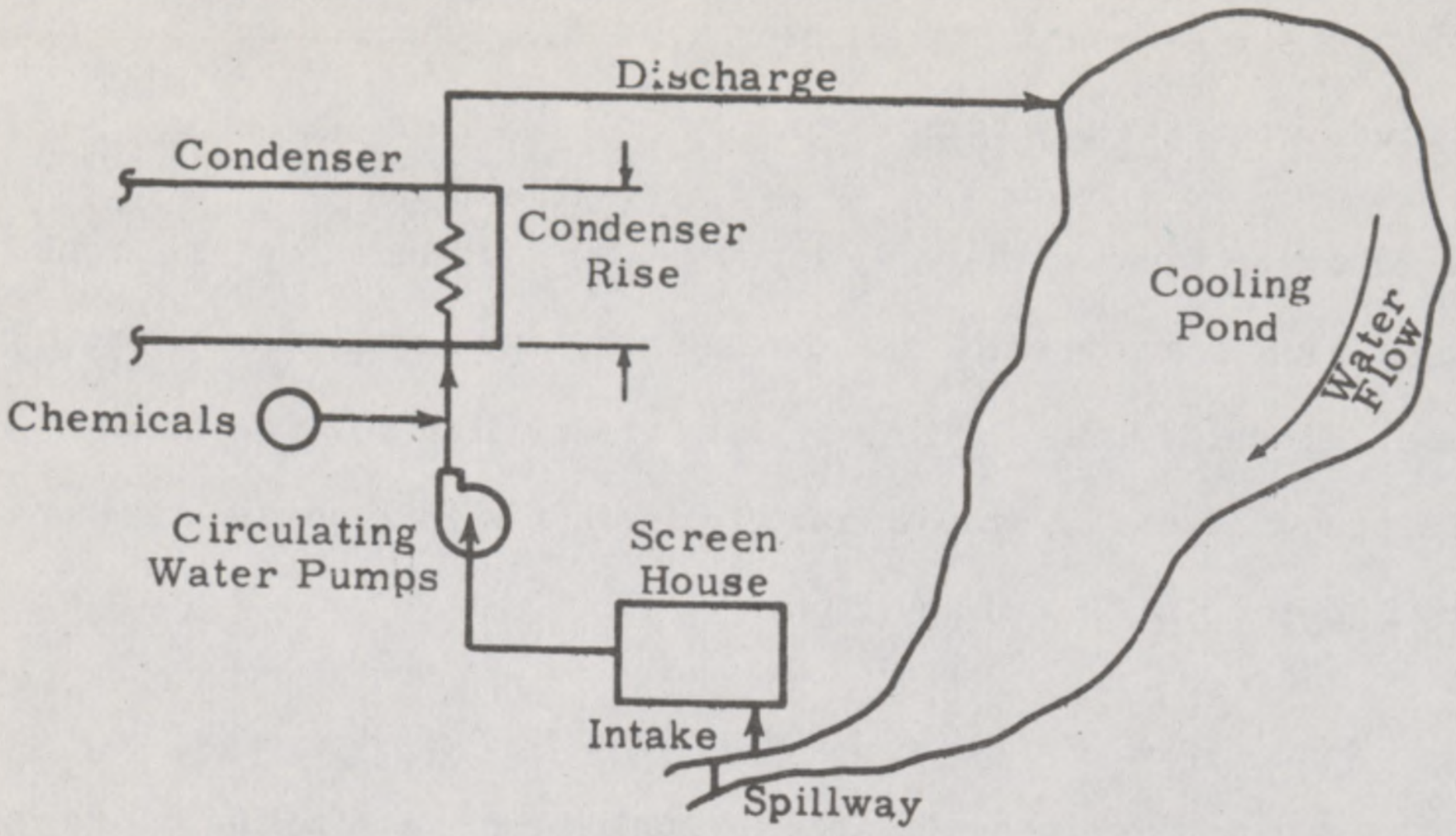
project of the Cherne thermal rotor system, sponsored by 23 electric utilities, was recently completed.

The Albritton floating thermal spray coolers produced by Ashbrook Corporation are currently in the research, development, and testing phase. Modular units for this system are available in four motor horsepower sizes. A unit or model consists of four nozzle assemblies per 19 motor Kw (25 hp) specified.

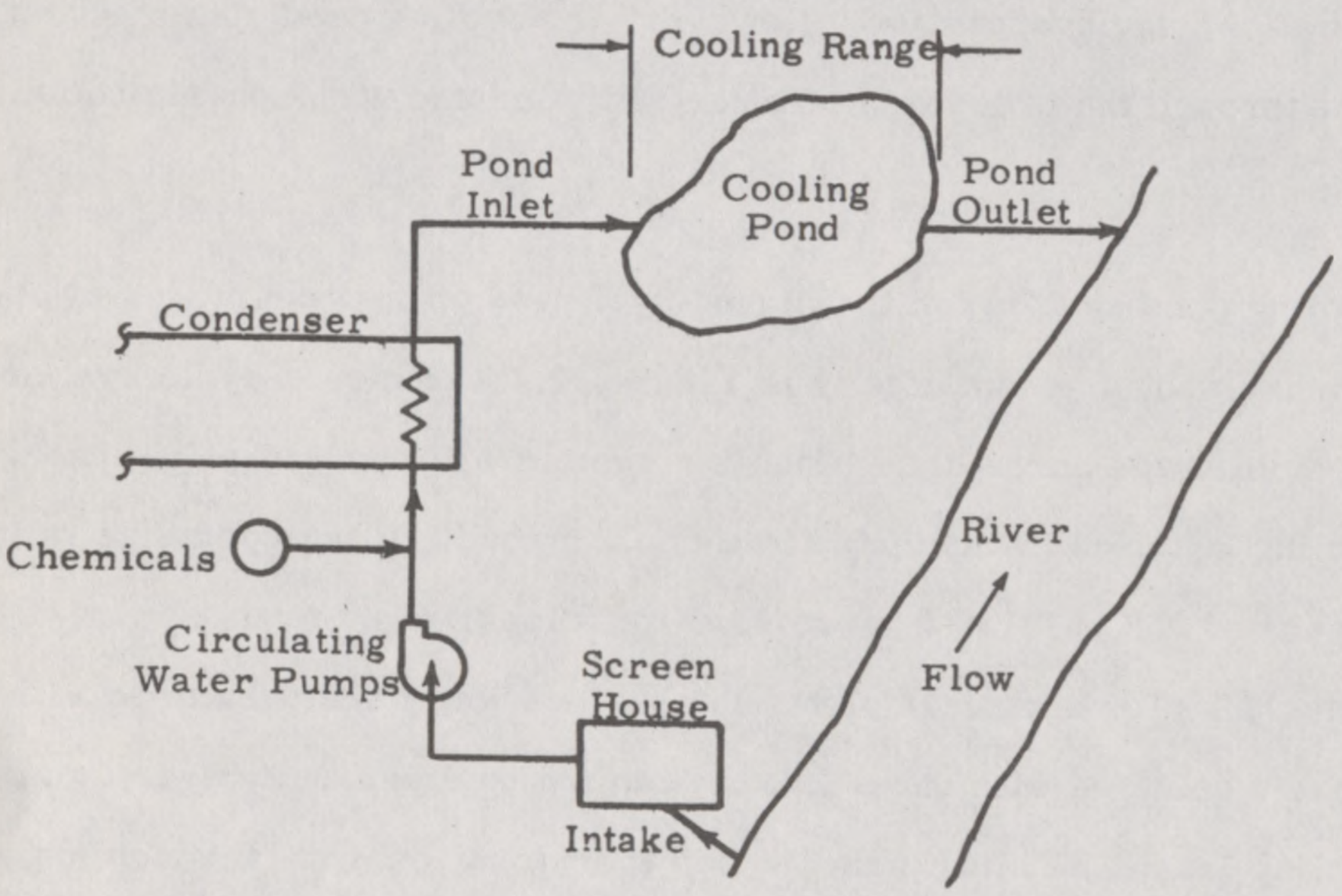
Cooling Ponds

Heat rejection from power plants through the use of cooling ponds is highly dependent upon site weather conditions. The heat is rejected from the pond surface by the natural effects of conduction, convection, radiation, and evaporation. However, the cooling pond also absorbs heat through the processes of solar radiation and atmospheric radiation to the pond.

Cooling pond systems in the closed cycle and open cycle modes of operation are shown schematically in Figure 11. The closed cycle system resembles the once-through cooling system with the exception that the cooling water is recirculated in a cooling pond. If the pond size is in excess of 0.8 ha/Mw (2 acres/Mw) for a fossil plant or 1.2 ha/Mw (3 acres/Mw) for a nuclear plant, the surface water temperatures will closely coincide with once-through cooling systems. However, many cooling lakes are much smaller and therefore, operate at much higher surface water temperatures.



Closed Cycle



Open Cycle

Figure 11. Cooling Pond Systems

Advantages of using cooling pond systems are: reasonable construction costs where soil conditions permit, their service as a settling basin for suspended solids, potential operation for extended periods without makeup water, and benefits from other purposes such as recreation. Disadvantages of cooling pond systems are: the requirement for large land area and the requirement for a soil basin of low permeability.

According to Reference 4, 57 cooling lakes are planned for power plants 300 Mw and larger on which construction has started or will start within two years.

Cooling ponds can be classified, on the basis of circulation pattern and temperature distribution, as completely mixed ponds and flow-through ponds (Ref. 10). In a completely mixed pond the flow between the inlet and outlet locations of the pond combined with wind mixing tend to keep the pond at a nearly uniform temperature. The drop in the temperature from the plant discharge temperature to the pond temperature takes place in a small portion of the pond. This condition seems to exist in ponds where the surface area is large compared to the water flow rate from the plant and the pond temperature is uniformly 0.6 to 1°C (1 to 2°F) above the equilibrium temperature. The equilibrium temperature, E, is defined as the pond surface temperature for which the heat leaving will exactly equal the heat entering a body of water.

In a flow-through pond the temperatures decrease continually along the pond. The pond effluent can either be returned to the plant intake

(closed cycle) or discharged to a natural receiving body (open cycle). The amount of temperature drop from one end of the pond to the other depends upon the water flow rate and the pond surface area. For a given pond volume and similar meteorological conditions, a pond with greater surface area and hence less depth will provide a greater temperature drop. The rate at which heat is lost decreases from the pond inlet to the pond outlet because the temperature excess gradually decreases along the pond. Flow-through ponds are more common.

A designer can estimate the size of a pond for his fossil or nuclear plant by determining the pond loading or Mw/ha (Mw/acre). For a flow-through pond under closed cycle operation, the pond loading depends upon the condenser rise, the residual temperature rise, ΔT, and the heat exchange coefficient. Residual temperature rise is defined as:

ΔT = pond outlet temperature - design equilibrium temperature (5)

It is similar to the "approach" parameter specified for the wet cooling towers and spray ponds. The heat exchange coefficient, k, describes the rate of heat lost across the air-water interface per unit area per unit temperature increase and depends upon the local site meteorology. For the sizing of open cycle, flow-through cooling ponds, the pond loading also depends upon the temperature of the water available from the stream in addition to condenser rise, ΔT and k.

Natural and Mechanical Draft Dry Towers

In the natural and mechanical draft dry tower heat rejection systems, the circulating water never comes into direct contact with the cooling air. Condensation by air cooling has been used in small industrial power plants for over 50 years. However, the application of air cooling to relatively large generating units has been limited. There are two basic types of air-cooled condensing systems, the indirect system and the direct system. The indirect system uses a condenser at the turbine to condense the exhaust steam. It is often referred to as the Heller system since the concept to use the indirect system of condensation by air cooling with a steam turbine generator was presented by Dr. Laszlo Heller in 1956. In the direct system, steam is condensed in the tower cooling coils without the use of a condenser or circulating water.

Indirect, dry-type heat rejection systems with a natural draft tower and with a mechanical draft tower are shown schematically in Figures 12 and 13, respectively. These diagrams present the principal components for the indirect systems according to Reference 11. Water from the condenser is pumped to the dry-type tower for cooling. Water from the tower cooling coils is sprayed into the direct contact steam condenser and mixes directly with the exhaust steam from the turbine. The water of condensate purity falls to the bottom where it is removed by circulating and condensate pumps. The greater part of the water flows through the pipes back to the cooling coils in the tower, and an amount equal to the exhaust steam from the turbine is directed back to the boiler feedwater circuit.

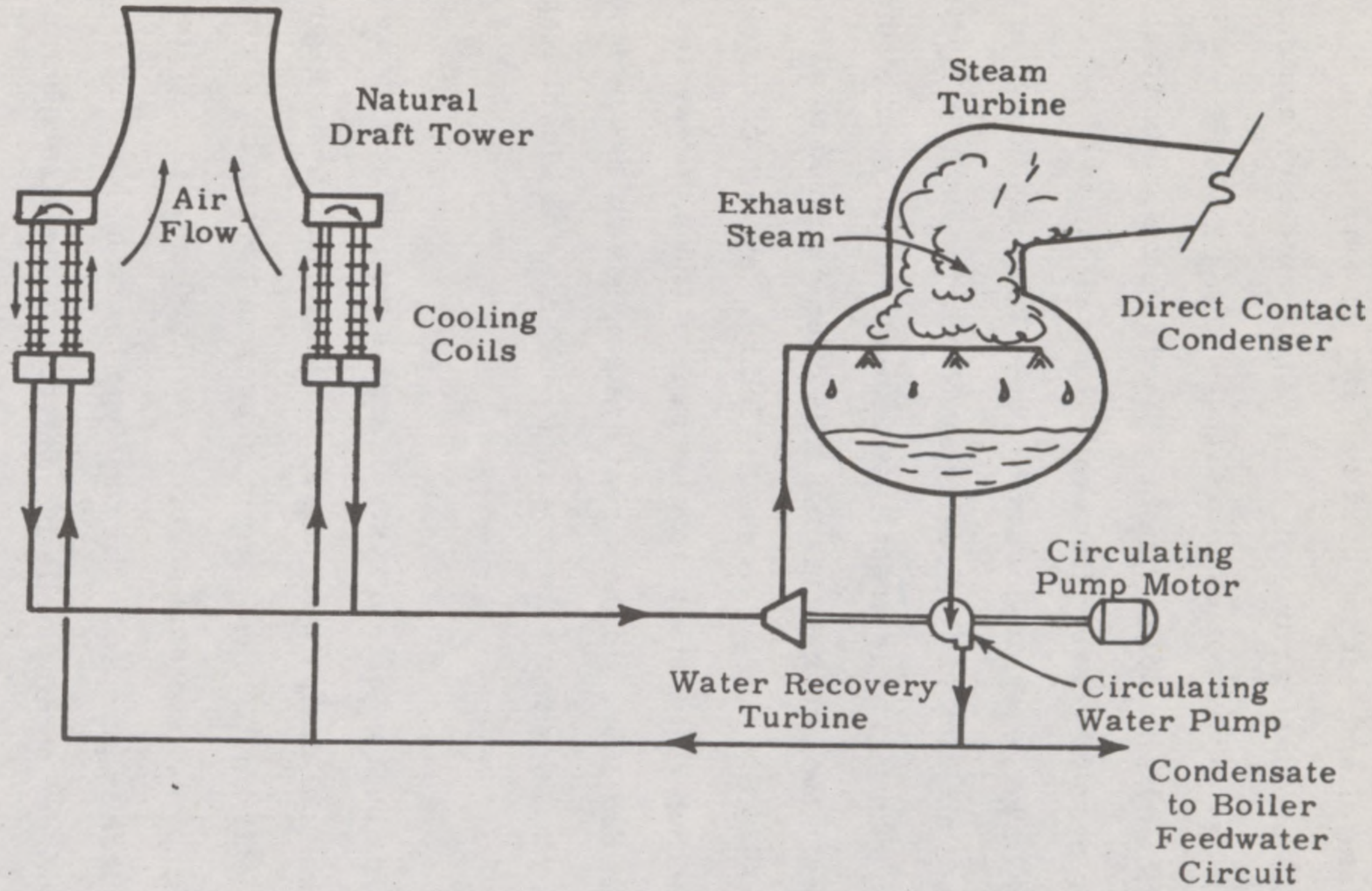


Figure 12. Indirect, Dry-Type Heat Rejection System with Natural Draft Tower

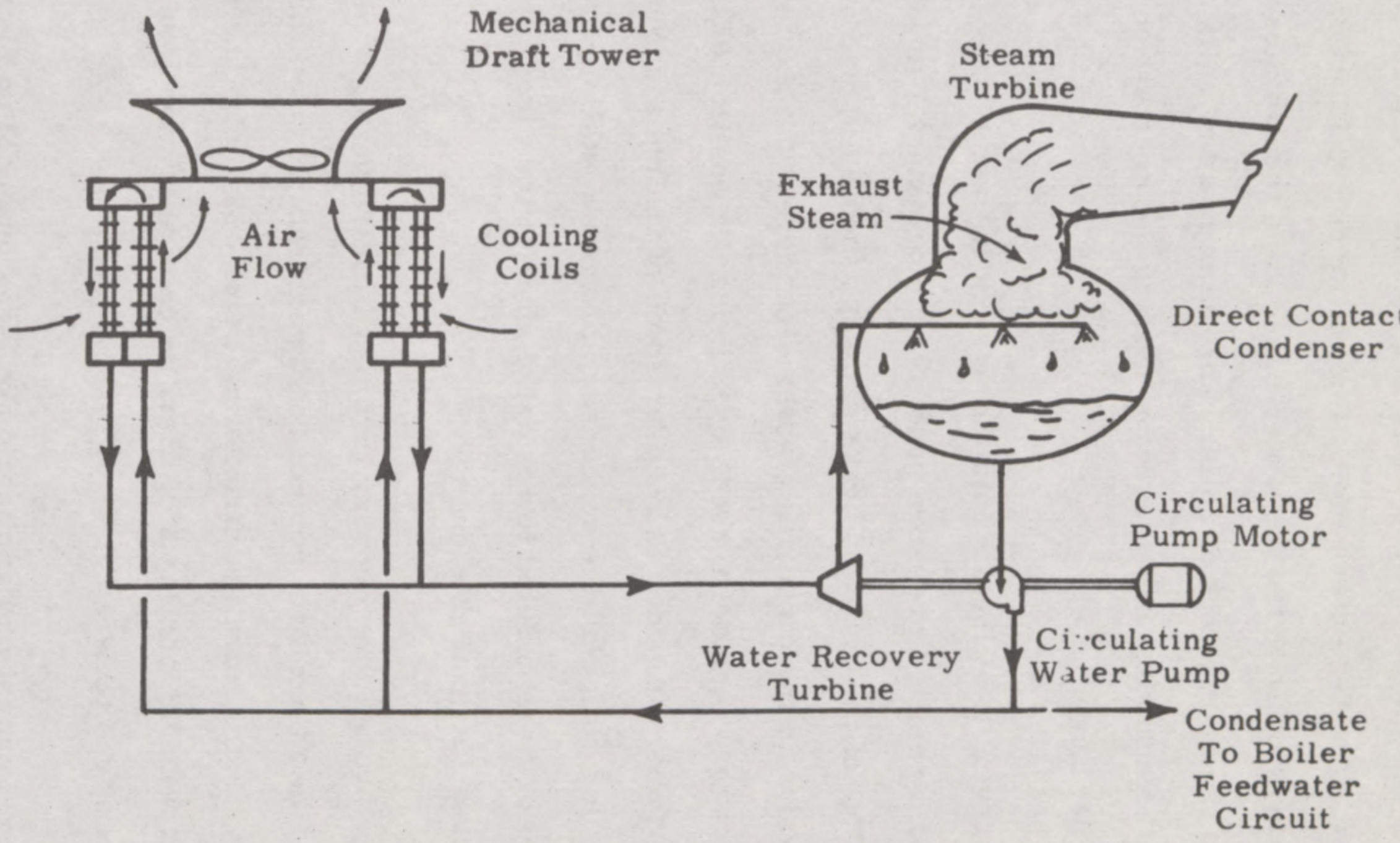


Figure 13. Indirect, Dry-Type Heat Rejection System with Mechanical Draft Tower

In the Heller system, the cooling coils are mounted vertically, and the warm circulating water enters the bottom of the coils, flows upward in the inner rows of coils to the top water boxes, and then is directed downward through the outer rows of coils. The outer rows of coils come into contact with the entering air, thereby providing the greatest cooling range in water temperature.

In order to prevent drawing air into the system in case of leaks in the cooling coils, a positive pressure head of approximately 1 m (3 ft) is imposed at the top of the coils. This is accomplished by means of either a throttling valve in the circulating water discharge from the tower, or, if a water recovery turbine is used, by varying the position of the adjustable turbine vanes. In order to recover some of the pressure head between the cooling coils and the condenser, in some installations water recovery turbines are coupled to the drive shaft of the circulating water pump to recover the available energy.

After passing through the recovery turbine, the circulating water is again sprayed into the direct contact condenser and recycled through the cooling system. Since the circulating water does not come into direct contact with the cooling air, there is no evaporative loss of water as with the wet-type towers.

The major development and application of large dry cooling towers has occurred in other countries. Table 5 presents the plants over 120 Mw in capacity and the types of dry towers employed. The largest dry tower system in the United States was installed in the Neil Simpson power plant of the Black Hills Power and Light Company at Wyodak, Wyoming. The

Company's Unit No. 4, a 20-Mw turbine-generator set, utilizes a direct, air-cooled steam condenser supplied by GEA of Germany. The 20 Mw unit went into commercial operation in December 1969.

TABLE 5. PLANTS OVER 120 MW WITH DRY COOLING TOWERS

Location	Rating Mw	Type of Dry Tower	Year Commissioned
Rugeley, England	120	Heller, natural draft	1962
Ibbenburen, Germany	150	Heller, natural draft	1967
Grootvlei, South Africa	200	MAN/Birwelco (Indirect)	1971
Gyongyos, Hungary	2 x 100	Heller, natural draft	1969
	2 x 200	Heller, natural draft	1972
Razdan, USSR	3 x 220	Heller, natural draft	1970, 1971, 1972

The future for large dry cooling towers in the United States may get a boost from several directions (Ref. 12). The first is the potential role in the nation's energy crisis of the development of the large low-sulfur coal deposits and minemouth power generation of the arid West (particularly the Powder River Basin). Secondly, Reference 13 described the aluminum-covered, steel natural draft tower structures designed to withstand high seismic and high wind loadings at the USSR's Razdan Plant. Hurricane and tornado resistance has been a deterrent to natural draft towers in some parts of the United States. Reference 13 reported that the Razdan natural draft cooling tower experience confirmed that cooling towers may be constructed even for 800 to 1200 Mw

capacities. The structural characteristics of towers much larger than that for the Razdan plant were assessed through computer analysis. The conclusion was that steel structures offer definite advantages over reinforced-concrete structures in reaching these larger sizes.

The performance of dry-type towers is governed by the following equation (Ref. 8):

$$ITD = AQ^b \qquad (5)$$

where:

ITD = initial temperature difference, ^oC (^oF)

= steam saturation temperature - dry bulb temperature

A = tower constant

Q = heat rejection rate, Kw (10^6 Btu/hr)

b = exponent dependent upon natural or mechanical draft towers

ITD is the design approach parameter for dry towers

Combined Cooling Systems or Wet-Dry Towers

The combined cooling system for removal of waste heat from discharged water consists of a combination of wet towers and dry towers. The wet-dry tower has several desirable characteristics which the dry tower and wet tower individually do not possess. Table 6 (Ref. 14) compares characteristics between dry and wet cooling towers. The combined cooling system presents a desirable happy medium between the performance extremes noted in the table.

TABLE 6. COMPARISON BETWEEN CHARACTERISTICS OF WET AND DRY TOWERS

Characteristic	Dry Towers	Wet Towers
Condenser Pressure	High	Low
Sensitivity of Plant Performance to the Ambient DBT	High	Very Low
Demand for Water Supply	None	Moderate
Vapor Plume with Potential for Fogging and/or Icing	No	Yes
Thermal Discharge to Natural Water Body	No	Yes
Blowdown Chemical Treatment	No	Yes
Drift Loss of Water	No	Yes

Combined cooling systems can be classified on the basis of the connection of fluid (water, air) flow circuits (series and/or parallel).

Parallel-flow designs have separate air passages through the convective (dry) and evaporative (wet) sections and rely on the fan to mix the warm dry air of low relative humidity with the warm saturated air. In series flow designs, the dry cooling section can be located either behind or ahead of the wet cooling section.

Combined cooling systems are also classified on the basis of the operating modes (Ref. 14). These modes are:

(1) The combined system with the dry tower as the helper

(2) The combined system with the wet tower as the helper

(3) The combined system with the wet tower and the dry tower operating continuously.

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There are several possible objectives for using the combined cooling system for removing waste heat from power plants. These objectives are:

(1) To incorporate dry towers into the wet cooling system in order to reduce or eliminate the vapor plume from towers

(2) To construct power plants at the location where not enough water is available for the wet cooling system

(3) To incorporate wet towers in the dry cooling system in order to reduce the condenser pressure

The Parallel Path Wet Dry (PPWD) cooling tower, being developed by Marley (Ref. 15), is shown in Figure 14. The design enables ambient air to be drawn through both the dry and wet sections in parallel paths. The air streams converge and are mixed within the cooling tower plenum before discharging to the atmosphere. The hot water to be cooled is passed through the dry air-cooled section and then through the wet section of the cooling tower. The heated dry air stream mixes with and dilutes the wet air stream to provide a less visible plume above the fan discharge. During certain weather conditions, the visible plume is virtually eliminated. During more adverse conditions, plume density and persistence are substantially reduced.

The developmental status for the PPWD tower (Ref. 15) includes a prototype test series where plume abatement levels have been observed and documented. A Marley tower has been serving St. Joseph Light and Power Company of Missouri since 1955. Four fan cells are used to

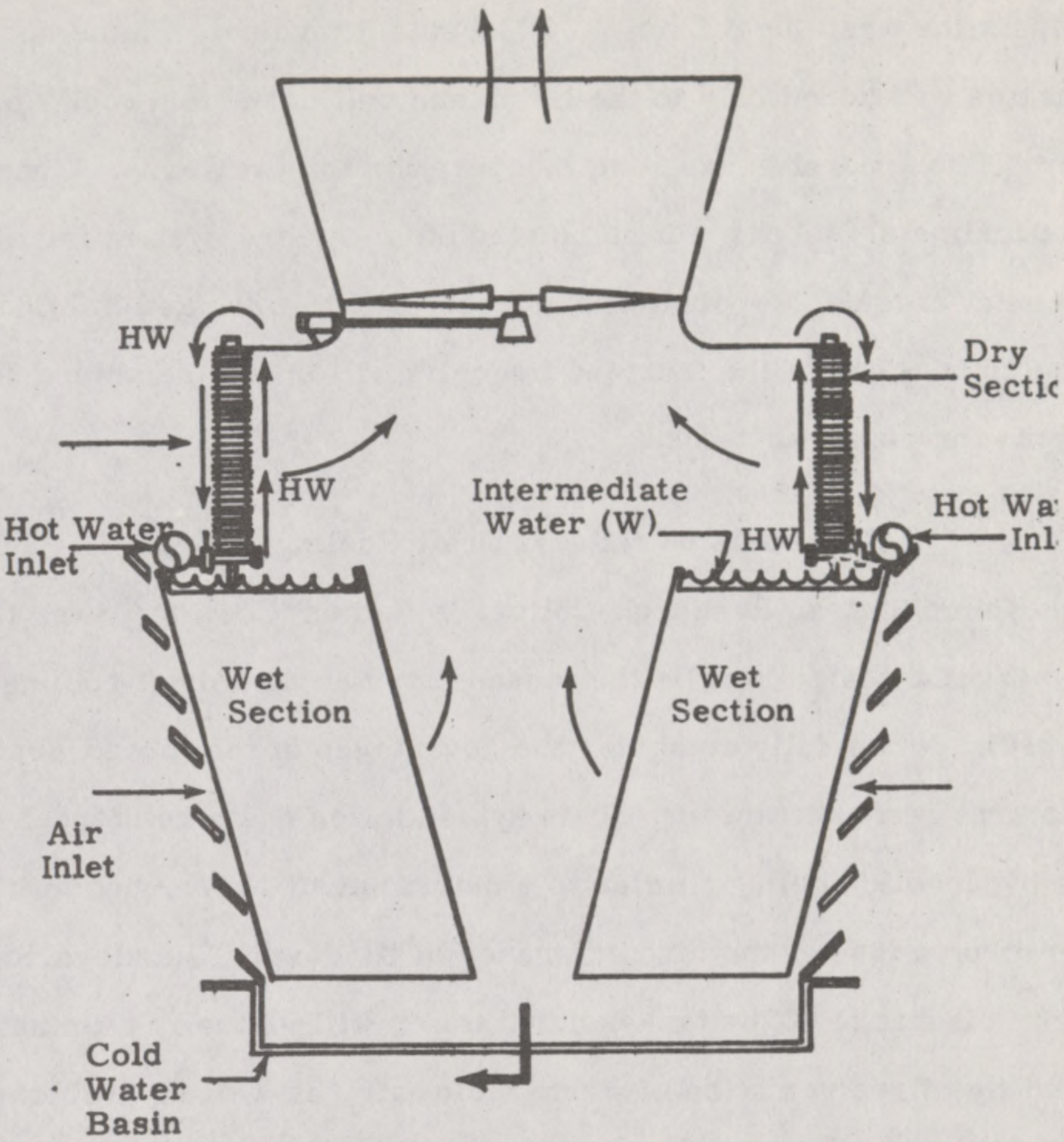


Figure 14. Parallel Path Wet-Dry Tower

dissipate the waste heat from a 30 Mw steam turbine. Plume abatement apparatus was added only to the North end cell of the four-cell cooling tower. The apparatus has been in operation for two years. Construction is approximately 90 percent completed on a wet-dry system for plume abatement at a 450 Mw plant of Northeast Utilities located in Middletown, Connecticut. Ten of the fourteen fan cells will utilize combined cooling systems for plume abatement.

Fan-Assisted Natural Draft Cooling Tower

In the United States, Research-Cottrell's Hamon Cooling Tower Division will market a design it calls the fan-assisted natural draft cooling tower (Ref. 16). It hopefully combines the advantages of the forced-draft and the natural draft wet towers. This hybrid tower has a reinforced-concrete hyperbolic shell, similar to a natural draft tower, but with large motor-driven fans at the circumference of its base. The elevated, high velocity discharge of the fan-assisted tower will virtually eliminate the possibility of recirculation of warm moist air, as well as problems of ground fog over local roads. Because of the fan assistance, total tower height usually need not be much greater than that of other buildings in the plant.

A fan-assisted tower will have roughly two-thirds the base diameter and half of the height of a natural draft wet tower designed for the same performance. It can be erected at about half the cost. However, it will require the continuing operating cost of, typically, 16 to 24 fans. Land area required by a fan-assisted tower will usually be less than that for the natural draft wet tower.

The concept is not entirely new. There are a few existing installations in Europe. Many are modifications of smaller natural draft wet towers. Great Britain's Central Electricity Generating Board announced in the Spring of 1972 that it planned to install an "assisted-draft" tower at its new 1000 Mw Ince-B station.

Costs

In Reference 6, the capital cost, auxiliary power requirements and power plant efficiency were computed for each type of thermal pollution control system assumed to be utilized in a closed cycle mode of operation in a new 800 Mw, fossil-fueled power plant. The results of these example cases are presented in Table 7. These results can not be used alone to evaluate the merits of one cooling method vs. another. In order to arrive at the most economical cooling method, at his particular plant site, the designer must not only consider capital costs of the cooling system components, but must also acquire data on total plant cost, electric power cost, fuel cost, water cost and availability, land cost and fixed charge rates, including interest, amortization, insurance and taxes. The results of Table 7 and some general trends are discussed in the following paragraphs. All costs are presented on a 1971 cost basis.

The presence of the alternative cooling method in the power plant system results in higher operating turbine back pressures or condenser pressures relative to those achieved when once-through cooling is used (an average of only 51 mm (2 in.) Mercury absolute). The higher turbine back pressure results in lower plant efficiency. This trend is seen in Table 7.

TABLE 7. ECONOMICS OF ALTERNATIVE COOLING METHODS*

(800 Mwe, Fossil-Fueled Power Plant)

Method	Design Conditions: WBT °C(°F)	Approach °C(°F)	Condenser Rise °C(°F)	Turbine Back Pressure mm Hg abs. (in Hg abs.)	Capital Cost 10^6 (1971 Basis)	Auxiliary Power Requirements Mw	Plant Efficiency %	Remarks
Natural Draft Wet Tower	21(70)	10(18.5)	16(28.7)	97(3.8)	4.9	2.8	35.2	
Mechanical Draft Wet Tower	21(70)	8(15)	14(25)	79(3.1)	1.55	6.9	35.5	
Spray Pond	21(70)	11(20)	11(20)	79(3.1)	3.6	10.0	35.5	Wind velocity of 8 Kn/hr (5 mph) assumed.
Cooling Pond	--	--	11(20)	69(2.7)	2.2	1.8	35.6	Pond outlet temperature - design equilibrium temperature= 1°C(2°F). Land unit cost equal to $4900/ha ($2000/acre).
DBT								
Natural Draft Dry Tower	32(90)	--	--	152(6.0)	19.5	7.1	34.1	Initial temperature difference = 28°C (50°F). Cost also includes condenser, piping, tanks, pumps, valves and controls.
Mechanical Draft Dry Tower	32(90)	--	--	152(6.0)	18.5	21.0	34.1	

* Estimates from Reference 6 for closed cycle mode of operation.

The natural draft wet tower has a higher capital cost than the mechanical draft wet tower. However, the mechanical draft wet tower requires more auxiliary power due to the presence of the fan. Consequently, the annual costs due to auxiliary power requirements are greater for the mechanical draft tower.

The capital cost in the table is for the conventional type of spray pond only. It is based on the installed cost for the spray pond at the Canadys station.

The capital cost of the cooling pond is based on a pond size of 445 ha (1100 acres) and an assumed unit cost of $4900/ha ($2000/acre) for land and excavation.

The capital cost for the dry tower is defined differently than the ones for each of the other cooling systems. Thus, the capital costs in Table 7 for the wet or evaporative systems are not directly comparable to those of the dry towers. For the dry tower, in addition to the cooling tower (with its heat exchanger), the capital cost also includes: the direct contact condenser, cooling system piping, water storage facilities, pumps, valves, and controls. The design conditions specified for the dry towers are the dry bulb temperature and the initial temperature difference shown. As seen in the table, the power plant employing either dry tower, under design conditions, operates at the highest turbine back pressure and the lowest plant efficiency.

The capital costs for wet-dry towers can range from approximately 1.6 (Ref. 17) to 2.4 (Ref. 18) times the cost of a conventional, mechanical draft wet tower.

Makeup Water Components

Makeup water requirements for the alternative wet cooling methods are due to three components: evaporative losses, drift losses, and blowdown. Evaporative losses for natural draft and mechanical draft wet towers, spray ponds and cooling ponds depend upon the site meteorological conditions and range. Evaporative losses for the wet towers are also a function of approach.

Drift is the loss of entrained water that is carried out of the top of a wet tower or from a spray pond. The typical drift guarantee of 0.2 percent of the water flow rate is far in excess of current engineering capability and practicality for large towers. Drift loss can be almost completely eliminated by control of air velocity and use of drift eliminators. Mechanical draft wet towers can be currently purchased with certification of drift elimination at the 0.02 percent level. According to Reference 19, natural draft wet towers can be certified at the 0.002 percent level. Also drift measurements on operating towers show levels as low as 0.005 percent for mechanical draft and 0.001 percent for natural draft towers.

Blowdown is also expressed as a percentage of the water flow rate. As water is lost by evaporation from the cooling water supply of wet cooling systems, nonevaporating substances are concentrated in the cooling water remaining. There is a practical limit of concentration of the substances if corrosion by scaling and general deterioration of the cooling structures are to be prevented. To avoid such problems, a certain amount of the cooling water customarily is drained off from the system for disposal. This water, termed blowdown, is replaced by fresh makeup water.

The equation for concentration factor or number of concentrations be given as:

$$C = \frac{E + D + B}{D + B} \quad (7)$$

where:

C = factor of concentration in the evaporative system

E = evaporative loss or evaporation, percent

D = drift loss, percent

B = blowdown, percent

The variables, E, D, and B, are all percentages of the water flow

Then this equation was rearranged to yield the blowdown:

$$B = \frac{E - D(C - 1)}{C - 1} \quad (8)$$

Cooling Method Selection

The selection of a cooling method depends upon the specific site and requirements. For each case, an optimization analysis must be pe: formed which considers the site meteorology, geography, plant characteristics, water supply availability, and local economic facto as well as the characteristics of the alternate methods. In general, one cannot say that one cooling method has advantages over the othe: A unique detailed evaluation must always precede the decision to use specific method for thermal pollution control.

SECTION III

COOLING WATER TREATMENT PROBLEMS

Significance of Water Treatment

Water treatment is required in cooling water systems to preclude the deterioration of heat transfer efficiency which is caused by the accumulation of scale, foulants, corrosion, and bacteria. Once-through systems are used if the temperature rise in the receiving body of water is acceptable. These systems generally do not require much chemical treatment. Treatment usually involves injecting chlorine as a bactericide and algacide (combined term: biocide) to prevent slimes on condenser tubes (Refs. 20, 21). In many instances, natural coolant water is sufficiently free from algae and slime-forming bacteria so that biocides are only needed seasonally such as in the spring when algal blooms may occur.

Recirculating cooling water systems are used in power station locations where sufficient quantity of natural waters are not available for once-through cooling or where effluent thermal pollution is a problem to receiving waters. To minimize water consumption, the water is recirculated and enough water is added to makeup for evaporative, drift, and blowdown losses. Natural waters contain dissolved and suspended solids and biological constituents which require treatment to preclude accumulation of concentrations sufficient to affect heat transfer efficiency in condensing systems. Cooling towers for most power plants often require chlorination and pH control as the only cooling water treatments (Ref. 19). In locations where the makeup water has significant concentrations of

dissolved solids, suspended solids, and biological constituents, the purpose of treating the recirculating water is to prevent or minimize the following (Ref. 20):

1. Scale formation on pipe walls and heat exchange surfaces
2. Corrosion of metallic parts of the system, particularly heat exchange surfaces
3. Fouling of heat exchange surfaces by growths of algae or slime mold
4. Rotting of wooden components, or other susceptible materials by fungus attack.

Careful control of chemical treatment is required to prevent pollution of receiving waters in cooling systems where water is removed (blowdown) to maintain a certain concentration of dissolved solids (Ref. 19). Commonly used chemical treatments involve adding acid, usually sulfuric, to control pH in the 6.0 to 7.0 range which allows concentration many times without precipitating calcium carbonate or calcium sulfate, adding chromate and phosphates to inhibit corrosion and scaling, and adding chlorine intermittently to control biological fouling and growth. Acid cooling water systems have advantages in that they provide excellent chemical treatment and are easily controlled. Acid systems have some severe disadvantages in that they require handling of acid, discharge chromates and metal ions which are toxicants, discharge phosphates which are algae nutrients, and discharge toxic microbiocides to receiving waters (Ref. 22).

The effect on the environment has caused development and use of new methods which satisfactorily perform and minimize need for toxic

corrosion inhibitors which require removal from the effluent. These methods generally require very careful control of operating variables since they depend upon controlled scale formation which cannot tolerate wide temperature changes, high heat-transfer rates, or pH fluctuations. They cannot control scale effectively in very hard, high alkalinity makeup waters (Ref. 22). The new treatment methods using scale inhibitors and antifoulants and operating under scaling conditions have been termed "non-polluting." However, corrosion data over the past few years have shown that these treatments are not as effective as the use of chromate-based corrosion inhibitors (Ref. 23).

Treatment Problems and Methods

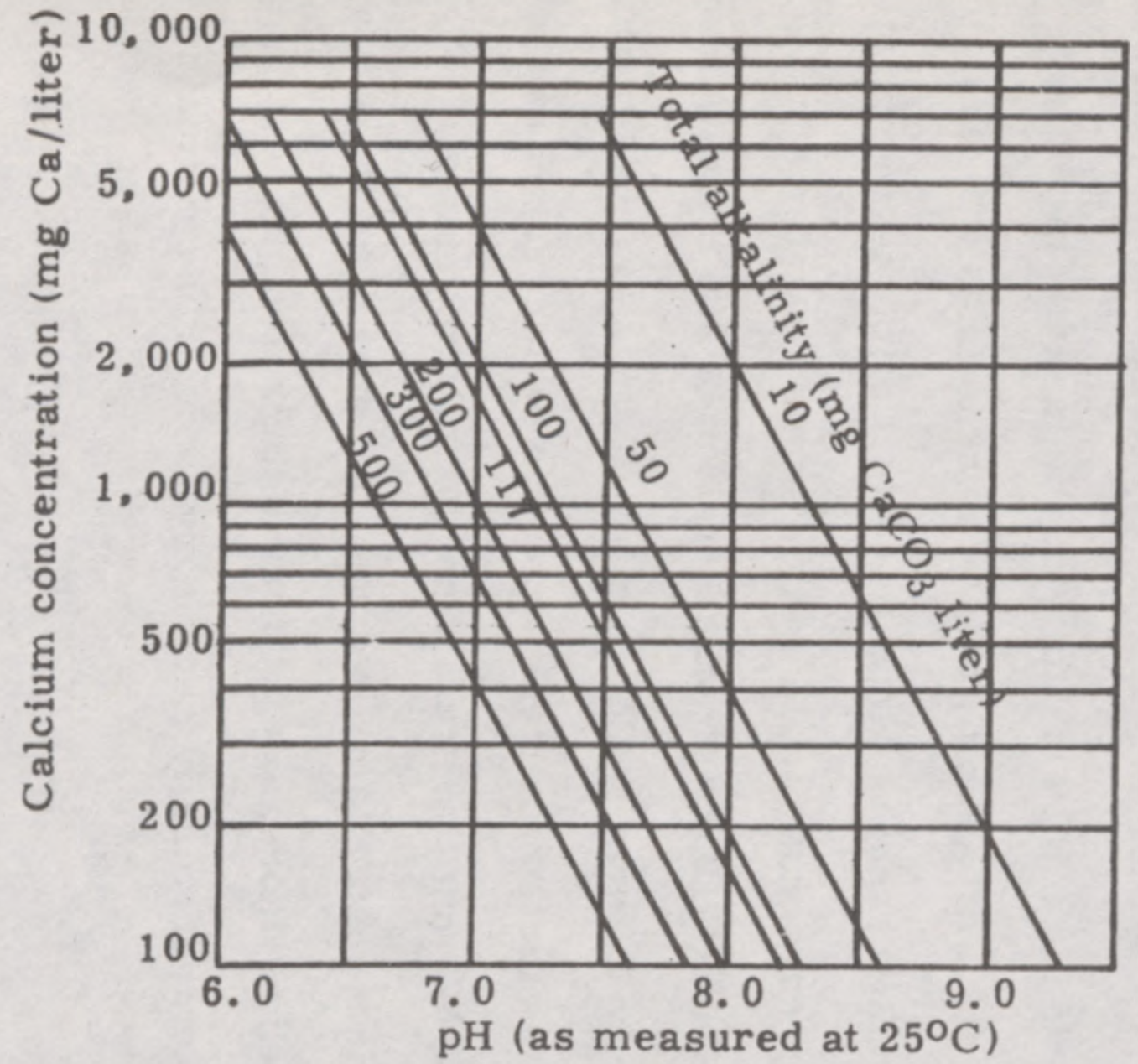
Scaling

Scale is the solid, adherent deposits of minerals precipitated from the process fluid which forms on surfaces and flow passages and decreases the effective heat transfer rate. The ultimate effect of scale formation is lost efficiency, reduced station generating capacity, increased down-time for maintenance, and increased cost of power generation (Ref. 24).

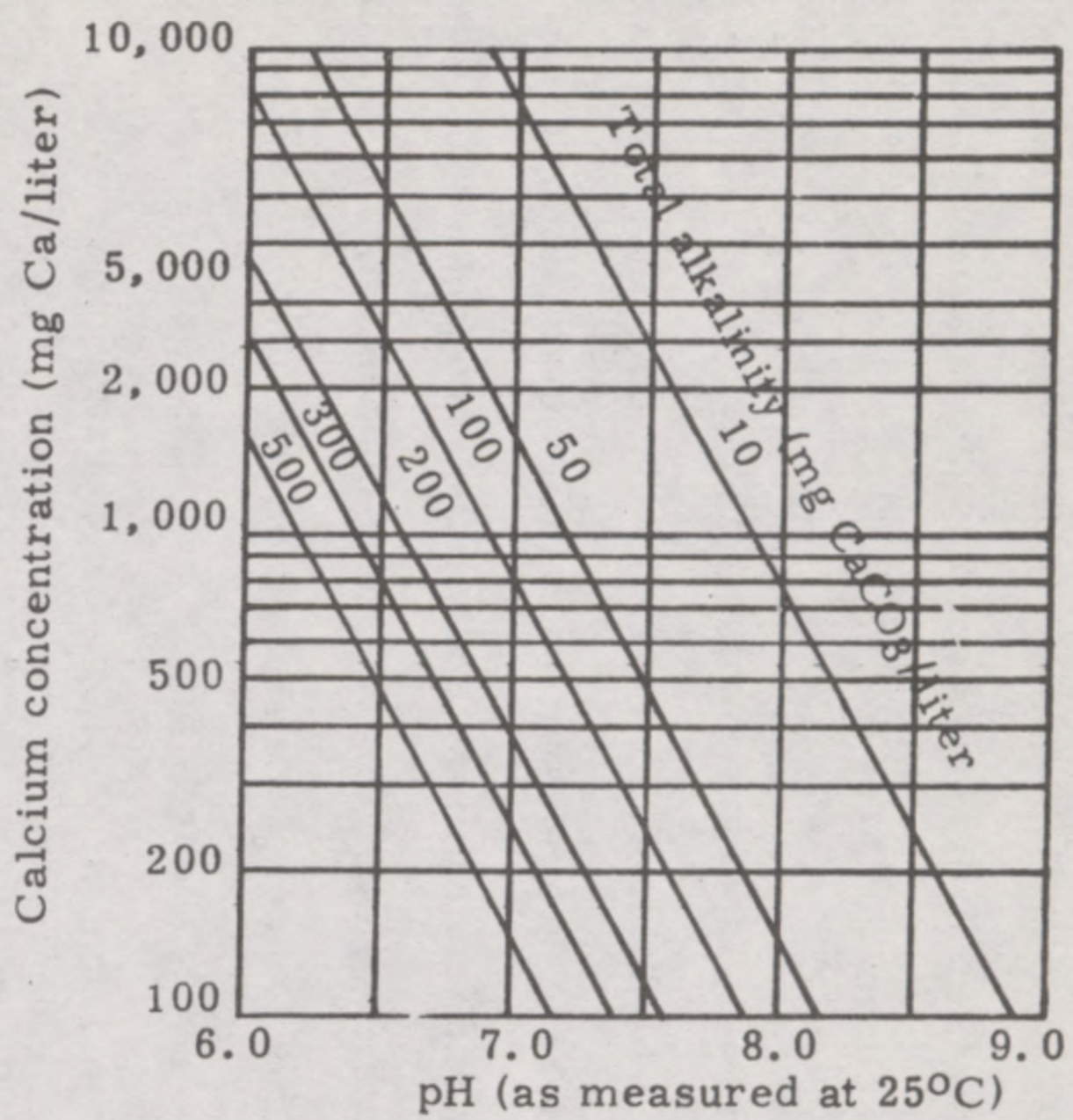
The types of scale are calcium carbonate, calcium sulfate, silica, magnesium compounds, iron and manganese compounds, and phosphate compounds (Ref. 5). The common constituents of scale are calcium carbonate, $CaCO_3$ (most common); magnesium hydroxide, $Mg(OH)_2$; and calcium sulfate, $CaSO_4$ (Ref. 25). The three common scale-forming compounds have an inverse solubility in water (Ref. 24). Calcium carbonate is the major potential contributor to scale at the operating temperatures of cooling water systems, 15-65°C (60-150°F). Calcium

sulfate scales predominate only in regions of concentrated brine or high temperatures. Magnesium hydroxide becomes predominant in the high temperature ranges above 77°C (170°F)(Ref. 24).

Calcium carbonate is very sparingly soluble in pure water. The solubility of less than 0.01 g/liter at 25°C (77°F) can be greatly increased by adding acid. Reference 26 presents a detailed discussion of calcium carbonate solubility and from this reference is taken Figure 15. Even though this figure was developed for seawater concentrations, it illustrates the combined effects of temperature and pH on the solubility of calcium carbonate in water. From Figure 15a, at an initial calcium concentration of 100 mg/liter and at a pH of 6.0, 40 concentrations can be achieved (increase to 4,000 mg Ca/liter) without precipitating calcium carbonate at 60°C (140°F) where the total alkalinity of the makeup is 500 mg $CaCO_3$/liter. This solubility limit greatly increases as the alkalinity of the makeup water decreases. Also, the effect of pH as an effective preventer of calcium carbonate scale can be seen. A water of total alkalinity of 10 mg Ca CO_3/liter at concentration of 200 mg Ca/liter and pH of 9.0 is likely to form scale whereas if pH is lowered to the 6.0 to 7.0 range, the calcium concentration can be increased at least 50 times (to over 10,000 mg Ca/liter) without scale formation. Figure 15b shows the effect of increasing temperature. All solubility lines moved toward the left and show decreases. Careful control of pH, calcium concentration, and temperature is necessary to control calcium carbonate scale formation.



(a) 60°C (140°F) Seawater



(b) 100°C (212°F) Seawater

Figure 15. Stability diagram for calcium carbonate for different alkalinities (a) at 60°C and (b) 100°C. Lines were calculated for average seawater and are also valid for other water of similar composition. Each line refers to water of specified alkalinity. Region on the right of respective line represents supersaturated, unstable solution likely to deposit calcium carbonate scale. Alkalinity is given in "mg $CaCO_3$/liter", (Ref. 26).

Scale prevention can be accomplished by several methods (Ref. 26):

1. Designing the cooling water system so that the number of concentrations does not form a supersaturated solution before blowdown.
2. Removing scale forming salts from makeup by softening
3. Adding chemicals such as acids which broaden the range of temperatures in which water is stable
4. Adding chemicals that retard scale deposition such as polyphosphates or cause the precipitation of soft, easily removed sludge, instead of scale which adheres to cooling surfaces
5. Causing precipitation of scale in special, easily cleaned towers such as by contact stabilization.

Acid treatment to control pH at about 7.0 is a common method to control scaling and it is the least costly method (Ref. 26). Sulfuric acid treatments can be used to remove already formed scale and neutralize the alkalinity of makeup water. Corrosion becomes a problem and generally requires the addition of corrosion inhibitors where acid treatments are used (Ref. 27). In evaporative cooling systems, the cooling water evaporates and increases the concentration of dissolved salts (salinity). The number of concentrations of recycled cooling water must be controlled to restrict salinity and to prevent scaling of heat exchangers, usually restricted to two or three recycles for condenser discharges in the 43°C (110°F) area. A portion of the recirculated water is removed (blowdown) and enough treated water is added (makeup) to replace evaporative losses and blowdown to control salinity. Temperature

effects (thermal pollution) of the blowdown are minimized by evaporation in wet cooling towers or by retention in holding ponds. Commonly used acid treatments include the addition of chromate and phosphate to inhibit corrosion. Chromates are toxic to biological life in receiving waters and must be diluted or removed from the effluent. Phosphates are nutrients for algae blooms in receiving waters and its concentration in effluents should be minimized.

Alkaline treatments have been developed in recent years to help meet increasingly stringent requirements for pollution control that acid-chromate and phsophate treatments would create if not removed. Alkaline treatments distort the growing calcium carbonate crystals and prevent the formation of large adhering crystals. Since they depend upon controlled scale formation, careful control of cooling tower operating variables is required. Alkaline treatments cannot tolerate wide temperature changes, high heat-transfer rates, or pH fluctuations that commonly occur in industrial cooling systems, and they cannot effectively control scale in very hard, highly alkaline waters (Ref. 22). The approach in alkaline systems is to concentrate the water in the cooling system to allow it to attain its natural equilibrium pH usually between 7.0 and 9.0. Chemicals are then added to stabilize the system and control corrosion, scaling, and fouling. Because of the many different water supplies, various treatments are required and the chemical dosage rates vary from intermittent to continuous. A complete analysis must be made of the water and the chemical treatment and then tailored to fit the requirements of system. Calcium carbonate crystal growth inhibitors for alkaline waters

are sulfonated lignins and tannins. Polyacrylates act as dispersants for crystalline scales. Polyphosphates act as crystal growth inhibitors. At sufficient dosages chelate calcium ion prevents scale formation. Polyphosphates are limited because they revert to orthophosphate at high temperature. At pH greater than 8 and at higher temperatures, scale growth can be inhibited using new scale control chemicals, namely the polyol-esters and phosphonates. These chemicals do not remove scale, however, and if scaling occurs, mechanical or acid cleaning is necessary (Ref. 22).

Millard (Ref. 28) and Puckorius (Ref. 29) reported the successful change-over from sulfuric-acid and polyphosphate treated water to polyol-ester and organic-inorganic polymeric water treatment systems which do not create pollution problems, perform well, and are easily controlled.

In some power station locations, design considerations include removal of scale formers prior to makeup by softening or precipitation. Fowlkes described in Reference 30 the successful pilot tests of a lime-soda-ash softening treatment for blowdown which allows blowdown blending with softened creek water as makeup. The chromate is recycled. Therefore, disposal of blowdown is no problem.

The acid-chromate phosphate treatment systems have in the past protected cooling water systems from scaling and corrosion, but chromates are toxic to life in receiving waters. Newer alkaline treatment methods must be tailored for each cooling water system to be successful in inhibiting scale formation on condensing surfaces. The alkaline treatments

24-642 O - 73 - pt. 2 - 10

do have limitations for preventing scale in very hard, high alkalinity makeup waters or where pH fluctuations, wide temperature changes, or high heat transfer rates occur.

Fouling

Fouling occurs from organics, algae, and bacteria forming slimes and growths on heat exchange surfaces. The operating temperature ranges for cooling systems form ideal conditions for producing bacterial growths. Microbiological growths are the most severe fouling problems in cooling towers. They enter from makeup water or scrubbing from the air in a wet tower. Bacterial growth is the precursor of other cooling tower problems such as severe rapid corrosion and wood rot. Natural waters used for makeup to cooling systems usually require some method to control silt which will form sludge and coatings on cooling system surfaces. Biological fouling not only plugs screens, restricts flow, creates growths, and reduces heat transfer, but it can release oxygen to accelerate corrosion (Ref. 5). Salt water systems generally require more antifouling treatment than fresh water. Shellfish will grow in or on pipe walls and other surfaces where if dislodged, they are swept into condenser tubes (Ref. 20) where they collect, block flow, and reduce efficiency.

Suspended solids or dissolved organic matter such as silt require treatment which is similar to the addition of scale inhibitors and which will keep them suspended. Suspended solids can be settled out in large retention basins. For natural water makeup, it is usual practice to add chemicals which act as dispersants and prevent coagulation and settling as sludge in the cooling water system. Polyol-esters, phosphonates,

natural organics, polyacrylates, and non-oxidizing biocides are anti-foulants. It is often more difficult to control fouling in alkaline than acid systems (Ref. 22). The makeup water may be microbiologically contaminated and contain substantial biological oxygen demand. More substances are insoluble in alkaline waters than acid waters. Colloidal organic matter tends to coagulate and precipitate easier in alkaline systems than under acid conditions. Microbiological deposits are sometimes more difficult to remove in alkaline systems. Fouling deposits come from: colloidal organic matter, silt and dirt, soluble iron, and microbiological contamination. The cooling air in evaporative cooling systems may contain dust, dirt, or be contaminated with reactive process gases such as hydrogen sulfide, sulfur dioxide, ammonia, etc. Process leaks are a common source of hydrocarbons and sulfides. Sulfides react with oxidizing biocides, zinc ion corrosion inhibitor, and may cause chromate reduction which results in additional fouling. Commonly used scale control chemicals are good fouling dispersants. Specification of particular dispersants requires knowledge of deposit-composition. In alkaline systems, deposit removal by new dispersants is gradual, and it is always preferable to prevent deposit formation than to remove deposits (Ref. 22). Another method to control fouling is mechanical cleaning. Mechanical condenser tube cleaning methods are being extensively used in Europe and in many power stations in the United States. Mechanical cleaning consists of circulating sponge rubber balls through the condenser tubes (Ref. 21).

Corrosion

Corrosion is the physiochemical destruction of materials by the action of the environment. The use of natural waters causes corrosion of materials used in cooling water systems. Acid systems used to control pH further contribute to corrosiveness of the cooling water. Alkaline systems are less prone to corrosion but prevention is still required.

Anionic corrosion inhibitors are used in both acid and alkaline cooling systems and include: chromates, zinc, phosphates, and some organic chemicals (Refs. 22 and 23). Chromate used with phosphate and zinc is an effective treatment but has toxic effects on aquatic life in receiving waters. Other corrosion inhibitors can sometimes be used such as silicates and molybdates. These are not as effective as synergized chromate products. At pH values above 7.0, corrosiveness is lessened and less corrosion inhibitor is required. Organic-polymer-silicate treatments used with zinc and an antifoulant are a common non-chromate treatment system which is most effective in the alkaline pH range (Refs. 23 and 27). Zinc is not restricted as a pollutant. However, this will change as more studies show effects of heavy metals on aquatic life (Ref. 23).

Phosphates are both scale and anionic inhibitors. Phosphates react with both calcium and iron. Phosphates react with iron and help prevent tuberculation or localized buildups of ferric hydroxide. Polyphosphates are suitable for use as a corrosion inhibitor and are commonly used with zinc and chromate treatment (Ref. 23). Phosphates

are nutrients for algae and for this reason, effluents containing phosphates are being restricted.

Biological Fouling

Microbiological growths are serious problems in cooling towers. Algae, fungi, bacteria, and crustaceans enter from makeup water or from scrubbing from the air (Refs. 27 and 31). Biological fouling not only plugs screens, restricts flow, creates growth, it can release oxygen to accelerate corrosion (Ref. 5). Thick growths decrease heat removal efficiency. Severe corrosion is caused by bacterial growth and wood rot is caused by fungi. It is possible to have simultaneous aerobic slime-forming bacteria growing under scale. If saltwater makeup is used, shellfish will grow in heat exchanger tubes and in a cooling tower (Ref. 27). Aesthetic and odor problems are also caused by biological growth and decay in cooling tower systems.

Cooling water systems form an ideal environment for biological growth since usual cooling tower operating temperatures range from 15°C to 75°C (60°F to 150°F). Optimum growth conditions for some biological species causing fouling problems can be found in Reference 31.

Biocides are usually intermittently added to control biological fouling (Ref. 31). The most commonly used biocide is chlorine. Other frequently used biocides are hypochlorite or nonoxidizing compounds such as chlorophenols, quaternary amines, and organo-metallics such as organo-tin compounds, organo sulfur, and organothiocyanate (Ref. 27). Massive chlorine dosages can deteriorate cooling tower wood and create

toxic effects in blowdown to receiving waters (Refs. 20, 22, and 27). Chlorine is more effective in acid systems than in alkaline systems.

Other biocides may be necessary in addition to chlorine, particularly for alkaline systems or if organic corrosion inhibitors are used. The nonoxidizing biocides are used when problems are severe and where the use of chlorine is not acceptable. Ozone is a powerful oxidant and biocide, compatible with alkaline systems, water pollution free, but unstable and expensive at present (Ref. 22) The use of biocides containing mercury, arsenic, lead, or boron is limited by stringent regulations because of their extreme toxicity when released to the environment (Ref. 27).

Saltwater cooling systems require more antifouling treatment than fresh water. Intermittent chlorination will control algae growths. Shellfish (mussels, barnacles, oysters, etc.) grow on pipe walls and other surfaces downstream of screens where if dislodged they are swept into condenser tubes. One control method is to recirculate heated water at frequent intervals which does not create unduly severe side effects but does require special valving and piping. Other methods include chemical treatment or use of copper or copper-alloy lined pipes and heat exchange surfaces but these are objectionable because of environmental effects (Ref. 20). Continuous mechanical cleaning could be used.

Cooling water systems require careful selection of water treatment chemicals to achieve efficient heat transfer and operation without incurring high costs or polluting natural waters.

Current development of new treatment methods appears centered on the use of alkaline treatment systems to minimize the requirements for chromates, zinc, phosphates, and organic-based chemicals. As previously stated, it should be noted that most cooling water systems require minimal treatment of the natural waters used, usually only pH control and chlorination (Ref. 19).

Blowdown and Effluent Quality

Blowdown is the cooling water which is taken or drained from an evaporative recirculating cooling water system to maintain a fixed concentration of dissolved solids by dilution with new water (makeup) to the system. Blowdown concentration and effluent quality is dependent upon the number of recycle concentrations and chemical treatment, respectively. Water quality considerations have already been discussed.

Concentration Vs. Recycle

The concentration of cooling water blowdown is measured by ratioing chemical content of blowdown water to that of the makeup water. The limits for allowable dissolved solid concentration in the cooling water system is dependent upon the operating variables and chemical treatment.

The discussion of scaling problems shows the relationship of calcium carbonate concentration, pH, alkalinity, and temperature. The concentration of the dissolved solids is governed by the rate of evaporation from the cooling water system. Drift losses and blowdown carry dissolved solids with them and consequently their removal (loss) does not chemically increase the concentration of the remaining water. Makeup

water dilutes the cooling water to maintain predetermined concentrations of dissolved solids in the system. The number of concentrations of a cooling water system is given by Equation (7) of Section II.

For a 1000 Mwe fossil-fueled power plant and various cooling methods, typical evaporation, drift, blowdown, and makeup water components are given in Table 8. Four and twenty concentration recycles were assumed for the three recirculating cooling systems (natural draft and mechanical draft towers and the spray canal). The values indicate rough magnitudes for blowdown and makeup for each cooling method (Ref. 3). The multiples of concentrations depend upon the makeup water chemistry: hard very alkaline waters, 2 to 4 recycles; waters which are fairly clean (free of dissolved solids), 30 to 50 recycles; and extremely clean or specially softened water where only drift losses occur and blowdown is not required, as high as 30,000 recycles. In this latter case, zero flow discharge is achieved except for drift which serves the blowdown requirements. There have been legislative proposals to regulate all industrial discharges to zero flow.

Blowdown Treatment Methods

Blowdown disposal is a serious problem. It often carries dissolved solids in high concentrations and chemical additives which are toxic to aquatic life or have other deleterious properties. Dilution in natural waters depends upon water quality regulations and may be a problem during periods of low flow (Ref. 20). Alternative disposal methods

TABLE 8. AVERAGE MAKEUP WATER COMPONENTS FOR COOLING SYSTEMS AT A 1000 Mwe FOSSIL FUELED POWER PLANT (ADAPTED FROM REF. 3)

Cooling Method	Flow Rate m^3/sec (cfs)	(a) Average Evaporative Loss m^3/sec (cfs)	(b) Drift Loss m^3/sec (cfs)(2)	(c) Average Blowdown m^3/sec (cfs) With Concentration Multiple: 4:1	20:1	Average Makeup m^3/sec (cfs), a + b + c, With Concentration Multiple: 4:1	20:1
Natural Draft Wet Tower	22.9(810)	0.30(10.6)	0.0006(0.02)	0.099(3.51)	0.015(0.54)	0.40(14.13)	0.32(11.16)
Mechanical Draft Wet Tower	27.9(984)	0.30(10.6)	0.0014(0.05)	0.098(3.48)	0.014(0.51)	0.40(14.13)	0.32(11.16)
Spray Canal	27.2(960)	0.30(10.6) (1,4)	0.0014(0.05) (4)	0.098(3.48)	0.014(0.51)	0.40(14.13)	0.32(11.16)
Cooling Pond (1857 acres)	28.9(1021)	0.29(10.2) (1)	0(0)	0(0)	0(0)	0(0)	0(0)
Once Through (3)	24.2(856)	0.23(8.2) (1)	0(0)	0(0)	0(0)	24.2(856) (5)	24.2(856) (5)

(1) Evaporative losses exclude evapo-transpiration losses.

(2) Assumed 0.002 percent (natural draft) and 0.005 percent (mechanical draft and spray canal) as indicated in Ref. 19.

(3) Assumed 11°C (20°F) condenser rise.

(4) Values approximated as equal to mechanical cooling towers.

(5) Once-through cooling is continuous makeup to condenser.

include:

1. Retention in ponds for subsequent release when natural water flow is high enough to permit dilution
2. Evaporation and concentration or seepage from ponds
3. Disposal into underground formations
4. Treatment with chemicals to remove or lower the concentrations of harmful substances (Ref. 20)
5. Desalting of blowdown to develop water suitable for other uses such as boiler makeup (Ref. 32)

Seasonal retention requires pond construction and costs for land as well as determination of the ability of the stream to absorb stored blowdown during its high flow period. The use of evaporation, seepage pits, and underground disposal require hydrological and geological surveys to insure that water contamination elsewhere will not occur. Evaporation requires extremely large ponds for large power plants. Chemical treatment of the blowdown is not usually warranted if nontreatment disposal methods can be used. The high toxicity of chromates and other chemicals usually results in mandatory requirements for removal prior to blowdown at most sites. Chemicals having sufficient salvage value to warrant recovery by ion-exchange methods should always be recovered (Ref. 20). Disposal of blowdown to municipal sewers is usually regulated. Exceeding specified concentrations usually results in surcharges to handle the blowdown. Methods of reducing quantity of blowdown are available but are not intensively used because of costs (Ref. 33). A

few of these treatment methods and some novel examples of blowdown treatment and control are given in the following paragraphs.

Biocides can be neutralized by dilution and organic biocides may possibly be oxidized to neutrality (Ref. 23). Chromates can be removed by reducing or by selective ion exchange. Phosphates can be precipitated, coagulated, settled, and filtered.

Blowdown might be combined with process waste water and treated (Ref. 23) prior to discharge. Organics are then removed by extended aeration in aerated lagoons.

Foulkes (Ref. 30) reported successful pilot testing of a lime-soda-ash softening treatment for blowdown which allows blending blowdown with softened creek water as makeup. The hot water recycle removes calcium carbonate and magnesium hydroxide, but allows chromate to pass through. By recycling chromate, disposal of blowdown is no problem.

Though not a blowdown treatment, preconditioning of makeup water may increase the concentration recycles to the point that minimal or zero blowdown flow is achieved. Farber (Ref. 23) outlines some processes to achieve zero flow discharges by removing scale forming dissolved solids by one or more of the following processes: cold lime softening; hot lime softening; ion exchange; reverse osmosis; coagulation, filtration and exchange with macroreticular resin (or chlorination); and recovery of extraneous blowdown streams such as losses from pump gland cooling, compressor cooling, steam traps, etc. If a chemically stable system can be used, chemical treatment with addition of biocides may accomplish

zero flow discharge. Chromate, zinc, phosphonate, and an antifoulant would be used to passivate metal surfaces and inhibit fouling and scale.

Consumptive Water Use

Consumptive water use is the non-return of makeup water to the source. Table 9 shows consumptive water usage for the cooling systems in Table 8.

TABLE 9. TYPICAL CONSUMPTIVE USAGE IN COOLING WATER SYSTEMS FOR A 1000 Mwe FOSSIL FUEL POWER STATION

Cooling Method	Consumptive Water Use m^3/sec(cfs)
Natural draft wet tower	0.30 (10.62)
Mechanical draft wet tower	0.30 (10.65)
Spray canal	0.30 (10.65)
Cooling pond	0.29 (10.2)
Once-through	0.23 (8.2)

Other consumptive uses include water lost from packing gland cooling or from leaks in the cooling water system. It should be noted that cooling ponds may not constitute consumptive losses unless water is made up to the pond from natural streams.

Dry Systems

Dry systems do not have blowdown because they are closed systems with heat transfer from water or from steam to the air across a heat exchange surface. The circulating water is intimately mixed with boiler feedwater, and it must, therefore, be of condensate purity (Ref. 11). The circulating water does not contact air; therefore, there is no evaporation loss. With no concentration of dissolved solids, there is no blowdown.

Cooling With Effluent From Secondary Sewage Treatment Plants

In arid or water short locations, it has become advantageous to use the effluent from secondary sewage treatment plants. Three characteristics of sewage plant effluent as it affects industry were given by Scherer and Terry (Ref. 34) as:

1. The average nonfilterable solids added to the potable water, which carries wastes from homes and industry, amounts to 0.24-0.36 kg/10^3 1(2-3 lb/1000 gallons). The additional 250-350 ppm total solids will be in the sewage plant effluent.
2. Wastewater treatment plants clean and purify the incoming water by varying degrees depending upon the design and operation of the plant. The quality of the effluent is affected by retention time, temperature, and the presence or absence of materials toxic to the bacterial life used to degrade the organic material present in the sewage.
3. The chemical and biological nature of the effluent from a sewage plant will vary from hour to hour, from day to day, and from season to season.

Orthophosphate content is a problem since tricalcium phosphate is an insoluble scale that forms at low temperatures. Tertiary wastewater treatment plant effluent treated with 0.3 kg of lime per 1000 liters (2-1/2 lb of lime per 1000 gallons) and coagulated with 0.1 kg (1/4 lb) of alum results in phosphate reduction to one ppm and lower. However,

the calcium is apparently sequestered since reductions do not follow the usable solubility tables. Gray, et al (Ref. 35) report that lime pretreatment of secondary sewage treatment plant effluent is not essential for cooling tower makeup in their Burbank, California plant. Nitrogen in the form of ammonia is found in significant amounts in the effluent from almost all biological treatment processes (Ref. 36). Even where extended aeration is used and the ammonia is ozidized to nitrate, it is not unusual to find 0.5-1.0 mg/liter NH_3-N. Ammonia in contact with chlorine forms chloramines which can be a significant toxicant to biological animals and vegetation.

Loss of heat transfer may result from inorganic scaling, organic fouling, or a combination of the two (Ref. 34). Organic fouling consists of deposits of suspended organics, oils or greases, and bacterial growths. Scaling problems by dissolved solids were discussed in earlier subsections except that phosphate scaling is an additional problem which is encountered when using wastewater treatment plant effluent. Another problem which may occur is foaming. Reference 35 reported foaming problems when ABS exceeds 0.5 ppm when using sewage plant effluent. Antifoam is injected to prevent foaming but even that has not adequately worked at times.

Disposal of blowdown is a problem when using wastewater treatment plant effluent as cooling tower makeup. Gray, et al (Ref. 35), report carrying four cycles of concentration in cooling water and the blowdown is diluted with the unused effluent from the treatment plant. Chlorine consumption is high. Slime forms in minor degrees and microscopic

pitting of admiralty tubes is believed due to organisms. The system uses mechanical condenser cleaning equipment to maintain cleanliness.

Condenser cleanliness is a problem when using effluent from wastewater treatment plant. Reference 35 reported a decrease in the cleanliness factor to 68 percent in two years operation. Their solution has been to reduce concentration cycles to 2-2.5 with pH of 6.5-7.0 and reduce phosphonate treatment level. An additional modification was made to reduce total hardness (as calcium carbonate) below 500 ppm. Ocassionally, suspended solids reach 200-300 ppm even though a 10 ppm warning limit is established (at which point, they switch to makeup from the city water supply). Soft organic matter accumulates and is removed by blowing nylon bristle brushes through tubes with compressed air and water. Condensers have sometimes been cleaned on stream by reducing the pH to 3.5 when heat transfer problems are initially realized.

Reference 37 reports satisfactory use of treated sewage from the city of Lubbock, Texas, as makeup to the cooling tower in the Clifford B. Jones generating station of the Southwestern Public Service Company. The water is extensively treated with 0.24 kg lime and 0.03 kg alum per 1000 1 (2.0 lb lime and 0.25 lb alum per 1000 gallons) of water clarified, and acid feed is used to control pH before pumping to a pond. Drawoff from the pond is filtered through anthracite beds then through a reverse osmosis system which provides 90-95 percent reduction in dissolved salts. It is further demineralized by demineralizer equipment. Dvorn and Wilcox indicated that cooling tower blowdown water could be ponded and used for irrigation of surrounding farm land.

In achieving zero flow discharge from a cooling tower system, Petrey (Ref. 32) suggested reuse of waste plant process water from air flotation processes for cooling tower makeup. The number of concentration cycles would be limited to 1.5-2.0 if chemical treatment were not applied because of calcium phosphate and organic and inorganic debris. Suitable wetting and dispersing agents should be used in addition to chlorination and pH adjustment to make the water suitable for the cooling tower.

Reference 34 states that in order for industry to make optimum and satisfactory use of sewage-disposal-plant effluent, it must receive treatment from a well designed, well operated plant. Incomplete organic decomposition produces effluent that becomes septic and nonsettleable in cold process softeners, regardless of chlorine residual. The treatment plant must be properly designed and operated, and adequate city ordinances must be instituted to protect the system from violent bacterial toxins. Lagoon storage, installed to be a water source in case of sewage plant upset, may be a problem due to algae growth. Acid injection is required to reduce pH, mechanical condenser cleaning is usually required, and increased chlorine demand requires large dosages of chlorine.

Water Conservation

Natural waters are sought which are clean and require minimal treatment for use in cooling systems because they minimize operating problems and total costs. These relatively clean waters are also valuable resources for potable water supplies, irrigation, recreation, and other uses. Consequently, excessive consumptive use, thermal pollution, and chemical contamination must be minimized or prohibited in order to

conserve the water supply and its quality. Water losses through uses in cooling systems constitute consumptive use of the water. Chemical contamination of the water has already been discussed. If the water is conscripted, the consumptive water usage may have to be purchased. Consumptive use of water may incur losses which affect water usage downstream.

Comparison of Evaporative and Drift Losses

Evaporative and drift losses are consumptive uses of water. Evaporative losses are far greater than drift losses. Magnitudes of losses for various cooling methods were shown in Table 8. The ratio of evaporative losses to drift losses is shown in Table 10. It can be seen that evaporative losses are by far the most significant. In addition to losses by evaporation, cooling towers, cooling ponds, and spray ponds must waste a certain percentage of the circulating water in order to maintain the concentration of dissolved solids to limits which preclude deposition of scale on the plant equipment. If the blowdown is concentrated by evaporation or for some other reason the blowdown is not returned to the makeup source, the blowdown water becomes a consumptive loss of water. If the blowdown is warmer than receiving waters, additional evaporation may occur causing a consumptive loss.

The typical values in Table 10 are not absolute. These are average annual values. Considerable variation may occur at any time due to plant capacity factor, cooling range, wet bulb temperature, relative humidity, cloud cover, and wind speed.

24-642 O - 73 - pt. 2 - 11

TABLE 10. TYPICAL EVAPORATIVE AND DRIFT LOSSES IN COOLING SYSTEMS FOR 1000 Mwe FOSSIL FUELED POWER STATIONS

Cooling Method	Evaporative Losses m^3/sec (cfs)	Drift Losses m^3/sec (cfs)	Ratio of Evaporative to Drift Losses
Natural draft wet tower	0.30(10.6)	0.0006(0.02)	530:1
Mechanical draft wet tower	0.30(10.6)	0.0014(0.05)	212:1
Spray canal*	0.30(10.6)	0.0014(0.05)	212:1
Cooling pond	0.29(10.2)	-	-
Once-through	0.23(8.2)	-	-

* Assumed that spray canal drift is the same as that for the mechanical draft wet tower.

Regional and National Aspects of Diversions

Diverting water from one location to another can have serious consequences if the water had "downstream" uses such as for potable water supply, hydroelectric power generation, or irrigation. Diversions in coastal areas of ocean or estuary waters generally have only minor impact such as the possibility of increased estuary salinity. References 1 and 38 have graphs which indicate that about $3x10^{12}$ Kw-hr of annual power generation will be generated by the year 1980. This generation will require an annual $4x10^{15}$ kcal ($16x10^{15}$ Btu) of heat rejected to cooling water. Hauser (Ref. 38) indicates that by the late 1970s fresh water bodies will reach a point where no further heat can be injected into them without damage to the ecology. The only natural heat sinks left will be the oceans. By the end of the 1970s, about 70 percent of new base load generation to be installed will be using some form of supplementary cooling method.

Table 11 shows the condenser requirements, withdrawn water, and consumptive uses (loss) of water for 1965 and projections to the year 2020. This table was taken from Reference 1. The data is given by regions. The regions of most concern are those where fresh water consumptive losses will occur (bracketed in Table 11). Other regions have access to salt water as a heat sink. Total fresh water consumptive losses through the year 2020 are projected and the mean natural runoff is shown. The total consumptive use in 2020 is 30.7×10^6 m^3/day (8.11×10^9 gpd). The total natural runoff is 6.8×10^9 m^3/day (1.79×10^{12} gpd). The projected total consumptive fresh water requirements including steam electric power for the year 2020 are 575×10^6 m^3/day (151×10^9 gpd) (Ref. 1). The steam-electric requirement represents five percent of the projected required water consumptive requirements and 0.45 percent of the total runoff.

As indicated in Table 11 these data show that on a national and regional basis, the consumptive use of water by evaporation, drift and other losses from power plant cooling systems is small compared to surface runoff. These data include allowance for the projected increases in the power generation capacity and use of cooling systems through 2020. It should be noted that these data are average annual runoff values and the seasonal variations could be significant unless storage is provided. In some areas a portion of the runoff will occur through small streams, and the diversions from rivers capable of supporting power plant installations can be significant particularly in the upper reaches. For this reason, each watershed and river basin must be analyzed on an individual basis to determine the impact of diversion of the stream water and consumptive loss to a cooling water system.

TABLE 11. NATURAL RUNOFF AND PROJECTED CONSUMPTIVE USE OF FRESH WATER FOR STEAM-ELECTRIC POWER GENERATION, 1965-2020(Ref. 1). Millions of cubic meters/day (millions of gallons/day)

Regions	Consumption Use			Mean Annual Natural Runoff
Utility Owned Plants:	1965	1980	2020	
North Atlantic	0.28(75)	0.46(120)	2.20(580)	617(163,000)
South Atlantic-Gulf	0.16(42)	0.72(190)	5.46(1440)	746(197,000)
Great Lakes	0.36(95)	0.70(184)	3.40(898)	239(63,200)
Ohio	0.52(138)	1.33(350)	4.51(1190)	473(125,000)
Tennessee	0.09(24)	0.25(65)	0.66(175)	157(41,500)
Upper Mississippi	0.23(61)	0.63(166)	2.30(607)	245(64,600)
Lower Mississippi	0.06(16)	0.23(60)	1.12(295)	183(48,400)
Souris-Red-Rainy	0.01(2)	0.02(4)	0.08(20)	23(6,170)
Missouri	0.09(24)	0.30(80)	1.21(320)	205(54,100)
Arkansas-White-Red	0.16(41)	0.36(95)	1.17(310)	363(95,800)
Texas - Gulf	0.22(57)	0.68(180)	2.24(590)	148(39,100)
Rio Grande	0.03(9)	0.08(20)	0.38(100)	19(4,900)
Upper Colorado	0.05(13)	0.06(17)	0.13(35)	51(13,450)
Lower Colorado	0.03(8)	0.13(35)	1.78(470)	12(3,190)
Great Basin	0.01(2)	0.10(25)	0.61(160)	22(5,890)
Columbia-North Pacific	-	0.05(13)	2.39(630)	795(210,000)
California	0.27(70)	0.30(80)	0.68(180)	247(65,100)
Alaska	-	0.004(1)	0.01(2)	2197(580,000)
Hawaii	-	-	-	50(13,300)
Subtotals	2.56(677)	6.36(1680)	30.30(8000)	
Industry Owned Plants:				
Subtotals	0.31(81)	0.30(80)	0.42(110)	
Total	2.87(758)	6.66(1760)	30.72(8110)	6795(1,794,000)

SECTION IV

PROBLEMS OF COOLING SYSTEM BACKFIT

The conversion of existing condenser and cooling water systems now designed to utilize circulated water from natural water bodies (once-through cooling) may be justified in special cases, but probably will not be widely done due to the problems involved (Ref. 39). For those special cases a number of solutions might be possible, but all must take into account the changed pumping pressures and the different cycle pressures and temperatures which may be the result of a cooling system backfit with wet cooling towers.

A cooling tower backfit operation could involve full conversion with the resulting tower system operating as a conventional recirculated system (closed cycle). This closed cycle system would require the replacement of circulating pumps with higher pressure pumps which in turn might require replacement of condenser water boxes with water boxes of higher design pressure. Alternatively, the conversion might consist of supplementary use of a tower such as a helper tower which would operate during certain periods of the year in order to satisfy terminal water temperature differences above some natural water temperature. As another possibility, the tower could be added to receive the discharge from the condenser in order to reduce the effluent temperature to acceptable limits. In the latter case, the addition of high pressure booster pumps would leave the original pumping and condenser system intact.

In Reference 40, an estimate was made of the costs required to retrofit an existing power plant with the wet-types of cooling systems under the closed cycle mode of operation. The subsequent paragraphs of this section present the findings and results from this reference.

The optimum design of the cooling system requires a match between the turbine-condenser combination and the cooling device. Normally, closed cycle cooling systems impose higher steam turbine back pressure and require higher temperature rises across the condenser than once-through cooling. Changing a once-through cooling system to a closed cycle system by backfitting a cooling device is more costly both in terms of capital cost and operating expenses than if the plant were initially designed with a closed cycle cooling system.

Limited generalized data are available on the cost of backfitted cooling facilities. Reference 41 showed that the cost of providing "thermal effect control" using wet towers retrofitted onto an existing plant was $10/Kw to $12/Kw. Woodson (Ref. 39) estimated the capital cost of converting an 800 Mw plant from once-through cooling to closed cycle cooling towers at roughly $3,000,000 or $3.8/Kw. In Reference 42, Warren estimated the cost of backfitting all of the 15,000 Mw of capacity existing and under construction on Lake Michigan as $150,000,000 or $10/Kw.

None of the references above were explicit in detailing what items were included in the cost estimates. It appears that capability losses, increased fuel costs and increased operating and maintenance expenses

were omitted. The capability or capacity loss may impose a cost penalty since the presence of the cooling tower necessitates the requirement of an additional heat input in order to maintain the rated plant output. Reference 40 estimates that these operating cost items could add $10/Kw to $15/Kw (equivalent capital investment) to the initial capital investment. Thus, the addition of these cost items to the range of capital costs for retrofit above yields a range of backfitting costs from $14/Kw to $27/Kw.

Since the power plant's primary function is the generation and sale of electricity, it is reasonable to assess the economic consequences of the use of closed-cycle cooling in terms of its effect on the cost of power. Thus, rather than provide cost data solely in terms of total capital cost in dollars or $/Kw, it is also expressed as the increase in power generation cost (or busbar cost) in mills/Kw-hr, and ultimately in terms of the increase in consumer cost. An example calculation is given. The numbers are illustrative and will change depending on plant load factor, fixed charge percent and backfitting costs. The numbers chosen for this example are 0.8, 14%/year and $14/kw for the three factors respectively. This results in:

$$\frac{\$14}{Kw} \times \frac{0.14}{yr} \times \frac{yr}{8760\ hr \times 0.8} \times \frac{1000\ mills}{dollar} = \sim 0.3\ mills/Kw\text{-}hr$$

Tichenor (Ref. 40) also found, from available data, that the additional cost of closed cycle cooling as compared to a basic once-through cooling system ranged from about 0.1 mills/Kw-hr for cooling ponds to about 0.2 mills/Kw-hr for evaporative cooling towers. Thus, one can

see the multiplications in cost roughly involved when one compares the increase in busbar cost due to cooling system backfit with that cost for closed cycle cooling designed into a new plant.

Estimates on the cost of backfitted cooling facilities are also available for a large number of specific plants. These data are, for the most part, contained in utility environmental reports and AEC draft environmental impact statements. The most striking aspect concerning these data is the lack of consistency in the methods of reporting. This results in widely different cost estimates. For example, total capital cost data for backfitting power plants on Lake Michigan reported by Argonne National Laboratory (Ref. 43) ranged from $19.4/Kw to $95.7/Kw for wet towers. Assuming a fixed charge rate of 14 percent and a plant load factor of 82 percent, the increase in busbar cost would be 0.38 and 1.86 mills/Kw-hr, respectively. Thus, these backfitting costs differ from one another by a multiplication factor of five.

In computing the increased busbar cost due to backfitting, care must be taken to use realistic values for plant load factor and fixed charge rate, since a short amortization period will increase the fixed charge rate. Reducing the load factor and/or increasing the fixed charge rate will increase the busbar cost range for the same total capital cost range. Thus, the 0.6 mills/Kw-hr value given above for backfitting applies to modern base loaded plants.

The cost of closed cycle cooling can be summarized based on the results presented thus far. For plants that were initially designed to utilize

closed cycle cooling systems, the increase in busbar cost over once-through cooling is about 0.2 mills/Kw-hr for a wet tower system. The increased busbar cost due to backfitting an existing plant with a wet tower system is about 0.6 mills/Kw-hr. However, unique problems associated with specific sites can cause wide variations, both up and down, from this general value.

If the economic effect of providing waste heat control is evaluated in terms of cost to the consumer, a true picture of the real cost burden is achieved. It is important to note that busbar cost variation is not the only factor influencing consumer cost. The amount the consumer pays for electric power is substantially higher than the actual production cost. Transmission, maintenance, advertising, etc., all add to the cost which the consumer pays for his electric power. For example the average U.S. residential electric power user paid 21.0 mills/Kw-h in 1970 (Ref. 44) when the average busbar cost was 7.2 mills/Kw-hr (Ref. 45) for stations put into service after 1967. Thus, for modern plants, the production cost is only approximately 30 percent of the residential electric power cost. In 1971, the average U.S. residential consumer paid 21.9 mills/Kw-hr for 7,380 Kw-hr, which gives an average annual electric bill of $161.62 (Ref. 44). Thus, increasing the busbar cost by 0.2 mills/Kw-hr due to closed-cycle cooling for future plants would increase the average 1971 U.S. residential consumer's electric bill by $1.48 per year or less than one percent. Similarly, a 0.6 mills/Kw-hr increase for backfitted cooling systems would cause a $4.43 annual increase, which is less than a three percent increase.

These data assume that the consumer buys all of his power from the plant in question. Cost increases of goods and services to the consumer due to increases in power rates to commercial and industrial users are not included.

SECTION V

BENEFICIAL USES OF WASTE HEAT

General

The problems associated with the discharging to watercourses of large quantities of heated condenser discharge water produced in steam-electric power generation have led to an investigation of beneficial uses of this "waste" heat. Strictly speaking, "waste" heat is the heat contained in the condenser discharge effluent from the normal operation of steam-electric turbines, that is, effluent discharged after a condenser rise of 5.5-16.7°C (10-30°F). As given in Reference 46, a "beneficial" use of this heat must either reduce the thermal water pollution problem directly or provide economic compensation to help offset the cost of cooling devices. These criteria have resulted in a large number of feasible and imaginative ideas on waste heat use which can be classified into two general approaches. They are direct utilization of low level (32-49°C or 90-120°F) waste heat and the integrated "total energy" complex.

Direct Utilization

Three areas of activity currently hold promise for the direct utilization of waste heat: secondary sewage treatment, agriculture, and aquaculture. Table 12 from Reference 47 identifies several other possible uses for heated condenser discharge water but, as can be seen, the supply temperature required for some of these applications is well above the 32-49°C (90-120°F) summertime temperatures realized with current steam-electric condenser discharge operations.

TABLE 12. ENERGY USE ESTIMATE

Energy Component	Supply Temperature* °C (°F)
Electricity	
Low Temperature Heat	
Space heat	93 (200)
Domestic hot water	93 (200)
Absorption air conditioning	121 (250)
Water distillation	129 (265)
Industry	149 (300)
Snow and ice melting	100 (212)
Transportation	149 (300)
Waste Heat	
Secondary sewage treatment	35 (95)
Agriculture	35 (95)
Aquaculture	35 (95)

* Approximate minimum temperature of transmitted steam or hot water.

Use of waste heat in sewage treatment plants is just now being given serious consideration. Preliminary studies have shown that biologica processing of sewage can be increased by a factor of ten by raising th temperature using low-grade waste heat (Ref. 48). The Environment Protection Agency is currently funding a study for New York State which will evaluate the acceleration of secondary sewage processing l heating (Ref. 47). These studies may indicate a potential use for hea ed condenser discharge water but it is very doubtful that this use cou be anything more than a supplementary application because of the lar quantities of waste heat involved.

Another possible use of waste heat is in agricultural applications. It appears technically feasible to use waste hot water in open-field agriculture and for temperature control in greenhouses and animal shelters. The question of economic feasibility is as yet unanswered.

Some of the potential benefits to accrue from the use of waste heat fo temperature control in open-field agriculture are: prevention of damage caused by temperature extremes, extension of the growing season, production of growth, and the improvement of crop quality. A significant pilot demonstration of these benefits is currently under way at the Thermal Water Horticultural Demonstration Project in Oregon's Willamette Valley. It is cosponsored by the Eugene Water & Electric Board and the Environmental Protection Agency and managed by the Vitro Division of Automotion Industries. Thermal water at 32-60°C (90-140^{0}F) from a nearby Weyerhaeuser Paper and

Pulp Company plant is sprayed over orchards and crops to provide frost protection, plant and crop cooling, and irrigation on 69 hectares (170 acres) of farm-land. Results indicate: 1) that thermal water has a definite advantage over cold water in providing complete plant frost protection, 2) that thermal water through evaporation is effective in plant cooling, and 3) that thermal water for irrigation is as good as normal cold water. Preliminary economics of this multi-use system also appear favorable as shown in Table 13 (Ref. 49).

Table 13. Total Annual Cost Per .4 Hectares (Acre) for Three Crop Protection and Irrigation Systems

System	Annual Fixed Cost	Annual Operational Cost	Total Annual Cost
Multi-Use	$81.54	$ 11.20	$ 92.74
Solid Fuel and Hand-Move Irrigation	$13.59	$265.05	$278.64
Central Distribution and Hand-Move Irrigation	$74.75	$295.05	$369.80

The importance of soil temperature to plant growth has long been recognized although basic knowledge in this area is somewhat limited. A number of programs currently underway are investigating the potential benefits of heating soils with waste hot water. An experimental project supported by the State of Oregon, the USDA, and the Pacific Power and Light Company showed that soil warming, in this case using electric heating cables, gave increased crop yields averaging 40 percent. Experiments at TVA have shown the combined effects of soil

heating and subirrigation to be most favorable in combination as indicated in Table 14 (Ref. 50).

Table 14. Effects of Soil Heating and Subirrigation on Vegetable Production, Muscle Shoals, Alabama, 1971

	Yield Tonne Per Hectare (Tons Per Acre)			
	Irrigation		No Irrigation	
Crop	Heat	No Heat	Heat	No Heat
String Beans	18.2 (8.1)	9.0 (4.0)	15.5 (6.9)	6.1 (2.7)
Sweet Corn	20.2 (9.0)	11.2 (5.0)	13.9 (6.2)	7.2 (3.2)
Summer Squash	68.6 (30.6)	60.3 (26.9)	46.2 (20.6)	39.5 (17.6)

Further experimental work on subsurface heating and subsurface irrigation is being performed at the Western Washington Research and Extension Center, while economic studies of these systems are in progress at Washington State University.

The utilization of thermal water in open field agricultural applications appears to offer significant benefits although several problem areas remain. Of great importance is the long-term implications of waste heat applications for soil management and disease and pest control. A more basic problem is the economic risk associated with implementing pilot scale research to large farms over extended years of operation. The problem of radioactive contamination of agricultural products from the use of cooling water from nuclear power plants must be solved and may require special precautions which could, in turn, diminish the economic attractiveness of these proposed ventures. Other pollutional side-effects could include changes in temperature or chemical characteristics of ground water and the spreading of pesticides.

The advantages of greenhouses for the cultivation of vegetables have long been acknowledged. These include larger crops, bigger yields, the ability to culture crops year round, and the ability to provide optimal environmental conditions for crop growth. Although the costs of producing vegetables in greenhouses vary with location, the two largest single operating costs are always labor and fuel. Heating costs for commercial greenhouse operations utilizing fossil fuels can be as much as $4900 to $27,200/hectare ($2000 to $11,000/acre)(Ref. 51).

The University of Arizona and TVA, among others, have performed work on the applicability of heating and cooling greenhouses using low level waste heat. At the University of Arizona's Puerto Penasco (Sonora, Mexico) greenhouse facilities about 300 cultivars of vegetables and six cultivars of strawberries have been tested for growth and yield characteristics. Results have shown that the cultivars developed in hot, humid areas respond best to the environments maintained in these greenhouses. Also, generally speaking, most vegetables tend to be more succulent and brittle and crop yields are much higher than is usually the case when they are grown outside. Table 15 (Ref. 52). presents a comparison of marketable crop yields grown under different conditions. It should be noted that the yields in the table were obtained under high light conditions which would not prevail in the northern latitudes. The success to date of this facility has led to the development of a two hectare (5 acre) greenhouse complex which is now in operation for the sheikdom of Abu-Dhabi.

TVA and Oak Ridge National Laboratory are collaborating on an

TABLE 15. A COMPARISON OF MARKETABLE CROP YIELDS

Kind of Vegetable	Puerto Penasco Greenhouses: Marketable Yield 0.4 hectare or 1 acre/yr	Puerto Penasco Greenhouses: Approximate Average Yield From Greenhouses	Comparative Data for U.S.: Approximate Average Yield Outdoors/ 0.4 hectare or 1 acre/yr	Comparative Data for U.S.: Good Yield Outdoors/0.4 hectare or 1 acre/yr
Cucumber (European Type)*				
Fall Crop	144 tonne(158 tons)	-	4 tonne(4.4 tons)	11 tonne(12 tons)
Spring Crop	159 tonne(175 tons)*			
Eggplant				
Fall Crop	60 tonne(66 tons)*	-	6.5 tonne(7 tons)	7.5 tonne(8.3 tons)
Spring Crop	60 tonne(66 tons)*			
Lettuce				
Bibb & Leaf				
Winter Crop	3500 ctn @ 2 dozen	3500 ctn	-	-
Okra				
Winter Crop	36 tonne(40 ton)	-	-	4.5 tonne(5 ton)
Peppers				
Bell				
Winter Crop	13.6 tonne(15 ton)	-	4.2 tonne(4.7 ton)	5.7 tonne(6.3 ton)
Radish				
Winter Crop	40,000 bunches @ 12/bunch	40,000 bunches	-	20,000 bunches
Tomato				
Fall Crop	68 tonne(75 tons)	36.3 tonne(40 ton)	6.2 tonne(6.8 ton)	27.2 tonne(30 ton)
Spring Crop	54.4 tonne(60 ton)	54.4 tonne(60 ton)	-	-

* Based on a harvest period of 90 days.

experimental greenhouse facility located adjacent to TVA's Browns Ferry Nuclear Power Plant. The greenhouse is to be cooled in the summer by evaporating the 32°C (90°F) water from the turbine condenser with once-through air and heated in the winter by operating the evaporative pads in an air-recirculating mode (Ref. 53). Objectives of this demonstration are to prove out the scaled-up heating and cooling system developed by ORNL which utilizes the waste hot water to establish the feasibility of producing vegetables commercially in the environment provided, and to evaluate the economic viability and commercial potential for large-scale greenhouse operations (Ref. 54).

One of the major problems associated with the use of waste heat in greenhouse applications is that of financing and marketing the large quantities of produce raised in any greenhouse complex that might conceivably utilize a small portion of the waste heat available from modern power plant operations. It is estimated, for example, that glass houses which could use one-fourth of the waste heat from a 100 mwe power plant would require a capital investment of about $25 million and would occupy some 101 hectare (250 acres) (Ref. 51). Other problem areas include the possibility of increased fungi growth and spread of bacteria in the near 100 percent humid greenhouse atmospheres, the effect of various water treatment chemicals used in the cooling water system on greenhouse plants, and the possibility of radioactive contamination of greenhouse produce by the cooling water discharged from nuclear power plants.

The same system for heating and cooling greenhouses has potential application for environmental control in livestock shelters. Proper temperature, humidity, and ventilation control in these shelters has been shown to decrease feed consumption and increase livestock productivity. An analysis of broiler and swine production costs indicate that feed costs represent 65 percent of total production expenses. It has been suggested that the use of waste heat could reduce fuel bills and increase feed efficiency and growth rate for both hogs and broilers by providing optimal temperature conditions (Ref. 51). TVA has further proposed a livestock waste recycling system in which algae would be cultivated on the nutrients from manures in a series of ponds and subsequently harvested and processed into a high-protein feed source for livestock (Ref. 50).

Significant problems must be overcome, however, before waste heat will find extensive utilization for environmental control in animal shelters. One of the problems is insufficient knowledge on the technical and economic feasibility of such systems, particularly the large production operations envisioned. It is estimated that current commercial operations are two or three orders of magnitude smaller than would be required to use 10 percent of the waste heat from a 1000 Mwe power plant (Ref. 51). Disease, odor, waste disposal, and land use are critical problems facing such large-scale production operations. Geographical concentration of livestock production facilities and seasonal demands for waste heat also appear to be limitations to widespread utilization of this concept. Problems with radioactivity

(in the case of nuclear plant supplied waste heat) and biocides in condenser cooling water still must be resolved.

Another potential area for direct utilization of waste heat from power plants is aquaculture. The Japanese have pioneered in this area since their initial culture experiments at the Sendai Power Plant in 1964. Presently five other demonstration programs utilizing heated effluent from fossil-fueled plants and a multi-species demonstration project at the Tokai-Mura Nuclear Power Station are under development. Much of the basis for the use of waste hot water for aquacultural applications has been established through years of extensive Japanese fish culturing experience. In 1967 aquacultural products in Japan represented 6 percent of the total catch and 15 percent of the total value (Ref. 51).

Of the 2500 known fish species, less than one percent have been successfully cultured at all and probably less than 0.5 percent have been intensively cultured as in animal husbandry. The simplest operation is the stocking of fish in pond cultures. Yields of a few hundred kg per hectare (pounds per acre) can be sustained on the natural food elements available in the water system. With nutrient enrichment by nitrogen and phosphorous fertilization, these yields can be increased to 670 kg per hectare year (600 lb per acre year) and with supplemental feeding the yields can be as high as 1800-2700 kg per hectare year (1600-2400 lb per acre year). At this stocking level, however, buildup of fish wastes, biological oxygen demand, and low dissolved oxygen content can lead to an overwhelming or unbalance of the aquatic system. Catfish, currently the most widely cultured

fish in the United States (24.5 million kg or 5.4 million lb in 1970), have traditionally been raised on a seasonal basis in pond cultures.

Dynamic culture systems offer a greater degree of environmental control and consequently offer larger potential yields. Such systems as the confinement of fish in cages submerged in a natural water body or cooling channel and flowing water culture in which fish are stocked in constructed multiple channels can allow a high degree of environmental control. Yields of 224,000 to 900,000 kg/hectare yr (200,000 to 800,000 lb/acre-year) have been reported for these systems (Ref. 51). A successful commercial operation of flowing water culture is the Thousand Springs Trout Company in Buhl, Idaho. This year-around operation is made possible by a 950,000 l/min (250,000 gpm) supply of constant temperature 15.6°C or (60°F) springwater which is distributed into high population density channels. Rainbow trout yields of 224,000 to 450,000 kg/hectare year (200,000 to 400,000 lb per acre-year) have been obtained. Several seawater species have been cultured on a seasonal, partial-environmental-controlled basis. This includes raft culture of oysters and mussels, cage culture of yellowtail, and the culture of shrimp, blue crab, abalone, squid, lobster and salmon (Ref. 54). The Japanese have also cultured several varieties of seaweed and algae.

Basic research has shown that optimal fish growth can be realized with the maintaining of proper temperatures. The concept of using power plant coolant to maintain optimal temperatures for fish cultures

was first demonstrated in Japan and more recently has been investigated in the United States. The oyster farms of Northport, Long Island have produced oysters on a commercial basis in the heated effluent of Long Island Light Company. By proper environmental control, selective breeding and seeding of oysters, this commercial operation has reduced by 1-1/2 years the four year oyster growing cycle. The use of thermal effluent permits accelerated growth over a four to six month period during which the oysters would normally be experiencing little growth.

Catfish culturing in thermal waters has also been practiced and at least one operation is now reported on a small-scale commercial operation basis. This operation uses the thermal discharge canal of a fossil fueled plant of the Texas Electric Service Company at Lake Colorado City, Texas for the cage culturing of catfish. Other pilot investigations are being performed in covered channels using discharge water from a TVA steam plant in Gallatin, Tennessee and at Houston Lighting and Power Company's Cedar Bayou Power Plant.

Cultivation of shrimp in heated effluent is being investigated at Florida Power Corporation's Crystal River site and at the Turkey Point facility of Florida Power and Light Company. Perhaps the largest shrimp farming venture anywhere is that of Marifarms Inc. of Panama City, Florida. This operation uses technology originally developed in Japan to cultivate and harvest some 1000 hectares (2500 acres) of sea-level impoundments and 240 hectares (600 acres) of land ponds. This operation utilizes the warm water from the local power plant to maintain water temperatures in the winter months.

Numerous other small scale efforts in the United States have been directed toward the culturing of the "luxury" seafoods, oysters and shrimp. Work on the culturing of lobsters in warm effluents is just now beginning to get underway. The Japanese, as noted earlier, have pioneered in the efforts to use waste warm water for fish cultivation purposes. Present operations include the culturing of shrimp, eel, yellowtail, seabream, ayn, and whitefish.

Several problem areas will have to be resolved for the development of large scale thermal aquaculture facilities. One of the major questions is that of economic feasibility and a dependable market for large scale operations. There have been several instances of technically successful operations which failed because of an inadequate marketing arrangement (Ref. 51). Another significant problem for large scale operations is the treatment of fish wastes and the requirement for adequate water reconditioning systems, including aeration, sedimentation, screening, chemical coagulation, and pH control (Ref. 54). A recent study found that 114 hatcheries were releasing 21 tonne (23 tons) of BOD per day - equivalent to a city of 270,000 people (Ref. 46). More work is needed to determine optimal growth conditions and food substances in order to maximize feed conversion to flesh. Although cultured species in adequately controlled environments do convert nutritionally balanced feed to flesh as efficiently or better than do chicken broilers, suitable feed formulation has been developed in this country only for the mass culture of rainbow trout. The possibility of radioactive contamination

of cultured species is another problem area which must be adequately solved if utilization of thermal water from nuclear power plants is to be achieved. It is also unlikely that any aquaculture facility could utilize all the waste heat from a typical modern day steam electric power plant. Furthermore, it is possible in certain locations that ambient water temperatures may preclude the use of any waste heat during the critical (for power plant waste heat disposal) summer months. Thermal aquaculture does not necessarily reduce the heat disposal problem of the power plant but it may provide additional profitability.

In summary, the direct utilization of power plant waste heat has potential application in the areas of secondary sewage treatment, agriculture, and aquaculture although each of these areas shares a number of problems along with several proposed uses such as ice-free shipping lanes which have not gone beyond the preliminary investigation stage in common. One of the major problems is the high distribution costs associated with pumping large quantities of low grade waste hot water. In an effort to minimize these costs, facilities would have to be located in the reactor exclusive area if the waste heat were supplied by a nuclear power plant, and this introduces questions of radioactive contamination by condenser cooling waters. Another problem is the large mismatch which exists between the amount of heat available from a typical steam electric plant and that which could be used by any process or combination of processes. This mismatch may not impose any penalty on the potential user, but the ability of the utility to market only a small fraction of the heat produced may reduce the incentive for

utility participation and steer the utility along the more conventional lines of auxiliary cooling towers. The demand for heat is also largely seasonal in nature and may further restrict the usefulness of these applications. Of critical importance to the utility is the capability of disposing of waste heat in summer months.

Finally and most importantly the economics of such applications have not yet been adequately demonstrated on a large commercial scale basis. The planning, financing, and coordination of a commercial size operation have yet to be delineated.

Total Energy Complex

The concept of "total energy" is not entirely new. Over 400 commercial, industrial, and institutional installations fulfill their heat requirements and electricity demands with total energy systems (Ref. 55). These systems utilize relatively small capacity gas turbines and diesel engines to generate their power heat requirements. The total energy complex, in contrast, would involve the use of high quality steam from the steam electric power plant cycle to provide both process heat and electricity.

Figure 16 (Ref. 56) shows conceptually some of the different ways of using the energy input to a steam turbine power system. The top illustration is the familiar steam-electric generating system with about 40 percent of the input energy converted to electricity and 60 percent dissipated to the environment as waste warm water (or air). The second diagram shows that extraction of some of the steam before

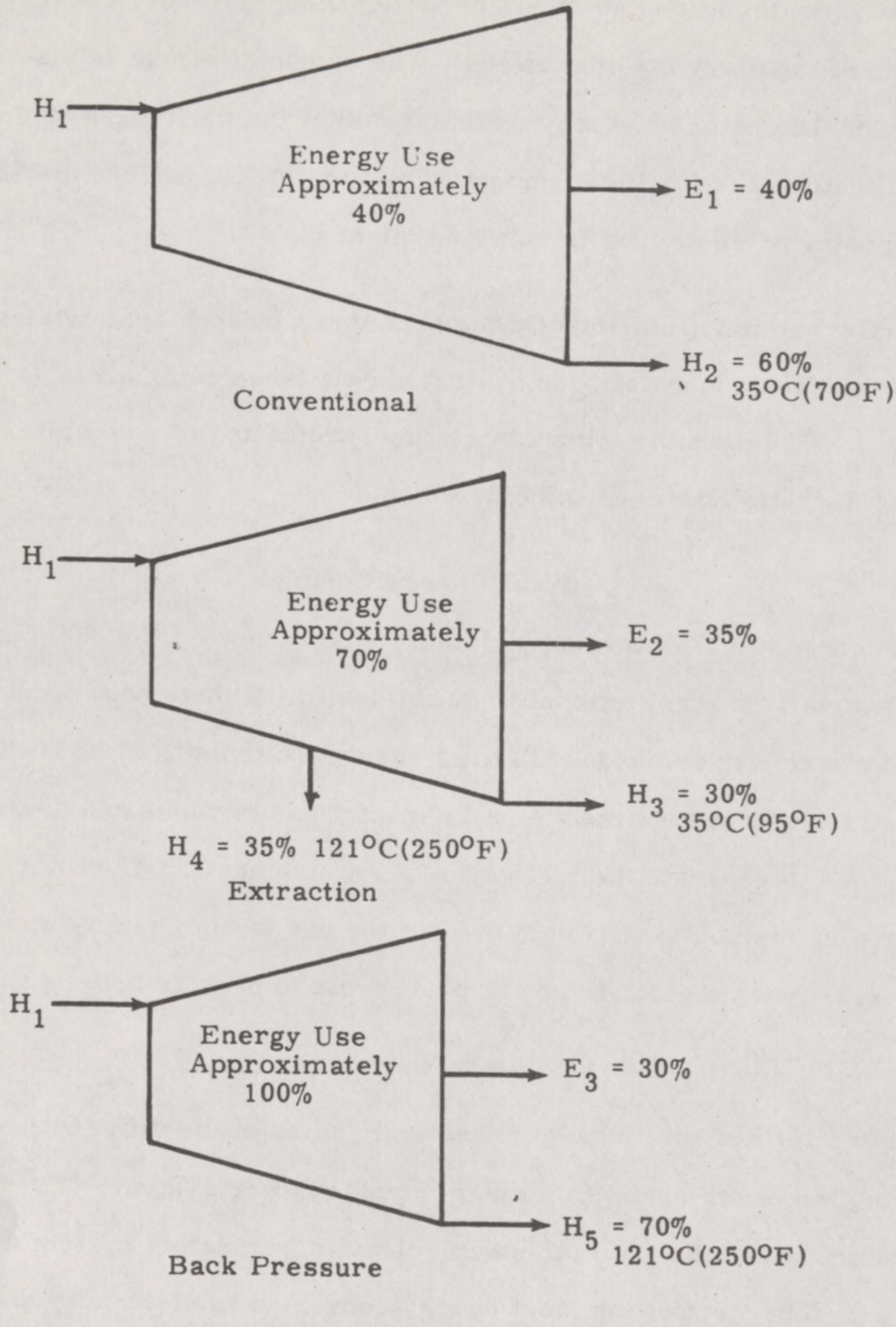


Figure 16. Conventional and Dual-Purpose Steam Turbine Performance

or after it has generated some electricity makes better use of the total energy input. Thirty-five percent of the energy is converted to electricity and 35 percent is extracted for other purposes and would replace energy that would otherwise be supplied by another source. Energy utilization in this case is about 70 percent with the remainder being dissipated to the environment. The third diagram illustrates the ultimate in energy utilization if there is a very large need for low temperature heat. In this case the steam expansion in the turbine is stopped short of full expansion to produce the process heat required. Energy utilization in this case would be very nearly 100 percent.

Extraction and back-pressure turbine concepts for the production of process heat are not at all new. District heating systems both in this country and abroad have used these systems in providing power and space heat for many years (Ref. 57,58) with Consolidated Edison of New York being the largest district heating system in this country. Industrial process steam has also been supplied by combination heat/electric power plants as in the case of Consumer Power's Midland Nuclear Plant (Ref. 59). What is new, however, is the concept of combining the turbine systems shown in Figure 16 into a composite arrangement so as to fully integrate power generation and process heat requirements for an active city and its industry, commerce, and residences.

Oak Ridge National Laboratory has done extensive work in this area, and has conceptualized a number of integrated systems for the pro-

duction/use of electricity/heat (Ref. 60). In one study a reference city with a population of 400,000 and a climate similar to Philadelphia was investigated. It was found that heat supplied from a steam extraction turbine could be competitive with present heat sources. The combined utilization of thermal energy and electricity in this total energy complex was found to result in significant reductions in thermal emissions and air pollution and in the conservation of fossil-fuel resources.

The institutional, financial, and management problems facing the establishment of such an integrated total energy complex are enormous. Transmission and distribution costs (a function of population density) for the delivery of thermal energy are a major determinant in the economic viability of any total energy complex and will probably dictate a case by case investigation. Nevertheless the potential benefits of a total energy complex warrant serious consideration. The total energy complex could very well be a solution to several environmental problems in the reduction of thermal pollution from power plants.

SECTION VI

TECHNOLOGY OF INTAKE STRUCTURES

At each plant site, it shall be required that the location, design, construction, and capacity of cooling water intake structures reflect the best technology available for minimizing adverse environmental impacts. Thus, the existing technology with respect to intake structures will be defined. The research, development, and demonstration programs currently underway to influence intake designs will also be discussed.

The passage of young fish through power plants and into unscreened irrigation diversions has resulted in heavy, undesirable mortality. The U.S. Bureau of Commercial Fisheries has been searching over the years for efficient, relatively low cost means for deflecting the fish away from these potentially dangerous intake areas (Ref. 61). In Figure 17, on the left, there is illustrated the manner in which fish screens were installed years ago, normal to the flow. Downstream fish migrants on their way to the ocean, upon reaching this facility, were required to stop and search in an effort to find the bypasses provided. This caused delay and an undue expenditure of their physical effort.

In the center of Figure 17, the next advanced step is shown. A fish deflecting structure is placed on an angle of 30 degrees to the direction of flow. Fish passing downstream upon approaching the structure

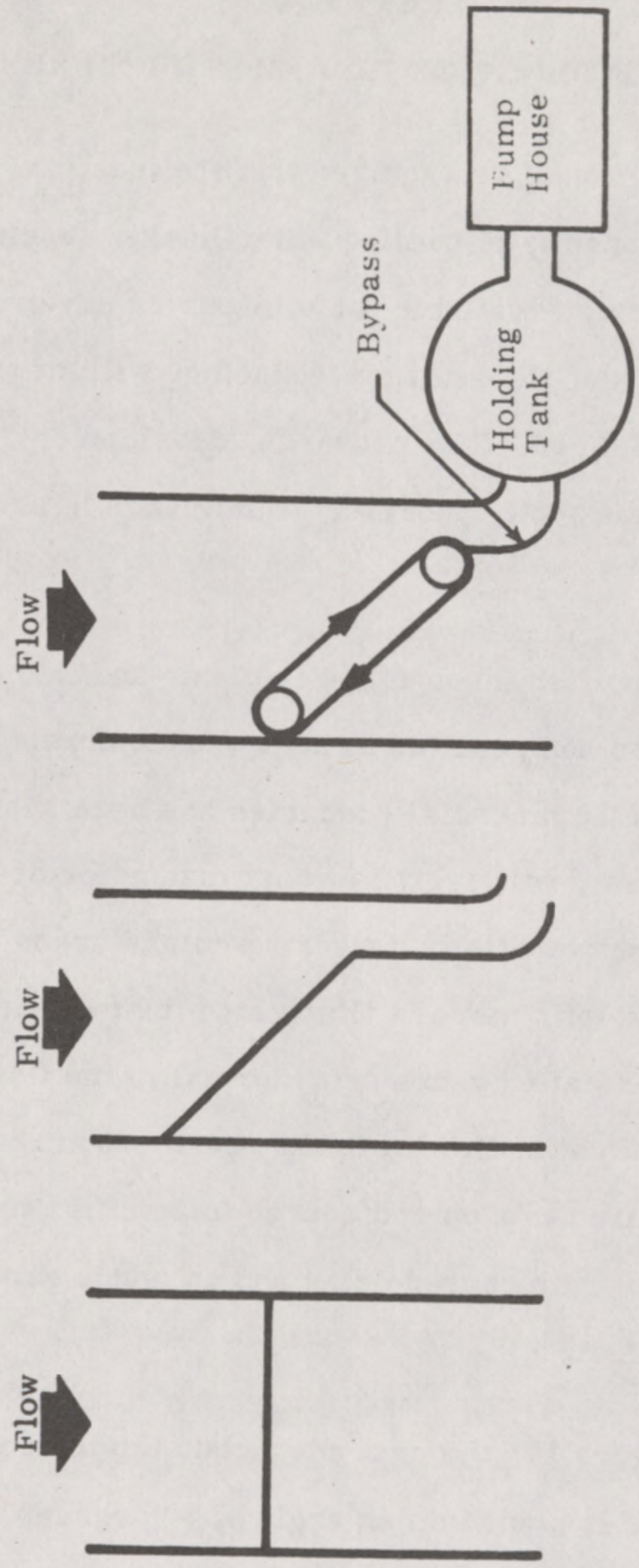


Figure 17. The Placement and Design of Fish Guidance Systems

position themselves head-first into the flow. This apparently provides them with increased control over their movements, making it easier to avoid obstacles as they drift downstream. When the structure is placed on an angle to the flow, fish moving downstream and into the bypass do so without hestiation.

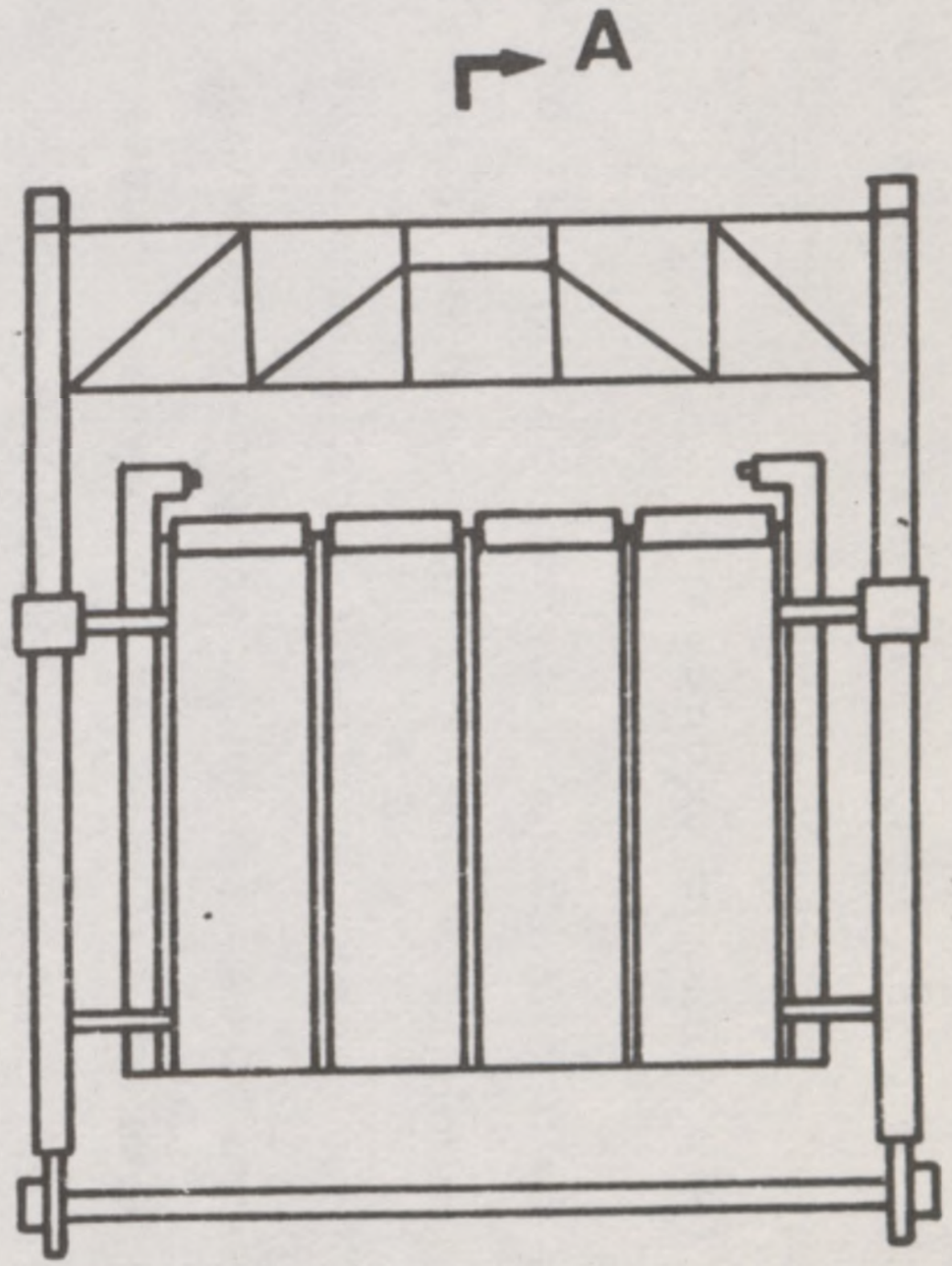
On the right of Figure 17, the horizontal traveling screen for guiding fish is illustrated. Travel of the screen is across the full width of the canal toward the bypass. At this point the screen makes a 180-degree turn and travels back upstream. The netting of the screen hangs full depth. Fish that are following the movement of the water through the canal are quickly deflected through the bypass and into the holding tank.

The advantages of the horizontal traveling screen system are low cost of screen structures, high efficiency in the diversion of juvenile fish migrants, easy deflection of fish, minimum effects due to water depth fluctuation, minimal head loss with single screening, screen self-cleaning, higher velocities of approach can be handled and simplicity of operation. According to Reference 61, higher than normal approach velocities can be used. Should fish be impinged onto the screen by the force of the motion, the impingement would be quite gentle, since the travel rate of the screen can be matched to the velocity of approach. For this same reason, debris impinging gently onto the screen is released readily. Impinged fish are carried directly into the bypass for

release, another very distinct advantage of the traveling-screen system. With other screens, impinged fish cannot be carried into the bypass and must somehow struggle off the screen or be carried up and over as in the case of drum and industrial water screens.

The National Marine Fisheries Service has been working with two methods for diverting anadromous fish out of intake structures (Ref. 62). They are the horizontal travelling screen and the vertical travelling screen. The horizontal travelling screen is still in the development stage. It appears that it will be a useful device for the diversion of fish in certain applications, such as canals, hydroelectric dams, irrigation and perhaps power plants later on. The horizontal travelling screen was recently installed in the Troy test plume on one branch of the Grande Ronde River in northeast Oregon. It can travel from 0.4 to 1.2 m/s (1.3 to 4 fps). Water from the river can be diverted into a concrete canal measuring 44 m (143 ft) long, 12.2 m (40 ft) wide and 3.7 m (12 ft) deep. Hydraulic tests of the travelling screen will be made.

Vertical travelling screens will become operational this year at Little Goose Dam near Starbuck, Washington. They will serve the Snake River hydroelectric plant. There will be nine screens operating at this dam, one for each intake. The vertical travelling fish screen for this dam is shown in Figure 18. On the right, an elevation view shows the screen retracted as one looks downstream. There are four separate screen sections, each driven to travel vertically. On the left of the figure, a sectional view shows the screen in the operating position. It is inclined



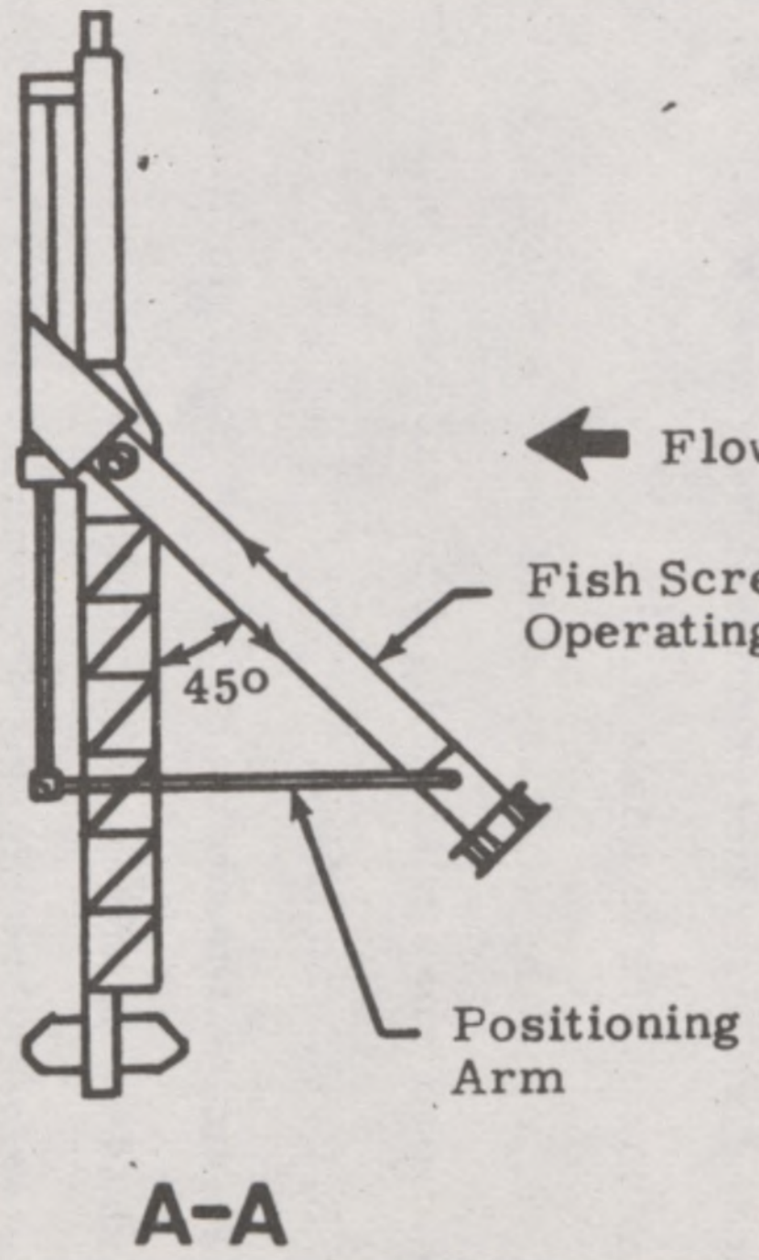


Figure 18. Vertical Travelling Screen

forward at 45° into the oncoming flow. Although the screens will be operational, development effort is continuing to obtain a screen that will be maintenance free for a minimum of three years.

Since 1957, Southern California Edison Company (S.C.E.) has investigated various methods of minimizing the intake of fishes at their coastal generating facilities. These methods include the installation of velocity caps over offshore intake structures, fish pumps and protective netting devices. As a continuation of these efforts, a series of behavioral studies with coastal marine fishes was conducted from March through October of 1972 at the Redondo Beach Generating Station, situated south of Los Angeles (Ref. 63). The program goals are concerned basically with determining and investigating those behavioral characteristics of marine fishes which can be used as parameters in the modification of existing, and in the design of future, fish diversion-removal systems at S.C.E. coastal generating stations. These goals are:

1. Determine the efficacy of screens and/or louvers in guiding fishes which might be expected in the vicinity of S.C.E. facilities.
2. Determine the optimum method for returning guided fishes back to sea unharmed.
3. Determine how intake structure velocity caps function in preventing fishes from entering intake waters and attempt to improve the performance of these structures.
4. Determine the impingement tolerance of key fishes to screens set at various vertical and horizontal angles to various approach velocity levels.

5. Determine the maximum burst and sustainable swimming speeds of prominant marine species indigenous to the area.

Research on the first two objectives has been completed. Research is currently underway on the remaining three objectives and should be completed sometime in late 1973. Coincident with the start of these behavioral studies, designs for the circulation water system for Units 2 and 3 of the San Onofre Nuclear Generating Station were being evaluated. Fish study guidelines have been premised, in part, upon the possible application of the positive results to prototype installations, and close liaison has been maintained with design engineers.

The results obtained from tests performed under the first two objectives are reported in Reference 63. A simulated intake screenwell in the form of a redwood flume of dimensions, 15 m by 1.8 m by 1.2 m (50 ft by 6 ft by 4 ft), was installed at S.C.E.'s Redondo Beach Generating Station. Stainless steel, 1.6 cm (5/8-in.) mesh screen panels and various louver configurations were installed at angles of from 90 degrees to 20 degrees to the direction of flow. Groups of indigenous marine fishes were introduced at flow velocity levels of from 0.15 m/s to 1.2 m/s (0.5 fps to 4.0 fps) at the different structural settings. The reactions of test specimens to diversion structures at these velocity levels were observed, photographed and analyzed. The screen was non-travelling.

Optimum guidance occurred at a mean approach velocity of 0.61 m/s (2.0 fps) to louvers spaced 2.54 cm (one in.) apart arranged in, and perpendicular to, a frame set at 20 degrees to the flow (Figure 19). Screens alone were not nearly as effective as louvers in diverting test specimens from the main flume flow into holding chambers. Fish guidance effects increased dramatically through settings of 45 degrees to 30 degrees, and an advantage at 20 degrees over 30 degrees was strongly indicated. Air bubble curtains were tried in conjunction with certain screen settings but met with only marginal success.

Equally as important as louver and velocity settings to successful diversion of fishes is the configuration of the bypass channel and holding-removal chamber. A successful model was designed into which fishes moved readily and from which they could be safely removed and returned unharmed to sea. It was reportedly demonstrated that test species moved into and through a bypass channel and remained in the holding chamber only if the flow were as smooth as possible and free from turbulences. The test effort was a modeled study in which all parameters except fish size, velocity, and louver spacing were on a reduced scale.

The Johns Hopkins University, under a three year grant from the Edison Electric Institute, is studying the biological effects of power plant cooling systems (Ref. 64). This study may influence the design of plants to minimize environmental impact such as the proposed Brandon Shores facility of the Baltimore Gas and Electric Company. The research is focusing on the design of fish screens at cooling water intakes, the effects of sudden environmental changes on small organisms that pass

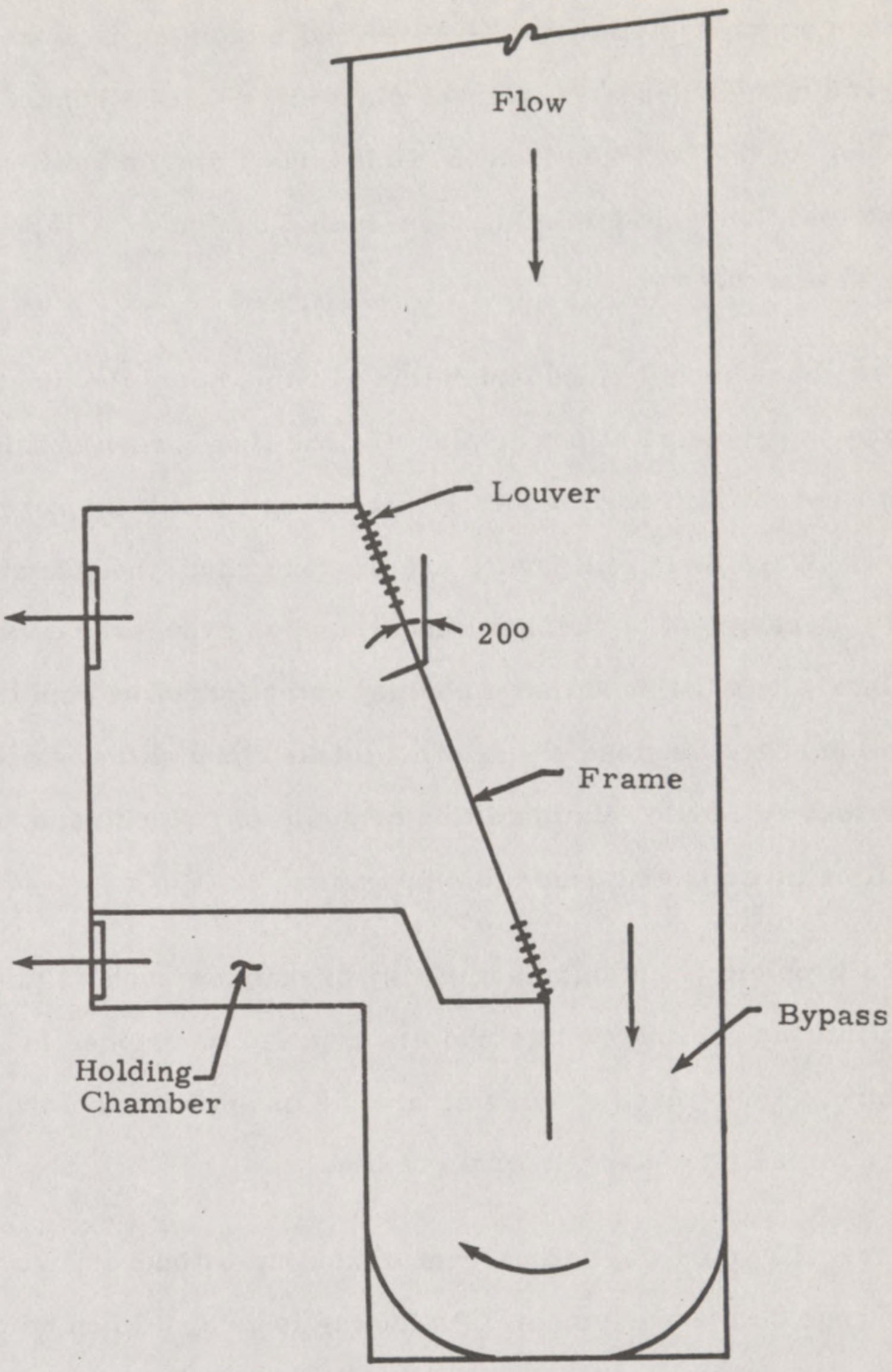


Figure 19. Plan View of Test Flume Showing Bypass Design With Louver Frame at 20 Degrees to Flow

through the cooling system with the water and biofouling of system parts by slime and marine deposits. Power plant sites will be studied at the Great Lakes, in the Far West, on the Gulf Coast, and on the Chesapeake Bay. Two test flumes, simulating plant intake systems, will be built to aid in the research.

Three areas have been defined under this work as being the most relevant ecologically to problems at power plants. The fish screen problem is important whereby fish are frequently sucked up against the screen by the intake flow. When their gill covers are pressed shut, the fish suffocate. Maryland's Department of Natural Resources has expressed concern about this problem. It is believed that a cooling water intake system that is flush with the shore, instead of use of an intake channel that extends into the waterway, could eliminate this problem of fish entrapment. This theory will be investigated under this program.

The second problem is entrainment of tiny organisms such as plankton, which pass into the cooling system and are exposed to changes in temperature and pressure. Since these organisms are the base of the aquatic food chain, their fate affects that of larger forms of life.

Researchers will study ways to prevent biofouling without inflicting an adverse change on the ecosystem. Biofouling is caused when bacteria form a slime on a wet surface, followed by tiny organisms that eat the bacteria and which are then followed by even larger organisms. The cooling systems provide a large surface area for this natural process to take place. As biofouling increases, friction is created, heat transfer is reduced and the efficiency of the entire cooling system declines.

Chlorination has been the principal means of cleaning these surfaces. However, its extensive use has prompted questions as to its environmental impact.

The research, development, and demonstration efforts presented in this section are only a part of the large amount of work being performed. At a recent workshop on entrainment and intake screening (Ref. 65) approximately 20 presentations were given by researchers from government agencies, utilities, universities, and private industries. The reports covered the entrainment of fish, shrimp, zooplankton, phytoplankton, and minute organisms by various intake configurations. These data will ultimately contribute to optimum designs of intake and discharge structures.

SECTION VII

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SECTION IX

NOMENCLATURE

The following terminology is defined in this report:

allowable temperature difference	The temperature of the hot water discharged from the heat rejection system into the stream minus the temperature of the water available from the stream
approach	The difference between the cold water temperature out of the tower and the wet bulb temperature
blowdown	The amount of cooling water drained off for disposal and replaced by fresh makeup water
closed cycle	The system wherein all heat is rejected from a cooling tower or pond and no natural receiving body is necessary except possibly for makeup water
cold water temperature	Temperature of the water being supplied to the power plant
completely mixed pond	The flow between the inlet and outlet locations of the pond combined with wind mixing tend to keep the pond at a nearly uniform temperature
condenser rise	Temperature difference between the hot water leaving and the cold water entering the condenser
consumptive water use	The non-return of makeup water to the source
drift	The loss of entrained water that is carried out of the top of a wet tower or from a spray pond
equilibrium temperature	The pond surface temperature for which the heat leaving will exactly equal the heat entering a body of water

flow-through pond	A pond in which the temperatures decrease continually along the pond
heat exchange coefficient	A coefficient that describes the rate of heat lost across the air-water interface
initial temperature difference	The steam saturation temperature minus the dry bulb temperature (dry tower only)
once-through cooling	The system wherein cooling water is taken from a natural receiving body, passes through the condenser, and is discharged downstream
open cycle	Hot water from the condenser is passed through a supplementary heat rejection system for cooling prior to discharge into a natural receiving body
plant efficiency	Thermal efficiency of the total plant
plant heat rate	Heat energy required for production of electricity expressed in kcal or Btu/Kw-hr
range	The water temperature decrease in the tower
residual temperature rise	The difference between the cooling pond outlet temperature and the design equilibrium temperature
turbine back pressure	Condenser pressure

TEMPERATURE DISTRIBUTION ANALYSIS

BY

JOHN ERIC EDINGER

(769)

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Table of Contents

List of Tables

List of Figures

Scales of Processes 4

Surface Area Descriptions 7

Time-Temperature Relationships 9

Initial Mixing Processes 11

Non-buoyant Two-Dimensional Jet Discharges 13

Non-buoyant Three-Dimensional Jet Discharges 16

Buoyant Surface Discharges 18

Submerged Buoyant Discharges 21

General Properties of Initial Mixing 23

Intermediate Mixing Processes 28

Two-Dimensional Intermediate Mixing 29

Three-Dimensional Intermediate Mixing 36

Large Scale Processes 38

Surface Heat Exchange 39

River Situations 41

Run of River Impoundments 44

Estuarine Situations 45

Coastal Water Situations 47

Summary 51

Nomenclature 52

References 54

Tables

Table 1 - Comparative evaluation of different initial mixing area relationships for similar discharge conditions. 27

Table 2 - Scales of separate heat dissipation mechanisms for a typical 2000 MW Powerplant Discharge. 50

Figures

Figure 1 - Two dimensional intermediate mixing unbounded case generalized plume.

Figure 2 - Two dimensional intermediate mixing bounded case, generalized distribution.

Figure 3 - Observed temperature distributions for a deep narrow river with vertical mixing of a surface heat discharge.

Figure 4 - Comparison of observed temperature rise and predictions for vertically mixing river using two-dimensional advective dispersive heat balance with boundary reflections.

Figure 5 - Three dimensional intermediate mixing scaling area compared to its parameters for plumes from a number of plants sited along a sectionally homogenous estuary, and for river sites.

Figure 6 - Comparison of observed upstream to downstream temperature rise for a mixed river with plant production per unit river flow.

Figure 7 - Observed temperature profiles along a river with a cold water release and cooling water use.

Figure 8 - Comparison of observed and predicted temperatures for a river with cold water release and cooling water use, for selected weeks throughout the year.

Figure 9 - Outline of reservoir stratification density underflow analysis including warming between dams and underflow hydraulics.

Figure 10 - Observed River Temperature Profiles for a Number of Years. Mean monthly tailrace temperatures.

Figure 11 - Comparison of Distance to Duckunder Point and Density Flow Parameters. Based on upstream area required for heating between dams.

Figure 12 - Comparison of Observed and Reconstructed Tailrace temperatures for density flow through reservoirs.

Figure 13 - Fully Mixed Temperature Rise per unit heat load for single point along sectionally homogenous estuary, $^{o}C/10^{6}$ Joules Hr^{-1}

Figure 14 - Comparison of observed temperature profiles for a number of years along a sectionally homogenous estuary, and prediction of temperature excess profile due to multiple sources.

Figure 15 - Comparison of predicted temperature excess and observed mean weekly estuarine temperatures for 1067 surveys using a one-dimensional sectionally homogenous model.

Figure 16 - Comparison of predicted upper and lower layer temperature excess and observed mean weekly upper and lower layer temperatures for 1967 surveys using a two-layered circulation analysis.

Prediction and analysis of temperature distributions resulting from thermal powerplant cooling water circulation are primarily a single problem in hydrodynamics and waterbody mechanics. Basically, the distribution of temperature can be predicted only to the degree of detail with which the temporal and spatial velocity field of a waterbody is known. The equations of fluid motion, combined with the equation of energy conservation fully define the prediction problem; however, even in the case of available numerical representations and programmed formulations, solutions are obtained as approximations to three different scales of processes.

The three scales of processes related to cooling water discharges are: the initial mixing scale dictated by discharge design, extending over 10^2 to 10^4 square meters of surface area and extending over minutes to an hour in time-temperature relationships; the intermediate scale describing further advection and dispersion of heat by ambient currents extending over 10^4 to 10^6 square meters of surface area and over a time scale of hours; and, large scale processes related to overall waterbody configurations at which surface heat dissipation becomes important extending over 10^6 to 10^8 square meters and a time scale of days. More commonly, the initial mixing

processes are referred to as near field phenomena and the intermediate and large scale processes are referred to as far field phenomena. The three scales exist primarily as an analytic artifact but are also physically significant in relating the size of the heat source to the size of the waterbody.

It is intended in this report to present a summary of all three scales of processes as they relate to each other. This is accomplished at the sacrifice of extensive detail required to present the analytic bases of numerous relationships that have been formulated and are still being developed for use in temperature prediction. A common basis used in this study for comparison of the different formulations chosen to illustrate the physical processes operating at each of the scales is the waterbody surface area required to reach a specified temperature reduction. Whenever possible,time temperature relationships of importance to the biologist in assessing the pattern of organism temperature exposure are presented. An attempt is made to present critical commentary on the interrelationships of the numerous independent formulations as they relate to the different scales of phenomena and impinge on each other.

Comparison of predicted temperature distributions to field observations represents the ultimate test of tem-

perature distribution models. However, a model for a particular siting problem is usually composed of many different parts, each covering a different scale and representing one or more different degrees of approximation ranging from rules of thumb and experienced judgement to detailed spatial and temporal predictions. Attempts to relate experimental observations to particular formulations for initial and intermediate scale processes are presented in Tokar (1971), Policastro and Tokar (1972), and Policastro and Paddock (1972). Many prediction relationships and programmed computations apply to plants not yet in operation, hence it will be some time before final verification and modification is available. Comparisons presented in this report are generally for large scale processes where historic data have been available. The few cases chosen are those that are known by this author to be independent comparisons of predictions and formulations that illustrate unique phenomena of complex temperature distributions, and that can be compared to basic temperature distribution relationships.

Scales of Processes

Classification of temperature distributions into three analytic scales of phenomena and further subclassification within these scales provides a measure of the diversity of situations encountered in powerplant siting. There are at least two types of initial mixing conditions having at least three types of design configurations: Large scale distributions may be subdivided into riverine, estuarine, lake and coastal situations with each of these further subdivided, for example, into free flowing rivers or run-of-river impoundments, or different estuarine configurations. Each combination of discharge design configuration and subgroup of waterbody classification would result in a particular intermediate mixing region. Neglecting the further compounding effect of time varying conditions, the effects of wind mixing, and additional combinations of boundary conditions, these combinations result in over 1,000 possible permutations of problems for analysis.

Comparing the 1,000 possible analytic cases with the fact that the present growth in electric generation

capacity from 250,000 mw to 500,000 mw is scheduled for approximately 150 sites, not all of which utilize direct circulation cooling, it is obvious that temperature distribution analysis is limited to site specific studies. Each site becomes a special case for analysis with only limited detail that can be translated from one configuration to another. An outline of typical cases serves to further illustrate the complexity of the problem.

Lake and storage reservoir situations can be categorized on the basis of the size of the heat source relative to the overall waterbody heat budget. A lake situation that is large relative to the heat source, for example, thermal discharges into one of the Great Lakes reduces the temperature prediction problem to a study of immediate shoreline effects. The problem is compounded by the importance of shoreline and wind driven circulation to provide dilution water to the initial mixing region of the discharge and by the prevalence of offshore temperature gradients resulting from the large scale circulation. The design problem becomes a choice between surface discharges that can reduce the potential interaction with benthic conditions and cooling water intake design, or submerged discharges that limit surface temperatures and immediate shoreline conditions. A discharge that is large relative to the overall lake heat budget as in the case of the Finger Lakes requires development of the description

of the large scale processes controlling the seasonal temperature structure without the discharge, the mechanics of the processes by which the discharge interacts with the seasonal temperature structure, and the mechanics of localized circulation between the discharge and intake.

Estuarine situations, like lake situations, are dependent on the relative magnitude of the cooling water circulation to the natural circulation. Siting on a large complex estuary, such as Chesapeake Bay, reduces to an initial and intermediate scale problem that is compounded by the localized temperature and salinity structure. Cold, higher salinity waters used as the cooling water source may have an intermediate density relative to the receiving waterbody and interact with the large scale circulation as a density interflow. The total amount of heat reaching the waterbody from the source is small compared to the overall heat budget. Siting on a smaller estuary such as the Delaware River Estuary will encounter a wide range of conditions extending from simple river dilution at the headwaters to those as complex as Chesapeake Bay in the more tidally influenced Bay region. When an estuary is considered sectionally homogenous for water quality purposes, limits on initial and intermediate mixing are imposed by the completely mixed condition resulting from such an analysis.

Run-of-river situations appear to present the simplest analytic configuration for theoretical consideration with the upper limit on initial and intermediate mixing

dictated by available river flow. However, the existence of impoundments with large surface area, the potential for coldwater density underflows, and the potential for flow reregulation eliminate from practical consideration simple hypothetical river problems as encountered in other types of water quality analysis.

Coastal or open waterbody situations, already mentioned in relation to large lakes and estuaries, present equally complex problems. Near shore circulation may be controlled by tidal and wind-driven circulation and by shoreline upwelling. Available dilution water due to these processes may be limited by shoreline topography and tributary embayments. Knowledge of limitations on initial and intermediate mixing, and consequently the basis for choice of outfall design, rests on an understanding of the processes controlling offshore circulation. These in turn may be dictated by conditions far away from a particular site.

Surface Area Descriptions

The site specific characteristics of temperature distribution analysis and the large number of possible formulations that can be permuted from hydrodynamic and temperature distribution theory makes a generalization of processes difficult. One basis of comparison of many different formulations, particularly for the initial and intermediate scale processes, is to express the formulations algebraically in terms of the surface area within a temperature con-

tour. Reasons for making this approximation are given by Edinger and Polk (1971).

Surface area descriptions are conceptually reasonable for heated discharges, because of buoyancy and because of the ultimate large scale fate of dissipation to the atmosphere. Pritchard (1972) has used surface area descriptions to place surface heat dissipation in perspective relative to the mixing and dilution processes. Surface area descriptions do not, however, represent the ultimate in detail often required. In particular, they do not include the detail of temperature distributions along shoreline or bottom boundaries that may be needed by the biologist to evaluate temperature exposures of benthic and littoral planktonic species.

Formulations of temperature distributions from reduced forms of the differential heat balance, alone and in combination with the similarity solutions of the equations of motion, are of the form of the mathematical normal distribution function. The resulting area-temperature excess formulation is of the form:

$$\frac{A}{A_n} = (\theta/\theta_o)^{-P} \int_{u=\theta/\theta_o}^{1} u^m [\mathrm{Ln}(1/u)]^n du \qquad 1$$

where the integral can be approximated as:

$$I(\theta/\theta_o) = \frac{\Gamma(n+1)}{(m+1)^{n+1}} [1-\theta/\theta_o] \qquad 2$$

in which $\Gamma(n+1)$ is the gamma function value of n+1. Comparison by this author of a number of cases of the initial and intermediate mixing processes indicate that p=m+1 and that $n=^{1/2}$. The value of m depends on the form of the dynamic relationships describing the velocity field and the number of spatial dimensions incorporated in a description of the temperature field. The approximation in Equation 2, suggested by Yeh (1973), enhances the original graphical descriptions of Edinger and Polk (1971) and provides a description of the relationship between different scales of phenomena.

Time-temperature Relationships

The relationship between temperature and time of travel through the temperature field is an important feature to the biologist in examining the advantages and disadvantages of different discharge and mixing configurations with regard to temperature exposure of organisms. Time and temperature may be a more important biological combination of parameters than surface area and temperature.

Given the physical processes which enter the area temperature relationships, it is possible to deduce the time temperature relationships for individual cases. This has been carried out by Pritchard (1972) for the case of the vertically mixed two-dimentional jet by employing empirical arguments related to the shape of the plume.

That analysis is extended in this paper to cover all the cases for which area-temperature relationships are formulated. This analysis is considered as an integral part of the problem of determining the scales of temperature distribution phenomena.

Initial Mixing Processes

The initial mixing region can be defined as that region of the temperature distribution over which the velocity field is dictated by discharge design. Generally, there are two types of initial discharge configurations; the surface discharge and the submerged diffuser discharge.

The surface discharge may take many configurations depending on the discharge momentum and buoyancy. It may tend to spread on the water surface as a buoyant plume entraining dilution water through the bottom. The rate of spreading is related to the lateral pressure gradient caused by the difference in density of the plume and the ambient water. For very high momentum discharges and in regions of the buoyant plume where entrainment has reduced the density difference, the discharge will entrain without regard to the buoyancy. Analytic description of the processes is based on the use of similarity relationships that exist for the separate cases of buoyant and non-buoyant plumes, and is a necessary artifact for each case since the similarity relationships are asymptotic in character. Even the case of non-buoyant plumes must be further subdivided into three-dimensional and two-dimensional rela-

24-642 O - 73 - pt. 2 - 15

tionships since each solution is separately asymptotic.

Submerged discharges entrain dilution water during both stages of momentum mixing and buoyant rise to the surface. Generally, the greater the depth of submergence and the greater the initial horizontal velocity, the more dilution that will be achieved. Submerged discharges are affected by ambient currents and stratification of the waterbody where the latter can result in the rising buoyant plume spreading at an intermediate depth.

Surface discharges are applicable in regions of shallow water where there is insufficient depth for effective submerged discharge design. Surface discharges tend to keep the heat away from benthic areas in the immediate vicinity of the discharge as contrasted to influencing the whole water column with a submerged discharge. Surface discharges have the disadvantage that they are strongly influenced by wind-driven and tidally-driven currents, and that the maximum temperature at the surface is the plant discharge temperature.

Programmed formulations of the initial mixing region have been developed for submerged discharges by Fan (1967) and Koh and Fan (1970); for surface buoyant discharges by Stolzenbach and Harleman (1971); and for vertically mixed momentum discharges into an ambient current by Carter (1969) and Motz and Benedict (1972). With the exception of submerged discharge configurations, each

of the formulations are detailed descriptions that can be approximated by area-contour methods.

Hirst (1972) has formulated the buoyant jet with horizontal and vertical deflection with formal reference to the basic hydrodynamic relationships. He provides comparisons to experimental data on submerged buoyant jets, surface buoyant and non-buoyant jets, and jets into a cross-current. The Hirst formulation appears to present the most generalized analysis as of 1973, and should encourage further discussion leading to a consolidation of applicable jet principles. Note that Hirst concludes: "The predictions made with the new method are often no better than those made with existing methods."

Non-Buoyant Two Dimensional Jet Discharges

Two dimensional jet discharges are considered to be vertically mixed through a constant depth and expand laterally by entrainment through the sides. Similarity relationships from the equations of motion show that: expansion is linear with distance, and centerline velocity decreases with the square root of distance. Concentration is similarly reduced with the square root of distance. Surface area relationships for two-dimensional jets have been developed by Edinger (1971) and utilized by Pritchard (1972) in a case analysis comparing the different regions of temperature distributions.

The scaling relationship given by Edinger (1971) is:

$$A = \frac{A_o x_{o2}}{D_o} \left(\frac{\theta}{\theta_o}\right)^{-4} \qquad 3$$

where A_o is the discharge cross-sectional area, x_{o2} is the two-dimensional jet virtual source distance (usually 4-6 times the discharge diameter), D_o is the jet diameter or depth, and θ_o is the initial temperature rise.

For a typical case of a 3 meter discharge,the area to 0.25 times the condenser temperature rise over ambient temperature is about 6×10^3 square meters. The two-dimensional jet is assumed to extend through the water column an amount equal to the D_o dimension of the jet and entrains dilution water only laterally through its sides.

The influence of an ambient current in the bending of a two-dimensional jet is considered in the analysis of Carter (1969) and Motz and Benedict (1972). Formulations of two-dimensional expansion into a cross-current treat the jet region as a solid body and ignore the influence of the jet on the ambient current; it is also assumed that there is a source of dilution water available to both the upstream and downstream side of the jet. When the inshore dilution water cannot be provided, such as when the jet swings against the shoreline, higher temperatures exist in this region than are predicted by the formulations. Present formulations of jets in a cross-current therefore

do not account for near shore boundary effects or limitations due to variations in the ambient current due to the jet.

Carter, et al (1973) examine a number of different entrainment relationships used in deriving the properties of the vertically mixed jet in a cross-current. They show that most formulations differ widely because of the assumed entrainment function.

Pritchard (1972) shows by numerical calculation for a case example that the effect of an ambient current is to extend the two-dimensional jet more rapidly along its axis with the result that the area within a temperature rise contour is increased over that given by Equation 3.

The time-temperature relationship through the non-buoyant two-dimensional plume can be determined from the relationship that the centerline velocity decreases with the square-root of distance from the discharge and that the temperature excess is similarly diluted with distance. The time-temperature relationship is:

$$t_\theta = \frac{4\ D_o}{U_o} \left[(\theta/\theta_o)^{-3} - 1 \right] \qquad 4$$

for which it is assumed that the two-dimensional virtual source distance is six times the discharge width.

The lack of dependency of surface area on discharge rate as indicated by Equation 3 requires explanation. If the rate of discharge is doubled through the same

discharge with constant A_o, D_o and at constant θ_o, entrainment will take place at a much more rapid rate, producing the same amount of dilution over the same surface area. However, if the discharge velocity is maintained the same while doubling the rate, then the cross-sectional area of the discharge must be doubled resulting in twice the surface area to achieve the same dilution. If for the same heat rejection the discharge rate is doubled, the θ_o is reduced by one-half, and the discharge takes place through the same cross-sectional area, then the area required to reach the same θ is reduced; however, this reduction comes about through a reduction of θ_o, and this choice cannot be made without consideration of changes in the discharge cross-sectional area. The rate of discharge is therefore implicit in the formulation through the choice of A_o and θ_o.

Non-buoyant Three-Dimensional Discharges

A high momentum discharge into water many times deeper than the vertical dimension of the outfall structure will expand as a three-dimensional jet. Entrainment can take place from all sides of the plume and is not limited by the depth of the water column as in a two-dimensional jet. Using first-order circular jet similarity relationships, it can be shown that the surface area contained within a temperature contour for a jet expanding radially is:

$$A = \frac{A_o^{1/2} x_{o3}}{\sqrt{2\pi}} \left[\frac{\theta}{\theta_o}\right]^{-2} \qquad 5$$

where A_o is the cross-sectional area of the discharge and x_{o3} is the virtual source distance for a three-dimensional jet.

For the example given for the two-dimensional jet with a circular cross-section of diameter the same as D_o it is found that a 4:1 dilution is reached in approximately 3×10^3 square meters of surface area. It is more efficient than the two-dimensional jet because of the greater exposure of the plume to new dilution water.

Limitations on three-dimensional jet expansion are reached when the jet begins to interact with the bottom allowing dilution water to reach it only through the sides over the depth of water column. If there is sufficient momentum remaining in the plume it will continue to expand as a two-dimensional jet beyond the point of interaction with the bottom.

Further limitations on three-dimensional jet expansion are due to the confined area into which dilution water must reach. The lack of longshore currents or the influence of bottom topography will prevent new water from reaching the vicinity of the jet and it will entrain water already circulated through it. The result will be a rapid dissipation of momentum within a smaller region than for the unconfined jet and less dilution over a given surface area.

The time-temperature relationship for a non-buoyant three-dimensional discharge can be found for centerline conditions to be:

$$t_\theta = \frac{3D_o}{U_o}\left[(\theta/\theta_o)^{-2} - 1\right] \qquad 6$$

and gives a more rapid travel time through the plume than the non-buoyant two-dimensional case.

Buoyant Surface Discharges

The fundamental hydrodynamic relationships that apply to buoyant surface spreading and their evaluation by similarity relationships has recently been presented by Engelund and Pedersen (1973). Their development is a formalization of the earlier empirical work of Jen and Wiegel (1966), and is an analytic description of a portion of the problem programmed by Stolzenbach and Harleman (1971). Although the latter is programmed to give temperature-area relationships, the Engelund and Pedersen formulation allows algebraic approximation to the area within a surface temperature contour as:

$$A = 43.4 D_o b_o R^{1/2}\left(\frac{\theta}{\theta_o}\right)^{-2} \qquad 7$$

where A is the area contained within the θ contour, θ_o is the plant condenser temperature rise, b_o is the half width of the discharge structure and R is the discharge Richardson number. The latter is given by:

$$R = F_o^{-2} = \frac{\Delta\rho}{\rho} \frac{gD_o}{U_o^2} \qquad 8$$

where F_o is the discharge densimetric Froude number, $\Delta\rho/\rho$ is the density difference ratio between the discharge and ambient fluid, D_o is the discharge depth, and U_o is the discharge velocity.

Stolzenbach, et. al. (1971) perform a computation of the surface area contained within the 2.2°C isotherm of a $56 m^3 s^{-1}$ discharge with an initial rise of 8.8°C and maximum velocity of $1.8 ms^{-1}$. Their results show that the required dilution is achieved over a surface area of 9×10^3 square meters. In order to achieve the 4:1 dilution over this area, $224 m^3 s^{-1}$ must be moved within the vicinity of the discharge.

The buoyant discharge has the advantage that heat can be limited to the surface layers and leave the benthic populations in the vicinity of it unaffected except by changes induced in the ambient current patterns to provide the dilution water. Entrainment takes place over such a small surface area that, despite the high temperature excess in the initial regions of the plume, the amount of heat dissipated to the atmosphere is very small compared to the plant heat rejection.

When the limits of buoyant plume entrainment are reached the intermediate advective and dispersive processes

begin to act on the remaining heat to distribute it further throughout the waterbody. The initial mixing process thus establishes the source condition relative to the intermediate mixing processes.

The buoyant plume relationships of Stolzenbach, et. al. (1973) and of Engelund and Pedersen (1973) apply for densimetric Froude number greater than 3. Physically, this means that the change in longitudinal momentum is large compared to the longitudinal pressure gradient due to surface slope and longitudinal density gradients, but the latter are dominant in the lateral direction. For densimetric Froude numbers less than unity, the longitudinal pressure gradient due to longitudinal density differences becomes significant and two-layered stratified flow regimes develop with little vertical entrainment across the interface.

The time-temperature relationship through a buoyant plume is derived for the centerline velocity conditions given by Engelund and Pedersen. Integrating the time of travel at the centerline velocity over the centerline distance and using the centerline distance temperature rise relationship results in a time-temperature relation of:

$$t_\theta = \frac{3\ D_o}{8\ U_o} \left[(\theta/\theta_o)^{-8/5} - 1 \right] \qquad 9$$

Thus, the higher the discharge velocity, the shorter the

travel time over a specified temperature rise, but the larger the discharge orifice, the greater the volume of the buoyant plume, and the longer the travel time over a given temperature rise.

Submerged Buoyant Discharges

Submerged buoyant discharges are applicable where there is sufficient water column depth to achieve dilution as the plume rises to the surface and where sufficient dilution water can be provided to the vicinity of the jet by ambient currents. This type of discharge has has been formulated by Kohn and Fan (1971) for cases of ambient currents in a stratified receiving water body, and nomograms for application have been developed by Shirazi and Davis (1972).

The formulations are much too complex to yield simple relationships for the surface area contained within a temperature contour after the plume reaches the surface. Computations by Shirazi and Davis for a typical case indicate that dilutions of the order of 20:1 are obtainable within a surface radius of 15 times the water column depth for a single port carrying a fraction of the discharge.

Powerplant cooling water discharges are of such large volume that multiple ports must be employed. The

design criteria require that each port should expand independently without entraining water from an adjacent port. As in other types of momentum mixing, entrainment can be limited by the ability of the ambient fluid to provide adequate new water in the vicinity of the discharge.

Submerged discharges can be limited by ambient stratification. Stratification will cause a rising plume to expand laterally at an intermediate depth without reaching the surface. Cases are also possible where the density of the discharge is greater than the ambient fluid density at the outfall location. An example is the case of a plant designed to withdraw cold hypolimnetic water in a stratified lake or high salinity bottom water in an estuary. The plume will plunge but entrain to an intermediate depth between the elevation of the intake and discharge.

Time-temperature relationships for the submerged buoyant discharge, as in a long outfall canal, are characterized by the long time of transit at the temperature rise experienced across the powerplant condensor. The need of a long outfall to reach sufficiently deep water for the submerged buoyant discharge to be effective has potentially poor biological payoff in comparison to surface discharges and must be compared to those conditions requiring limited surface temperatures in the immediate vicinity of the outfall.

General Properties of Initial Mixing

Proper design of an outfall to mix a discharge as rapidly as possible with the ambient fluid, will allow substantial dilutions to be achieved over a small area of a waterbody as long as sufficient dilution water is available. The asymptotic nature of known analyses do not provide for a determination of limitations of available dilution water. The design is empirical relative to available dilution water requiring an assessment of the source of the new water. This has led to the use of physical hydraulic models to study the interaction of discharge dilution and ambient current conditions, but these models are limited in application because they may not simulate ambient stratification conditions.

The choice between surface discharges and submerged discharges is usually made on the basis of the depth of the receiving water. In shallow coastline areas, the use of a submerged discharge is limited by the distances through which the outfall must be piped. Surface buoyant initial mixing may be applicable in areas where there is some reason to keep the heat away from benthic populations. It cannot be justified on the basis of surface heat dissipation because of the limited surface area over which the mixing takes place. The choice between surface and submerged discharges is abrogated by criteria that limit

maximum surface temperatures in the initial mixing region, often negating the use of the former without consideration of other criteria.

Criteria to protect aquatic organisms suggest that temperature time of travel relationships are important for organisms passing through a cooling water system and entrained in the initial mixing region. Long outfalls maintain entrained organisms at the condenser discharge temperature for a longer time than shoreline outfalls. In either case there is the problem of the advantages and disadvantages of using large amounts of cooling water at low temperature rise or small amounts of cooling water at higher temperature rise. The former subjects more organisms to a lower temperature rise but makes discharge design more difficult because of the larger amount of cooling water that must pass through the system. Pritchard (1972) has shown that rapidly mixing discharges expose the entrained organisms to the higher temperature rises for shorter periods of time than do buoyant discharges and gives additional considerations of the relationship for time of exposure of organisms throughout the mixing area.

Analytic formulations of initial mixing, particularly for surface discharges, are for independent hydrodynamic conditions. There is presently no single formulation that covers the full range of conditions from non-buoyant conditions to a buoyant discharge or the trans-

ition between a three-dimensional and two-dimensional plume expansion. Buoyant plume formulations are valid for densimetric Froude numbers greater than three and the area over which mixing takes place decreases with increasing discharge densimetric Froude number.

Stolzenbach, et. al. (1973) indicates that a non-buoyant three-dimensional expansion takes place for IF_o greater than 15, and the buoyant jet region begins for IF_o less than 10. Another possibility for a shallow shoreline or confining thermocline is for a non-buoyant two-dimensional expansion to take place initially and then merge to a buoyant jet region.

For the case of jet development beginning with a non-buoyant three-dimensional expansion, the local densimetric Froude number would decrease with increased dilution as:

$$IF^2 = IF_o^2(\theta/\theta_o)^2 \qquad 10$$

and for the case of jet development beginning with a non-buoyant two-dimensional expansion, the local densimetric Froude number would decrease with increase dilution as:

$$IF^2 = IF_o^2(\theta/\theta_o)^3 \qquad 11$$

where IF is the local densimetric Froude number along the axis of the plume and IF_o is the discharge densimetric Froude number. In either case, the non-buoyant expansion

essentially expands the discharge to a greater depth, low velocity and lower density difference to a point where longitudinal acceleration and inertia are reduced to the order of magnitude of the lateral pressure gradient due to the density differences.

The relative size of the initial mixing region for each of the different cases is computed in Table 1. Initial conditions are assumed typical of a 1000 mw nucle plant discharge. For the non-buoyant three dimensional expansion it is assumed that there is sufficient off-shor depth that entrainment is uninhibited. For the non-buoya two-dimensional expansion, it is assumed that the depth o the discharge is the same as the off-shore depth.

At all temperature rise ratios, the three-dimen sional non-buoyant plume produces the smallest surface ar because it has more directions in which to expand and a greater area over which entrainment can take place.

Comparison of the non-buoyant two-dimensional expansion and the buoyant case shows that the former init ly has the smaller surface area at the higher temperature rise ratios, but that the latter provides greater dilutio at the lower temperature rise ratios. Basically, initial mixing of the buoyant plume is inhibited by stratificatio but at lower temperatures rise ratios presents a greater area to the ambient fluid than lateral mixing of the non-buoyant two dimensional case.

Table 1

Comparative Evaluation of Different Initial Mixing Area Relationships for Similar Discharge Conditions

Q_o=28 $m^3 s^{-1}$ θ_o= 11°C U_o= 2.4ms^{-1}

D_o= 4.5m A_o=11.5m^2 IF_o= 8.15

θ/θ_o	Three-Dim. non-buoyant area, m^2	Two-Dim. non-buoyant area, m^2	Buoyant case area, m^2
0.80	6.9	28	54
0.60	39	89	194
0.40	232	452	655
0.20	930	7240	3430

24-642 O - 73 - pt. 2 - 16

Intermediate Mixing Processes

Beyond the near field jet mixing region of a discharge, further mixing can take place as the excess heat is advected and dispersed throughout an expanse of waterbody. In unconfined waterbodies, it is the advection and dispersion processes due to natural currents and turbulence that spread the excess heat over sufficient surface area where atmospheric dissipation can become effective. Numerical models of the hydrodynamic equations, most generally available for vertically mixed situations (leendertse, 1970), can be used to describe the intermediate mixing processes if refined to small grid sizes. Short of this, however, it is possible to develop scaling laws in the intermediate mixing region for simplified assumptions about the ambient current and dispersion.

Intermediate scaling relationships for the two cases of vertically mixed conditions and for vertically stratified conditions have been developed by Edinger and Polk (1971) for point source discharges. These relationships are extended here for the consideration of finite source conditions resulting from initial mixing. An unresolved problem still exists, however, of quantifying the conditions under which initial mixing is terminated and the larger scale advective and dispersive processes commenc

Two-Dimensional Intermediate Mixing

The two-dimensional intermediate mixing process is considered to be a balance between the horizontal advection and dispersion processes of heat mixed vertically through the water column. The two-dimensional heat balance equation is:

$$\frac{\partial\theta}{\partial t} + U\frac{\partial\theta}{\partial x} + V\frac{\partial\theta}{\partial y} = \frac{\partial[D_x\frac{\partial\theta}{\partial x}]}{\partial x} + \frac{\partial[D_y\frac{\partial\theta}{\partial y}]}{\partial y} \qquad 12$$

where the horizontal velocity components U and V must be known for evaluation. The velocity components may be determined from the vertically integrated equations of motion most generally utilizing a numerical finite difference formulation.

Short of a detailed description of the velocity field from numerical models the most elementary case to consider analytically is the balance between longitudinal advection in a uniform current with speed U and depth d and lateral dispersion of heat described by a laterial dispersion coefficient D_y as:

$$U\frac{\partial\theta}{\partial x} = \frac{\partial D_y\frac{\partial\theta}{\partial y}}{\partial y} \qquad 13$$

For constant lateral dispersion coefficient the most general solution to the balance in Equation 13 is:

$$\Theta(x,y) = \frac{H_p}{\rho C_p d\ 2\ D_y} \exp\left(\frac{Ux}{D_y}\right) \quad K_o[U(x^2+y^2)^{1/2}/2D_y] \qquad 1$$

where H_p is the heat source strength, and K_o is the modifie Bessel function of the second kind. For Ux/D_y much greater than unity Equation 14 converges to the more familiar normal distribution solution of:

$$\Theta(x,y) = \frac{H_p}{2\rho C_p d(\pi UD_y x)^{1/2}} \exp\left(-\frac{U\ y^2}{4D_y x}\right) \qquad 15$$

This applies to cases where the source temperature rise after jet mixing Θ_o, is less than 5 times the fully mixed temperature rise Θ_m as in a confined river situation. This latter restriction has become evident recently in determining temperature distributions for sources that are of relatively low volume compared to the volume of flow available for dilution as in the case of cooling tower blowdown discharges.

The laterally unbounded solution of Equation 15 is presented in Figure 1 for the dimensionless lateral width of $z' = y/W$, downstream length of $x' = xD_y/W^2U$, and fully mixed temperature rise defined as $\Theta_m = Q_o\Theta_o/WdU$. In the laterally unbounded case, the width W can be given any convenient value. The laterally bounded solution of Equation 15 is presented in Figure 2 for reflections off the centerline and the boundary at $z' = 1$. In the laterally bounded case, the width W is the lateral distance between the two

boundaries. Both solutions are presented for comparative purposes to illustrate the influence of boundaries on heat dispersion.

When boundaries exist as in a river or estuary, all the heat released is contained and reaches a fully mixed condition long before surface heat dissipation becomes effective. Centerline temperatures decrease more rapidly with distance due to lateral mixing for the unbounded case than for the bounded case. Centerline temperatures approach the fully mixed temperature rise for the bounded case but decrease to zero for the unbounded case. In both cases, the fully mixed temperature value does not extend beyond $z'=0.5$ while the heat is spreading. Temperature rise decreases laterally more rapidly for the bounded case than for the unbounded case. In effect the plume is relatively shorter but wider for the unbounded case than for the bounded case, indicating that the effects of the boundary are to confine the plume laterally but stretch it out longitudinally.

The two-dimensional relationships presented in Figure 1 and Figure 2 apply to a source of heat located on the plume centerline at the appropriate value of θ_o/θ_m. The closer this value is numerically to one, the less mixing there is to take place in the bounded case. Brooks (1959) has considered solutions to the two-dimensional

Figure 1

Two dimensional intermediate mixing unbounded case generalized plume

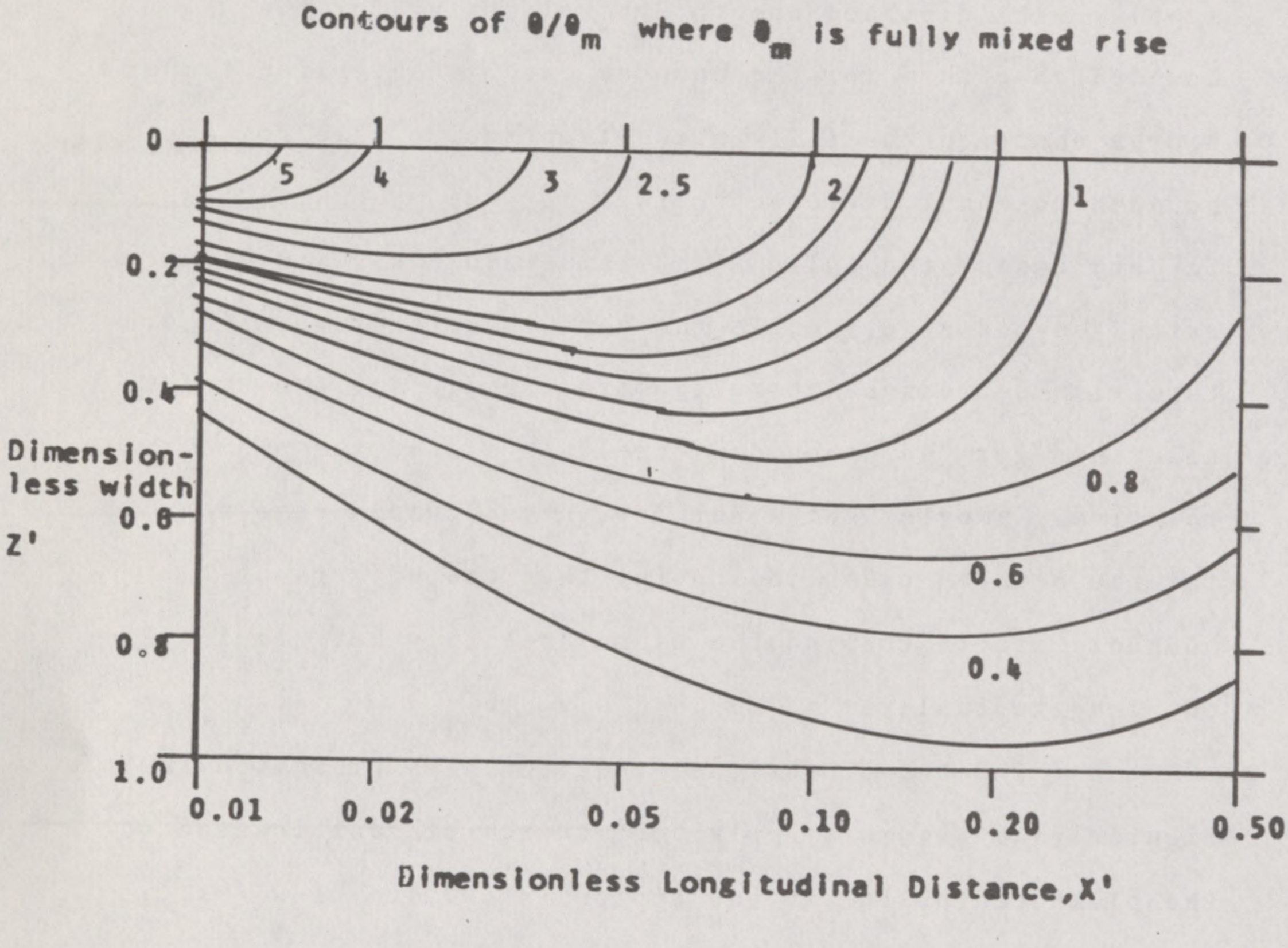
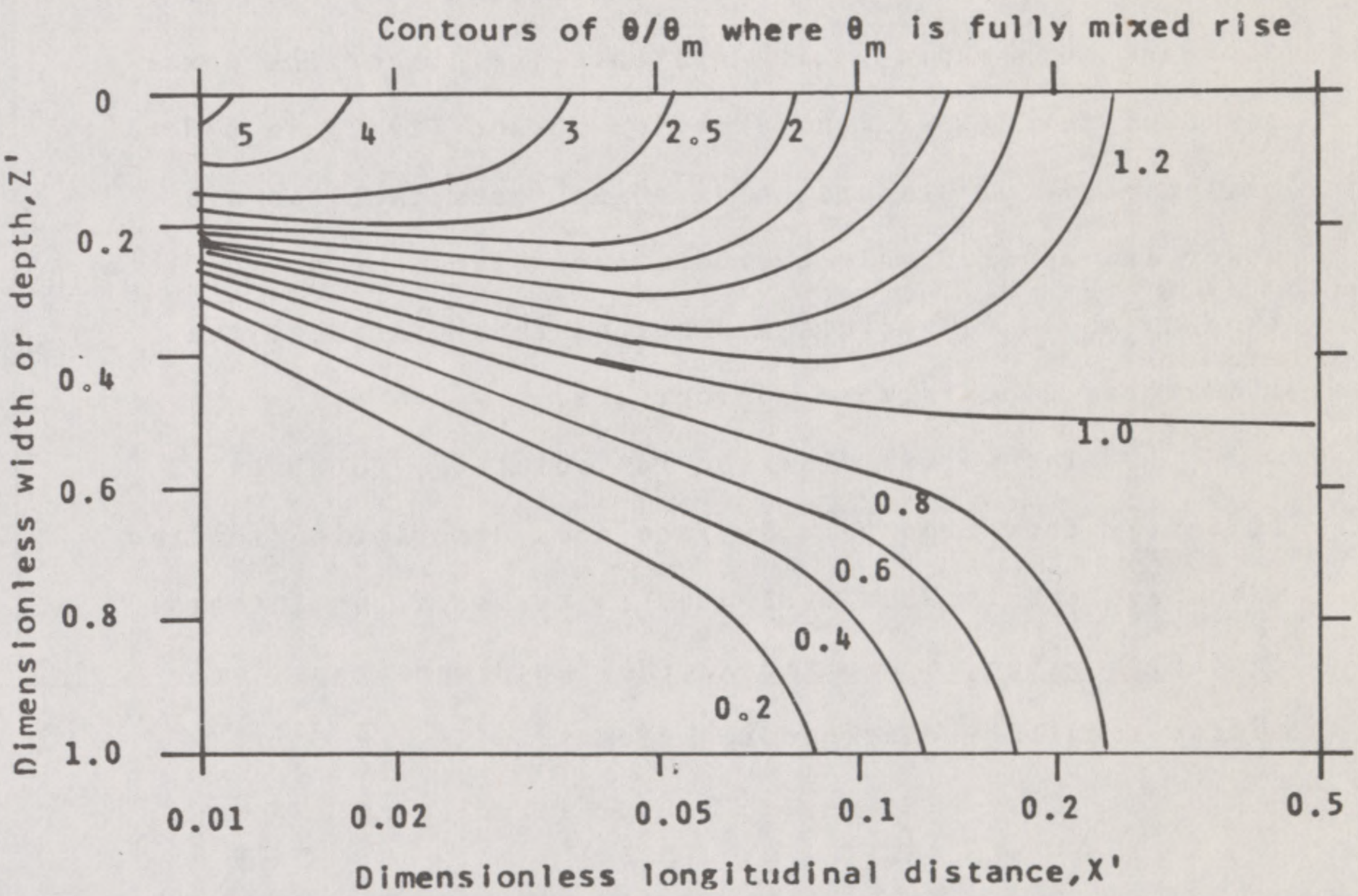


Figure 2

Two dimensional intermediate mixing bounded case, generalized distribution.



unbounded case beginning with a finite width source resulting from initial mixing into the current. Initial mixing would reduce the value of θ_o/θ_m and must match width of the finite source to determine the value of W for the unbounded case of Figure 2.

In addition to the finite width source, Brooks considers the cases where the lateral dispersion coefficient increases linearly and with the 4/3 power with longitudinal distance as well as the case of constant lateral dispersion. His analysis shows that centerline concentrations decrease more rapidly with distance the higher the power law used for dispersion. However, Okubo (1962) in a detailed study of dispersion data indicates that the 4/3 power law applies only over distances from the source location up to 10,000 meters and beyond that distance, the linear law appears more appropriate.

The normal distribution solution, Equation 15 is easily converted to a surface area description for the unbounded case. When evaluated in terms of the integral condition given in Equation 2 the two-dimensional intermediate scaling relationship becomes:

$$\frac{A}{A_n} = 0.168[(\theta_o/\theta)^3-(\theta_o/\theta)^2] \qquad 16$$

where A_n is the scaling area given by:

$$A_n = \frac{4\ Q_o^3}{\pi^{3/2}\ D_y\ U^2\ d^3}$$

32

where Q_o is the plant discharge rate at temperature rise θ_o .

Equation 16 assumes that there is no initial mixing to immediately reduce the temperature rise over a smaller area. If, however, it is assumed that there is some initial mixing of the discharge from temperature θ_o to temperature θ_m then the intermediate mixing area beyond the θ_m contour is given by:

$$\frac{A}{A_n} = 0.168[(\theta_o/\theta)^3-(\theta_o/\theta_m)^3 + (\theta_o/\theta_m)^2 - (\theta_o/\theta)^2] \quad 17$$

which applies for θ less than θ_m .

One result of Equation 17 is that the area contained within small θ contours of the far field is only slightly influenced by near field mixing. The initial mixing processes do, however, perform the important function of reducing the higher temperature excess as rapidly as possible.

Two-dimensional intermediate mixing processes take place wherever there is a current existing over sufficient time for the temperature field to develop, and where vertically mixed conditions are achieved as in a shallow waterbody or in the epilimnion of a stratified waterbody. These conditions often exist in tidal situations particularly in coastal waters where an ebb tide or flood tide persists for a long time period compared to slack water.

An application of the two-dimensional advective dispersive relationships has been made for the narrow deep

river situation described by Churchill (1970) and shown in Figure 3. The downstream heat balance is between longitudinal advection and vertical mixing from a line source across the river at the point of discharge. In this case, Equation 13 will apply if the y direction is taken vertically. The bounded solution in Figure 2 will apply with the longitudinal dimensionless coordinate given as $x'=xD_y/d^2U$ and the dimensionless depth given by $z'=y/d$, where D_y is taken as the vertical dispersion coefficient and d is the river depth. A comparison between computed temperature rise and observed temperature rise is given in Figure 4 and indicates that for this case temperature rise is reasonably described by the simple two-dimensional model. The data in Figure 4 indicate that the theoretical relationship gives too high a temperature rise prediction in the immediate vicinity of the discharge where some initial mixing is taking place.

The significance of surface heat dissipation during the intermediate mixing processes has been investigated by Edinger and Polk (1971) for the two-dimensional case. It is found that surface heat dissipation does not influence the area-temperature rise power law, and becomes significant only after mixing to θ/θ_o of 0.20 or less is achieved. Thus most surface heat loss takes place over very large surface areas at low values of temperature excess for unbounded waterbody situations.

Figure 3

Observed temperature distributions for a deep narrow river with vertical mixing of a surface heat discharge.

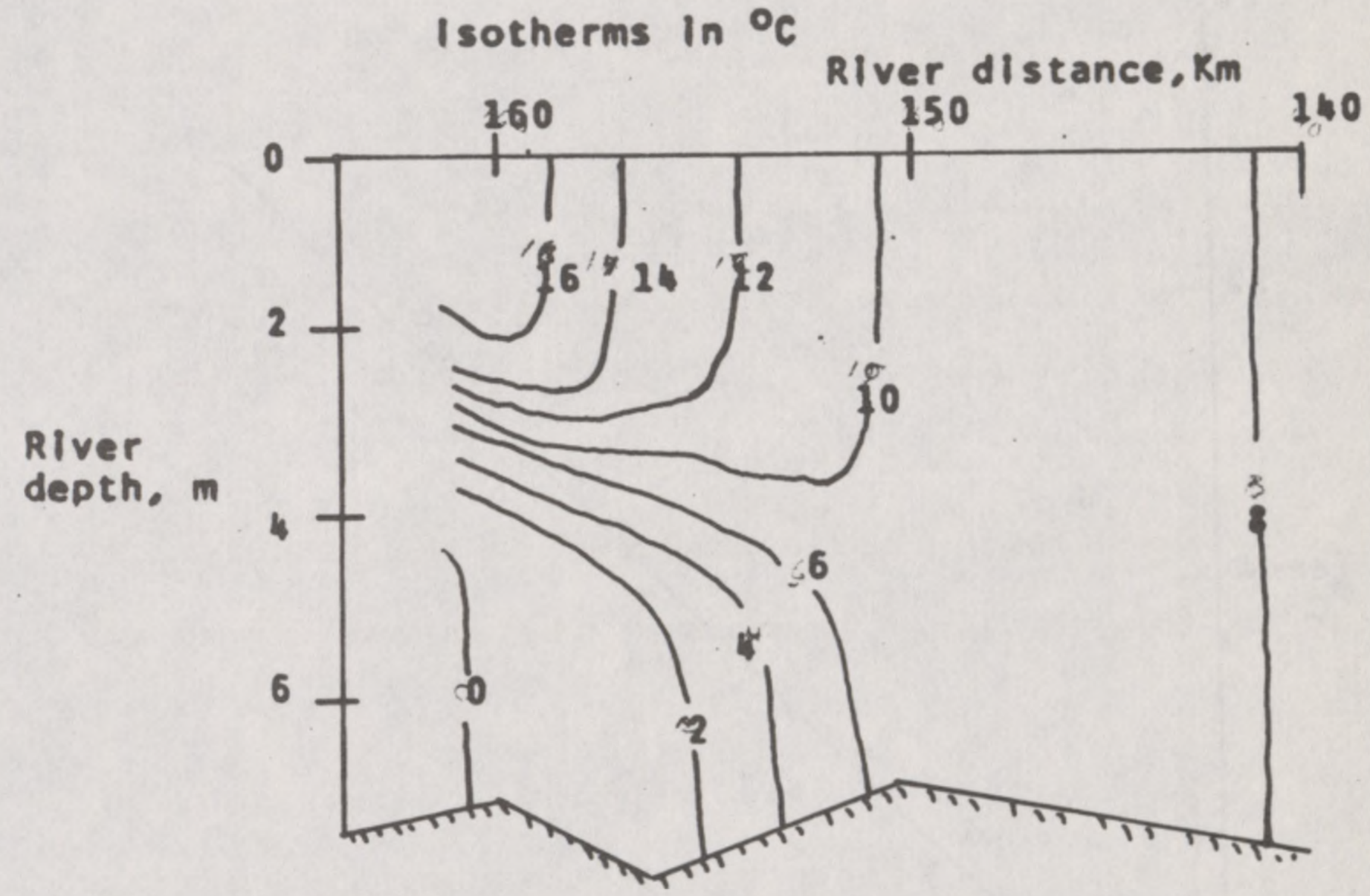
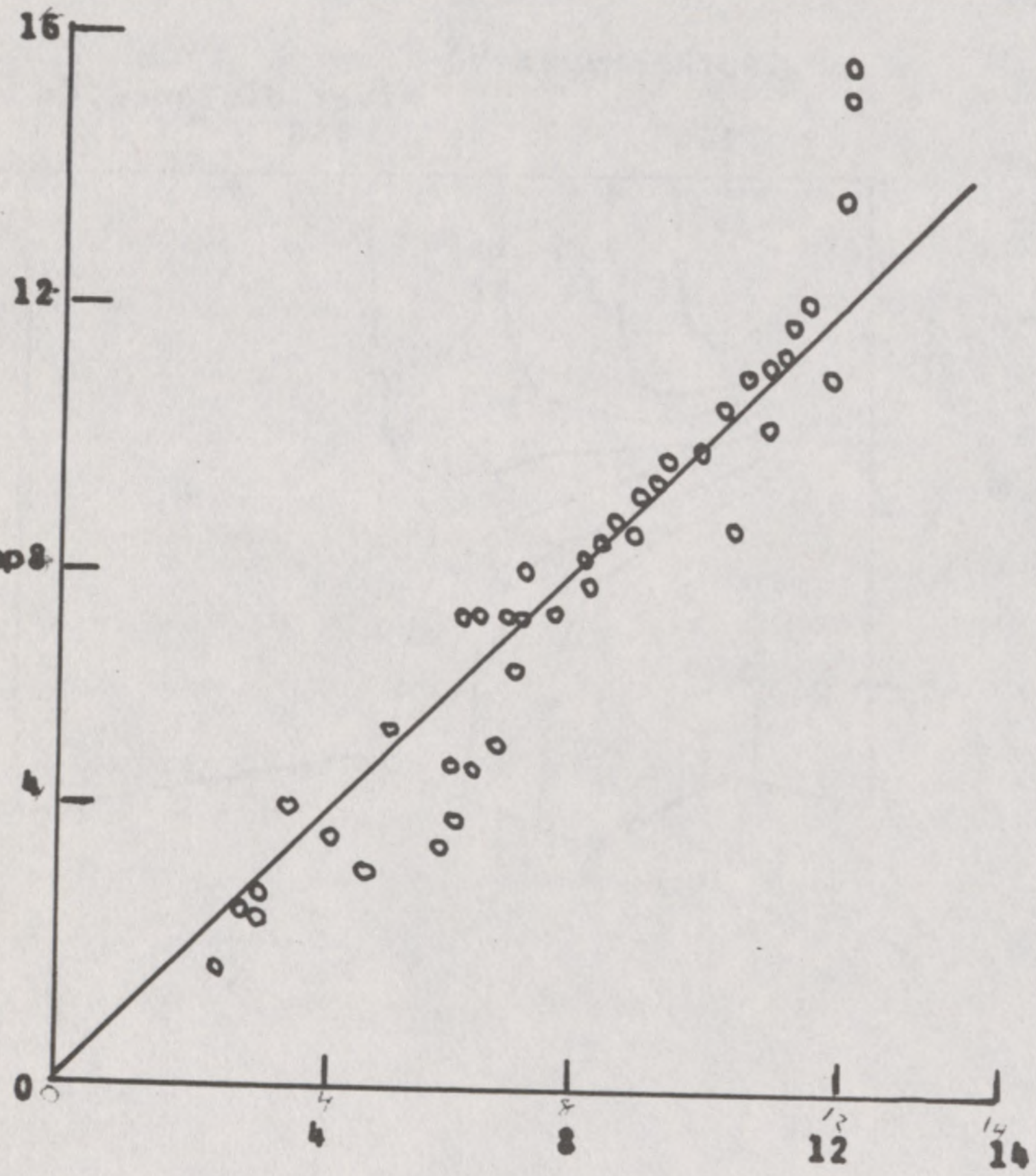


Figure 4

Comparison of observed temperature rise and predictions for vertically mixing river using two-dimensional advective dispersive heat balance with boundary reflections



Time of travel relationships can be determined for the two-dimensional case for transport along the centerline of the plume with the current velocity U. When the centerline is along a shoreline or bank in the unbound- ed case, the time of travel-temperature rise relationship becomes:

$$t_\theta = \frac{1}{\pi D_y} (Q_o/Ud)^2 [(\theta_o/\theta)^2 - 1] \qquad 18$$

When the plume is unbounded on either side, or heat can be dispersed in two lateral directions, the time of travel to a given isotherm is reduced to one-half the value calculat from Equation 18.

In the intermediate field, only that fraction of the organisms passing through the condenser with the plant flow Q_o will experience the time-temperature rise relation ship given in Equation 18. Organisms passing with the ambient current through the remainder of the width of the plume will experience a lower temperature rise the greater the lateral distance from the plume centerline. In the case of a confined river, Figure 2, organisms passing with one-half the river width of the discharge bank are success ively subjected to an increase in temperature then a de- crease in temperature, while organisms passing through the outer half of the river width are subjected to only an in- crease in temperature rise up to the fully mixed temperati

Three-Dimensional Intermediate Mixing

Relaxation of the assumption of vertical homogeniety is achieved by considering the balance between longitudinal advection in a uniform current and vertical and lateral mixing by turbulent dispersion. This case illustrates the reduction in scale that results from an additional degree of spatial complexity.

When evaluated in terms of temperature and surface area, the three-dimensional intermediate scaling relationship from Edinger and Polk (1971) as modified by Equation 2 becomes:

$$\frac{A}{A_n} = 0.496\left[(\theta_o/\theta)^{3/2} - (\theta_o/\theta)^{1/2}\right] \qquad 19$$

where A_n is the scaling area given by:

$$A_n = \frac{2\ Q_o^{3/2}}{\pi^{1/2} U^{1/2} D_y^{1/4} D_z^{3/4}} \qquad 20$$

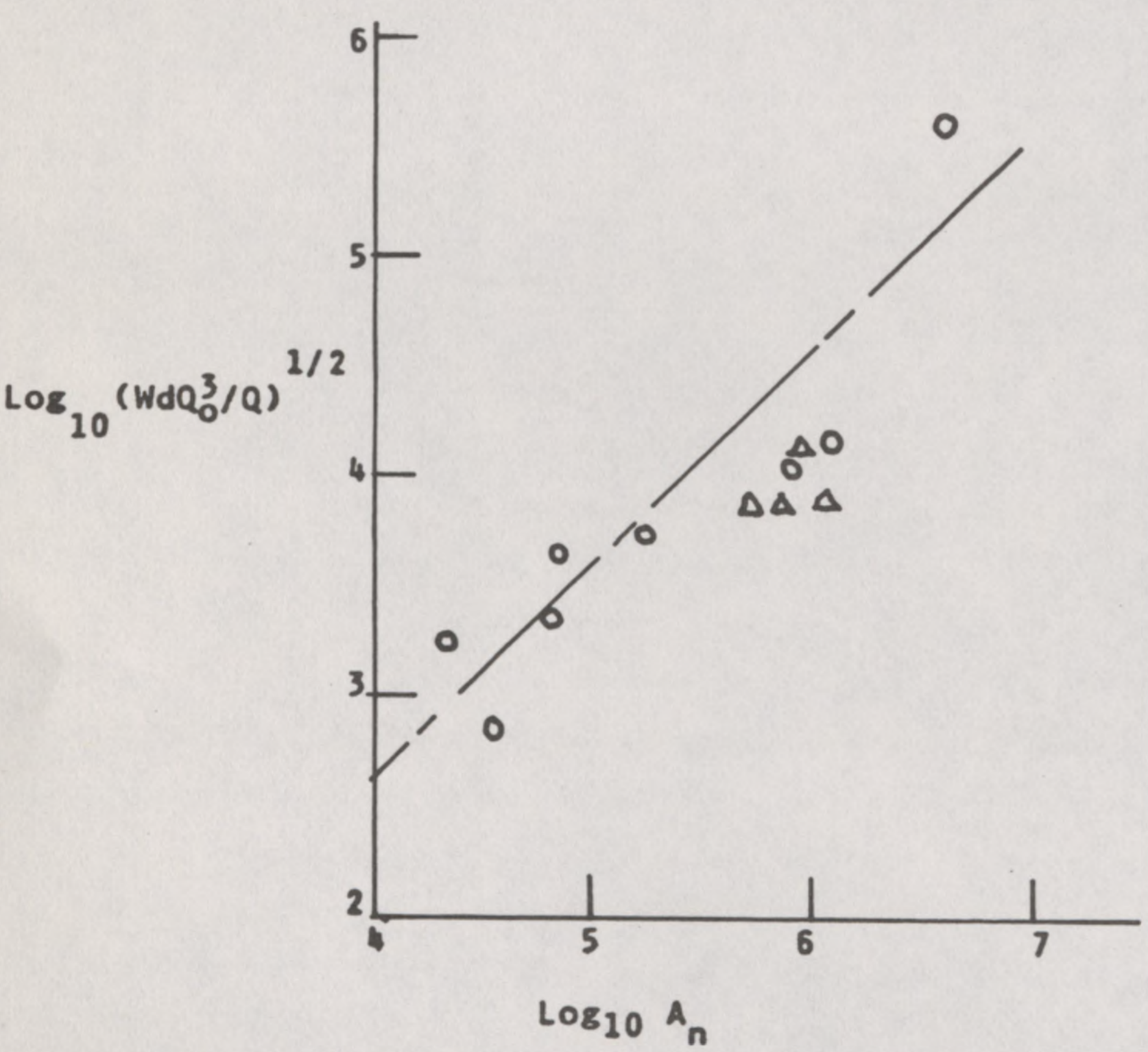
and where D_z is the vertical turbulent diffusivity. The three-dimensional scaling relationship can be modified for initial mixing producing a result similar in form to that presented in Equation 17 for the two-dimensional case.

Compared to the two-dimensional case, the additional degree of spatial freedom results in the temperature rise decreasing more rapidly with surface area for a given set of plant pumping rate, waterbody current and waterbody dispersion conditions. Also, surface area increases less rapidly with changes in plant pumping rate.

Results of application of the three-dimensional intermediate mixing area scaling relations are presented in Figure 5. Plume data from a number of different power plants sited along a sectionally homogenous estuary was fit to Equation 19 to determine the scaling area A_n. The plants varied in size and location along the estuary giving a wide variation in w, d, and Q_o. The flow rate, Q, was determined from the freshwater inflow for the day of survey. Reasonable scaling between the plants on the estuary and the river plants presented by Edinger and Polk (1971) is shown.

Figure 5

Three dimensional intermediate mixing scaling area compared to its parameters for plumes from a number of plants sited along a sectionally homogenous estuary, and for river sites.



△ River plants (Edinger and Polk, 1971)
○ Estuarine plants

Large Scale Processes

: The relative size of cooling water circulation to the overall configuration of a waterbody determines the importance of large scale processes. It is the scale at which final dissipation of heat to the atmosphere takes place. Surface heat exchange may be important in determining spatial temperature distributions far away from the discharge and may be of the order of the thermal gradients. More realistically, surface heat exchange is of the same order of magnitude as temporal heat storage making large scale prediction an unsteady or time varying problem.

Large scale temperature distribution analysis is often made for steady state conditions as a first approximation despite the relative magnitudes of surface heat exchange and heat storage. Comparison of predictions and observed temperatures for a number of different waterbody situations illustrate the discrepancies.

Modeling of large scale temperature distributions cannot be generalized beyond reference to a particular waterbody configuration. A limited number of cases are assembled that illustrate some of the complexities of comparing fundamental analytic relations to observed temperatures, including run-of-river situations, run-of-river

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reservoirs, and estuarine situations. The choice of cases is based on situations for which comparisons are available between predicted and observed temperatures.

Coastal water siting is becoming a significant consideration in the choice of available powerplant locations. A discussion of large scale processes and the relative importance of initial mixing and intermediate scales would be incomplete without presenting a few of the basic features of the coastal siting problem. Little comparative data exists because new units for which predictions have been made are not yet operating.

Surface heat dissipation to the atmosphere becomes an important feature of large scale temperature predicition. Fundamentals of its description are summarized before proceeding with a discussion of the related comparative studies.

Surface Heat Exchange

The seven physical processes by which heat is exchanged across the water surface are, incoming short-wave solar radiation; incoming long-wave radiation; relfection of short-wave radiation at the water surface; relfection of long-wave atmospheric radiation; heat loss by back radiation; heat loss by conduction; and, heat loss by evaporation. The algebraic sum of the rates of the seven mechanisms represent the net rate of surface heat exchange.

In order to simplify the development of temperature prediction models, it has been necessary to reduce the expression of net rate of surface heat exchange to a few fundamental relationships.

Simplification of the description of the water surface temperature dependent heat exchange processes is achieved by defining an equilibrium temperature as that temperature the water surface must have for the net rate of heat exchange across the water surface to be zero. It is therefore that temperature at which the rate of incoming radiation is balanced by the sum of the heat loss processes.

The equilibrium temperature is computed from meteorological and solar radiation data independently of water surface temperature. Details of its formulation are given in Edinger, et. al. (1968). Further simplifications, modifications and extensions are given by Brady, et. al. (1969) and more recently by Yotsukura, et. al. (1973). The result of these derivations is that the description of the net rate of surface heat exchange can be simplified to:

$$H_n = - K(T_s - T_e) \qquad 21$$

Where H_n is the net rate of surface heat exchange, T_s is the water surface temperature, T_e is the equilibrium temperature, and K is the coefficient of surface heat exchange. The exchange coefficient, K, incorporates the wind-speed functions of evaporation formulae, the Stephan-Boltzmann constant of backradiation, and the water surface emissivity.

The equilibrium temperature, T_e, incorporates the meteorological variables of incoming radiation, air temperature, and dew point temperature. Its definition allows summarizing a large number of variables into a single parameter which has physical significance in temperature prediction relationships. Basically, when the water temperature is below the equilibrium temperature it is warming up; when it is higher the water is cooling down. The heating and cooling processes occur continuously.

The simplest and one of the most descriptive formulation of the equilibrium temperature is, (Brady, et. al., 1969):

$$T_e = \frac{H_s}{K} + T_d \qquad 22$$

where H_s is the rate of incoming short-wave solar radiation and T_d is the dew point temperature. The equilibrium temperature varies daily and seasonally as it follows the variations of short-wave solar radiation and dew point temperature.

In cases where spatial temperature distributions are important, the description of surface heat exchange can be further simplified by determining the temperature excess, Θ, as the difference in temperature with and without an added heat source, (Edinger, 1971). This eliminates the need to consider large amounts of meteorological data in most cooling water related temperature prediction problems.

River Situations

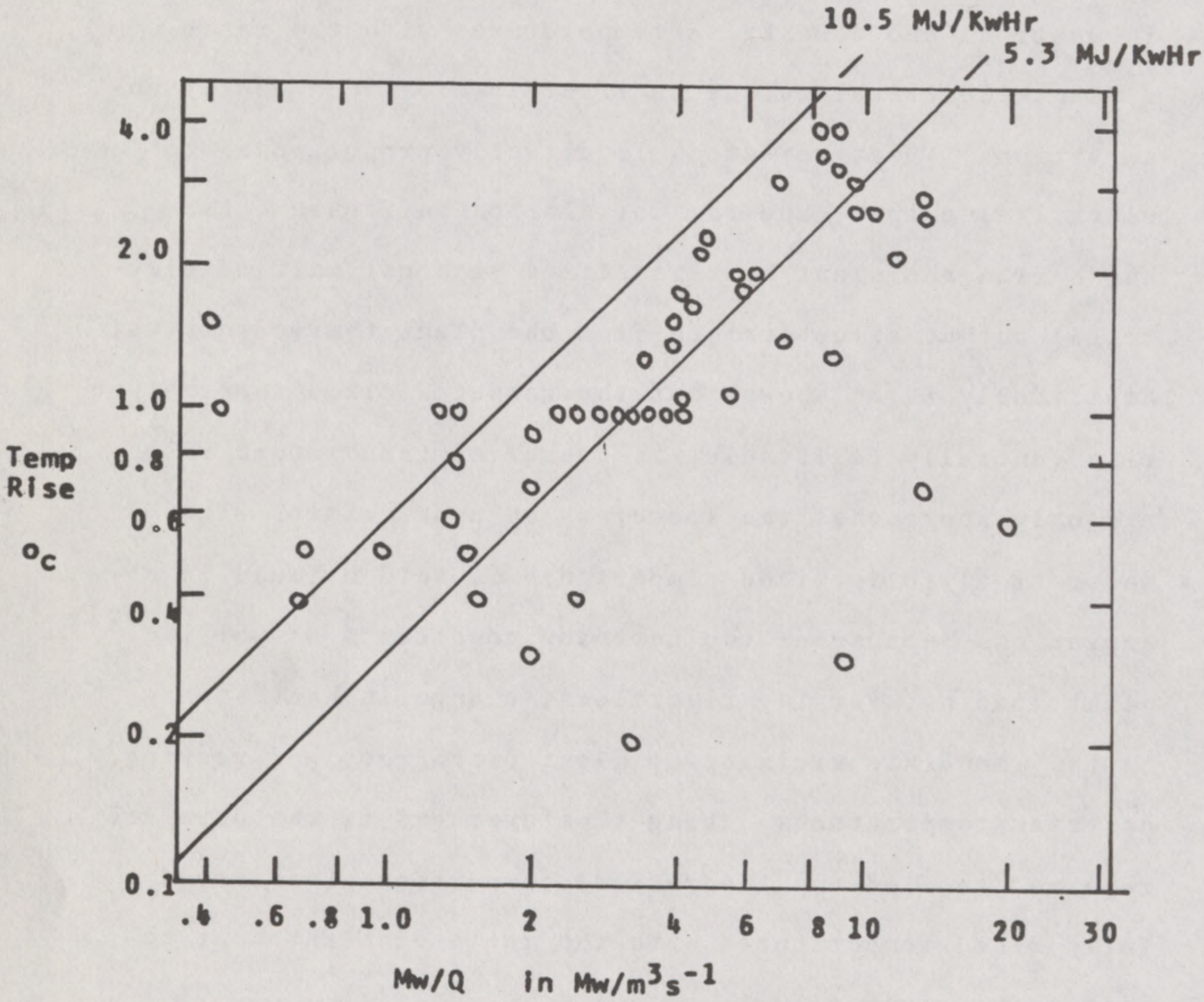
The simplicity of the concept of cooling water

circulation on a flowing river has led to an over-emphasis on this type of situation beyond its importance relative to the powerplant siting problem. The fully mixed temperature rise can be computed from the condenser temperature rise and the ratio of plant pumping rate to river flow. Under steady state conditions the temperature profiles should follow a well-behaved dieaway. But steady state conditions are hardly ever observed.

Figure 6 presents a comparison of the difference in upstream and downstream temperatures with the ratio of a plant electrical output to riverflow for mean weekly observations. Heat rejection is directly proportional to electrical output, and the correlation in Figure 6 is known from the plant heat rejection rate per unit of electrical output as determined from the plant thermodynamics. Empirically it is shown that the computed mixed temperature rise generally falls below the observed temperature rise and only approaches the latter as an upper limit. The theoretical fully mixed temperature is seldom found in observations because of the unsteady conditions of varying plant loading, varying riverflows, change in heat storage in the immediate vicinity of plant discharge, and varying upstream temperatures. Long time averages of the data are required to find the theoretical comparison of observed fully mixed temperatures with the ratio of plant heat rejection to river flow.

Figure 6

Comparison of observed upstream to downstream temperature rise for a mixed river with plant production per unit river flow.



Temperatures vary along a river reach due to upstream releases and tributary inflows as well as cooling water circulation. With tributary inflows at a temperature T_i, an equilibrium temperature T_e, an upstream flow release Q, a tributary inflow rate per unit river surface area q, and a coefficient of surface heat exchange of $k=K/\rho c_p$ the steady state temperature profile becomes:

$$T-T_a = (T_o-T_a)[1+\frac{q}{Q} A]^{-(1+k/q)} \qquad 23$$

where T_a is the approach temperature given as:

$$T_a = \frac{q\ T_i + k\ T_e}{q + k} \qquad 24$$

For no tributary inflows, Equation 23 reduces to the more familiar exponential decay law of:

$$T - T_e = (T_o - T_e)\ \exp(-kA/Q) \qquad 25$$

The river surface area determined from where $T = T_o$ is A, and the initial temperature T_o is determined at each new source point.

A case of a river temperature profile perturbed by a number of different source conditions along a river stretch is given in Figure 7. An upstream impoundment maintains the initial temperature at a very low value throughout the year. During the summer, the river is warming toward the approach temperature and during the winter, it is cooling toward the approach temperature. Each of the cooling water sources perturb the stream temperature and

Figure 7

Observed temperature profiles along a river with a cold water release and cooling water use

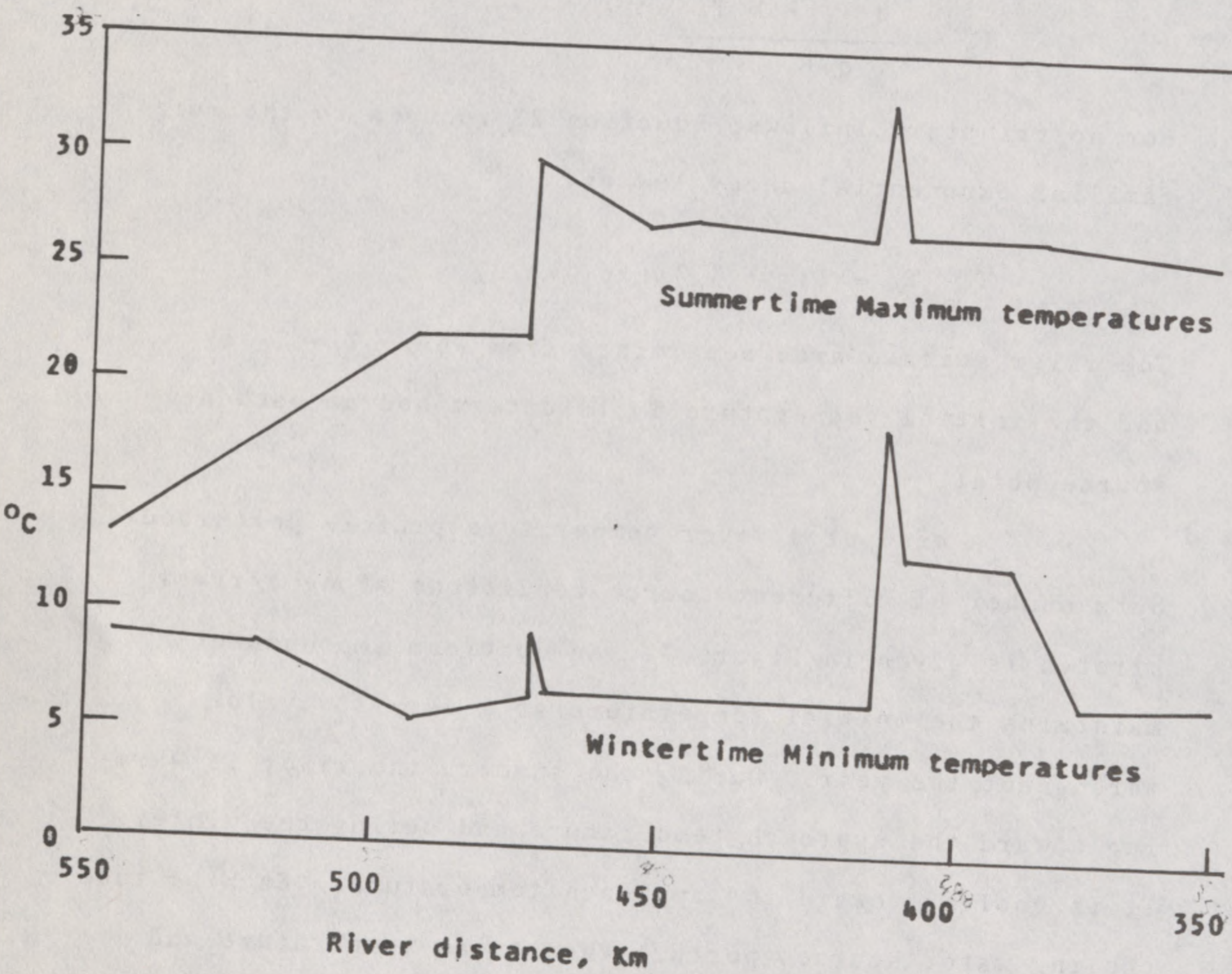
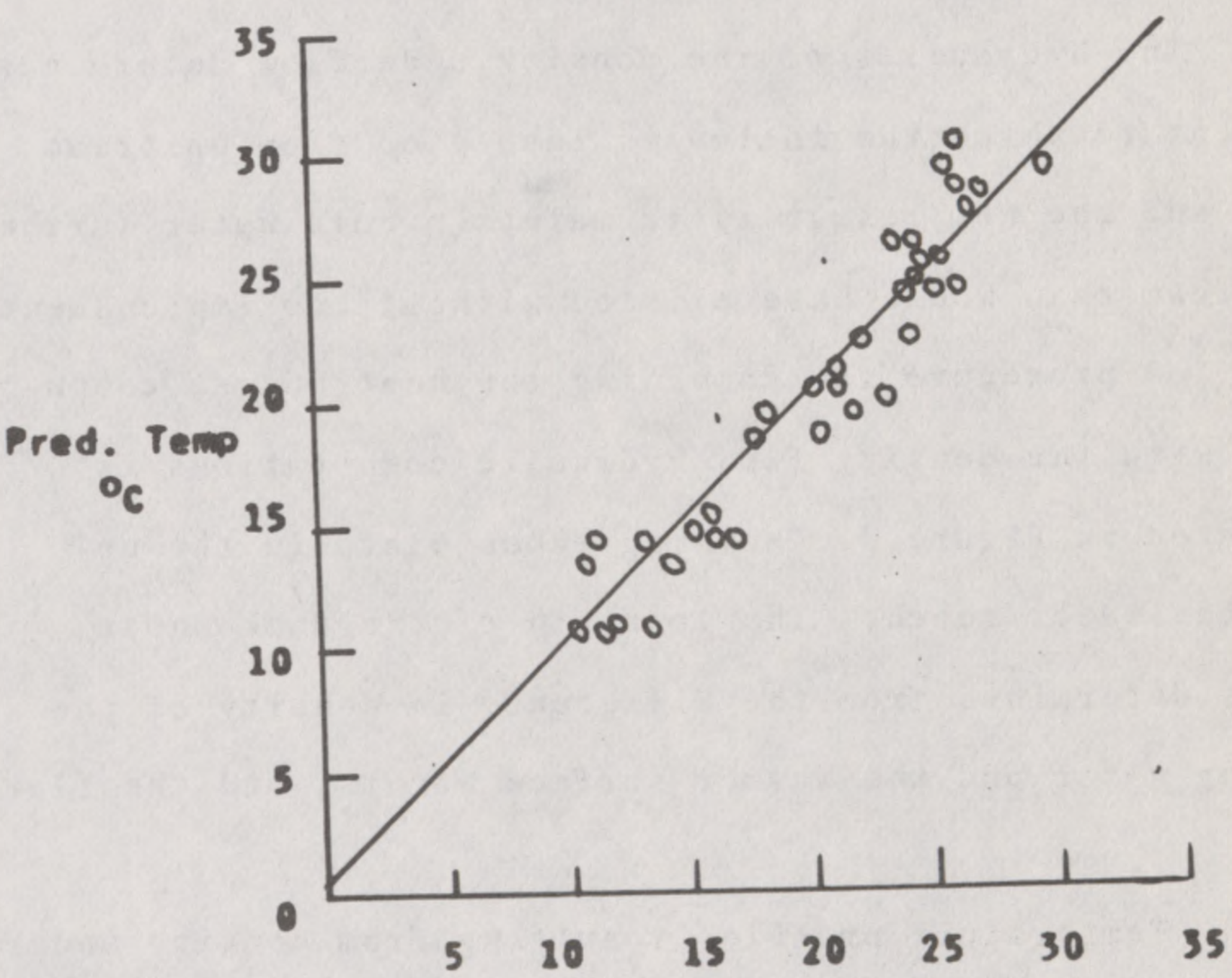


Figure 8

Comparison of observed and predicted temperatures for a river with cold water release and cooling water use, for selected weeks throughout the year.



the downstream profile can result from the perturbation being above the approach temperature and cooling down or being below the approach temperature and continuing to warm further downstream. A comparison of computed and observed temperature for this case is given in Figure 8 for weekly profiles throughout the year and indicates that prediction results can be improved through the consideration of change in heat storage, unsteady flows, and more detail about tributary inflow conditions.

Run-of-River Impoundments

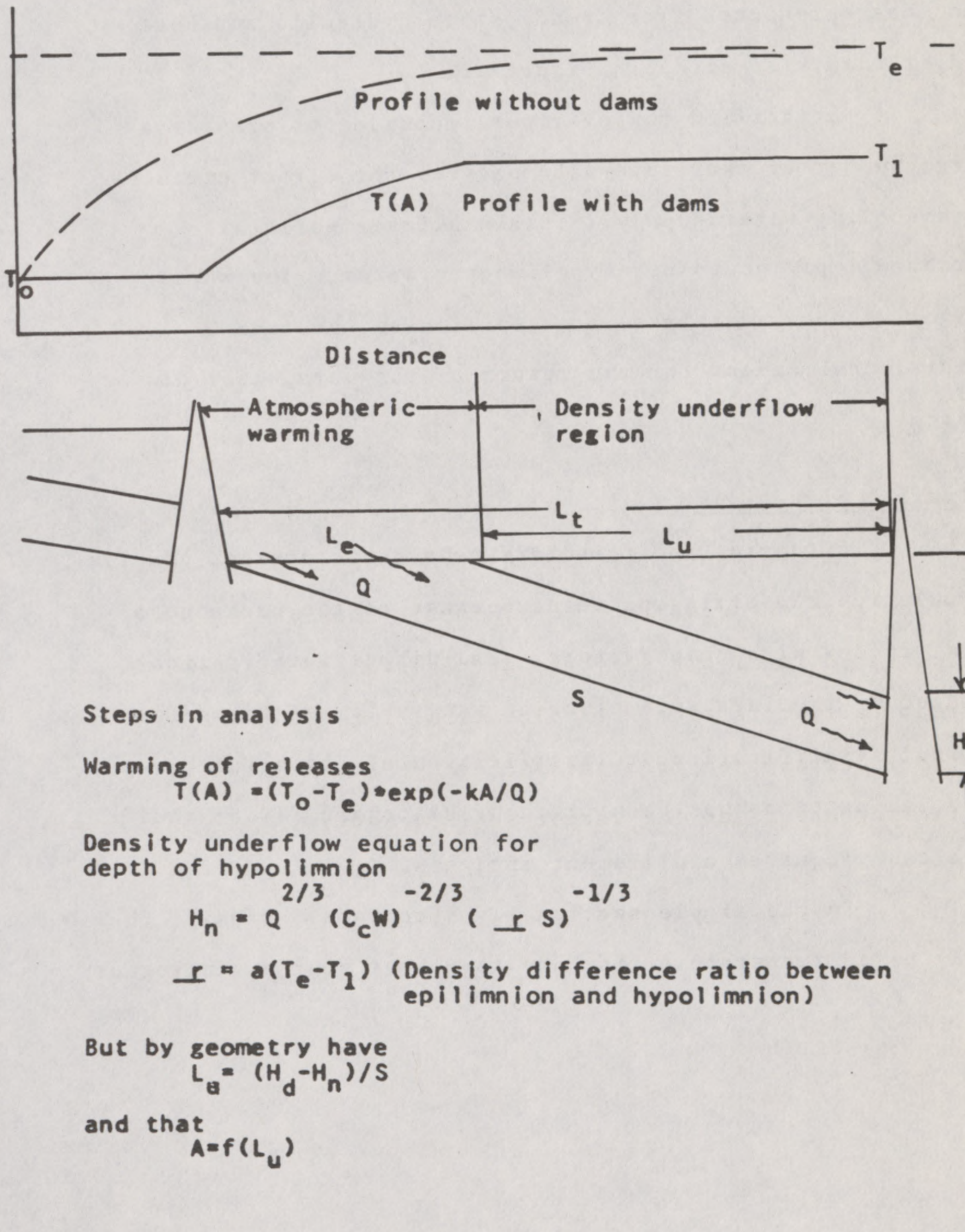
Run-of-river impoundments add substantial surface area to a river reach and provide an opportunity for stratification of a cold water inflow from warmed surface waters. The hydraulics of the density underflow determines the extent to which the inflow is insulated from upstream heating and the net result is to maintain cold water further down stream than would have existed without the impoundment.

A procedure for combining the heat budget computations with the density flow hydraulic computations is illustrated in Figure 9. Warming takes place in the upstream tailwater reach. The location of the duck-under point is determined from the difference in density of the inflowing water and the warmer surface waters, and the flow rate.

Temperature profiles resulting from density under-

Figure 9

Outline of reservoir stratification density underflow analysis including warming between dams and underflow hydraulics



Steps in analysis

Warming of releases

$$T(A) = (T_o - T_e) * \exp(-kA/Q)$$

Density underflow equation for depth of hypolimnion

$$H_n = Q^{2/3} (C_c W)^{-2/3} (\underline{r}\, S)^{-1/3}$$

$\underline{r} = a(T_e - T_1)$ (Density difference ratio between epilimnion and hypolimnion)

But by geometry have

$$L_u = (H_d - H_n)/S$$

and that

$$A = f(L_u)$$

flows through a series of run-of-river impoundments for a number of different years are given in Figure 10. The profiles vary from year to year due to the different flows and different meteorological conditions. A comparison of the distance to the duck-under point and the hydraulic parameters for two impoundments of Figure 10 is shown in Figure 11. A comparison of observed tailrace temperatures and those predicted from steady state hydraulic and heat budget theory is given in Figure 12.

Stratified run-of-river impoundments present a large number of available alternatives for direct circulation cooling water supply. Intake skimmer walls allow withdrawal of the colder hypolimnetic water, The warmer larger volume and surface area epilimnion, provide a natural environment for the return of the warm water discharge.

Estuarine Situations

Estuaries and tributary embayments present complex circulation and mixing patterns because of the exchange of river inflow with ocean waters. Salinity stratification induced by the intrusion of ocean waters is reflected in thermal stratification. Classification of estuarine circulation patterns has been given by Pritchard (1958) and each case requires a different analysis.

In the simple sectionally homogenous estuary, the fully mixed temperature rise due to a heat source, analogous

Figure 10

Observed River Temperature Profiles for a Number of Years. Mean monthly tail-race temperatures.

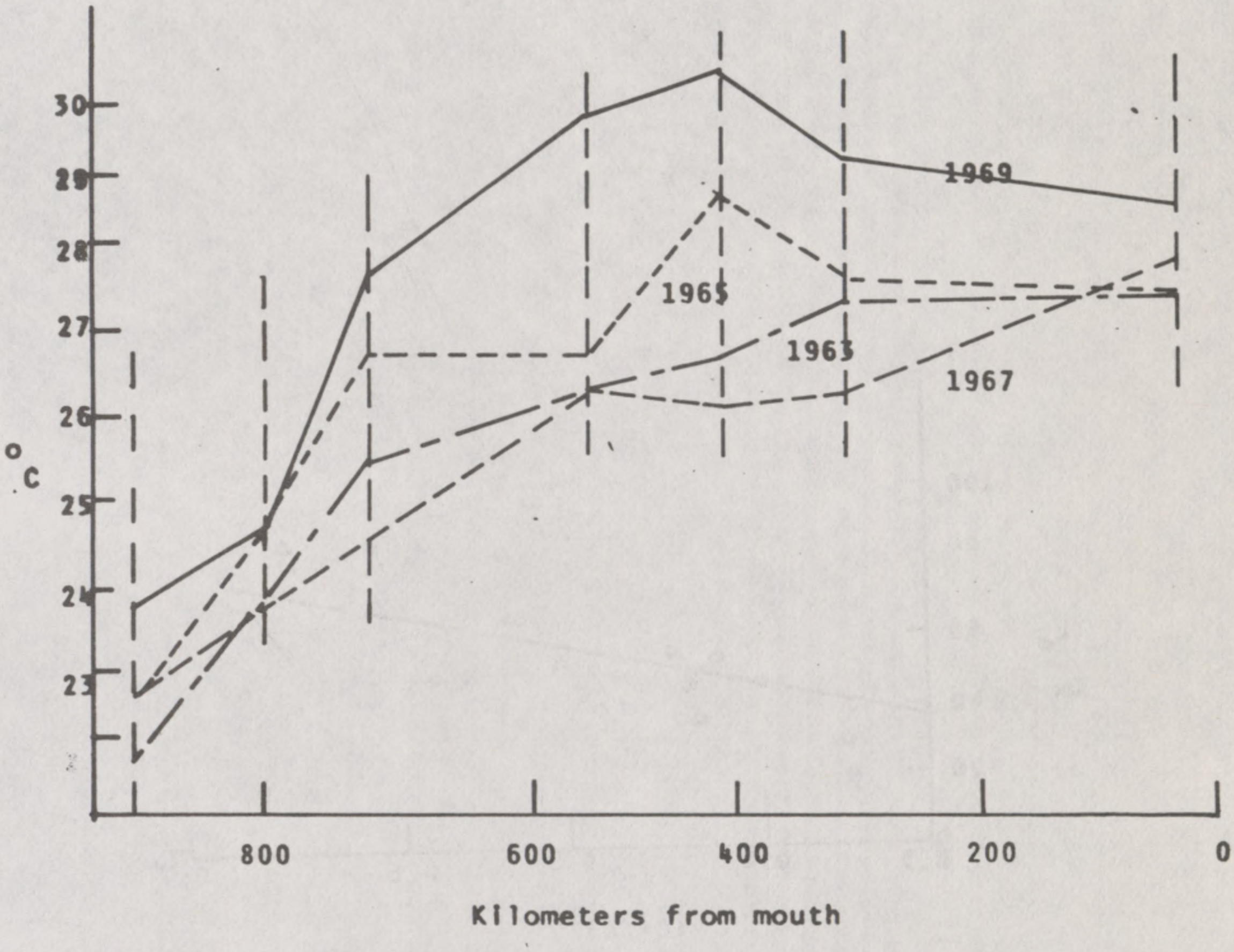
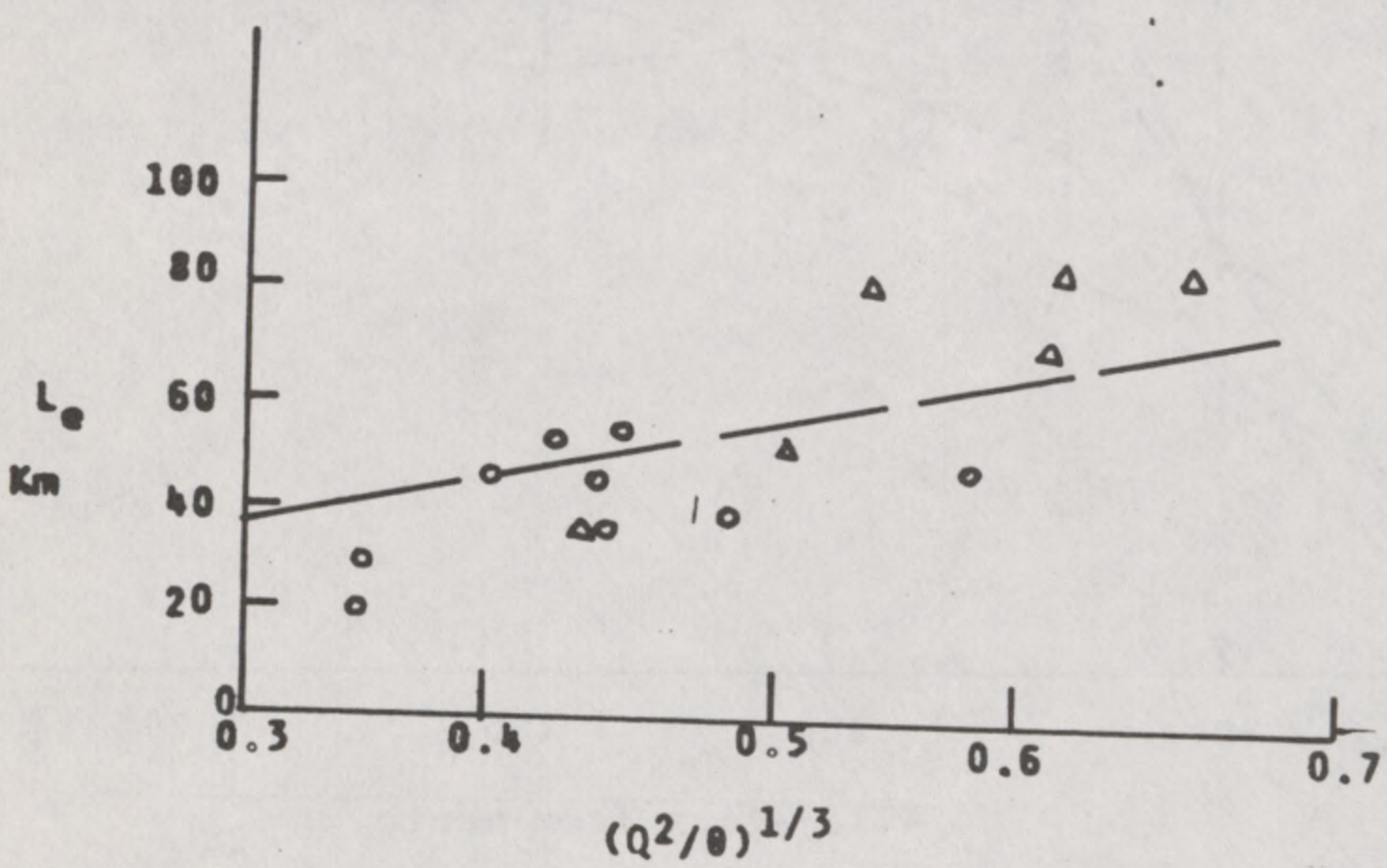


Figure 11

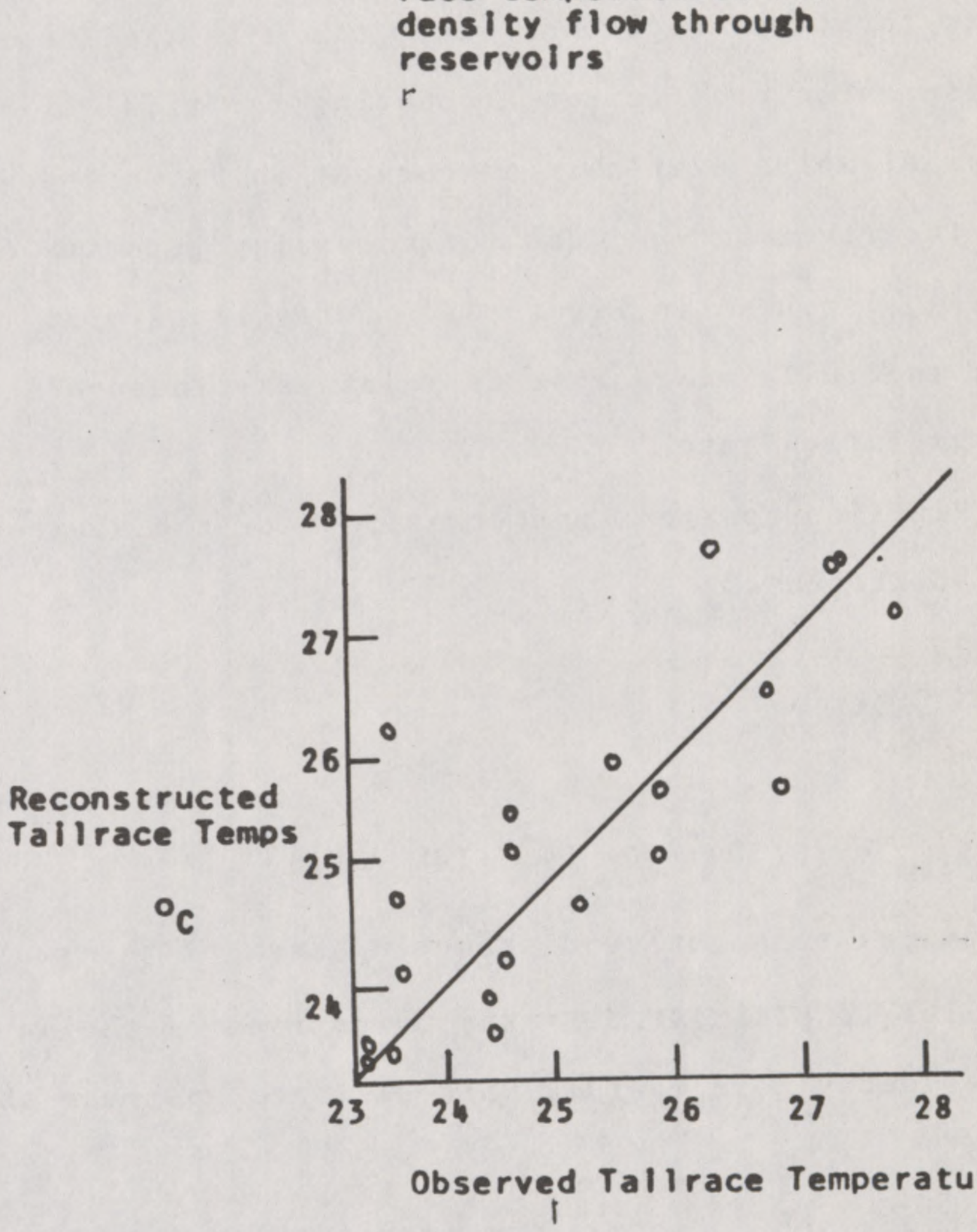
Comparison of Distance to Duckunder Point and Density Flow Parameters. Based on upstream area required for heating between dams.



Q in thds $m^3 s^{-1}$
θ in deg C

Figure 12

Comparison of Observed and Reconstructed Tailrace temperatures for density flow through reservoirs



to the fully mixed rise for a flowing river, is given as:

$$\Theta_m = \frac{H_p}{\rho c_p Q[1 + (4WSDk/Q^2)]^{1/2}} \qquad 26$$

where H_p is the heat source strength, W is the estuarine width, S is the cross-sectional area, and D is the longitudinal dispersion coefficient accounting for tidal mixing. The greater dilution available throughout an estuary downstream of the river inflow, due to increasing geometry and tidal mixing, is shown in Figure 13. Sufficiently far downstream the fully mixed rise is relatively independent of the river inflow rate.

Profiles upstream and downstream of the source decay with distance as:

$$\Theta = \Theta_m e^{a_i x} \qquad 27$$

where:

$$a_{1,2} = [Q/SD \pm ((Q/SD)^2 + (4Wk/SD))^{1/2}]/2 \qquad 28$$

where a_1 applies to negative distance upsteam of the source and a_2 applies to positive distance downstream of the source. Temperatures decay more rapidly with distance upstream than downstream.

Steady state temperature profiles for a sectionally homogeneous estuary computed for a number of sources along an estuarine reach are compared to mean monthly temperature gradients in Figure 14. The steady state tempera-

Figure 13

Fully Mixed Temperature Rise per unit heat load for single point along sectionally homogenous estuary, $^{o}C/10^{6}$ Joules Hr^{-1}

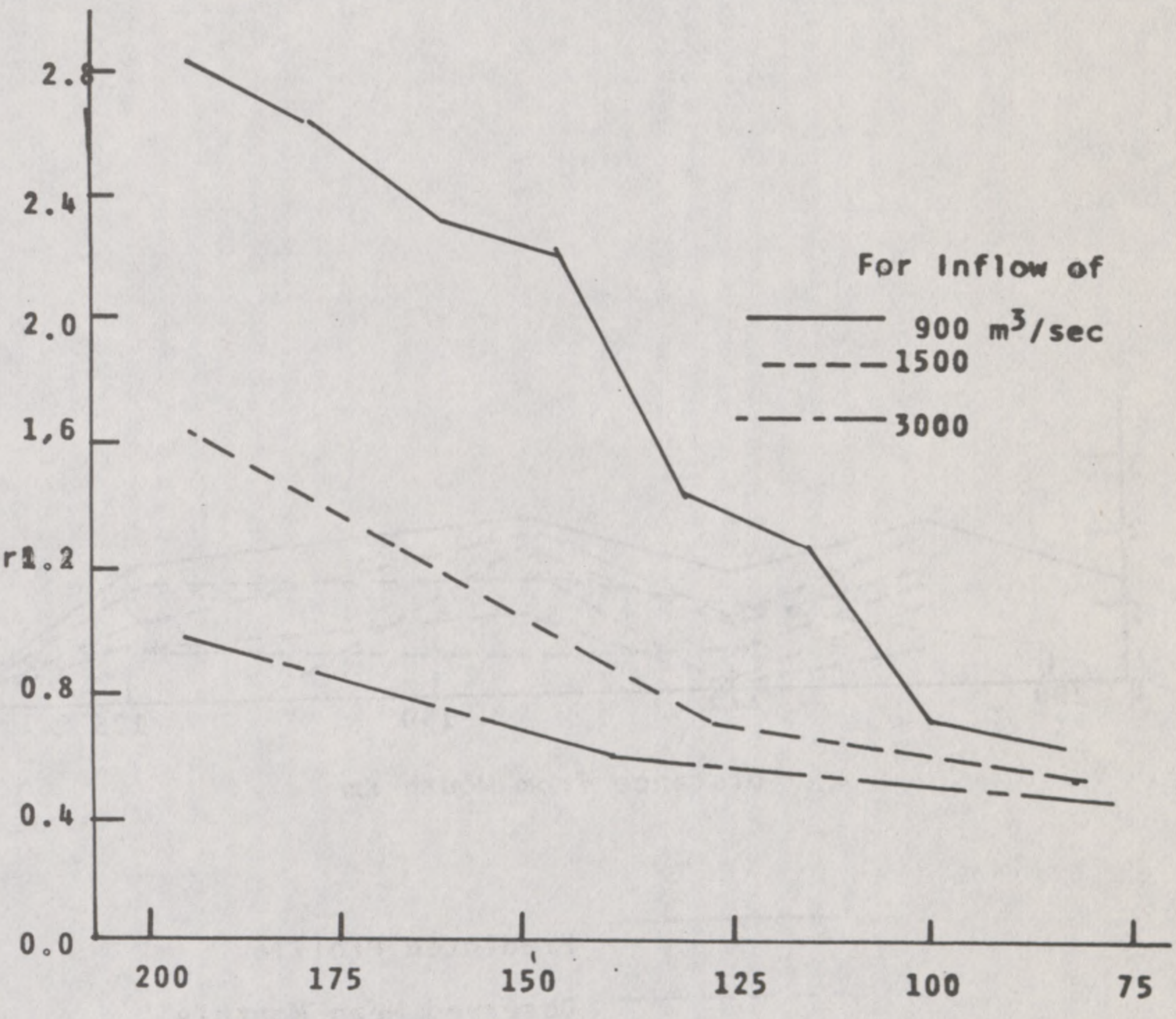
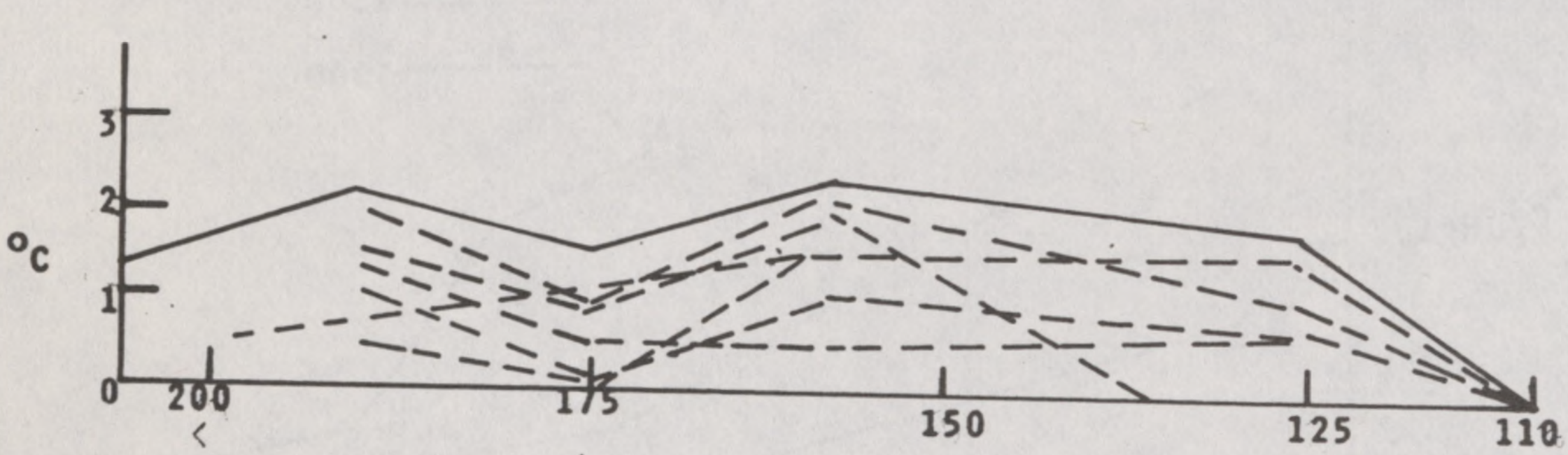


Figure 14

Comparison of observed temperature profiles for a number of years along a sectionally homogenous estuary, and prediction of temperature excess profile due to multiple sources.



Predicted Profile

Observed Mean Monthly July Temperature Rise

ture predictions tend to envelope the observed gradients because the latter reflect the effects of changes in heat storage, varying heat source strength, and varying meteorological conditions.

Proper representation of the estuarine circulation pattern is critical to accurate prediction of temperature profiles due to a heat source. Edinger and Bornstein (1973) examined an estuary used for cooling water supply as if it were sectionally homogeneous and as a two-layered circulation. Results of the sectionally homogeneous computations are given in Figure 15 and two-layered circulation computations, for the same estuary, are given in Figure 16. The sectionally homogeneous computations over-estimate temperature excess particularly in the vicinity of the source. The more detailed two-layer computations produce results that are more in agreement with the observed temperature gradients and illustrate the importance of ocean intrusion over freshwater inflow in providing the dilution water.

Coastal Water Situations

Coastal water siting presents thermal analysis problems over all three scales of temperature distribution phenomena. Without detailed hydrographic studies over a specific coastal region, it is possible only to postulate events of circulation that might be related to the coastal water siting problem.

figure 15

Comparison of predicted temperature excess and observed mean weekly estuarine temperatures for 1067 surveys using a one-dimensional sectionally homogenous model

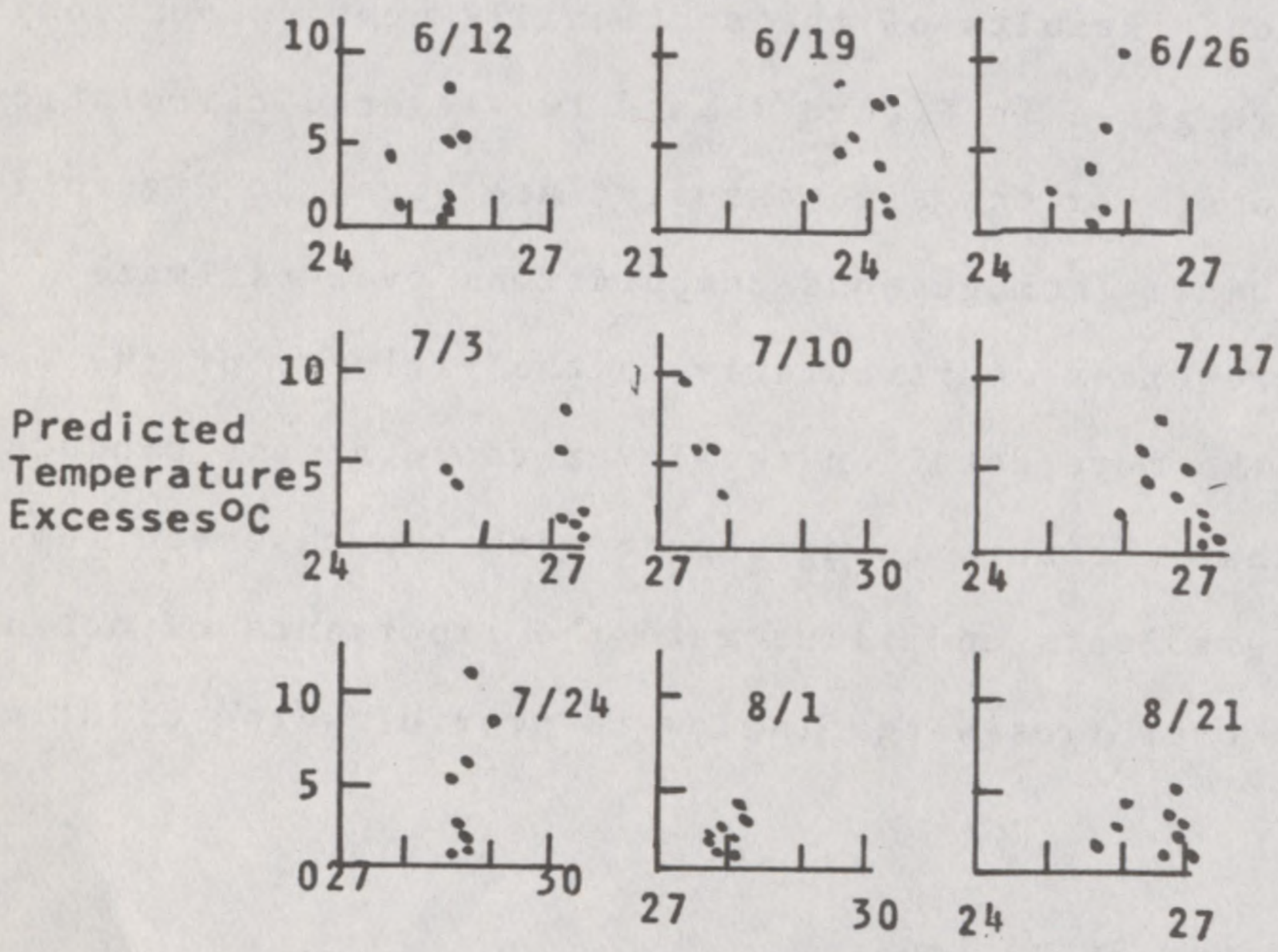
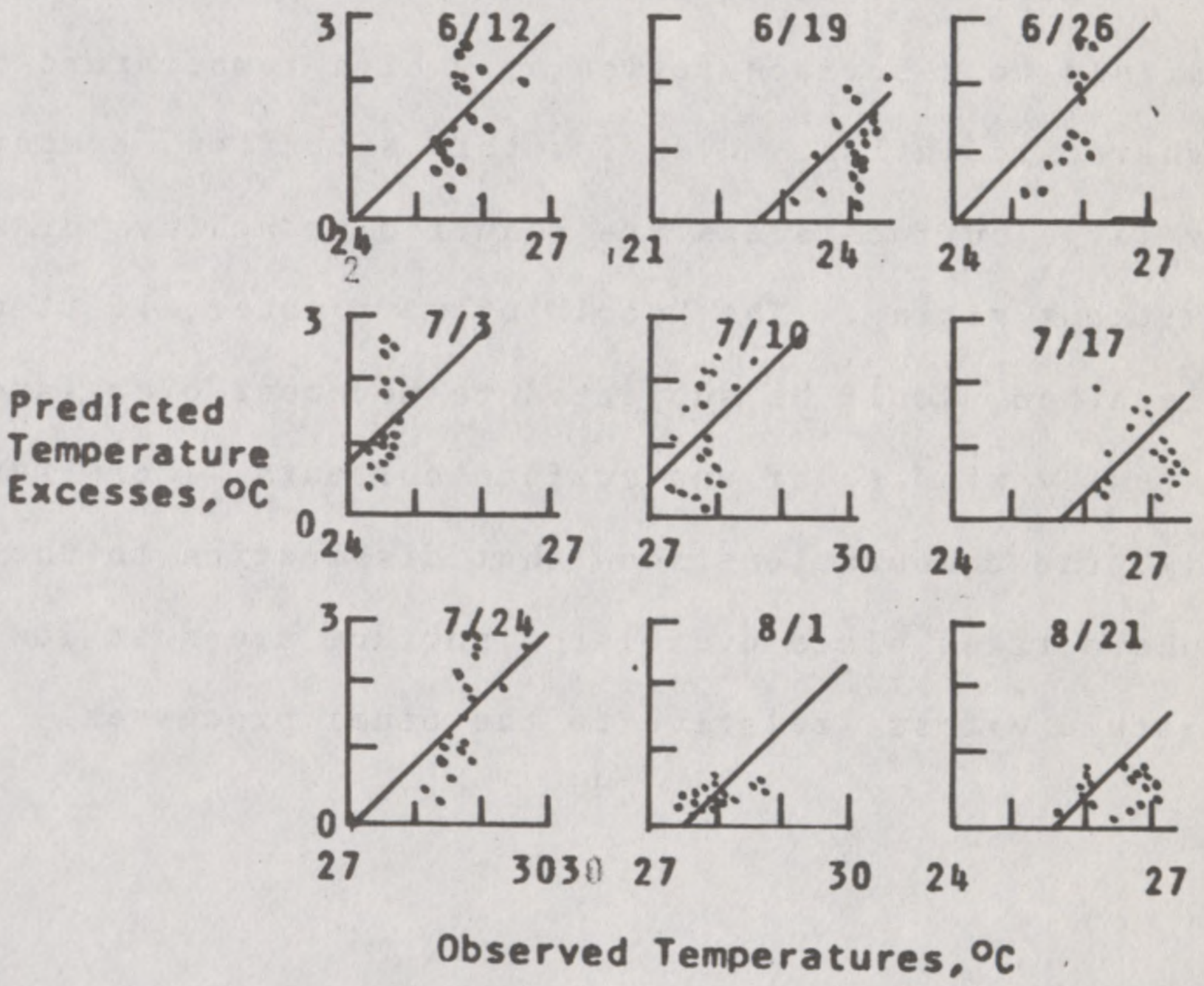


Figure 16

Comparison of predicted upper and lower layer temperature excess and observed mean weekly upper and lower layer temperatures for 1967 surveys using a two-layered circulation analysis.



trolling the distribution of excess heat. Considered in Table 2 is the temperature excess surface area relationships for the separate processes of jet mixing, mixing into a coastal current with no jet dilution, and surface cooling with no mixing and dispersion for a hypothetical discharge of flow rate $56 m^3 s^{-1}$ and condenser temperature rise of $11^{o}C$. There is an order of magnitude difference in the effectiveness of each of the separate processes in controlling the size of the temperature distribution and the influence of forced jet dilution is evident.

Surface cooling is effective only if the heat can be confined to a surface region at a high temperature excess through recirculation. Even for this situation, comparatively large surface areas are required to achieve dissipation without mixing. The "pool" of warm water, if it could be maintained, would be subjected to movement over large distances by wind shear and surface currents. More realistically, the computations show that dissipation to the atmosphere takes place over large surface areas at low temperature excess, relative to the other processes.

Table 2

Scales of Separate Heat Dissipation Mechanisms for a Typical 2000 MW Powerplant Discharge

Temperature Excess Ratio	Buoyant Jet Dilution Surface Area, m^2	Three-Dimensional Intermediate Area, m^2	Surface Heat Dissipation Area, m^2
0.75	1.4×10^2	0.93×10^4	1.7×10^6
0.50	5.8×10^2	6.5×10^4	4.5×10^6
0.25	5.4×10^3	2.3×10^5	9.0×10^6
0.10	8.6×10^4	7.4×10^5	1.4×10^7

Summary

This attempt to provide a comparative classification of cooling water discharge situations is not without its shortcomings. Temperature distributions from steam electric powerplant operations are treated independent of the problem of predicting the natural temperature structure of a waterbody. However, naturally occurring water temperatures are often as variable as the temperatures found around cooling water discharges. Analysis of temporal variations of temperature due to meteorological conditions, changing plant operations, and time varying hydrodynamic conditions require vast amounts of input data that can be handled efficiently only by computer.

Powerplant cooling operations present unique problems in water resource decisions. Alternatives to direct circulation cooling on large waterbodies include extensive land use for single purpose cooling ponds or development of water supply for cooling tower operations. Comparison of these alternatives is usually between different sites where their application is obvious rather than as choices available at a given site. Hydrodynamic considerations are but a small technical component of these larger economic and social choices.

Nomenclature

a_i = Estuarine temperature decay rate

a_i = Upstream decay rate

a_i = Downstream decay rate

A = Surface area within a temperature contour

A_n = Scaling area for intermediate mixing relationsl

A_o = Cross-sectional area of jet discharge

b_o = Rectangular discharge half-width

d = Waterbody depth

D_o = Jet diameter or depth

D = Longitudinal dispersion sufficient sectionally homogeneous estuary.

D_x = x-direction dispersion coefficient

D_y = y-direction dispersion coefficient

D_z = z-direction dispersion coefficient

F = Froude number in plume

F_o = Initial Froude number

g = Gravitational accleration

H_n = Net rate of surface heat exchange

H_s = Rate of incoming shortwave solar radiation

H_p = Powerplant heat rejection rate

K = Coefficient of surface heat exchange

K = $K/\rho C_p$, Kinematic exchange coefficient

K_o = Modified Bessel function

Q = Riverflow rate

Q_o = Powerplant pumping rate

q = Tributary inflow rate per unit river surface area

R = Richardson number

S = Estuarine cross-sectional area

t = time

t_θ = Time of travel to temperature excess contour

T = Water temperature

T_a = Approach temperature

T_d = Dewpoint temperature

T_e = Equilibrium temperature

T_i = Tributary inflow temperature

T_o = Initial water temperature

T_s = Water surface temperature

U = Waterbody x-component of velocity

U_o = Jet initial velocity

V = Waterbody y-component of velocity

W = Estuarine or river width

x = x-direction coordinate

y = y-direction coordinate

z' = Non-dimensional width or depth

X_{o2}= Two-dimensional jet virtual source distance

X_{o3} = Three-dimensional jet virtual source distance

θ = Temperature excess

θ_o = Powerplant condenser temperature rise

θ_m = Mixed temperature excess

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THERMAL ASPECTS OF AQUATIC CHEMISTRY

PART I

BY

W. DROST-HANSEN

TABLE OF CONTENTS

Part I

Page

I. INTRODUCTION

A. Objectives 1

B. Biotic responses to Temperature 2

C. Modeling of Environmental Aquatic Systems 4

II. PHYSICO-CHEMICAL CHANGES - THERMAL EFFECTS

A. General Observations 11

B. Densities, Specific Volumes, Compressibility and Thermal Expansion Properties 12

C. Vapor Pressure 15

D. Heat of Vaporization 16

E. Specific Heat 17

F. Thermal Conductivity 20

G. Viscosity 21

H. Diffusion 22

I Surface Tension 23

J Dielectric Constant 24

K Index of Refraction 24

L. Electrical Conductivity 25

III. SOLUTION PROPERTIES

A. Ionic Effects

1. ion activities 27

2. Dissociation constants 36

3. osmotic pressures 38

4. pH and P relationships 39

Table of Contents Continued...

Part I

Page

B. Gas solubilities

1. O_2 40

2. N_2 42

3. Other Gases 43

C. General Solubility Relations

1. CO_2-Carbonates; Sulfates 44

2. Miscellaneous Solubility Tables 50

IV. SURFACE AND COLLOID CHEMICAL ASPECTS

A. Introduction 54

B. Colloid Stability 63

C. Adsorption Desorption Phenomena 64

PART I

SECTION I: INTRODUCTION

I. INTRODUCTION

A. Objectives

The purpose of this review is threefold: first, to examine the effects of temperature on the physical and chemical properties of natural waters (specifically waters of interest to the continental United States); second, to discuss some of the influences of the chemical changes - effected by temperature changes - on the suitability of these waters to support life; and finally, to delineate some of the effects and the underlying mechanisms of temperature changes on the cell chemistry of the aquatic biota - that is, a thermochemical perspective of the aquatic biology under possible heat stress.

B. Biotic Responses to Temperature

In Part I, Section I,C, is discussed the effects of temperature changes on model systems - serving as approximations to real, natural water systems - in terms of both physical properties and a number of chemical equilibria and rate processes. In principle, since attention is restricted to the temperature range from approximately 0°C to approximately 40°C,* the problem is essentially "straightforward" - at least to within the approximations afforded by the model systems chosen to represent the actual natural waters. Standard physical chemistry accounts reasonably well for temperature effects on dilute but aqueous solutions of electrolytes. The second task, to determine the effects of the chemical changes (effected by temperature variations) on the biota is far more complex. For this reason, the second task will be reduced to considerations of two different, distinct problems. First, it will be demonstrated that the chemical changes effected by small temperature changes are probably without any dramatic influence on the overall ecology of a local region. Obviously, any temperature change will change the ecology. This statement is almost axiomatic. However, while nearly obviously true, it is also likely, as will be evidenced, that the changes are relatively minor, though likely readily detectable. Whether these changes will be beneficial or detrimental is beyond the realm of this investigation (and

*Thus excluding such unique environments as hot springs.

beyond the ability of the present investigator to determine). In the second major aspect of this study, some specific influences of aquatic temperature changes directly on various organisms will be considered in some detail.

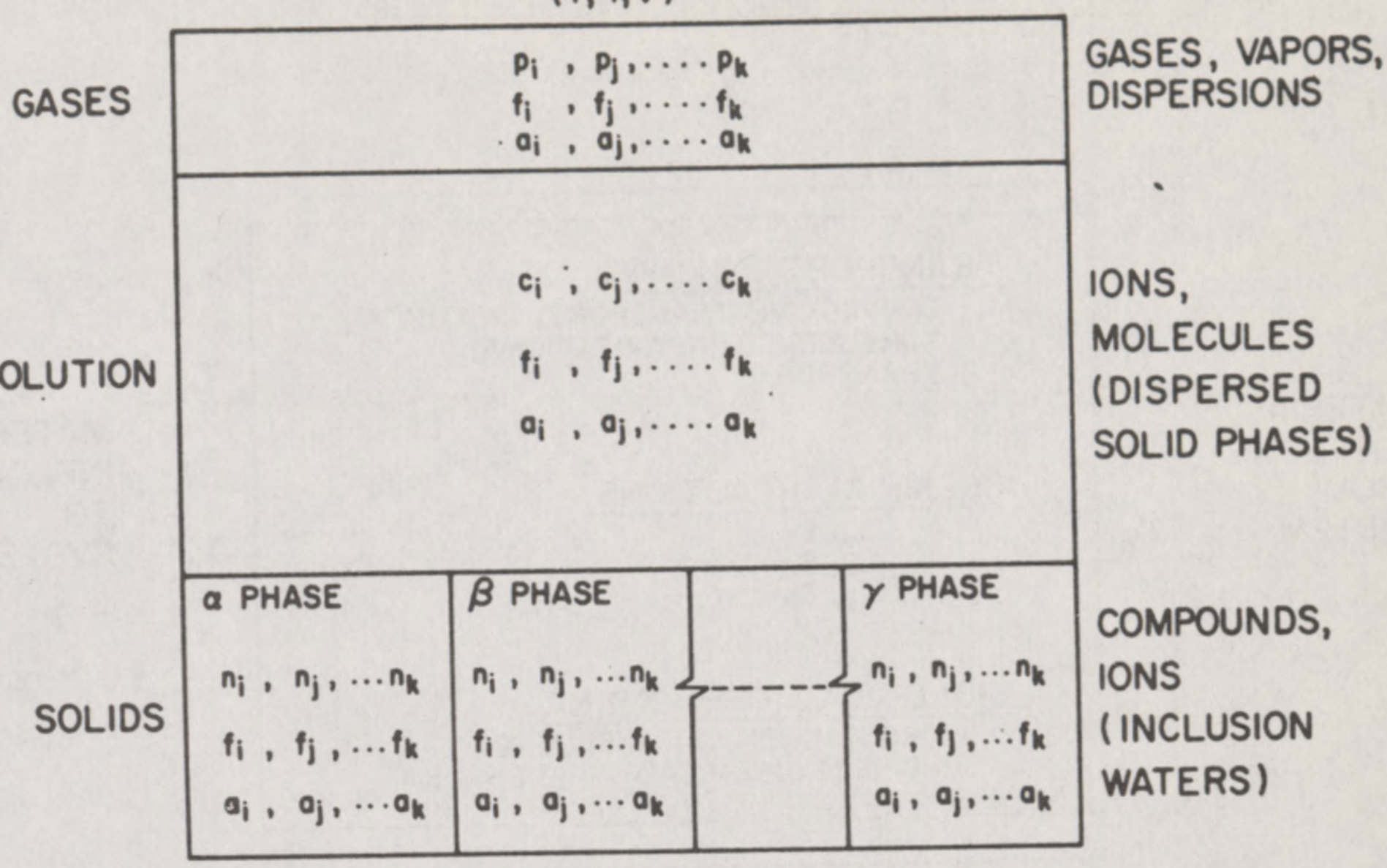
We conclude this brief introduction by stressing one of the main results of the investigation: the effects of temperature on the aquatic chemistry are probably of minimal consequences, at least for the ecology for small temperature changes, in "safe temperature intervals" (the meaning of the expression "safe temperature intervals" to be discussed at length below, in Section 2.IV-V). However, near certain "critical temperature ranges" (also to be explicitly defined and discussed in a subsequent section), dramatic and generally highly deleterious ecological effects can be expected. These latter changes are brought about at characteristic, narrow temperature intervals, apparently as the result of chemical changes internal to the organism (rather than due to the relatively modest chemical changes in the chemistry of the external, bulk environment).

C. Modeling of Environmental, Aquatic Systems

Morgan (1967) has discussed the "applications and limitations of chemical thermodynamics in natural water systems". This study delineates some conceptual models by which a "real" situation may be approximated by generalized models to which at least in principle, thermodynamics is applicable. The two systems primarily advocated by Morgan allow, respectively, for a thermodynamic description of an essentially closed system, and for a chemical dynamics description, allowing for material exchanges (inputs and outflows) and energy exchanges. The natural extension of this system would be to the inclusion of biological phenomena. Figure I-01 and Figure I-02 show, respectively, Morgan's two systems. Unfortunately, Morgan mentions only briefly the principle by which a connection can be made between the thermodynamic description of a chemical reaction system and the actual kinetics. The link is provided via the general field of irreversible chemical thermodynamics. Formally, the simplest expression is the formula for the rate of internal energy production, dS_i/dt. This rate of entropy production is related to the overall velocity of the chemical reaction, as seen in equation (1).

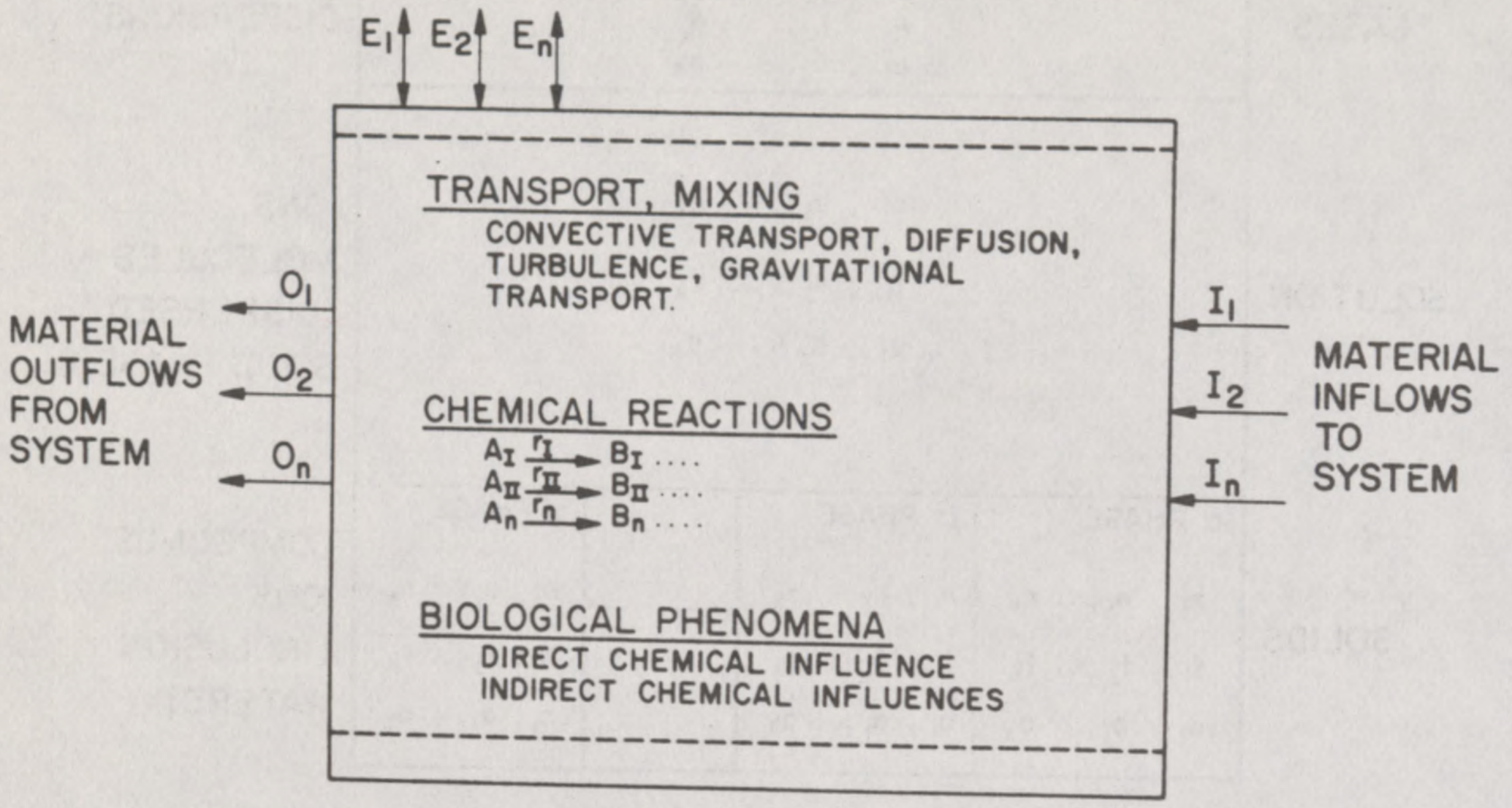
$$\frac{dS_i}{dt} = \frac{A}{T} \cdot \frac{d\xi}{dt} = \frac{A}{T} \cdot v \qquad (1)$$

Here $v = d\xi/dt$ is the velocity of the chemical reaction. dS_i/dt is the rate of internal energy production. ξ_i is the degree of advancement of the reaction. In Equation (1), A is the affinity ($= -\Sigma v_i \mu_i$).



A Generalized Model for the Thermodynamic Description of Natural Water Systems (Morgan, in Stumm, 1967, page 9).

Figure 1-01



Generalized Model for a Chemical, Dynamic Description of Natural Water Systems with Material and Energy Exchanges Across Boundaries.

(Morgan, in Stumm, 1967, page 14).

Figure I-02

In the present review, it is not possible to take into account the effects of a temperature change on an open, dynamic model system. The theory for this is only being developed right now (see, for instance, Glansdorff and Prigogine, "Thermodynamic Theory of Structure, Stabilility and Fluctuations", 1971). The problem is complicated in the sense that the actual natural water system may be far from equilibrium initially (and even further from equilibrium after a change in the temperature has been imposed via a man-made energy exchange). Thus, the obvious changes - such as enhanced vapor pressure and rate of evaporation - will obviate the possibility of obtaining accurate answers by considering merely closed equilibrium thermodynamic systems.

For an open system the stationary state is one characterized by an entropy production (assuming fixed affinities or concentrations in the environment). The stationary state has been described by Prigogine (1961) as the state of minimum entropy production; in other words, the least free energy dissipation.

In his treatment of open and dynamic model systems, Morgan calls attention to the general equation for a system in which the concentration of any constituent (i) is a function of space and time.

$$\frac{\partial C_i}{\partial t} + u\frac{\partial C_i}{\partial x} + v\frac{\partial C_i}{\partial y} + w\frac{\partial C_i}{\partial z} = \frac{\partial}{\partial x}\left(D_x\frac{\partial C_i}{\partial x}\right) + \frac{\partial}{\partial y}\left(D_y\frac{\partial C_i}{\partial y}\right) + \frac{\partial}{\partial z}\left(D_z\frac{\partial C_i}{\partial z}\right) + r_{i,n} \qquad (2)$$

Where terms of the form a . $\frac{\partial C_i}{\partial P}$ are the advective or convective terms and expressions of the form $\frac{\partial}{\partial p}(D_p \cdot \frac{\partial C_i}{\partial p})$ are terms related to diffusion or turbulent transport (depending on the hydrodynamic situation). $r_{i,n}$ is the rate of formation or disappearance of the constituent i by any process (N) in the vicinity of point of interest. It is seen that the equation is composed of advective or convective terms, diffusion or turbulent transport terms and rates of disappearance or formation of a constituent.

In the present review, attention is concentrated on two types of systems: idealized model systems, consisting of closed equilibrium thermodynamic systems for which changes in parameters and properties are calculated (either from theory or based on experimental data) for properties as a function of temperature. The second facet to be dealt with are temperature changes in a non-equilibrium (and sometimes non-steady) state, such as living systems; here the temperature effects are directly on the functioning of the cellular organism. Kinetic phenomena, per se, will receive only relatively little attention. The treatment primarily deals, in this case, with the kinetics of processes in colloidal systems, specifically rate variations as a function of temperature.

In the "realistic" model systems - which is, at best, a first order approximation - it is specifically assumed that one needs to be concerned only with the effects of temperature on a constant chemical environment as opposed to a

real system in which large-scale random changes may occur. Thus, the treatment does not allow for the effects of temperature, on an otherwise "steady-state" system, suddenly subject to dumping of major or minor chemical constituents into the system (such as may occur as the result of a heavy rainfall, unexpected runoff from fertilized water sheds, or variable inputs from private or municipal water treatment plants which may be operating subject to large fluctuations).

Please note, unless specifically stated otherwise, all measurements are in cgs units. Also note particularly the consistent use of temperatures in degrees Celsius ("Centigrade"); or, where appropriate, degrees Kelvin. Where temperatures are discussed which are derived from quotes in the literature - in all but direct quotes - the temperatures have been converted to degrees Celsius. Generally, the conversion is at least to within the nearest degree Celsius.

Finally, it should be observed that the aim of the present review is twofold: estimating temperature effects on the intrinsic ("equilibrium") chemistry - i.e., concentration, ion activities and general properties. The second major aspect is the effects of temperature on the organisms as effected through the internal chemical changes. The connection between the chemical changes effected by temperature and the suitability of these natural waters to support life are thus deliberately separated into two distinctly differing aspects. What is left out of consideration, then, is the "feedback"; the effects which the temperature exerts on the organisms and which, in turn, alters the chemistry - often dramatically - (for instance, through metabolic use of oxygen, exchange of ions, etc.).

In Section II, thermal effects on physico-chemical properties of water and selected electrolyte solutions are examined in some detail. Attention is restricted essentially to the temperature range from 0 to 40° - the principal limits for naturally occurring aquatic environments. It is obvious that the properties of both pure water and aqueous solutions are functions of temperature. These temperature dependencies have, in many cases, been determined with great accuracy and extreme precision. In the present context, however, only essential features of these temperature variations have been considered for practical reasons. Where available, data are reported, over the temperature range from 0 to (at least) 40° in sufficiently small increments to allow reasonably accurate interpolations to be made.

The main objective of the first part of this study may be stated simply as the determination of the changes in the chemistry of natural waters effected by a reasonable thermal input into a localized body of water. Somewhat arbitrarily, for sake of discussion, a maximum of 5 or 10°C temperature increase has been adopted in this analysis. In other words, if the ambient temperature of the water body in question is 15° on the average, a maximum temperature rise of 10° (to 25°C) will be considered. The question is: what effects does such a temperature increase have on the chemistry and, in turn, on the population of organisms in this body of water? In the first part of the study, the effect is treated, in a sense, as an abstraction. In other words, the emphasis is on the change in the suitability of the water as a medium for sustaining life due to the resulting changes in the chemistry. What is excluded, then, in this discussion is the intrinsic effects of the temperature on the organisms internally which will ultimately be reflected in the chemistry of the environment.

The above limitation is, in a sense, highly unfortunate from the point of view of the ecology. For this reason, the second part of this review deals specifically with some selected (but not general) aspects of temperature effects on cellular organisms. However, the simplification proposed may be justified pragmatically in terms of the enormous complexity of the natural system - requiring some simplifications to be made - and in part by the conclusion which results from this study; namely, that the relatively minor changes in chemical composition, which are brought about by a 10° temperature change, are not likely to affect significantly the overall ecology. Thus, further studies of temperature changes on aquatic ecology may be better served by increased attention to the changes in the cellular chemistry, rather than in excessive efforts to monitor in detail the overall "bulk" chemistry of the natural waters.

PART I

SECTION II: PHYSICO-CHEMICAL CHANGES - THERMAL EFFECTS

A. General Observations

In classical physical chemistry, the effect of temperature on equilibria and on rate processes are traditionally represented by van't Hoff plots and Arrhenius plots, respectively. In either case, the logarithm of the quantity in question is plotted as a function of reciprocal absolute temperature. Traditional interpretations (subject to many limitations) are usually restricted to straight line segments of such curves. As an example, for solubility data, the slope gives the heat of solution; for rate processes, the slope is the Arrhenius energy of activation. Enumerable detailed treatments of these quantities can be found in standard texts on physical chemistry.

In Table I is shown a general survey of some characteristic physical properties of water as a function of temperature. More detailed information about these variables are fuond in Section II-B.

TABLE I

GENERAL SURVEY:

PHYSICAL PROPERTIES OF WATER AT ATMOSPHERIC PRESSURE

t_{68}, °C	Vapor Pressure bar	Density, kg m^{-3}	Isothermal compressibility, bar^{-1}	Isobaric specific heat, Jg^{-1}	Temp. °C	Dielectric constant	Viscosity centipoise
0	0.00611	999.840	50.866	4.2174	0	$87{\cdot}74_0$	1·787
5	0.00872	999.964	49.170	4.2019	5	$85{\cdot}76_3$	1·516
10	0.01228	999.700	47.810	4.1919	10	$83{\cdot}83_2$	1·306
15	0.01705	999.100	46.735	4.1855	15	$81{\cdot}94_5$	1·138
20	0.02338	998.204	45.894	4.1816	20	$80{\cdot}10_3$	1·002
25	0.03169	997.045	45.249	4.1793	25	$78{\cdot}30_3$	0·8903
30	0.04245	995.648	44.773	4.1782	30	$76{\cdot}54_6$	0·7975
35	0.05627	994.032	44.443	4.1779	35	$74{\cdot}82_3$	0·7194
40	0.07382	992.215	44.243	4.1783	40	$73{\cdot}15_1$	0·6531
45	0.09591	990.212	44.158	4.1792	45	$71{\cdot}51_1$	0·5963
50	0.12346	988.033	44.179	4.1804	50	$69{\cdot}91_0$	0·5467
55	0.15754	985.691	44.297	4.1821	55	$68{\cdot}34_4$	0·5044
60	0.19936	983.193	44.504	4.1841	60	$66{\cdot}81_3$	0·4666
65	0.25027	980.548	44.797	4.1865	65	$65{\cdot}31_9$	$0{\cdot}434_2$
70	0.31181	977.761	45.171	4.1893	70	$63{\cdot}85_5$	$0{\cdot}404_9$

B. Densities, Specific ___ ____ Volumes of Water and Seawater

Extensive discussion of the density of water can be found both in Dorsey (1940) and in Gmelin (loco cit., page 1317-1323). Table 1-02 shows the tabulated values reported in Gmelin (page 1322-1323) based on the recalculated data of Chappui, according to Tilton and Taylor (1937).

t	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
0°	0.9998676	0.9998743	0.9998808	0.9998871	0.9998933	0.9998993	0.9999051	0.9999107	0.9999161	0.9999214
1°	0.9999265	0.9999314	0.9999362	0.9999407	0.9999451	0.9999493	0.9999534	0.9999573	0.9999610	0.9999645
2°	0.9999678	0.9999710	0.9999740	0.9999769	0.9999796	0.9999821	0.9999844	0.9999866	0.9999886	0.9999905
3°	0.9999922	0.9999937	0.9999950	0.9999962	0.9999972	0.9999981	0.9999988	0.9999993	0.9999997	0.9999999
4°	1.0000000	0.9999999	0.9999996	0.9999992	0.9999986	0.9999979	0.9999970	0.9999960	0.9999948	0.9999934
5°	0.9999919	0.9999902	0.9999884	0.9999864	0.9999843	0.9999820	0.9999796	0.9999770	0.9999742	0.9999713
6°	0.9999683	0.9999651	0.9999618	0.9999583	0.9999546	0.9999508	0.9999469	0.9999428	0.9999386	0.9999342
7°	0.9999297	0.9999250	0.9999202	0.9999153	0.9999102	0.9999049	0.9998995	0.9998940	0.9998883	0.9998825
8°	0.9998765	0.9998704	0.9998642	0.9998578	0.9998513	0.9998446	0.9998378	0.9998309	0.9998238	0.9998166
9°	0.9998092	0.9998017	0.9997941	0.9997863	0.9997784	0.9997704	0.9997622	0.9997539	0.9997454	0.9997368
10°	0.9997281	0.9997193	0.9997103	0.9997012	0.9996919	0.9996825	0.9996730	0.9996634	0.9996536	0.9996437
11°	0.9996336	0.9996234	0.9996131	0.9996027	0.9995922	0.9995815	0.9995706	0.9995597	0.9995486	0.9995374
12°	0.9995261	0.9995146	0.9995030	0.9994913	0.9994795	0.9994675	0.9994554	0.9994432	0.9994309	0.9994184
13°	0.9994059	0.9993932	0.9993803	0.9993674	0.9993543	0.9993411	0.9993278	0.9993143	0.9993007	0.9992870
14°	0.9992732	0.9992593	0.9992453	0.9992311	0.9992168	0.9992024	0.9991879	0.9991732	0.9991584	0.9991436
15°	0.9991286	0.9991134	0.9990982	0.9990828	0.9990674	0.9990518	0.9990360	0.9990202	0.9990043	0.9989882
16°	0.9989721	0.9989558	0.9989394	0.9989229	0.9989062	0.9988895	0.9988726	0.9988557	0.9988386	0.9988214
17°	0.9988041	0.9987867	0.9987691	0.9987515	0.9987337	0.9987158	0.9986979	0.9986798	0.9986616	0.9986433
18°	0.9986248	0.9986063	0.9985877	0.9985689	0.9985501	0.9985311	0.9985120	0.9984928	0.9984735	0.9984541
19°	0.9984346	0.9984150	0.9983953	0.9983754	0.9983555	0.9983355	0.9983153	0.9982950	0.9982747	0.9982542
20°	0.9982336	0.9982130	0.9981922	0.9981713	0.9981503	0.9981292	0.9981080	0.9980867	0.9980653	0.9980438
21°	0.9980221	0.9980004	0.9979786	0.9979567	0.9979346	0.9979125	0.9978903	0.9978679	0.9978455	0.9978230
22°	0.9978003	0.9977776	0.9977547	0.9977318	0.9977088	0.9976856	0.9976624	0.9976390	0.9976156	0.9975921
23°	0.9975684	0.9975447	0.9975208	0.9974969	0.9974729	0.9974487	0.9974245	0.9974002	0.9973758	0.9973512
24°	0.9973266	0.9973019	0.9972771	0.9972522	0.9972272	0.9972021	0.9971769	0.9971516	0.9971262	0.9971007
25°	0.9970751	0.9970494	0.9970237	0.9969978	0.9969718	0.9969458	0.9969196	0.9968934	0.9968671	0.9968406
26°	0.9968141	0.9967875	0.9967608	0.9967340	0.9967071	0.9966801	0.9966530	0.9966258	0.9965986	0.9965712
27°	0.9965437	0.9965162	0.9964886	0.9964608	0.9964330	0.9964051	0.9963771	0.9963490	0.9963208	0.9962926
28°	0.9962642	0.9962358	0.9962072	0.9961786	0.9961499	0.9961211	0.9960922	0.9960632	0.9960341	0.9960049
29°	0.9959757	0.9959463	0.9959169	0.9958874	0.9958578	0.9958281	0.9957983	0.9957684	0.9957384	0.9957084
30°	0.9956783	0.9956480	0.9956177	0.9955874	0.9955569	0.9955263	0.9954956	0.9954649	0.9954341	0.9954032
31°	0.9953722	0.9953411	0.9953099	0.9952787	0.9952473	0.9952159	0.9951844	0.9951528	0.9951211	0.9950894
32°	0.9950575	0.9950256	0.9949936	0.9949615	0.9949293	0.9948970	0.9948647	0.9948322	0.9947997	0.9947671

t	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
33°	0.9947344	0.9947016	0.9946688	0.9946359	0.9946028	0.9945698	0.9945366	0.9945033	0.9944700	0.9944365
34°	0.9944030	0.9943694	0.9943358	0.9943020	0.9942682	0.9942343	0.9942003	0.9941662	0.9941320	0.9940978
35°	0.9940635	0.9940291	0.9939946	0.9939600	0.9939254	0.9938907	0.9938559	0.9938210	0.9937860	0.9937510
36°	0.9937159	0.9936807	0.9936454	0.9936100	0.9935746	0.9935391	0.9935035	0.9934678	0.9934321	0.9933962
37°	0.9933604	0.9933244	0.9932883	0.9932522	0.9932160	0.9931797	0.9931433	0.9931068	0.9930703	0.9930337
38°	0.9929970	0.9929603	0.9929234	0.9928865	0.9928495	0.9928125	0.9927753	0.9927381	0.9927008	0.9926634
39°	0.9926260	0.9925884	0.9925508	0.9925132	0.9924754	0.9924376	0.9923997	0.9923617	0.9923236	0.9922855
40°	0.9922473	0.9922090	0.9921707	0.9921323	0.9920938	0.9920552	0.9920165	0.9919778	0.9919390	0.9919001
41°	0.9918612	0.9918221	0.9917830	0.9917439	0.9917046	0.9916653	0.9916259	0.9915864	0.9915469	0.9915073

Table 1-02

Table 1-03

Specific Volume $\bar{V}$ of Ordinary Water under Pressure[a]

P, kbar	t, °C								
	0	25	50	75	100	125	150	175	200
0.5	0.97666	0.98185	0.99135	1.00421	1.02008	1.03887	1.0607	1.0860	1.1149
1.0	0.95656	0.96344	0.97321	0.98552	1.00016	1.0171	1.0363	1.0578	1.0826
1.5	0.9385	0.9471	0.9572	0.9696	0.9839	0.9995	1.0174	1.0366	1.0588
2.0	0.9241	0.9341	0.9447	0.9561	0.9681	0.9822	0.9989	1.0166	1.0368
2.5	0.9117	0.9218	0.9321	0.9430	0.9544	0.9675	0.9824	0.9987	1.0172
3.0	0.9005	0.9106	0.9209	0.9317	0.9426	0.9550	0.9689	0.9839	1.0004
3.5	0.8901	0.9002	0.9105	0.9212	0.9320	0.9440	0.9572	0.9707	0.9860
4.0	0.8805	0.8906	0.9009	0.9114	0.9220	0.9338	0.9465	0.9595	0.9733
4.5	0.8715	0.8815	0.8918	0.9022	0.9128	0.9241	0.9361	0.9485	0.9617
5.0	0.8627	0.8727	0.8829	0.8933	0.9038	0.9148	0.9264	0.9385	0.9511
5.5	0.8551	0.8649	0.8749	0.8851	0.8952	0.9059	0.9171	0.9289	0.9410
6.0	0.8481	0.8577	0.8675	0.8773	0.8872	0.8976	0.9084	0.9199	0.9316
6.5	(0.8417)	0.8510	0.8605	0.8701	0.8798	0.8901	0.9004	0.9116	0.9229
7.0	—	0.8451	0.8543	0.8636	0.8730	0.8829	0.8929	0.9037	0.9147
7.5	—	0.8393	0.8483	0.8574	0.8666	0.8772	0.8871	0.8971	0.9071
8.0	—	0.8339	0.8427	0.8516	0.8606	0.8709	0.8805	0.8902	0.8999

24-642 O - 73 - pt. 2 - 20

Table 1-04

VOLUME PROPERTIES OF ORDINARY WATER

G. S. KELL

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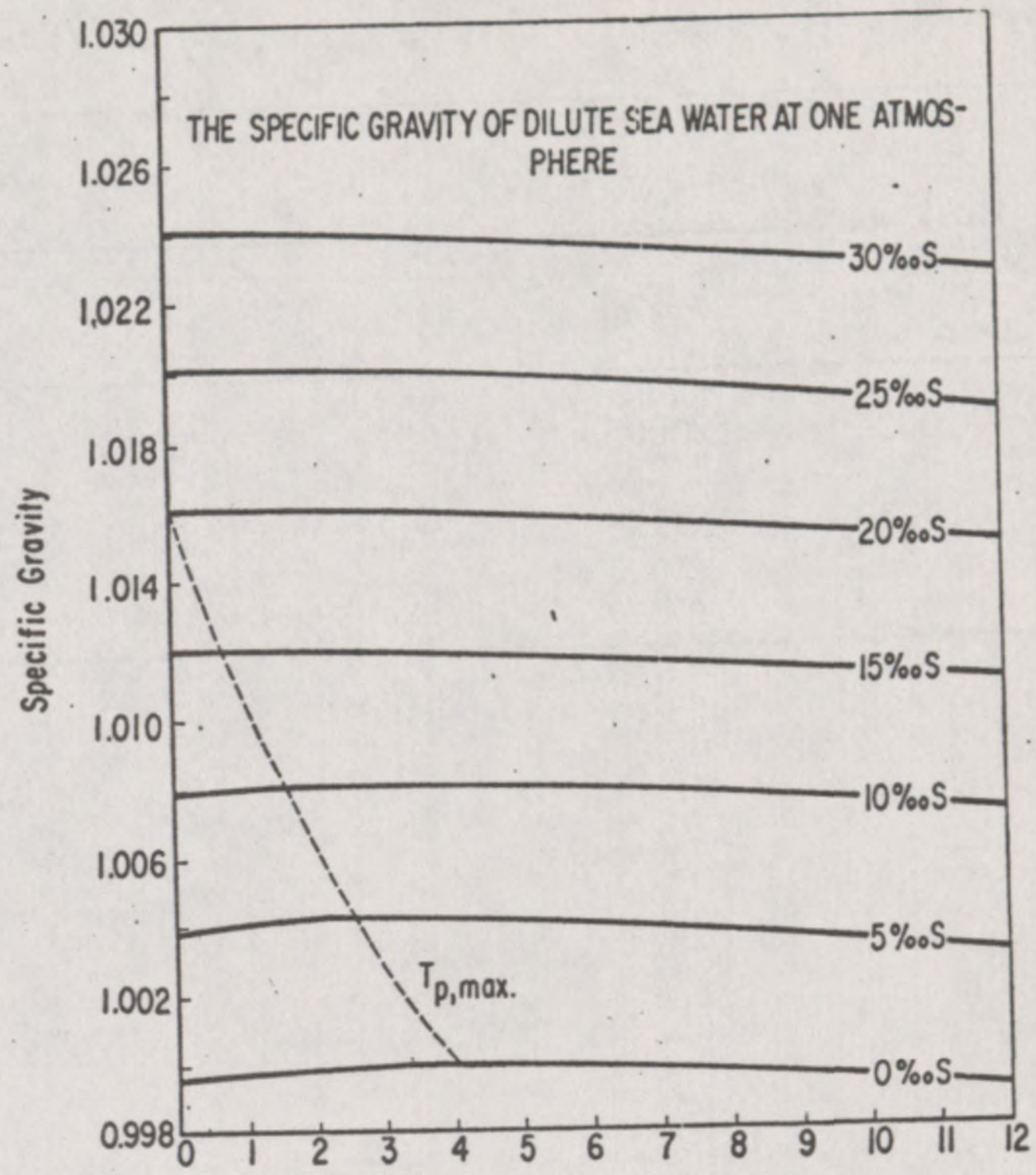
(Specific volume v, density ρ, thermal expansivity $\alpha = \mathrm{d} \ln v/\mathrm{d}t = -\mathrm{d} \ln \rho/\mathrm{d}t$, compressibility $\kappa = -\mathrm{d} \ln v/\mathrm{d}p = \mathrm{d} \ln \rho/\mathrm{d}p$)

t, °C.	v, Cc./G.	ρ, G./Ml.	$10^6\alpha$, Deg.$^{-1}$	$10^6\kappa$, Bar^{-1}
−20	1.00658	0.99349	−678.48	61.94
−18	1.00532	0.99474	−580.83	60.48
−16	1.00424	0.99581	−495.74	59.11
−14	1.00332	0.99672	−420.85	57.83
−12	1.00254	0.99749	−354.33	56.64
−10	1.001895	0.998137	−294.73	55.52
−9	1.001614	0.998417	−267.18	54.99
−8	1.001359	0.998671	−240.95	54.48
−7	1.001131	0.998899	−215.94	53.98
−6	1.000926	0.999102	−192.06	53.50
−5	1.000746	0.999283	−169.22	53.04
−4	1.000587	0.999441	−147.34	52.60
−3	1.000451	0.999578	−126.36	52.17
−2	1.000334	0.999694	−106.20	51.76
−1	1.000238	9.999790	−86.81	51.36
0	1.000160	0.999868	−68.14	50.98
1	1.000101	0.999927	−50.14	50.61
2	1.000060	0.999968	−32.77	50.26
3	1.000036	0.999992	−15.98	49.92
4	1.000028	1.000000	0.26	49.59
5	1.000036	0.999992	15.98	49.28
6	1.000060	0.999968	31.23	48.98
7	1.000098	0.999930	46.01	48.69
8	1.000151	0.999877	60.37	48.41
9	1.000219	0.999809	74.33	48.15
10	1.000300	0.999728	87.90	47.89
11	1.000395	0.999634	101.12	47.65
12	1.000502	0.999526	113.99	47.42
13	1.000623	0.999406	126.54	47.19
14	1.000755	0.999273	138.78	46.98
15	1.000900	0.999129	150.73	46.78
16	1.001057	0.998972	162.41	46.59
17	1.001225	0.998804	173.82	46.40
18	1.001405	0.998625	184.99	46.23
19	1.001596	0.998435	195.91	46.06
20	1.001797	0.998234	206.61	45.91
21	1.002010	0.998022	217.10	45.76
22	1.002232	0.997801	227.37	45.62
23	1.002465	0.997569	237.45	45.48
24	1.002708	0.997327	247.34	45.36
25	1.002961	0.997075	257.05	45.24
26	1.003224	0.996814	266.59	45.13
27	1.003496	0.996544	275.96	45.02
28	1.003778	0.996264	285.17	44.93
29	1.004069	0.995976	294.23	44.84
30	1.004369	0.995678	303.14	44.75
31	1.004678	0.995372	311.92	44.67
32	1.004995	0.995057	320.55	44.60
33	1.005322	0.994734	329.06	44.54
34	1.005657	0.994403	337.44	44.48
35	1.006000	0.994063	345.71	44.42
36	1.006352	0.993716	353.85	44.37
37	1.006713	0.993360	361.89	44.33
38	1.007081	0.992997	369.81	44.29
39	1.007457	0.992626	377.64	44.25
40	1.007842	0.992247	385.36	44.22
41	1.008234	0.991861	392.99	44.20
42	1.008634	0.991467	400.52	44.18
43	1.009042	0.991067	407.97	44.16
44	1.009458	0.990659	415.33	44.15
45	1.009881	0.990244	422.60	44.15
46	1.010311	0.989822	429.80	44.14
47	1.010749	0.989393	436.91	44.15
48	1.011194	0.988957	443.95	44.15
49	1.011647	0.988515	450.92	44.16
50	1.012107	0.988066	457.81	44.17
51	1.012574	0.987610	464.64	44.19
52	1.013048	0.987148	471.40	44.21
53	1.013529	0.986680	478.10	44.24
54	1.014017	0.986205	484.74	44.26
55	1.014512	0.985723	491.32	44.29
56	1.015014	0.985236	497.84	44.33
57	1.015522	0.984743	504.30	44.37
58	1.016038	0.984243	510.71	44.41
59	1.016560	0.983737	517.07	44.45
60	1.017089	0.983226	523.38	44.50
61	1.017625	0.982708	529.64	44.55
62	1.018167	0.982185	535.85	44.61
63	1.018716	0.981655	542.02	44.66
64	1.019271	0.981120	548.14	44.72
65	1.019833	0.980580	554.22	44.79
66	1.020402	0.980034	560.26	44.85
67	1.020977	0.979482	566.26	44.92
68	1.021558	0.978924	572.22	45.00
69	1.022146	0.978361	578.15	45.07
70	1.022740	0.977793	584.04	45.15
71	1.023340	0.977219	589.89	45.23
72	1.023947	0.976640	595.72	45.32
73	1.024560	0.976056	601.51	45.40
74	1.025180	0.975466	607.27	45.49
75	1.025805	0.974871	613.00	45.59
76	1.026437	0.974271	618.71	45.68
77	1.027076	0.973665	624.39	45.78
78	1.027720	0.973055	630.04	45.88
79	1.028371	0.972439	635.67	45.99
80	1.029027	0.971819	641.27	46.10
81	1.029690	0.971193	646.86	46.21
82	1.030360	0.970562	652.42	46.32
83	1.031035	0.969926	657.96	46.44
84	1.031716	0.969286	663.48	46.56
85	1.032404	0.968640	668.98	46.68
86	1.033098	0.967990	674.47	46.81
87	1.033797	0.967335	679.94	46.94
88	1.034503	0.966674	685.40	47.07
89	1.035216	0.966009	690.84	47.20
90	1.035934	0.965340	696.26	47.34
91	1.036658	0.964665	701.68	47.48
92	1.037389	0.963986	707.08	47.63
93	1.038125	0.963302	712.48	47.77
94	1.038868	0.962613	717.86	47.93
95	1.039617	0.961920	723.24	48.08
96	1.040372	0.961222	728.60	48.24
97	1.041133	0.960519	733.96	48.40
98	1.041900	0.959812	739.32	48.56
99	1.042673	0.959100	744.67	48.73
100	1.043453	0.958384	750.01	48.90
101	1.044239	0.957662	755.36	49.07
102	1.045030	0.956937	760.70	49.25
103	1.045828	0.956207	766.03	49.43
104	1.046633	0.955472	771.37	49.62
105	1.047443	0.954733	776.71	49.80
106	1.048260	0.953989	782.05	50.00
107	1.049083	0.953240	787.39	50.19
108	1.049912	0.952488	792.73	50.39
109	1.050747	0.951730	798.07	50.59
110	1.051589	0.950968	803.42	50.80

Table 1-05



Specific Gravity and Temperature of Maximum Density of Seawater.

Table 1-06

Specific Volume of Distilled Water, in cm^3/g

P, bars[a]	T, °C				
	0	10	20	30	40
1	1.0000	1.0003	1.0017	1.0043	1.0078
100	0.9950	0.9956	0.9972	0.9999	1.0035

Table I-06 Continued.

Specific Volume of Seawater

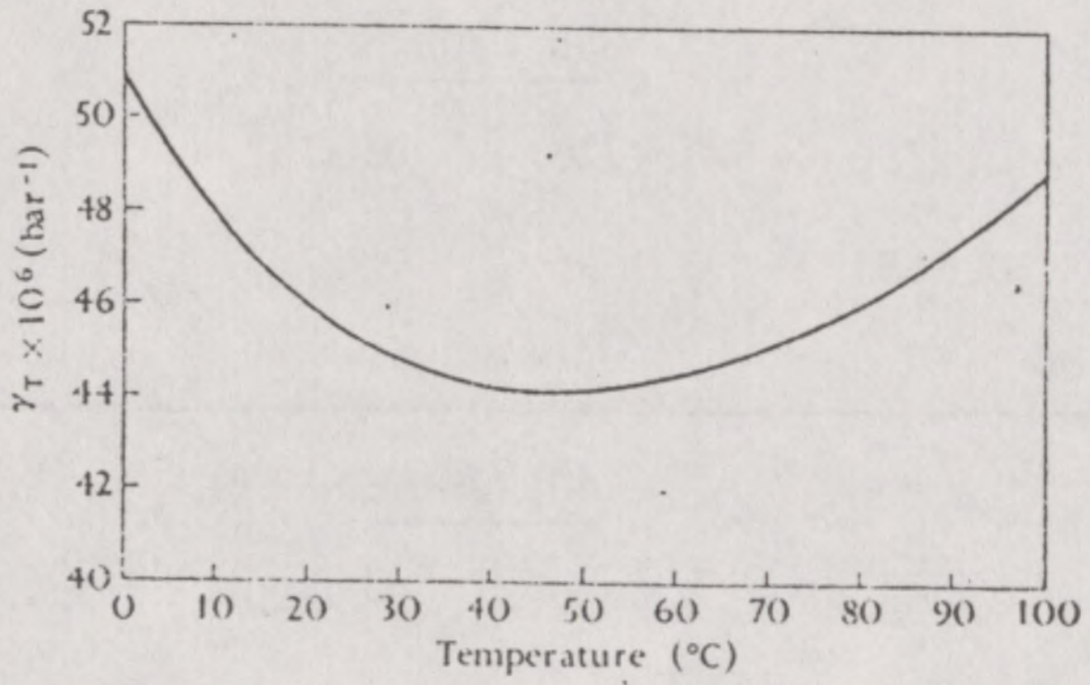
P, bars[a]	T, °C				
	0	10	20	30	40
			10 °/00 S		
1	0.9921	0.9926	0.9942	0.9968	1.0004
100	0.9873	0.9881	0.9899	0.9926	0.9961
			20 °/00 S		
1	0.9842	0.9850	0.9868	0.9894	0.9930
100	0.9796	0.9806	0.9826	0.9853	0.9888
			30 °/00 S		
1	0.9764	0.9775	0.9794	0.9821	0.9856
100	0.9719	0.9732	0.9753	0.9781	0.9816
			35 °/00 S		
1	0.9726	0.9738	0.9757	0.9784	0.9819
100	0.9681	0.9695	0.9717	0.9745	0.9780
			40 °/00 S		
1	0.9687	0.9700	0.9720	0.9748	0.9783
100	0.9644	0.9659	0.9680	0.9709	0.9744

Compressibility

The compressibility of water is relatively low (of the order of fifty parts per million per atmosphere at ordinary temperatures). Furthermore, it varies only relatively little with temperature. On a global scale, however, one could hardly afford to ignore the compressibility of water - especially if one lives in southern Florida - since were water completely incompressible, the level of the sea would be higher by about 40 meters (reducing the global land area by 5%).

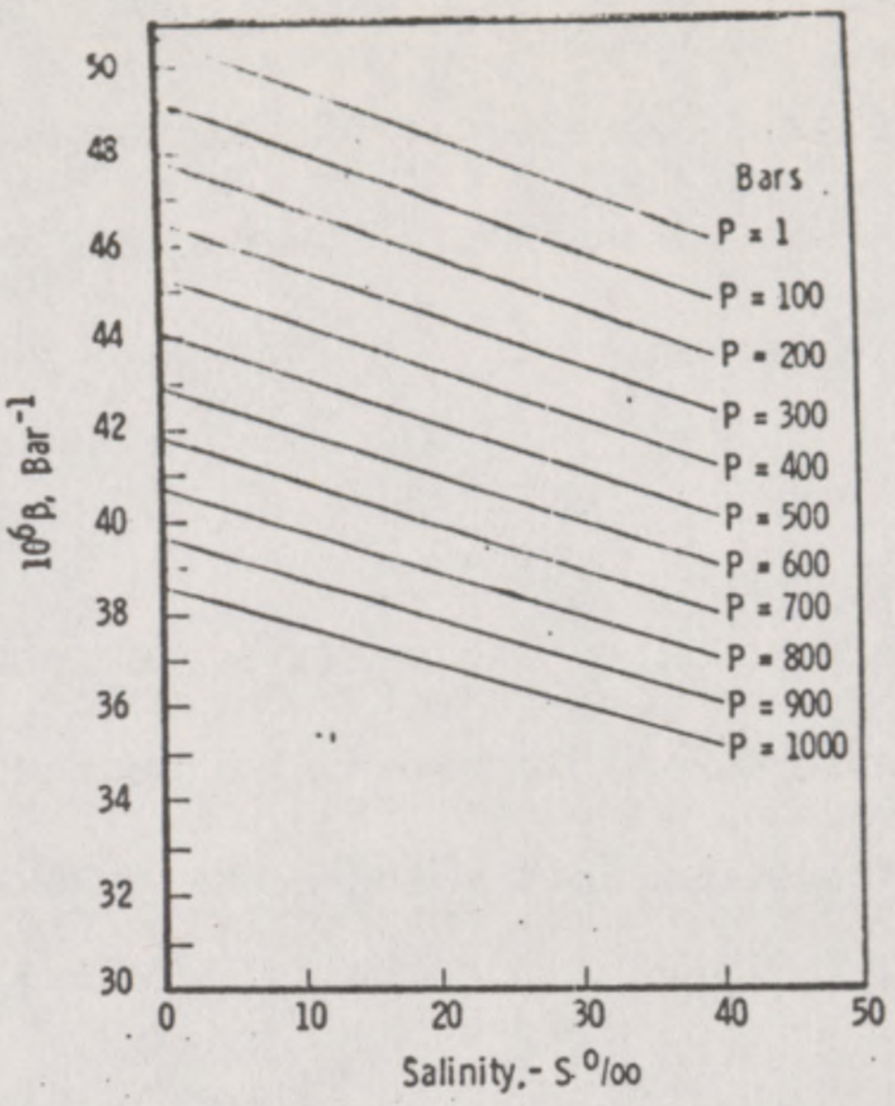
For extensive discussion of the compressibility of water, see Gmelin (loco cit., page 1331-1339).

For more recent studies of the isothermal compressibility of water, see the data by Millero, Curry and Drost-Hansen (1969).

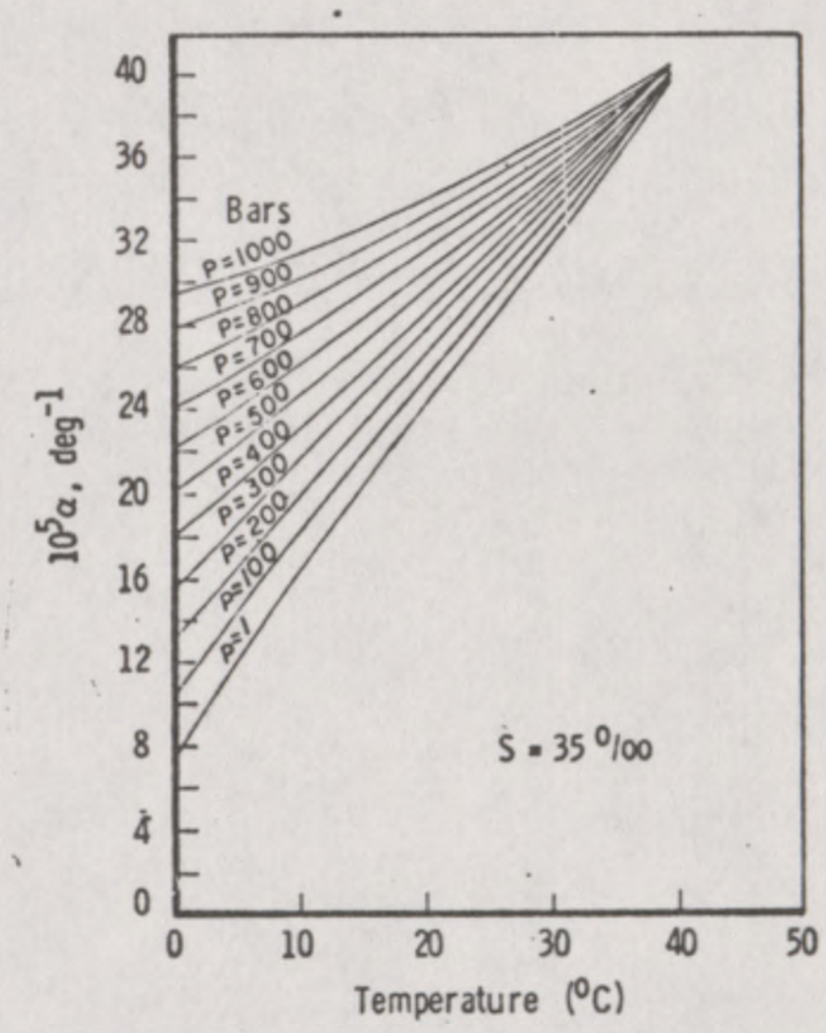


The coefficient of isothermal compressibility, γ_T, for liquid water at 1 atm pressure. Data from Kell (1967).

Figure 1-03



The Compressibility of Seawater at 0°C. From Wilson and Bradley (1966).



Coefficient of Thermal Expansion of Seawater as a Function of Temperature and Pressure. From Wilson and Bradley (1966).

Figure I-04

Specific gravity is defined as the ratio of density of solution to the density of distilled water at 4°, expressed as a function of temperature for various salinities. The results are given in terms of σ, defined by the equation:

$$\sigma_{s,T,p} = (\rho_{s,T,p} - 1)1000$$

where $\rho_{s,T,p}$ is the density of the seawater, depending on salinity, temperature and pressure. At (or near) 1 atmosphere pressure, it is customary to drop the subscripts s and p; as an example, $\sigma_T = 25.50$ implies a density of 1.02550. Figure 1-05 is taken from the illustration in the treatise edited by Kinne (1970, based on data by Knudsen, 1901).

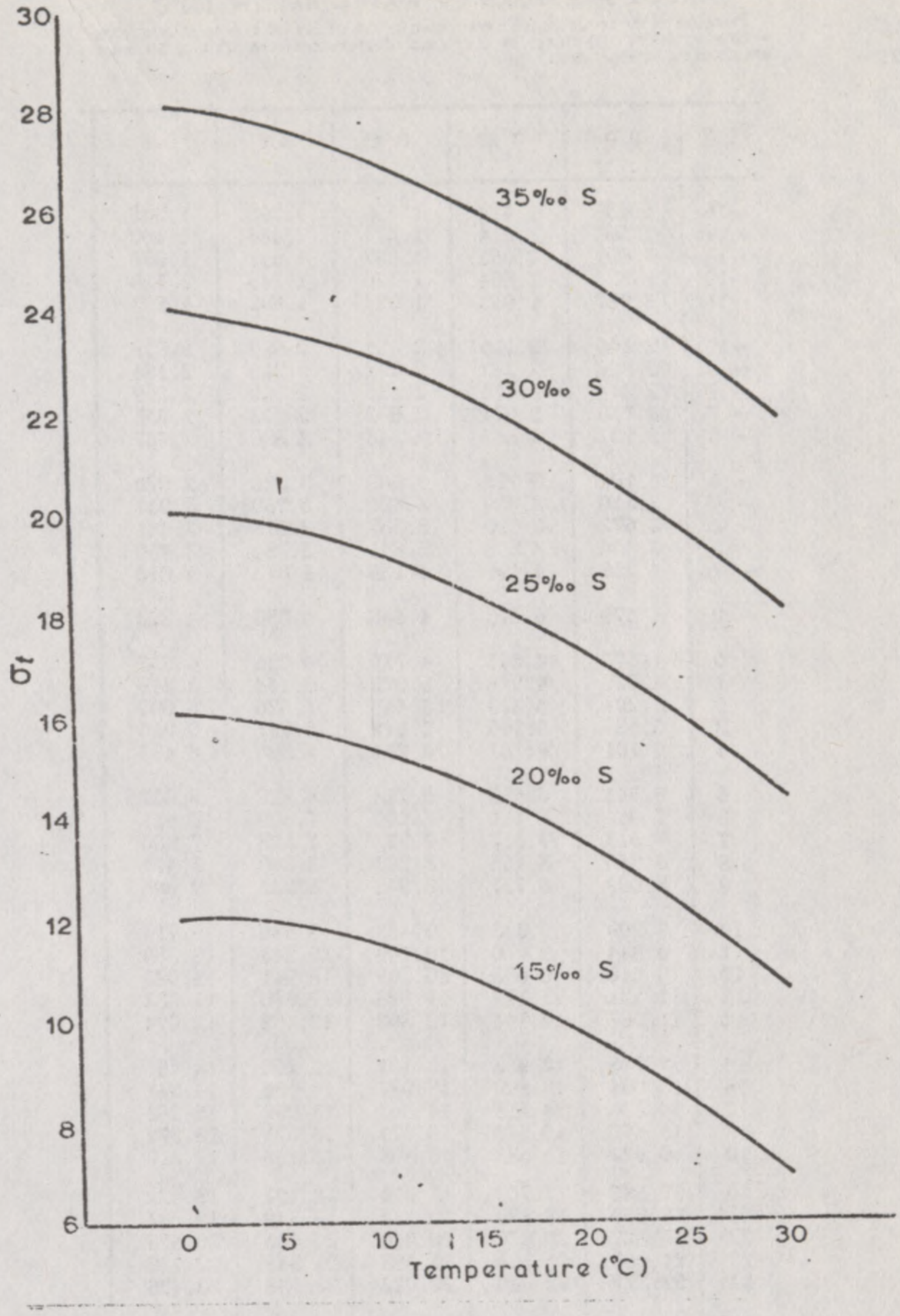

30
28
26
24
22
20
18
16
14
12
10
8
6
σt
35‰ S
30‰ S
25‰ S
20‰ S
15‰ S
0
5
10
15
20
25
30
Temperature (°C)

Figure I-05

C. Vapor Pressure

VAPOR PRESSURE OF WATER BELOW 100°C

Pressure of aqueous vapor over water in mm of Hg for temperatures from −15.8 to 100°C. Values for fractional degrees between 50 and 89 were obtained by interpolation.

Temp. °C	0.0	0.2	0.4	0.6	0.8
−15	1.436	1.414	1.390	1.368	1.345
−14	1.560	1.534	1.511	1.485	1.460
−13	1.691	1.665	1.637	1.611	1.585
−12	1.834	1.804	1.776	1.748	1.720
−11	1.987	1.955	1.924	1.893	1.863
−10	2.149	2.116	2.084	2.050	2.018
− 9	2.326	2.289	2.254	2.219	2.184
− 8	2.514	2.475	2.437	2.399	2.362
− 7	2.715	2.674	2.633	2.593	2.553
− 6	2.931	2.887	2.843	2.800	2.757
− 5	3.163	3.115	3.069	3.022	2.976
− 4	3.410	3.359	3.309	3.259	3.211
− 3	3.673	3.620	3.567	3.514	3.461
− 2	3.956	3.898	3.841	3.785	3.730
− 1	4.258	4.196	4.135	4.075	4.016
− 0	4.579	4.513	4.448	4.385	4.320
0	4.579	4.647	4.715	4.785	4.855
1	4.926	4.998	5.070	5.144	5.219
2	5.294	5.370	5.447	5.525	5.605
3	5.685	5.766	5.848	5.931	6.015
4	6.101	6.187	6.274	6.363	6.453
5	6.543	6.635	6.728	6.822	6.917
6	7.013	7.111	7.209	7.309	7.411
7	7.513	7.617	7.722	7.828	7.936
8	8.045	8.155	8.267	8.380	8.494
9	8.609	8.727	8.845	8.965	9.086
10	9.209	9.333	9.458	9.585	9.714
11	9.844	9.976	10.109	10.244	10.380
12	10.518	10.658	10.799	10.941	11.085
13	11.231	11.379	11.528	11.680	11.833
14	11.987	12.144	12.302	12.462	12.624
15	12.788	12.953	13.121	13.290	13.461
16	13.634	13.809	13.987	14.166	14.347
17	14.530	14.715	14.903	15.092	15.284
18	15.477	15.673	15.871	16.071	16.272
19	16.477	16.685	16.894	17.105	17.319
20	17.535	17.753	17.974	18.197	18.422
21	18.650	18.880	19.113	19.349	19.587
22	19.827	20.070	20.316	20.565	20.815
23	21.068	21.324	21.583	21.845	22.110
24	22.377	22.648	22.922	23.198	23.476
25	23.756	24.039	24.326	24.617	24.912
26	25.209	25.509	25.812	26.117	26.426
27	26.739	27.055	27.374	27.696	28.021
28	28.349	28.680	29.015	29.354	29.697
29	30.043	30.392	30.745	31.102	31.461
30	31.824	32.191	32.561	32.934	33.312
31	33.695	34.082	34.471	34.864	35.261
32	35.663	36.068	36.477	36.891	37.308
33	37.729	38.155	38.584	39.018	39.457
34	39.898	40.344	40.796	41.251	41.710
35	42.175	42.644	43.117	43.595	44.078
36	44.563	45.054	45.549	46.050	46.556
37	47.067	47.582	48.102	48.627	49.157
38	49.692	50.231	50.774	51.323	51.879
39	52.442	53.009	53.580	54.156	54.737
40	55.324	55.91	56.51	57.11	57.72
41	58.34	58.96	59.58	60.22	60.86

Table 1-07

D. Heat of Vaporization

The heat of vaporization of water has been discussed by Dorsey (1940) and Gmelin (loco cit., page 1363-1367). Table 1-08 gives the values for the heat of vaporization (in international calories/gram from Gmelin (page 1364).

Table 1-08

Temperature	ΔH_{l-g}
0°	597.3
10°	591.7
20°	586.0
30°	580.4
40°	574.7
50°	569.0
60°	563.2
70°	557.3
80°	551.3
90°	545.2
100°	539.0

E. Specific Heat

The physico-chemical properties of water which are most important in determining global ecology are vapor pressure, heat of vaporization and specific heat. Vapor pressure data are shown in the overview of physical properties of water, Table I-01. The heat of vaporization is discussed very briefly in Section D. Detailed Tables of the specific heat are given below. Franks (1968) has reminded us of the enormous influence of the large heat capacity of water in affecting our terrestrial environment. Franks observes: "If we consider a warm ocean current such as the Gulfstream, 100 miles wide and a quarter mile deep, flowing at one mile/h from a warm to a cold region, with a temperature gradient of 20° C, then the thermal energy transport every hour is equivalent to that supplied by 1.75×10^8 tons of coal. All the coal mined in the world in one year is able to supply heat at this rate for only one and a half hours."

The specific heat of the water has been discussed in detail by Dorsey (1940) and in Gmelin (loco cit., page 1370-1375).

Figure I-06 shows the overall behavior of c_p, and c_v between 0 and 100° C (from Eisenberg and Kauzmang, 1969). A more detailed graph is shown in Figure I-07 (data by Ginnings and Furukawa, 1953; see Kinne, 1970 (Vol. I, Pt. I, Chapter 3.0 - p. 323). It is seen that the specific heat at constant pressure goes through a shallow maximum in the vicinity of 35° C.

A Table of recommended values (Table I-08) is taken from Gmelin (pp. 1372-1373). (c_p is expressed in absolute joules/gram/degree).

Figure 1-06

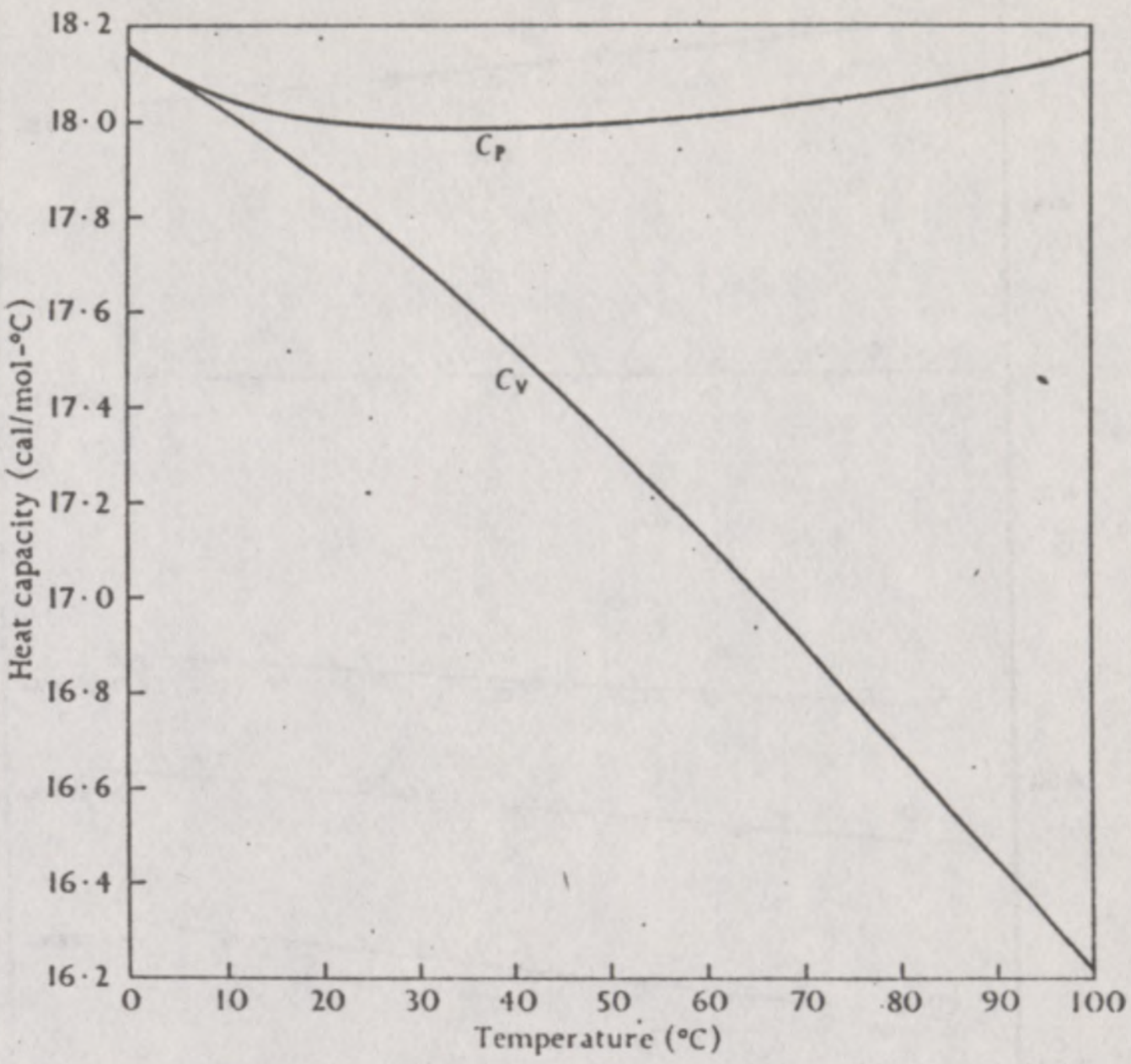
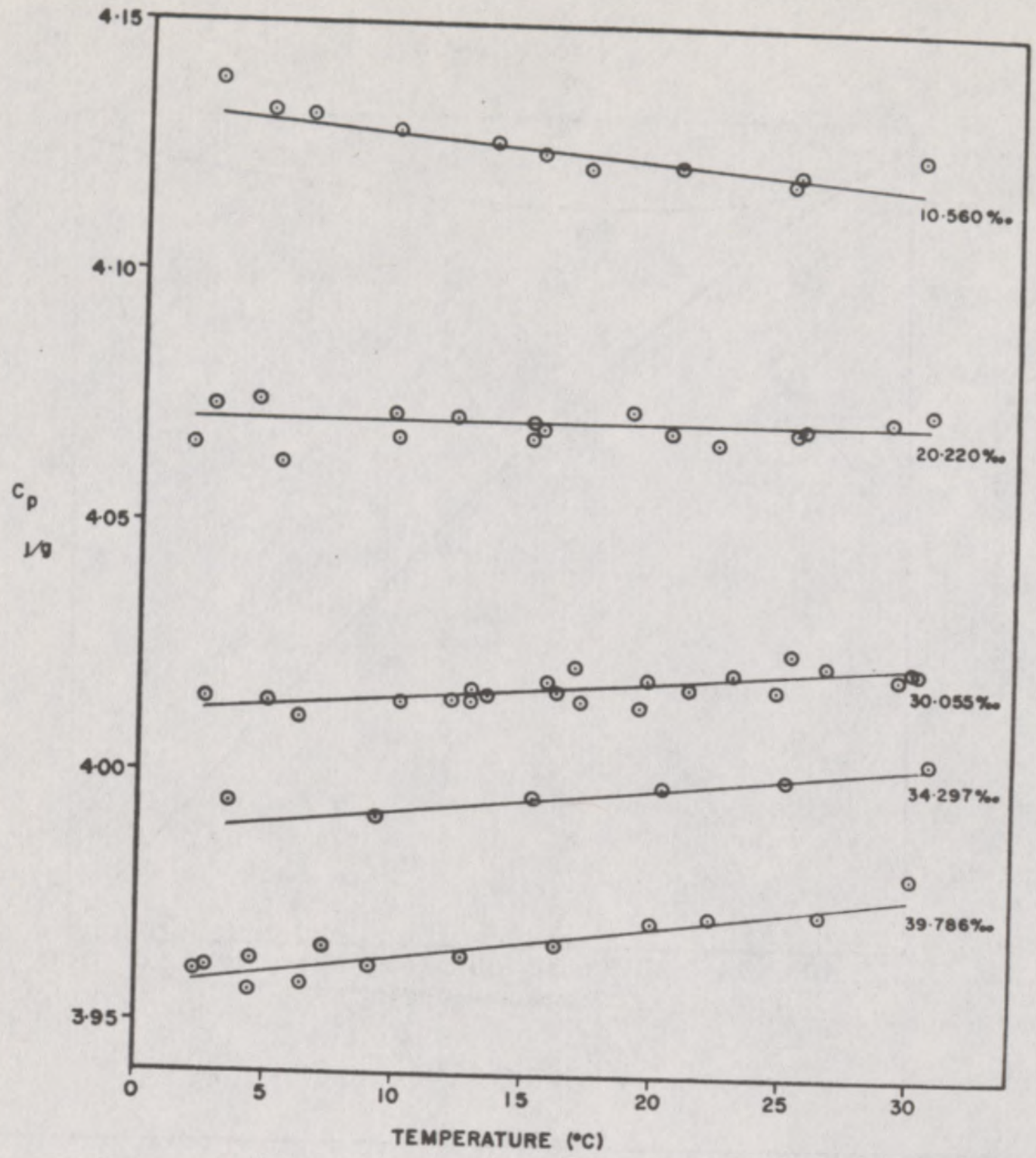


Figure 1-07



Temperature Dependence of the Specific Heat of Various Concentrations of Seawaters (in Joules per Gram). Data point indicated by Circle (Cox and Smith, 1959; Straight lines are Derived from Theoretical Expression by Conners, 1970).

Figure I-08

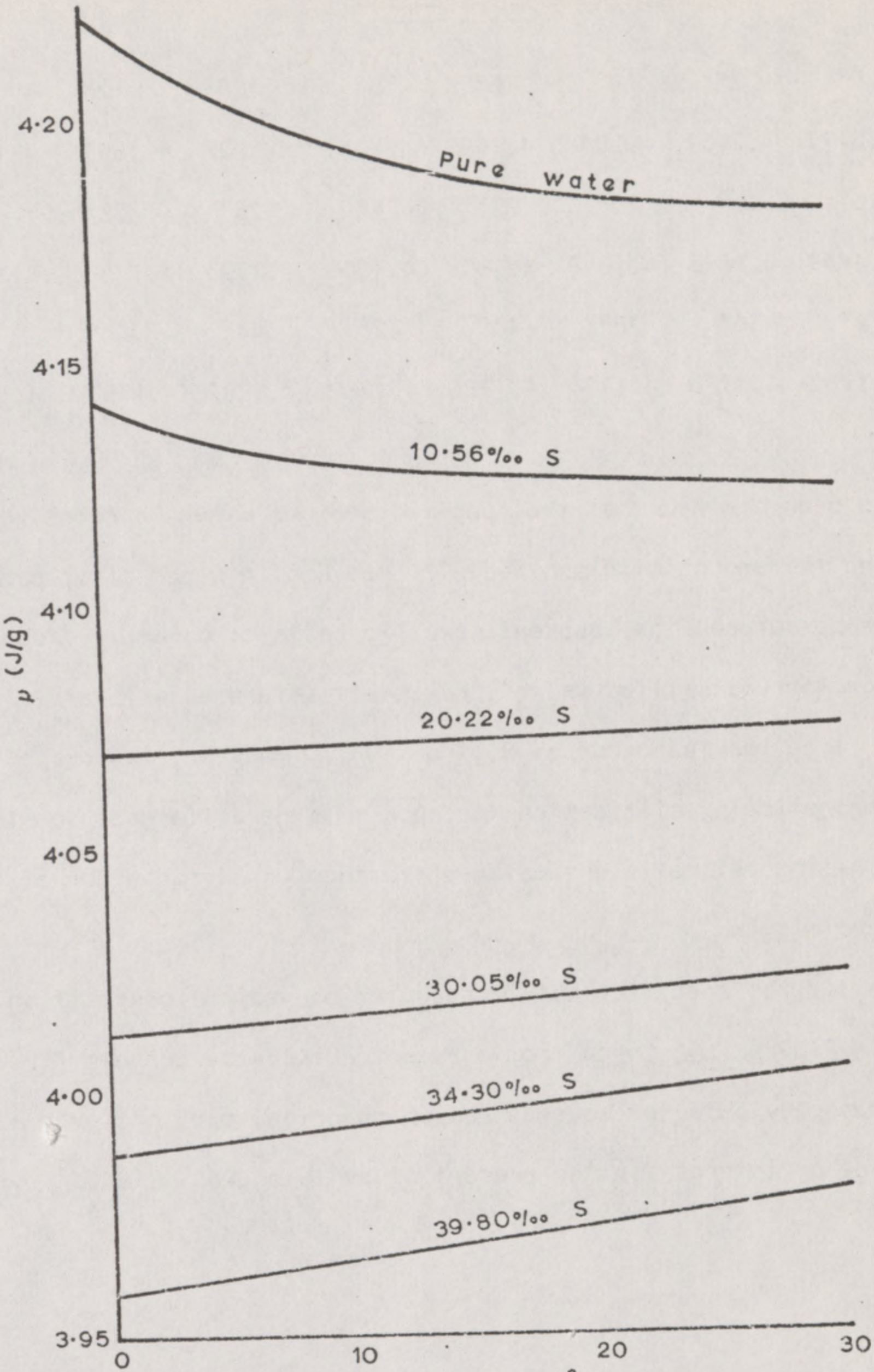

4·20
4·15
4·10
4·05
4·00
3·95
μ (J/g)
Pure water
10·56‰ S
20·22‰ S
30·05‰ S
34·30‰ S
39·80‰ S
0
10
20
30
Temperature (°C)

Figure 1-09

Table I-08

t	0°	2°	4°	6°	8°	10°	12°	14°	15°
c_p	4.2177	4.2107	4.2048	4.1999	4.1957	4.1922	4.1893	4.1869	4.1858
t	16°	18°	20°	22°	24°	26°	28°	30°	32°
c_p	4.1849	4.1832	4.1819	4.1808	4.1800	4.1793	4.1788	4.1785	4.1783
t	34°	36°	38°	40°	42°	44°	46°	48°	50°
c_p	4.1782	4.1783	4.1784	4.1786	4.1789	4.1792	4.1797	4.1802	4.1807

It has been claimed that the specific heat of water is relatively dependent on the amount of dissolved air (see Gmelin, loco cit., page 1374). The difference between the apparent specific heats of carefully degassed water and ordinary distilled water (presumably saturated with air) is remarkably large (of the order of 0.5% at 40°). However, there appears to be no theoretical justification for such a large difference; on the contrary, the theoretically estimated difference is of the order of only six parts per million.

Values for the specific heat of seawater of variant composition are shown in Figure I-08 taken from a recent article by Conners (1970).

Heat capacity data for aqueous sodium chloride solutions over a partial range of interest in the present study is shown in Table I-09.

Heat capacity data for aqueous sodium chloride solutions are shown for four different temperatures over a wide concentration range in Table I-09 (Parker, 1965). The concentrations are expressed in molal concentrations (m; the variable n is the ratio of water molecules to "molecules" of sodium chloride).

Table I-09

Φ_C, cal/deg mole

n	m	15°	20°	25°	30°
∞	0.00	−25.2	−23.3	−21.5	−20.1
100,000	.000555	−25.1	−23.2	−21.4	−20.0
50,000	.00111	−25.0	−23.1	−21.3	−19.9
20,000	.00278	−24.9	−23.0	−21.2	−19.8
10,000	.00555	−24.8	−22.9	−21.1	−19.6
7,000	.00793	−24.7	−22.8	−21.0	−19.5
5,000	.01110	−24.6	−22.7	−20.9	−19.4
4,000	.01388	−24.5	−22.6	−20.8	−19.3
3,000	.01850	−24.4	−22.5	−20.7	−19.2
2,000	.02775	−24.2	−22.3	−20.4	−19.0
1,500	.03700	−23.9	−22.0	−20.2	−18.8
1,000	.05551	−23.4	−21.6	−19.8	−18.4
900	.0617	−23.3	−21.4	−19.6	−18.2
800	.0694	−23.1	−21.3	−19.5	−18.1
700	.0793	−22.8	−21.0	−19.3	−17.9
600	.0925	−22.5	−20.8	−19.0	−17.6
500	.1110	−22.0	−20.3	−18.6	−17.3
400	.1388	−21.4	−19.8	−18.2	−16.9
300	.1850	−20.5	−19.0	−17.5	−16.2
200	.2775	−19.0	−17.5	−16.3	−15.1
150	.3700	−17.7	−16.4	−15.2	−14.1
100	.5551	−15.5	−14.8	−13.4	−12.5
75	.7401	−13.6	−12.6	−11.7	−10.9
50	1.1101	−10.4	−9.6	−8.8	−8.2
40	1.3877	−8.3	−7.6	−7.0	−6.4
30	1.8502	−5.7	−5.1	−4.6	−4.1
25	2.2202	−3.5	−2.9	−2.4	−2.0
20	2.7753	−0.8	−0.4	0.0	+0.2
15	3.7004	.....	.....	+3.3	3.5
12	4.6255	.....	.....	6.3	.....
10	5.5506	.....	.....	9.0	.....
9.5	5.8427	.....	.....	9.7	.....
9.0	6.1674	.....	.....	10.5	.....

24-642 O - 73 - pt. 2 - 21

F. Thermal Conductivity

For a discussion of the heat conductivity of water (and ice), see Dorsey (1940) and particularly Gmelin (loco cit., p. 1403-1408). In passing, it is noted that the heat conductivity of ice is notably larger- as would be expected theoretically - than that of liquid water. Values for the heat conductivity of ice single crystals appears to depend on the orientation (parallel to or perpendicular to the C-axis - a difference of about 5%). Values reported in the literature for ice at -4° range from 0.016 to 0.020 w/cm/°. Values for the heat conductivity of liquid water are shown in the Table below.

Table 1-10

Temp.	0°	10°	20°	30°	40°	50°	60°	70°	80°
$10^5 k''$	560	581	600	614.5	628.5	641	653	662	669.5

(all values in watts/centimeter/degree. Note conversion factor 1 watt/cm/° = 0.23899 cal/cm/sec/°.)

G. Viscosity

Recent data for the viscosity of pure water as a function of temperature are shown in Table I-II, which gives the viscosity (in centipoises) by five different sets of co-workers. Within the limits of primary interest, the data generally seem to be in good agreement nutually.

Pressure exerts a notable effect on the viscosity of water. Some viscosity isotherms are shown in Figure I-10.

Finally, Figure I-11 shows a comparison between the viscosity and the thermal conductivity for water (and heavy water) over a wide temperature range.

Some older data for the viscosity of seawater (reported in millipoise) are reported in Table I-12 (data by Miyake and Koizumi, 1948).

More recent data are shown in survey form for an extended temperature range for salinities varying from 10.0 grams/kilogram to 150 grams/kilogram (and up to high temperatures). (Data by Isdale, Spence and Tudhope, 1972). (See Table I-13).

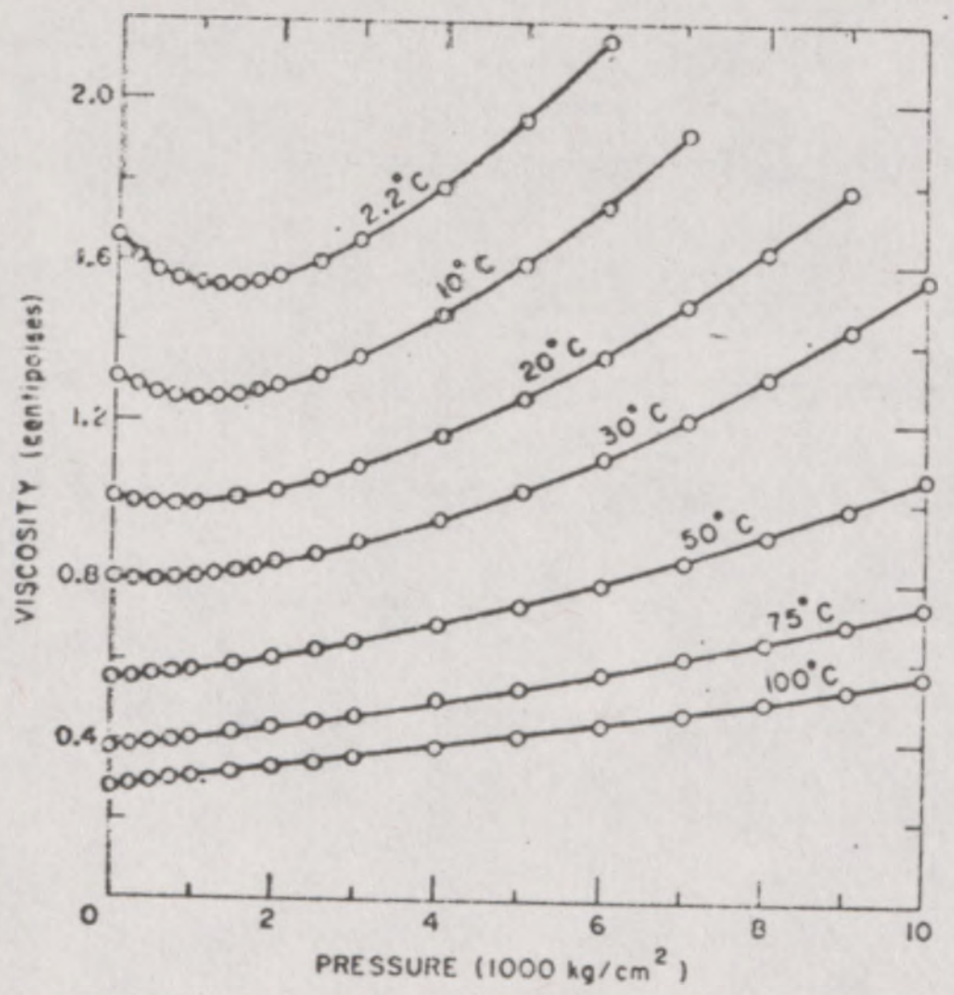
Other recent viscosity measurements of seawater have been made by various authors. Figure I-12 shows the results reported by Horne et al (1965). Other data have been reported by Fabuss and Korosi (1967, 1969). See also Emerson and Jamieson (1967). Recent data of high precision have also been obtained in the present author's laboratory by Dexter (1970). Low temperature data have been reported by Eicher and Zwolinski (1971).

Table 1-11

Viscosity of H_2O at Atmospheric Pressure[a]

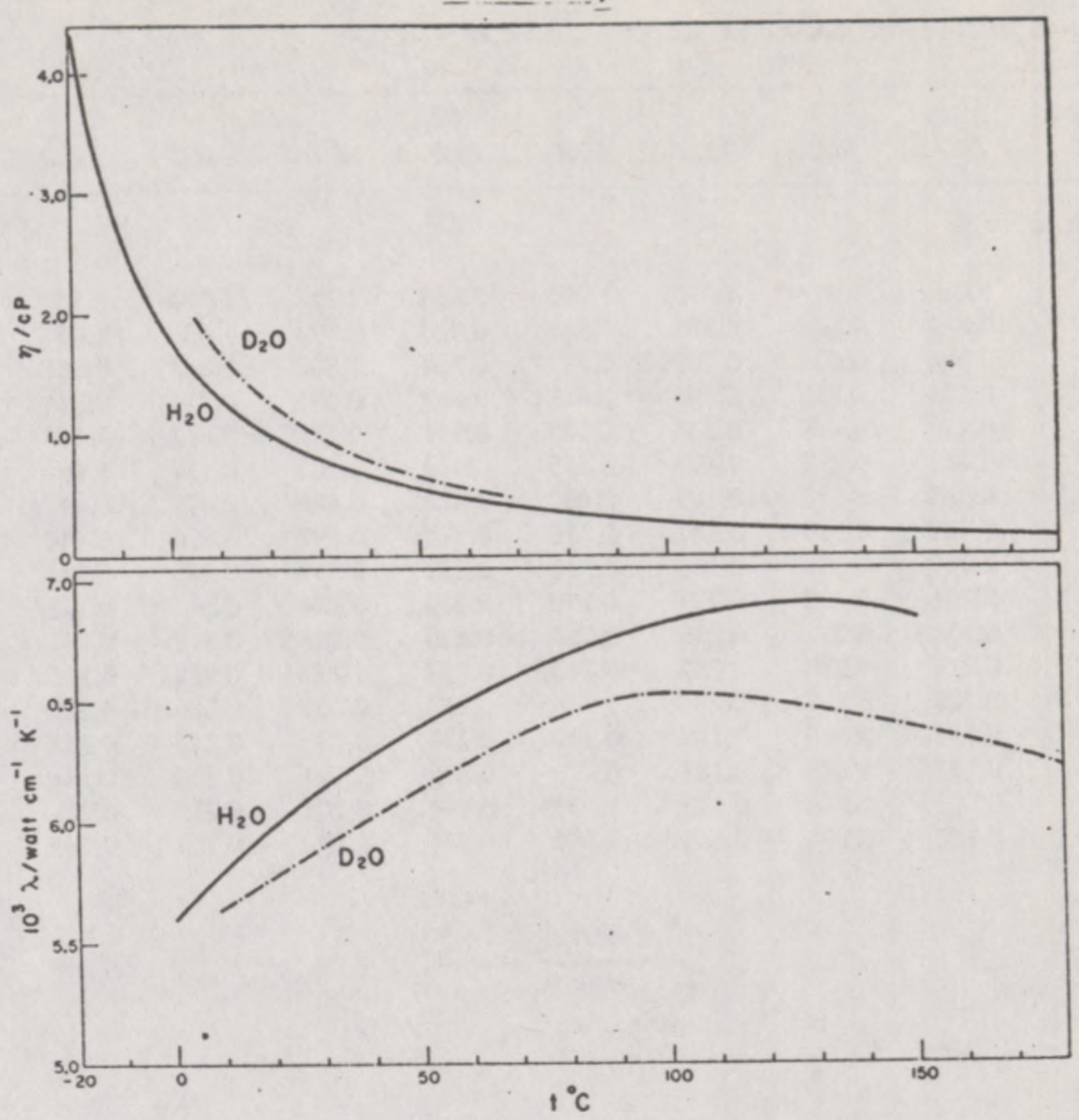
t_{48}, °C	Viscosity, cP				
	Stokes and Mills[1032]	Korosi and Fabuss[626,627]	Korson *et al.*[628]	Weber[1156]	Hardy and Cottington[459,460]
0	1.787	—	1.7916	1.792	—
5	1.516	—	1.5192	1.520	1.5184
10	1.306	—	1.3069	1.3069	—
15	1.138	—	1.1382	1.1383	—
20	1.002	1.0020	1.0020	1.0020	—
25	0.8903	0.8903	0.8903	0.8903	—
30	0.7975	—	0.7975	0.7975	—
35	0.7194	—	0.7195	0.7193	—
40	0.6531	0.6527	0.6532	0.6531	0.6531
45	0.5963	—	0.5963	—	—
50	0.5467	—	0.5471	—	—
55	0.5044	—	0.5042	—	—
60	0.4666	0.4665	0.4666	—	0.4665
65	0.4342	—	0.4334	—	—
70	0.4049	0.4045	0.4039	—	—
75	0.3788	0.3784	0.3775	—	—
80	0.3554	0.3546	0.3538	—	0.3548
85	0.3345	—	0.3323	—	—
90	0.3156	0.3143	0.3128	—	0.3148
95	0.2985	—	0.2949	—	0.2976
100	0.2829	0.2820	0.2783	—	0.2822

[a] All values here are adjusted to a value of 1.002 cP at 20°C.



Viscosity of water under pressure. The data shown indicate that $(\partial\eta/\partial P)_T = 0$ at 33.5°C. Reproduced from Bett and Cappi.[80] (Reprinted with permission from *Nature*, copyright 1965.)

Figure 1-10



Transport properties of liquid at atmospheric pressure. (a) Viscosity η. (b) Thermal conductivity λ. For D_2O, the values up to 60°C are the means given by Powell,[866] and those above 75°C are from Ziebland and Burton.[1200]

Figure 1-11

Table 1-12

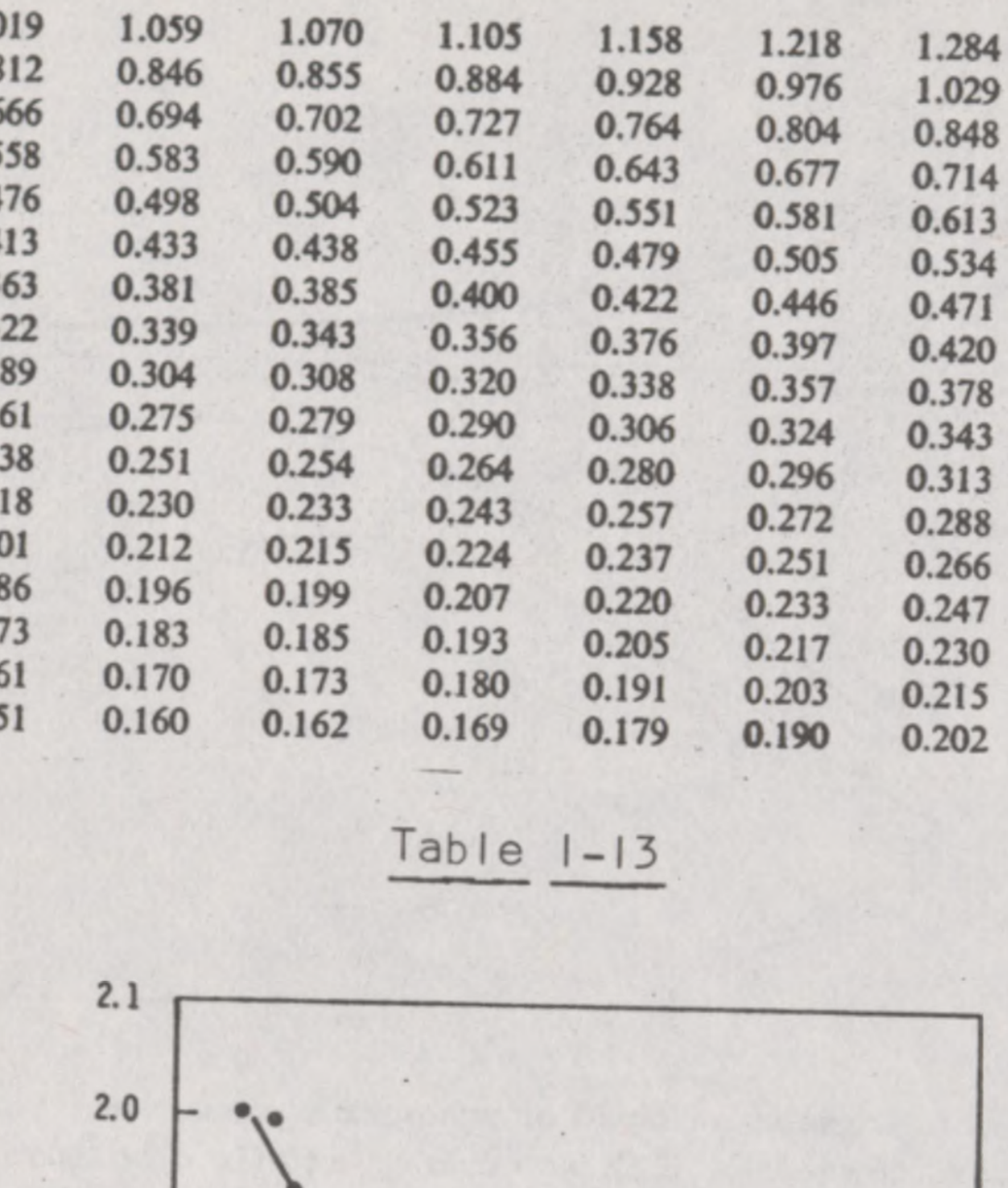
Viscosity coefficients of sea water in millipoise
(After MIYAKE and KOIZUMI, 1948)

	Cl ‰					
°C	0	4	8	12	16	20
0	17·94	18·11	18·29	18·45	18·62	18·90
2	16·76	16·92	17·10	17·29	17·46	17·74
4	15·71	15·85	16·03	16·23	16·41	16·68
6	14·75	14·89	15·07	15·28	15·46	15·71
8	13·81	14·03	14·20	14·41	14·59	14·83
10	13·10	13·24	13·41	13·62	13·80	14·03
12	12·39	12·52	12·69	12·89	13·07	13·29
14	11·73	11·87	12·04	12·23	12·40	12·60
16	11·13	11·27	11·43	11·61	11·79	11·97
18	10·58	10·72	10·88	11·05	11·21	11·39
20	10·07	10·21	10·36	10·52	10·68	10·85
22	9·60	9·74	9·89	10·03	10·19	10·35
24	9·16	9·30	9·45	9·58	9·73	9·88
26	8·75	8·90	9·04	9·16	9·31	9·44
28	8·37	8·52	8·65	8·77	8·91	9·04
30	8·02	8·17	8·30	8·40	8·54	8·66

DYNAMIC VISCOSITY OF SEA WATER SOLUTIONS, mNs m^{-2} (cP)

Salinity *g/kg*	*10.0*	*30.0*	*35.0*	*50.0*	*70.0*	*90.0*	*110.0*	*130.0*	*150.0*
Temperature °C									
20.0	1.019	1.059	1.070	1.105	1.158	1.218	1.284	1.357	1.437
30.0	0.812	0.846	0.855	0.884	0.928	0.976	1.029	1.087	1.150
40.0	0.666	0.694	0.702	0.727	0.764	0.804	0.848	0.896	0.947
50.0	0.558	0.583	0.590	0.611	0.643	0.677	0.714	0.754	0.797
60.0	0.476	0.498	0.504	0.523	0.551	0.581	0.613	0.647	0.684
70.0	0.413	0.433	0.438	0.455	0.479	0.505	0.534	0.564	0.595
80.0	0.363	0.381	0.385	0.400	0.422	0.446	0.471	0.497	0.525
90.0	0.322	0.339	0.343	0.356	0.376	0.397	0.420	0.444	0.469
100.0	0.289	0.304	0.308	0.320	0.338	0.357	0.378	0.399	0.422
110.0	0.261	0.275	0.279	0.290	0.306	0.324	0.343	0.363	0.383
120.0	0.238	0.251	0.254	0.264	0.280	0.296	0.313	0.331	0.351
130.0	0.218	0.230	0.233	0.243	0.257	0.272	0.288	0.305	0.323
140.0	0.201	0.212	0.215	0.224	0.237	0.251	0.266	0.282	0.298
150.0	0.186	0.196	0.199	0.207	0.220	0.233	0.247	0.262	0.277
160.0	0.173	0.183	0.185	0.193	0.205	0.217	0.230	0.244	0.259
170.0	0.161	0.170	0.173	0.180	0.191	0.203	0.215	0.229	0.243
180.0	0.151	0.160	0.162	0.169	0.179	0.190	0.202	0.215	0.228

Table 1-13



Temperature Dependence of the Viscosities of Pure Water (open circles) and 35‰ *S* Seawater (closed circles). From Horne, Courant, Johnson, and Margosian (1965), with permission of American Chemical Society.

Figure 1-12

H. Diffusion Coefficient

For a discussion of the self-diffusion coefficient of water (i.e., water in water) determined by the use of various tracers (such as D_2O, DHO, HTO, H_2O^{18} and $D_2{}^{18}O$) see Gmelin (loco cit., page 1472). Characteristic values from Gmelin are shown in Table I-14.

Table I-14

t	0°	5°	15°	25°	35°	45°	55°
$D \cdot 10^5$	1.00	1.20	1.61	2.13	2.76	3.45	4.16
$D \cdot 10^5$	----	----	1.62 ±0.03	2.04	2.73 ±0.04	3.34 ±0.08	----

as reported by two different investigators.

The effect of electrolytes on the self-diffusion of water has been studied by Devell (1962), and a thorough discussion of diffusion in water in aqueous solutions in general, has been presented by McCall and Douglass (1965).

Table I-15 lists some values for the diffusion coefficients of some electrolytes in water at 25°, as a function of concentration.

Table I-15

Diffusion Coefficients of Some Seawater Electrolytes at 25°C

Concentration, *M*	NaCl	KCl	CsCl	$CaCl_2$	$SrCl_2$	Na_2SO_4	$MgSO_4$
				$cm^2/sec \times 10^5$			
0.005	1.560	1.934	1.978	1.179	1.219	1.123	0.710
0.01	1.545	1.917	1.958	—	—	—	—
0.05	1.507	1.864	—	—	—	—	—
0.10	1.483	1.844	1.971	—	—	—	—
0.50	1.474	1.850	1.860	—	—	—	—
1.00	1.404	1.892	1.902	—	—	—	—
1.50	1.473	1.943	—	—	—	—	—

1. Surface Tension

The surface tension of water has been determined repeatedly. The values recommended in Gmelin (loco cit., page 1420) are shown in Table 1-16 below.

Table 1-16

Temp.	0	1	2	3	4	5	6	7	8	9
0°	75.626	75.470	75.312	75.155	75.006	74.860	74.713	74.555	74.410	74.263
10°	74.113	73.957	73.800	73.653	73.497	73.350	73.203	73.045	72.889	72.732
20°	72.583	72.427	72.270	72.113	71.957	71.810	71.652	71.495	71.339	71.192
30°	71.035	70.869	70.710	70.559	70.397	70.230	70.073	69.906	69.740	69.573
40°	69.416	69.249	69.083	68.925	68.759	68.592	68.424	68.257	68.091	67.914
50°	67.799	67.571	67.405	67.238	67.072	66.894	66.717	66.541	66.374	66.208

Note, however, that more recent determinations with likely greater accuracy and precision have been reported by a number of authors (Gitten, 1969); Johansson and Eriksson (1972); and Cini and co-workers (1972).

Surface tension values for seawater have been reported infrequently: the reason for the lack of data is the frequent incident of naturally-occurring surface-active agents tending to yield significantly lower values than theoretically predicted (and often with considerable scatter). A table of "Surface Tension of Clean Seawater" presented in the Table below.

Table 1-17

Surface Tension of Clean Seawater
(From Fleming and Revelle, 1939, with permission of American Association of Petroleum Geologists)

S, ‰	Temperature, °C			
	0	10	20	30
0	75.64	74.20	72.76	71.32
10	75.86	74.42	72.98	71.54
20	76.08	74.64	73.20	71.76
30	76.30	74.86	73.42	71.98
35	76.41	74.97	73.53	72.09
40	76.52	75.08	73.64	72.20

J. Dielectric Constant

The static dielectric constant of water decreases with temperature. For a review of measurements of this quantity, see Gmelin (loco cit., page 1591-1592). The dielectric constant of water is obviously one of the most important parameters in connection with the suitability of water to support life, through its role in determining the solubility and dissociation of electrolytes. Figure 1-13 shows the dielectric constant of water as a function of temperature, taken from the review of seawater in the treatise by Kinne (1963), based on data by Weast.

Table 1-18 shows the microwave dielectric data and relaxation parameters for water as a function of temperature. These measurements were reported by Hasted and co-workers (see Franks, 1972, page 277). In this Table is given the static dielectric constant (ε_s), the high-frequency dielectric constant (ε_∞), the relaxation time (τ) x 10^{-11} seconds.

Table 1-18

Microwave Dielectric Data and Relaxation Times

T, °C	ε_s	ε_∞	τ, X10^{-11} sec
0	88.3	4.46	1.79
10	84.1	4.10	1.26
20	80.4	4.23	0.93
30	76.8	4.20	0.72
40	73.2	4.16	0.58
50	70.0	4.13	0.48
60	66.6	4.21	0.39
75	62.1	4.49	0.32

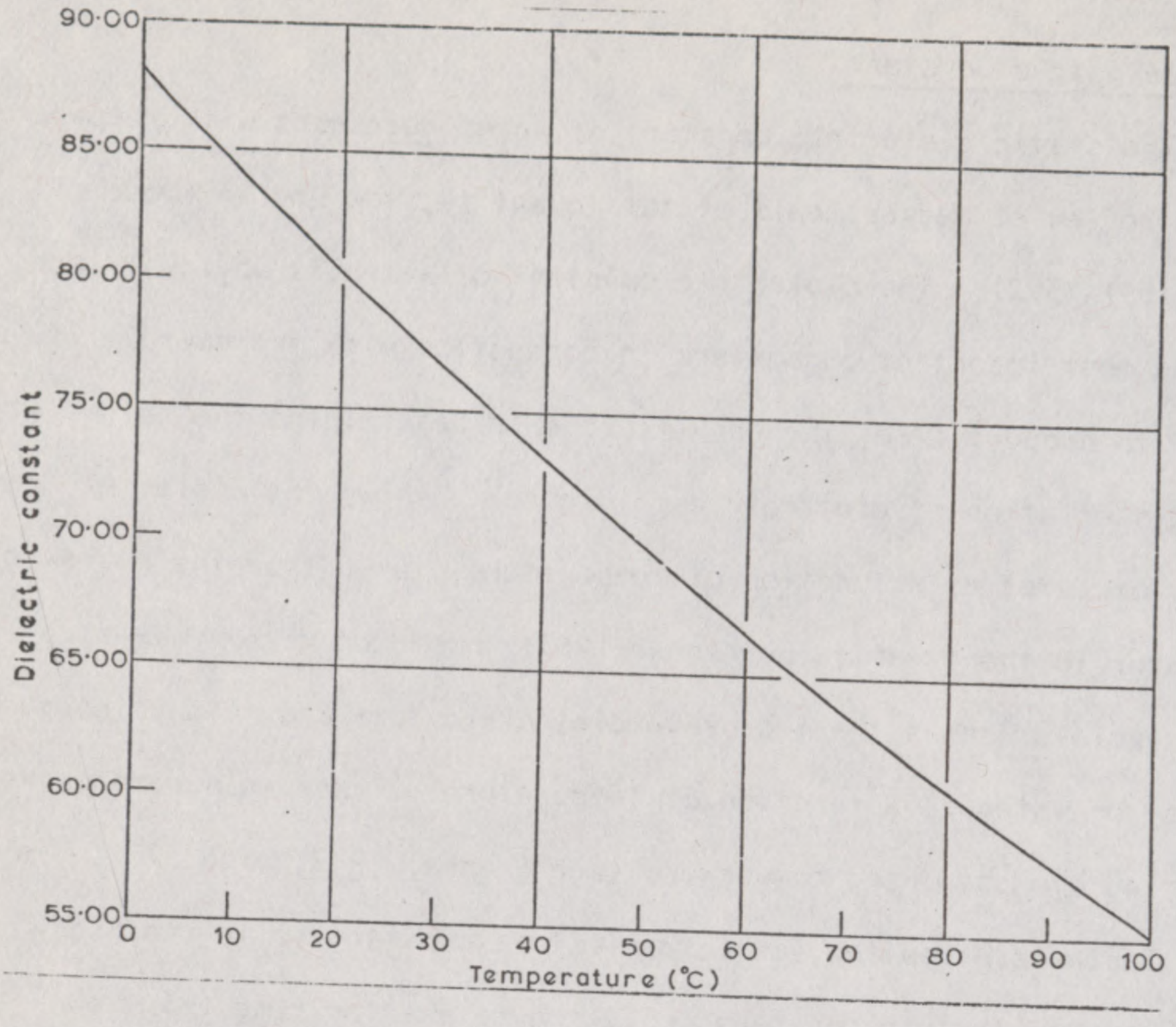

90·00
85·00
80·00
75·00
70·00
65·00
60·00
55·00
Dielectric constant
0
10
20
30
40
50
60
70
80
90
100
Temperature (°C)

Figure 1-13

K. Index of Refraction.

Table 1-19

Refractive Index of Seawater[a]
(From C. L. Utterback, T. G. Thompson, and B. D. Thomas, *J. Conseil Exploration Mer*, **9**, 35 (1934) with permission of Conseil International pour l'Exploration.)

	Temperature, °C											
S, ‰	0		5		10		15		20		25	
0	1.3	3395	1.3	3385	1.3	3370	1.3	3340	1.3	3300	1.3	3250
5		3500		3485		3465		3435		3395		3345
10		3600		3585		3565		3530		3485		3435
15		3700		3685		3660		3625		3580		3525
20		3795		3780		3750		3715		3670		3620
25		3895		3875		3845		3805		3760		3710
30		3991		3966		3935		3898		3851		3798
31		4011		3985		3954		3916		3869		3816
32		4030		4004		3973		3934		3886		3834
33		4049		4023		3992		3953		3904		3851
34		4068		4042		4011		3971		3922		3868
35		4088		4061		4030		3990		3940		3886
36		4107		4080		4049		4008		3958		3904
37		4127		4099		4068		4026		3976		3922
38		4146		4118		4086		4044		3994		3940
39		4166		4139		4105		4062		4012		3958
40		(4185)		(4157)		(4124)		(4080)		(4031)		(3976)
41		(4204)		(4716)		(4143)		(4098)		(4049)		(3994)

[a] For sodium D light.

The value for the Index of Refraction of seawater as a function of both temperature and salinity. Reported by Horne (1969), p. 517).

L. Electrical Conductivity

The electrical conductivity of pure water has been reported by various authors. For a summary, see, for instance, Gmelin (1963). Because the electrical conductivity of water is extremely sensitive to electrolytic impurities and particularly to the presence of dissolved CO_2, data for the conductivity of pure water are not listed here.

A large literature exists on the problem of the electrical conductivity of seawater. For specific applications, the reader is referred to the oceanographic literature for details. A survey taken of the specific conductivity of water as a function of temperature and salinity is shown in Table I-20. See also Figure I-14.

Table 1-20

Specific Conductivity of Seawater[a]

[Values calculated from the equation of P. Weyl, *Limnol. Oceanog.*, 9, 75 (1964), based on data of B. D. Thomas, T. G. Thompson, and C. L. Utterback, *J. Conseil Perm. Intern. Exploration Mer.*, 9, 28 (1934)]

	Temperature, °C						
S, ‰	30	25	20	15	10	5	0
10	(19.127)	17.345	15.628	13.967	12.361	10.816	9.341
20	(35.458)	32.188	29.027	25.967	23.010	20.166	17.456
30	(50.856)	46.213	41.713	37.351	33.137	29.090	25.238
31	(52.360)	47.584	42.954	38.467	34.131	29.968	26.005
32	(53.859)	48.951	44.192	39.579	35.122	30.843	26.771
33	(55.352)	50.314	45.426	40.688	36.110	31.716	27.535
34	(56.840)	51.671	46.656	41.794	37.096	32.588	28.298
35	(58.323)	53.025	47.882	42.896	38.080	33.457	29.060
36	(59.801)	54.374	(49.105)	(43.996)	(39.061)	(34.325)	(29.820)
37	(61.274)	55.719	(50.325)	(45.093)	(40.039)	(35.190)	(30.579)
38	(62.743)	57.061	(51.541)	(46.187)	(41.016)	(36.055)	(31.337)
39	(64.207)	58.398	(52.754)	(47.278)	(41.990)	(36.917)	(32.094)
40	(65.667)	(59.732)	(53.963)	(48.367)	(42.962)	(37.778)	(32.851)

[a]Conductivity in $ohm^{-1}\ cm^{-1} \times 1000$.

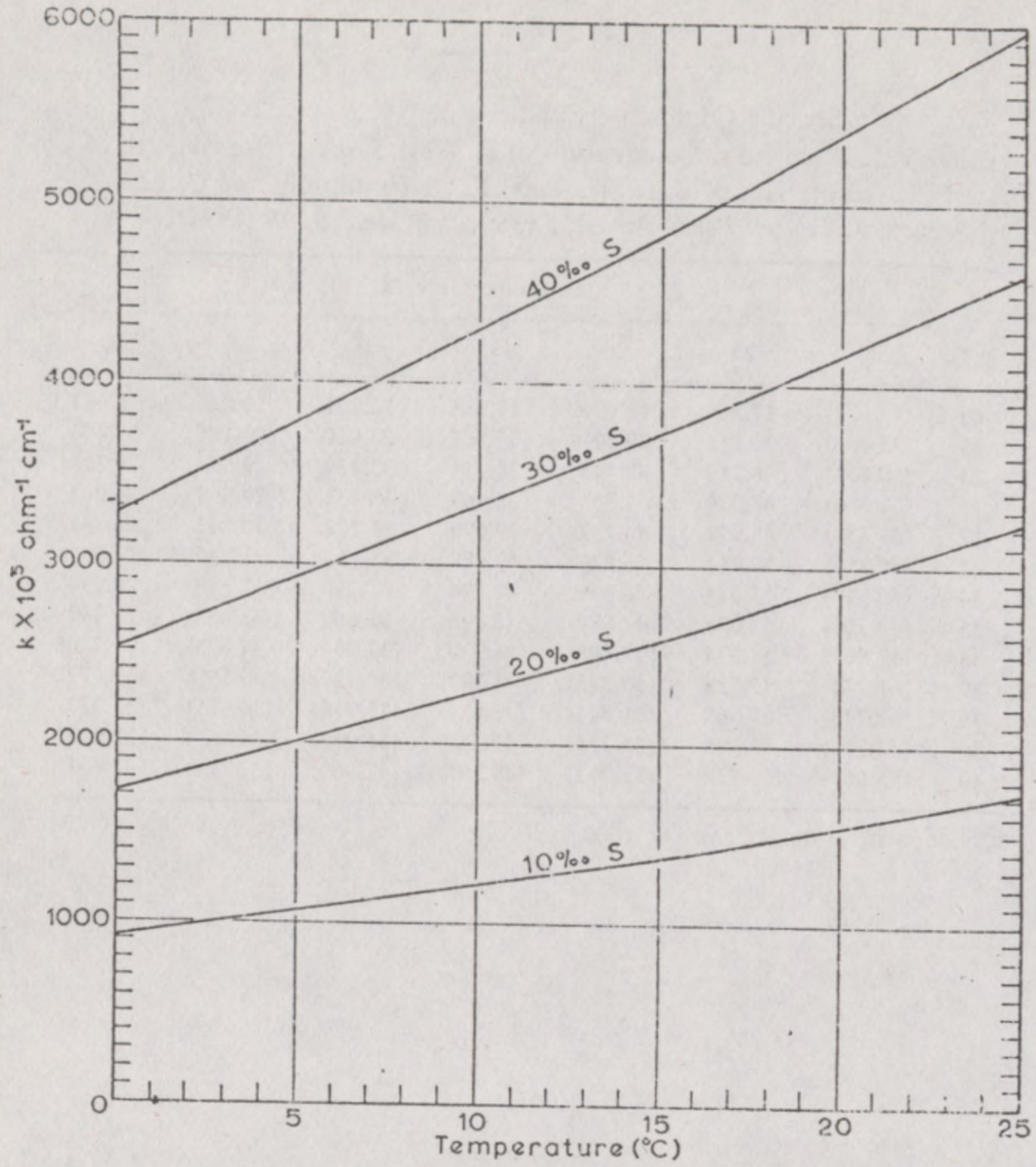

6000
5000
4000
3000
2000
1000
0
k X 10⁵ ohm⁻¹ cm⁻¹
40‰ S
30‰ S
20‰ S
10‰ S
5
10
15
20
25
Temperature (°C)

Figure 1-14

Table 1-21 shows the temperature dependencies of cation and anion equivalent conductances (at infinite dilution).

	0 °C	18 °C	25 °C	100 °C
$l'_{1\infty}$				
H^+	224	315	349,6	631
Li^+	19,3	32,6	38,7	114
Na^+	25,7	42,6	50,1	148
K^+	40,3	63,7	73,5	193
Rb^+	43,5	66,3	77	—
Cs^+	43	66,8	77,7	200
Ag^+	33	53,3	62,2	180
Tl^+	43,3	64,8	74	—
NH_4^+	40,0	63,6	74	184
$N(CH_3)_4^+$	23,0	39,7	41,5	—
$N(C_2H_5)_4^+$	15,8	27,2	32	100
$^1/_2\ Be^{++}$	—	—	45	—
$^1/_2\ Mg^{++}$	31	44,6	58	170
$^1/_2\ Ca^{++}$	30,5	50,4	59	187
$^1/_2\ Sr^{++}$	30	50,6	60	—
$^1/_2\ Ba^{++}$	32	54,4	63,2	200
$^1/_2\ Ra^{++}$	(33)	56,5	(66,8)	—
$^1/_2\ Mn^{++}$	23,5	44,5	50	—
$^1/_2\ Fe^{++}$	28	(44,5)	(53,5)	—
$^1/_2\ Co^{++}$	28	45	49	—
$^1/_2\ Ni^{++}$	23	45	49	—
$^1/_2\ Cu^{++}$	28	45,3	55,5	—
$^1/_2\ Zn^{++}$	27,0	45	54	—
$^1/_2\ Cd^{++}$	28	45,1	54	—
$^1/_2\ Pb^{++}$	37,5	60	65	—
$^1/_3\ Al^{+++}$	29	—	61	—
$^1/_3\ Sc^{+++}$	—	—	64,7	—
$^1/_3\ Y^{+++}$	32	—	62	—
$^1/_3\ La^{+++}$	35	59,2	69,7	220
$^1/_3\ Ce^{+++}$	—	—	67	—
$^1/_3\ Pr^{+++}$	—	—	65,4	—
$^1/_3\ Nd^{+++}$	—	—	64,3	—
$^1/_3\ Sm^{+++}$	32	—	62	—
$^1/_3\ Gd^{+++}$	31,9	—	62	—
$^1/_3\ Co(NH_3)_6^{+++}$	56	—	109	—
$l'_{2\infty}$				
OH'	105	174	197	449
F'	—	47,6	55	—
Cl'	41,4	66,3	76,4	213
ClO_3'	36	55,8	65,3	172
ClO_4'	37,3	59,1	67	183
Br'	43,1	68,3	78	150
BrO_3'	30,7	49,0	56,0	155
J'	42,6	66,8	77,1	—
JO_3'	20,7	34,8	41,6	127
NO_3'	40,2	62,6	71,1	191
CN'	—	—	82	—
SCN'	37,0	57,4	66	—
MnO_4'	36	53	61	—
$HCOO'$	—	48	56	86
CH_3COO'	23,5	35	41,4	66
$^1/_2\ SO_4^{--}$	40,7	68,7	79	256
$^1/_2\ S_2O_3^{--}$	—	—	84,9	—
$^1/_2\ CO_3^{--}$	36	60,5	74,0	—
$^1/_2\ CrO_4^{--}$	44	72	83	—
$^1/_3\ Fe(CN)_6^{---}$	—	—	94	—
$^1/_4\ Fe(CN)_6^{----}$	57,5	—	100	272

PART I

SECTION III: SOLUTION PROPERTIES

III.A.1. Ion Activities

The effect of temperature on thermodynamic equilibrium properties is generally well understood, and readily described. For the systems of interest to natural waters all the necessary input data for a systematic description of the chemistry as a function of temperature, however, not necessarily available. Theoretical estimates are readily obtained by the use of the Debye-Hückel equation or one of its extensions. Yet, it is recognized that serious limitations are implied in either more concentrated solutions (say, for ionic strength of 0.5 or above) or in the presence of several types of ionic species, particularly those prone to form ion complexes. A good discussion of a chemical model for seawater is presented by Garrels and Thompson (1962); see also Garrels and Christ). Generally, for seawater, an ionic strength of 0.7 is accepted - a value certainly sufficiently accurate for the purposes of the present discussion. Note that an ionic strength of 0.7 is high enough to cause interactions between ions which change their thermodynamic properties so as to yield quantitative data notably different from those one would obtain by ignoring complex formation. The average composition of surface seawater (19 parts per thousand chlorinity) at 25° is given below (Garrels and Christ, p. 101): see Table I-22

Table I-23, taken from Garrels and Christ (p. 103) gives the activity coefficients of individual species at ionic strength of 0.7 (chlorinity 19 parts per thousand; 25°C).

Of interest in the present connection is the change of these activities - differing from those estimated on the simple use of a Debye-Hückel type of equation - due to temperature.

However, it is obvious that while no accurate estimates can be made through extensions of the Debye-Hückel equation, some generalities of

Table 1-22

Composition of Average Surface Sea Water with 19‰ (parts per thousand) Chlorinity at 25 °C (pH = 8.15)

Ion	Molality
Na^+	0.48
Mg^{++}	0.054
Ca^{++}	0.010
K^+	0.010
Cl^-	0.56
SO_4^{--}	0.028
HCO_3^-	0.0024
CO_3^{--}	0.00027

Table 1-23

Activity Coefficients of Individual Species in Sea Water.[a] (Ionic Strength, 0.7; Chlorinity, 19‰, 25 °C)

Dissolved Species	Activity Coefficient	Method Used
$NaHCO_3^\circ$	1.13	Analogy with H_2CO_3
$MgCO_3^\circ$	1.13	Same
$CaCO_3^\circ$	1.13	Same
$MgSO_4^\circ$	1.13	Same
$CaSO_4^\circ$	1.13	Same
HCO_3^-	0.68	Figure 4.5, A
$NaCO_3^-$	0.68	Analogy with HCO_3^-
$NaSO_4^-$	0.68	Same
KSO_4^-	0.68	Same
$MgHCO_3^+$	0.68	Same
$CaHCO_3^+$	0.68	Same
Na^+	0.76	Meas. glass electrode
K^+	0.64	$\gamma_{K^+} = \gamma_{\pm KCl}$
Mg^{++}	0.36	$\gamma_{Mg^{++}} = (\gamma^3_{\pm MgCl_2})/(\gamma^2_{\pm KCl})$
Ca^{++}	0.28	$\gamma_{Ca^{++}} = (\gamma^3_{\pm CaCl_2})/(\gamma^2_{\pm KCl})$
Cl^-	0.64	$\gamma_{Cl^-} = \gamma_{\pm KCl}$
CO_3^{--}	0.20	Figure 4.5, D
SO_4^{--}	0.12	See text

significance can still be derived. Thus, the temperature effects will be reflected, respectively, in the A and B coefficients, primarily. The temperature variations of these constants are shown in Table I-24 (taken from the extensive calculations by Hamer, 1968).

It is obvious that no sudden or abrupt changes are to be expected over the temperature range of interest in connection with natural waters.

Table 1-24

Values of the Debye-Hückel constants for activity coefficients based on the values of the dielectric constant of water determined by Owen et al. [12]

t °C	ϵ [a]	A		B	
		Weight basis	Volume basis	Weight basis	Volume basis
		$kg^{1/2}\ mol^{-1/2}$	$l^{1/2}\ mol^{-1/2}$	$kg^{1/2}10^{8}\ cm\ mol^{-1/2}$	$l^{1/2}10^{8}\ cm\ mol^{-1/2}$
0	87.90	0.4905	0.4905	0.3245	0.3246
5	85.90	.4941	.4941	.3254	.3254
10	83.95	.4979	.4979	.3262	.3262
15	82.04	.5018	.5021	.3270	.3271
18	80.93	.5042	.5045	.3274	.3276
20	80.18	.5059	.5064	.3277	.3280
25	78.36	.5103	.5110	.3285	.3290
30	76.58	.5148	.5159	.3294	.3301
35	74.85	.5194	.5209	.3302	.3311
38	73.83	.5223	.5241	.3307	.3318
40	73.15	.5243	.5263	.3310	.3323
45	71.50	.5293	.5319	.3318	.3334
50	69.88	.5345	.5378	.3327	.3347
55	68.30	.5400	.5439	.3335	.3359
60	66.76	.5455	.5502	.3344	.3372
65	65.25	.5514	.5568	.3353	.3386
70	63.78	.5573	.5636	.3362	.3400
75	62.34	.5635	.5707	.3371	.3414
80	60.93	.5699	.5781	.3380	.3429
85	59.55	.5766	.5859	.3389	.3444
90	58.20	.5835	.5939	.3399	.3459
95	56.88	.5906	.6022	.3409	.3475
100	55.58	.5981	.6110	.3419	.3492

[a] Values for the dielectric constant of water as determined by Owen et al. [12]; values above 70 °C were calculated from their equation expressing ϵ as a function of temperature.

The interionic distance parameter, $\mathring{a}_i$, is shown in Table I-25, from the monograph by Garrels and Christ (1965, pp. 61, 62).

In Table I-24, note the rather small variation in A and B, as a function of temperature. As an example, increasing the temperature from 15 to 25° changes A by only 1.7%, and B by only 0.05%. These variations are minimal, especially compared to the "uncertainty" in the choice of the "ionic diameter" ($\mathring{a}_i$ listed in Table I-25). Recall in passing, however, that the activity coefficients themselves will vary exponentially with the listed values, but note that some "compensation" occurs as A and B enter the equation as a ratio (both increasing with temperature.)

Table I-25

Values of $\mathring{a}_i$ for Some Individual Ions in Aqueous Solutions

$\mathring{a}_i \times 10^8$	Ion
2.5	Rb^+, Cs^+, NH_4^+, Tl^+, Ag^+
3.0	K^+, Cl^-, Br^-, I^-, NO_3^-
3.5	OH^-, F^-, HS^-, BrO_3^-, IO_4^-, MnO_4^-
4.0–4.5	Na^+, HCO_3^-, $H_2PO_4^-$, HSO_3^-, Hg_2^{++}, SO_4^{--}, SeO_4^{--}, CrO_4^{--}, HPO_4^{--}, PO_4^{3-}
4.5	Pb^{++}, CO_3^{--}, SO_3^{--}, MoO_4^{--}
5.0	Sr^{++}, Ba^{++}, Ra^{++}, Cd^{++}, Hg^{++}, S^{--}, WO_4^{--}
6	Li^+, Ca^{++}, Cu^{++}, Zn^{++}, Sn^{++}, Mn^{++}, Fe^{++}, Ni^{++}, Co^{++}
8	Mg^{++}, Be^{++}
9	H^+, Al^{3+}, Cr^{3+}, trivalent rare earths
11	Th^{4+}, Zr^{4+}, Ce^{4+}, Sn^{4+}

SOURCE: Adapted from I. M. Klotz, *Chemical Thermodynamics.* Englewood Cliffs, N.J., Prentice-Hall, 1950, p. 331.

The most extensive calculations of the theoretical mean activity coefficients (of strong electrolytes in aqueous solutions) have been presented by Hamer (1968). As these calculations represent the presently best available (theoretically calculated) data, several representative sets are quoted directly from the publication by Hamer. Thus, the following pages show the theoretical background on which the data have been calculated, and the actual values are shown in Table I-27 through I-32. The main point of interest in the present connection is to demonstrate that A) the (calculated) changes in the mean activity coefficients as a function of temperature are relatively minor, and B) that no "surprising", abrupt changes with temperature occur.

Theoretical Expressions for Activity Coefficients

Activity coefficients give a measure of the deviations of real solutions from ideality and include the magnitude of all effects that lead to these deviations.

In dilute solutions the main effect is that of interionic attraction, i.e., the attraction between electrical (ionic) charges of unlike sign, and for which Debye and Hückel [3] assuming that ions are point charges derived a solution which led to the following expression for the mean activity coefficient, $\gamma_\pm$, of an electrolyte (γ shall be used hereafter for $\gamma_\pm$):

$$\log \gamma_c = -z_+ z_- A_c \sqrt{I_c} \qquad (1)$$

where the subscript c refers to concentrations on the volume basis and

$$A_c = \left(\frac{2\pi N}{1000}\right)^{1/2} \frac{e^3}{2.302585 k^{3/2}} \left(\frac{1}{T^{3/2}\epsilon^{3/2}}\right)$$

$$= \frac{1.824829238 \times 10^6}{(T\epsilon)^{3/2}},$$

where the symbols have the following meanings and numerical values [4]:

N (or N_A) = Avogadro constant = $6.02252(28) \times 10^{23}$ mol^{-1}.
e = elementary charge (sometimes called the electronic or protonic charge) = 4.80298(20) esu.
k = Boltzmann constant = $1.38054(18) \times 10^{-16}$ erg K^{-1}.
T = absolute temperature in K (defined in the thermodynamic scale by assigning 273.16 K (Kelvin) to the triple point of water (freezing point of water, 273.15 K = 0 °C (Celsius). (The 13th General Conference on Weights and Measures in 1967 changed the unit of temperature and temperature interval from "degrees Kelvin" to simply "Kelvin," symbol: K.)
ϵ = dielectric constant of the solvent.

The values given in parentheses above represent established limits of error based on three standard deviations applied to the last digits in the listed value.

The following values of π and ln 10 were used in the calculations:

$$\pi = 3.14159265$$

$$\ln 10 = 2.302585$$

A_m on the molality (or weight) basis is given by $A_m = A_c(d_0)^{1/2}$ where d_0 is the density of the solvent. Values of ϵ, the dielectric constant, and of d_0, the density of water, from 0 to 100 °C, inclusive, are given in table 2 [5, 6]. Values of A_c and A_m for aqueous solutions from 0 to 100 °C, inclusive, are given in table 3.

Values of γ_c as calculated by equation (1) for 1–1, 1–2 (or 2–1), 1–3 (or 3–1), 1–4 (or 4–1 or 2–2), 2–3 (or 3–2), 2–4 (or 4–2), 3–3, 3–4 (or 4–3), and 4–4 electrolytes are given, respectively, in tables 4 to 12, inclusive, for ionic strengths of 0.1 and below and for temperatures from 0 to 100 °C, inclusive. Similar data for γ_m are given in tables 13 to 21, inclusive.

When the size, a_i, of the ions is taken into account, the Debye-Hückel equation becomes:

$$\log \gamma_c = \frac{-z_+ z_- A_c \sqrt{I_c}}{1 + B_c a_i \sqrt{I_c}}$$

where

$$B_c = \left(\frac{8\pi N}{1000}\right)^{1/2} \frac{e}{k^{1/2}} \left(\frac{1}{T^{1/2}\epsilon^{1/2}}\right) = \frac{50.29158649 \times 10^8}{(T\epsilon)^{1/2}}$$

in which the symbols have the significances given above. B_m on the molality (or weight) basis is given by $B_m = B_c(d_0)^{1/2}$. Values of B_c and B_m for aqueous solutions from 0 to 100 °C, inclusive, are given in table 3.

Güntelberg [7] suggested the simpler form

$$\log \gamma_c = \frac{-z_+ z_- A_c \sqrt{I_c}}{1 + \sqrt{I_c}} \qquad (2)$$

which is equivalent to assigning a value of approximately 3Å as calculated by equation (2) to the ion size at all temperatures. Güntelberg values of γ_c for 1–1, 1–2 (or 2–1), 1–3 (or 3–1), 1–4 (or 4–1 or 2–2), 2–3 (or 3–2), 2–4 (or 4–2), 3–3, 3–4 (or 4–3), and 4–4 electrolytes are given, respectively, in tables 22 to 30, inclusive, for ionic strengths of 0.1 and below and for temperatures from 0 to 100 °C, inclusive. Güntelberg values for γ_m for these same valence types and ranges of ionic strength and temperature are given in tables 31 to 39, inclusive.

A modified or extended Güntelberg equation would be

$$\log \gamma_c = \frac{-z_+ z_- A_c \sqrt{I_c}}{1 + 3B_c \sqrt{I_c}} \qquad (3)$$

where the denominator is now temperature dependent since B_c is a function of temperature. Extended Güntelberg values of γ_c as calculated by equation (3) for 1–1, 1–2 (or 2–1), 1–3 (or 3–1), 1–4 (or 4–1 or 2–2), 2–3 (or 3–2), 2–4 (or 4–2), 3–3, 3–4 (or 4–3), and 4–4 electrolytes are given, respectively, in tables 40 to 48, inclusive, for ionic strengths of 0.1 and below and for temperatures from 0 to 100 °C, inclusive. Extended Güntelberg values for γ_m for the same valence types and ranges of ionic strength and temperature are given in tables 49 to 57, inclusive.

These Güntelberg expressions for the activity coefficient give a fair representation of a number of electrolytes up to $I = 0.1$. However, a better representation is obtained if a term linear in the ionic strength is added to the right side of the equations. Thus, Guggenheim [8] proposed the equation

$$\log \gamma_c = \frac{-z_+ z_- A_c \sqrt{I_c}}{1 + \sqrt{I_c}} + bI_c$$

where b is an adjustable parameter.

Davies [9] altered the Guggenheim equation by putting $b=0.2Az_+z_-$, thus:

$$\log \gamma_c=\frac{-z_+z_-A_c\sqrt{I_c}}{1+\sqrt{I_c}}+0.2Az_+z_-I_c \qquad (4)$$

where the denominator of the first term on the right is again independent of temperature. Davies values of γ_c as calculated by equation (4) for 1–1, 1–2 (or 2–1), 1–3 (or 3–1), 1–4 (or 4–1 or 2–2), 2–3 (or 3–2), 2–4 (or 4–2), 3–3, 3–4 (or 4–3), and 4–4 electrolytes are given, respectively, in tables 58 to 66, inclusive, for ionic strengths of 0.1 and below and for temperatures from 0 to 100 °C, inclusive. Davies values for γ_m for the same valence types and ranges of ionic strength and temperature are given in tables 67 to 75, inclusive.

Scatchard [10] suggested that a better average fit is obtained if $(1+1.5\sqrt{I})$ is used in the denominator of the first term on the right for the expression for $\log \gamma_c$, thus:

$$\log \gamma_c=\frac{-z_+z_-A_c\sqrt{I_c}}{1+1.5\sqrt{I_c}} \qquad (5)$$

Scatchard actually used an additional linear term in I with an adjustable coefficient on the right side of the above equation but this additional term is omitted here. Scatchard values of γ_c as calculated by equation (5) for 1–1, 1–2 (or 2–1), 1–3 (or 3–1), 1–4 (or 4–1 or 2–2), 2–3 (or 3–2), 2–4 (or 4–2), 3–3, 3–4 (or 4–3), and 4–4 electrolytes are given, respectively, in tables 76 to 84, inclusive, for ionic strengths of 0.1 and below and for temperatures of 0 to 100 °C, inclusive. Scatchard values for γ_m for the same valence types and ranges of ionic strength and temperature are given in tables 85 to 93, inclusive.

A modified or extended Scatchard equation results if the denominator, $1+1.5\sqrt{I_c}$, in the above equation is made temperature dependent, thus:

$$\log \gamma_c=\frac{-z_+z_-A_c\sqrt{I_c}}{1+4.5B_c\sqrt{I_c}} \qquad (6)$$

Extended Scatchard values for γ_c as calculated by equation (6) for 1–1, 1–2 (or 2–1), 1–3 (or 3–1), 1–4 (or 4–1 or 2–2), 2–3 (or 3–2), 2–4 (or 4–2), 3–3, 3–4 (or 4–3), and 4–4 electrolytes are given, respectively, in tables 94 to 102, inclusive, for ionic strengths of 0.1 and below and for temperatures from 0 to 100 °C, inclusive. Extended Scatchard values for γ_m for the same valence types and ranges of ionic strength and temperature are given in tables 103 to 111, inclusive.

Bjerrum [11] has shown that ion pairs (associated ions with charges of unlike sign) occur if the diameter of the ion is less than

$$a_B=\frac{z_+z_-e^2}{2\epsilon kT}$$

Values of a_B for aqueous solutions from 0 to 100 °C, inclusive, are given in table 112. The Bjerrum expression for the activity coefficient is:

$$\log \gamma_c=\frac{-z_+z_-A_c\sqrt{I_c}}{1+B_ca_B\sqrt{I_c}} \qquad (7)$$

Bjerrum values of γ_c as calculated by equation (7) for 1–1, 1–2 (or 2–1), 1–3 (or 3–1), 1–4 (or 4–1 or 2–2), 2–3 (or 3–2), 2–4 (or 4–2), 3–3, 3–4 (or 4–3), and 4–4 electrolytes are given, respectively in tables 113 to 121, inclusive, for ionic strengths of 0.1 and below and for temperatures of 0 to 100 °C, inclusive. Bjerrum values for γ_m for the same valence types and ranges of ionic strength and temperature are given in tables 122 to 130, inclusive.

Table 1-26

Bjerrum's minimum ion-parameter for uni-univalent electrolytes in aqueous solutions from 0 to 100 °C based on the dielectric constant of water determined by Owen et al. [12].

Temperature	Ion-parameter	Temperature	Ion-parameter
t	a_B	t	a_B
°C	10^8 cm	°C	10^8 cm

(On weight or volume basis)

0	[a] 3.48 (3.49)	50	3.70
5	3.50	55	3.73
10	3.52	60	3.76 (3.75)
15	3.53 (3.54)	65	3.79 (3.78)
18	3.55	70	3.82 (3.81)
20	3.56	75	3.85 (3.84)
25	3.58	80	3.88
30	3.60	85	3.92 (3.91)
35	3.62	90	3.95 (3.94)
38	3.64	95	3.99 (3.98)
40	3.65	100	4.03 (4.02)
45	3.67		

Table 1-27

Mean activity coefficients of electrolytes in aqueous solutions on a volume basis—Debye-Hückel limiting law

(Electrolyte, $z_+z_- = 1$)

Ionic strength	Temperature in degrees Celsius											
	0	5	10	15	18	20	25	30	35	38	40	45
.0001	.9887	.9887	.9886	.9885	.9884	.9884	.9883	.9882	.9881	.9880	.9880	.9878
.0002	.9841	.9840	.9839	.9838	.9837	.9836	.9835	.9833	.9832	.9831	.9830	.9828
.0003	.9806	.9804	.9803	.9801	.9800	.9800	.9798	.9796	.9794	.9793	.9792	.9790
.0004	.9776	.9774	.9773	.9771	.9770	.9769	.9767	.9765	.9763	.9761	.9761	.9758
.0005	.9750	.9748	.9746	.9744	.9743	.9742	.9740	.9738	.9735	.9734	.9733	.9730
.0006	.9726	.9725	.9722	.9720	.9719	.9718	.9716	.9713	.9710	.9709	.9708	.9705
.0007	.9705	.9703	.9701	.9698	.9697	.9696	.9693	.9690	.9687	.9686	.9684	.9681
.0008	.9685	.9683	.9680	.9678	.9676	.9675	.9672	.9669	.9666	.9664	.9663	.9660
.0009	.9666	.9664	.9661	.9659	.9657	.9656	.9653	.9650	.9646	.9644	.9643	.9639
.0010	.9648	.9646	.9643	.9640	.9639	.9637	.9634	.9631	.9628	.9626	.9624	.9620
.0020	.9506	.9503	.9499	.9495	.9493	.9491	.9487	.9482	.9477	.9475	.9472	.9467
.0030	.9399	.9394	.9390	.9385	.9382	.9380	.9375	.9370	.9364	.9360	.9358	.9351
.0040	.9309	.9304	.9299	.9294	.9290	.9288	.9282	.9276	.9269	.9265	.9262	.9255
.0050	.9230	.9225	.9220	.9214	.9210	.9207	.9201	.9194	.9186	.9182	.9179	.9171
.0060	.9160	.9154	.9148	.9142	.9138	.9135	.9128	.9120	.9112	.9107	.9104	.9095
.0070	.9096	.9090	.9083	.9077	.9072	.9069	.9061	.9053	.9045	.9039	.9036	.9026
.0080	.9037	.9030	.9023	.9016	.9011	.9008	.9000	.8991	.8982	.8977	.8973	.8963
.0090	.8981	.8975	.8967	.8960	.8955	.8951	.8943	.8934	.8924	.8918	.8914	.8903
.0100	.8929	.8922	.8915	.8907	.8901	.8898	.8889	.8879	.8869	.8863	.8859	.8847
.0200	.8520	.8510	.8500	.8489	.8483	.8478	.8465	.8453	.8439	.8431	.8425	.8410
.0300	.8219	.8208	.8195	.8183	.8175	.8169	.8154	.8139	.8123	.8113	.8107	.8089
.0400	.7973	.7960	.7947	.7933	.7924	.7917	.7901	.7884	.7866	.7855	.7848	.7828
.0500	.7763	.7749	.7734	.7719	.7709	.7702	.7684	.7666	.7646	.7635	.7626	.7605
.0600	.7578	.7563	.7547	.7530	.7520	.7512	.7493	.7474	.7453	.7440	.7432	.7409
.0700	.7411	.7395	.7379	.7361	.7350	.7342	.7322	.7302	.7280	.7266	.7257	.7233
.0800	.7259	.7243	.7225	.7207	.7195	.7187	.7166	.7145	.7122	.7108	.7098	.7073
.0900	.7120	.7102	.7084	.7065	.7053	.7044	.7023	.7001	.6977	.6962	.6952	.6926
.1000	.6990	.6972	.6953	.6934	.6921	.6912	.6890	.6867	.6842	.6827	.6817	.6789

Mean activity coefficients of electrolytes in aqueous solutions on a volume basis—Debye-Hückel limiting law—Continued

(Electrolyte, $z_+z_- = 1$)

Table 1-28

Mean activity coefficients of electrolytes in aqueous solutions on a volume basis—Debye-Hückel limiting law

(Electrolyte, $z_+z_- = 2$)

Ionic strength	Temperature in degrees Celsius											
	0	5	10	15	18	20	25	30	35	38	40	45
.0001	.9776	.9774	.9773	.9771	.9770	.9769	.9767	.9765	.9763	.9761	.9761	.9758
.0002	.9685	.9683	.9680	.9678	.9676	.9675	.9672	.9669	.9666	.9664	.9663	.9660
.0003	.9615	.9613	.9610	.9607	.9605	.9604	.9600	.9597	.9593	.9590	.9589	.9585
.0004	.9557	.9554	.9551	.9547	.9545	.9544	.9540	.9536	.9531	.9529	.9527	.9522
.0005	.9506	.9503	.9499	.9495	.9493	.9491	.9487	.9482	.9477	.9475	.9472	.9467
.0006	.9460	.9457	.9453	.9449	.9446	.9444	.9439	.9434	.9429	.9426	.9424	.9418
.0007	.9418	.9414	.9410	.9406	.9403	.9401	.9396	.9390	.9385	.9381	.9379	.9373
.0008	.9379	.9375	.9371	.9366	.9363	.9361	.9355	.9350	.9344	.9340	.9337	.9331
.0009	.9343	.9339	.9334	.9329	.9326	.9323	.9318	.9312	.9305	.9301	.9299	.9292
.0010	.9309	.9304	.9299	.9294	.9290	.9288	.9282	.9276	.9269	.9265	.9262	.9255
.0020	.9037	.9030	.9023	.9016	.9011	.9008	.9000	.8991	.8982	.8977	.8973	.8963
.0030	.8833	.8826	.8817	.8809	.8803	.8799	.8789	.8779	.8768	.8761	.8757	.8745
.0040	.8665	.8657	.8647	.8637	.8631	.8627	.8616	.8604	.8592	.8584	.8579	.8565
.0050	.8520	.8510	.8500	.8489	.8483	.8478	.8465	.8453	.8439	.8431	.8425	.8410
.0060	.8391	.8380	.8369	.8358	.8350	.8345	.8332	.8318	.8303	.8295	.8288	.8272
.0070	.8274	.8263	.8251	.8239	.8231	.8225	.8211	.8196	.8181	.8171	.8165	.8147
.0080	.8166	.8155	.8142	.8129	.8121	.8115	.8100	.8085	.8068	.8058	.8051	.8033
.0090	.8067	.8054	.8041	.8028	.8019	.8012	.7997	.7981	.7964	.7953	.7946	.7927
.0100	.7973	.7960	.7947	.7933	.7924	.7917	.7901	.7884	.7866	.7855	.7848	.7828
.0200	.7259	.7243	.7225	.7207	.7195	.7187	.7166	.7145	.7122	.7108	.7098	.7073
.0300	.6755	.6736	.6716	.6696	.6682	.6673	.6649	.6625	.6599	.6583	.6572	.6543
.0400	.6357	.6337	.6315	.6293	.6278	.6268	.6243	.6216	.6188	.6170	.6159	.6127
.0500	.6026	.6005	.5982	.5958	.5943	.5932	.5905	.5877	.5847	.5829	.5816	.5783
.0600	.5742	.5719	.5696	.5671	.5655	.5643	.5615	.5586	.5555	.5536	.5523	.5489
.0700	.5492	.5469	.5444	.5419	.5402	.5390	.5362	.5332	.5299	.5280	.5266	.5231
.0800	.5270	.5246	.5221	.5194	.5177	.5165	.5136	.5105	.5072	.5052	.5038	.5002
.0900	.5069	.5045	.5019	.4992	.4975	.4962	.4932	.4901	.4867	.4847	.4833	.4796
.1000	.4886	.4861	.4835	.4808	.4790	.4778	.4747	.4715	.4681	.4661	.4647	.4610

Mean activity coefficients of electrolytes in aqueous solutions on a volume basis—Debye-Hückel limiting law—Continued

(Electrolyte, $z_+z_- = 2$)

Table 1-29

Mean activity coefficients of electrolytes in aqueous solutions on a volume basis—Debye-Hückel limiting law

(Electrolyte, $z_+z_-=4$)

Ionic strength	Temperature in degrees Celsius											
	0	5	10	15	18	20	25	30	35	38	40	45
.0001	.9557	.9554	.9551	.9547	.9545	.9544	.9540	.9536	.9531	.9529	.9527	.9522
.0002	.9379	.9375	.9371	.9366	.9363	.9361	.9355	.9350	.9344	.9340	.9337	.9331
.0003	.9245	.9240	.9235	.9229	.9225	.9223	.9216	.9210	.9202	.9198	.9195	.9187
.0004	.9134	.9128	.9122	.9115	.9111	.9108	.9101	.9093	.9085	.9080	.9076	.9067
.0005	.9037	.9030	.9023	.9016	.9011	.9008	.9000	.8991	.8982	.8977	.8973	.8963
.0006	.8950	.8943	.8935	.8927	.8922	.8919	.8910	.8901	.8891	.8885	.8880	.8869
.0007	.8871	.8863	.8855	.8847	.8841	.8837	.8828	.8818	.8807	.8801	.8796	.8785
.0008	.8797	.8789	.8781	.8772	.8766	.8762	.8752	.8742	.8730	.8724	.8719	.8706
.0009	.8729	.8721	.8712	.8703	.8697	.8692	.8682	.8671	.8659	.8652	.8647	.8633
.0010	.8665	.8657	.8647	.8637	.8631	.8627	.8616	.8604	.8592	.8584	.8579	.8565
.0020	.8166	.8155	.8142	.8129	.8121	.8115	.8100	.8085	.8068	.8058	.8051	.8033
.0030	.7803	.7789	.7775	.7759	.7749	.7742	.7725	.7707	.7688	.7676	.7668	.7647
.0040	.7509	.7494	.7478	.7461	.7450	.7442	.7423	.7403	.7382	.7369	.7360	.7336
.0050	.7259	.7243	.7225	.7207	.7195	.7187	.7166	.7145	.7122	.7108	.7098	.7073
.0060	.7041	.7023	.7005	.6985	.6973	.6964	.6942	.6919	.6895	.6880	.6870	.6843
.0070	.6846	.6827	.6808	.6787	.6774	.6765	.6742	.6718	.6692	.6677	.6666	.6638
.0080	.6669	.6650	.6629	.6608	.6595	.6585	.6561	.6536	.6509	.6493	.6482	.6453
.0090	.6507	.6487	.6466	.6444	.6430	.6420	.6395	.6370	.6342	.6325	.6314	.6283
.0100	.6357	.6337	.6315	.6293	.6278	.6268	.6243	.6216	.6188	.6170	.6159	.6127
.0200	.5270	.5246	.5221	.5194	.5177	.5165	.5136	.5105	.5072	.5052	.5038	.5002
.0300	.4563	.4538	.4511	.4483	.4465	.4452	.4421	.4389	.4354	.4333	.4319	.4281
.0400	.4042	.4016	.3988	.3960	.3942	.3929	.3897	.3864	.3829	.3808	.3793	.3755
.0500	.3632	.3606	.3578	.3550	.3531	.3518	.3487	.3454	.3418	.3397	.3383	.3345
.0600	.3297	.3271	.3244	.3216	.3198	.3185	.3153	.3121	.3086	.3065	.3050	.3013
.0700	.3017	.2991	.2964	.2936	.2918	.2906	.2875	.2843	.2808	.2788	.2773	.2737
.0800	.2777	.2752	.2725	.2698	.2680	.2668	.2637	.2606	.2572	.2552	.2538	.2502
.0900	.2569	.2545	.2519	.2492	.2475	.2462	.2433	.2402	.2369	.2349	.2336	.2301
.1000	.2387	.2363	.2338	.2311	.2295	.2283	.2254	.2224	.2191	.2172	.2159	.2125

Mean activity coefficients of electrolytes in aqueous solutions on a volume basis—Debye-Hückel limiting law—Continued

(Electrolyte, $z_+z_-=4$)

Mean activity coefficients of electrolytes in aqueous solutions on a weight basis—Extended Scatchard

(Electrolyte, $z_+z_- = 1$)

Ionic strength	Temperature in degrees Celsius											
	0	5	10	15	18	20	25	30	35	38	40	45
.0001	.9889	.9888	.9887	.9887	.9886	.9886	.9885	.9884	.9883	.9882	.9882	.9881
.0002	.9844	.9843	.9842	.9841	.9840	.9840	.9838	.9837	.9836	.9835	.9834	.9833
.0003	.9811	.9809	.9808	.9806	.9806	.9805	.9803	.9802	.9800	.9799	.9798	.9796
.0004	.9782	.9781	.9779	.9778	.9777	.9776	.9774	.9772	.9770	.9769	.9768	.9766
.0005	.9758	.9756	.9754	.9753	.9751	.9751	.9749	.9747	.9744	.9743	.9742	.9740
.0006	.9736	.9734	.9732	.9730	.9729	.9728	.9726	.9724	.9721	.9720	.9719	.9716
.0007	.9716	.9714	.9712	.9710	.9708	.9707	.9705	.9703	.9700	.9698	.9697	.9695
.0008	.9697	.9695	.9693	.9691	.9689	.9688	.9686	.9683	.9680	.9679	.9678	.9675
.0009	.9680	.9678	.9675	.9673	.9671	.9670	.9668	.9665	.9662	.9660	.9659	.9656
.0010	.9664	.9661	.9659	.9656	.9655	.9654	.9651	.9648	.9645	.9643	.9642	.9639
.0020	.9536	.9533	.9529	.9526	.9524	.9522	.9519	.9515	.9511	.9508	.9506	.9502
.0030	.9442	.9438	.9434	.9430	.9428	.9426	.9421	.9417	.9412	.9409	.9407	.9402
.0040	.9365	.9361	.9357	.9352	.9349	.9347	.9342	.9337	.9332	.9328	.9326	.9320
.0050	.9300	.9295	.9291	.9285	.9282	.9280	.9275	.9269	.9263	.9259	.9257	.9250
.0060	.9242	.9237	.9232	.9227	.9223	.9221	.9215	.9209	.9203	.9199	.9196	.9189
.0070	.9190	.9185	.9180	.9174	.9170	.9168	.9162	.9155	.9148	.9144	.9141	.9134
.0080	.9143	.9138	.9132	.9126	.9122	.9119	.9113	.9106	.9099	.9094	.9091	.9083
.0090	.9100	.9094	.9088	.9081	.9078	.9075	.9068	.9061	.9053	.9048	.9045	.9037
.0100	.9059	.9053	.9047	.9040	.9036	.9033	.9026	.9019	.9011	.9006	.9003	.8994
.0200	.8757	.8749	.8741	.8733	.8728	.8724	.8715	.8705	.8695	.8689	.8685	.8674
.0300	.8551	.8542	.8533	.8524	.8518	.8513	.8503	.8492	.8481	.8473	.8469	.8456
.0400	.8392	.8383	.8373	.8362	.8356	.8351	.8340	.8328	.8315	.8308	.8302	.8289
.0500	.8263	.8252	.8242	.8231	.8224	.8219	.8207	.8194	.8181	.8172	.8167	.8152
.0600	.8153	.8142	.8131	.8119	.8112	.8107	.8094	.8080	.8067	.8058	.8052	.8037
.0700	.8057	.8046	.8034	.8022	.8015	.8009	.7996	.7982	.7967	.7959	.7952	.7937
.0800	.7972	.7961	.7949	.7936	.7929	.7923	.7909	.7895	.7880	.7871	.7864	.7848
.0900	.7896	.7885	.7872	.7859	.7852	.7846	.7832	.7817	.7802	.7792	.7786	.7769
.1000	.7828	.7816	.7803	.7790	.7782	.7776	.7762	.7746	.7731	.7721	.7714	.7697

Mean activity coefficients of electrolytes in aqueous solutions on a weight basis—Extended Scatchard—Continued

(Electrolyte, $z_+z_- = 1$)

Table 1-31

Mean activity coefficients of electrolytes in aqueous solutions on a weight basis—Extended Scatchard

(Electrolyte, $z_+z_-=2$)

Ionic strength	Temperature in degrees Celsius											
	0	5	10	15	18	20	25	30	35	38	40	45
.0001	.9779	.9778	.9776	.9774	.9773	.9773	.9771	.9769	.9767	.9766	.9765	.9763
.0002	.9691	.9689	.9687	.9684	.9683	.9682	.9679	.9677	.9674	.9672	.9671	.9668
.0003	.9625	.9622	.9619	.9617	.9615	.9614	.9611	.9607	.9604	.9602	.9601	.9597
.0004	.9569	.9566	.9563	.9560	.9558	.9557	.9553	.9550	.9546	.9544	.9542	.9538
.0005	.9521	.9518	.9515	.9511	.9509	.9507	.9504	.9500	.9495	.9493	.9491	.9486
.0006	.9478	.9475	.9471	.9467	.9465	.9463	.9459	.9455	.9450	.9447	.9445	.9440
.0007	.9439	.9436	.9432	.9428	.9425	.9423	.9419	.9414	.9409	.9406	.9404	.9399
.0008	.9403	.9399	.9395	.9391	.9388	.9386	.9381	.9376	.9371	.9368	.9366	.9360
.0009	.9370	.9366	.9361	.9357	.9354	.9352	.9347	.9341	.9336	.9332	.9330	.9324
.0010	.9338	.9334	.9329	.9324	.9321	.9319	.9314	.9309	.9303	.9299	.9297	.9291
.0020	.9093	.9087	.9081	.9074	.9070	.9067	.9060	.9053	.9045	.9040	.9037	.9029
.0030	.8915	.8908	.8901	.8893	.8888	.8885	.8876	.8868	.8859	.8853	.8849	.8839
.0040	.8771	.8763	.8755	.8746	.8741	.8737	.8728	.8718	.8708	.8702	.8697	.8686
.0050	.8649	.8640	.8631	.8622	.8616	.8612	.8602	.8591	.8580	.8573	.8569	.8557
.0060	.8542	.8533	.8523	.8513	.8507	.8503	.8492	.8480	.8469	.8461	.8456	.8443
.0070	.8446	.8437	.8427	.8416	.8410	.8405	.8393	.8381	.8369	.8361	.8356	.8342
.0080	.8360	.8350	.8339	.8328	.8321	.8316	.8304	.8292	.8279	.8270	.8265	.8251
.0090	.8280	.8270	.8259	.8247	.8240	.8235	.8223	.8209	.8196	.8187	.8182	.8167
.0100	.8207	.8196	.8185	.8173	.8165	.8160	.8147	.8134	.8119	.8111	.8105	.8089
.0200	.7669	.7655	.7641	.7626	.7617	.7611	.7595	.7578	.7561	.7550	.7542	.7523
.0300	.7312	.7297	.7282	.7265	.7255	.7248	.7230	.7211	.7192	.7180	.7172	.7151
.0400	.7043	.7027	.7011	.6993	.6982	.6974	.6955	.6935	.6915	.6902	.6893	.6871
.0500	.6827	.6810	.6793	.6774	.6763	.6755	.6735	.6714	.6692	.6679	.6670	.6646
.0600	.6646	.6629	.6611	.6592	.6580	.6572	.6551	.6529	.6507	.6493	.6483	.6459
.0700	.6491	.6473	.6455	.6435	.6423	.6414	.6393	.6371	.6348	.6334	.6324	.6299
.0800	.6356	.6337	.6318	.6298	.6286	.6277	.6256	.6233	.6209	.6195	.6185	.6159
.0900	.6235	.6217	.6198	.6177	.6165	.6156	.6134	.6110	.6086	.6072	.6061	.6035
.1000	.6127	.6108	.6089	.6068	.6056	.6046	.6024	.6001	.5976	.5961	.5951	.5924

Mean activity coefficients of electrolytes in aqueous solutions on a weight basis—Extended Scatchard—Continued

(Electrolyte, $z_+z_-=2$)

Mean activity coefficients of electrolytes in aqueous solutions on a weight basis—Extended Scatchard
(Electrolyte, $z_+z_-=4$)

Ionic strength	Temperature in degrees Celsius											
	0	5	10	15	18	20	25	30	35	38	40	45
.0001	.9563	.9560	.9557	.9554	.9552	.9551	.9547	.9543	.9539	.9537	.9535	.9531
.0002	.9392	.9388	.9383	.9379	.9376	.9374	.9369	.9364	.9359	.9355	.9353	.9347
.0003	.9263	.9258	.9253	.9248	.9245	.9242	.9236	.9230	.9224	.9220	.9217	.9210
.0004	.9157	.9152	.9146	.9140	.9136	.9133	.9127	.9120	.9112	.9108	.9105	.9097
.0005	.9066	.9060	.9053	.9046	.9042	.9039	.9032	.9024	.9016	.9011	.9008	.8999
.0006	.8984	.8977	.8970	.8963	.8959	.8955	.8948	.8939	.8931	.8925	.8921	.8912
.0007	.8910	.8903	.8896	.8888	.8883	.8880	.8871	.8862	.8853	.8847	.8843	.8833
.0008	.8842	.8835	.8827	.8819	.8814	.8810	.8801	.8792	.8782	.8776	.8772	.8761
.0009	.8779	.8771	.8763	.8754	.8749	.8745	.8736	.8726	.8716	.8709	.8705	.8694
.0010	.8720	.8712	.8704	.8694	.8689	.8685	.8675	.8665	.8654	.8648	.8643	.8631
.0020	.8268	.8257	.8246	.8234	.8227	.8222	.8209	.8196	.8182	.8173	.8167	.8152
.0030	.7948	.7935	.7922	.7908	.7900	.7894	.7879	.7864	.7847	.7837	.7831	.7813
.0040	.7693	.7679	.7665	.7650	.7641	.7634	.7618	.7601	.7583	.7572	.7565	.7545
.0050	.7480	.7466	.7450	.7434	.7424	.7417	.7400	.7381	.7362	.7350	.7342	.7322
.0060	.7297	.7281	.7265	.7247	.7237	.7229	.7211	.7192	.7172	.7159	.7151	.7129
.0070	.7134	.7118	.7101	.7083	.7072	.7064	.7045	.7025	.7004	.6991	.6982	.6959
.0080	.6989	.6972	.6954	.6935	.6924	.6916	.6896	.6875	.6853	.6840	.6831	.6807
.0090	.6856	.6839	.6821	.6802	.6790	.6782	.6761	.6740	.6717	.6703	.6694	.6670
.0100	.6735	.6717	.6699	.6679	.6667	.6659	.6638	.6615	.6592	.6578	.6569	.6544
.0200	.5881	.5860	.5839	.5816	.5802	.5792	.5768	.5743	.5716	.5700	.5689	.5660
.0300	.5347	.5325	.5302	.5278	.5264	.5253	.5227	.5200	.5172	.5155	.5143	.5113
.0400	.4961	.4938	.4915	.4890	.4875	.4864	.4838	.4810	.4781	.4764	.4752	.4721
.0500	.4661	.4638	.4614	.4589	.4574	.4563	.4536	.4508	.4479	.4461	.4449	.4417
.0600	.4417	.4394	.4370	.4345	.4330	.4319	.4292	.4263	.4234	.4216	.4204	.4172
.0700	.4214	.4190	.4167	.4141	.4126	.4115	.4088	.4059	.4030	.4012	.3999	.3968
.0800	.4040	.4016	.3992	.3967	.3952	.3940	.3913	.3885	.3856	.3838	.3825	.3794
.0900	.3888	.3865	.3841	.3815	.3800	.3789	.3762	.3734	.3704	.3686	.3674	.3643
.1000	.3755	.3731	.3708	.3682	.3667	.3656	.3629	.3601	.3572	.3554	.3541	.3510

Mean activity coefficients of electrolytes in aqueous solutions on a weight basis—Extended Scatchard—Continued
(Electrolyte, $z_+z_-=4$)

Thickness of the Ionic Atmosphere

Table 1-33 gives the thickness of the ionic atmosphere ($1/\kappa$; in Å) at different temperatures and concentrations for a number of electrolytes (uni-univalent, uni-divalent, etc). The Table is taken from the monograph by Falkenhagen (1971). Note that, as a rough approximation, the thickness of the ionic atmosphere is approximately equal to:

$$1/\kappa \simeq 10^{-8}/\sqrt{c} \quad \text{(in cm.)}$$

As the concentration increases from 10^{-4} to 10^{-2} molar, the thickness of the ionic atmosphere decreases by a factor of 10.

Table 1-33

c in $\frac{mol}{l}$	Valence					
	1-1	1-2	2-2	1-3	1-4	2-4
t = 0°C; D_0 = 87.91						
10^{-4}	306.89	177.12	153.45	125.27	97.03	88.58
10^{-3}	97.03	56.03	48.53	39.62	30.69	28.01
10^{-2}	30.69	17.72	15.35	12.53	9.71	8.86
10^{-1}	9.71	5.60	4.85	3.99	3.07	2.80
t = 18°C; D_0 = 80.82						
10^{-4}	303.79	175.33	151.89	124.00	96.05	87.68
10^{-3}	96.05	55.46	48.04	39.22	30.38	27.73
10^{-2}	30.38	17.54	15.19	12.41	9.61	8.77
10^{-1}	9.61	5.55	4.80	3.93	3.04	2.77
t = 25°C; D_0 = 78.25						
10^{-4}	302.45	174.55	151.23	123.46	95.63	87.30
10^{-3}	95.63	55.22	47.82	39.05	30.24	27.61
10^{-2}	30.24	17.46	15.13	12.35	9.57	8.73
10^{-1}	9.57	5.52	4.78	3.91	3.03	2.76
t = 100°C; D_0 = 56.23						
10^{-4}	286.88	165.56	143.43	117.10	90.70	82.80
10^{-3}	90.91	52.37	45.36	37.04	28.69	26.19
10^{-2}	28.69	16.56	14.35	11.71	9.07	8.28
10^{-1}	9.09	5.24	4.53	3.71	2.87	2.62

The prefactor in many potentiometric expressions is given by:

$$k = 2.30258 \cdot \frac{RT}{F} \text{ (Absolute Volts)}$$

For the sake of convenience, this parameter has been tabulated in Table 1-34 (Ives and Janz, page 67, Table IV).

Table 1-34

VALUES OF $k = 2.30258(RT/F)$ (ABSOLUTE VOLTS)

Temp., °C	k (references *102*, *23*); ice-point = 273.16	k (reference *109*); ice-point = 273.150
0	0.054197	0.054195
5	0.055189	0.055187
10	0.056182	0.056179
15	0.057173	0.057171
18	0.057768	0.057766
20	0.058165	0.058163
25	0.059158	0.059155
30	0.060149	0.060147
35	0.061141	0.061139
40	0.062133	0.062131
45	0.063126	0.063123
50	0.064117	0.064115
55	0.065109	0.065107
60	0.066102	0.066099

24-642 O - 73 - pt. 2 - 23

A.2. Dissociation Constants

The effects of temperature on the dissociation constant of water are reflected in Table I-35; however, these data are, to a large extent, primarily of theoretical interest. Superimposed on the relatively small changes in pH, induced by the temperature effects on the dissociation equilibrium of water, must be added the generally far more significant effects of changes in carbon dioxide concentration which will significantly affect the pH. This problem is treated in the Section on CO_2 and carbonate solubility relations. Lee (1973) points out that water with an alkalinity of 3.4 milliequivalent/liter (in the form of calcium carbonate) has a pH of 8.0 at 0° temperature in equilibrium with a partial pressure of CO_2 of 0.25 millimeter Hg. Increasing the temperature of this water to 25° results in a change in the pH of this system from 8.0 to 8.76 (Lee and Delfino, 1969), rather than the decrease which would be predicted from the dissociation constants quoted in Table I-35.

Table I-35

Ionization Constant of Water, K_w	
t °C	$K_w \times 10^{14}$
0	0.1139
5	0.1846
10	0.2920
15	0.4505
20	0.6809
25	1.008
30	1.469
35	2.089
40	2.919
45	4.018
50	5.474
55	7.297
60	9.614

Values for a number of ionization constants as functions of temperature are shown in Tables[1-36], [37], [38], and [39]. The Tables are all taken from the Monograph by Harned and Owen (1958). The first two Tables represent the more commonly encountered acids, including carbonic acid in water and in a number of sodium chloride solutions. Tables [1-38] and [1-39] give some ionization constants which may be of use in connection with the specific occurrence of organic compounds; these are generally present only in minute quantities in naturally-occurring water, except under circumstances where man-made pollution may be significant.

Table 1-36

OBSERVED IONIZATION CONSTANTS IN WATER. ALL VALUES ARE ON THE *m*-SCALE

Acid	Solvent		0°	5°	10°	15°	20°	25°	30°	35°	40°	45°	50°
Carbonic	Water	$K_{1A} \times 10^7$	2.64	3.04	3.44	3.81	4.16	4.45	4.71	4.90	5.04	5.13	5.19
	0.1*M* NaCl	"	4.48	5.16	5.84	6.49	7.11	7.66	8.14	8.54	8.85	9.06	9.16
	0.2*M* NaCl	"	5.15	5.93	6.70	7.44	8.14	8.78	9.33	9.79	10.15	10.39	10.51
	0.5*M* NaCl	"	6.23	7.14	8.04	8.90	9.70	10.41	11.03	11.53	11.92	12.19	12.32
	0.7*M* NaCl	"	6.62	7.56	8.47	9.34	10.15	10.81	11.51	12.03	12.45	12.75	12.93
	1.0*M* NaCl	"	7.02	7.98	8.92	9.80	10.63	11.37	12.02	12.58	13.02	13.37	13.58
Phosphoric	Water	$K_{2A} \times 10^8$	4.85	5.24	5.57	5.89	6.12	6.34	6.46	6.53	6.58	6.59	6.55
Phenolsulphonic	"	$K_{2A} \times 10^{10}$	4.45	5.20	6.03	6.92	7.85	8.85	9.89	10.94	12.00	13.09	14.16
Glycine	"	$K_{1A} \times 10^7$	....	3.82	3.99	4.17	4.32	4.46	4.57	4.66	4.73	4.77	4.79
Benzoic	"	$K_{1A} \times 10^5$	....	....	....	....	6.24	6.29	6.27	6.24	....	....	....
Citric	"	$K_{1A} \times 10^4$	6.03	6.31	6.69	6.92	7.21	7.45	7.66	7.78	7.96	7.99	8.04
	"	$K_{2A} \times 10^5$	1.45	1.54	1.60	1.65	1.70	1.73	1.76	1.77	1.76	1.76	1.75
	"	$K_{3A} \times 10^7$	4.05	4.11	4.14	4.13	4.09	4.02	3.99	3.78	3.69	3.45	3.28

Table 1-37

OBSERVED IONIZATION CONSTANTS IN WATER. ALL VALUES ARE ON THE *m*-SCALE.

Acids		0°	5°	10°	15°	20°	25°	30°	35°	40°	45°	50°	55°	60°
Formic	$K_A \times 10^4$	1.638	1.691	1.728	1.749	1.765	1.772	1.768	1.747	1.716	1.685	1.650	1.607	1.551
Acetic	$K_A \times 10^5$	1.657	1.700	1.729	1.745	1.753	1.754	1.750	1.728	1.703	1.670	1.633	1.589	1.542
Propionic	$K_A \times 10^5$	1.274	1.305	1.326	1.336	1.338	1.336	1.326	1.310	1.280	1.257	1.229	1.195	1.160
n-Butyric	$K_A \times 10^5$	1.563	1.574	1.576	1.569	1.542	1.515	1.484	1.439	1.395	1.347	1.302	1.252	1.199
Chloro-acetic	$K_A \times 10^3$	1.528	.....	1.488	1.440†	.....	1.379	1.308‡	.....	1.230	.....	.....	.....	.....
Lactic	$K_A \times 10^4$	1.287	.....	1.361*	.....	.....	1.374	.....	1.336**	.....	.....	1.270	.....	.....
Glycolic	$K_A \times 10^4$	1.334	.....	1.427*	.....	.....	1.475	.....	1.471**	.....	.....	1.415	.....	.....
Sulfuric	$K_{2A} \times 10^2$	.....	1.80	.....	1.36	.....	1.01	.....	0.75	.....	0.56	.....	0.41	.....
Carbonic	$K_{2A} \times 10^{11}$	2.36	2.77	3.24	3.71	4.20	4.69	5.13	5.62	6.03	6.38	6.73	.....	.....
Oxalic	$K_{2A} \times 10^5$	5.91	5.82	5.70	5.55	5.40	5.18	4.92	4.67	4.41	4.09	3.83	.....	.....
Malonic	$K_{2A} \times 10^6$	2.140	2.165	2.152	2.123	2.076	2.014	1.948	1.863	1.768	1.670	1.575	1.469	1.362
Phosphoric	$K_{1A} \times 10^3$	8.968	.....	8.394*	.....	.....	7.516	.....	6.531**	.....	.....	5.495	.....	.....
	$K_{2A} \times 10^8$	.....	.....	.....	.....	6.056	6.226	6.349	6.430	6.471	6.475	6.439	.....	.....
Boric	$K_A \times 10^{10}$	.....	3.63	4.17	4.72	5.26	5.79	6.34	6.86	7.38	.....	8.32	.....	.....
Amino-Acids														
Glycine	$K_A \times 10^3$	.....	.....	3.94	.....	4.31	4.47	4.50	.....	4.81	.....	.....	.....	.....
	$K_B \times 10^5$	.....	.....	4.68	5.12	5.57	6.04	6.52	6.98	7.43	7.87	.....	.....	.....
Alanine	$K_A \times 10^3$	.....	.....	.....	.....	4.47	4.57	4.66	4.71	4.74	4.76	.....	.....	.....
	$K_B \times 10^5$	.....	.....	.....	.....	6.90	7.47	8.08	8.61	9.10	9.60	.....	.....	.....

Table 1-38

OBSERVED IONIZATION CONSTANTS IN WATER.

		0°	10°	20°	25°	30°	40°	50°	60°
Ammonia	$K_B \times 10^5$	1.374	1.570	1.710	1.774	1.820	1.862	1.892	
Ethylene diammonium ion	$K_{1B} \times 10^6$	2.73	5.42	10.35	14.2	10.2	34.4	60.1	102.3
	$K_{2B} \times 10^{11}$	1.94	4.14	8.41	11.8	16.5	30.9	56.0	98.8
Hexamethylamine	$K_{1B} \times 10^{11}$	1.73	4.22	9.68	14.8	21.2	44.3	88.7	171.0
Diammonium ion	$K_{2B} \times 10^{12}$	1.39	3.40	7.85	11.7	17.3	36.2	73.0	141.9
Valeric acid	$K_{1A} \times 10^5$	1.504	1.501	1.463	1.436	1.409	1.329	1.241	1.147
Hexoic acid	$K_{1A} \times 10^5$	1.445	1.448	1.416	1.390	1.364	1.287	1.201	1.110
Iso-butyric acid	$K_{1A} \times 10^5$	1.497	1.489	1.447	1.417	1.387	1.301	1.208	1.110
Iso-valeric acid	$K_{1A} \times 10^5$	1.879	1.810	1.709	1.657	1.605	1.477	1.345	1.216
Iso-hexoic acid	$K_{1A} \times 10^5$	1.491	1.491	1.455	1.429	1.402	1.322	1.235	1.141
Trimethylacetic acid	$K_{1A} \times 10^5$	0.965	0.968	0.944	0.929	0.911	0.858	0.797	0.732
Diethyl acetic acid	$K_{1A} \times 10^5$	2.384	2.169	1.948	1.835	1.744	1.540	1.353	1.131

Table 1-39

OBSERVED IONIZATION CONSTANTS OF AMINO-ACIDS° IN WATER.
ALL VALUES ARE ON THE m-SCALE

	1°	12.5°	25°	37.5°	50°
dl-Alanine, $K_A \times 10^3$	3.75	4.14	4.49	4.68	4.66
$K_B \times 10^5$	4.83	6.10	7.40	8.73	9.86
dl-α-Amino-n-butyric acid, $K_A \times 10^3$	4.63	4.90	5.18	5.15	5.05
$K_B \times 10^5$	4.25	5.50	6.81	8.22	9.38
dl-α-Amino-n-valeric acid, $K_A \times 10^3$	4.21	4.57	4.81	4.91	4.86
$K_B \times 10^5$	4.04	5.18	6.47	7.64	8.63
dl-Norleucine, $K_A \times 10^3$	4.04	4.41	4.62	4.74	4.70
$K_B \times 10^4$	4.41	5.62	6.87	8.05	9.16
α-Aminoisobutyric acid, $K_A \times 10^3$	3.81	4.17	4.40	4.46	4.41
$K_B \times 10^4$	1.14	1.38	1.61	1.84	1.99
dl-Valine, $K_A \times 10^3$	4.79	5.05	5.18	5.11	4.90
$K_B \times 10^5$	3.24	4.21	5.27	6.28	7.28
dl-Leucine, $K_A \times 10^3$	4.14	4.49	4.70	4.71	4.65
$K_B \times 10^5$	3.57	4.52	5.60	6.71	7.59
dl-Isoleucine, $K_A \times 10^3$	4.32	4.59	4.81	4.82	4.66
$K_B \times 10^5$	3.61	4.57	5.77	6.79	7.85

A.3. Osmotic Pressure

In Table 1-40, 41, and 42, are listed, respectively, the osmotic pressures of seawater for various salinities, at the respective freezing points.

Table 1-41 shows the vapor pressure and the osmotic equivalent of seawater at 25°, as a function of chlorinity (in ppt) at 25°. As is to be expected, to a fair approximation, the osmotic pressure increases nearly linearly with the chlorinity over the limited range indicated.

Table 1-42 gives the osmotic pressure in atmospheres of seasalt solutions as a function of concentration (in weight percent of salts), at a few temperatures. At the lower concentrations, the osmotic pressure is again seen to increase roughly linearly with concentration. The increase in the osmotic pressure with increasing temperature is essentially proportional to the ratios of the temperatures (in °K).

Table 1-40

Freezing point and osmotic pressure of sea water at various salinities
(After DÉFANT, 1961)

Salinity (‰)	5	10	15	20	25	30	35	40
Freezing point (°C)	−0·267	−0·534	−0·802	−1·074	−1·349	−1·627	−1·910	−2·196
Osmotic pressure (atm)	3·23	6·44	9·69	12·98	16·32	19·67	23·12	26·59

Table 1-41

Vapor Pressure and Osmotic Equivalent of Seawater at 25°C
(From R. A. Robinson *J. Marine Biol. Assoc. U.K.*, **33**, 449 (1954), with permission of Marine Biological Association of the United Kingdom)[a]

Cl, ‰	*R*	NaCl	KCl	$CaCl_2$	$MgCl_2$	$MgSO_4$	Na_2SO_4	Sucrose	Urea	V.P. Lowering[b]	Osmotic Pressure, atm
10	0.02861	0.2861	0.2908	0.2039	0.2005	0.5056	0.2374	0.5065	0.5400	0.00946	12.87
11	0.02869	0.3156	0.3211	0.2240	0.2199	0.5597	0.2643	0.5560	0.5965	0.01042	14.19
12	0.02877	0.3452	0.3516	0.2441	0.2393	0.6138	0.2918	0.6053	0.6534	0.01139	15.51
13	0.02885	0.3751	0.3825	0.2642	0.2588	0.6675	0.3196	0.6546	0.7112	0.01237	16.85
14	0.02893	0.4050	0.4134	0.2481	0.2780	0.7206	0.3477	0.7040	0.7695	0.01334	18.19
15	0.02901	0.4352	0.4447	0.3043	0.2975	0.7738	0.3762	0.7534	0.8285	0.01433	19.55
16	0.02908	0.4653	0.4760	0.3243	0.3165	0.8264	0.4051	0.8025	0.8880	0.01532	20.91
17	0.02916	0.4957	0.5077	0.3445	0.3356	0.8786	0.4347	0.8516	0.9482	0.01631	22.28
18	0.02924	0.5263	0.5397	0.3645	0.3546	0.9300	0.4648	0.9008	1.010	0.01732	23.66
19	0.02932	0.5571	0.5719	0.3845	0.3738	0.9803	0.4954	0.9497	1.071	0.01833	25.06
20	0.02940	0.5880	0.6043	0.4044	0.3929	1.028	0.5264	0.9982	1.133	0.01936	26.47
21	0.02948	0.6191	0.6370	0.4243	0.4122	1.076	0.5578	1.047	1.197	0.02039	27.89
22	0.02956	0.6503	0.6698	0.4440	0.4313	1.123	0.5896	1.095	1.260	0.02142	29.33

[a] This column gives the relative pressure lowering $\Delta p/p^\circ = (p^\circ - p)/p^\circ$, where p is the vapor pressure of seawater and p^0 is the vapor pressure of pure water. $p^0 = 23.756$ mm at 25°C.
[b] A. B. Arons and C. F. Kientzler, *Trans. Am. Geophys. Union*, 35, 722 (1954), also give vapor pressure information for sea salt solutions.

Table 1-42

Osmotic Pressure (in atm) of Sea Salt Solutions
(From R. W. Stoughton and M. H. Lietzke, *J. Chem. Eng. Data*, **12**, 101 (1967), with permission of American Chemical Society)

	Wt % Salts								
T, °C	1.00	2.00	3.45[a]	5.00	7.50	10.00	15.00	20.00	25.00
25	7.11	14.29	25.15	37.49	59.30	83.97	144.93	228.59	348
40	7.42	14.93	26.34	39.35	62.41	88.53	152.81	239.86	362
60	7.80	15.70	27.74	41.51	65.98	94.69	161.53	252.06	376
80	8.13	16.37	28.94	43.32	68.69	97.82	168.27	261.17	386
100	8.42	16.94	29.92	44.79	71.17	100.97	173.16	267.47	393

A.4. pH and pε Relationships

In natural waters, the pH is determined primarily by CO_2 in equilibrium with various carbonates. Silicates also play a role in the buffering of naturally-occurring waters. In Tables I-43, & I-44 are outlined some of the more important equations used for calculating pH and buffering of natural waters.

Table I-43 also includes some of the more important expressions for determining redox potentials.

For a detailed discussion of pH, buffering and redox potentials,, particularly of sediments, see the standard treatises by Pourbaix (1949), Garrels and Christ (1965), Horne (1969) or Stumm and Morgan (1970).

Table 1-43

pH **and** pε

$pH = -\log\{H^+\}$		$p\epsilon = -\log\{e\}$	
Acid–base reaction: $HA + H_2O = H_3O^+ + A^-$; K_1	(1*a*)	Redox reaction: $Fe^{3+} + \frac{1}{2}H_2(g) = Fe^{2+} + H^+$; K_1	(1*b*)
Reaction (1*a*) is composed of two steps:		Reaction (1*b*) is composed of two steps:	
$HA = H^+ + A^-$; K_2	(2*a*)	$Fe^{3+} + e = Fe^{2+}$; K_2	(2*b*)
$H_2O + H^+ = H_3O^+$; K_3	(3*a*)	$\frac{1}{2}H_2(g) = H^+ + e$; K_3	(3*b*)
According to thermodynamic convention: $K_3 = 1$		According to thermodynamic convention: $K_3 = 1$	
Thus: $K_1 = K_2 = K_2K_3 = \{H^+\}\{A^-\}/\{HA\}$	(4*a*)	Thus: $K_1 = K_2 = K_2K_3 = \{Fe^{2+}\}/\{Fe^{3+}\}\{e\}$	(4*b*)
or $pH = pK + \log[\{A^-\}/\{HA\}]$	(5*a*)	or $p\epsilon = p\epsilon^\circ + \log[\{Fe^{3+}\}/\{Fe^{2+}\}]$	(5*b*)
Since $pK = -\log K = \Delta G^\circ/2.3RT$		Since $p\epsilon^\circ = \log K = -\Delta G^\circ/2.3RT$	
$pH = \Delta G^\circ/2.3RT + \log[\{A^-\}/\{HA\}]$	(6*a*)	$p\epsilon = -\Delta G^\circ/2.3RT + \log[\{Fe^{3+}\}/\{Fe^{2+}\}]$	(6*b*)
or for the transfer of 1 mole of H^+ from acid to H_2O:		or for the transfer of 1 mole of e to oxidant from H_2:	
$\Delta G/2.3RT = \Delta G^\circ/2.3RT + \log[\{A^-\}/\{HA\}]$	(7*a*)	$-\Delta G/2.3RT = -\Delta G^\circ/2.3RT + \log[\{Fe^{3+}\}/\{Fe^{2+}\}]$	(7*b*)
For the general case where n protons are transferred:		For the general case where n electrons are transferred:	
$H_nB + nH_2O = nH_3O^+ + B^{-n}$; β^*	(8*a*)	$ox + \{n/2\}H_2 = red + nH^+$; $ox + ne = red$; K^*	(8*b*)
$pH = \{1/n\}p\beta^* + \{1/n\}\log[\{B^{-n}\}/\{H_nB\}]$	(9*a*)	$p\epsilon = \{1/n\}\log K^* + \{1/n\}\log[\{ox\}/\{red\}]$; $p\epsilon = p\epsilon^\circ + \{1/n\}\log[\{ox\}/\{red\}]$	(9*b*)
$pH = \Delta G/n2.3RT$			
$= \Delta G^\circ/n2.3RT + \{1/n\}\log[\{B^{-n}\}/\{H_nB\}]$	(10*a*)	$p\epsilon = -\Delta G^\circ/n2.3RT + \{1/n\}\log[\{ox\}/\{red\}]$	(10*b*)
$\Delta G = -nFE$ (E = acidity potential)	(11*a*)	$\Delta G = -nFE_H$ (E_H = redox potential)	(11*b*)
$pH = -E/\{2.3RTF^{-1}\}$		$p\epsilon = E_H/\{2.3RTF^{-1}\}$	
$= -E^\circ/\{2.3RTF^{-1}\} + \{1/n\}\log[\{B^{-n}\}/\{H_nB\}]$	(12*a*)†	$= E^\circ/2.3RTF^{-1} + \{1/n\}\log[\{ox\}/\{red\}]$	(12*b*)†
Acidity potential:		Redox potential (Peters-Nernst equation):	
$E = E^\circ + \{2.3RT/nF\}\log[\{H_nB\}/\{B^{-n}\}]$	(13*a*)	$E_H = E_H^\circ + \{2.3RT/nF\}\log[\{ox\}/\{red\}]$	(13*b*)

† At 25 C, $2.3RTF^{-1} = 0.059$ (V/eq). From (10) and (12): 25°C, $p\epsilon = E/0.059$, $p\epsilon^\circ = E_H^\circ/0.059$.

Most frequently used equations for calculating pH and pε (Stumm and Morgan, 1970, page 304).

Table 1-44

Buffering of Aqueous Carbonate System

Titration Curve	Buffer Intensity
I. C_T = constant Addition of strong acid or base:	
$C_B - C_A = C_T(\alpha_1 + 2\alpha_2) + [OH^-] - [H^+]$ (1) $dC_B = d[Alk]$	$\frac{d[Alk]}{dpH} = \beta_{C_T}^{C_B} = 2.3\{C_T[\alpha_1(\alpha_0 + \alpha_2) + 4\alpha_2\alpha_0] + [H^+] + [OH^-]\}$ (2) $\beta_{C_T}^{C_B} \approx 2.3\alpha_1(\alpha_0 + \alpha_2)C_T$ (3)
II. [Alk] = constant Addition or removal of CO_2:	
$C_T = ([Alk] - [OH^-] + [H^+])/(\alpha_1 + 2\alpha_2)$ (4) $dC_T = \frac{1}{2}d[Acy]$	$\frac{d[Acy]}{dpH} = \beta_{Alk}^{2C_T} \simeq -4.6\,\frac{\alpha_1\alpha_0 + \alpha_1\alpha_2 + 4\alpha_2\alpha_0}{(\alpha_1 + 2\alpha_2)^2}\,[Alk]$ (5) $\beta_{Alk}^{2C_T} \approx -4.6[(\alpha_0 + \alpha_2)/\alpha_1][Alk]$ (6)
III. [Acy] = constant Addition or removal of $NaCO_3(CaCO_3)$:	
$C_T = ([Acy] - [H^+] + [OH^-])/(\alpha_1 + 2\alpha_0)$ (7) $dC_T = \frac{1}{2}d[Alk]$	$\frac{d[Alk]}{dpH} = \beta_{Acy}^{2C_T} \simeq 4.6\,\frac{\alpha_1\alpha_0 + \alpha_1\alpha_2 + 4\alpha_2\alpha_0}{(\alpha_1 + 2\alpha_0)^2}\,[Acy]$ (8) $\beta_{Acy}^{2C_T} \approx 4.6[(\alpha_0 + \alpha_2)/\alpha_1][Acy]$ (9)
IV. p_{CO_2} = constant Addition of strong base or strong acid:	
$C_B - C_A = (K_H(\alpha_1 + 2\alpha_2)/\alpha_0)p_{CO_2} + [OH^-] - [H^+]$ (10) $dC_B = d[Alk]$	$\frac{d[Alk]}{dpH} = \beta_{pCO_2}^{C_B} = 2.3\left\{K_H p_{CO_2}\,\frac{\alpha_1(\alpha_0 + \alpha_2) + 4\alpha_2\alpha_0 + (\alpha_1 + 2\alpha_2)^2}{\alpha_0} + [H^+] + [OH^-]\right\}$ (11) $\beta_{pCO_2}^{C_B} \approx 2.3K_H p_{CO_2}/\alpha_0 \approx 2.3C_T$ (12)

Principle equations for evaluating buffering capacity of aqueous carbonate systems (Stumm and Morgan, 1970, page 138).

B.1 Solubility of Oxygen

An extensive discussion of the problem of the solubility of oxygen in natural waters is presented in Vol. I of the treatise by Hutchinson on Limnology. See also the recent data by Carpenter (1966) on the solubility of oxygen in pure water and natural waters. Table I-47 shows the smoothed data for the oxygen solubility in saline waters of varying chlorinity (0.0 to 20.0 ‰) for 20.94% atmosphere oxygen at 100% relative humidity.

Other solubility data for oxygen as a function of chlorinity and temperature have been reported by Green and Carritt (1967). One of the interesting results by these authors is the observation that while the solubility of oxygen in seawater decreases essentially exponentially with concentration, the salting out was observed to decrease with increasing temperature, contrary to the predictions by the Debye theory.

Although the problems associated with determining accurately the solubilities of gases in water are not inconsiderable, at least the problem belongs in the realm of standard classical physical chemistry and is amenable to straightforward experimentation, the accuracy and , precision of which can usually be improved by sheer preseverance. Far more difficult is the problem of rates of approach to various equilibria, particularly in solubility phenomena. Hutchinson has reviewed briefly some of the known aspects of the rate of changes in oxygen concentration. Relatively little has been done on the effects of temperature on this process. The reader is referred to the data by Adeney and Becker (reported by Hutchinson [1957] loco cit., p. 589).

Table 1-45

SOLUBILITY OF OXYGEN IN WATER

Some early determinations give slightly high values at lower temperatures (see Bohr and Bock, below). Recent determinations indicate that the lower values are probably correct (Morrison and Billet, also table following)

β = ml O_2 (at S.T.P.) absorbed by 1 ml H_2O at a pressure of O_2 of 1 atm.

	β				β		
t°	Winkler 1891	Morrison and Billet 1952	Bohr & Bock 1891	t°	Winkler 1891	Morrison and Billet 1952	Bohr & Bock 1391
0	0.0489	-	0.0496	40	0.0231	0.0232	0.0233
5	0.0429	-	0.439	50	0.0209	0.0208	0.207
10	0.0380	-	0.390	60	0.0195	0.0196	0.189
15	0.0342	0.0341	0.350	70	0.0183	0.0186	0.178
20	0.0310	0.0308	0.317	80	0.0176	0.0177	0.172
25	0.0283	0.0284	0.290	90	0.0172	-	0.169
30	0.0261	0.0265	0.268	100	0.0170	-	0.168

SOLUBILITY OF OXYGEN IN WATER IN CONTACT WITH AIR

These results, of considerable commercial and biological importance have been measured directly and calculated from data on pure oxygen. Morgan and Richardson, 1930 found that the values obtained in these two ways are the same. Extensive data upon the rate of solution of atmospheric oxygen and nitrogen in water are given in a series of papers by Adeney and Becker 1916-1920, 1919, 1920 and 1921.

Recent data again tend toward lower solubility values (see also table above). The following table was compiled by Truesdale, Downing and Lowden, 1955 for comparison of the various results these authors found the solubility at one atmosphere pressure (air and water vapor) to be: $C = 14.161 - 0.3943t + 0.007714t^2 - 0.0000646t^3$ where C is the concentration of oxygen in water in parts per million, and t is °C.

t°	Fox 1909	Winkler 1889[a]	Winkler 1891[b]	Roscoe & Lunt 1889	Jacobsen 1905[c]	Bohr & Bock, 1891	Royal Comm. 1908[d]	Truesdale, Downing and Lowden 1954, 1955
0	14.65	14.56	14.55	-	14.30	14.79	-	14.16
5	12.80	12.72	12.73	12.41	12.48	13.02	-	12.37
10	11.33	11.27	11.24	11.11	11.01	11.58	11.11	10.92
15	10.15	10.09	10.06	9.98	9.85	10.32	9.98	9.76
20	9.17	9.10	9.10	8.96	8.91	9.30	8.99	8.84
25	8.38	8.29	8.24	8.25	8.16	8.46	8.18	8.11
30	7.63	7.53	7.52	-	-	7.71	-	7.52
35	7.10	-	-	-	-	7.08	-	7.02

[a]titrametric analysis [b]gasometric [c]as quoted by Fox, 1909 [d]Royal Commission on Sewage Disposal, 5th Report, 1909, Appendix 6, Part XIII

Table 1-46

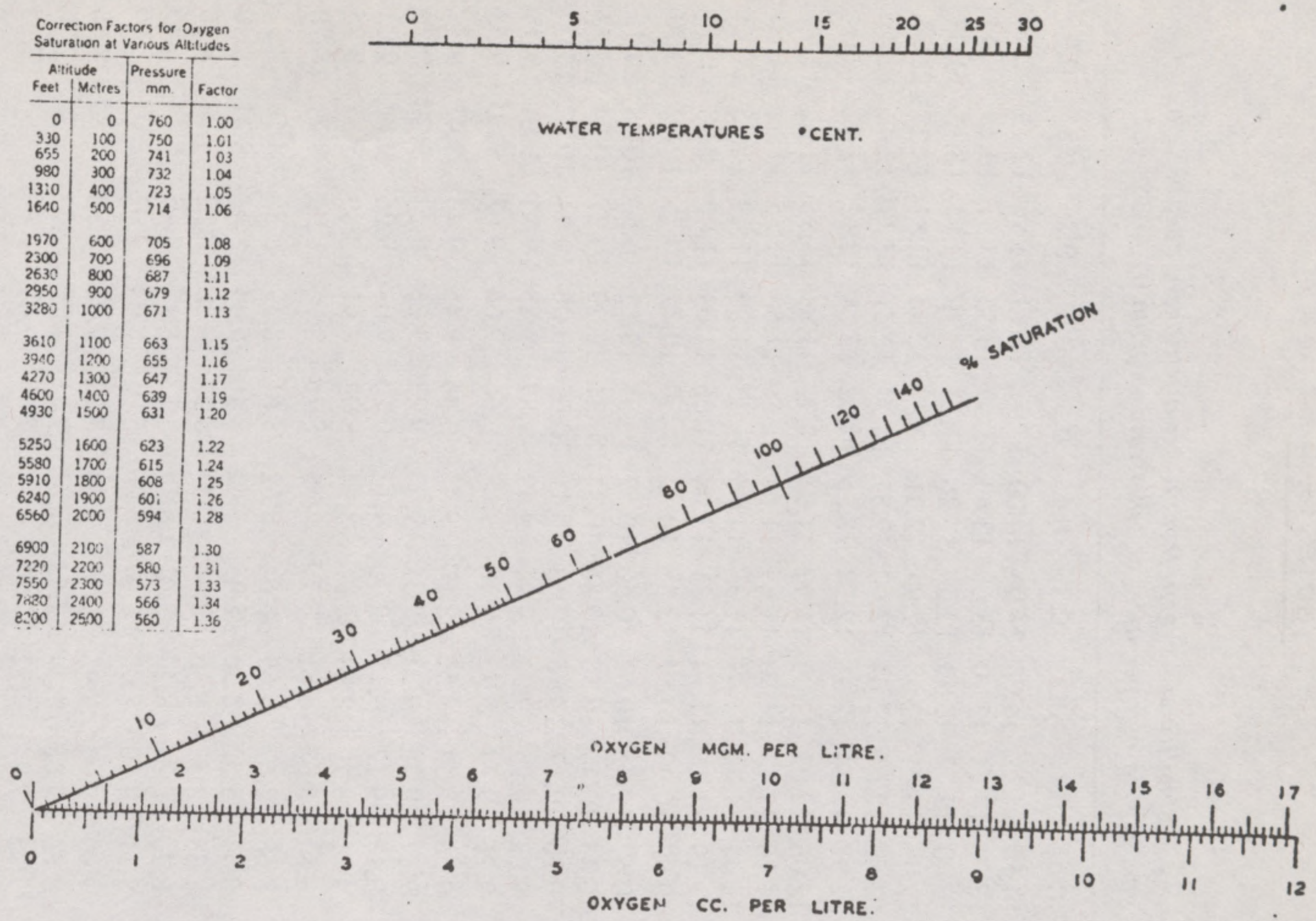
*Solubility of oxygen, from a wet atmosphere at a pressure of 760 mm. Hg, in mg. per liter, at temperatures from 0° to 35° C.**

Temp.	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
0	14.16	14.12	14.08	14.04	14.00	13.97	13.93	13.89	13.85	13.81
1	13.77	13.74	13.70	13.66	13.63	13.59	13.55	13.51	13.48	13.44
2	13.40	13.37	13.33	13.30	13.26	13.22	13.19	13.15	13.12	13.08
3	13.05	13.01	12.98	12.94	12.91	12.87	12.84	12.81	12.77	12.74
4	12.70	12.67	12.64	12.60	12.57	12.54	12.51	12.47	12.44	12.41
5	12.37	12.34	12.31	12.28	12.25	12.22	12.18	12.15	12.12	12.09
6	12.06	12.03	12.00	11.97	11.94	11.91	11.88	11.85	11.82	11.79
7	11.76	11.73	11.70	11.67	11.64	11.61	11.58	11.55	11.52	11.50
8	11.47	11.44	11.41	11.38	11.36	11.33	11.30	11.27	11.25	11.22
9	11.19	11.16	11.14	11.11	11.08	11.06	11.03	11.00	10.98	10.95
10	10.92	10.90	10.87	10.85	10.82	10.80	10.77	10.75	10.72	10.70
11	10.67	10.65	10.62	10.60	10.57	10.55	10.53	10.50	10.48	10.45
12	10.43	10.40	10.38	10.36	10.34	10.31	10.29	10.27	10.24	10.22
13	10.20	10.17	10.15	10.13	10.11	10.09	10.06	10.04	10.02	10.00
14	9.98	9.95	9.93	9.91	9.89	9.87	9.85	9.83	9.81	9.78
15	9.76	9.74	9.72	9.70	9.68	9.66	9.64	9.62	9.60	9.58
16	9.56	9.54	9.52	9.50	9.48	9.46	9.45	9.43	9.41	9.39
17	9.37	9.35	9.33	9.31	9.30	9.28	9.26	9.24	9.22	9.20
18	9.18	9.17	9.15	9.13	9.12	9.10	9.08	9.06	9.04	9.03
19	9.01	8.99	8.98	8.96	8.94	8.93	8.91	8.89	8.88	8.86
20	8.84	8.83	8.81	8.79	8.78	8.76	8.75	8.73	8.71	8.70
21	8.68	8.67	8.65	8.64	8.62	8.61	8.59	8.58	8.56	8.55
22	8.53	8.52	8.50	8.49	8.47	8.46	8.44	8.43	8.41	8.40
23	8.38	8.37	8.36	8.34	8.33	8.32	8.30	8.29	8.27	8.26
24	8.25	8.23	8.22	8.21	8.19	8.18	8.17	8.15	8.14	8.13
25	8.11	8.10	8.09	8.07	8.06	8.05	8.04	8.02	8.01	8.00
26	7.99	7.97	7.96	7.95	7.94	7.92	7.91	7.90	7.89	7.88
27	7.86	7.85	7.84	7.83	7.82	7.81	7.79	7.78	7.77	7.76
28	7.75	7.74	7.72	7.71	7.70	7.69	7.68	7.67	7.66	7.65
29	7.64	7.62	7.61	7.60	7.59	7.58	7.57	7.56	7.55	7.54
30	7.53	7.52	7.51	7.50	7.48	7.47	7.46	7.45	7.44	7.43
31	7.42	7.41	7.40	7.39	7.38	7.37	7.36	7.35	7.34	7.33
32	7.32	7.31	7.30	7.29	7.28	7.27	7.26	7.25	7.24	7.23
33	7.22	7.21	7.20	7.20	7.19	7.18	7.17	7.16	7.15	7.14
34	7.13	7.12	7.11	7.10	7.09	7.08	7.07	7.06	7.05	7.05
35	7.04	7.03	7.02	7.01	7.00	6.99	6.98	6.97	6.96	6.95

* From Truesdale, Downing, and Lowden (1955).

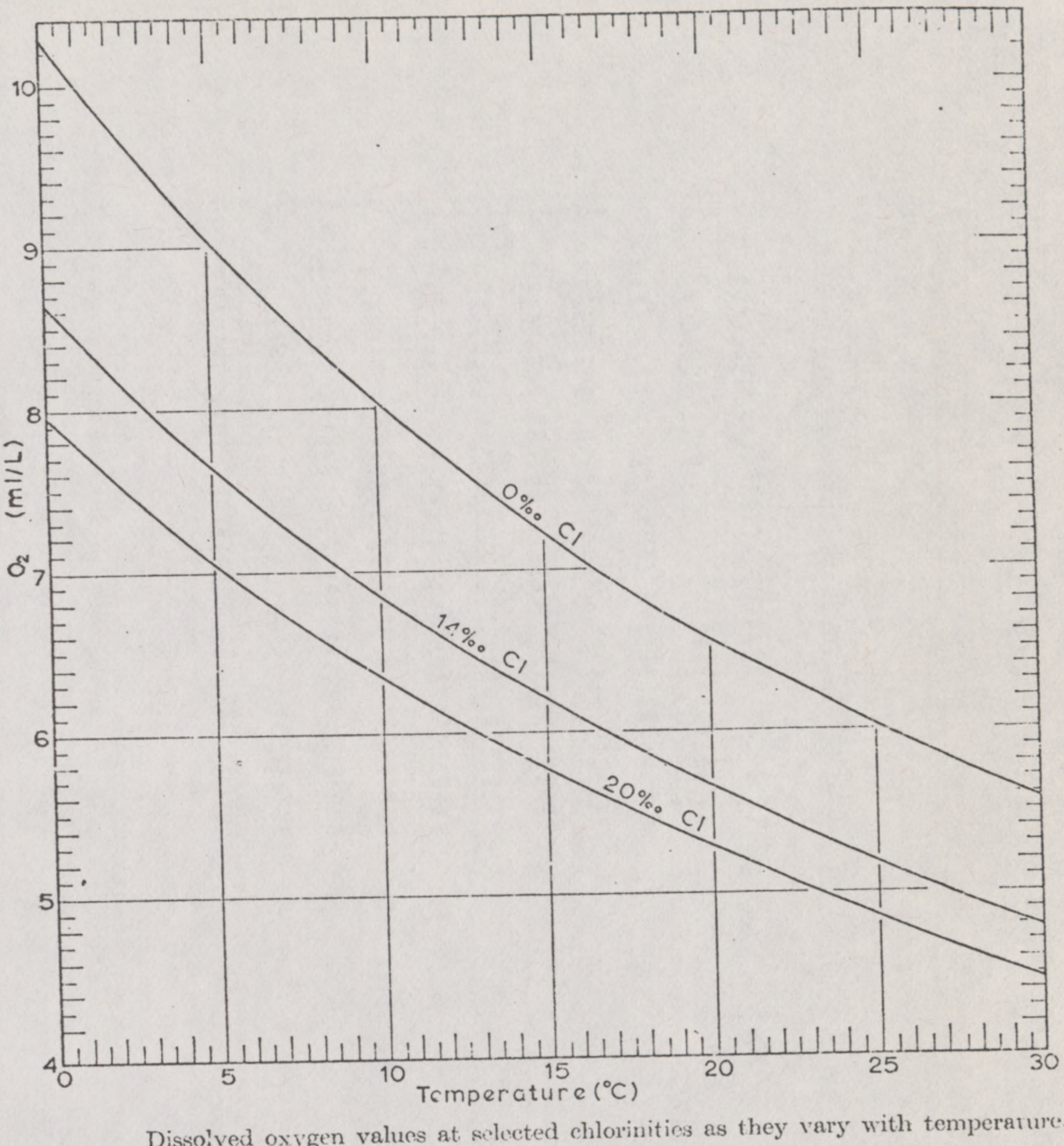
Correction Factors for Oxygen Saturation at Various Altitudes

Altitude Feet	Altitude Metres	Pressure mm.	Factor
0	0	760	1.00
330	100	750	1.01
655	200	741	1.03
980	300	732	1.04
1310	400	723	1.05
1640	500	714	1.06
1970	600	705	1.08
2300	700	696	1.09
2630	800	687	1.11
2950	900	679	1.12
3280	1000	671	1.13
3610	1100	663	1.15
3940	1200	655	1.16
4270	1300	647	1.17
4600	1400	639	1.19
4930	1500	631	1.20
5250	1600	623	1.22
5580	1700	615	1.24
5910	1800	608	1.25
6240	1900	601	1.26
6560	2000	594	1.28
6900	2100	587	1.30
7220	2200	580	1.31
7550	2300	573	1.33
7880	2400	566	1.34
8200	2500	560	1.36



Nomogram for determining O_2 saturation at different temperatures and altitudes (Mortimer).

Figure 1-15



Dissolved oxygen values at selected chlorinities as they vary with temperature. (Drawn from data of Fox as given by RICHARDS, 1965.)

Figure 1-16

Table 1-47

Interpolated values of oxygen solubility (μg-at./liter) from an atmosphere of 20.94% O_2 and 100% relative humidity

Temp. (C)	Chlorinity (‰)										
	0.0	2.0	4.0	6.0	8.0	10.0	12.0	14.0	16.0	18.0	20.0
0.5	902	879	857	835	814	794	774	756	737	720	703
1.0	889	867	846	825	804	785	765	747	729	711	694
2.0	864	844	823	804	784	765	747	729	711	694	677
3.0	840	821	802	783	764	746	728	711	694	677	660
4.0	817	799	780	762	745	727	710	693	677	660	644
5.0	796	778	760	743	725	709	692	676	660	644	629
6.0	775	758	741	724	707	691	675	659	644	629	614
7.0	756	739	722	706	690	674	659	643	629	614	600
8.0	737	721	704	689	673	658	643	628	614	600	586
9.0	720	704	688	672	657	642	628	614	600	586	573
10.0	703	688	672	657	642	627	613	600	586	573	561
11.0	688	672	657	642	627	613	600	586	573	561	549
12.0	674	658	643	628	614	600	586	573	561	549	537
13.0	659	644	629	614	600	587	574	561	549	537	526
14.0	645	630	616	601	588	574	562	549	538	526	515
15.0	631	617	603	589	576	563	550	538	527	516	505
16.0	618	603	590	577	564	551	539	528	516	506	495
17.0	604	591	578	565	553	540	529	517	507	496	486
18.0	591	578	566	554	542	530	519	508	497	487	477
19.0	579	567	555	543	531	520	509	498	488	478	468
20.0	568	556	544	532	521	510	499	489	479	469	460
21.0	556	545	533	522	511	500	490	480	470	461	452
22.0	546	534	523	512	501	491	481	471	462	453	444
23.0	535	524	513	502	492	482	472	463	454	445	436
24.0	525	514	504	493	483	473	464	455	446	437	429
25.0	516	505	494	484	474	465	455	447	438	430	421
26.0	506	496	485	475	466	457	447	439	430	422	414
27.0	497	487	477	467	458	448	440	431	423	415	407
28.0	488	478	468	459	450	441	432	424	415	408	400
29.0	480	470	460	451	442	433	425	416	408	401	393
30.0	471	462	453	443	435	426	418	410	402	394	387
31.0	464	454	445	436	427	419	411	403	395	388	381
32.0	456	447	438	429	420	412	404	396	389	382	375
33.0	448	439	430	422	414	406	398	390	383	376	369
34.0	441	432	423	415	407	399	391	384	377	370	363
35.0	433	425	417	408	400	393	385	378	371	364	358
36.0	426	418	410	402	394	387	379	372	365	359	352

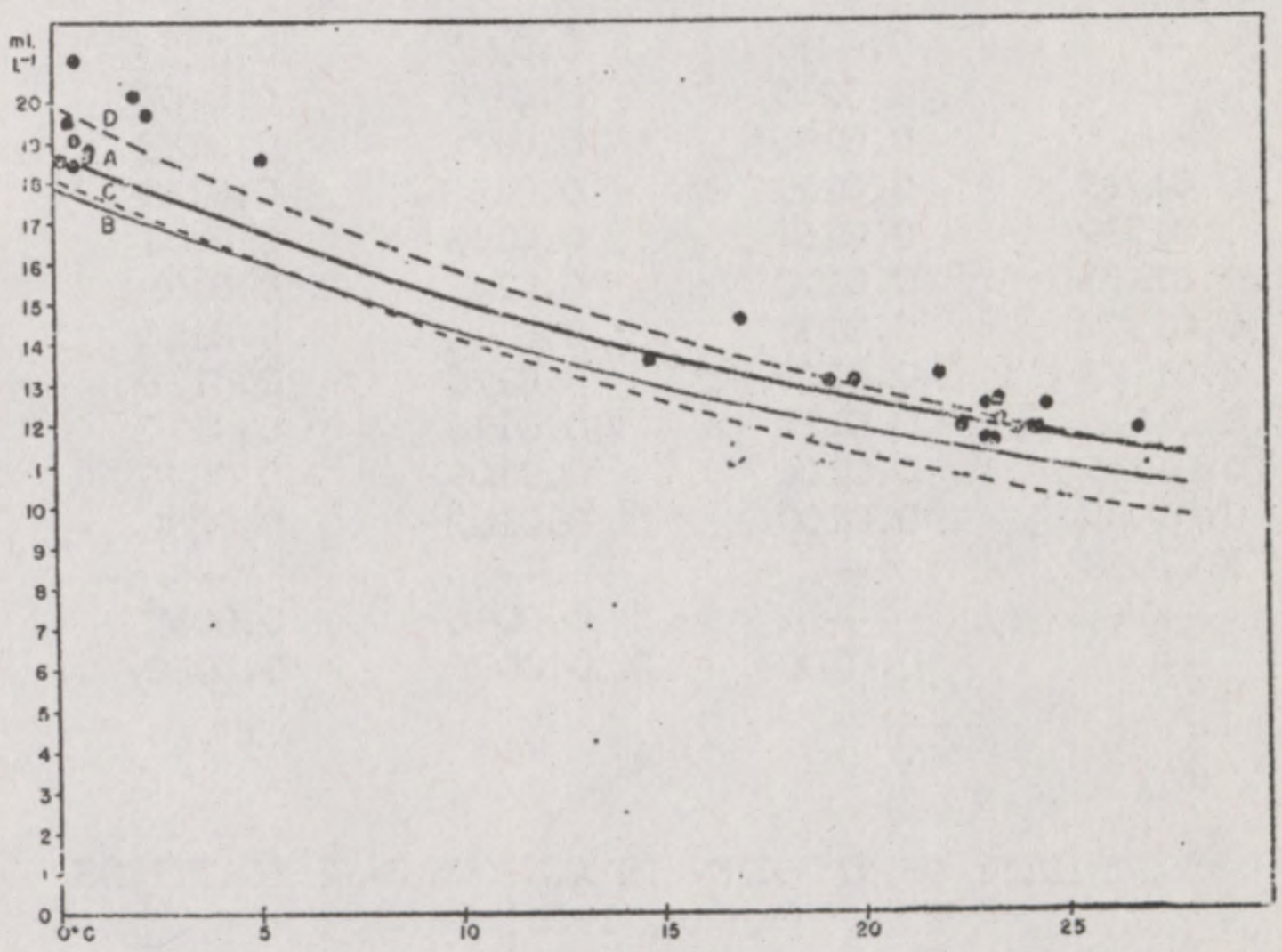
Oxygen Solubility Data as a Function of Temperature and Chlorinity.

(Data by Carpenter, 1966).

Solubility of Nitrogen

Because of its chemical relative inertness (as a molecular species), relatively little interest attaches to the solubility of nitrogen. Various estimates of the solubility of nitrogen in water as a function of temperature are shown in Figure 1-17

One important aspect of nitrogen solubility is the possibility of supersaturation. Mortality in salmon and trout have been ascribed to gas bubble disease. With an increase in temperature, the originally saturated water becomes supersaturated and the effect of this supersaturation has been discussed for the Chinook salmon "jacks", by Snyder and Blahm (1971).



The solubility of molecular nitrogen (ml. per liter) in waters at various temperatures.. A, solubility computed for dry air at sea level from the determinations of Fox; B, solubility computed for wet air at an elevation of 278 m.; C, curve B corrected for the apparent supersaturation effect in Fox's experiments; D, curve drawn by eye, parallel to C, to fit the determinations made by Birge and Juday on surface waters of Wisconsin Lakes, and presumably a suitable working standard for estimation of saturation in vertical series of analyses by these investigators.

Figure 1-17

24-642 O - 73 - pt. 2 - 24

Table 1-48

NITROGEN N_2

SOLUBILITY IN WATER
(Winkler, 1891; Bohr and Bock, 1891; Morrison and Billett, 1952)

Results in reasonable agreement with these are given by Braun, 1900; Hufner, 1906-07; Bohr, 1910; Muller, 1912-13; von Hamel, 1915; Cassuto, 1904; Orcutt and Seevers, 1936, 1937; Van Slyke, 1939.

Of the several determinations, Winkler's are generally lowest; above 35° the recent values of Morrison and Billet are considerably higher than the older work.

β = Bunsen absorption coefficient = ml N_2 (at 0°, 760 mm.) dissolved by 1 ml. H_2O when partial pressure N_2 = 760 mm.

β' = "Solubility" = ml N_2 (at 0°, 760 mm) dissolved by 1 ml. H_2O when total pressure (N_2 + H_2O) = 760 mm.

q = gms. N_2 per 100 gms. H_2O when total pressure = 760 mm.

	(M.&B. 1952)	(B.&B. 1891)	(W., 1891)		
t°	β	β	β	β'	q
0	--	0.0239	0.0235	0.0233	0.00239
5	--	0.0215	0.0208	0.0206	0.00259
10	--	0.0196	0.0186	0.0183	0.00230
15	0.01745	0.0179	0.0168	0.0165	0.00208
20	0.01599	0.0164	0.0154	0.0151	0.00189
25	0.01485	0.0150	0.0143	0.0139	0.00174
30	0.01377	0.0138	0.0134	0.0128	0.00161
35	0.01283	0.0127	0.0125	0.0118	0.00148
40	0.01215	0.0118	0.0118	0.0110	0.00139
50	0.01125	0.0106	0.0109	0.0096	0.00121
60	0.01085	0.0100	0.0102	0.0082	0.00105
70	0.01058	--	--	--	--
80	--	--	0.0096	0.0051	0.00069
100	--	0.0100	0.0095	0.0000	0.00000

SOLUBILITY OF NITROGEN IN AQUEOUS SALT SOLUTIONS
(Braun, 1900)

	Coefficient of Absorption of N_2 in Barium Chloride Solutions of:				
t°	13.83%	11.92%	6.90%	3.87%	3.33%
5	0.0127	0.0137	0.0160	0.0180	0.0183
10	0.0117	0.0125	0.0147	0.0166	0.0168
15	0.0104	0.0114	0.0132	0.0148	0.0150
20	0.0092	0.0098	0.0118	0.0132	0.0135
25	0.0078	0.0086	0.0104	0.0114	0.0119

	Coefficient of Absorption of N_2 in Sodium Chloride Solutions of:				
t°	11.73%	8.14%	6.4%	2.12%	0.67%
5	0.0102	0.0127	0.0138	0.0179	0.0200
10	0.0093	0.0113	0.0126	0.0164	0.0185
15	0.0081	0.0101	0.0113	0.0147	0.0164
20	0.0066	0.0087	0.0098	0.0131	0.0148
25	0.0047	0.0075	0.0083	0.0113	0.0130

Table I-48

SOLUBILITY OF NITROGEN IN SALT SOLUTIONS
(Morrison and Billet, 1952)

Values of "salting-out" constants $k = \frac{\log So/S}{C}$

So = Solubility in pure H_2O (β)

C = Moles salt per 1000 gms. H_2O.

		k		
t°	So	NaCl	LiCl	KI
12.6	0.01837	0.145	0.125	0.134
30	0.01377	0.121	0.095	0.100
50	0.01125	0.106	0.084	0.086
72	0.1054	0.106	0.092	0.084

SOLUBILITY OF NITROGEN IN SEA WATER
(Fox, 1909a)

Before using the sample of sea water for the solubility determinations it was found necessary to add acid, otherwise the CO_2 could not be boiled out or the precipitation of neutral carbonates prevented. The very small amount of acid was titrated back, using phenolphthaleine as indicator.

The results are in terms of number of cc. of nitrogen (containing argon) absorbed by 1000 cc. of sea water from a free dry atmosphere of 760 mm. pressure.

The calculated formula expressing the solubility is:

$$1000\underline{a} = 18.639 - 0.4304\underline{t} + 0.007453\underline{t}^2 - 0.0000549\underline{t}^3 - Cl(0.2172 - 0.007187\underline{t} + 0.0000952\underline{t}^2).$$

Parts Chlorine per 1000	t°=0°	4°	8°	12°	16°	20°	24°	28°
0	18.64	17.02	15.63	14.45	13.45	12.59	11.86	11.25
4	17.74	16.27	14.98	13.88	12.94	12.15	11.46	10.89
8	16.90	15.51	14.32	13.30	12.44	11.70	11.07	10.52
12	16.03	14.75	13.66	12.72	11.93	11.25	10.67	10.16
16	15.18	14	13	12.15	11.73	10.81	10.27	9.80
20	14.31	13.27	12.34	11.57	10.92	10.36	9.87	9.44

A critical examination of the available data upon the Solubility of Nitrogen in pure water and in sea water has been made by Coste, 1917, 1927. It is concluded that "When proper allowances have been made for the effect of argon in the solubility of atmospheric nitrogen, considerable uncertainty exists as to the absorption coefficients of both this mixed gas and pure nitrogen in distilled Water. A similar uncertainty exists in the case of sea water.

B.3. Solubility of Argon and Carbon Monoxide

Solubility data for argon and for carbon monoxide are shown in the Tables included, taken from the solubility listings by Seidell (edited by Linke, 1958).

Table 1-49

ARGON A

THE SOLUBILITY OF ARGON IN WATER

The data of Lanning, 1930 (0°-40°), Morrison and Johnstone, 1954 (10°-80°), Friedman, 1954 (15°, 25°), and Eucken and Hertzberg, 1950 (0°, 20°) are in excellent agreement. The values listed below were read from a smooth curve drawn through the combined data. The average deviation of the original data from the curve is 0.0002.

The results of various earlier workers were not in agreement with each other and were up to 20% higher than these. For earlier work, see: Ramsey, 1895; Estreicher, 1899; Winkler, 1897, 1905; Von Antropoff, 1910, 1919; Valentiner, 1927, 1930; Åkerlof, 1935; Behnke and Yarbrough, 1939.

α = Bunsen adsorption coefficient. α = ml. of gas (measured at S.T.P.) dissolved by 1 ml. of solvent when the partial pressure of the gas is 1 atmosphere. - See page 2 .

°C	α	°C	α	°C	α
0	0.0528	30	0.0288	60	0.0209
5	.0466	35	.0269	65	.0202
10	.0413	40	.0251	70	.0196
15	.0370	45	.0237	75	.0189
20	.0337	50	.0226	80	.0184
25	.0311	55	.0217		

Table 1-50

CARBON MONOXIDE CO

SOLUBILITY IN WATER

The data below are determined by Winkler, 1901. In the following table are some results which do not agree too well with these. See also O'Brien and Parker, 1922. There is no very recent work.

β = Vol. of CO (measured at 0°, 760mm) absorbed by 1 volume of liquid at a partial pressure of CO of 760mm.
β' = Vol. of CO (measured at 0°, 760mm) absorbed by 1 volume of liquid at a total pressure (CO + vapor) of 760mm.
q = Grams of CO dissolved by 100 gms. H_2O at a total pressure of 760mm.

t°	β, "Absorp. Coef."	β', "Solubility."	q	t°	β, "Absorp. Coef."	β', "Solubility."	q
0	0.03537	0.03516	0.0044	40	0.01775	Q.01647	0.0021
5	0.03149	0.03122	0.0039	50	0.01615	0.01420	0.0018
10	0.02816	0.02782	0.0035	60	0.01488	0.01196	0.0015
15	0.02543	0.02501	0.0031	70	0.01440	0.00998	0.0013
20	0.02319	0.02266	0.0028	80	0.01430	0.00762	0.0010
25	0.02142	0.02076	0.0026	90	0.01420	0.00438	0.0006
30	0.01998	0.01915	0.0024	100	0.01410	0.00000	0.0000

SOLUBILITY OF CARBON MONOXIDE IN PHYSIOLOGICAL SOLUTIONS

SOLUBILITY OF PURE CARBON MONOXIDE IN SERUM AND IN PLASMA (O'Brien and Parker, 1922)

As a check on the determinations the authors also determined the solubility of carbon monoxide in water and obtained results in good agreement with those of Winkler.

t°	Cc. of CO absorbed per 1.0 cc. of Beef serum	Sheep serum	Human serum	Beef plasma
15	0.203	0.0206	....	0.0198
20	0.181	0.0187	0.0180	0.0181
25	0.161	0.0156	0.0183	0.0169
30	0.145	0.0153	0.0158	0.0147
37	0.129	0.0144	0.0142	0.0134

Data for the solubility of CO in ox blood and ox serum at 25° are given by Findlay and Creighton, 1910-11.

Data for the influence of time on the absorption of CO by blood are given by Grehaut (1894). The author passed air containing from one part CO per 1000 to one part CO per 60,000, through 100 cc. portions of blood and found that the maximum absorption, 18.3 cc. CO per 100 cc. of blood (for the 1 : 1000 mixture) occurred in three hours.

Data for the solubility of CO in aqueous hemoglobin solutions are given by Hufner (1895) and Hufner and Kulz (1895).

Treatment of CO_2-Carbonate Systems (with some notes on Calcium sulphate)

In this section, data are shown for the solubility of CO_2 in pure water and, where available, in salt solutions including seawater.

A general treatment of carbonate equilibria has been presented by Garrels and Christ (1965). The discussion is divided by the authors into the following set of typical conditions:

1. Pure calcite and pure water, with negligible gas phase present.
2. Calcium in pure water system open to CO_2 (i.e., in contact with a reservoir such as the atmosphere of fixed partial pressure CO_2).
3. Equilibrium relations with fixed quantity of dissolved carbonate species, but pH arbitrarily fixed (controlled by other reactions).
4. Equilibrium in a system connected to an external reservoir of fixed partial pressure of CO_2 but with pH arbitrarily determined.
5. Equilibrium resulting from addition of $CaCO_3$ to a system originally open to a CO_2 reservoir but closed to that reservoir before addition to $CaCO_3$.

For System 1, the temperature dependence can be illustrated. Table 3.2 shows carbonate equilibria (see Garrels and Christ, page 89) at temperatures from 0 to 80° C. Lee has also dealt with the carbonate equilibria; see particularly the survey article (1968). Additional data for carbonate systems were discussed by Kramer (1967). Kramer's data are interesting as they show actual data and calculated values, revealing a complete lack of agreement between theory and experiment. Figures 1-18, 19, 20, 21, 22, 23, and 24 are taken from Kramer's paper.

Table 1-51

Solubility of CO_2 in pure water

Temp., °C.	0.03%	0.033%	0.044%	Temp., °C.	0.03%	0.033%	0.044%
0	1.00	1.10	1.47	16	0.57	0.62	0.84
1	0.96	1.06	1.41	17	0.55	0.60	0.81
2	0.93	1.02	1.36	18	0.54	0.59	0.79
3	0.89	0.99	1.30	19	0.52	0.58	0.76
4	0.86	0.94	1.26	20	0.51	0.56	0.74
5	0.83	0.91	1.22	21	0.49	0.54	0.72
6	0.80	0.88	1.17	22	0.48	0.52	0.70
7	0.78	0.86	1.14	23	0.46	0.51	0.68
8	0.75	0.82	1.10	24	0.45	0.50	0.66
9	0.72	0.79	1.06	25	0.44	0.48	0.64
10	0.70	0.76	1.02	26	0.42	0.46	0.62
11	0.67	0.74	0.98	27	0.41	0.45	0.60
12	0.65	0.72	0.95	28	0.40	0.44	0.59
13	0.63	0.69	0.92	29	0.39	0.43	0.57
14	0.61	0.67	0.89	30	0.38	0.42	0.56
15	0.59	0.65	0.87				

Table 1-52

CARBON DIOXIDE CO_2

SOLUBILITY IN WATER

(1) Bohr (1899); Geffcken (1904); Just (1901); (2) Morgan and Payne, 1930; (3) Markham and Kobe, 1941, 1941a; (4) v. Kiss, Lajtai and Thury, 1937; (5) Showalter and Ferguson, 1936; (6) Gatterer, 1926; (7) Kobe and Williams, 1935; (8) Orcutt and Seevers, 1936, 1937; (9) Kobe and Williams, 1935; (10) Shedlovsky and McInnes, 1935; (11) Curry and Hazelton, 1938; (12) Morrison and Billett, 1952.

The data listed below are those of Bohr (1899), Geffcken (1904) and Just (1901) when unmarked (unmarked values of q and β are not necessarily from the same author). The recent determinations of Morrison and Billett (1952) were plotted and the values of β given in parentheses ( ) were read from the graph. The results of various other authors are in excellent agreement with these. The data of Harned and Davis (1943) are apparently too high by about +.01 in β over the entire 0-50° range. Kunerth's (1922) results 20-34° seem too low (about -.02 in β), as are those of Morgan and Maass (1931) from 0-25° (-.02 to -.1 in β). The data of Buch (1925) at very low partial pressures of CO_2 are erratic. Additional results are given by Bhagwat and Dahr (1929), Appel (1921), Schwab and Berninger (1928), Hantzsch and Vagt (1901) and [of the supersaturation limits] by Metschl (1924).

q = gms. CO_2 dissolved by 100 gms. H_2O at a total pressure of 760mm.
β = ml CO_2 (measured at 0°, 760mm) dissolved in 1 ml. of H_2O when the partial pressure of CO_2 is 760mm.

SOLUBILITY OF CO_2 IN WATER--Cont.

t°	q	β	Other values for β
0	0.335	1.713	1.713 (4) 1.702 (0.2°) (3)
5	.277	1.424	1.419 (6)
10	.231	1.194	1.197 (6)
12.5	...	... (1.075)	1.159 (4)
15	.197	1.019(1.000)	1.022 (5) 1.014 (6)
20	.169	0.878(.865)	0.872 (6)
23	...	...	.802 (7)
24	...	...	.776 (7)
25	.145	.759(.754)	.758 (7) .757 (6)(2) .753 (8) .754(9) .756(3) .750(4) .7553(10) .752(11)
30	.126	.664(.664)	
35		(.595)	
40	.097	.530(.533)	
45		(.480)	
50	.076	.436(.438)	
55		(.397)	
60		(.365)	
70		(.319)	

Table 1-53

Henry's Law Constants for the Dissolution of CO_2 in Pure Water and Aqueous NaCl Solutions

From H. S. Harned and R. Davis, Jr., *J. Am. Chem. Soc.*, **65**, 2030 (1943).

	$-\log C$			
Temp., °C	Pure Water	0.2 *M*, NaCl	0.5 *M* NaCl	1 *M* NaCl
0	1.1144	1.1383	1.1738	1.2313
5	1.1938	1.2167	1.2510	1.3065
10	1.2695	1.2920	1.3259	1.3800
15	1.3412	1.3638	1.3970	1.4482
20	1.4063	1.4285	1.4605	1.5110
25	1.4635	1.4842	1.5152	1.5645
30	1.5209	1.5410	1.5712	1.6191

Table 1-54

Carbonate Equilibria

Temperature, °C	pK_1[a]	pK_2[b]	pK_s[c]	pK_{CO_2}[d]
0	6.58	10.62	8.02	1.12 (0.2°)
5	6.52	10.56	8.09	
10	6.47	10.49	8.15	
15	6.42	10.43	8.22	
20	6.38	10.38	8.28	
25	6.35	10.33	8.34	1.47
30	6.33	10.29	8.40	
40	6.30	10.22	8.52	1.64
50	6.29	10.17	8.63	
80	(6.32)	(10.12)	8.98	

$pK_1 = -\log K_{H_2CO_3}$; $pK_2 = -\log K_{HCO_3}$; $pK_s = -\log K_{CaCO_3}$; $pK_{CO_2} = -\log K_{CO_2}$. Values of original authors rounded to two decimal places in present table.

Table 1-55

Solubility of $CaCO_3$ *at various temperatures for two important* CO_2 *pressures*

Temp., °C.	0.033%	0.044%	Temp., °C.	0.033%	0.044%
0	96	106	15	67	74
1	95	104	16	65	71
2	93	101	17	63	70
3	90	99	18	62	68
4	88	96	19	60	67
5	86	94	20	59	65
6	84	92	21	57	63
7	82	89	22	56	62
8	79	87	23	55	61
9	77	85	24	54	60
10	75	83	25	54	59
11	73	81	26	52	58
12	71	79	27	51	57
13	69	77	28	50	56
14	68	76	29	49	54

Table 1-56

CO CALCIUM CARBONATE $CaCO_3$

SOLUBILITY IN WATER

Since the reactions $CO_3^{=} \rightleftharpoons HCO_3^{-}$ and $HCO_3^{-} \rightleftharpoons CO_2$ aq. are appreciable, the solubility of $CaCO_3$ is dependent on the concentration of CO_2 in solution, and therefore on the partial pressure of CO_2 in the atmosphere above the solution.

Much of the older work has been evaluated by Johnston (1915) and Frear and Johnston (1929) and only data representing some of the more reliable results are reproduced here. For additional (older) data see:

Cossa, 1869; Schloesing, 1872; Caro, 1874; Reid, 1887-88; Irving and Young, 1888; Anderson, 1888-89; Engel, 1888; Lubavin, 1892; Pollacci, 1896; Leather and Sen, 1909; Cavazzi, 1917; Seyler and Lloyd, 1909; Holleman; Treadwell and Renter, 1896; Ramann and Sallinger, 1921.

SOLUBILITY OF CALCIUM CARBONATE IN WATER IN CONTACT WITH ORDINARY AIR (Wells, 1915)

Joplin, Mo., calcite was used. The solutions were kept in a thermostat and agitated by a current of out-door air filtered through cotton and washed by water. The CO_2 content of the air varied from 3.02 to 3.27 parts per 10,000. The calcium content of the solutions was determined by titrating with 0.02 n $NaHSO_4$, using methyl orange as indicator. The solutions were slightly acid to phenolphthalein, showing that the calcium was present chiefly as bicarbonate.)

SOLUBILITY OF CALCIUM CARBONATE IN WATER IN CONTACT WITH ORDINARY AIR--Cont.

Results in parentheses are by Kendall (1912). In connection with these it is stated by Johnston (1915), that assurance is wanting that the partial pressure of CO_2 was the same at both temperatures and the results are, therefore, not necessarily comparable.

t°	Gms. $CaCO_3$ per Liter	t°	Gms. $CaCO_3$ per Liter
0	0.081	30	0.052
10	0.070	40	0.044
20	0.065	50	0.038 (0.029)
25	0.056 (0.046)		
	0.052*		

*Frear and Johnston, 1929.

SOLUBILITY OF CALCIUM CARBONATE IN WATER ESSENTIALLY FREE OF CARBON DIOXIDE

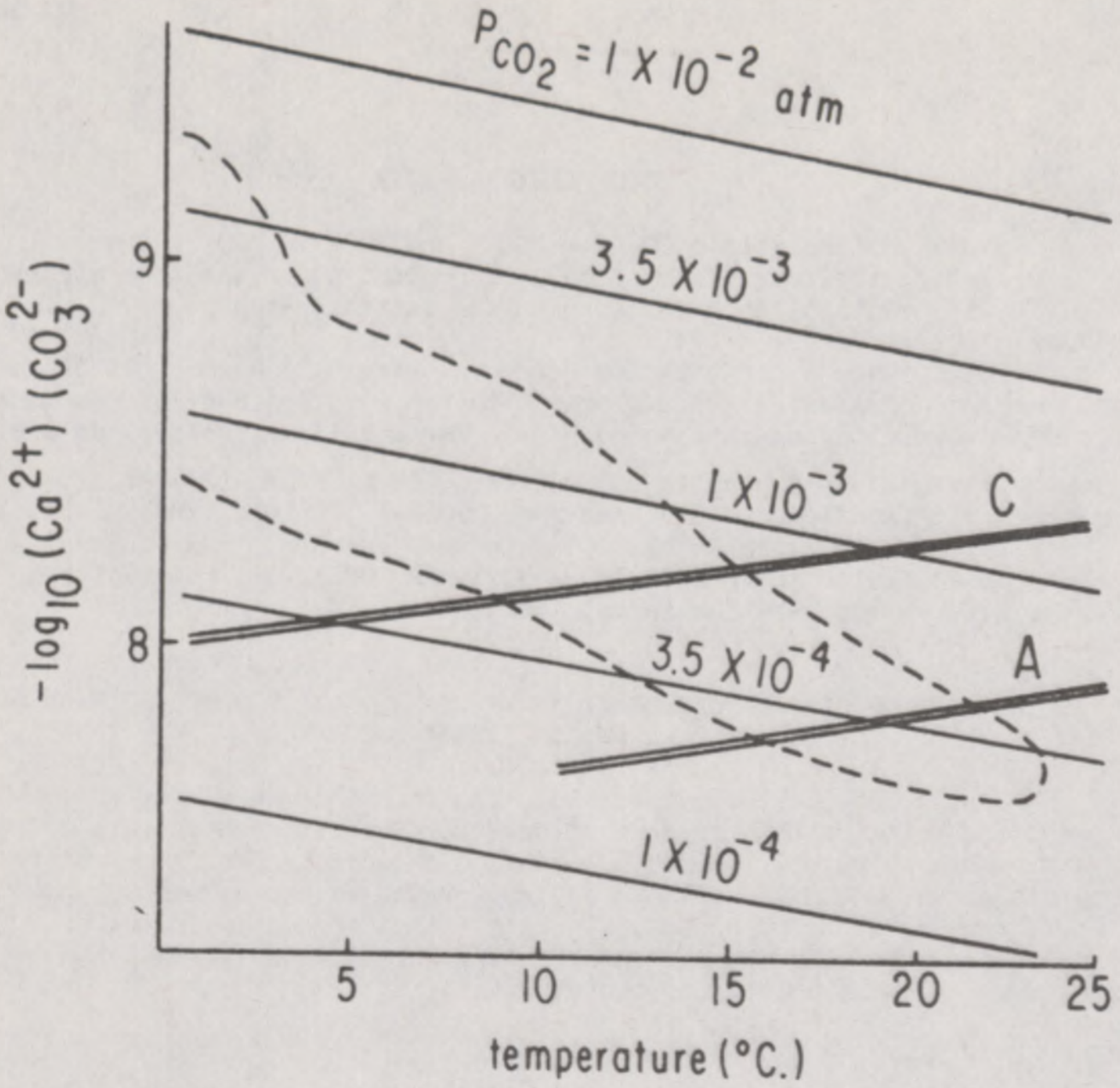
t°	Gms. $CaCO_3$ per liter	Author
15	0.238 (?)	Treadwell and Renter, 1896
17	0.0145	Stumper, 1925
18	0.0128	LeBlanc and Novotny, 1906
25	0.0132	Franquin and Marecaux, 1938
25	0.013	Askew, 1923
"Room t°"	0.013	Wesley, 1944
95	0.024	"
95-100	0.0207	LeBlanc and Novotny, 1906
100	0.0375	Leick, 1932, 1933
182	0.025	Straub, 1932
207	0.014	"
244	0.011	"
316	0.08	"
370	0.39 (200 atm.)	Schleomer, 1952

SOLUBILITY OF CALCIUM CARBONATE IN WATER AT LOW PARTIAL PRESSURES OF CO_2

THE SOLUBILITY OF CALCIUM CARBONATE (CALCITE) IN WATER AT 16° IN CONTACT WITH AIR CONTAINING PARTIAL PRESSURE P OF CO_2
(Calc. from Schloesing, 1872, and Engel, 1888, by Johnston, 1915)

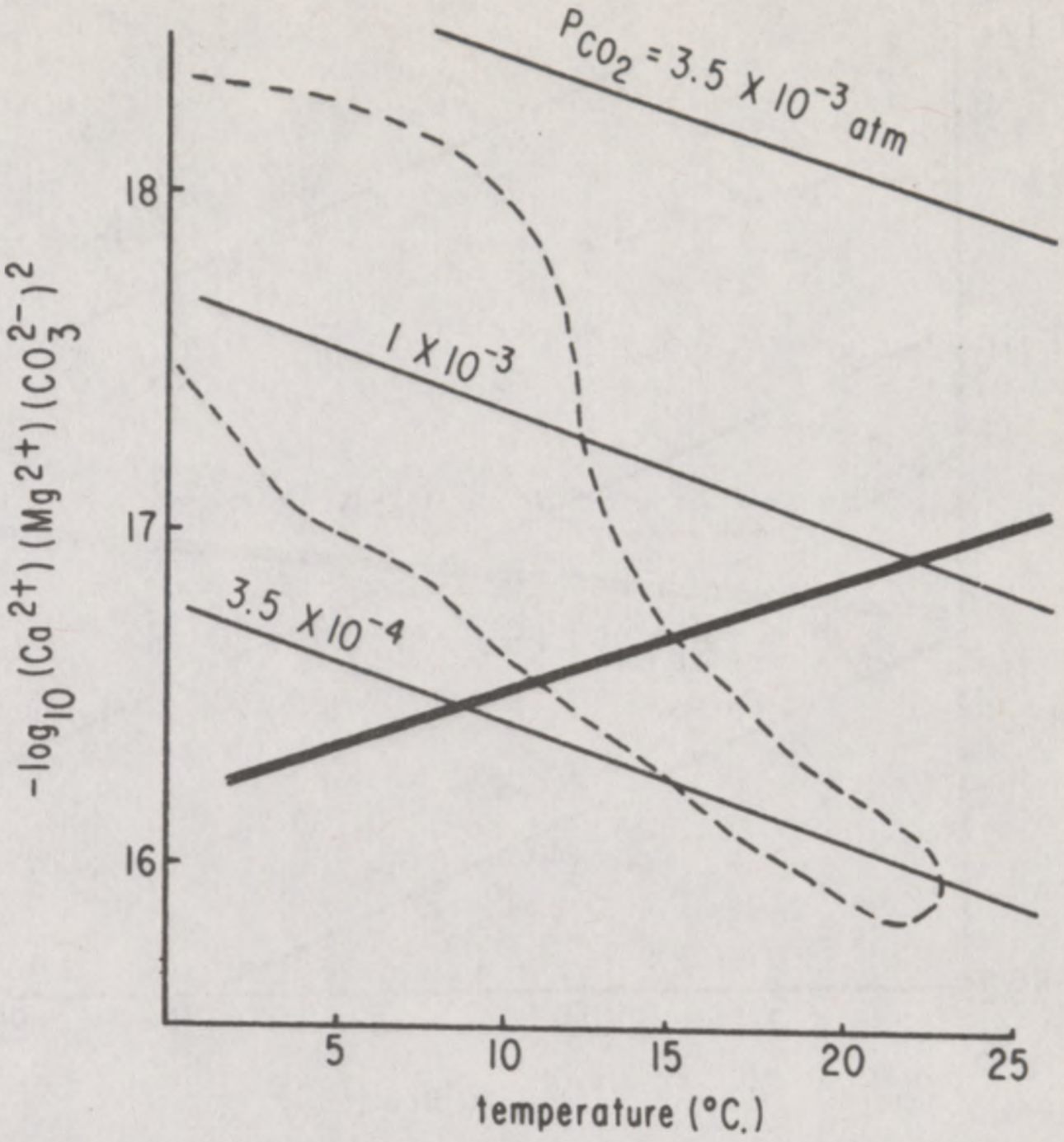
Partial Pressure P of CO_2 in Atmospheres	Total Ca. Mols. per Liter	Total $Ca(HCO_3)_2$ Mols. per Liter
0.000504	0.000746	0.000731
0.000808	0.000850	0.000837
0.00333	0.001372	0.001364
0.01387	0.002231	0.002226
0.02820	0.002965	0.002961
0.05008	0.003600	0.003597
0.1422	0.005330	0.005328
0.2538	0.006634	0.006632
0.4167	0.007825	0.007874
0.5533	0.008855	0.008854
0.7297	0.009772	0.00972

(Cont.)



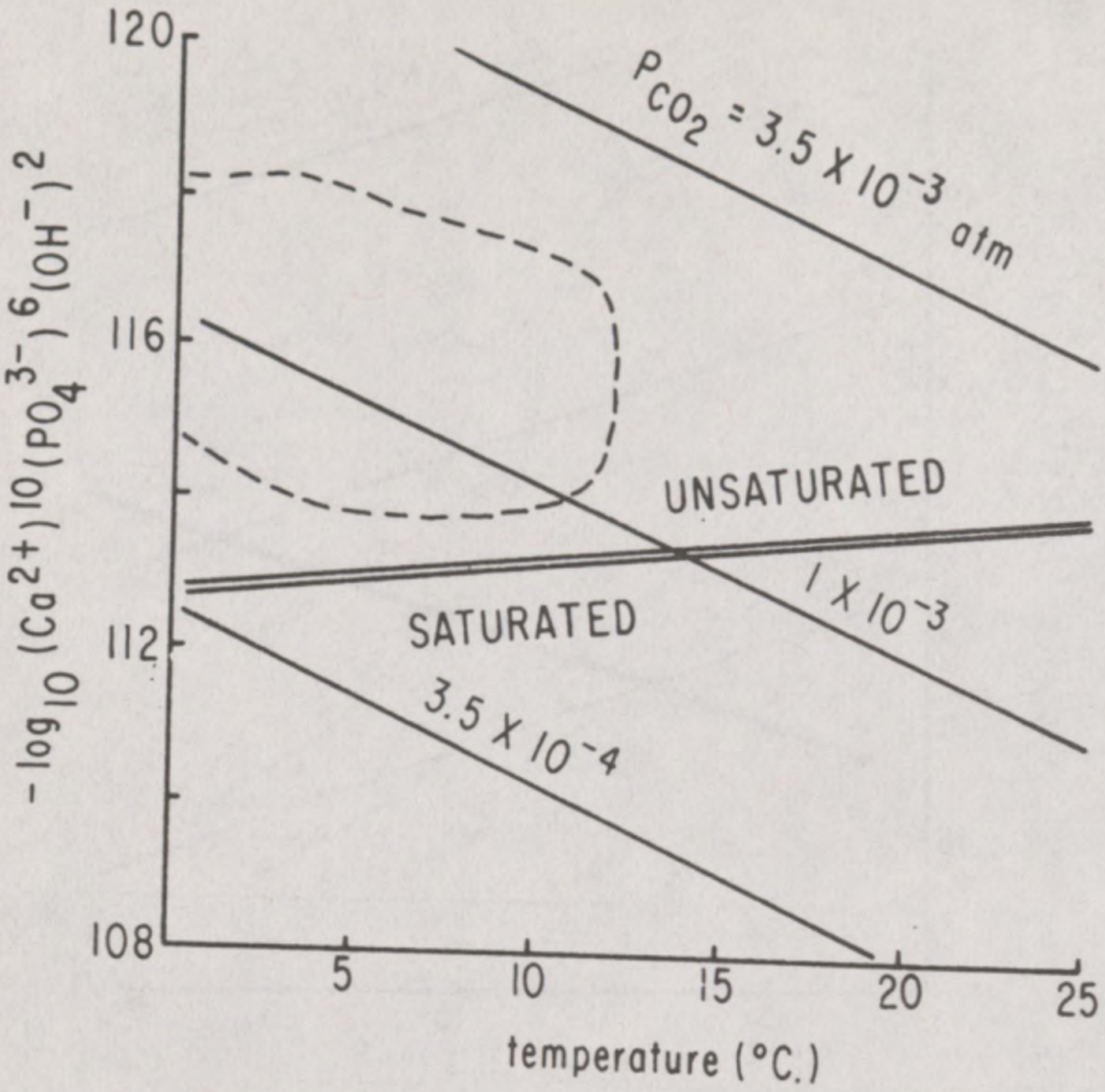
Ion Products for Calcite (c) and Aragonite (a) as functions of Temperature and Partial Pressure of Carbon Dioxide. The actual data from Lake Water Studies Fall Within the Dashed Lines. Double Lines Represent Solubility Constants. (Kramer, in Stumm, 1967, Page 251).

Figure I-18



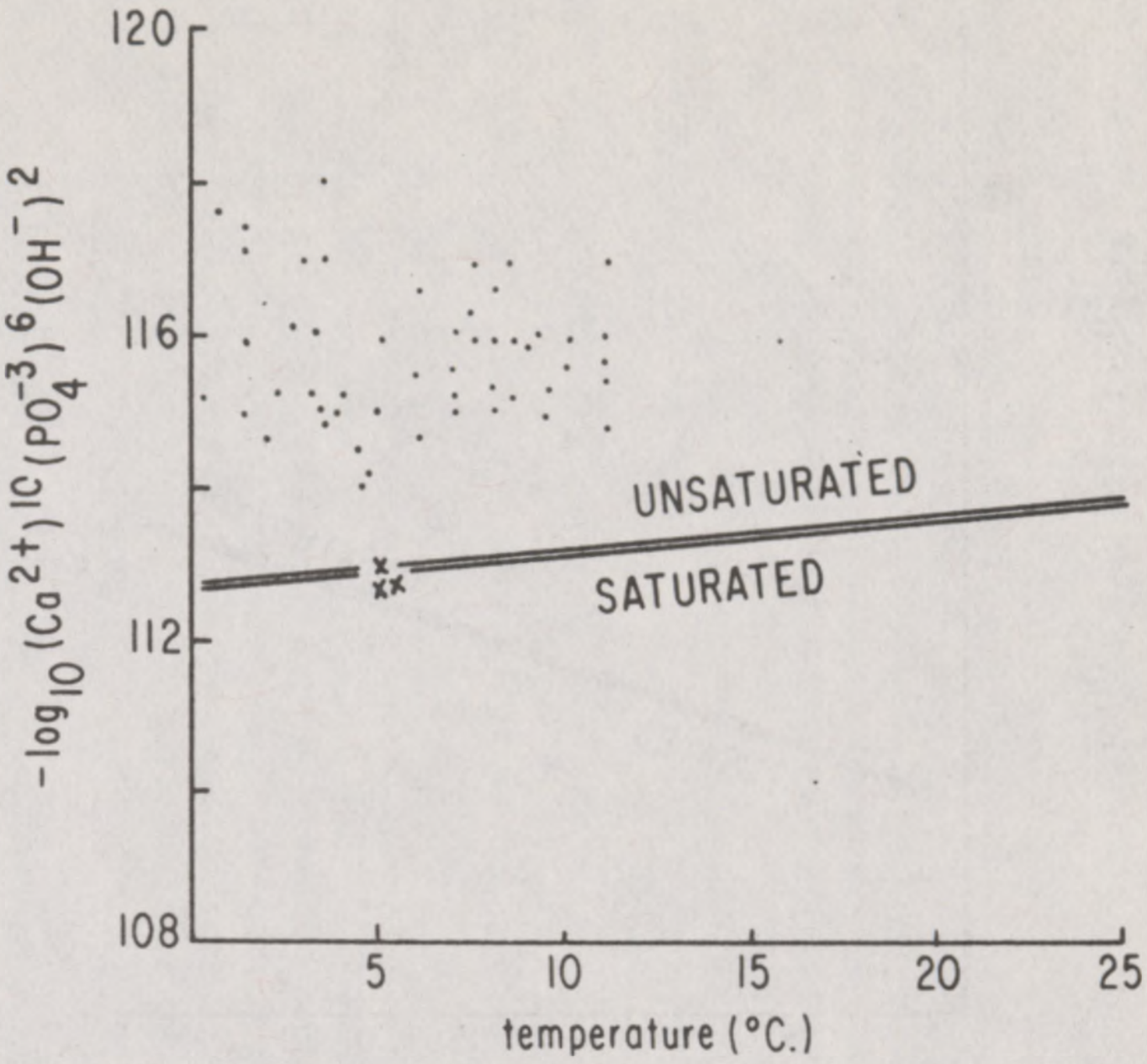
Ion Product for Dolomite as a Function of Temperature and Partial Pressure of CO_2. Double Line Represents Solubility Constant. Areas Indicated by Dashed Line Include Data from Actual Lake Water Analysis (Kramer, See Stumm, 1967, page 252).

Figure I-19



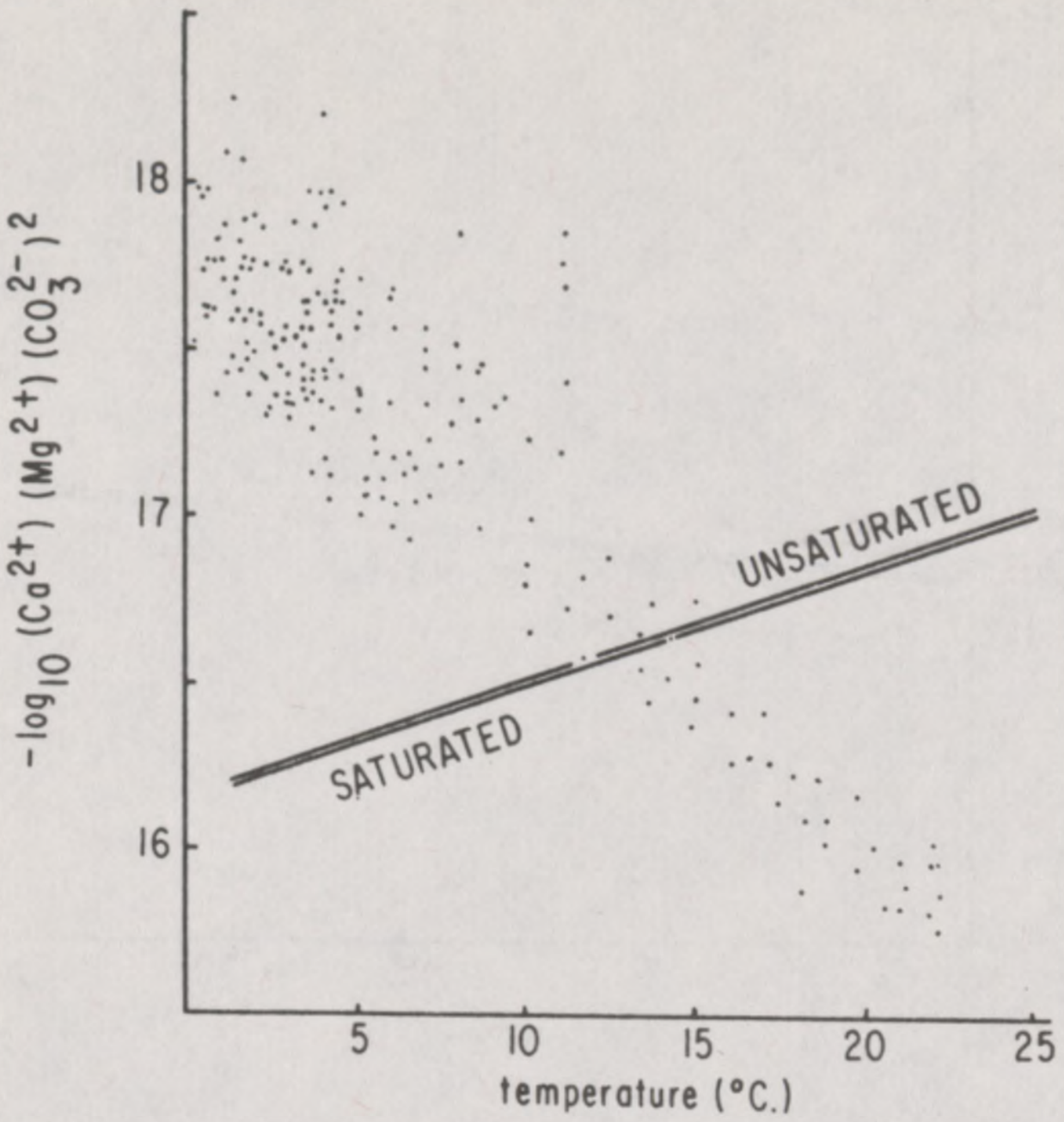
Ion Product for Hydroxyapatite as a Function of Temperature and Pressure. Dashed Line Indicates Actual Values for Observed Data (only during Winter). Double Line Represents Solubility Constant. (Data by Kramer, see Stumm, 1967, page 253).

Figure I-20



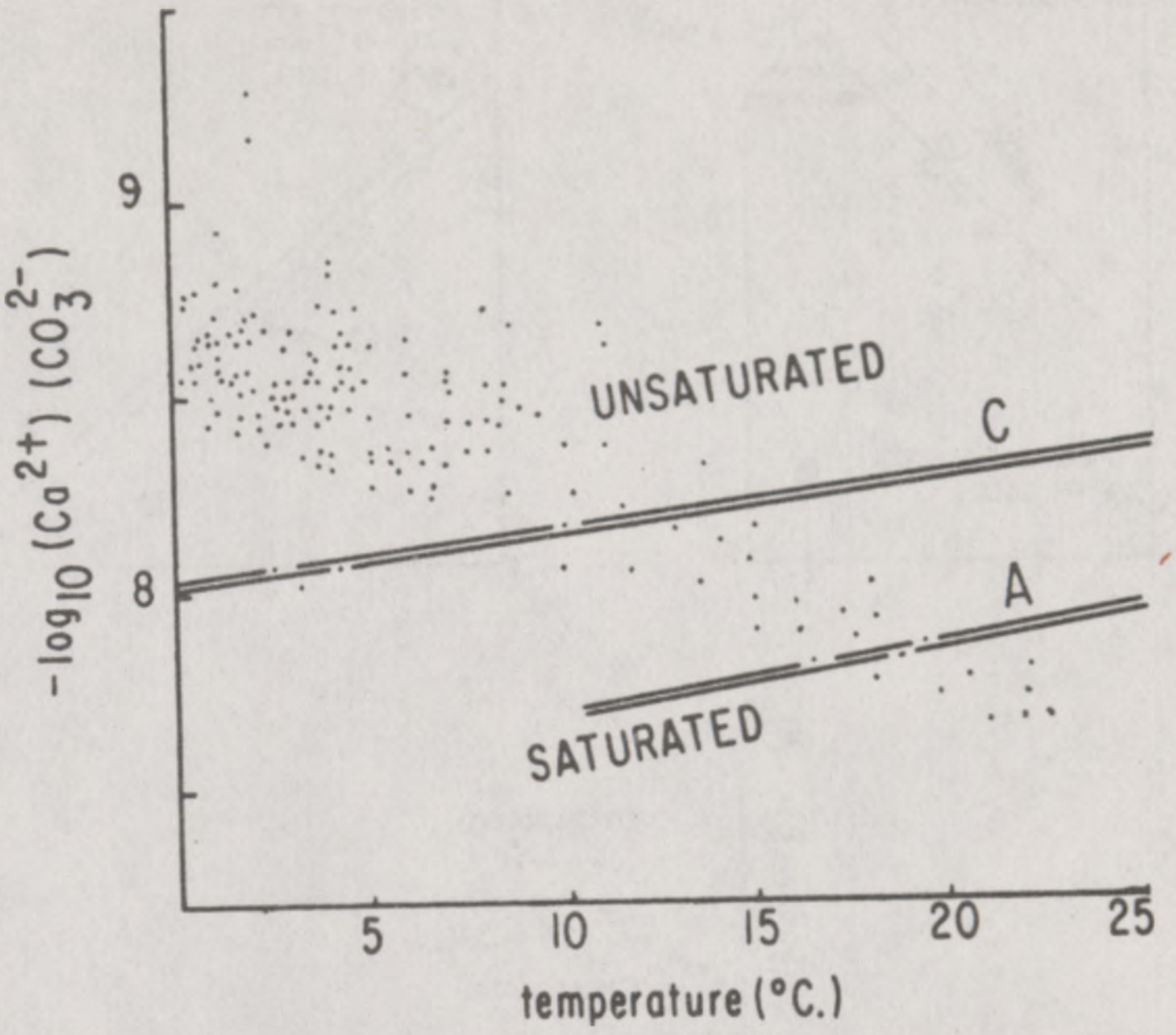
Saturation of Lake Water with Respect to Hydroxyapatite as a function of temperature. Low temperature data available only. (Kramer, in Stumm, 1967, page 249).

Figure I-21



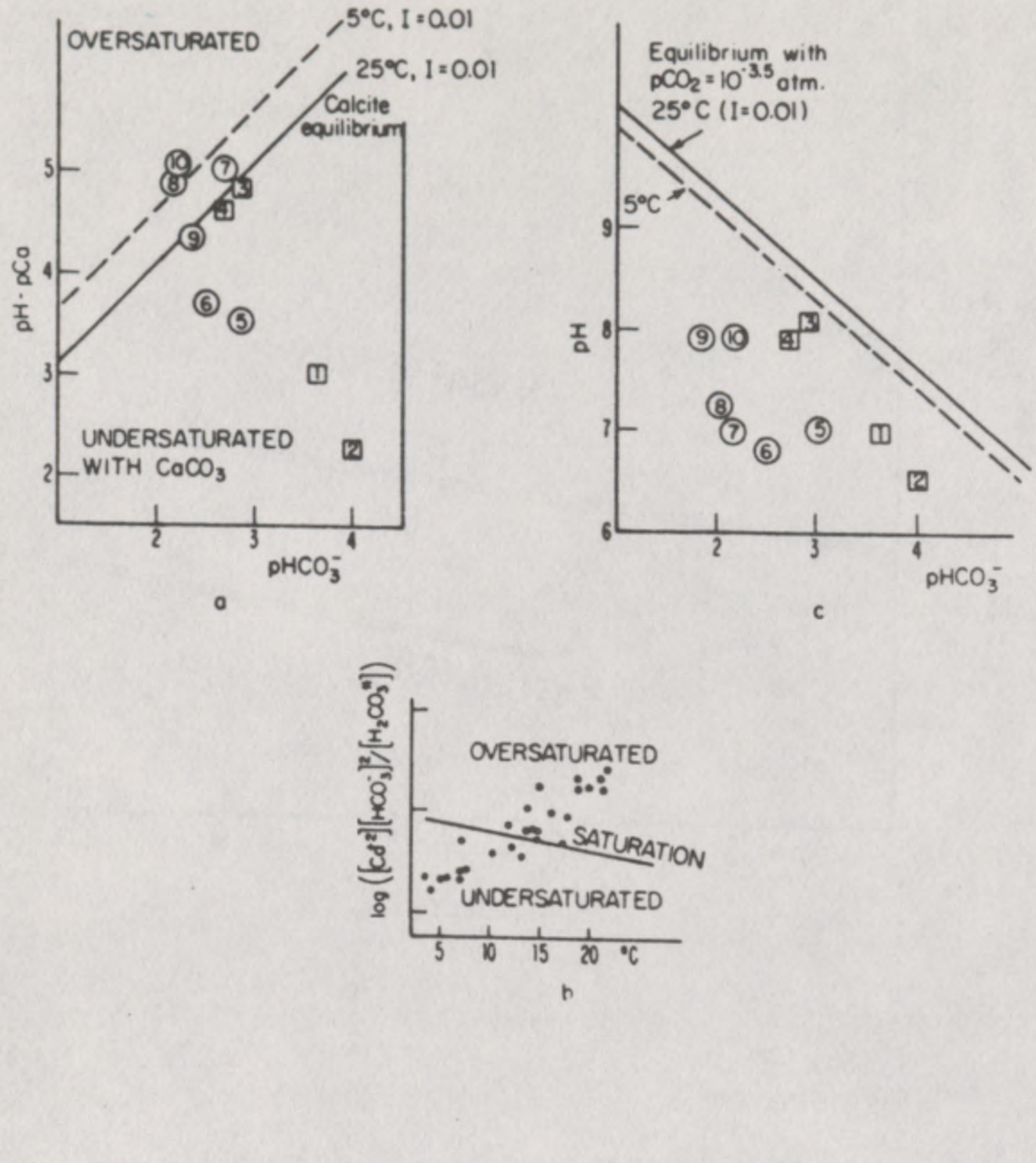
Saturation of Lake Water with Respect to Dolomite as a Function of Temperature. Points Above the Double Line Indicate Unsaturated Conditions; Points Below the Double Line Saturated Conditions. Note the Vastly Different (in fact, opposite) Temperature Coefficient Between Actually Observed and Theoretically Predicted Solubilities. (Kramer, in Stumm, 1967, page 248).

Figure I-22



Saturation of Lake Water with Respect to Dolomite. Points Above Double Line Correspond to Unsaturated Conditions; Below Dotted Line To Saturated Systems. (Kramer, in Stumm, 1967, Page 248).

Figure I-23



Actual composition values for carbonates in various lakes and streams. Figure a: actual data from various sources, compared with equilibrium composition for the reaction $CaCO_3(s) + H^+ \rightleftharpoons Ca^{++} + HCO_3^-$. Figure b: water from Lake Zürich; note oversaturation with calcium carbonate at high temperatures (upper layers) and undersaturation at lower temperatures. The deviation from equilibrium is, in part, explainable in terms of photosynthesis (upper layers, with increased pH) and by respiration in deeper layers (decrease in pH). Figure c: oversaturation with respect to CO_2 content of the atmosphere. Actual data from variou locales (streams and lakes). Theoretical lines indicate the equilibrium $CO_2(g) + H_2O \rightleftharpoons H^+ + HCO_3^-$.

Figure I-24

For additional discussions of various aspects of the carbon dioxide carbonate equilibria, see the writings by Sillen (particularly 1961). More recent papers include a study by Pytkowicz (1968), concerned with the carbon dioxide-carbonate equilibria at high pressures. See also the paper by Bischoff (1969) which provides a number of kinetic data (although mostly for temperatures above those of immediate interest in the present connection.

Extensive discussion of the carbon dioxide hydrogen ion concentration and calcium carbonate solubility can also be found in Vol. I of Hutchinson's treatise on limnology (1967).

The effects of temperature on the various equilibrium constants for carbonate equilibria are shown in Table $\frac{1\text{-}54}{\quad}$, from the data by Garrels and Christ (1965, page 89). No reference is made in this review to the changes with pressure as only pressures exceeding about twenty-five atmospheres appear to play a role (corresponding to an effective depth of 250 meters, or roughly 750 feet).

Most of the organic matter in seawater is nitrogenous. The major part of the organic compounds are in the form of peptides, proteins and "heteropolycondensates" (see E. T. Degens in "Organic Matter in Natural Waters", edited by Donald W. Hood, 1970, p. 99). According to Degens, free monomers such as amino acids, fatty acids and sugar amounts to less than 10% of total amount of organic matter. Degens proposes that clathrate-type molecular structures form the heteropolycondensates. As would be expected, Degens concludes that the majority of the organic matter is the result of metabolism of planktons and microorganisms. The contribution to the oceans of land-based sources of organic matter is probably negligible, except in the immediate vicinity of river discharges (estuarine environments).

The difficulties which surround the description of the carbonate equilibria in natural water, brackish water and seawater have been indicated above. Chave (in "Organic Matter in Natural Waters", edited by Donald W. Hood, 1970, p. 373) has contributed to the problem of the calcium carbonate-seawater system, particularly through the suggestion that rates of reactions may be significantly influenced by adsorption of organic material onto the initially-formed carbonates.

Chave summarizes the main problem areas within the carbonate system in the following way:

1) "The supersaturation of most surface and near surface seawaters with respect to calcium carbonate (Wattenberg and Timmerman, 1966, MacIntyre and Platford, 1964).

2) "The complex minerality of shelf carbonate sediments (Land, 1961, Figure 1).

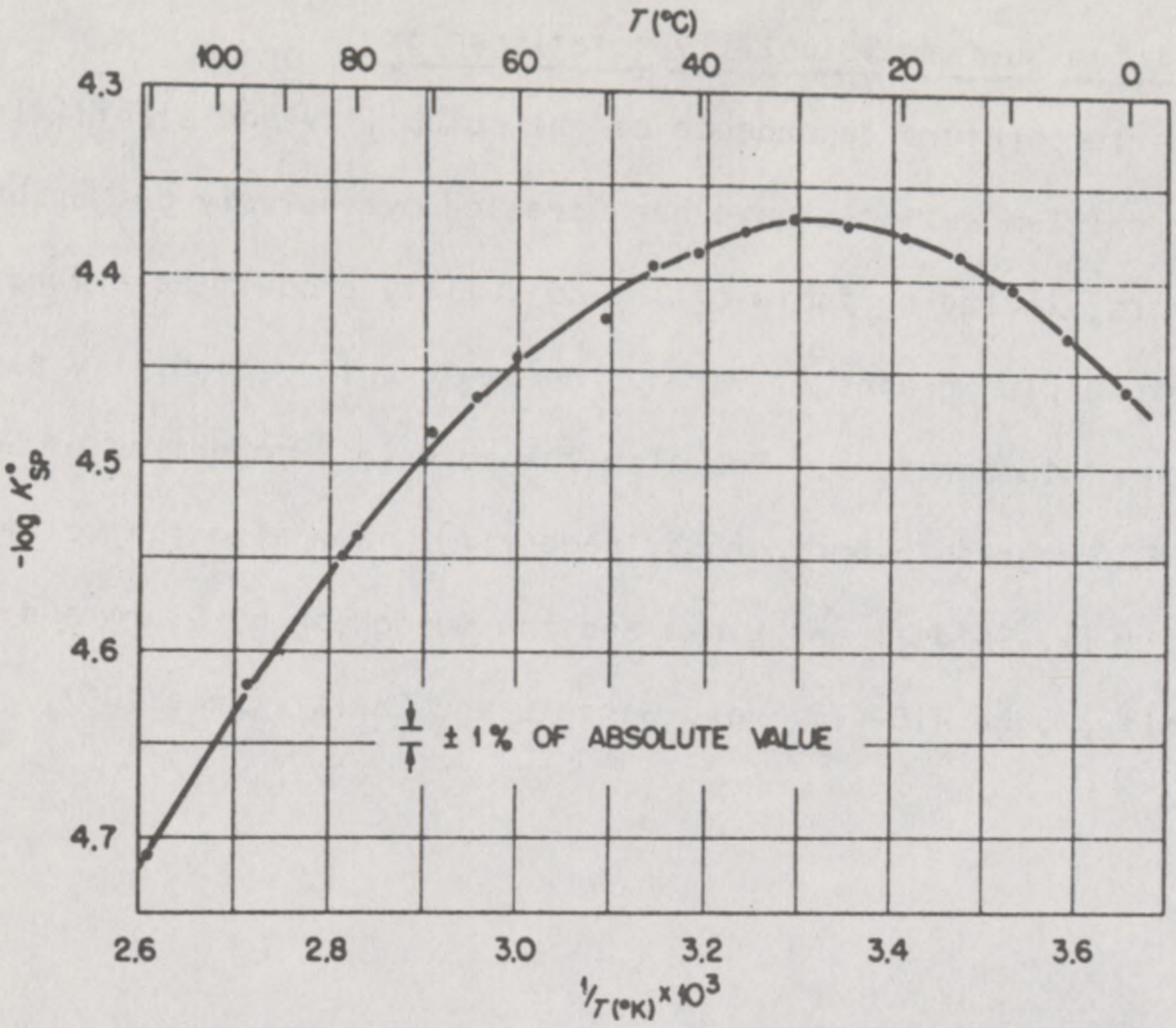
3) The occurrence of $CaCO_3$ in pelagic sediments from all depths of the ocean (Bramlette, 1961; Smith, et al., 1968)".

Chave points out that these features suggest the lack of equilibrium in the carbonate-seawater. Thus, solution of calcium carbonate should not remain supersaturated indefinitely (i.e., exhibit the properties of a diuternal supension; see further discussion of colloidal aspects in Section IV). Chave also points out that a complex of calcium carbonate mineral basis cannot be in equilibrium with a single aqueous phase. Finally, the deep ocean waters are undersaturated with respect to calcium carbonate, and hence, carbonates should be absent in deep pelagic sediments. An important conclusion by Chave and Chave and co-workers is that independend work has shown that any seawater sample will equilibrate with (at least) the surface of any marine carbonate mineral within a relatively short time (of the order of an hour). Hence, some aspects other than simply a slow ionic reaction between the inorganics of the system must be involved. This missing aspects appears from the studies by Chave and Chave and co-workers to be the interaction between dissolved organic molecules and the carbonated minerals. The reader is referred to the detailed studies by Chave and co-workers (see Chave, loco cit., 1970). The important aspect to stress at this point is that it apparently is not sufficient to have available temperature coefficients for solubility products, dissociation constants, or even individual rate reactions of carbonate systems in well defined systems. In addition, it is necessary to know in detail the nature of the organic species present in the natural waters, and specifically the degree and rate of adsorption (and co-precipitation) of organic material on freshly formed carbonate particles. Such data are obviously completely lacking at present. Furthermore, an enormous complexity must be anticipated in view of the literally infinite number of possible

combinations of concentrations and types of organic solute species. Finally, and this may be particularly significant, although difficult to demonstrate, the rates and the types of reactions may be determined to a large extent by the hydration structures of both the adsorbates and adsorbents.

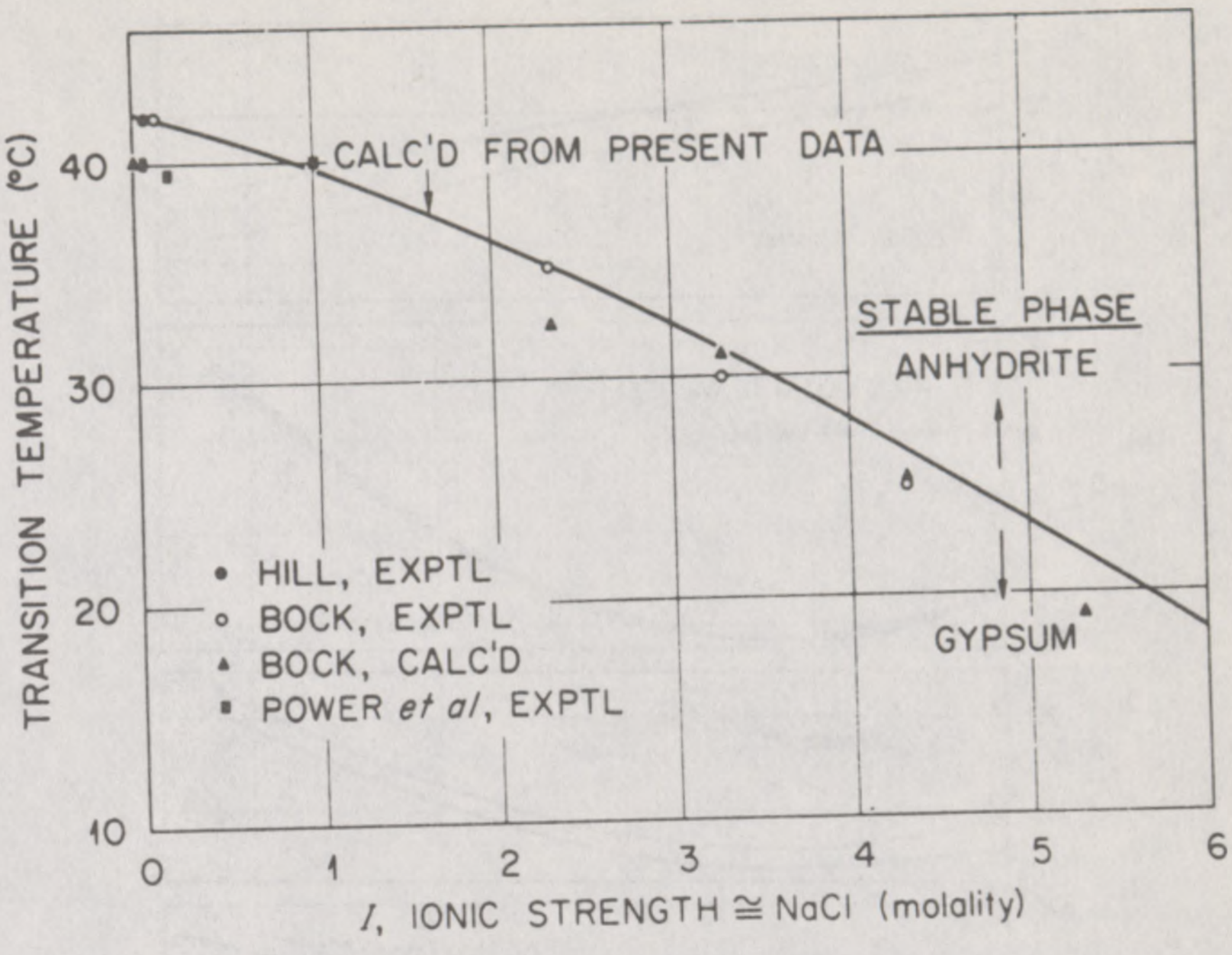
Calcium-Sulfate Solubility Relationships

The temperature dependence of the solubility and stabilities of various calcium sulfates have been treated extensively by Marshall and co-workers, including table of the solubility product as a function of temperature plus graphs of various parameters for solubility as a function of temperature. See also the note in "Properties of Solutions" [OSW, R&D Progress Report, #685, page 117]. See also the volume on solubility by Seidell and Linke and the monograph by Stumm and Morgan (loco cit., page 416-417); and Garrels and Christ (page 106).



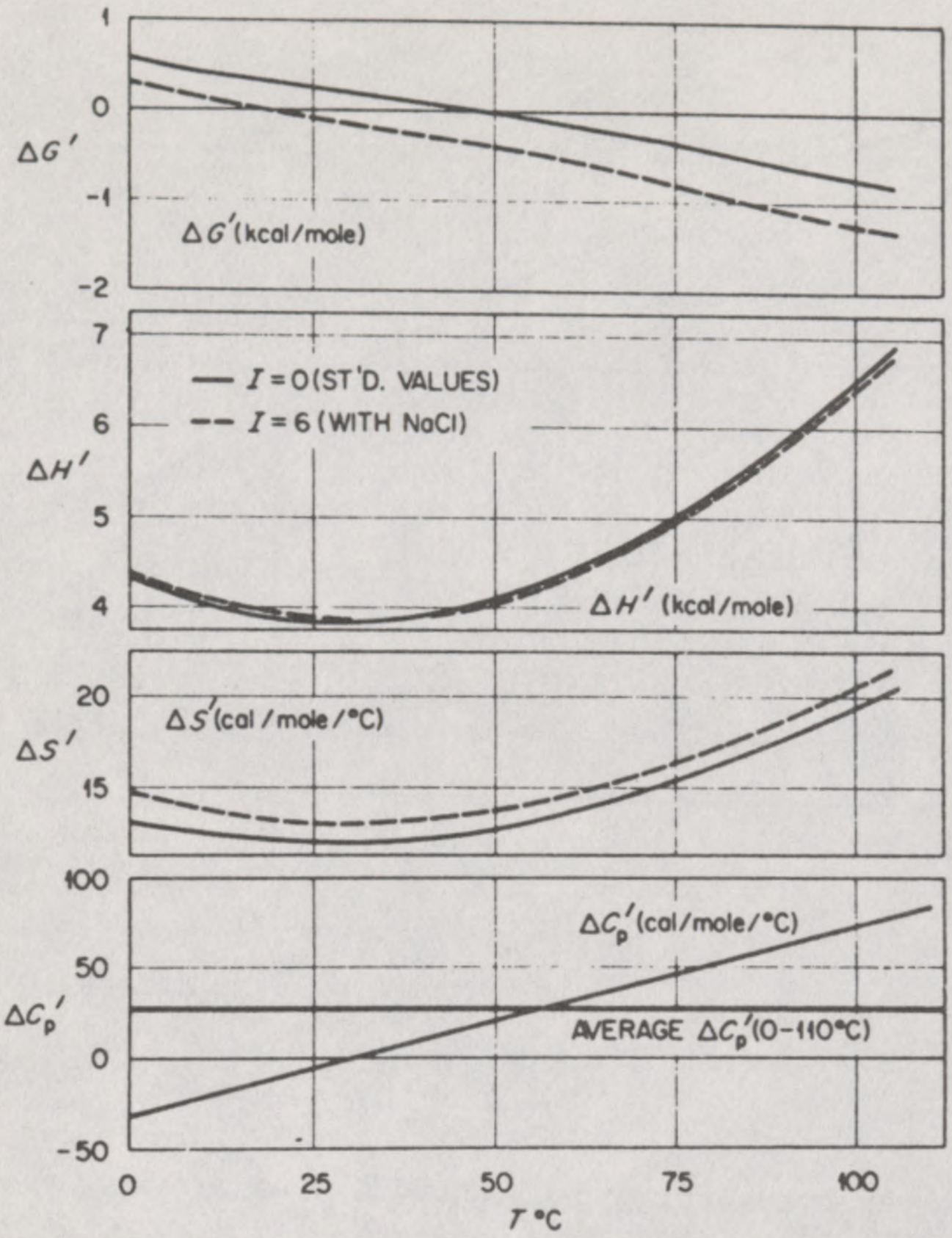
Negative values of logarithmic solubility product constant for $CaSO_4$, $2H_2O$ at *zero* ionic strength, over a wide range of temperatures. (Marshall and Slusher, 1966).

Figure 1-25A



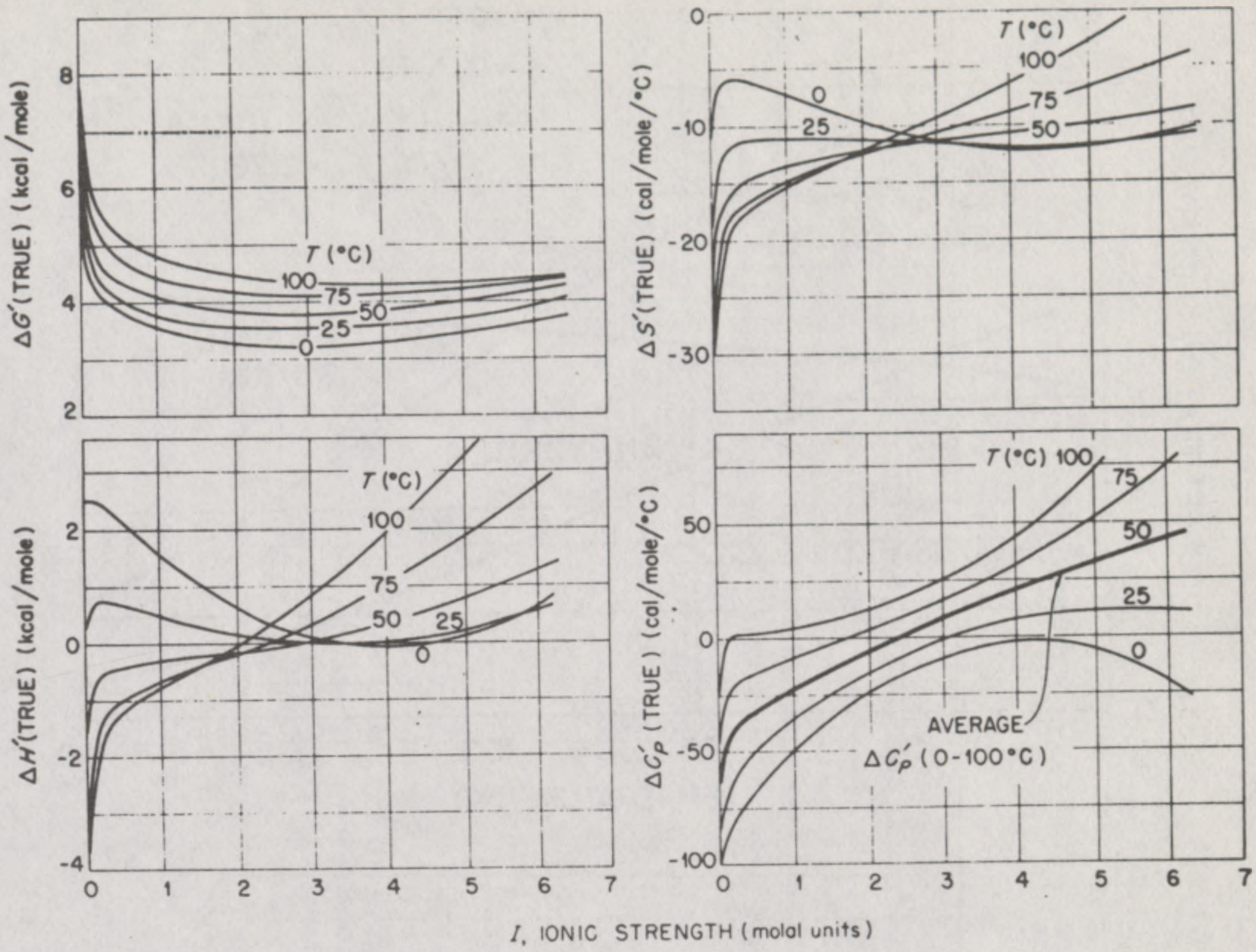
Transition temperatures for gypsum-anhydrite as a function of ionic strength (approximately equal to sodium chloride molality). (Marshall and Slusher, 1966).

FIGURE 1-25B



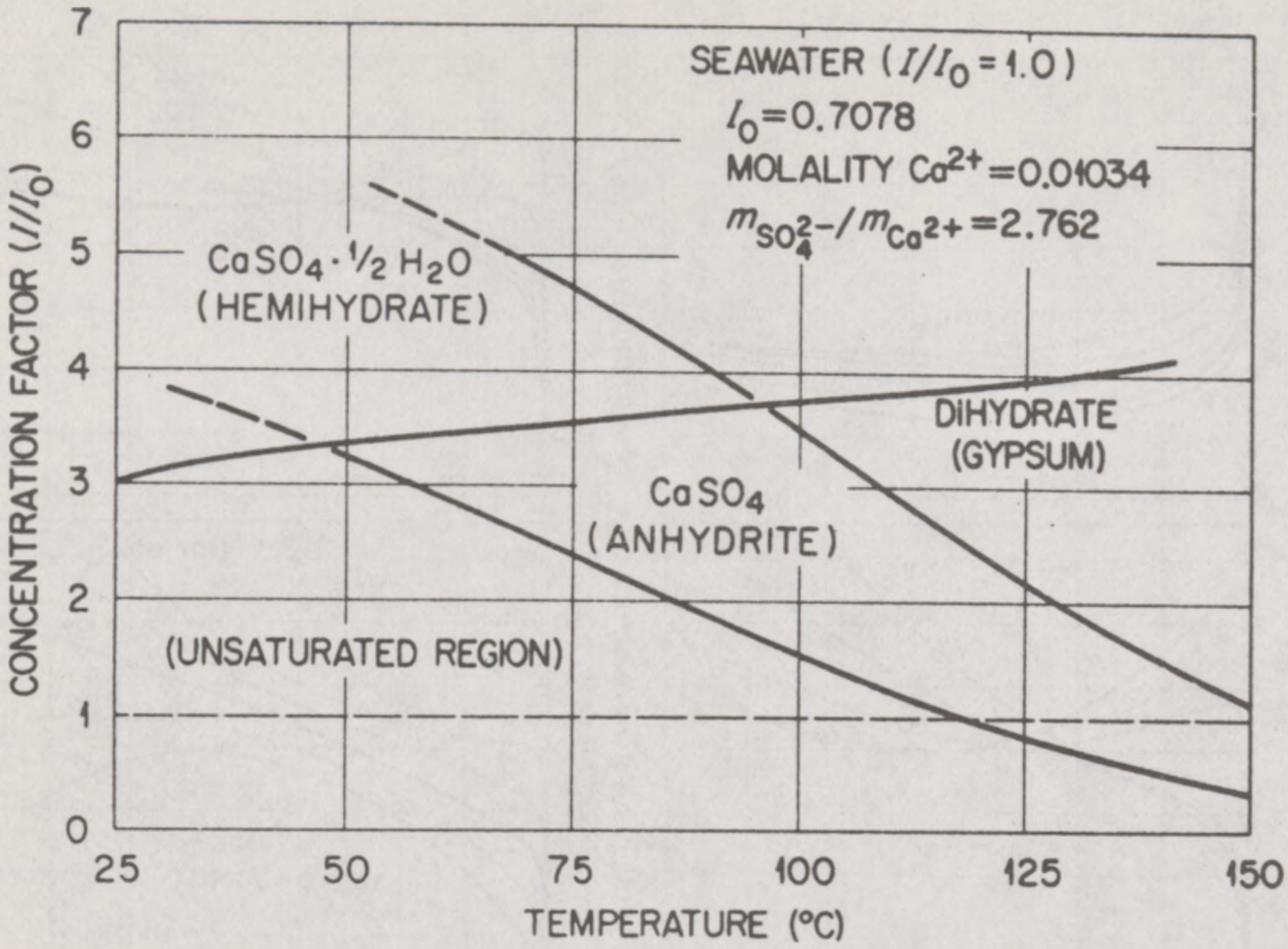
Some thermodynamic values for the reaction $CaSO_4 \cdot 2H_2O^{(s)} \rightleftharpoons CaSO_4{}^{(s)} + 2H_2O^{(liq)}$. (Marshall and Slusher, 1966).

Figure 1-25C



Generalized thermodynamic quantities for the solubility of gypsum ($CaSO_4 \cdot 2H_2O$) in sodium chloride-water solution. 0 to 6 molar from 0 to 100° C. (Marshall and Slusher, 1966).

Figure 1-25D



Temperature-concentration limits for precipitation of calcium sulfate and its hydrates in seawater. (Marshall, 1971).

Figure 1-25E

CO MAGNESIUM CARBONATE $MgCO_3$
HCO MAGNESIUM BICARBONATE $Mg(HCO_3)_2$

SOLUBILITY IN "CO_2-FREE" WATER

At 15°

Extrapolation of the data of Treadwell and Reuter, 1898 shows that at 0 partial pressure of CO_2 and at 15° and mean barometric pressure, one liter of saturated aqueous solution contains 0.641 gm. of $MgCO_3$ plus 1.954 gms. $Mg(HCO_3)_2$.

At 100°
(Leick, 1932, 1933)

The determinations showed that 0.030 gm. MgO = 0.063 gm. $MgCO_3$ per liter was dissolved at 100°. It was found that the solubility is increased by NaCl and Na_2SO_4. NaOH and Na_2CO_3 do not reduce the solubility of $MgCO_3$ as much as they do that of $CaCO_3$. Results for the simultaneous solubility of $MgCO_3$ and $CaCO_3$ in water at 100° show that with increasing time of boiling, from 1-1/2 to 48 hours, the dissolved CaO increased about 5 times while the dissolved MgO decreases about 10 times. The results are of interest in connection with the purification of boiler waters.

RESULTS IN WATER WITH UP TO 1 ATM. PARTIAL PRESSURE OF CO_2

At 15°

Considerable data are given by Treadwell and Reuter, 1898, giving total Mg^{++}, HCO_3^-, and $CO_3^=$, but it is pointed out by Johnston (1915) that although Treadwell and Reuter made very painstaking analyses, their mode of working did not secure equilibrium conditions, a fact which is borne out by the lack of constancy of the calculated solubility-product constant.

At 18°
(Johnston, 1915)

It is shown that if the CO_2 pressure is kept constant at P and the water evaporated off so slowly at 18° that equilibrium conditions are continuously maintained, the following amounts of $Mg(OH)_2$ or of $MgCO_3 \cdot 3H_2O$ will be obtained.

Partial Pressure P of CO_2 in Atms.	Total Mg Mols./l	Gms. per Liter	
0	0.00015	0.0087	$Mg(OH)_2$
0.00020	0.01934	1.13	"
0.00025	0.02218	1.29	"
0.00030	0.02486	1.45	" CO
0.00035	0.02742	1.60	" HCO
0.00040	0.02868	3.97	$MgCO_3 \cdot 3H_2O$
0.00045	0.02924	4.05	"
0.00050	0.02976	4.12	"

At 20°
(Wells, 1915)

Mixture	Milligrams per Liter of Sat. Solution: Mg	Free CO_2	CO_2 as Bicarbonate
Natural Magnesite in Distilled H_2O	0.018	trace	0.065
" in Aq. NaCl (27.2 g. per l)	0.028	trace	0.086
$MgCO_3 \cdot 3H_2O$ (equilibrium from bicarbonate end)	0.038	0.28*	0.83
$MgCO_3 \cdot 3H_2O$ (" " undersaturation")	0.034	0.32*	0.59

* = CO_2 as carbonate

Table 1-57

Table 1-57 Continued

At 25°
(Kline, 1929)

The saturated solutions were prepared by bubbling mixtures of carbon dioxide and air in constant proportions through conductivity water in contact with finely divided solid for periods of three to five days.

Partial Pressure of CO_2 in Atmospheres	Millimols per 1000 gms. H_2O			Partial Pressure of CO_2 in Atmospheres	Millimols per 1000 gms. H_2O		
	$[Mg^{++}]$	$[HCO_3^-]$	$[CO_2^{--}]$		$[Mg^{++}]$	$[HCO_3^-]$	$[CO_2^{--}]$
0.000107	0.00433	0.00488	0.00189	0.000510	0.01437	0.01710	0.00382
0.000113	0.00445	0.00501	0.00195	0.000680	0.01512	0.01872	0.00376
0.000170	0.00577	0.00745	0.00205	0.000845	0.01566	0.01990	0.00372
0.000179	0.00593	0.00763	0.00212	0.000887	0.01593	0.02046	0.00370
0.000197	0.00658	0.00795	0.00261	0.000930	0.01624	0.02119	0.00365
0.000210	0.00708	0.00806	0.00305	0.00160	0.01859	0.02698	0.00310
0.000233	0.00780	0.00837	0.00361	0.00334	0.02210	0.03548	0.00236
0.000251	0.00807	0.00855	0.00380	0.00690	0.02507	0.04468	0.00273
0.000310	0.01013	0.01184	0.00421	0.0150	0.03127	0.06022	0.00116
0.000376	0.01296	0.01404	0.00594	0.0432	0.04601	0.08998	0.00102
0.000380	0.01355	0.01432	0.00639	0.1116	0.06266	0.1236	0.00085
				0.9684	0.2135	0.4269	--

The activity product constant of magnesium carbonate at 25° is taken as 1×10^{-5} and that of magnesium hydroxide similarly as 5×10^{-12}.

Table 1-58

SOLUBILITY PRODUCTS OF VARICUS HYDRATES
(Lannung and Torborg-Jensen, 1949)

$MgCO_3 \cdot 3H_2O$	$Ksp = 8.9 \times 10^{-6}$
$MgCO_3 \cdot 2H_2O$	$Ksp = 2.3 \times 10^{-5}$
$MgCO_3 \cdot H_2O$	$Ksp = 2.7 \times 10^{-5}$

AT OTHER TEMPERATURES

EQUILIBRIUM IN THE SYSTEM MAGNESIUM OXIDE, CARBON DIOXIDE AND WATER
(Takahashi, 1927)

CO HCO t°	d. of sat. sol.	Gms. per 100 gms. sat. sol. CO_2	Gms. per 100 gms. sat. sol. MgO	Solid Phase
-2.80	1.0411	3.410	1.526	$MgCO_3 \cdot 5H_2O$
0	1.0407	3.219	1.496	"
+5	1.0395	2.942	1.423	"
10	1.0383	2.962	1.363	"
15	1.0373	2.744	1.312	"
20	1.0363	2.606	1.256	"
5	1.0407	3.232	1.530	$MgCO_3 \cdot 3H_2O$
10	1.0360	2.736	1.314	"
15	1.0320	2.270	1.143	"
20	1.0287	2.109	0.9858	"
25	1.0250	1.839	0.8654	"
30	1.0210	1.572	0.7634	"
35	1.0170	1.381	0.6780	"
40	1.0135	1.206	0.6017	"
45	1.0097	1.044	0.5323	"
50	1.0050	0.922	0.4718	"
55	1.0008	0.833	0.4083	"
60	0.9980	0.746	0.3648	"

Results are also given for the solubility of $5MgO \cdot 4CO_2 \cdot 7H_2O$ in Water saturated with CO_2 at one atmosphere pressure.

Determinations of the equilibrium in the system $MgCO_3 + CO_2 + H_2O$ made by passing CO_2 at atmospheric pressure through mixtures of H_2O + MgO and H_2O + $MgCO_3$ at temperatures from 0° to 40°, are given by Tereda, 1928. There is, however, some uncertainty in regard to the exact terms in which the results are expressed.

Data for the system magnesium carbonate-carbonic acid-water at 20°, 25°, 30°, 34° and 39° are given by Leather and Sen (1914). In connection with these results, it is pointed out by Johnston (1915), that it is questionable whether equilibrium was really obtained and furthermore, the accuracy of the analytical results cannot be trusted since the ratio of total amount of CO_2 in solution, to the magnesia is very irregular. The results when plotted directly show great inconsistencies.

Solubility Tables

The most extensive listings of solubilities have been presented in the treatise by Seidell (new edition, edited by Linke, 1958). From these tables are taken some illustrative examples of available solubility data (various lead compounds, etc.).

Solubility of Silver Chloride in Water

†°	Gms. AgCl per liter	†°	Gms. AgCl per liter
0	0.00070	40	0.0036
5	0.00085	45	0.0043
10	0.00105	50	0.0054
15	0.00125	100	
20	0.00155	220	
25	0.00193	250	
30	0.0024	269	
35	0.0029	289	

Table 1-59

Table 1-60

Cl LEAD CHLORIDE $PbCl_2$

SOLUBILITY IN WATER

(1) Demassieux, 1923; (2) Flöttmann, 1928; (3) Deacon, 1927; (4) Weber, 1929; (5) Burvage, 1926; (6) Herz and Hellebrandt, 1923; (7) Sowerby, 1927; (8) Lichty, 1903; (9) Carmody, 1929; (10) Lewin, Vance and Nelson, 1953; (11) Benrath, Gjedebo, Schiffers and Wunderlich, 1937; (12) Goulden and Hill, 1945.

For more recent data on the solubility between 100 - 370° see Malinin, 1957.

Solid phase is anhydrous

t°	Gms. $PbCl_2$ per 100 gms. sat. sol.		t°	Gms. $PbCl_2$ per 100 gms. sat. sol.		t°	Gms. $PbCl_2$ per 100 gms. sat. sol.	
0	0.668	(8)	15	0.866	(12)	25	1.076	(2)[c]
15	0.902	(8)	20	0.971	(2)[b]		1.075	(3)
	0.85	(1)		0.968	(12)		1.059	(10)
	0.876	(2)[a]	25	1.073	(8)(9)		1.028	(4)

(Cont.)

[a]d. = 1.0071 [b]d. = 1.0070 [c]d. = 1.0069

SOLUBILITY IN WATER--Cont.

(1) Demassieux, 1923; (2) Flöttmann, 1928; (3) Deacon, 1927; (4) Weber, 1929; (5) Burvage, 1926; (6) Herz and Hellebrandt, 1923; (7) Sowerby, 1927; (8) Lichty, 1903; (9) Carmody, 1929; (10) Lewin, Vance and Nelson, 1953; (11) Benrath, Gjedebo, Schiffers and Wunderlich, 1937; (12) Goulden and Hill, 1945.

Solid phase is anhydrous

t°	Gms. $PbCl_2$ per 100 gms. sat. sol.		t°	Gms. $PbCl_2$ per 100 gms. sat. sol.		t°	Gms. $PbCl_2$ per 100 gms. sat. sol.	
20	1.083	(5)(6)	65	2.082	(8)	230	11.3	(11)
	1.075	(12)	80	2.555	(8)	257	14.3	(11)
30	1.17	(8)	95	3.068	(8)	276	16.7	(11)
	1.179	(12)	100	3.234	(8)	287	18.4	(11)
35	1.307	(8)		3.10	(1)	345	24 - 76*	(11)
	1.298	(12)	141	4.74	(11)	351	81.2	(11)
45	1.543	(8)	160	5.67	(11)	362	87.8	(11)
50	1.75	(1)	187	7.39	(11)	407	84.4	(11)
55	1.709	(8)	195	8.47	(11)			

*Two liquid layers are formed and there is present salt solution, melt and vapor.

SOLUBILITY OF LEAD CHLORIDE IN WATER - DEUTERIUM OXIDE MIXTURES AT 25° (Noonan, 1948)

% D_2O	Moles $PbCl_2$ per 100 moles Solvent
91.6	0.0471
100.0	.0449

Table 1-61

LEAD SULFATE $PbSO_4$

SOLUBILITY IN WATER

(Average curve from gravimetric results of Dibbits (1874), Beck and Stegmüller (1910) and Pleissner (1907) and conductivity results of Böttger (1903) and Kohlrausch (1904-05).

t°	Gms. $PbSO_4$ per Liter	t°	Gms. $PbSO_4$ per Liter
0	0.028	20	0.041
5	0.031	25	0.045
10	0.035	30	0.049
15	0.038	35	0.052
18	0.040	40	0.056

Later determinations of the solubility of lead sulfate in water by Crockford and Brawleys, 1934; Purdum and Rutherford, 1933; Kolthoff and Rosenblum, 1933; and Huybrechts and de Langeron, 1930, gave an average curve from which the following values were taken.

t°	Gms. $PbSO_4$ per Liter	t°	Gms. $PbSO_4$ per liter
0	0.0330	25	0.0452
5	0.0354	30	0.0476
10	0.0380	35	0.0500
15	0.0403	40	0.0526
20	0.0427	50	0.0574

Koizumi, 1950 reports that the effect of dissolved CO_2 on the solubility of $PbSO_4$ is negligible.

Table 1-62

MANGANESE CARBONATE $MnCO_3$

SOLUBILITY OF MANGANESE CARBONATE IN WATER
(Smurov, 1938)

(The total pressure of CO_2 + H_2O was one atmosphere)

Partial Pressure CO_2 in atm.	Gms. Mn per 100 gms. Sat. Sol. 5°	15°	40°	50°	80°
0.0005	0.0011	0.0009	0.0003	0.0002	0.0001
0.005	.0026	.0022	.0008	.0006	.0002
0.05	.0061	.0052	.0019	.0014	.0005
0.10	.0078	.0068	.0025	.0018	.0007
1.0	--	.04 (18°)*	--	--	--
56	--	.080 (18°)*	--	--	--

Table 1-63

STRONTIUM SULFATE $SrSO_4$

SOLUBILITY OF PRECIPITATED STRONTIUM SULFATE AND OF CALCINED "CELESTINA" (96.67% $SrSO_4$) IN WATER
(Gallo, 1935)

t°	Gms. $SrSO_4$ per 100 cc sat. sol. Solid Phase Pptd. $SrSO_4$	Solid Phase "Celestina"	t°	Gms. $SrSO_4$ per 100 cc sat. sol. Solid Phase Pptd. $SrSO_4$	Solid Phase "Celestina"
5	0.0121	0.0119	60	0.0131	0.0125
10	0.0129	0.0123	70	0.0123	0.0119
20	0.0132	0.0132	80	0.0116	0.0111
30	0.0138	0.0136	90	0.0115	0.0107
40	0.0141	0.0136	95	0.0113	0.0108
50	0.0135	0.0128			

Results of Kohlrausch, 1908

2.85°	0.01133 gms. per 100 cc H_2O
17.4	0.01143 gms. per 100 cc H_2O
32.3	0.01143 gms. per 100 cc H_2O

In general, temperature changes result in measureable and sometimes significant changes in ion concentration due to dissolution or precipitation of relatively insoluble compounds. Examples of temperature-dependent solubility data are shown in a number of tables. In this review, attention is called, in passing, to these solubility data as indicative of the orders of magnitude which one can expect. However, the reader is warned against drawing inferences about the direct applicability of these data to natural water systems. As will be discussed briefly in Section IV, the actual precipitation or degassing from a slightly supersaturated solution (resulting, for instance, from a lowering of temperature, or say, loss of CO_2) is often slow, and frequently highly dependent on the concentration and nature of heterogeneous nuclei for gas bubble formation or for the initial condensation of the insoluble precipitate. Conversely, the process of dissolution is time-dependent, and an immediate increase in temperature does obviously not immediately result in a new level of concentration of all species to an equilibrium value. Kinetic effects are important and unfortunately these are frequently poorly understood; furthermore, they are highly dependent on specific details on the nature of water and solutes adjacent to the dissolving or precipitating particle (stagnant layers, diffusion boundaries, adsorbed ions or co-precipitated, etc.).

For some comments on complex ions in brine and particularly the difficulties in predicting solubilities of minerals in more concentrated brines, see the discussions by Garrels and Christ (p. 108). These authors particularly note, regarding solubility problems, that theoretical predictions are nearly impossible at the present time. The reason is the unknown contributions to solubility from species for which dissociation constants are not known. Furthermore, the authors also point out that a very large number of simultaneous equations would have to be solved and that the problem, therefore, exceeds what is practical. Accumulation of errors from various uncertainties is presumably known dissociation constants might add up sufficiently to obviate any accuracy in prediction of the activity coefficients. This problem is of some interest in connection with the thermal changes in a natural water system where sediments in contact with the waters may or may not be affected by solubility changes.

Regarding the complex problem of the solubility of silicates, see Garrels and Christ (1965) and also Stumm and Morgan (1970 , loco cit., p. 409).

SECTION IV: SURFACE AND COLLOID CHEMICAL ASPECTS

IV. SURFACE AND COLLOID CHEMICAL ASPECTS

A. Introduction

The stability of a closed system - any chemical system, and in this case specifically natural waters - is determined by the free energy, ΔF, and for this reason, much interest attaches to the question of possible compensation between enthalpy and entropy; the compensation problem is treated in Section 2-IIIB. For most simple inorganic solutes in water, the thermodynamic properties are fairly well known, permitting various types of calculations of stabilities. However, for more "complicated" solutes, particularly polypeptides, and enzymes, ΔF may be numerically very small, and rather minute "environmental" changes (that is, in the chemical or physical nature of the aqueous system), may affect stability severely. We are presently a long way from a rational - let alone complete - description of natural waters in such terms.

While many unknowns still remain to be determined quantitatively in free energy relationships, the principles of thermodynamics must apply. However, the rate with which the various equilibria may be reached are subject to far greater uncertainty. The problem of colloidal stability continues to be a field of active research. This Section presents a brief outline, in qualitative terms, of the problem of colloid stability. The kinetics of approach to equilibrium in colloidal systems is exceedingly complex. Even in its simplest form, in terms

of "classical approaches", the problem is difficult. To these difficulties, the present author feels must be added the very poorly understood (and still incompletely documented) roles of vicinal water structures.

Tables I-64 and I-65 outline in an exceedingly schematic fashion, the standard approach to problems such as colloidal stability, based primarily on theories for the electrical double-layer. Extensive treatments can be found in standard references such as Kruyt (1949, 1952), Adamson (1960), Sheludko (1966), or Davies and Rideal (1963).

In nearly all of the commonly employed descriptions of surface and colloid phenomena, the assumption is made that "water is water is water"; in other words, that a colloidal system can be considered a heterogeneous mixture of some "extraneous material" in a matrix of water, the latter retaining its bulk structure and properties. Some evidence is accumulating which indicates that water near interfaces is not bulk-like but is indeed differently structured. Furthermore, and perhaps more significantly, the distances over which these different structures extend may be considerable. In this context, "considerable" means large on a molecular scale, say 100 to 1,000 molecular diameters. This is significant in connection with the subject at hand, namely the suitability of natural waters to support life. First of all, the extensive hydration phenomena which may accompany the presence of colloidal material in actual waters may play an important role in determining the overall properties. However, perhaps far more significant is the fact that if indeed water structure is affected over distances of 1,000 molecular diameters

(i.e., 0.3 microns), structural effects apparently occur over distances which are of the same order of magnitude as intracellular dimensions. For this reason, it is important first to review briefly some of the available evidence which suggests structuring of water near interfaces. Secondly, attention is directed toward biological systems. Here it is necessary and important to realize that the structural effects observed in cellular systems are found as well in physico-chemically well described, completely non-living systems.

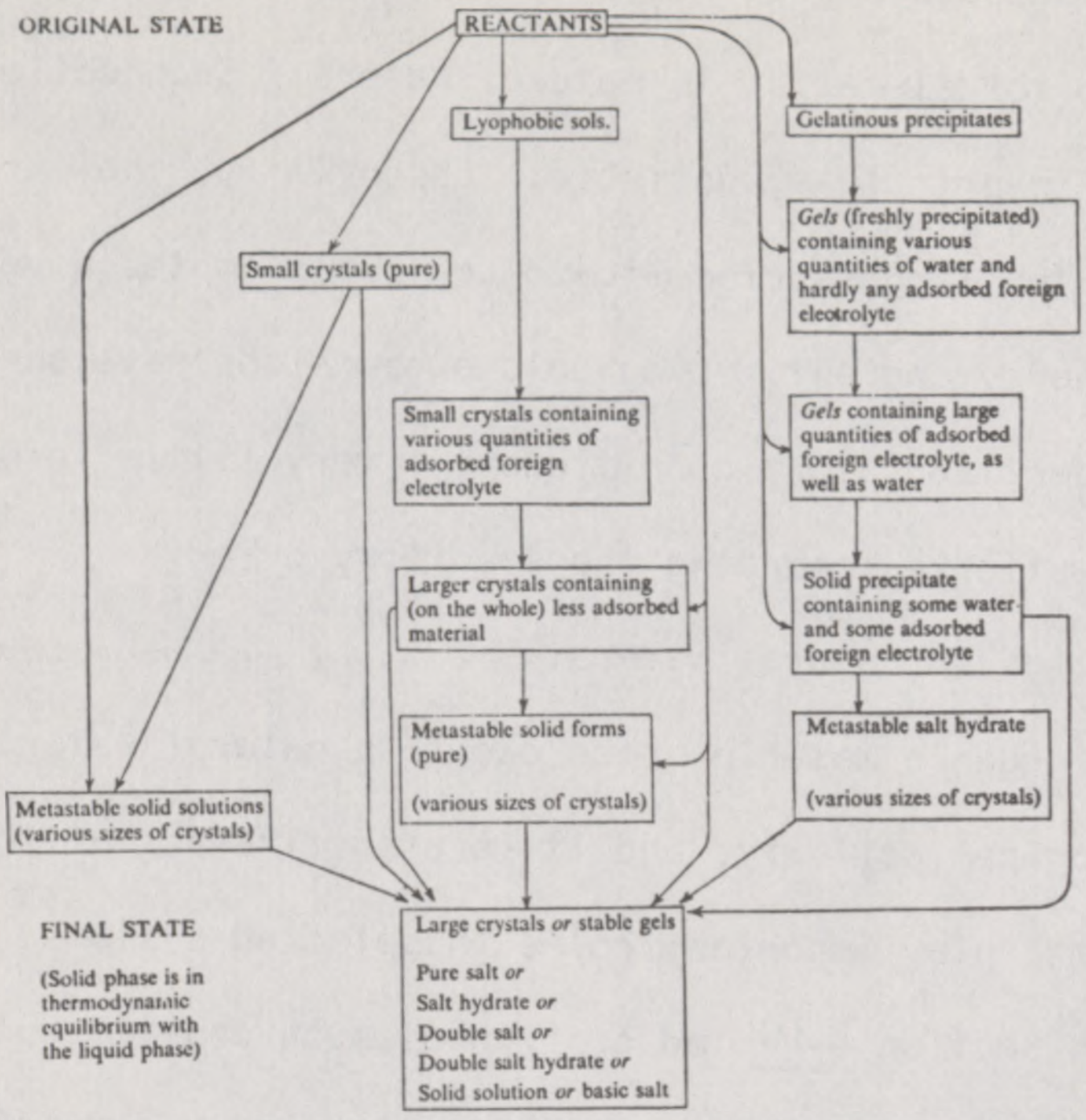
While temperature effects on thermodynamic equilibrium properties may be predicted with some degree of certainty - and generally with predictably small net changes—the behavior of kinetic phenomena is notably different. Rates of reactions are often significantly affected by temperature. However, to the degree of approximation used in this review, the temperature effects on rates are essentially predictable from simple analysis. No sudden or unexpected large changes in the rates of reactions are to be expected for "standard simple processes" such as rate of dissociation of H_2CO_3 - or rate of complexing of magnesium ions. However, unfortunately, these reactions - of the type which occur wholely in bulk - are fairly few and in many respects unimportant for the natural waters. Of far greater importance are those reactions which take place at interfaces. Indeed, these are, by far, the more abundant and include such important properties as rates of transfer of gases at the air/water interface; rates of dissolution or precipitation; rates of reactions involving colloidal suspended matter and the constituents of the natural waters, etc. For reactions involving interfacial aspects, the simple predictions made on the basis of homogeneous bulk reaction rates are often totally incomplete and, in fact, erroneous. The reason for these difficulties is due to the complexities of interfacial phenomena, particularly in aqueous systems where various types of hydration of interfaces is not only still poorly understood, but obviously exceedingly complex.

As will be apparent from the preceding discussion, the bulk properties of water (both physical and chemical properties) may be expected to change in relatively predictable, "smooth" fashion with temperature

at least over the temperature interval of practical interest (here chosen to be approximately 0 to 45°C). However, large surface-to-volume ratio systems (such as colloidal suspensions) may be expected to show abrupt and unexpected changes at a number of critical temperatures. The ranges of temperature which have been previously described, particularly by the present author (1973, 1971) are 14 to 16°; 29 to 32°; 44 to 46°; and 59 to 62°. Note that the changes are abrupt, but not of the type of abruptness observed at the freezing or boiling point . This corresponds to the contention made earlier that the anomalies are reflections of higher-order phase transitions (not first order phase transitions). In order to observe higher-order phase transitions, it is necessary to have some structured elements and these are most likely stabilized water structures at the water/solid interface. The higher-order phase transition, in a sense, resembles "smeared out" melting processes of different predominant structures, or rather the transition from one type of structure to another type of structure (with greater stability in a different temperature interval).

Lyophobic suspensions undoubtedly represent an important class of suspended colloidal matter in natural waters. Such colloidal solutions are, in principle, unstable. Essentially, they are unstable because the large surface-to-volume ratio imples a very high surface-free energy content. Lyophobic suspensions have been studied extensively under laboratory conditions but very little information is currently available regarding the stability or even nature of lyophobic colloids in natural waters. However, it seems reasonable that colloidal organic material does occur in natural waters as the result of biological activity, and it is also likely that these colloids in turn, play important roles in selected systems. Thus, as mentioned in Section III C1 adsorption of such organic colloids as denatured proteins may seriously affect nucleation and precipitation rates of carbonates. Again, one is dealing with an interfacial system for which it is to be expected that hydration structures play a role over and above that recognized in the traditional treatment of colloidal stability.

Lewin (1960) has indicated some possible steps in the creation of a simple precipitate or stable gel from the reactions via various types of precipitates. These include (in order of increasing complexity and practical and theoretical "messiness" metastable solids [crystallites], stable but small crystals, lyophobic sols and gels and gelatinous precipitates of various types (see Figure I-26). The question of the role of water structure in the stability and properties of gels remains unresolved at this time.



Non-stable Intermediary States Which may Form in a Typical Precipitation Reaction (Lewin, 1960).

Figure I-26

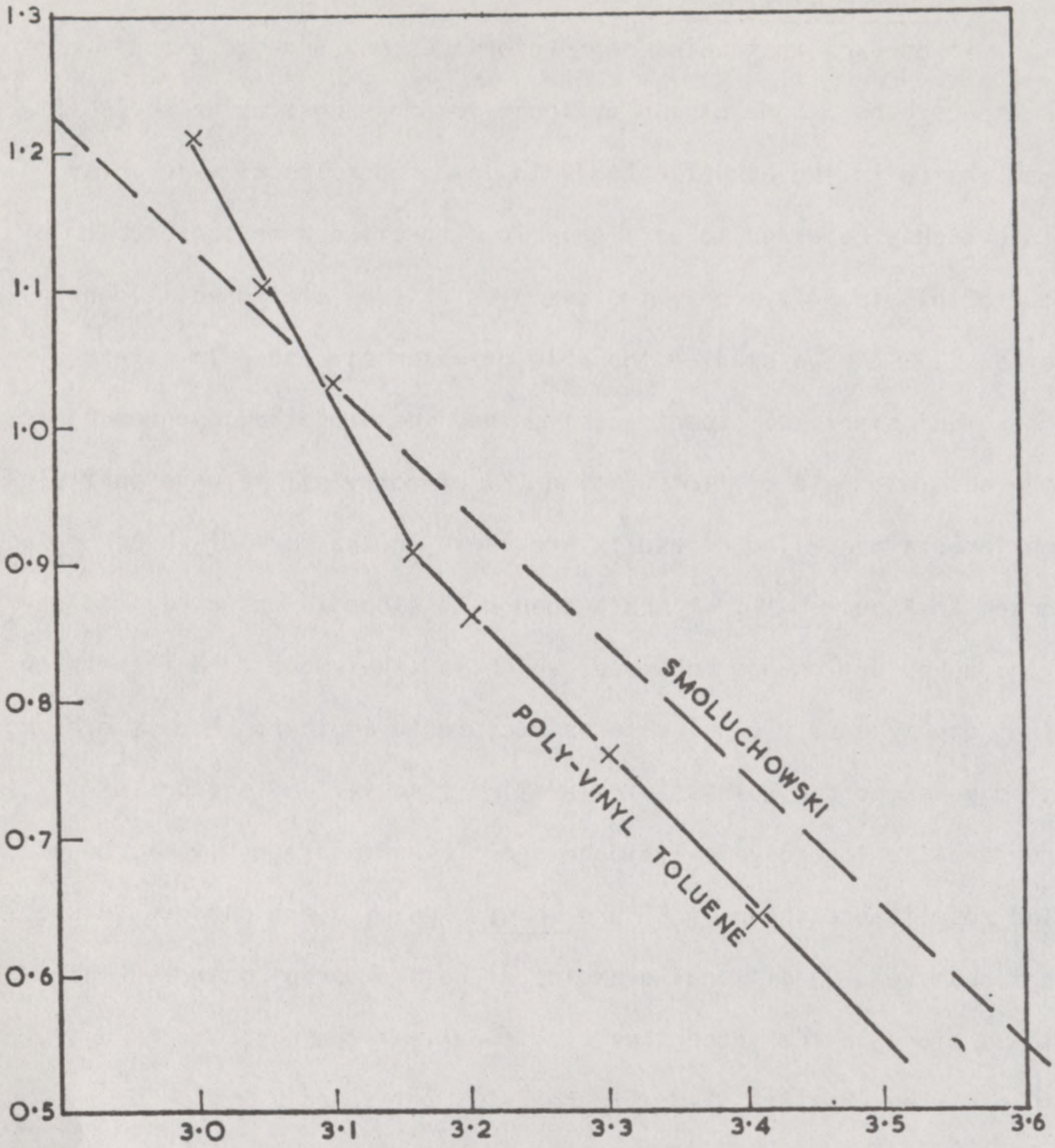
As indicated in the preceding sections, only the most elementary aspects of colloidal stability have yet been elucidated theoretically. The expressions available for determining colloidal stability usually contain in the rate expressions reference to the linear or exponential temperature dependencies. However, as stressed before, most theoretical predictions would indicate relatively simple and certainly "smooth" temperature-dependent behavior. The complexity of the problem, however, for actual systems, can be seen quite readily from the simple case discussed by Lewin (1960). The major problem is the formation of many types of non-stable states which may be formed. Thus, for simple reactions leading to an insoluble product, a "full accounting" of possible temperature effects would involve kinetic rate expressions for each of the many consecutive and/or simultaneous reactions - each no doubt with differing enthalpies and entropies of activation. For this reason, theoretical predictions of the kinetics of precipitation of insoluble products generally cannot be expected to yield reliable results - nor can rates of solution be predicted theoretically. In addition to the complexity indicated in Figure I-26, one need most likely also include distinct differences in the role played by the water of hydration for each of the metastable states indicated.

In practical terms, assessments of expected changes in equilibrium properties in composition of natural water systems may be obtained by the approach discussed in Sections II, III of this review. However, the rate with which these changes will be effected may become highly tmeperature-dependent wherever aqueous, interfacial processes are involved, particularly those involving the solid/water interface such as a mineral grain/water interface, or the interface between a dispersed organic material or a cellular organism and the water.

In this section, we review some unexpected anomalous temperature effects on colloidal phenomena to illustrate the points discussed above. It will become obvious that few generalizations can be made, but that caution must be urged in predicting the effects of ambient temperature changes on the overall composition of natural waters involving colloidal phenomena.

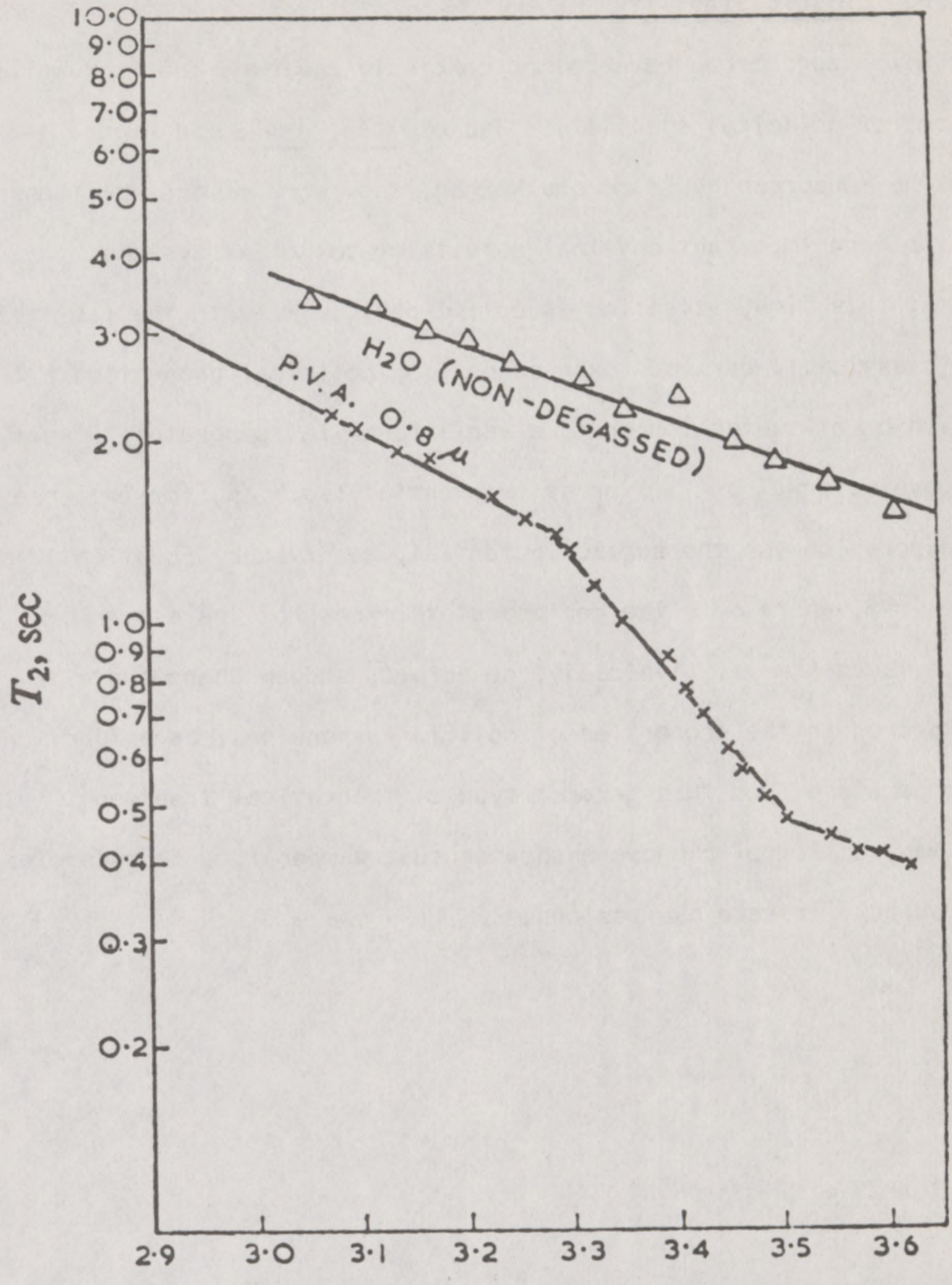
Thermal Anomalies.

It appears that water near interfaces may undergo extensive restructuring. Some of the evidence for this restructuring is manifested in the abrupt changes in the properties of water near interfaces, referred to earlier. In connection with the problem of colloidal stability, only two examples will be mentioned. Johnson et al (1966) have studied the role of water structure in determining colloidal stability; specifically, they measured the dependence of the absolute rate of flocculation (K) of polyvinyl toluene particles on temperature. Their results are shown in the form of an Arrhenius graph in Figure I-29. A sharp change in slope is observed, indicating an abrupt change in slope, which is likely due to a transition from one type of vicinal water structure to another. The same authors also measured the spin-spin relaxation time (T_2) as a function of temperature for polyvinyl alcohol particles (average 0.8 micron diameters). The results are shown in Figure I-30. Again, sharp changes in slope are observed. Additional examples of rather abrupt changes with temperature in the properties of vicinal water are shown in Part 2 of this review (Section II-B; Figure 2-10; 2-11; and 2-12). For a detailed discussion of various aspects of water structure near solid surfaces, the reader is referred specifically to an article by Drost-Hansen (1969).



Log flocculation rate (K 10^{12}) as function of 1/T for PVT particles (Johnson et. al., 1966).

Fig. 1 - 29



Spin - spin relaxation rate as function of 1/T for 0.8 PVA particles (and for degassed water) (Johnson et al., 1966)

Figure 1 -30

B. Colloid Stability

Stumm and Morgan have rather concisely reviewed the "conventional wisdom" of colloidal stability. Tables I-64, I-65, and Figure I-27 from the monograph by Stumm and Morgan, show some of the equations for the more important physical aspects of colloidal systems.

At this time, attention is called particularly to the fact that the "classically derived" expressions for colloidal properties all contain or allow for temperature variations via temperature itself as a prefactor (T or T^{-1}) or as exponential (such as, for instance, the expression for the surface potential, as given by Equation 12-a, Table I-64, where κ is the reciprocal thickness of the electric double layer (cm^{-1}). Typically, no abrupt, sudden changes are to be expected in the properties of colloid suspensions, as a function of temperature from this general type of theoretical treatment. Yet, many colloidal phenomena show unusual temperature dependencies, particularly in rate expressions.

Table 1-64

Gouy–Chapman Theory of Single Flat Double Layer†

I. VARIATION OF CHARGE DENSITY IN SOLUTION

Equality of electrochemical potential, $\bar{\mu}$ $(=\mu + zF\Psi)$ of every ion, regardless of position.

Electrochemical Potential

$$\bar{\mu}_{+(x)} = \bar{\mu}_{+(x=\infty)}; \qquad \bar{\mu}_{-(x)} = \bar{\mu}_{-(x=\infty)} \tag{1}$$

$$zF(\Psi'_{(x)} - \Psi'_{(x=\infty)}) = RT \ln \frac{n_{+(x)}}{n_{+(x=\infty)}} = -RT \ln \frac{n_{-(x)}}{n_{-(x=\infty)}} \tag{2}$$

Cations
$$n_+ = n_{+(x=\infty)} \exp(-zF\Psi'_{(x)}/RT) \tag{3}$$

Anions
$$n_- = n_{-(x=\infty)} \exp(zF\Psi'_{(x)}/RT) \tag{4}$$

Charge Density
$$q = zF(n_+ - n_-) \tag{5}$$

II. LOCAL CHARGE DENSITY AND LOCAL POTENTIAL

Ψ' and q are related by Poisson's equation

Poisson's Equation
$$d^2\Psi'/dx^2 = -(4\pi/\epsilon)q \tag{6}$$

Combining (3), (4), and (5) with (6) and considering that $\sinh x = (e^x - e^{-x})/2$ gives the *Double-Layer Equation*

$$d^2\Psi'/dx^2 = \kappa^2/(zF/RT)\sinh(zF\Psi'/RT) \tag{7}$$

where

$$\kappa = \left(\frac{8\pi\tilde{n}e^2z^2}{\epsilon kT}\right)^{1/2} = \left[\frac{8\pi e^2}{\epsilon kT}\left(\frac{NI}{10^3}\right)\right]^{1/2} \tag{8}$$

For convenience the following substitutions can be made:

$$y = zF\Psi'/RT; \qquad z = zF\Psi'_0/RT; \qquad \xi = \kappa x \tag{9}$$

Considering (9), (8) becomes

Substituted Double-Layer Equation

$$d^2y/d\xi^2 = \sinh y \tag{10}$$

For boundary conditions, if $\xi = \infty$, $dy/d\xi = 0$ and $y = 0$

first integration: $dy/d\xi = 2\sinh(y/2)$, or (11)

$$d\Psi'/dx = \frac{RT}{zF} 2\kappa \sinh(y/2) \tag{11a}$$

and for boundary conditions, if $\xi = 0$, $\Psi' = \Psi'_0$ or $y = z$

second integration:
$$e^{y/2} = \frac{e^{z/2} + 1 + (e^{z/2} - 1)e^{-\xi}}{e^{z/2} + 1 - (e^{z/2} - 1)e^{-\xi}} \tag{12}$$

Simplified Equations for $\Psi'_0 < 25$ mV

Instead of (7)
$$d^2\Psi'/dx^2 = \kappa^2\Psi' \tag{7a}$$

Instead of (12)
$$\Psi' = \Psi'_0 \exp(-\kappa x) \tag{12a}$$

III. TOTAL DOUBLE-LAYER CHARGE AND Ψ'_0

Total Charge:
$$\sigma = -\int_0^\infty q\,dx = \epsilon/4\pi \int_0^\infty (d^2\Psi'/dx^2)dx$$

$$= -\epsilon/4\pi[d\Psi'/dx]_{x=0} \tag{13}$$

Gouy-Chapman theory of a single, flat electrical double layer (from Stumm and Morgan, 1970, page 460).

Table I-64 Continued

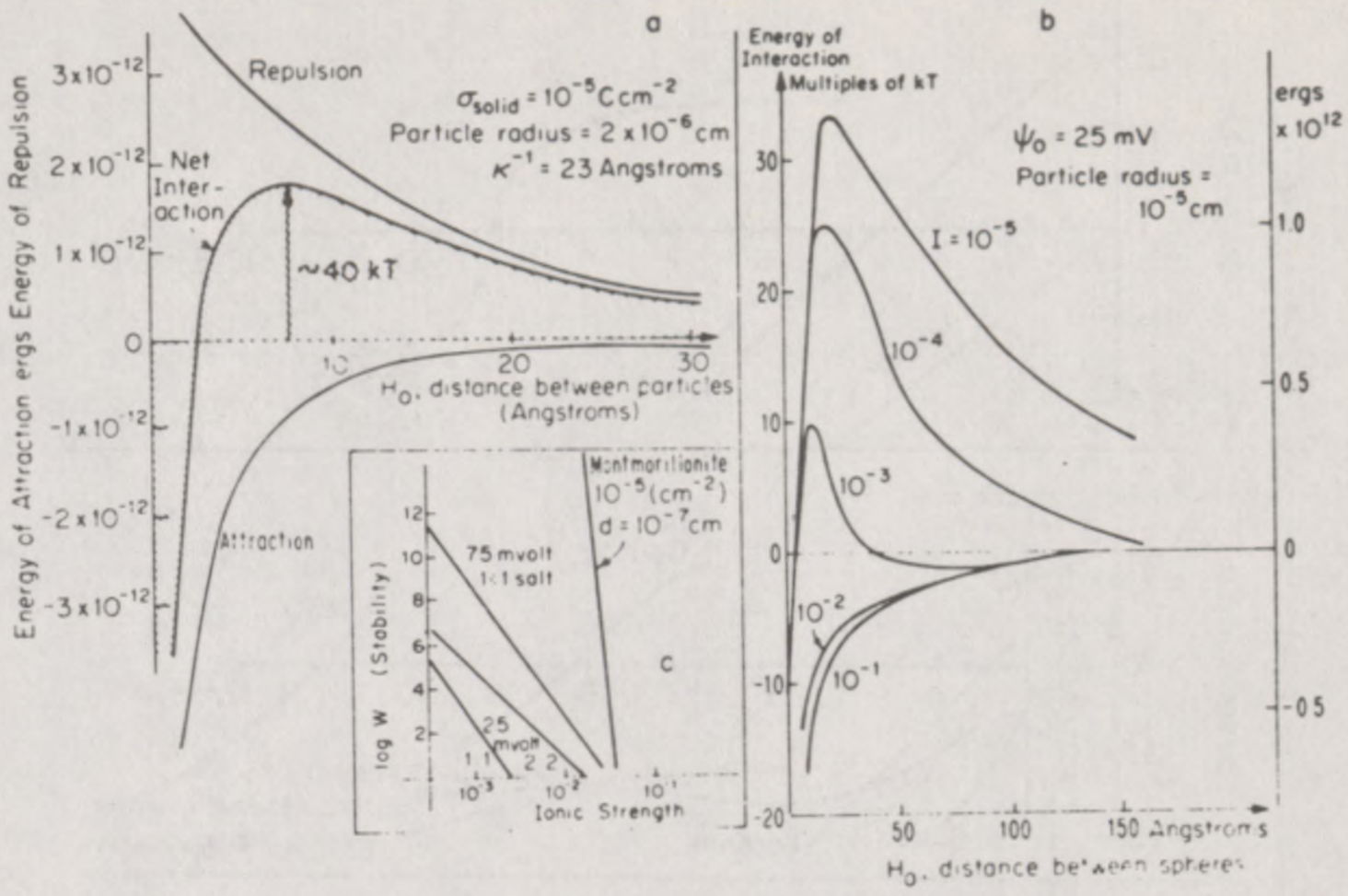
Inserting (11*a*):

$$\sigma = [(2/\pi)\epsilon kT\bar{n}]^{1/2} \sinh (zF\Psi_0/2RT) \quad (14)$$

Simplified equation for small Ψ_0:

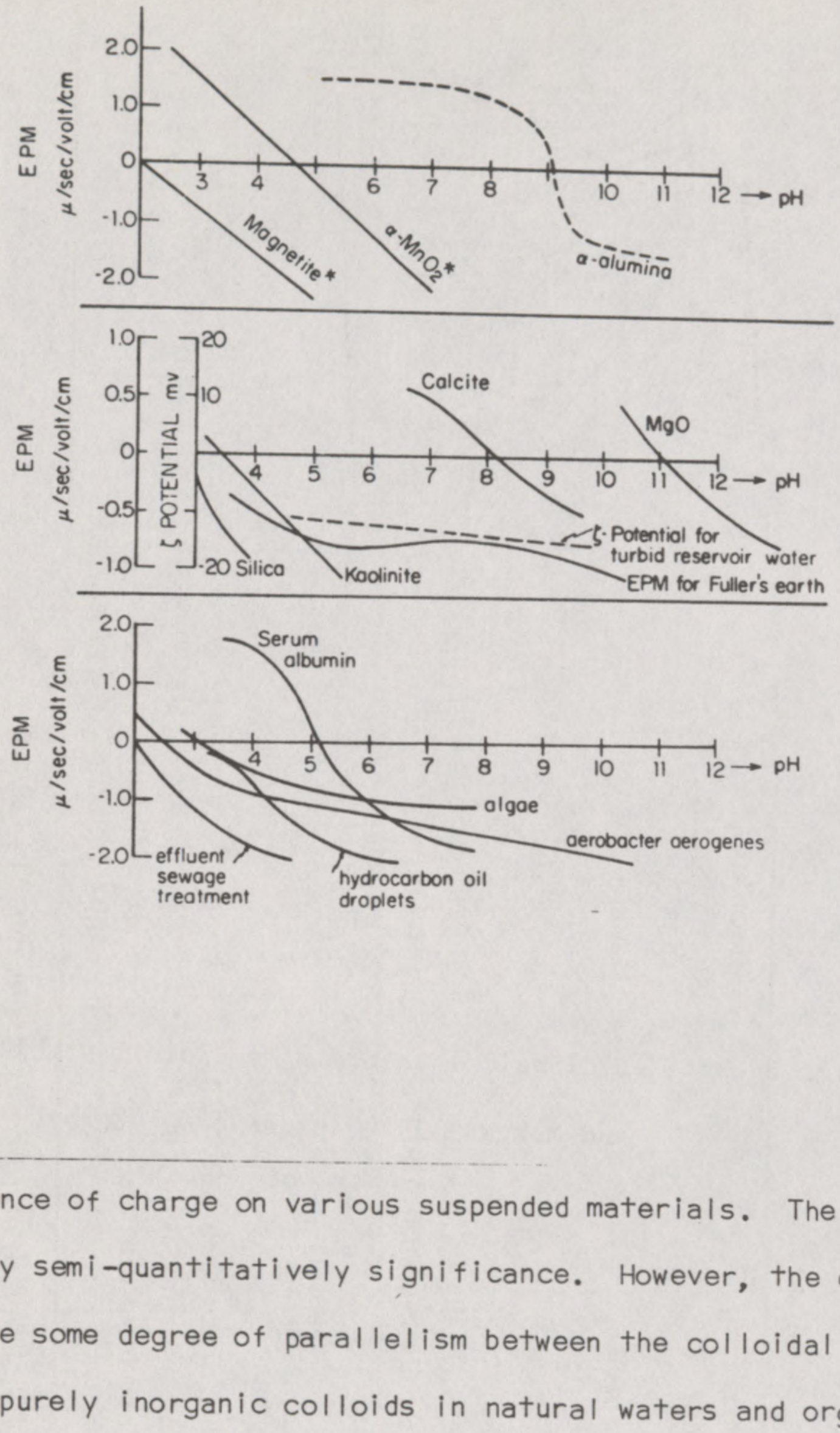
$$\sigma \simeq (\epsilon\kappa/4\pi)\Psi_0 \quad (14a)$$

† μ chemical potential
$\bar{\mu}$ electrochemical potential
Ψ local potential, V
Ψ_0 surface potential, V
q (volumetric) charge density, coulombs cm^{-3}
σ total surface charge, coulombs cm^{-2}
x distance from surface, cm
n_+ local cation concentration, moles cm^{-3}
n_- local anion concentration, moles cm^{-3}
$n_{(x=\infty)}$ bulk ion concentration, moles cm^{-3}
$\bar{n}$ number of ion pairs, cm^{-3} ($= Nn_{x=\infty}$)
N Avogadro's number, 6.03×10^{23} mole^{-1}
I ionic strength, mole liter^{-1}
z valence of ion
κ reciprocal thickness of double layer, cm^{-1}
e charge of electron, 1.6×10^{-19} coulombs
kT Boltzmann constant times absolute temperature, 0.41×10^{-20} V coulomb at 20 C
$RT = N \times kT = 2.46 \times 10^3$, V coulomb mole^{-1}
ϵ dielectric constant, 89×10^{-12} coulombs V^{-1} cm^{-1}
F Faraday $= 6 \times 10^{23} \times e$, coulombs equiv^{-1} = 96,500 coulombs equiv^{-1}
$F\Psi/RT = e\Psi/kT = 1$ for Ψ = 25 mV at 20 C



Energetics aspects of classical theory of colloidal stability (Stumm and Morgan, 1970, page 497).

Figure I-27



pH dependence of charge on various suspended materials. The data are of only semi-quantitatively significance. However, the data do indicate some degree of parallelism between the colloidal properties of purely inorganic colloids in natural waters and organic or living material (bacteria and algae). (Stumm and Morgan, 1970, p. 455).

Figure 1-28

Table I-65

Modes of Destabilization and Their Characteristics†

Phenomena	Physical Double-Layer Theory (Coagulation)	Chemical Bridging Model (Flocculation)	Aggregation by Adsorbable Species (Adsorption Coagulation)‡
Electrostatic interaction	Predominant	Subordinate	Important
Chemical interactions, and adsorption	Absent	Predominant	Important
Zeta potential for optimum aggregation	Near zero	Usually not zero	Not necessarily zero
Addition of an excess of destabilizing species	No effect	Restabilization due to complete surface coverage	Restabilization usually accompanied by charge reversal
Relationship between optimum dosage of destabilizing species and the concentration of colloid (or concentration of colloidal surface)	CCC virtually independent of colloid concentration	Stoichiometry, a linear relationship between flocculant dose and surface area	Stoichiometry possible but does not always occur
Physical properties of the aggregates which are produced	Dense, great shear strength but poor filtrability in cake filtration	Flocs of 3-dimensional structure; low shear strength but excellent filtrability in cake filtration	Flocs of widely varying shear strength and density

† From W. Stumm and C. R. O'Melia, *J. Amer. Water Works Assoc.*, 60, 514 (1968).
‡ Aggregation by hydrolyzed metal ions fits into this category.
Reproduced with permission from American Water Works Association.

Various aspects of stabilization of aqueous colloidal systems.

(Stumm and Morgan, 1970, page 501).

C. Adsorption-Desorption Phenomena

Various adsorption processes play a crucial role in determining the overall chemical properties of natural waters. The classical expressions for estimating adsorption equilibria are shown in Table I-66, from the monograph by Stumm and Morgan (1970). The Table shows the "conventional wisdom" with regard to adsorption phenomena, specifically the Gibbs and Langmuir adsorption isotherms. A vast literature exists on adsorption phenomena (from aqueous solutions) in general. However, far fewer data are available specifically on temperature effects on adsorption equilibria. Furthermore, the complications introduced in the preceding paragraph - namely those due to the possibility of different vicinal water structures - must be kept in mind in connection with all adsorption-desorption phenomena.

Table 1-66

Adsorption Equilibria†

	Gibbs‡§		Langmuir‡§	
Adsorbed substance per unit area $\Gamma = n_i/A$ $= \Gamma_\infty \theta$ (for monolayer adsorption)	$\Gamma_i = -\left(\frac{\delta\gamma}{\delta\mu_i}\right)_{\text{T, P, all } \mu\text{'s except } \mu_1 \text{ and } \mu_{H_2O}}$	(1)	$\frac{\theta}{1-\theta} = K^{-1}a_i$	(5)
	$\Gamma_i = -\frac{1}{RT}\left(\frac{\delta\gamma}{\delta \ln a_i}\right)_{\text{T, P, all } \mu\text{'s except } \mu_1 \text{ aud } \mu_{H_2O}}$	(2)	$\Gamma_i = \frac{\Gamma_{i\infty} a_i}{K + a_i}$	(6)
Example: Adsorption of a hydrocarbon (HC)	$d\gamma = -RT\Gamma_{HC} d \ln \{HC\}$	(3)	$\frac{1}{\Gamma_i} = \frac{1}{\Gamma_{i\infty}} + \frac{K}{\Gamma_{i\infty}}\frac{1}{\{HC\}}$	(7)
Example· Adsorption of a hydrocarbon (HC) and of an alcohol (ROH)	$d\gamma = -RT\Gamma_{HC} d \ln \{HC\} - RT\Gamma_{ROH} d \ln \{ROH\}$	(4)	$\Gamma_{ROH} = \frac{\Gamma_{ROH\infty} K_{ROH}^{-1}\{ROH\}}{1 + K_{ROH}^{-1}\{ROH\} + K_{HC}^{-1}\{HC\}}$	(8)
Basis for application: μ_i (interface) $= \mu_i$ (bulk phase)	Reversible equilibrium		(1) Reversible equilibrium up to monolayer ($\theta = 1$). K is related to the free energy of adsorption: $K = \exp[\Delta G^\circ/RT](G')$ (2) Fixed site adsorption (immobility of adsorbate)# (3) Homogeneity in surface (energy of adsorption independent of θ)	

Classical adsorption equilibria. (Stumm and Morgan, 1970, page 452).

(For an explanation of symbols, see next page).

† μ = chemical potential
γ = interfacial tension, erg cm^{-2}
a_i = activity of species i, M
θ = fraction of surface covered with adsorbate
R = gas constant
K = adsorption equilibrium constant, M (if $K = a_i$, $\theta = 0.5$)
Γ_i = adsorption density, moles cm^{-2}
‡ In most cases, concentrations may be used instead of activities; however, the bulk concentration can no longer be defined in terms of quantities added if the solutes have associated to form micelles. Similar difficulties arise when the adsorbates in the interface undergo irreversible changes, such as denaturation reactions.
§ Γ_i is defined in such a way that in dividing the interface, the adsorption density of water is zero (Gibbs convention).

A similar adsorption model for multilayer adsorption has been set forth in the *Brunauer, Emmett and Teller* (*BET*) equation which has the form:

$$X = \frac{X_\infty B a_i}{(a_{is} - a_i)[1 + (B - 1)a_i/a_{is}]}$$

where X and X_∞ are the observed and ultimate quantity of substance adsorbed per unit area, B, an energy related constant, and a_{is} is the saturation activity of the solute.
Varying energies of adsorption can arise because of heterogeneity of the surface, that is, the free energy decreased with coverage. The Tempkin isotherm is based on such a model. In the *Tempkin isotherm*, θ is a function of log a_i at intermediate coverages ($0.2 < \theta < 0.8$).

CREDITS

Part I of this review is based on a wealth of information gathered from the published literature. In the following section is acknowledged the origin of the tables and illustrations used.

FIGURES

Figure I-01. J. J. Morgan in volume edited by W. Stumm, 1967, "Equilibrium Concepts in Natural Water Systems", page 9.

Figure I-02. J. J. Morgan in volume edited by W. Stumm, 1967, "Equilibrium Concepts in Natural Water Systems", page 14.

Figure I-03. Data by G. S. Kell, 1967, as shown in volume by D. Eisenberg and W. Kauzmann, "The Structure and Properties of Water", page 184.

Figure I-04. Compressibility data by Wilson and Bradley, 1966, as shown in R. A. Horne, 1969, "Marine Chemistry", page 61.

Figure I-05. Data by Knudsen, 1901, as shown by A. W. Collier, 1970, in volume edited by O. Kinne, "Marine Ecology", Vol. I, Part I.

Figure I-06. Heat capacity of water, as shown by D. Eisenberg and W. Kauzmann, 1969, "The Structure and Properties of Water", page 172.

Figure I-07. Heat capacity of water, based on the data by Ginnings and Furukawa, 1953, as shown in volume edited by O. Kinne, 1970, "Marine Ecology", Vol. I, Part I, page 323.

Figure I-08. Specific heat of water and seawater, based on data by Cox and Smith, as shown by A. W. Collier in volume edited by O. Kinne, 1970, "Marine Ecology", Vol. I, Part I, page 54.

Figure I-09. Specific heat of seawater, as shown by Connors, 1970.

Figure I-10. Viscosity as a function of temperature and pressure. Data by Bett and Cappi, as quoted by G. S. Kell in Franks, 1972, "Water, A Comprehensive Treatise", page 409.

Figure I-11. Transport properties of liquid water and heavy water, as shown by G. S. Kell in Franks, 1972, "Water, A Comprehensive Treatise", page 406.

Figure I-12. Viscosity as reported by R. A. Horne, 1969, page 95.

Figure I-13. Static dielectric constant, based on data by Weast, 1964, as shown by A. W. Collier in O. Kinne, 1970, "Marine Ecology," Vol. I, Part I, page 65.

Figure I-14. Electrical conductivity of seawater from data by Dietrich, 1963, as shown by A. W. Collier in O. Kinne, 1970, "Marine Ecology", Vol. I, Part I, page 64.

Figure I-15. Nomogram for determining oxygen saturation, according to Mortimer, as shown in Hutchinson, 1957, "A Treatise on Limnology", page 582.

Figure I-16. Oxygen solubilities, based on data by Fox (as indicated by Richards), shown by A. W. Collier in O. Kinne, 1970, "Marine Ecology", vol. I, Part I, page 79.

Figure I-17. Solubility of nitrogen as shown by Hutchinson, 1957, page 840.

Figures I-18, I-19, I-20, I-21, I-22, I-23. Solubility relationships for carbonates, as shown by J. R. Kramer in volume edited by W. Stumm, 1967.

Figure I-24. Carbonate solubility relationships, as shown by W. Stumm, and J. J. Morgan, 1970, "Aquatic Chemistry", page 410.

Figures I-25A, I-25B, I-25C, I-25D. Solution properties of calcium sulfate, as shown by Marshall and Slusher, 1966.

Figure I-25E. Solubility relationships of calcium sulfate in seawater, as shown by Marshall, 1971 (in Research and Development Progress Report #685, "Properties of Solutions", July 1971, Office of Saline Water, U. S. Department of the Interior, Washington, D. C.).

Figure I-26. Intermediary states in precipitation reactions as shown by Lewin, 1960, "The Solubility Product Principle", page 49.

Figure I-27. Energetics of colloidal stability, as shown by W. Stumm and J. J. Morgan, 1970, "Aquatic Chemistry", page 497.

Figure I-28. Surface charge relationships, as shown by W. Stumm and J. J. Morgan, 1970, "Aquatic Chemistry", page 455.

Figure I-29. Fluctulation rate as a function of reciprocal absolute temperature, as shown by Johnson, et al., 1966, page 124.

Figure I-30. Spin-spin relaxation times vs. reciprocal absolute temperature, as shown by Johnson, et al., 1966, page 128.

TABLES

Table I-02. Density of water, as shown in Gmelin, 1963, pages 1322-1323.

Table I-03. Specific volume of water, as shown by G. S. Kell in Franks, 1972, "Water, A Comprehensive Treatise", page 385.

Table I-04. Volume properties of water, reported by G. S. Kell in "Handbook of Chemistry and Physics", 52nd edition, 1971-1972, page F-5.

Table I-05. Specific gravity and temperature maximum of seawater, as shown by R. A. Horne, "Marine Chemistry", 1969, page 63.

Table I-06. Specific volume of seawater. Data from tables by Wilson and Bradley, as quoted by R. A. Horne, 1969, "Marine Chemistry", pages 479-481.

Table I-07. Vapor pressure of water, as shown in "Handbook of Chemistry and Physics", 52nd edition, 1971-1972, page D-148.

Table I-08. Heat evaporization as shown in Gmelin, 1963, page 108.

Table I-09. Heat capacity data for sodium chloride solutions, as given by Parker, 1965, page 43.

Table I-10. Heat conductivity data from Gmelin, 1963.

Table I-11. Viscosity of water, as shown by G. S. Kell in Franks, 1972, "Water, A Comprehensive Treatise", page 407.

Table I-12. Viscosity of seawater. Data by Miyake and Koizumi, as shown by A. W. Collier in volume edited by O. Kinne, 1970, "Marine Ecology", Vol. I, Part I, page 57.

Table I-13. Viscosity of seawater from J. D. Isdale, C. M. Spence and J. S. Tudhope, 1972, "Desalination", Vol. 10, pages 319-328 (Elsevier Publishing Company, Amsterdam, Netherlands).

Table I-14.. Diffusion coefficients of water as shown in Gmelin, 1963, page 1472.

Table I-15. Diffusion coefficients of some seawater electrolytes, as shown in R. A. Horne, 1969, "Marine Chemistry", page 94.

Table I-16. Surface tension of water, as shown in Gmelin, 1963, page 1420.

Table I-17. Surface tension of seawater, as shown by R. A. Horne, 1969, "Marine Chemistry", page 323.

Table I-18. Microwave dielectric data by J. B. Hasted, in Franks, 1972, "Water, A Comprehensive Treatise", Vol. I, page 277.

Table I-19. Refracture index of seawater, as quoted by R. A. Horne, 1969, "Marine Chemistry", page 517.

Table I-20. Specific conductivity of seawater, as shown by R. A. Horne, 1969, "Marine Chemistry", page 487.

Table I-21. Cation and Anion equivalent conductances, as shown by Falkenhagen, 1971, "Theorie der Elektrolyte", pages 195-196.

Table I-22. Composition of seawater, as given by Garrells and Christ, 1965, "Solutions, Minerals, and Equilibria", page 101.

Table I-23. Activity coefficients of individual species of seawater, as shown by R. M. Garrells and C. L. Christ, 1965, "Solutions, Minerals, and Equilibria", page 103.

Table I-24. Debye-Hückel constants from W. J. Hamer, 1968, page 266.

Table I-25. Minimum ion-parameter, as given by R. M. Garrells and C. L. Christ, 1965, "Solutions, Minerals, and Equilibria", page 62.

Table I-26. Minimum ion-parameter, as given by W. J. Hamer, 1968, page 267.

Tables I-27, I-28, I-29, I-30, I-31, I-32. Theoretically calculated mean activity coefficients, as given by W. J. Hamer, 1968.

Table I-33. Thickness of ionic atmosphere, as given by Falkenhagen, 1971, "Theorie der Elektrolyte", page 117.

Table I-34. Pre-exponential term, as given by Ives and Janz, 1961, "Reference Electrodes", page 67.

Table I-35. Ionization constant of water from R. M. Garrells and C. L. Christ, 1965, "Solutions, Minerals, and Equilibria", page 70.

Tables I-36, I-37, I-38, I-39. Ionization constants, as shown in Harned and Owen, 1958, "The Physical Chemistry of Electrolytic Solutions", 3rd edition.

Table I-40. Freezing point and osmotic pressure, based on data by Defant, 1961, as shown by A. W. Collier in volume edited by O. Kinne, 1970, "Marine Ecology", page 56.

Table I-41. Vapor pressure and osmotic equivalent of seawater from R. A. Horne, 1969, "Marine Chemistry", page 533.

Table I-42. Osmotic pressure of sea salt solutions from R. A. Horne, 1969, "Marine Chemistry", page 533.

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Table I-44. Buffering capacity of carbonate systems from W. Stumm and J. J. Morgan, 1970, in "Aquatic Chemistry", page 138.

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Table I-46. Solubility of oxygen as shown by Hutchinson, 1957, "A Treatise on Limnology", Vol. I, page 580.

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Table I-48. Solubility of nitrogen in water, from Seidell, 1958, edited by Linke.

Table I-49. Solubility of argon in water, from Seidell, 1958, edited by Linke.

Table I-50. Solubility of carbon monoxide from Seidell, 1958, edited by Linke.

Table I-51. Solubility of CO_2 from Hutchinson, 1957, "A Treatise on Limnology", Vol. I, page 654.

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Tables I-57, I-58, I-59, I-60, I-61, I-62, I-63. Various solubilities, as shown by Seidell, 1958, edited by Linke.

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THERMAL ASPECTS OF AQUATIC CHEMISTRY
PART 2

BY

W. DROST-HANSEN

TABLE OF CONTENTS

	Page
PART 2	
I. Overview	
A. Thermal Transitions in Biological Systems	1
II. Structural Role of Water	
A. Hydration Phenomena	5
B. Specific Examples of Thermal Anomalies	9
C. Origins of Thermal Responses and of Anomalies	12
D. Miscellaneous Effects on Some Isolated Systems	15
III. Functional Aspects	
A. Rate Expressions	17
B. Enthalpy-Entropy Compensation	20
C. "Normal Behavior"	26
D. Anomalous Responses Near 23° C	27
E. Acclimatization and Adaptation	30
F. Multiple Temperature Optima	34
G. Thermal Death Mechanisms	40
H. Low Temperature Death	43
I. Neural Temperature-Sensitive Phenomena	45
IV. Effects of Temperature on Various Organisms	47
V. Ecological Aspects	
A. Introduction	59
B. Fluctuating Temperatures	61
C. Multivariant Analysis	63
D. Specific Examples	66
E. Cytoecology	68

Table of Contents Continued - Part 2

	Page
V. Ecological Aspects (Continued)	
F. Various Ecological Examples	73
VI: Summary and Discussion	75
Semantics Note	78
Acknowledgements	81
References	82

PART 2

SECTION I: OVERVIEW

I. OVERVIEW

A. Thermal Transitions in Biological Systems

Abrupt changes in biological processes are frequently observed at discrete temperatures (often in the vicinity of 14-16°C, 29-32°C, 44-46°C). If one allows for cooperativity* of the kind exhibited, for instance, in traditionally described higher-order phase transitions, it is reasonable to assume that many (but naturally not all) biological systems might exhibit transitions at nearly identical temperature intervals. Many cellular functions, principally the metabolic pathways for the oxidation of glucose, the utilization of ATP, and possibly the synthesis of nucleic acids and proteins, are essentially the same whether one is concerned with multicellular animals and plants, protists, or bacteria and blue-green algae. Similarly, many aspects of membrane structure and function appear to be similar in both animals and plants. Hence, a fundamental biochemical uniformity appears to exist from unicellular life to mammals at the cellular and subcellular levels of organization. Should any of the types of processes mentioned above depend in some way on temperature activation on a cooperative process, it would be expected that the same type of effects would be manifested in vastly different types of living systems. As an example, there are reasons to believe (Drost-Hansen, unpublished) that lipid/water interactions may exhibit an anomaly near 23°C. Hence, processes primarily controlled by interactions such as occurring in bimolecular leaflet-type membranes are likely affected at about the same temperature regardless of the type of cells studied. The effect seems intimately associated with the properties of both the water and the naturally-occurring lipids. However, while for instance, the functioning of ATP, protein synthesis, etc. may be ubiquitous to cellular

*The word cooperativity is used here in its physico-chemical sense: a "landslide effect" on structure, reflecting extensive intermolecular "self-helping", far exceeding the effects of any single molecular event.

functioning, so indeed is water and it is proposed that structural changes in vicinal water determine the frequently observed abrupt changes in this review. One particular reason for considering vicinal water to be the "site of action" is the fact that in purely inorganic (non-living) aqueous model-systems (of large surface-to-volume ratios), thermal anomalies are frequently observed at the temperature ranges discussed above, namely near 15, 31, and 45°C. On this basis, it is proposed that generalizations may be made - based on a physico-chemically reasonable concept - regarding biological systems, with respect to the responses to temperature. Not all individual cellular phenomena are controlled or determined by aqueous processes. Many biological systems show no evidence of abrupt changes at the critical temperatures discussed. However, within the entire organism, be it unicellular or multicellular, it is likely that one or more of the multitude of individual reactions occurring are affected by vicinal water structures. This being the case, it appears reasonable to propose that the temperatures at which vicinal water undergoes structural changes may serve as rather invariant, thermal pollution limits, or at least that such temperature regions call for particular caution. It may be sufficient for temperature to exert a noticeable effect on one stage of development of an organism, and thus affect an entire biotic community's development.

B. Effects of Chemical Changes on Cells and Organisms

In Part I of this review, the effects of temperature on the chemical properties of water and dilute aqueous solutions were reviewed. Restricting our attention to that range of temperatures in natural systems of environmental interest, 0 to 40°C, it was shown that the net effect on the chemistry of a 5 or 10°C temperature increase is often modest. From the point of view of physical chemistry, the changes may be highly significant, and frequently

measureable with extreme precision, but in many cases a 5°C increase in temperature will have only very slight effects on the (chemical and physical) parameters determining the suitability of the aqueous medium to support life. For example, increasing the temperature from 20 to 30°C decreases the viscosity by 20%. Such a change in viscosity is unlikely to affect the energetics in a significant way of the swimming speed of a fish or the "drift velocity" of an organism in the phytoplankton. Increasing the temperature of seawater from 20 to 30°C reduces the saturation levels of DO by approximately 18%. From a physico-chemical point of view, this could have a significant (but not necessarily devastating) effect. The changes in other physico-chemical parameters with temperature may be of limited importance. A fish most likely "would not notice" the 20% increase in electrical conductivity of the seawater, corresponding to a 10°C temperature increase (say, from 15 to 25°C). As long as changes in the chemical parameters of the natural waters vary either linearly, or even exponentially with temperature, variations in physical or chemical properties over reasonably small temperature intervals - (5 or 10°C increments) - are probably without major effects on ecosystem functioning. Yet, it is well known that rapid, and sometimes disastrous changes occur in biota as the result of temperature changes of only a few degrees! Some of the possible classical mechanisms described in the literature to explain sharp temperature optima are treated below. A prime example is the now classical treatment by Eyring and co-workers (see Johnson, Eyring and Polissar, 1954) on the effects of temperature on the luminescence of some bacteria as a function of temperature, interpreted in terms of consecutive and simultaneous biochemical reactions (enzymatic reactions) on the molecular level.

In this part of the review, it is proposed to demonstrate that large

and often profound changes may be induced in cellular organisms due to attendant changes in the internal chemistry. At the same time the effects of temperature - as discussed above - exerted via the changes in the external chemistry of natural waters, is likely relatively small, reasonably well understood and predictable.

The first two sections of this part of the review are concerned with some aspects of hydration phenomena (and hydration structures) of organic solutes and aqueous microphases (such as lipid-membrane systems). The second of these sections is also concerned with some biochemical and biophysical interpretations of cellular functions in terms of molecular models. Throughout the discussion, emphasis is placed on the effects of temperature on the nature and extent of hydration. A brief discussion is presented also of other possible "sites of action" of temperature in living systems, for instance, the effects expected due to phase changes in lipids or conformational changes in proteins.

The present treatment is restricted essentially to the separate review of changes in the chemistry of natural waters (as the result of temperature changes) and, independently, changes in the suitability of natural waters to support life in view of the temperature-induced changes in the chemistry. The standard approach has been to describe the effects of temperature effects on the properties of such a system in relation to the suitability of the system to support life. Only rarely have more complex than binary systems been studied in any detail as a function of temperature and only rarely have several external factors been considered operating at the same time. The simultaneous effects of multiple (ecological variables) been discussed in some detail (by D. F. Alderdice) in "Factor Combinations" in Kinne's volume on Marine Ecology (1972).

PART 2

SECTION II: STRUCTURAL ROLE OF WATER

II. STRUCTURAL ROLE OF WATER

A. Hydration Phenomena

During the past twenty years, several authors (Jacobson, [1955], Troshin [1956], Drost-Hansen [1956], Szent-Györgyi [1957], Klotz [1958], and Ling [1962] began to consider seriously possible "non-classical effects" of aqueous surface interactions and their roles in biological systems.

Several reviews are available, devoted in part or completely to interfacial aspects of water in biological systems. The following references are suggested: Ling (1962), Walter and Hope (1971), Drost-Hansen (1971), and Hazlewood (1973).

For a review of some pertinent aspects of the hydration of organic solutes in water, see Drost-Hansen (1971). This paper discussed briefly the nature of hydrophobic bonding; the nature of organic hydrates - including clathrate hydrates - the possible role of water structure in gels, and briefly, the role of water structure in the hydration of peptides, nucleic acids and proteins. For other articles on the role of water structure in aqueous protein solutions, see the papers by Privalov (1958), Richards (1963), von Hippel and Schleich (1969), Lumry and Rajender (1970), Lumry and Biltonen (1969), Meryman (1966), Kayushin (1969), Vuks and Sidorova (1971a,b). For a review of the solvation in general of polyelectrolytes, see the recent article by Conway (1972).

The majority of organic materials in natural waters - including seawater - consist of nitrogeneous compounds, composed of: amino acids, small peptides, and polypeptides. Concentrations of these compounds in ordinary natural waters are extremely low - particularly in the open ocean. The significance, however, is in the effects of temperature on the hydration structures of macromolecular solutes in the organisms rather than as bulk solutes.

A few "semi-classical" attempts at describing physiological fluids in terms of classical electrolyte theory have been made. One study by DeHaven and Shapiro calls attention to the fact that in applying classical physical chemistry to cell physiological problems, the "proper values" for various parameters must be used. While this would seem to be obvious, it is, nonetheless, rarely done - simply for lack of detailed knowledge of these parameters. Examples of the "proper" parameters for which the actual values are not known include dielectric constant, viscosity or activity.

In considering the interpretations of general physiological regulations in terms of solution chemistry, Pfister and Pauly (1972) have examined the concept of "apparent" single ion activities in complex solutions such as the cytoplasm of living cells. They conclude both from their experiments as well as from model calculations that the activity coefficient of uni-univalent salts in cytoplasm should be not more than 30% lower than in a salt solution of equal composition. Furthermore, "on the basis of the assumption that concentrated protein-salt solutions may serve as appropriate model systems for the cytoplasm, no evidence could be derived for the binding of a large portion of the intracellular simple ions". Compare this together with the analysis by DeHaven and Shapiro (1968) - with the approach advocated by Ling, on the one hand (the association-induction theory) and the present author's attempts, on the other hand, at describing the cytoplasm as an aqueous environment distinctly different from that ordinarily accounted for in classical electrolyte theory - due to the changes in water structure induced by mere proximity to an interface (regardless of the specific chemical nature of the vicinal solid).

For a general review of the hydration of macromolecules, particularly proteins, see the article by Brandts in Rose's monograph, Thermobiology (1967).

From the discussion by Brandts are shown some aspects of the hydration of protein molecules, emphasizing the likely role of hydration water structures (Figure 2-1 , 2-2). The article by Brandts is recommended as a concise review of the temperature dependence for the kinetics of enzyme reactions. Two illustrative examples from Brandt's article are shown in the Figures 2-3 and 2-4 .

The problem of extensive, stable hydration hulls has been summed up by Lumry and Rajender (1970) in the following statement: "For some years it was customary in studies of protein hydrodynamic properties to incorporate into the calculations a shell of water which was treated as moving with the protein. There was considerable experimental justification for this course of action provided by the results of drying experiments, calculated diffusion coefficients, transport of solvent by protein, buoyance measurements and so on, but the use of partial specific volumes computed on a dry weight basis makes it unnecessary to examine this problem in every hydrodynamic or equilibrium sedimentation experiment". Lumry and Rajender have also pointed out that, "The idea of stable hydration shells has not been very popular in recent years despite the skillful championing of the idea by Klotz ... It is probable that there are some very unusual features of water at protein surfaces and the experiments by Lauffer and co-workers on TMV protein ... are particularly important in this connection; but the idea of a structured shell with either ice-like or clathrate character has not been generally appealing for reasons which have been presented by Kauzmann ... However, if such shells exist, they are the most obvious places to look for the source of solvent-dependent compensation behavior and should have top priority in studies of compensation. Although the estimates of 'hydration' of water differ markedly from method to method, a frequent

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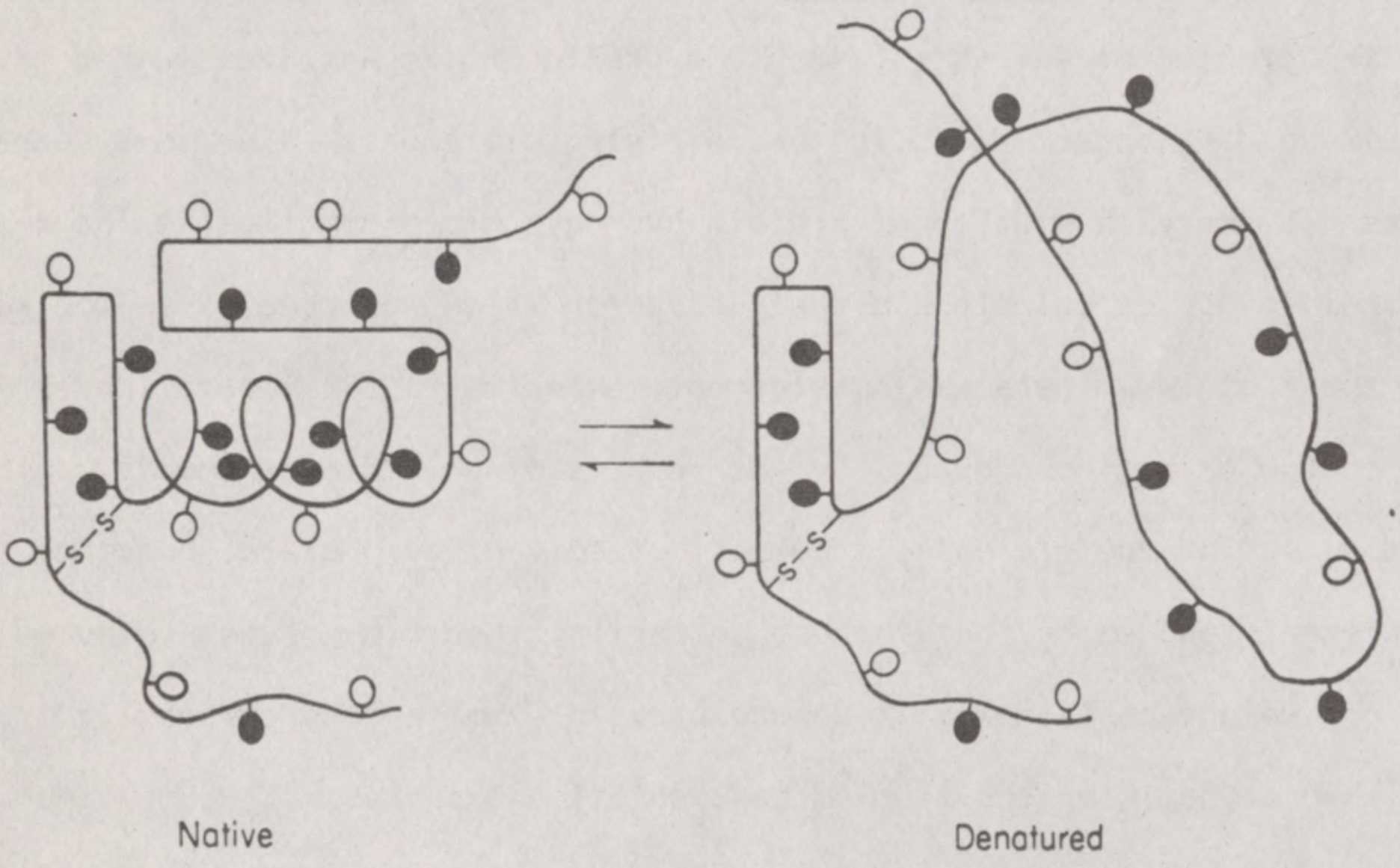
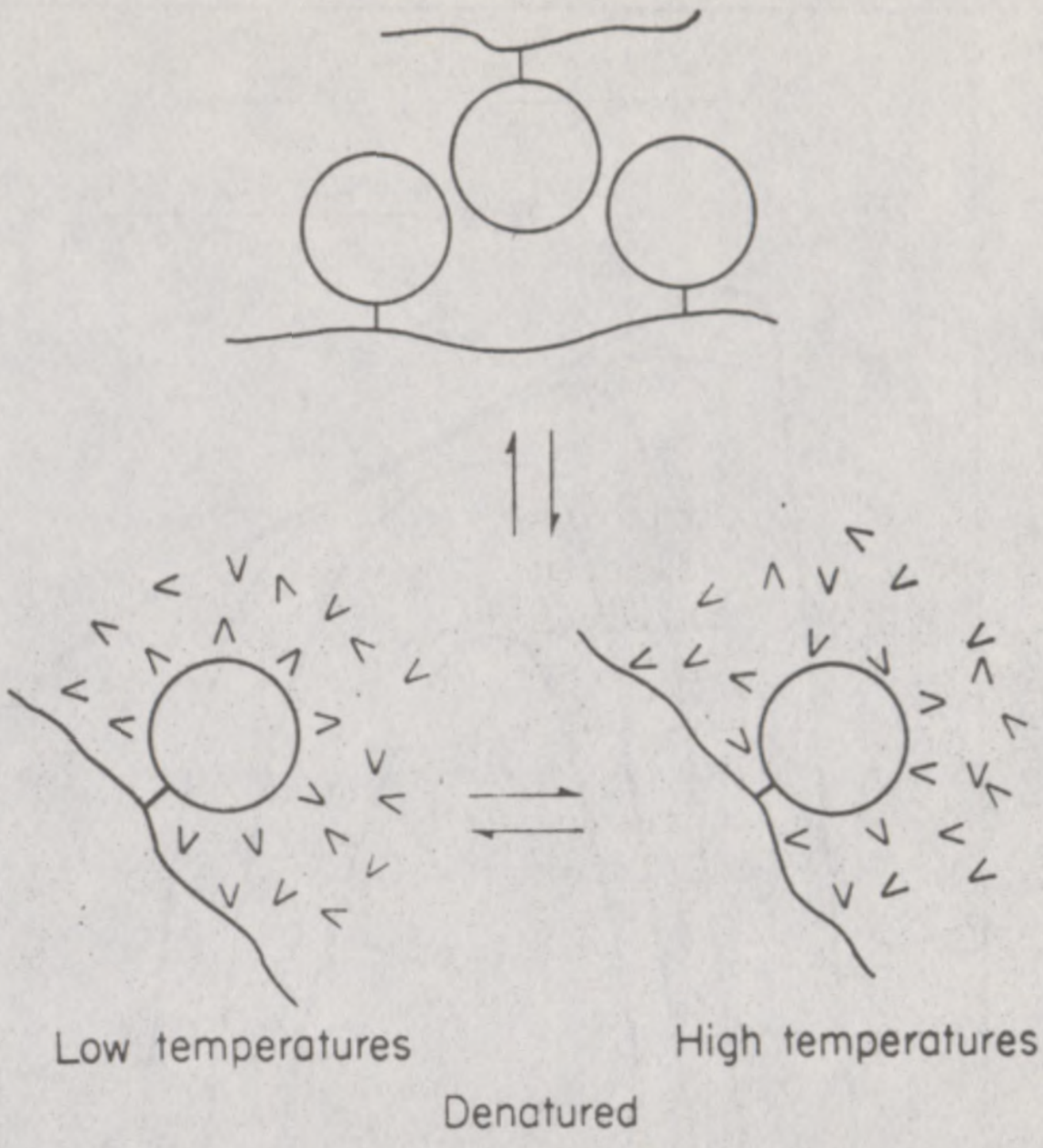
figure deducted from different types of experiments is 30% of the weight of the protein (see Glasel ... for a recent experimental approach to the problem)".



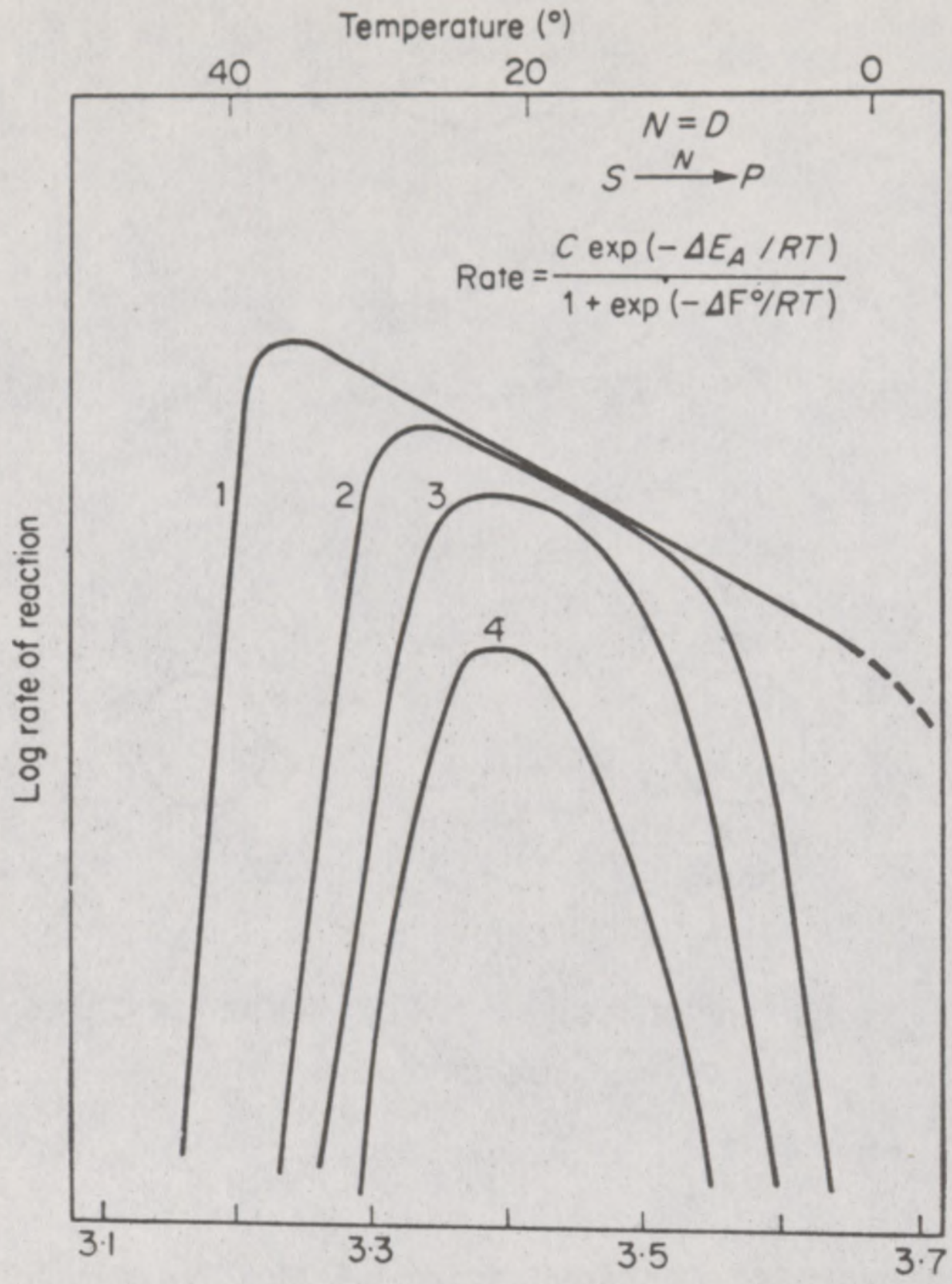
Highly Schematic Diagram of the Denaturation of a Protein Molecule. Most Hydrophobic Side Chains (Filled Circles) are Buried in the Molecule in the Native State, but become Exposed to the Solvent in the Denatured State; Polar and Ionic Side Chains [Corresponding to High Energy Interactions with the Solvent (water)], Shown as Open Circles; these are all largely Solvated, both in the Native and Denatured State (see Brandts in Rose, 1967, page 30).

Figure 2-1



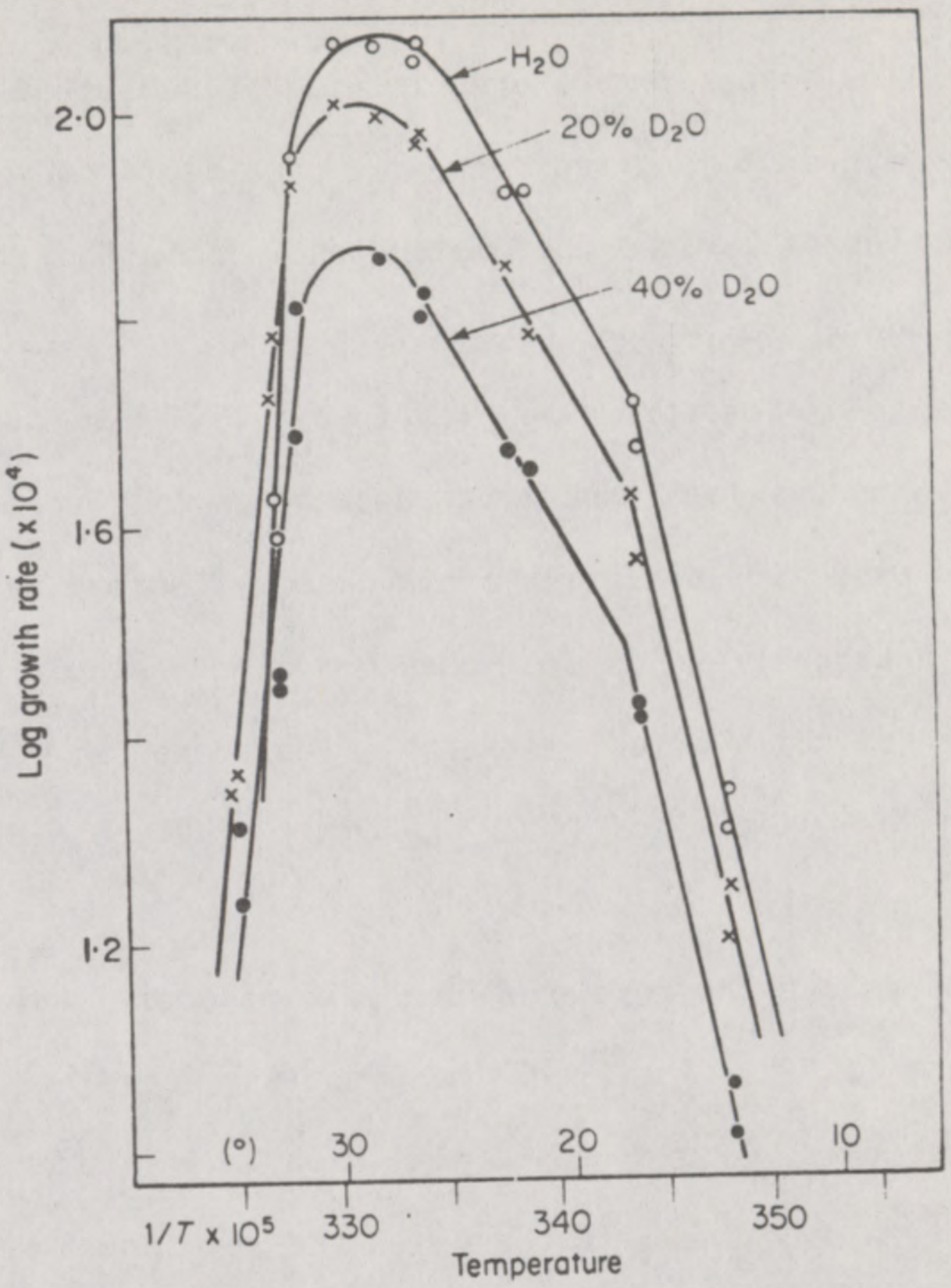
Extremely schematized Representation of the Hydrophobic Bonding Reaction and "Clathrate Melting Transition". Note Transition from Low Temperature, Ordered Solvation Shell of Water to Disordered Solvation Shell at Higher Temperature. (From Brandts, in Rose, 1967, Page 37).

Figure 2-2



Schematized Arrhenius plot for Reaction S → P, Catalyzed by an Enzyme N. Values shown for Different Heat Stabilities of the Enzyme. (Brandts, in Rose, 1967, page 64).

Figure 2-3



Typical Example of Arrhenius Plot for Growth of Tetrahymena pyriformis (in H_2O and D_2O). Note abruptness of Change near 15° (and Precipitous Drop in Growth Rate Above 30°). (Data by Moner, quoted by Brandts in Rose, 1967, page 67).

Figure 2-4

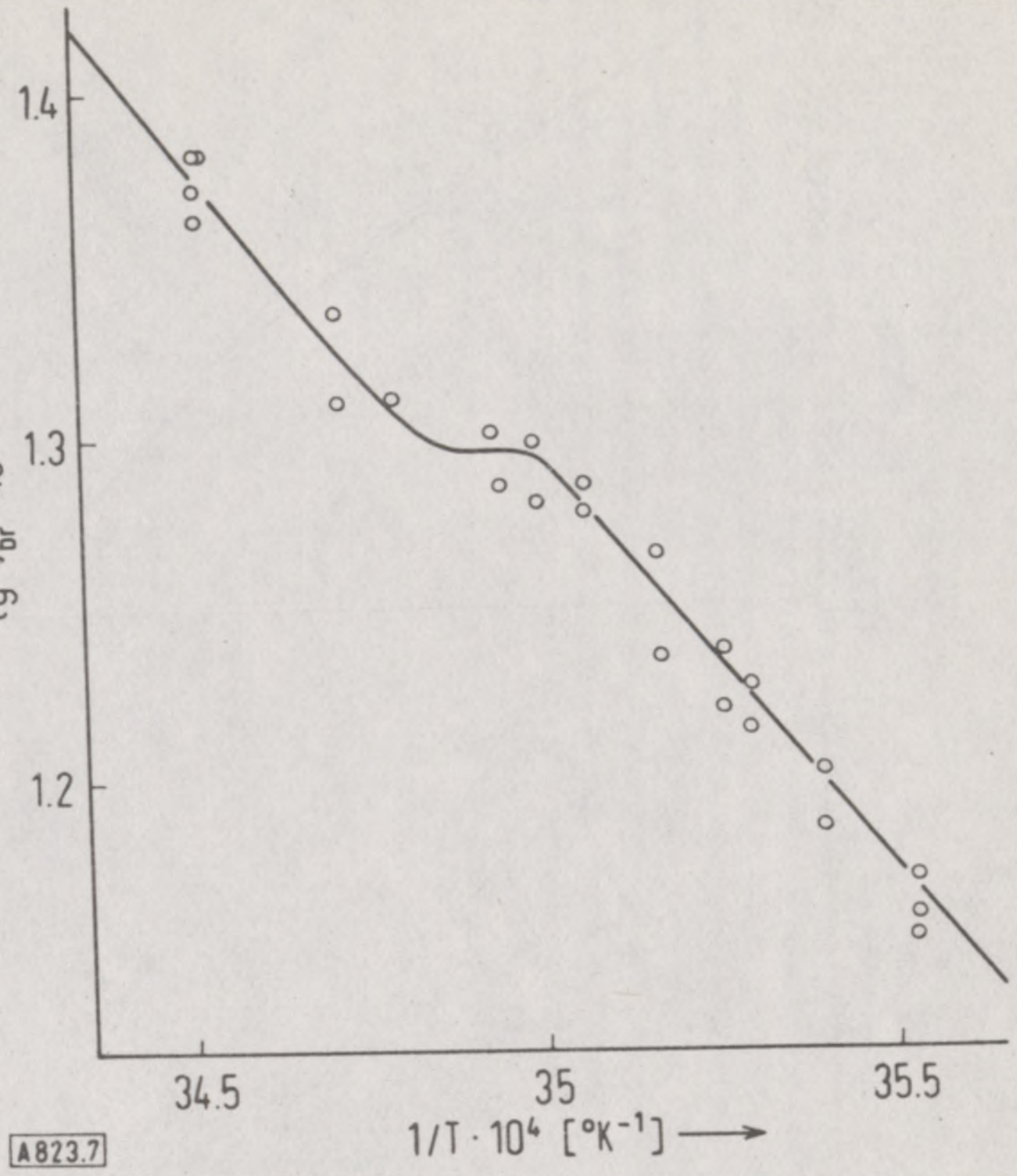
B. Specific Examples of Thermal Anomalies

In the following paragraphs are discussed a number of examples which illustrate the types of results frequently obtained from temperature studies of properties of various macromolecules in solution. Most of these examples have specifically been chosen from the enzyme systems because of the ubiquitous role these proteins play in all living systems.

Figure 2-5 shows the temperature dependence of the rate of hydrolysis of a synthetic ester (N^{α}-benzoyl-L-arginine ethyl ester) by trypsin (Talsky, 1971). The standard Arrhenius plot does not give a single straight line, but rather two "slightly offset" straight line segments. Change of slope is observed in the vicinity of 14°C. [Anomaly of "Type A-B", Drost-Hansen, 1967, p. 81]. See also Figure 2-5a.

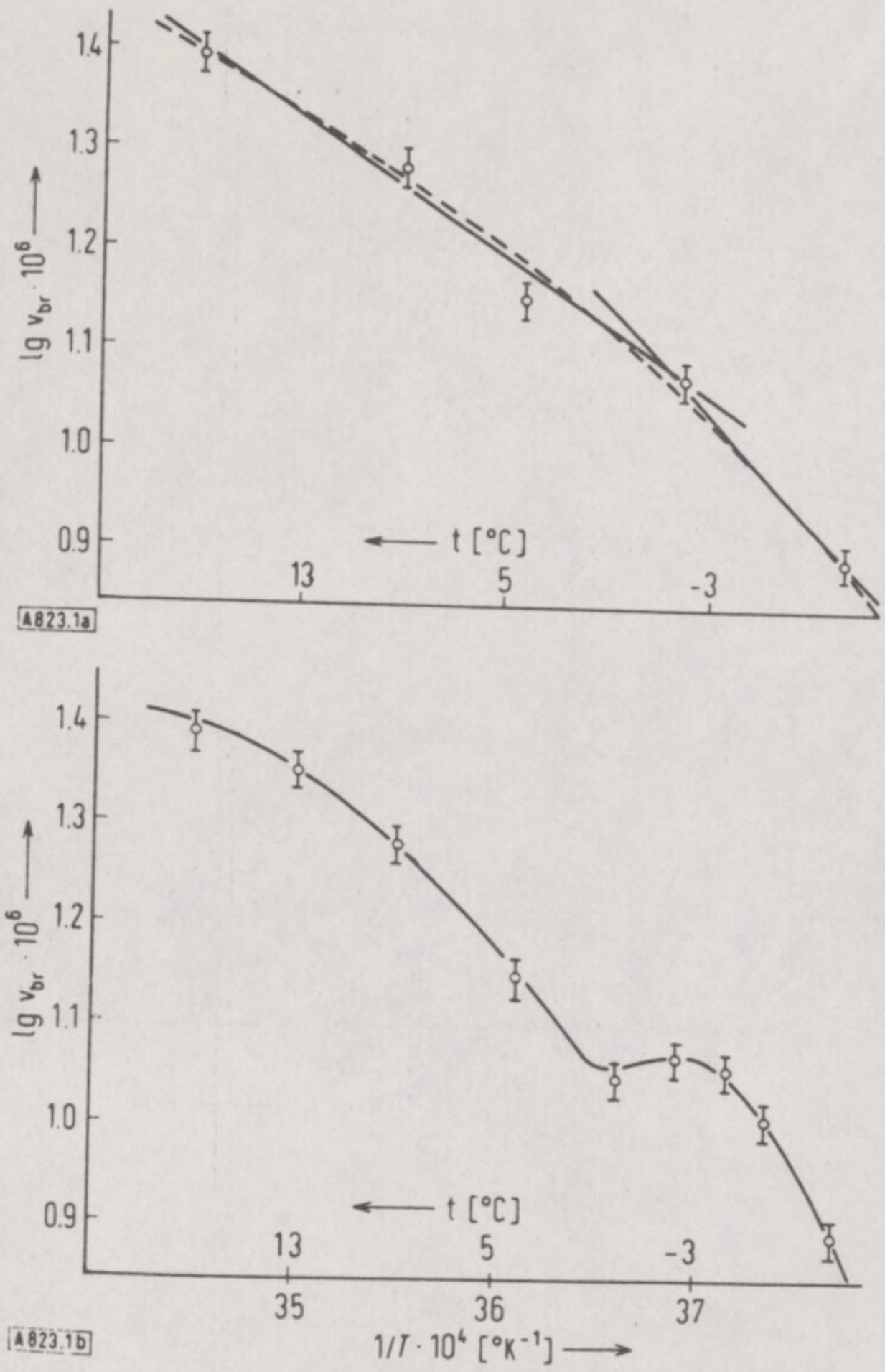
Figure 2-6 shows the rate of hydrolysis of acetyl thiocholine iodide (Ciliv and Özand, 1972). Acetylcholine hydrolase, obtained from human erythrocyte fragments, is a glycoprotein which is activated by polar substrates (acetyl thiocholine). A change in the rate and binding constant is observed in the vicinity of 31°C. [Anomaly of "Type E-F", Drost-Hansen, 1967, loco cit.].

Figure 2-7 shows the effect of temperature on the activation of trypsin by calcium from a study by Sipos and Merkel (1970). In the absence of calcium, the trypsin activity goes through a single maximum at 45°C. In the presence of calcium ions (0.02 molar), two distinct peaks are observed, respectively, near 45°C and near 60°C. The corresponding Arrhenius plot is shown in Figure 2-8 for the trypsin-catalyzed hydrolysis of p-Tos-L-Arg-OMe. One observes an effect in the enzyme activity as a function of temperature, and again, two essentially straight line segments one observes similar to the example discussed by Talsky (1971).



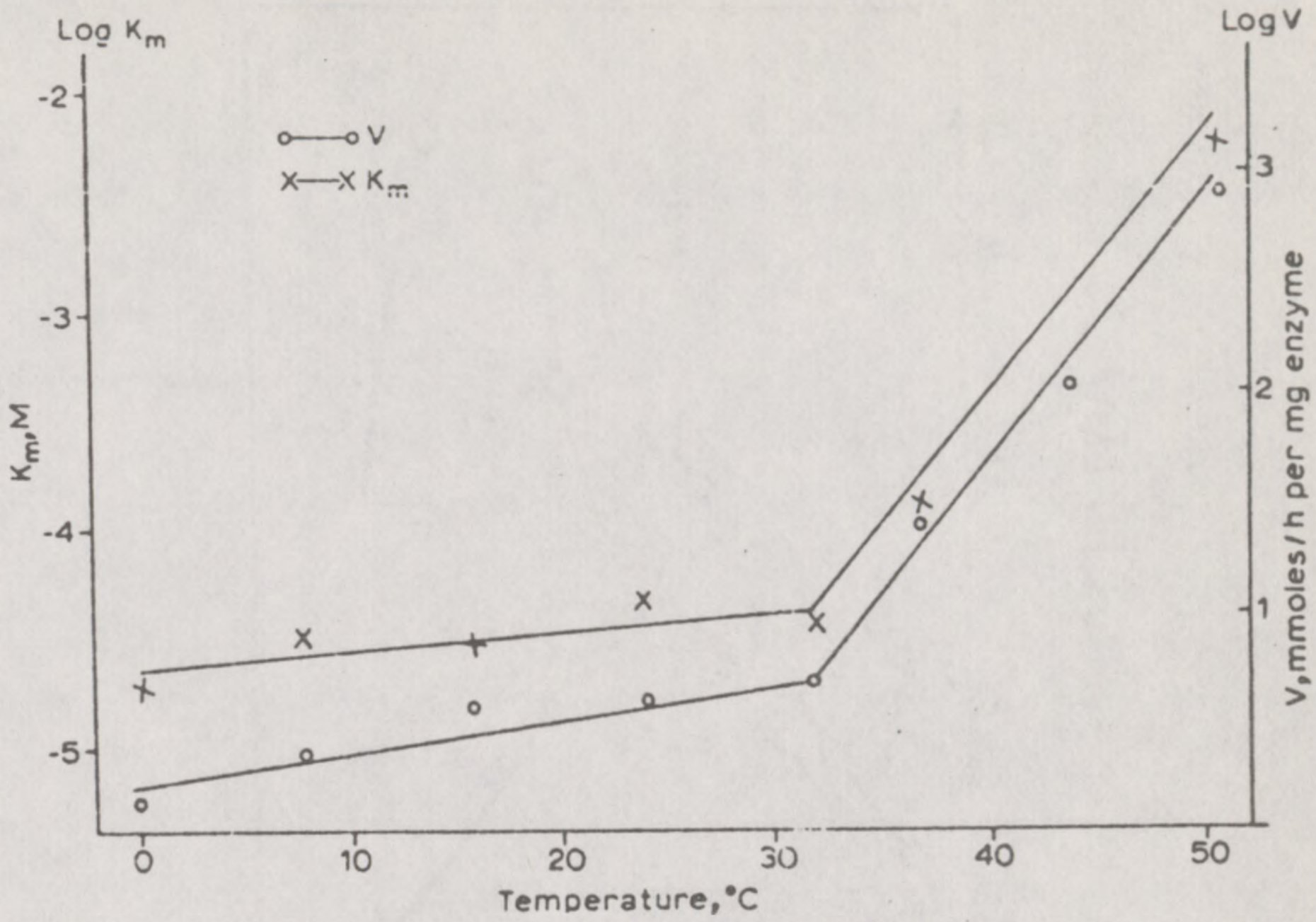
Temperature Dependence of the Rate of Hydrolysis of N^{α}-benzoyl-L-arginine ethyl ester by trypsin. Note anomaly near 14° C. (Talsky, 1970).

Figure 2-5



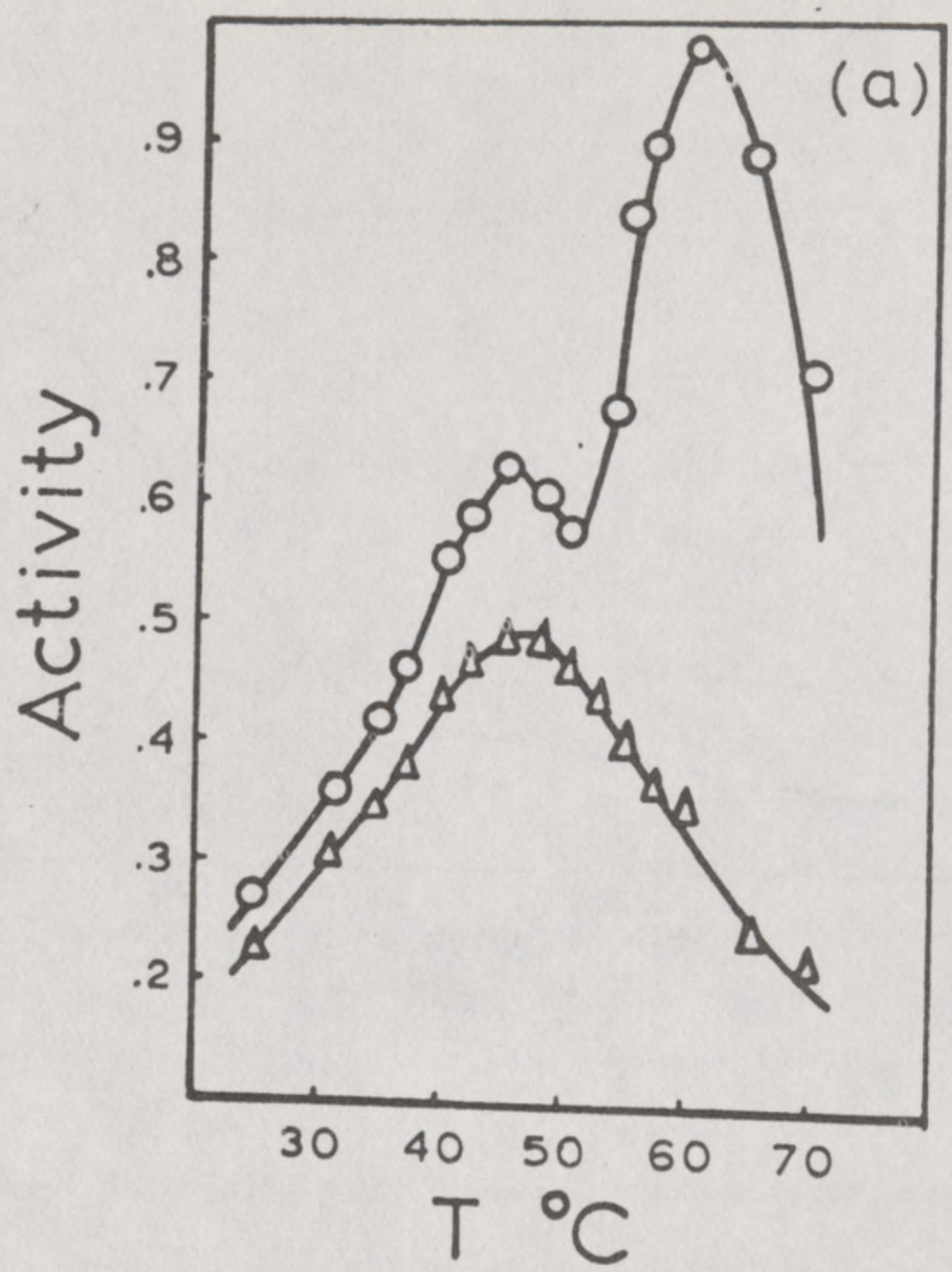
Temperature Dependence of the Hydrolysis of Tributyrin by Lipase from Pig Pancreas. Note that Measurements as Shown in Top Part of This Figure - Obtained Approximately at 5 to 10° Intervals, could be highly Misleading. The lower Curve shows the Identically same Conditions as for the top Figure, but with Careful Measurements at Approximately 1 to 2° intervals. As stressed by the present author (Drost-Hansen, 1960, 1965), studies of this type require closely-spaced temperature measurements.(Talsky, 1971).

Figure 2-5a



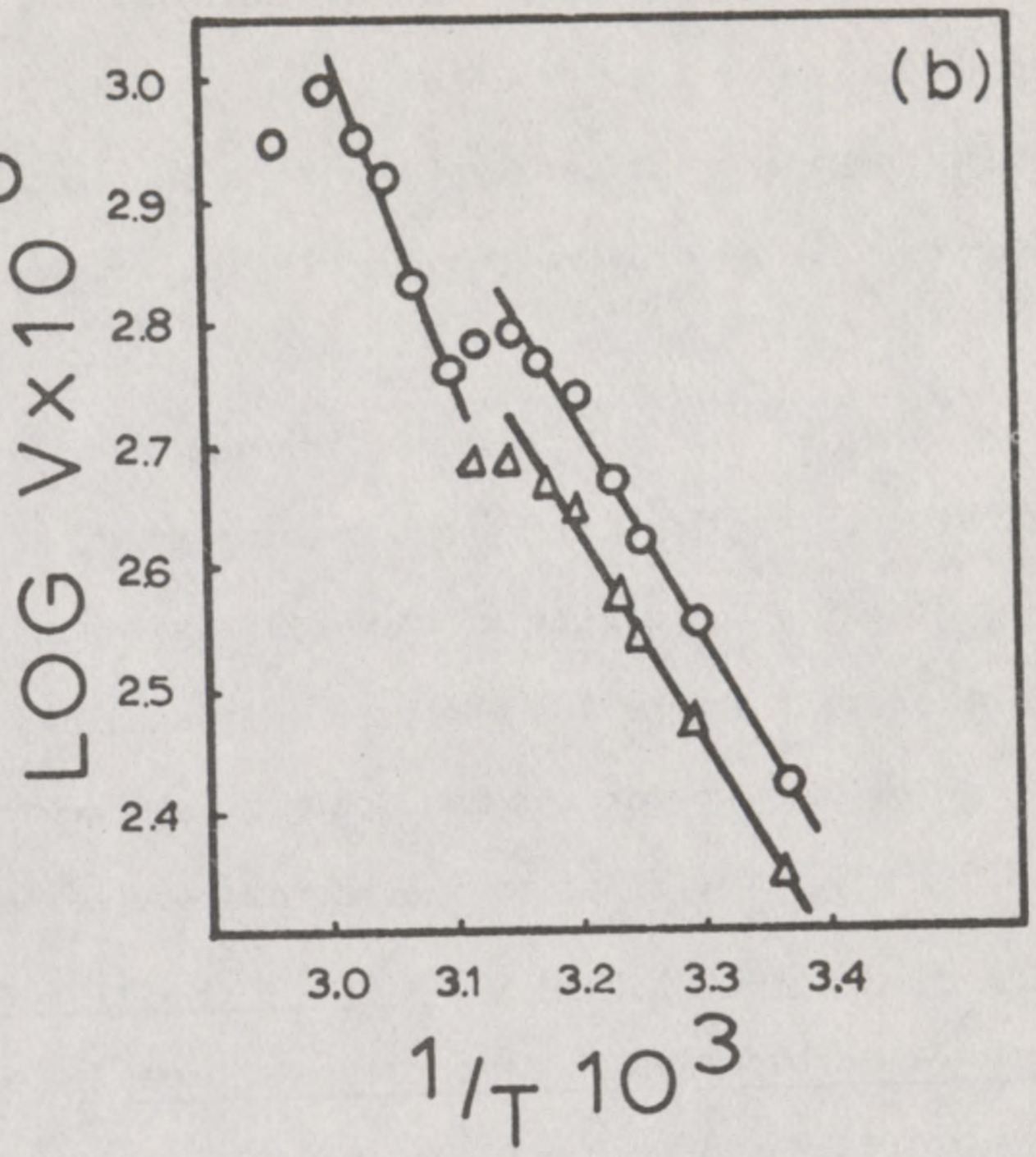
Michaelis-Menten Kinetic Data (K_m and V) for Effects of Temperature on Acetyl Thiocholine Iodide Hydrolysis (Ciliv and Özand, 1972).

Figure 2-6



Temperature-Dependent Activation of Trypsin by Calcium; trypsin concentration: 6.3 microgram/milliliter. Rate: millimoles hydrolyzed per minute per milligram trypsin. (Circles: activity in the presence of 0.02 molar $CaCl_2$; Δ: trypsin activity in the absence of calcium). (Sipos and Merkel, 1970).

Figure 2-7



Arrhenius Plot of Trypsin Catalyzed Hydrolysis of p-Tos-L-ArgOMe.

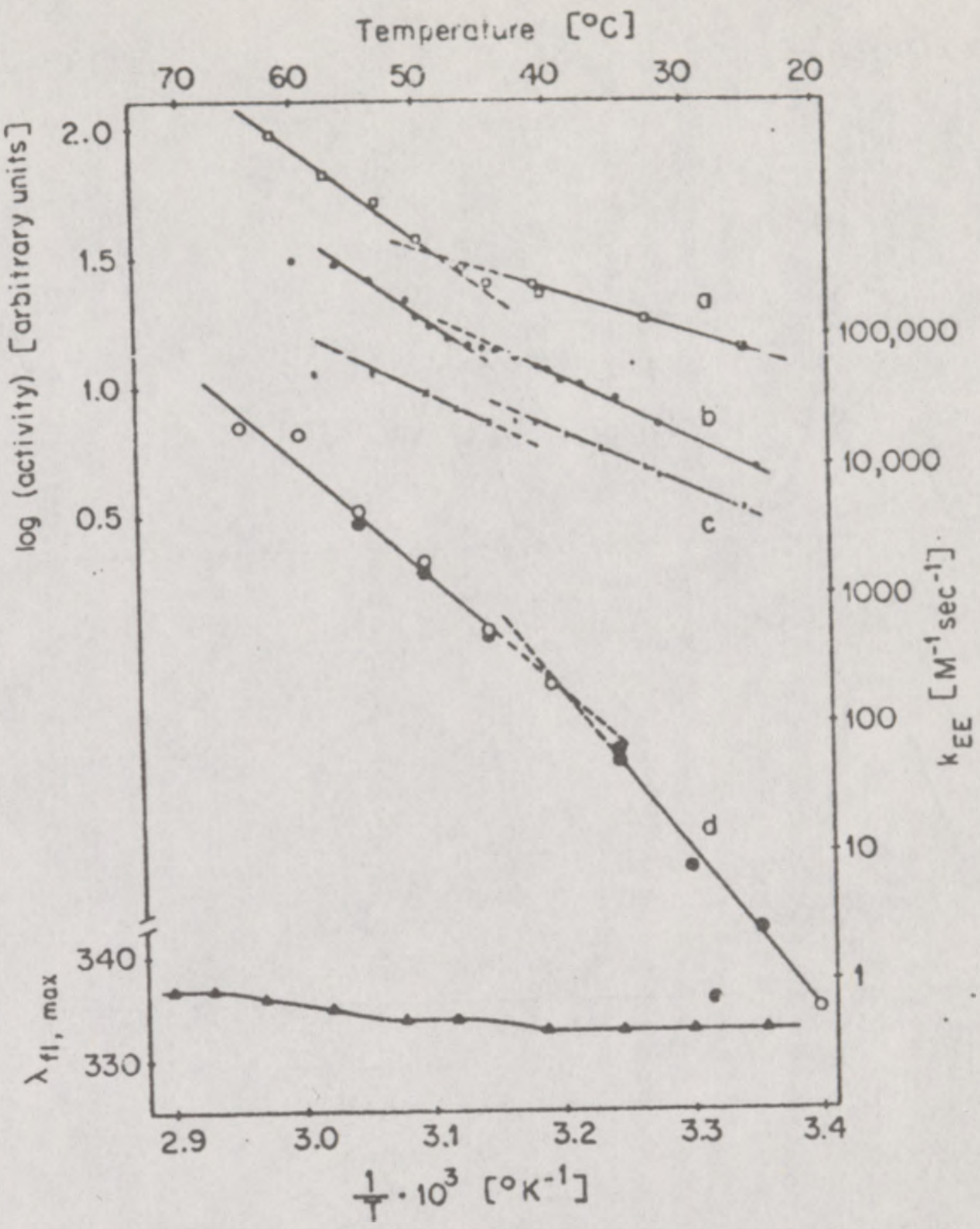
(Sipos and Merkel, 1970).

Figure 2-8

Figure 2-9 shows an Arrhenius plot for the activity and inactivation of different trypsins as determined by Gabel and Kasche (1972). They studied the temperature dependence of catalysis by free and immobilized α- and β-trypsin. The curves have a relatively abrupt change in slope near 45°C [Type E-F].

The preceeding examples are indicative of the wealth of available data in the literature, suggesting the occurrence of unexpected, abrupt and notable changes in properties of simple biochemical systems as a function of temperature. The present author has proposed that such changes, far from being unusual, are relatively common and owe their existence to higher-order phase transitions in the water vicinal to the macromolecules in question. Such anomalies may play a dominant role in determining cellular as well as organismic and ecological responses to temperature changes. Detailed analysis of these phenomena are discussed by Drost-Hansen (1973, 1972[a], 1971, 1969, 1965).

Thermal anomalies of the types suggested in Figures 2-5 through 2-9 have been observed in many aqueous macromolecular solutions. They are, however, not believed due directly to major conformational changes of the macromolecules - such as observed in classical irreversible denaturation of a protein. Rather, the anomalies appear to be manifestations of changes in the water structure adjacent to various types of interfaces, since they are frequently observed in completely inorganic, physico-chemically well characterized systems. Anomalies have been described in the temperature-dependence of the disjoining pressure between quartz plates submerged in water as shown in Figure 2-10 (Peschel and Adlfinger, 1971) or in the diffusion coefficient for thiourea in water (determined in capillary experiments) in Fig. 2-11 (Dreyer et al 1969). Again, the reader is referred to the writings by the present author (1973, 1972[a], 1971) since it is not appropriate to repeat the detailed arguments in this review.



Arrhenius plots (curves a-d) for β-trypsin, and β-trypsin sephadex. Logarithm of rate of P-tosyl-L-arginine methyl ester. (Gabel and Kasche, 1972). Note the author's proposed interpretation in terms of "several independent unfolding processes - multistate unfolding."

Figure 2-9

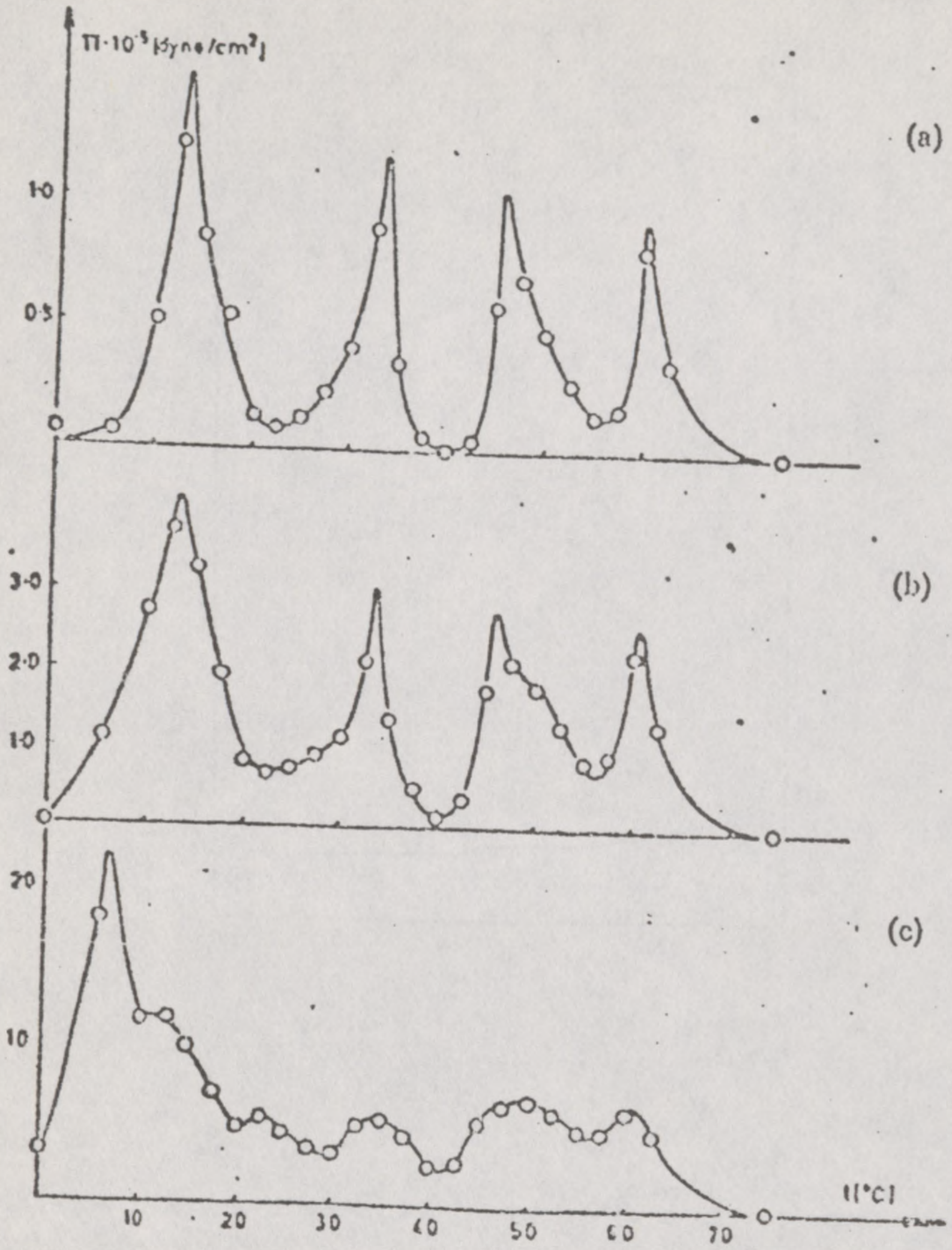
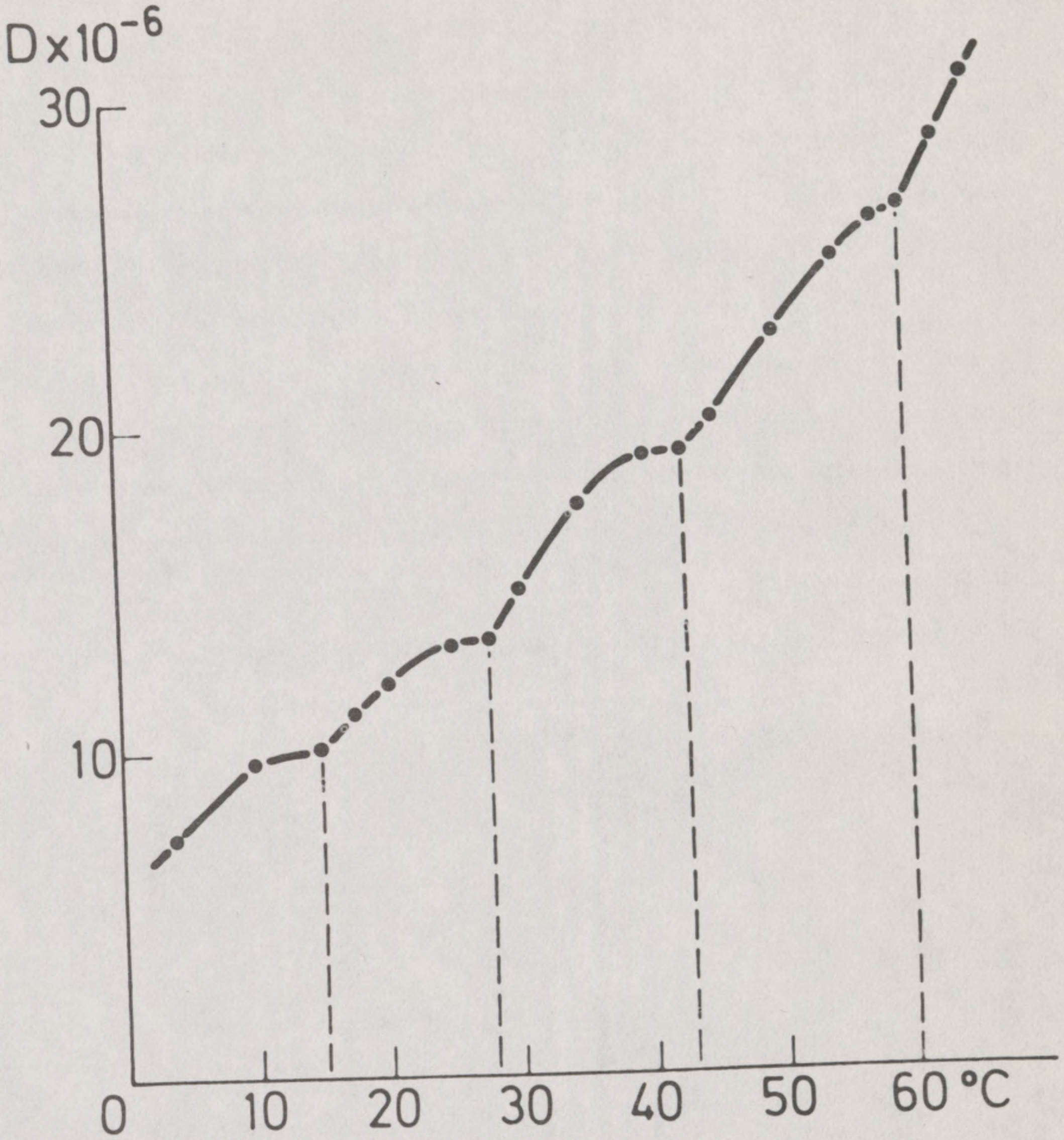


Fig. 2. Temperature dependence of the disjoining pressure for plate distances (a) 500 Å, (b) 300 Å, and (c) 100 Å.

[17] G. Peschel and K. H. Adlfinger, Naturwiss. 54, 614 [1967].

Figure 2-10



Diffusion Coefficient of Thiourea in Water Contained in Relatively Narrow Capillaries (Dreyer et al., 1969).

Figure 2-11

Finally, Figure 2-12 shows a typical example of a temperature-dependent property of an artificial membrane system. In this figure is shown the bi-ionic potential (E_{BI}) for a toluene-impregnated Millipore filter ("Ilani membrane") separating two solutions, respectively, 1.0 molar KCl and 1.0 molar NaCl. Below 31°C, the slope approaches the theoretically expected value, given by the expression ($E_{BI} = \frac{RT}{F} \text{ in } (U_+^{(1)}/U_+^{(2)})$; above 31°C, the slope (temperature coefficient) becomes larger. This example illustrates the fact that in pure, non-living membrane systems - devoid of any active transport mechanisms or any kind of macromolecular solutes in solution - thermal anomalies may be observed. In terms of the concept of water structure changes adjacent to solid interfaces, however, the phenomenon may be seen as an example of changes in the state of water adjacent to and/or in the "micropores" of the hydrophobic cellulose membrane matrix.

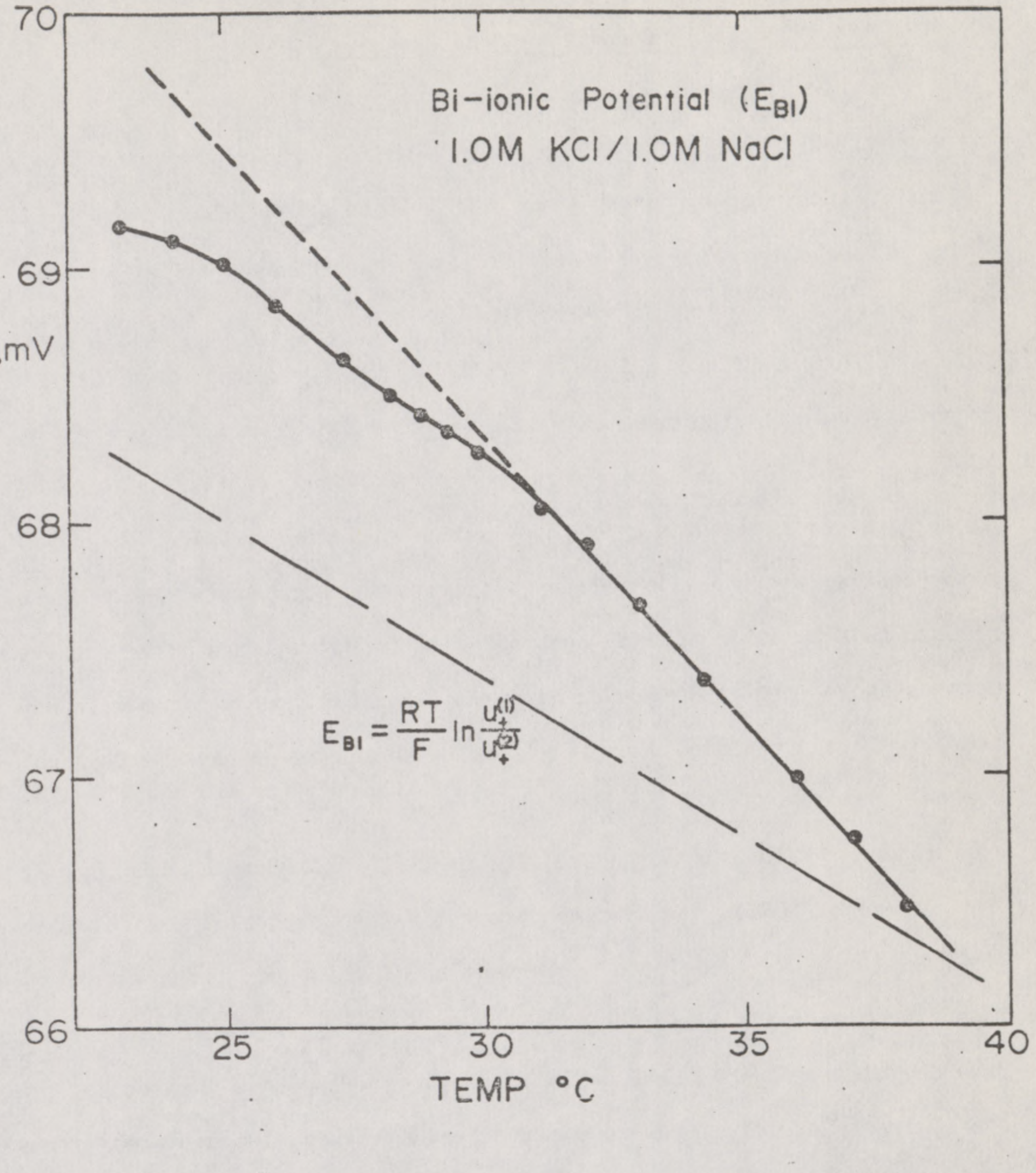
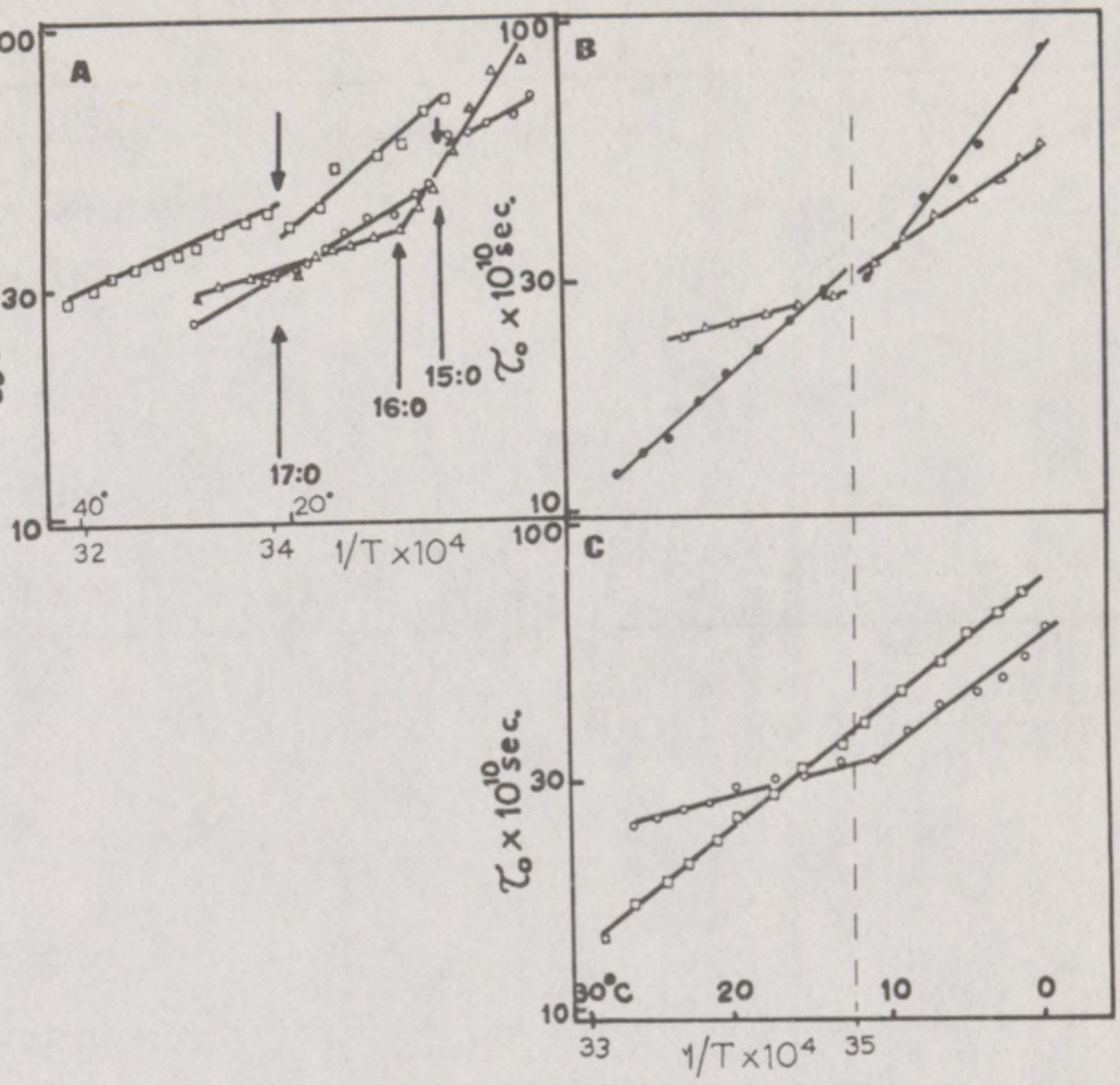

Bi-ionic Potential (E_{BI})
1.0M KCl / 1.0M NaCl
$E_{BI} = \frac{RT}{F} \ln \frac{u_+^{(1)}}{u_+^{(2)}}$
E_{BI}, mV
70
69
68
67
66
25
30
35
40
TEMP °C

Figure 2-12

C. Origins of Thermal Responses and of Anomalies

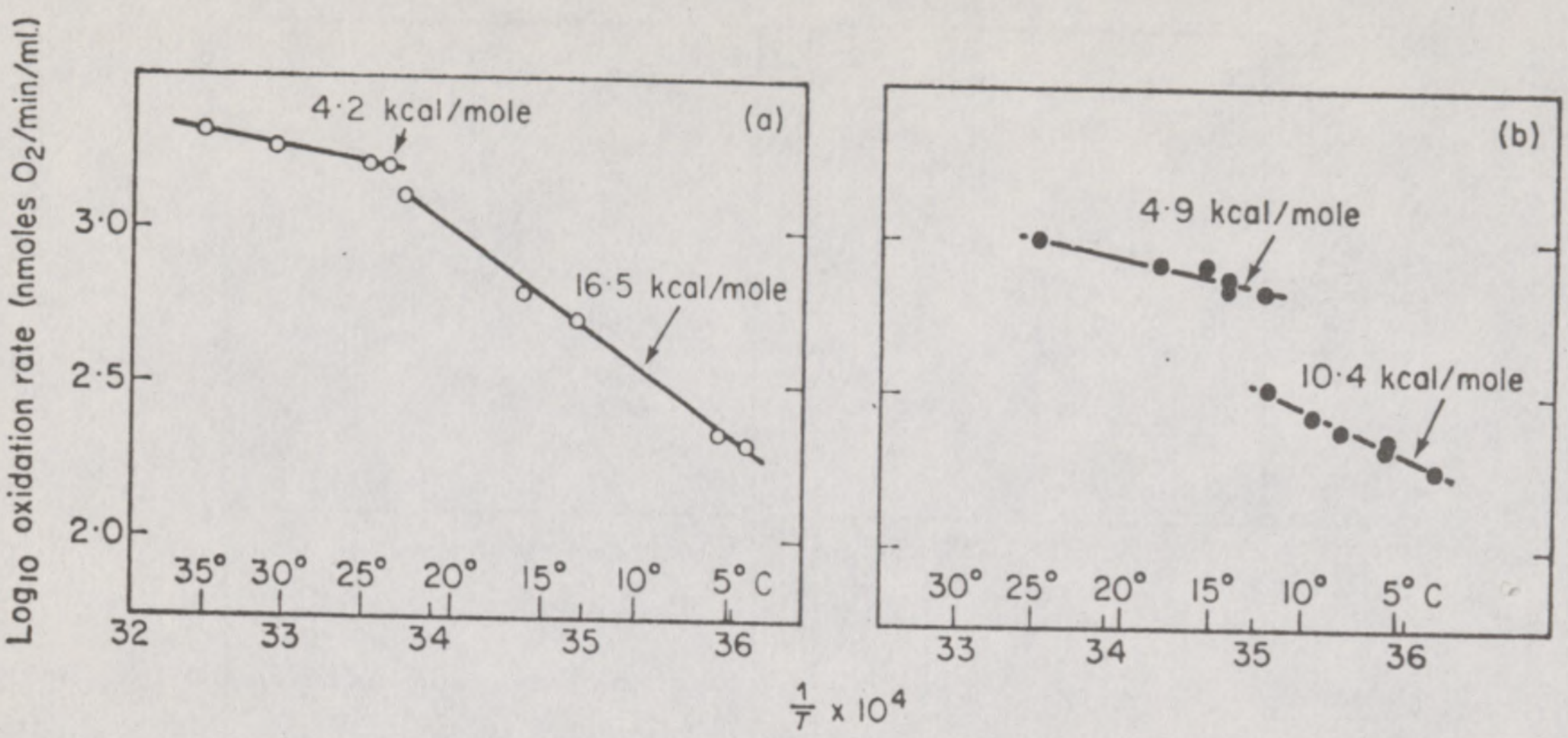
The thermal anomalies discussed in the present paper have sometimes been referred to as "discontinuities", "kinks", "breaks" and occasionally "knees". (See, for instance, Lumry and Rajender, 1970, loco cit., p. 1129). Only in rare situations are genuine discontinuities observed in biochemical and biological functioning. A possible example was shown in Figure 2-13 from the study by Henry and Keith (1971) on the lipids from a saturated fatty acid-mutant of a yeast. Another example is shown in Figure 2-14 from a paper by Raison and co-workers (see Kumamoto, 1971). The examples shown give the rates of succinate oxidation by, respectively, (a) rat-liver mitochondria, and the (b) chilling-sensitive cucumber fruit. Note the case of succinate oxidation by the cucumber mitochondria. More often, curves such as shown for the rate succinate oxidation by liver mitochondria may probably be approximated by a single curve, but with an extremely sharp change in slope near the temperature of the thermal anomaly. This is the most common type of thermal anomaly [Type E-F, Drost-Hansen, 1967, p. 81].

Kumamoto (1971) in discussing breaks in Arrhenius plots, specifically observes that "...the point of intersection of these two lines tells us that these two transition states should co-exist at this temperature, have equal free energies $(\Delta F)^{\neq}$ and because they are in equilibrium with a mutual ground state, are in equilibrium with one another. If these two different transition states are composed of the same material and can exclude each other from their own respective domains, we have a two-phase system with the attendant loss of a degree of freedom (the temperature becomes invariant)". This author feels that the different states may represent the identical molecule but with different conformations, dictated by the specific nature of the vicinal water structures, changing abruptly at the point of the thermal anomaly.



Motion Parameter (Related to the Rotational Correlation Time as Determined by Spin Relaxation Measurements) as an Arrhenius plot for Yeast Mutants. See text and Original Article for Details (Henry and Keith, 1971).

Figure 2-13



Log Rate Plots of Succinate Oxidation by, Respectively, Rat Liver Mitochondria and Mitochondria from Chilling-Sensitive Cucumber Fruit (Kumamoto et al., 1971).

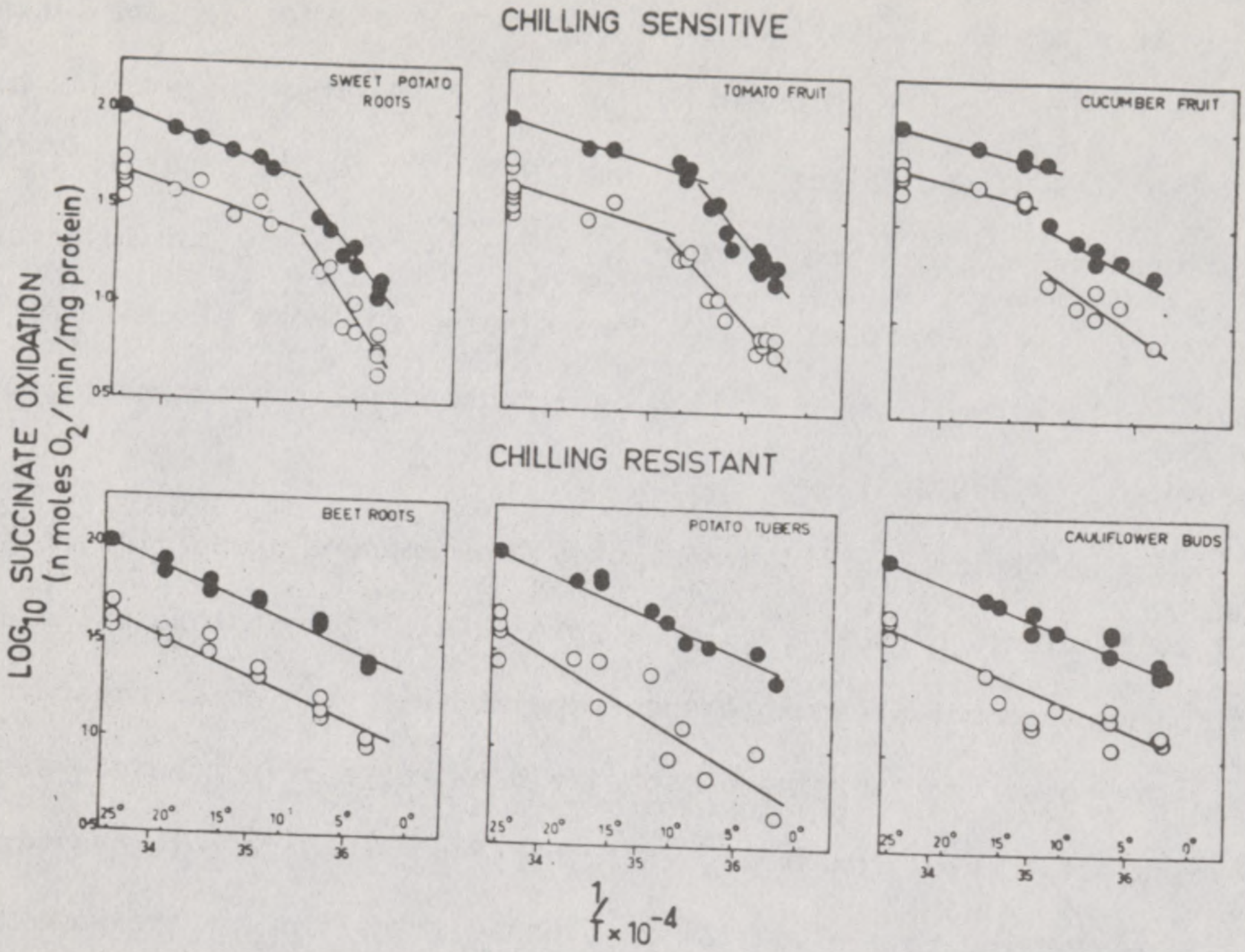
Figure 2-14

Other examples of distinct breaks in rate plots for various biochemical functioning are shown in Figures 2-15, and 2-16, from the studies by Lyons and Raison (1970) and Raison and Lyons (1971). Note, in general, that while abrupt changes in slope are frequently - though certainly not invariably - observed, only one example clearly demonstrates an overt discontinuity (namely for the succinate oxidation by mitochondria from cucumber fruit as previously discussed).

Henry and Keith (1971) have studied the membrane properties of saturated fatty acid mutants of yeast, using a spin-labelling technique using a Varian electron paramagnetic resonance spectrometer, with variable temperature accessory. They observed that the phospholipid extracts of untreated yeast cells, cells subject to heat treatment, and others subjected to both heat treatment and freeze-thawing, all give rise to a phase transition at the same temperature - about 13°C (within ± 1.5°C - the latter reflecting the instrumental precision of temperature control, rather than a statistical estimate of the variance of point of intercept of the differing slopes). Arrhenius plots obtained in this manner are shown in Figures 2-13 and 2-17. The authors observed that yeast cells treated with phospholipase-C, pronase, sodium azide* and microbial lipase also showed a phase transition at approximately the same temperature. They conclude, "since the temperature of phase transition is unchanged with different treatments, and τ_0 at various temperatures is not drastically changed among the different preparations, it appears that these properties are contained in the lipids and not in the proteins".

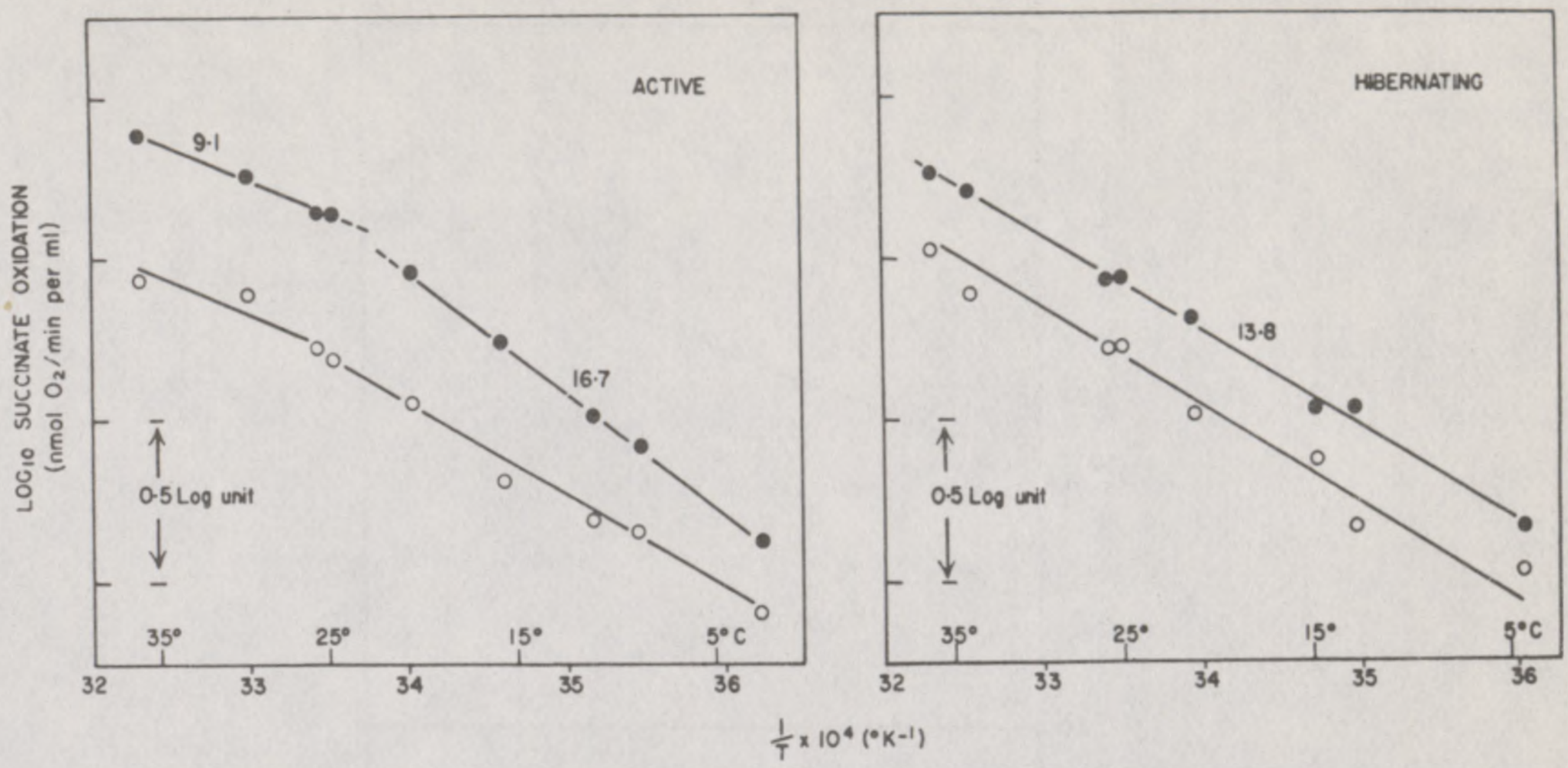
Henry and Keith (1971) speculated on the origin of the phase transition in terms of "pools" of impurity (nitrous oxide). Henry and Keith also discussed the transitions which have been reported by Raison and Lyons (1971)

*Azide is a specific enzyme inhibitor frequently used in such studies.



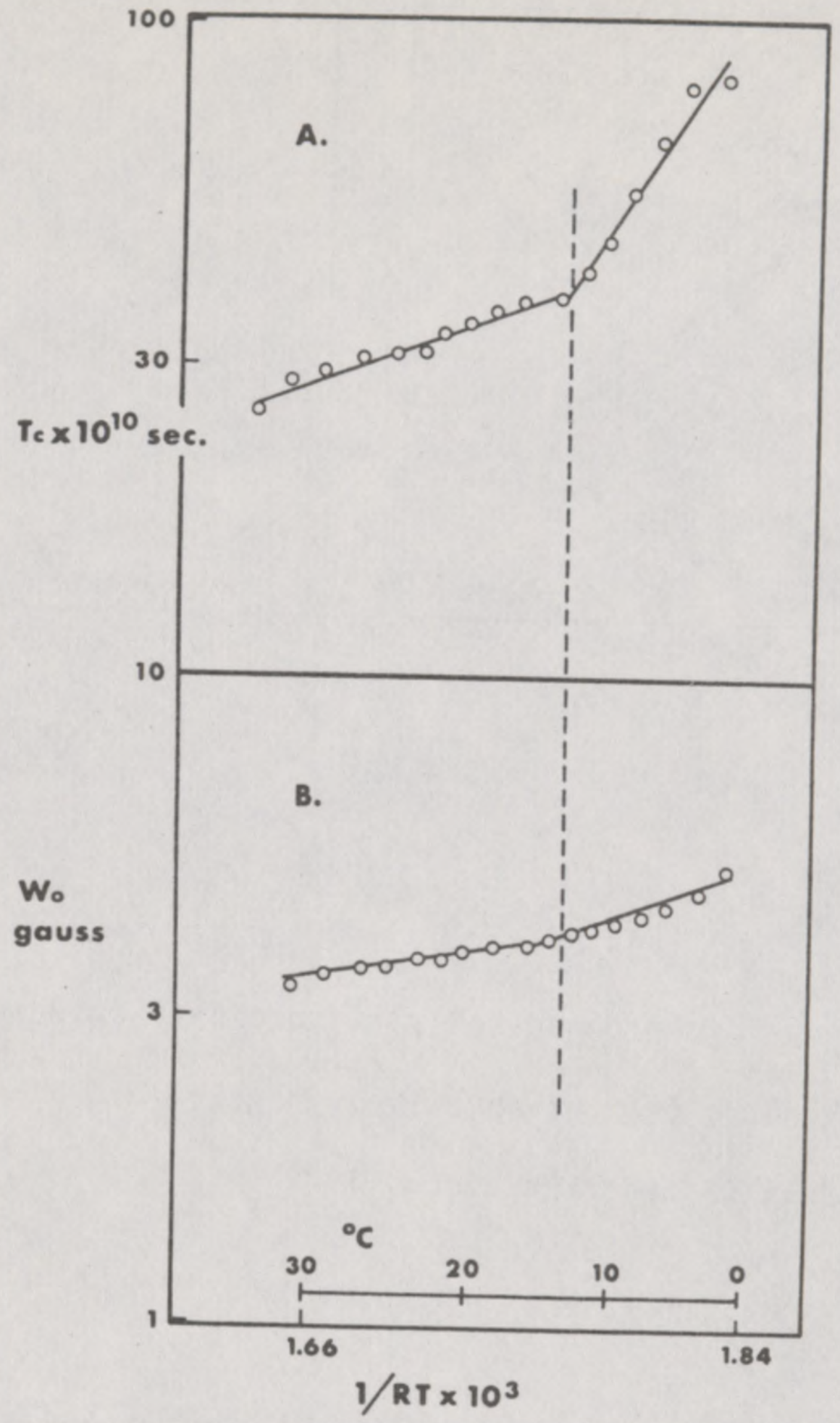
Arrhenius Plot of Succinate Oxidation by Mitochondrial Enzyme, Obtained from the Various Plants Indicated. Note Overt Discontinuity in the Data Obtained with Mitochondria from Cucumber Fruit. (Lyons and Raison, 1970).

Figure 2-15



Effect of temperature on activity of succinate oxidase from intact liver mitochondria from, respectively, active and hibernating brown squirrels (Raison and Lyons, 1971).

Figure 2-16



Rotational Correlation Time and Line Width as a Function of Temperature of 12 NS in Yeast Mutant. Note Pronounced Break in the Vicinity of 13° (Henry and Keith, 1971).

Figure 2-17

for mitochondria (where the rat liver mitochondria shows a transition at about 12°C).

The study by Henry and Keith is interesting as it is a clear example of a thermal anomaly in a lipid system, occurring near 15°C rather than 25°C. As discussed in Section 2-III many water/lipid systems (in vivo and in vitro) suggest the occurrence of an anomaly near 23°C.

D. Miscellaneous Thermal Effects on Some Isolated Systems

Space limitations allow only a few illustrative examples of abrupt changes in thermal properties of some biological systems. Innumerable examples of this type are found in the literature. There, the changes have not been interpreted in terms of vicinal water structures; rather, a large number have been interpreted in terms of directly-induced conformational changes of the biologically interesting macromolecules, or in terms of specific interactions between intracellular solutes. Many explanations have been offered, sometimes for the same phenomenon by different authors, and at other times completely different explanations have been employed.

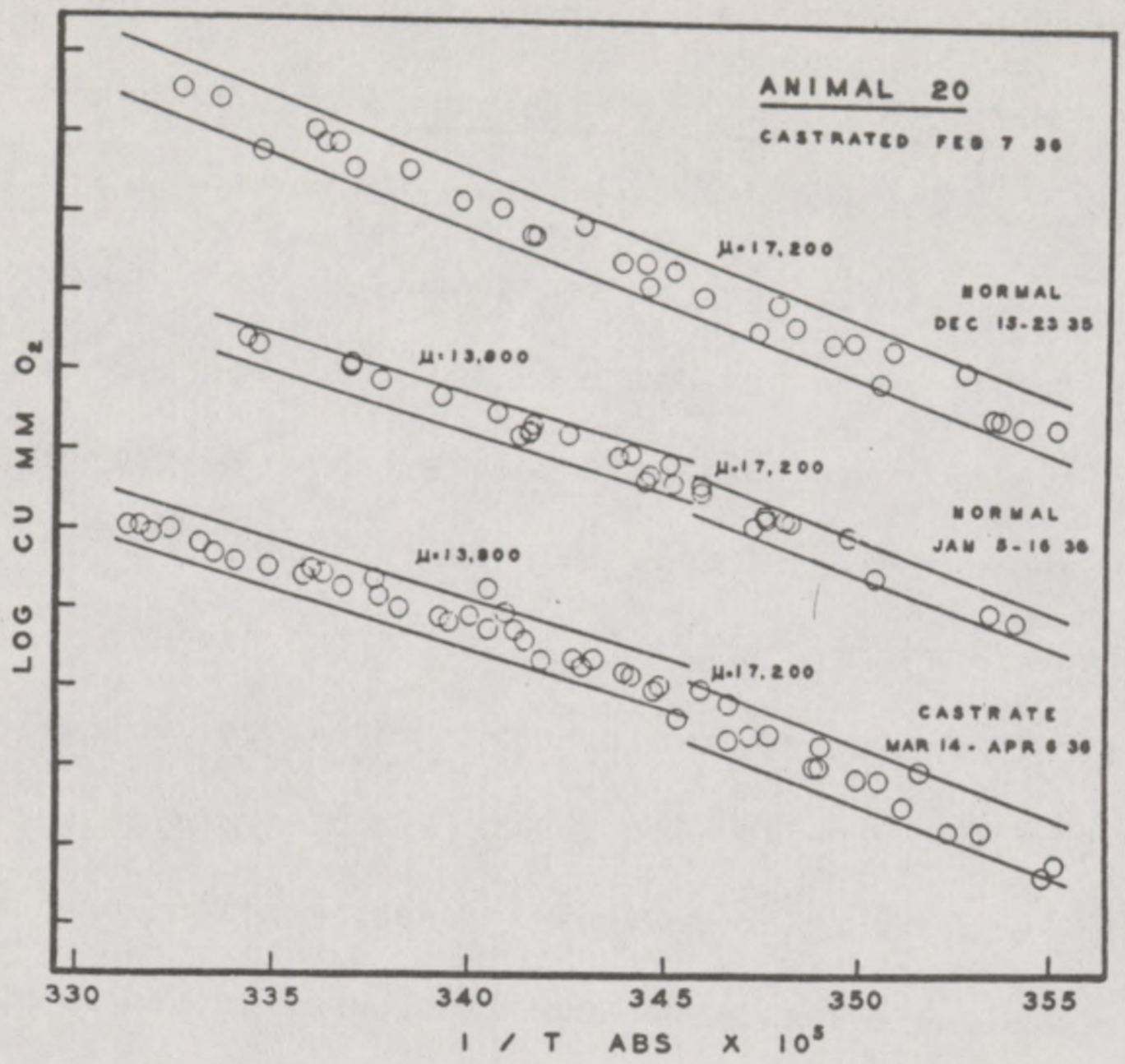
Bowler and Duncan (1967) have studied the temperature sensitivity of ATPase activity in microsomal preparations from the muscle of the crayfish, Astacus pallipes. Among the conclusions arrived at by the authors, is the suggestion that the results show a "close similarity between the properties of the magnesium ion-dependent ATPase and the phenomenon of heat death in this species. In both cases, a $1^{o}C$ rise (above $32^{o}C$) produces a marked effect, and both thermal inactivation of the enzyme and heat death occur in the same narrow temperature range ($33-36^{o}C$)".

Davison (1971) has demonstrated temperature minima around $34^{o}C$ (usually a decrease in activity between 30 to $34^{o}C$) in the oxygen consumption of sarcomes (mitochondria) from flight muscle of the blow-fly, Calliphora erythrocephala. Davison also calls attention to the anomalies in the Arrhenius plots observed by Kemp, et al. (1969) for succinate oxidation of isolated rat-liver mitochondria, where an abrupt change occurs near $17^{o}C$; similar changes were obtained also from P_i-ATP exchange, ADP-ATP exchange reactions, and also DNP stimulated magnesium ATPase activity in the same mitochondria.

Pomerat and Zarrow (1937) determined the oxygen consumption and CO_2 production from the Newt Triturus viridescens over a temperature range from 6 to 28°C. Some of their results are shown in Figures 2-18, and 2-19. Note that anomalies, when present, occur in both the O_2 and CO_2 data. The scatter is large but not unreasonable. Whatever was lacking in reproducibility of individual data points is, to a very large extent, compensated by the number of individual observations. In some of the figures presented distinct changes in slope in the Arrhenius plot are observed near 15.5°C. However, in many other cases, no indications are obtained for an abrupt change in slope. It is not a rare characteristic of many studies of biological functioning that in experiments on presumably identical populations, anomalous effects are sometimes observed and sometimes not.

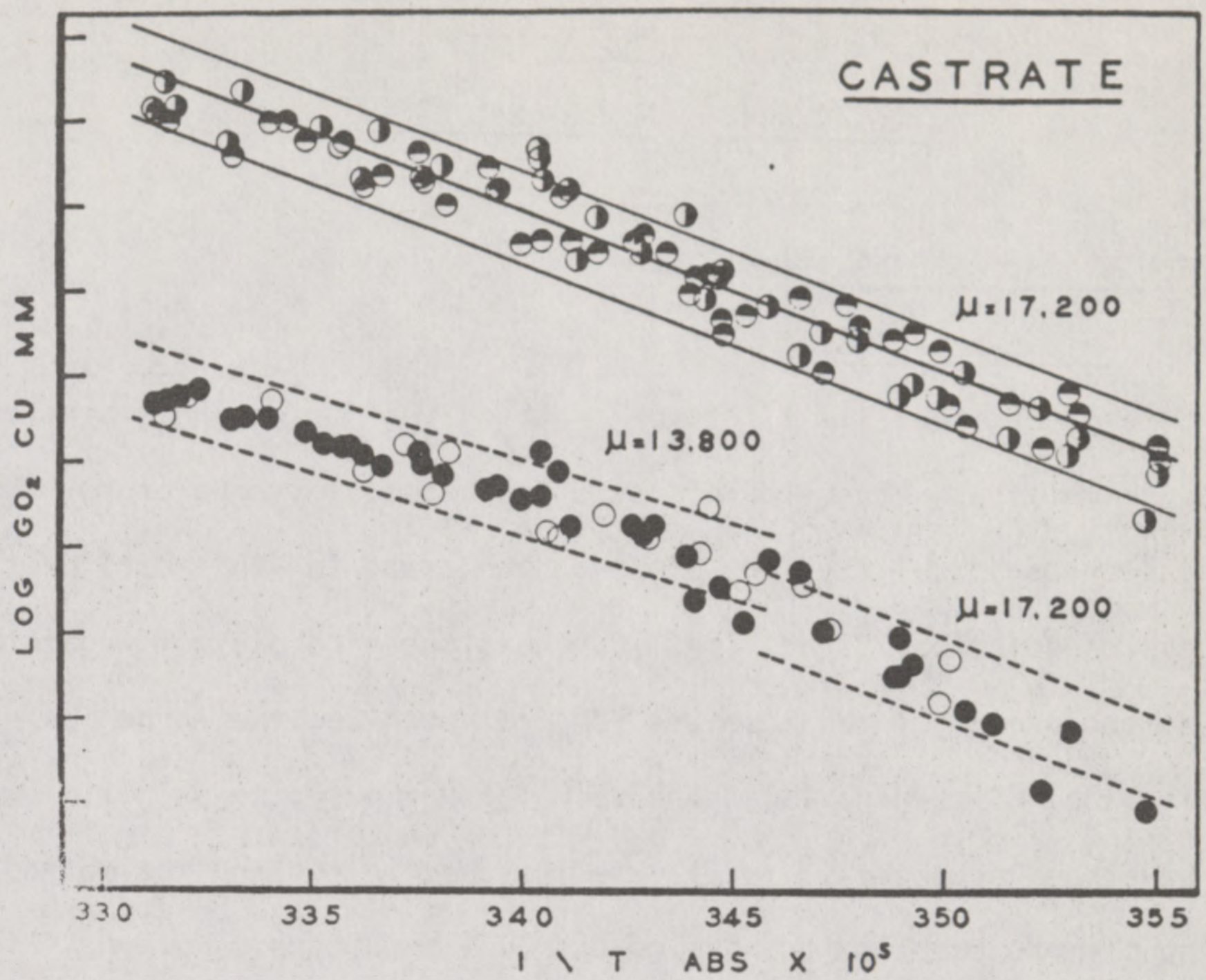
Lagerspetz, et al. (1973) have also studied the magnesium ATPase and sodium-potassium ATPase activities in nerve cord homogonates from earthworms. Characteristically, for earthworms acclimated to 14°C, the magnesium ATPase shows a sharp change in slope around 10 to 12°C, with a rather broad maximum between 40 to 45°C. Earthworms acclimated at a higher temperature (25°C) show notably less sodium-potassium ATPase activity at the lower temperatures, but approximately the same activity and the same abrupt decrease near 45°C, as for the low temperature acclimated worms.

In summary, thermal anomalies are often observed over relatively narrow temperature intervals for a variety of isolated systems. There is good reason to believe that these changes occur in marine organisms and, as will be discussed in the remainder of this review, in turn influence many processes eventually reflected in the ecological responses to temperature.



Respiratory response to temperature of Newt. Note absence of thermal anomaly in initial measurements (December 15-23); a thermal anomaly near 16° at a later time (January 5-16) and a similar anomaly in the same specimen, castrated approximately one month before last series of measurements. (Data by Pomerat & Zarrow, 1937).

Figure 2-18



Arrhenius plot of carbon dioxide production by a Newt (castrated). Note two sets of data on a single population, showing respectively presence and absence of anomaly in the vicinity of 16° C;(Pomerat and Zarrow, 1936).

Figure 2-19

PART 2

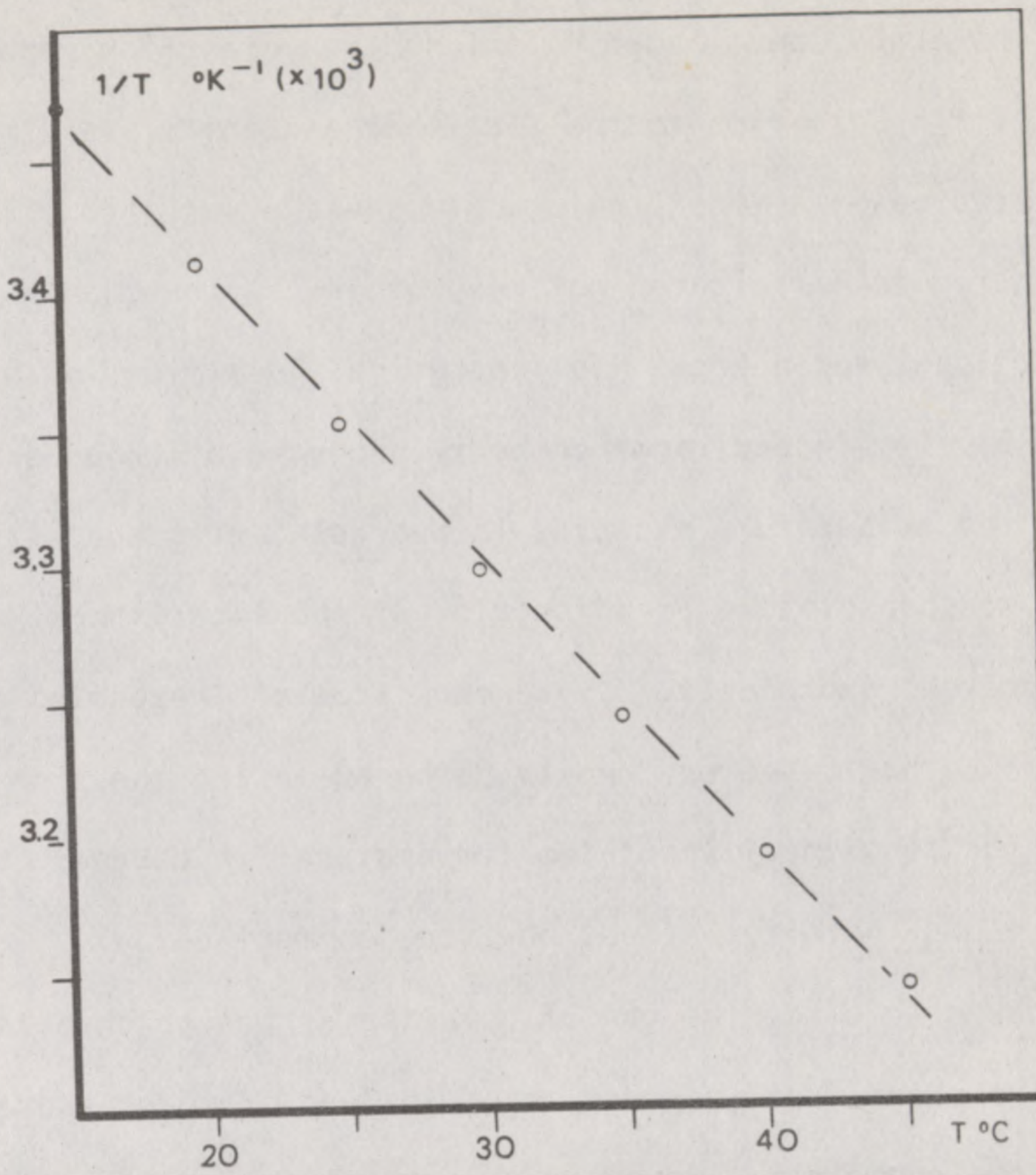
SECTION III: FUNCTIONAL ASPECTS

III. FUNCTIONAL ASPECTS

A. Rate Expressions

Some theoretical justification can be given for making graphs of properties or rates as a function of reciprocal absolute temperature. For properties such as solubility, the slope of the graph (a van't Hoff plot) gives the heats of solution. Traditionally, the slope of a plot of logarithmic rate vs. reciprocal of the absolute temperature gives the Arrhenius energy of activation. Elsewhere is a discussion of various other kinetic expressions which have been advanced to facilitate the description and the molecular understanding of more complicated physico-chemical phenomena. However, it should be observed that measurements determining "thermal stability" are often made over rather narrow temperature intervals (say, $6^{o}C$ to around $30^{o}C$) - corresponding to $303^{o}K$. The reciprocal of $303^{o}K$ is 3.298×10^{-3}. From $20^{o}C$ to $45^{o}C$ the temperature in degrees Centigrade and the reciprocal absolute temperature show an approximately linear relationship (see Figure 2-20). Belehradek had mentioned this point in 1935. For measurements carried out around $30^{o}C$ (within $\pm$ $10^{o}C$, and possibly even $\pm$ $20^{o}C$) and particularly for measurements carried out over very narrow intervals in this range, an artificial linear dependence is obtained for which no theoretical justification is possible. Somewhat similar objections can be made to the attempts, for instance, by Belehradek (1935) to justify various empirical equations. The nearly linear dependency between $t^{o}C$ and $1/T$ is illustrated in Figure 2-20. Within the limits of error which most biologists work, this indeed, is a "straight line".

Belehradek (1935) has frequently advocated expressions for temperature dependencies where the particular property studied (or its logarithm) was expressed directly as a function of the logarithm of the temperature - measured



Graph Showing Approximate Linear Relationship Between Reciprocal Absolute Temperature (in Degrees K) as a Function of Temperature, in °C, over the Range from 15 to 45°.

Figure 2-20

in degrees Centigrade, and linear relationships were often reported. Belehradek paid little attention to the fact that a quantity varying by a factor of ten when studied on a logarithmic scale shows a variation, reduced to 1.0, thus tending to "straighten out" any otherwise reasonable (and even notable) functional dependency. No theoretical justification exists for this procedure. If, indeed, some property produces a linear graph, using logarithm of the temperature measured in degrees Centigrade, it surely would not do so when plotted as a function of the logarithm of the temperature measured in degrees Fahrenheit. It appears from an inspection of Belehradek's small monograph, that he nevery really bothered facing the problem of the proper value for the logarithm of the temperature (in degrees Centigrade) at $0^{o}C$; namely, minus infinity! (See, however, comment below).

Belehradek criticized the use of both the Arrhenius equation and other (at that time popular) rate expressions. Instead of these expressions, he suggested a simple empirical equation to account for many biological phenomena:

$$y = a/t^{b}.$$

Taking logarithms on both sides of this equation, yields:

$$\log y = \log a - \log t$$

which appears to be the foundation for the rest of Belehradek's "theory". Only one other modification was introduced. Belehradek, in examining equations 1 or 2 did notice that "it may be seen that at $0^{o}C$ the reaction should be stopped. Yet this is not always the case". To avoid the problem, Belehradek therefore introduced a new constant (α) which is denoted the "temperature threshold" from which the temperature is calculated; (this presumably coincides with the

"biological zero" for the process), thus the modified equation becomes:

$$y = \frac{a}{(t-\alpha)^b}$$

Many biologists still pursue a description in terms of such simple, exponential forms with temperature expressed in °C. That leaves little room in those theories for detailed molecular considerations.

Several examples of theoretical rate curves, fitted to various biological rate data, are shown in Figures 2-21, 2-22, and 2-23. It is interesting to observe that in all three figures, reasonably good to excellent fits with experimental data are obtained over a limited temperature range. However, in each case, the temperatures above 30°C to 32°C, the agreement ceases to hold completely - often with such dramatic changes as opposite sign for the temperature coefficient. Curve fitting programs of the type illustrated in the four figures are merely that: empirical, parametric fits over limited temperature intervals, not allowing for any interpretation in terms of underlying phenomena. Other examples of biological phenomena showing abrupt changes over narrow temperature ranges are mentioned in Andreawartha and Birch (1954), particularly in the section on temperature (loco cit., Part III, "Analysis of Environment", Chapter 6, pp. 129-205).

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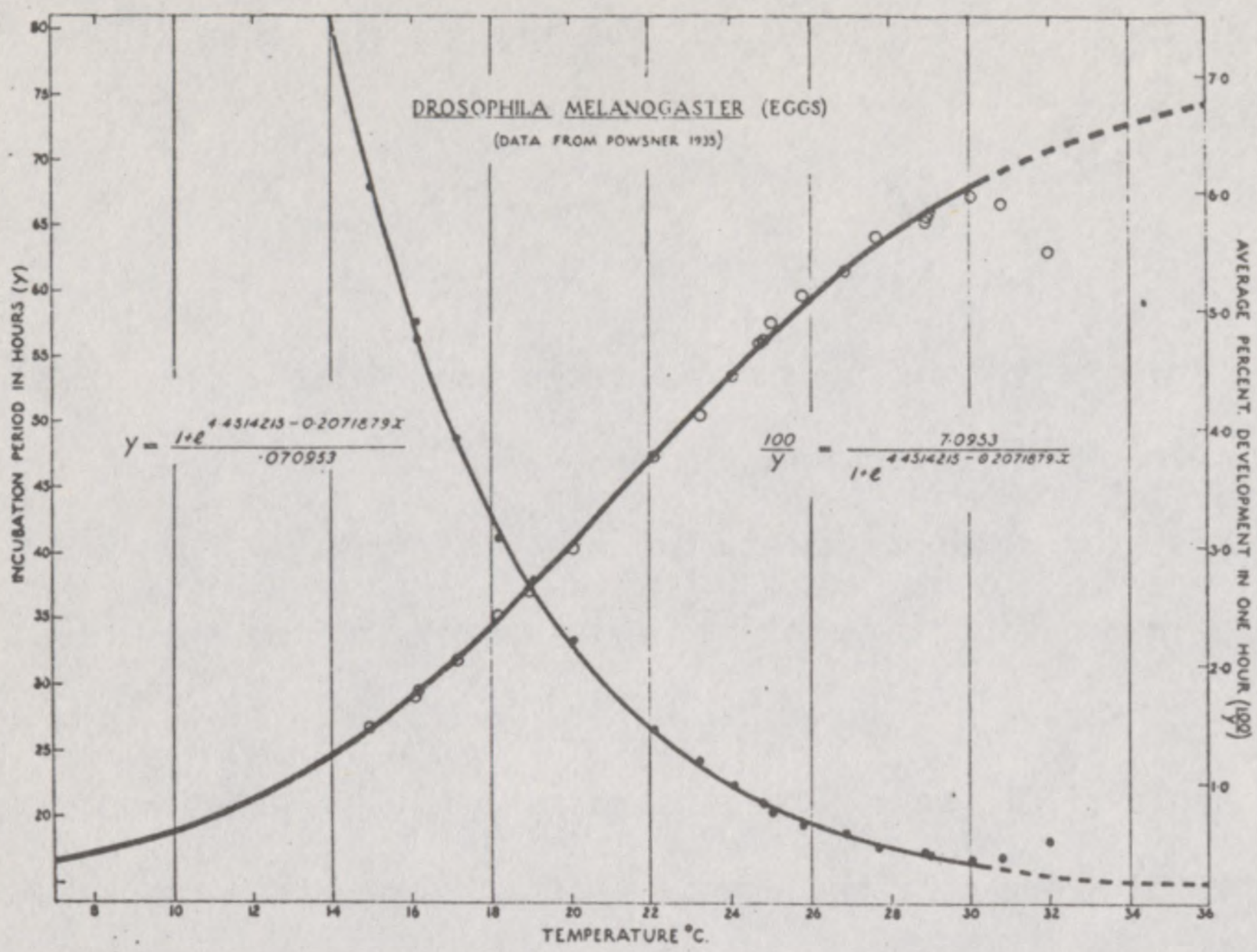
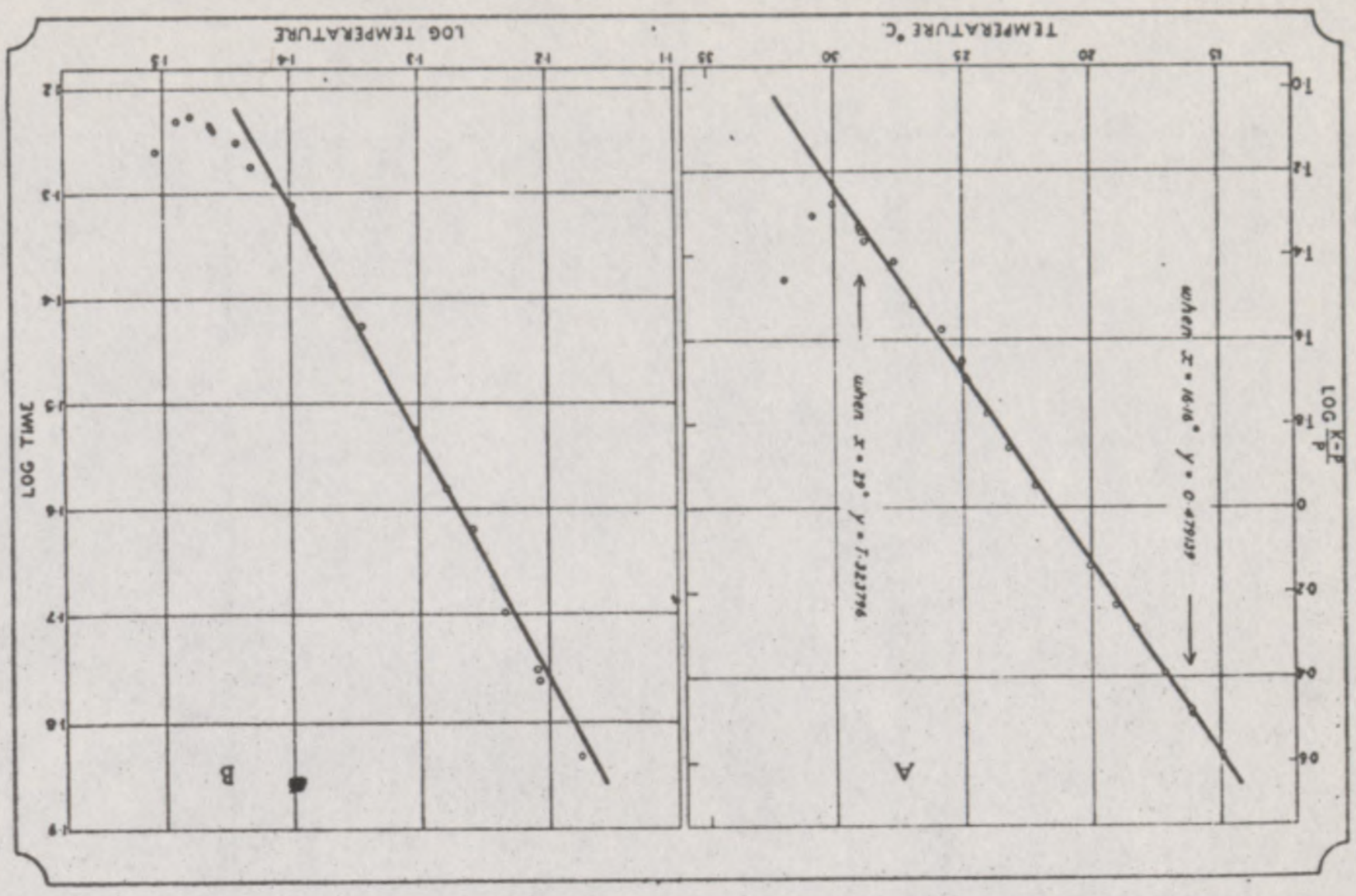


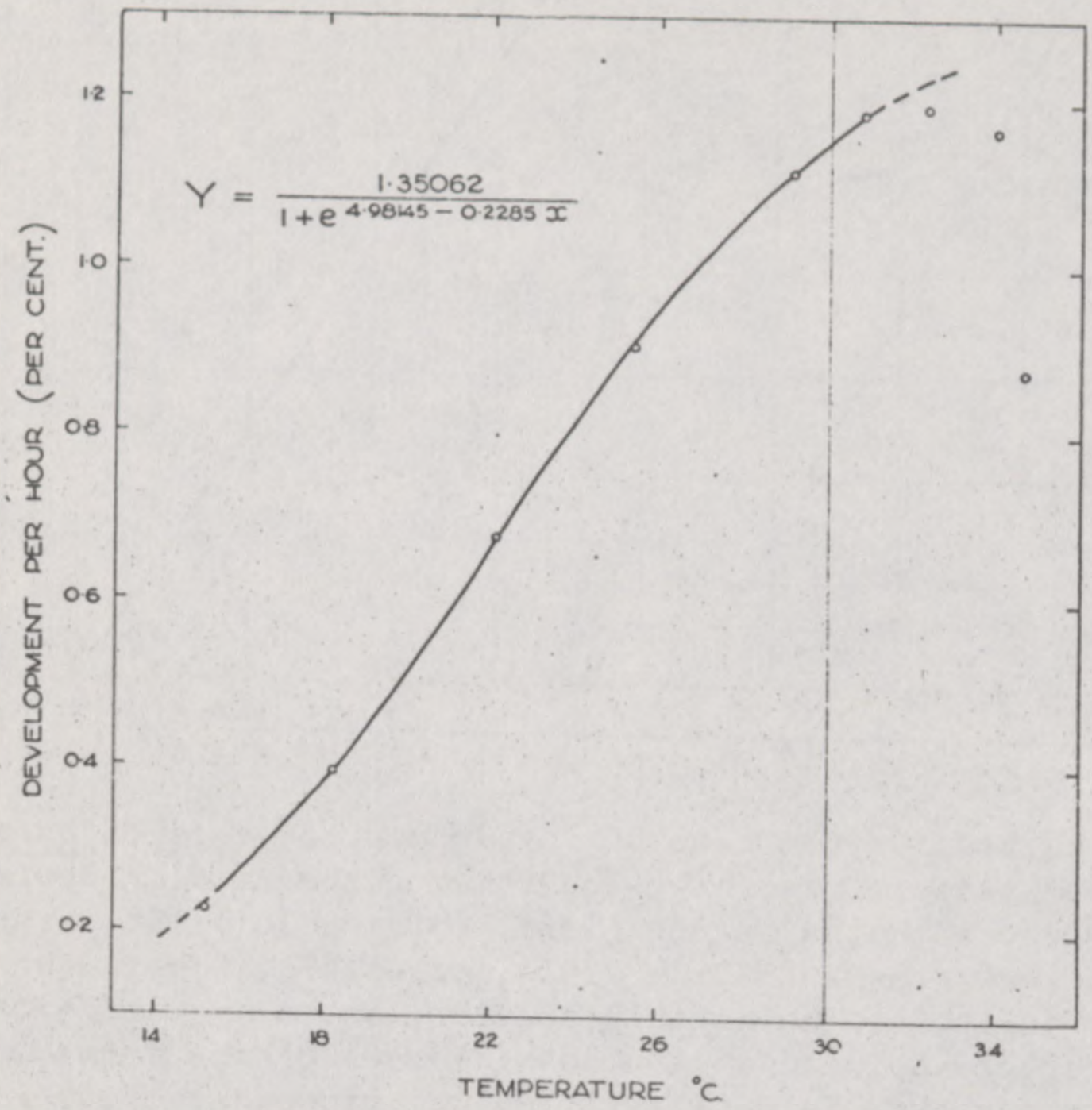
Rate of Development of Drosophila melanogaster Eggs as a Function of Temperature. Note Abrupt Deviation from Predicted Curve Above 30° (Data by Powsner, Quoted by Andreawartha and Birch, 1954).

Figure 2-21



Two empirical curves for the rate of development of eggs of Drosophila as a function of temperature. The logistics curve used by Davison (1944) is compared with the degree of fit obtainable by Belehradek's equation. (Andreawartha and Birch, 1954, page 149). The authors claim the superiority of the logistics curve, but acknowledge the fit is only satisfactory between 15 and 30° ("above 30° the harmful influence of temperature is manifest from the pronounced decrease in the speed of development above that temperature", Andreawartha and Birch, loco cit., page 150).

FIGURE 2-22



Rate of development of the egg state of Calandra oryzae (after Birch, 1944a). Note the pronounced difference between calculated and observed values for temperatures above 31 to 32°. (Andreawartha and Birch, 1954, page 153).

FIGURE 2-23

B. Enthalpy-entropy Compensation

In the physico-chemical description of any system in equilibrium (with the environmental variables of temperature, pressure and concentrations) the general expression applies:

$$\Delta F^0 = \Delta H^0 - T\Delta S^0$$

Equilibrium in multi-phase systems implies that $\Delta F = 0$. Variations in either or both ΔH and ΔS can alter the prevailing equilibria. However, it has been known (Barclay and Butler, 1938) for many years that a compensation mechanism operates such that ΔH appears to be related to ΔS. This relationship cannot be derived from first principles of thermodynamics; it is an extra-thermodynamic statement. Its explanation is lacking. Frequently observed is the relationship, $\Delta H^0 = \alpha + T_c\Delta S^0$. Of importance is the remarkable fact that the values for T_c frequently fall in relatively narrow ranges from about 250 to 320°K (-23°C to +47°C) for processes as diverse as solvation of ions and electrolytes, hydrolysis, oxidation-reduction reactions, ionization of weak electrolytes, and many others (see Lumry and Rajender, 1970, for details). One interpretation of the existence of the enthalpy-entropy compensation is that it manifests an intrinsic aspect of water structure. This statement must be taken guardedly. It is frequently true that regardless of the solute and the solute processes studied (thus including both thermodynamic equilibrium properties and transport phenomena properties), similar compensation regularities for aqueous systems are observed. This applies also to proteins of functional importance in physiological processes. On this basis, Lumry and Rajender suggested that the enthalpy and entropy relationship may be used as a diagnostic test for the participation of and specifically the controlling role of the water in protein processes. While values for T_c generally fall in the range from 250 to 320°K,

the values far more often cluster around 270 to 290°K - notably between 285 and 290°K, or in other words, in the interval from 12° to 17°C. The present author has speculated that the compensation temperature, T_c, may be one of the "critical temperatures" for the stability of one or another type of vicinal water structures stabilized by the proximity to an interface.

Specifically with regard to the interaction between water and some macromolecules of biologically interesting systems (proteins and especially enzymes) again note Lumry and Rajender (1970): "The similarity of T_c values for small solute and protein compensation processes in water has provided the basis for the proposal that all Vaslow-Doherty processes have a common source. Systematic studies of the effects of solvents on the linear compensation processes of proteins now underway should provide definite evidence for or against this generalization, which is only an hypothesis at the present time. In the protein cases there are other alternatives. For example, it is a natural consequence of any cooperative structure that enthalpy and entropy changes must, to some extent, compensate each other. Protein unfolding processes are weak first-order phase transitions, weak because the cooperative unit is very small so that the transition-temperature range is very much broader than that for the melting of ice. Compensation behavior due to the protein conformation is clearly apparent in the thermodynamic changes in protein unfolding which are discussed at length elsewhere. However, this type of compensation process is not quantitatively similar to Vaslow-Doherty compensation, except for changes involving the exposed non-polar groups as demonstrated in the ribonuclease and trypsin examples".

Lumry and Biltonen (1969) have discussed the probable importance of the enthalpy-entropy compensation phenomenon. They state: "Indeed it is probable

that the enthalpy and entropy change during conformational changes of proteins is the single most important physico-chemical characteristic of protein function".

Compensatory behavior is perhaps particularly important in ecological systems when one attempts to dissect the complexities of intraorganism relationships in terms of molecular events effected by temperature. Compare in this connection the coarse outline presented in Table 2-2, p. 49a.

Problems exist regarding the phenomenon of entropy-enthalpy compensation. Exner (1972), and more recently, Wold and Exner (1973, in press), are critically examining the foundation of the experimental utilization of the compensation phenomenon.

The most serious objections have come from Banks, Damjanovic and Vernon (1972). They have demonstrated, based on the suggestion by Leffler, that the "compensation law" may essentially be an artifact due to a very human shortcoming, namely, the tendency to measure that which is readily measured - for instance, rates which are within a relatively narrow range. Thus, values for first-order rate constants (r) are frequently in the range of 10^{-3} to 10^{-6} sec^{-1} (corresponding to reaction half-lives of from 10 minutes to a week). Rewriting the Eyring equation in the form

$$\log r - \log \frac{kT}{h} = \frac{\Delta S^{\neq}}{2.303R} - \frac{\Delta H^{\neq}}{2.303RT}$$

one sees that since log (kT/h) is assumed to be essentially constant, a variation by a factor of 10^3 in r will affect the left-hand side only to the extent of a variation between -16 and -19; in other words, essentially constant. The right-hand terms, i.e., the entropy and the enthalpy, would exhibit rather compensatory behavior. Still more critical (at least as far as rate phenomena are concerned) is the observation made by Banks, et al.: "fifty arbitrarily selected

hypothetical values of rate coefficients between 10^{-3} and 10^{-6} s^{-1}, temperatures between 295 and 345°K and apparent enthalpies of activation between 10 and 200 kcal mol^{-1}, were randomly associated and the corresponding values of $\Delta S^{\neq}$ calculated from equation (2)". The result, shown in the Figure 1, of the article by Banks, et al, is indeed an "impressively straight line" of $\Delta S^{\neq}$, plotted as a function of $\Delta H^{\neq}$ (note misprint in original - activation symbol missing from ΔH) with a value of T_c of 322°K. More recently, Wold (1973, personal communication) has indicated that he fears that somewhat similar objections may be applied to equilibrium properties and indeed to the "conventional wisdom" implied in the Barclay-Butler* rule.

Possible compensatory behavior between entropy and enthalpy should not be disregarded. Too many examples in the literature appear well founded and work along these lines continues, particularly in the Laboratory of Professor Lumry (1973, personal communication). Enthalpy-entropy compensation has also been discussed by Lovrien (1969) in terms of activation diagrams of enzyme catalysis (i.e., in the framework of the transition state theory). Lovrien stresses that if compensation relationships - being of an extra thermodynamic nature - do occur, then it must be expected that a "particular mechanism, class of mechanisms, or common controlling features to them, are underlying". Furthermore, Lovrien proceeds to suggest that where the compensation of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ in enzyme reactions is strictly obeyed, "the effect of water seems manifest because of values of T_c, corresponding to reactions in that solvent rather precisely". Again, this statement must now be taken with some reservation in view of the criticism by Banks, et al. (1972).

*"... all the entropies of vaporization of solutes from non-associated solvents ..... approximate to a single linear relation between the entropy and heat of vaporization" [Barclay and Butler, 1938, p. 1445].

However, if indeed in these cases there are reasons to believe that a non-accidental compensation occurs between enthalpy and entropy, these quantities must be "coupled by means of macromolecular structures, or more properly, by means of actions intimately involving the dynamics of macromolecular structure. In turn these are controlled partly or largely by the structure or other properties of water". Lovrien proceeds to consider that in the process of a reaction, along the "reaction coordinate", the "enthalpy change is not simply irreversibly lost to its surroundings. It may be stored temporarily in the macromolecular framework, probably as entropy (multiplied by T_c), and probably under the aegis of water governing the conformational changes which must occur in most activation processes as described above". Assuming that a reversible exchange of $\Delta H^{\neq}$ and $T_c \cdot \Delta S^{\neq}$ occurs between the substrate and its immediate surroundings, "it is perhaps easier to see an advantage macromolecular catalysts would have over small molecule catalysts. The latter simply may not have the bulk or control needed to act as such a reservoir". This suggestion is important and may parallel, or be identical with, the proposal by the present author (1971, 1972a,1973) of an "energy delocalization" as the cause of the "paradoxial effect" (the observation that vicinal water structures undergo thermal transitions at essentially identical temperature ranges, regardless of the nature of the vicinal solid). Thermal anomalies are not observed in pure bulk water nor in solutions of small molecules (electrolytes or non-electrolytes) but in aqueous macromolecular solutions or near "solid" interfaces. The macromolecule has the ability to accomodate and redistribute local high-energy fluctiations which, in the pure bulk, would have destroyed the possible stabilizable water structures. Thus, it is via the cooperative nature of the states of vicinal water (differing in structure, but with only minor differences in the energetics) that stability is produced by proximity to the "interface" (with a macromolecular solute) which, as suggested by Lovrien, has the "bulk" (i.e., total mass and no doubt vibrational modes) sufficient "to act as such a reservoir".

C. "Normal Behavior"

Biological systems may show either little change in functioning with temperature, at least over reasonably small temperature ranges, while others show nothing but "normal" behavior. "Normal behavior" in this sense would, for instance, be illustrated by rate processes yielding essentially straight line Arrhenius plots, or Arrhenius plots with mild curvature rather than abrupt changes in slopes. As an example of authors who have considered "normal behavior", Fuhrman and Fuhrman (1959) studied the rate of oxygen consumption of animals and tissues as a function of temperature, and concluded that "little influence of temperature is a regular one, and respiration increases with rising temperature so that when rates of oxygen consumption are plotted against temperature, the resulting curve is regular, without dips or peaks except the maximum expected at the optimum temperature". Fuhrman and Fuhrman (1959) did quote some of the earlier evidence for abrupt and unexpected changes such as noted by O'Conner (1955) and O'Conner and coworkers (Crozier and others).

The overall effects on the cellular level and particularly in higher organisms is one of superposition of a vast number of simultaneous and independent biochemical and biophysical events, each with their own characteristic temperature dependencies. This, for instance, has been invoked to explain the body temperature of mammals and of birds (Drost-Hansen, 1965, 1971). Yet - while body temperatures and temperatures for "optimum performance" may center around relatively narrow ranges of temperatures - in all these cases (i.e., mammals and birds), 45 to 46°C is found to be an abrupt, upper thermal limit.

D. Anomalous Responses near 23°C

Anomalies near 14-16°C, 29-32°C and 44-46°C are not the only ones that have been observed. Thus, some systems instead exhibit anomalous properties near 21 to 23°C. These changes are sometimes far less dramatic, but nonetheless appear to be real. Studies are currently underway to investigate this observation; it appears that vicinal water structures may be involved only indirectly. It seems that in many of the cases where a distinct anomaly is observed near 23°C, one is dealing with a lipid/water system. It is well known that pure anhydrous lipids can undergo higher-order phase transitions (see Chapman *et al*, 1966; Chapman and Wallach, 1968; Ladbrooke and Chapman, 1969). However, such need not necessarily play a particularly dominant role in biological systems which are, after all, highly aqueous. It is desired to point out here that very likely, the "sensitive" part of this system is the combined water/lipid interactions, rather than either of the separate phases alone.

Because anhydrous lipids do show phase transitions at various temperatures this phenomenon may play a role in determining the temperature responses of some biological systems. However, it is proposed that the detailed nature of the water/lipids interfacial properties are even more important. Vicinal water is structured and these structures, in turn, impose conformational restraints on the substrate - in the present case, the hydrocarbon chains on the lipids. There are mutual interactions resulting in restraings on the geometrical possibilities of vicinal water due to the specific nature of the lipid and, conversely, there are specific structural constraints imposed upon the lipids by virtue of whatever vicinal water structure happens to be stabilized within the particular temperature interval in question. Of all the biologically interesting water/"solid" interfaces, the lipids are undoubtedly the materials

most readily "mechanically deformable". As temperature is changed, the vicinal water structure will pass from one particular type of stabilized geometry to another, and these changes therefore will be reflected in the specific structure and properties of the underlying lipid at the water/lipid interface. The water/water interactions involved in the vicinal structuring may be weak, but the interactions in question are cooperative, and the sizes of the cooperating units are undoubtedly rather large.

As indicated earlier, Oppenheimer and Drost-Hansen proposed that an organism might exhibit optimal growth at different temperature intervals by utilizing different metabolic pathways. Sinesky (1971) has studied the fatty acids in bacterial phospholipids as a function of the temperature of growth. He found that the palmitate-to-oleate ratio in the phospholipids isolated from E. coli shows a distinct and sharp maximum at 30°C. Furthermore, Sinesky points out that "as expected, the ratio of palmitate-to-oleate incorporated into phospholipid rises with increasing growth temperature, but shows a peculiar inflection at 30°C". Sinesky discusses this in terms of carbon chain length and the effects of this parameter on the melting point of the fatty acids. It is tempting here to suggest that the sharp maximum at 30°C in the palmitate-to-oleate ratio in the total phospholipids is a manifestation of some water structure-induced change in metabolic processes and that the "peculiar inflection at 30°C" is also such a manifestation.

Recently, Smolen and Hagman (1973) have been concerned with the nature of diffusion across biological membranes. To simplify the study of actual biological diffusion across lipid/aqueous-type membranes (lipoid barriers), the authors chose to study polyanion-polycation salt complex membranes prepared by casting from various solvent mixtures. Permeability coefficients were determined for several solutes, specifically those for which previous

measurements had been made on diffusion permeability in actual biological membrane systems. Good correlations were obtained between the biological membrane permeabilities reported and the data they obtained on the poly-salt membranes. The authors concluded that the observed permeability behavior of the membranes could not be related to the water structures within the polymer matrices of the membranes and likewise suggested that the lipoid barrier properties of actual biomembranes may be similarly understood in terms of the amount of structured water.

E. Acclimatization and Adaptation

For various aspects of temperature adaptations, see the extensive writings by Hochachka and Somero (both individually and in joint papers); also Precht (1968), Precht, et al. (1955), Rose (1967). Prosser (1967) edited the Symposium Proceedings on "Molecular Mechanism of Temperature Adaptation" and introduced the volume in which is defined physiological responses in terms of "acclimation", "acclimatization", "adaptations", etc.

Further discussions of biochemical adaptation are in writings by Hochachka and by Somero; both authors have been concerned with adaptive processes as studied by measurements on isolated enzymes. More recently Smith (1973) determined the thermal stability of various mitochondrial enzymes and pointed out that in none of the fishes included in his study are all the enzymes fully stable when incubated at 37°C with one exception (cytochrome oxidases) even in the most stable loses some 20% of its activity at that temperature. "This is perhaps to be expected for, although fish such as goldfish, tench, and carp can withstand higher temperatures, they can also still live in quite cold water without becoming completely inactive. It may be that the properties of enzymes such as these which are involved in energy producing reactions would correlate better with parameters such as the temperature optima for growth, rather than with extremes of temperature which can be endured". The danger of drawing extensive conclusions from isolated enzyme studies is indicated by the illustration given in the paper by Smith (1973) on the thermal stability of some mitochondrial enzyme systems from fresh-water teleost fishes compared with the respective upper lethal and the preferred temperatures. In that article, the preferred temperature (based on data by Varley [1967] exceeds the quoted

upper lethal temperature for carp [based on data by Jones, 1964]). The apparent inconsistencies probably are no more than a reflection of the inevitable errors in biological observations carred out independently by different authors and the experimental uncertainties associated with measuring (or even properly defining) an "upper lethal temperature".

Somero and Hochachka (1971) have introduced what they termed a "paradigm" of biochemical adaptation to the environment. Specifically, they suggest that "biochemical adaptation to the environment is effected by producing the proper molecules in the proper quantity at the proper time to insure satisfactory biological function in the face of new environmental conditions". They have been particularly interested in biochemical adaptation to different environmental temperatures. Two major types of changes are possible in principle: the concentrations of certain molecular species in cells may change; or in the alternative, the actual types of molecules may vary. The latter is exemplified by the different types of isozymes present in, respectively, cold and warm-acclimated organisms. The authors propose that for adult poikilotherms, a "considerable degree of 'biochemical restructuring' on a seasonal basis" occurs. Oppenheimer and Drost-Hansen (1960) have considered thermal effects on the growth of some microorganisms (on minimal media), and proposed that in different temperature intervals, different metabolic pathways are utilized. Such a proposal is consistent with Somero and Hochachka's notions and would suggest that different molecular species and different chemical processes occurred above or below a thermal transition region (for instance, around 30 to 32°C). In this view, the mechanism of adaptation represents selecting "certain proper molecular species" to permit optimal functioning.

The second suggestion by Somero and Hochachka represents the utilization

of different types of isozymes. This brings to mind the changes that Privalov and co-workers (1969) observed by physico-chemical techniques (particularly DTA), and referred to as "subdenaturation of proteins". This author proposes that Privalov's "subdenaturation" may be merely a manifestation of minor conformational changes, induced in the macromolecules in question, due to the changes in the structure of the vicinal water.

Regardless of the detailed mechanism, it appears that the type of adaptation discussed above does occur in biological systems. However, only rarely is the adaptation profound: specifically, temperatures for maximum rate of growth, or optimum feeding behavior, may be changed through acclimatization by several degrees. However, while exceptions certainly occur, it seems that many changes are frequently restricted to very limited temperature intervals. For instance, upper thermal limits for fishes rarely vary more than one or a few degrees, regardless of acclimatization. A tabulation of such data for fishes is available in a report in this series. For a discussion of these aspects, the reader is referred to the papers by the present author (1971, 1972a). Confer also with the writings by Hochachka and Somero (1971) and by Precht (1968).

Table 2-1 shows the basic ideas expressed by Somero and Hochachka (1971) regarding the biochemical changes effected during temperature acclimatization in poikilothermic organisms. The Table is modified to contain two separate interpretations: Part A is the proposed interpretations by Somero and Hochachka; Part B is the (rather tentative) interpretation proposed by the present author based on current understanding.

Recently, Davison (1971) has studied the interrelationships between age, acclimatization temperature, and thermal death point in adult moth

Table 2-I

Constituent	Change: Part A	Change: Part B
Enzymes	Different variants in winter and summer rainbow trout	Different variants (winter vs. summer) due to minor conformational changes, imposed by changed vicinal water structures.
Lipids	Changes in saturation, chain length and quantity of lipid	As proposed by Somero and Hochachka.
Metabolic pathways	Increases in activities of pathways associated with biosynthesis in cold-acclimated fish, e.g. increase in hexose monophosphate shunt	Different metabolic pathways over different temperature intervals (See Section __,__ and Oppenheimer and Drost-Hansen, 1960, Schmidt and Drost-Hansen, 1961, and Drost-Hansen, 1971).
Protein synthesis	Change in rate	Change in rate, determined by changes in vicinal water structure (rather abruptly changing at the temperatures of the thermal anomalies).
Nucleic acid synthesis	Change in rate	Changes in rate, determined by changes in vicinal water structure (rather abruptly changing at the temperatures of the thermal anomalies).
Blood ions	Changes in relative concentrations	Changes in relative concentrations, effected by changes in membrane functioning due to changes in vicinal water structure - interpretable in terms of either changes in active transport and/or different ion activities (see Drost-Hansen, 1971, and Hazlewood, 1973).

Constituent	Change: Part A	Change: Part B
Tissue ions	Changes in relative concentrations	Changes in relative concentrations, effected by changes in membrane functioning due to changes in vicinal water structure - interpretable in terms of either changes in active transport and/or different ion activities (see Drost-Hansen, 1971, and Hazlewood, 1973).
Ribosomes	Differences in ribosome melting temperatures between summer and winter trout	Melting temperatures affected by nature and extent of vicinal water structures.
Hemoglobins	Changes in O_2 affinity likely due to changes in modulator concentrations	Changes in O_2 affinity, affected by vicinal water structures.

Calliphora erythrocephala. Only one point is of interest in the present context. The data presented by Davison suggest that physiological acclimatization does occur at temperatures above 29°C, but the increase in LD_{50} does not form a reproducible, consistent pattern. Davison speculates that the acclimatization is complicated by a simultaneous age-dependent decline in LD_{50} which is also accelerated by increasing the temperature of acclimatization. Furthermore, "physiological acclimatization" does not become superimposed upon this decline until 32°C. Moreover, the increase in resistance between 31 and 32°C is so great as to suggest that this temperature range may be critical for physiological acclimatization to become manifested. The cause of the abrupt increase in resistance in this temperature range remains obscure. I would like to suggest here that the obscure cause is a direct manifestation of changes in the vicinal water structure at some regulatory "site of action".

F. Multiple Temperature Optima

Multiple temperature optima for growth have been discussed, particularly by Drost-Hansen (1965, 1971; see also Mitchell and Houlahan, 1946; and Davey and Miller, 1964) for a variety of microorganisms. An interesting example for a multicellular organism may be seen in a study of the marine nematode, Rhabditis marina by Tietjen, et al. (1970). They showed that its growth is minimal near 15°C, with a relatively sharp optimum between 25 and 30°C. As is often the case, the growth maximum is skewed and reveals a precipitous drop above 30°C, approaching zero at 35°C.

Extremely complex, multiple-growth optima curves have been reported by Sieburth (1964) for cultures of a marine bacterium, genus Arthrobacter. Relative growth minima were frequently seen at 15°C, but with several narrow growth optima at other temperatures, depending on added nutrients.

Binodal response curves have been reported for various types of organisms. Gessner (see Kinne, Marine Ecology) reported photosynthesis and respiration data for three species of marine algae based on data by Ehrke (1930) (Fucus serratus; Plocamium coccineum; Enteromorpha compressa). In all three cases, multiple optima or at least curves with very distinct "shoulders" were observed for both respiration and photosynthesis.

It is difficult to pinpoint the "site of action" responsible for binodal growth curves. Oppenheimer and Drost-Hansen (1960) and later elaborated on by Drost-Hansen (1971) have suggested that different metabolic pathways may be involved above or below the temperature ranges of thermal transition. It seems reasonable to postulate the involvement of different water structures in "metabolic switching" in the different temperature intervals. For instance, Kohonen, et al. (1973) have determined the activities of brain Mg_2^+ ATPases and the sodium-potassium ATPases of the fishes, roach and

gourami. In the case of the latter species (Helostoma temmicki) the sodium potassium ATPase activity shows a distinct shoulder, while for the roach (Leucisus rutilus) two distinct optima were observed with a minimum around 30°C. The activities also decreased fairly rapidly above 45°C (particularly for the roach). By differentially affecting the activities of key enzymes, temperatures may induce the selection of certain pathways to be favored at particular temperatures

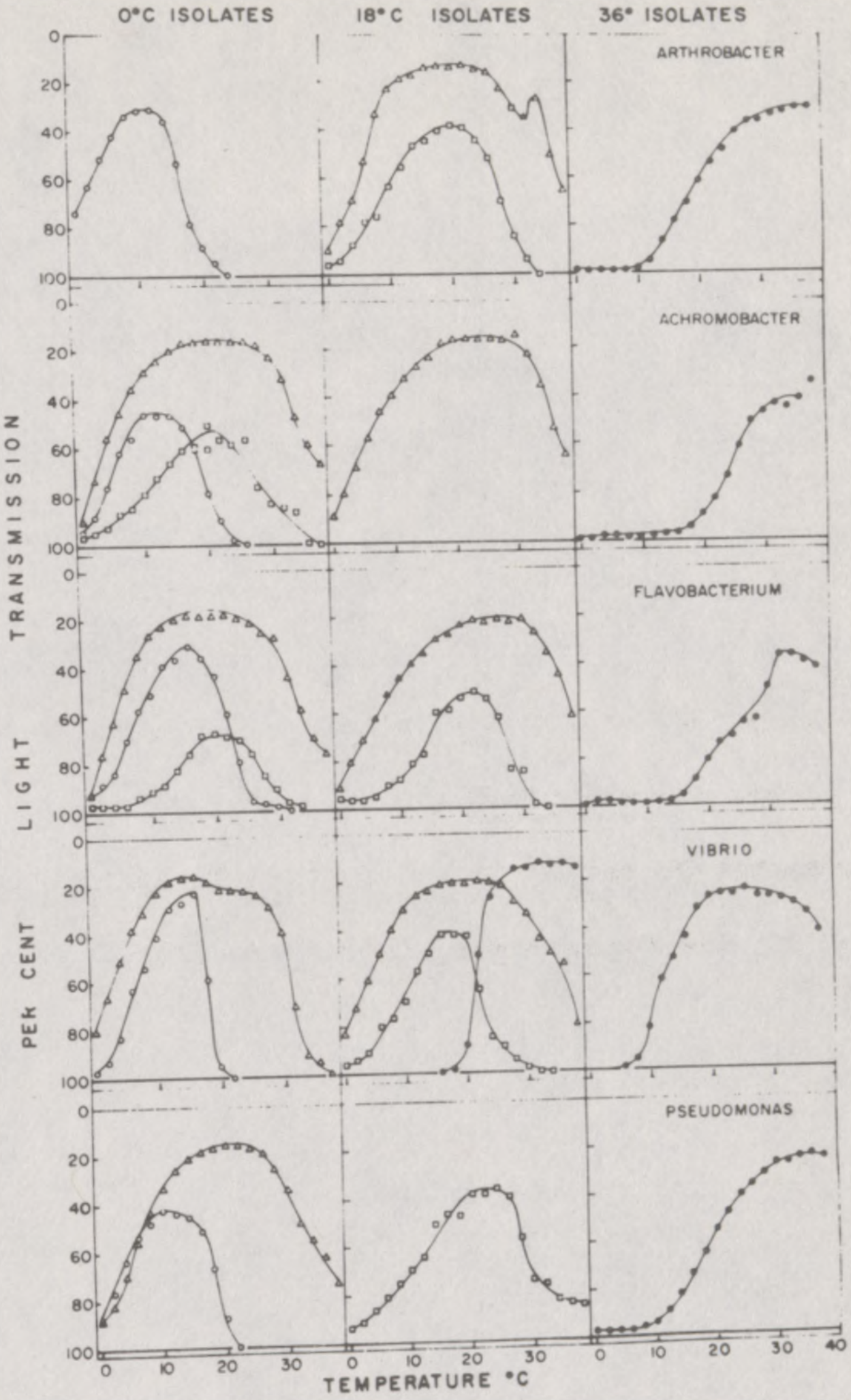
An example of the sometime abrupt changes in algae in response to temperature has been reported by Bonaventura and Kindergan (1971). These authors studied the delayed light emission from the green alga Chlorella pyrenoidosa. The purpose of this study was to gain some insight into the photosynthetic events as related to the electron transport mechanisms. Ecologically, the study is of interest because of the relationship between light saturation and the properties of the photosynthetic unit. The point stressed in the present connection, however, is merely that abrupt changes appear to occur at the temperature where the cellular water also appears to undergo changes. Thus, Bonaventura and Kindergan observed notable binodal distribution of emission intensity in the fast emission (12 milliseconds after 12.7 milliwatt/cm^2 excitation at 488 nm). The emission exhibits a relatively sharp maximum around 10°C with a precipitous drop between 10 and 15°C. The emission intensity remains essentially constant up to 30°C, where a second peak occurs. It is of interest, also, that the intensity drops to zero at about 48°C. The delayed emission (measured after 30 milliseconds after excitation with 0.9 milliwatt/cm^2 radiation of same wavelength) shows only one peak corresponding to the higher temperature peak for the prompt emission. The intensity drops to nearly zero at about the same temperature as for the prompt emission. It is proposed that these results are also consistent with the notion of vicinal water structure, i.e., that in the photosynthetic pro-

cesses involved in green algae, a component exists which is sensitive to water structure.

Wanka and Geraedts (1972) studied the effect of temperature on DNA replication in Chlorella pyrenoidosa. In one experiment, the relative amount of DNA and total number of cells were measured as a function of temperature. The experiment showed two relative optima for both total cell counts and DNA contents. A well-defined minimum occurred at 15°C.

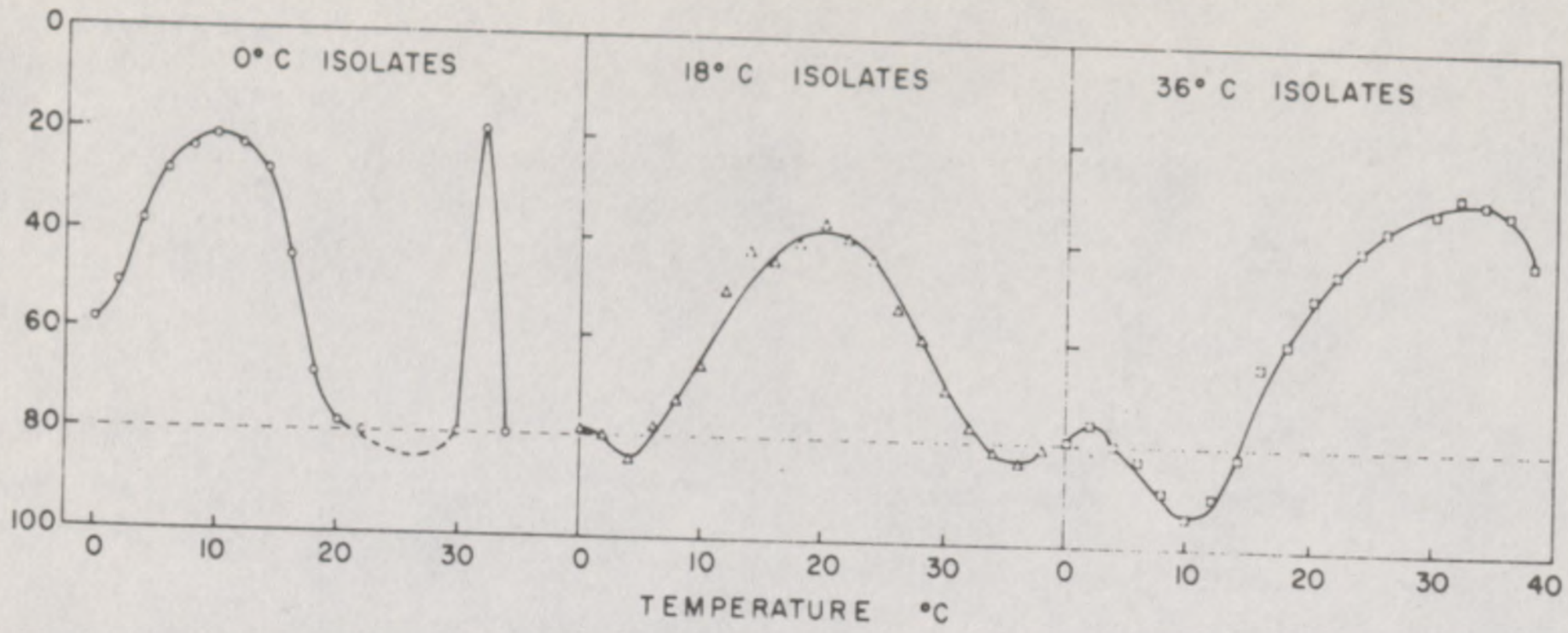
A remarkable example of multiple temperature optima for a biological process has been reported by Wulff, et al. (1972). These authors measured the germination of seeds of Jussiaea suffruticosa as a function of light intensity and temperature. The authors observed in the case of seeds incubated at constant light intensity during germination a remarkable minimum in germination near 30°C. The lower the light intensity, the more pronounced this effect. Relative optima were observed near 25 and around 35 to 40°C. Oppenheimer and Drost-Hansen (and later Schmidt and Drost-Hansen, and Drost-Hansen, 1971) had noted that many microorganisms exhibit binodal growth phenomena, especially when grown on minimal media. The types of organisms included both bacteria and fungi. However, the example by Wulff, et al. (1972) suggests a similar effect for organisms other than unicellular microorganisms. Furthermore, for seeds from various tree-species, binodal growth curves have been reported earlier by P. A. Thompson (1970).

Sieburth has contributed to the study of multiple temperature optima. He has been interested in the growth of marine organisms. Some of his results are shown in Figures 2-24 and 2-25 and show very complex patterns. Yet, it would, no doubt, be a great mistake to ignore for long the phenomena of multiple growth optima, particularly in connection with the specific effects which may result from the presence of various nutrients - be they



"Growth temperature spectra" of some five hundred representative isolates of Arthrobacter, Achromobater, Flavobacterium, Vibrio and Pseudomonas, isolated at three different temperatures (0, 18 and 36°) from Narrangansett Bay, Rhode Island. (Sieburth in Oppenheimer, 1968, page 199).

Figure 2-24



Multiple Growth Temperatures for Arthrobacter (0° C Isolates); Flavobacterium (18° C) and a Pseudomonad (36° C). The data below the Dotted Line Represents Decreases in the Initial Turbidity Due to Cell Lysis (Sieburth; See Oppenheimer, 1968, page 203).

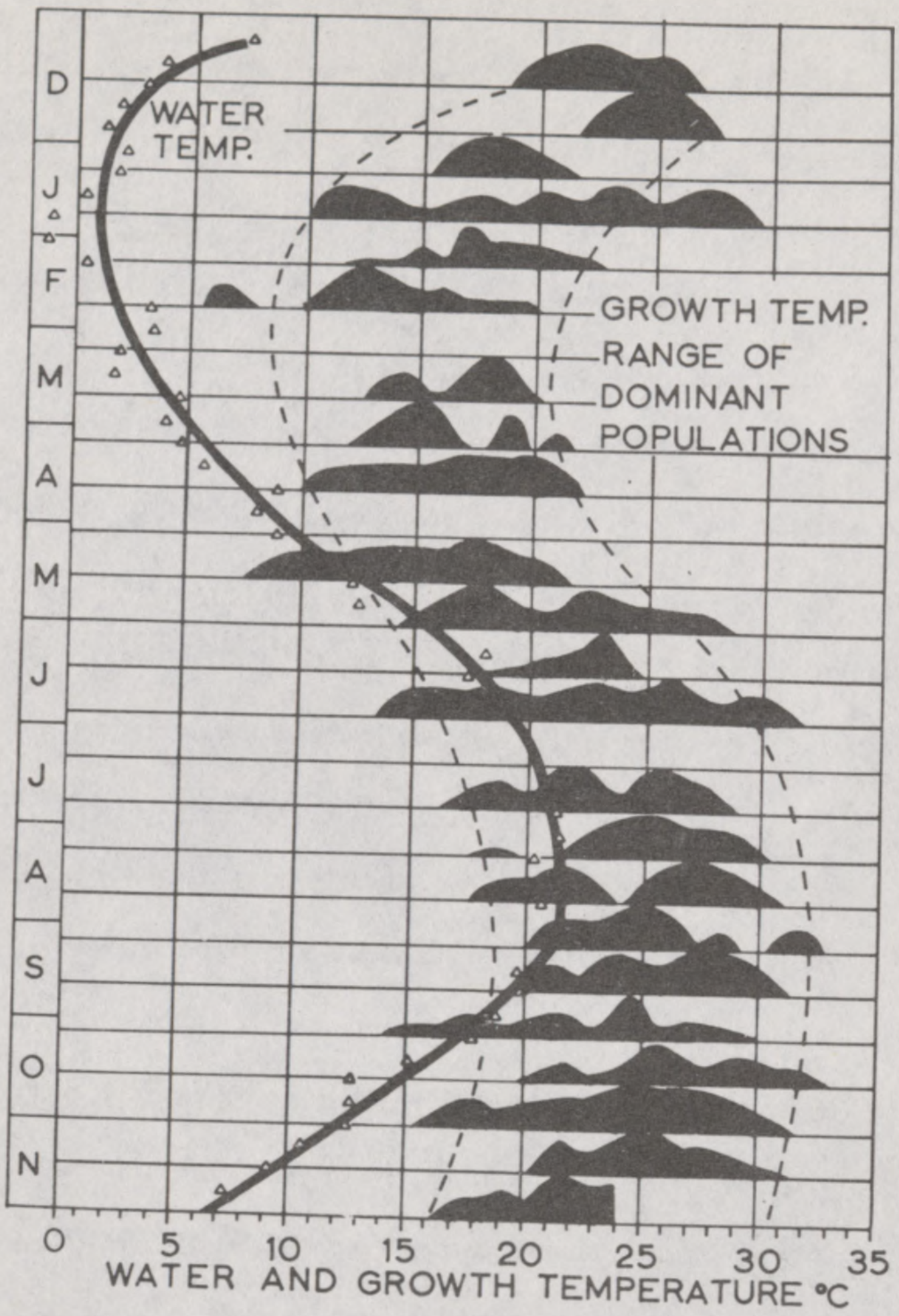
Figure 2-25

naturally occurring or the result of man-made pollution.

Sieburth has also studied the predominant microflora in Narragansett Bay. His results are shown in Figure 2-26. Note that a rather sharp cutoff occurs between 30 and 33° C.

Many physiological responses of individual cells or organisms to temperature yield curves which go through a maximum, but sometimes with a noticeable "shoulder" (making the curve appear skewed to various extents). To remind the reader of this type of curve, a number of hypothetical examples are shown in Figures 2-27A through 2-27D. Frequently, it can be assumed that such temperature dependencies reflect the operation of two different processes. Figure A shows a typical curve with a "shoulder". Shown also are two individual curves which have been superimposed to give the resultant total, "skewed" peak. In this and the other cases discussed here, the peaks have been synthesized on the computer from superposition of simple Gaussian functions. A very obvious example of the superposition of two curves is shown in Figure B, and a rather subtle example in Figure C. Finally, Figure D shows a curve which appears to be an almost symmetrical, "simple" curve, and two identical (but highly overlapping) curves from which the resultant, net curve was made up.

The preceding examples deserve some comment. Multiple growth optima may be identified with two separate growth processes. However, a description in terms of superposition of simple Gaussian functions is unrealistic. This is shown in the illustrations in this Section, where rather than Gaussian "bell shaped" curves, the growth curves show very abrupt changes in slope near 15 to 18° C, and near 27 to 31° C, with a very much broader maximum in the mid-range of the interval. Secondly, in such more complex cases as Figure 2-27A or Figure 2-27D, the resolution of the net curve into its component curves is



Ranges of Growth for the Dominant Microflora in Narrangansett Bay (December 1960-November 1961). Note Relatively Sharp Cutoff Between 30 and 33° During Summer Months. Data by Sieburth, 1967, quoted by Hedgepeth and Gonor in Krenkel and Parker, 1969, page 98).

Figure 2-26

Theoretical Net "Growth" Curves, Representing the Sum of

the Individual, Separate Gaussian Curves Shown. All Calculated.

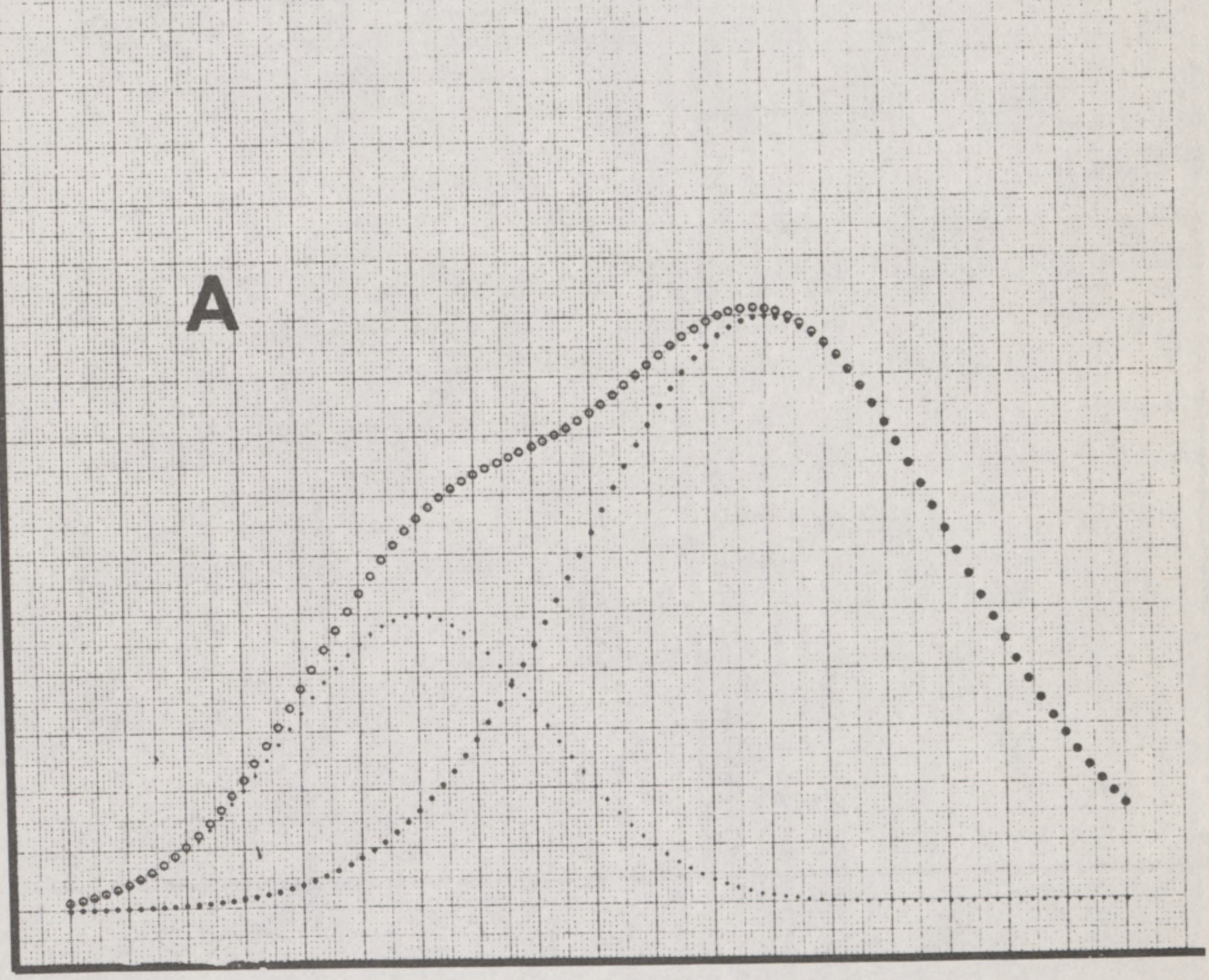
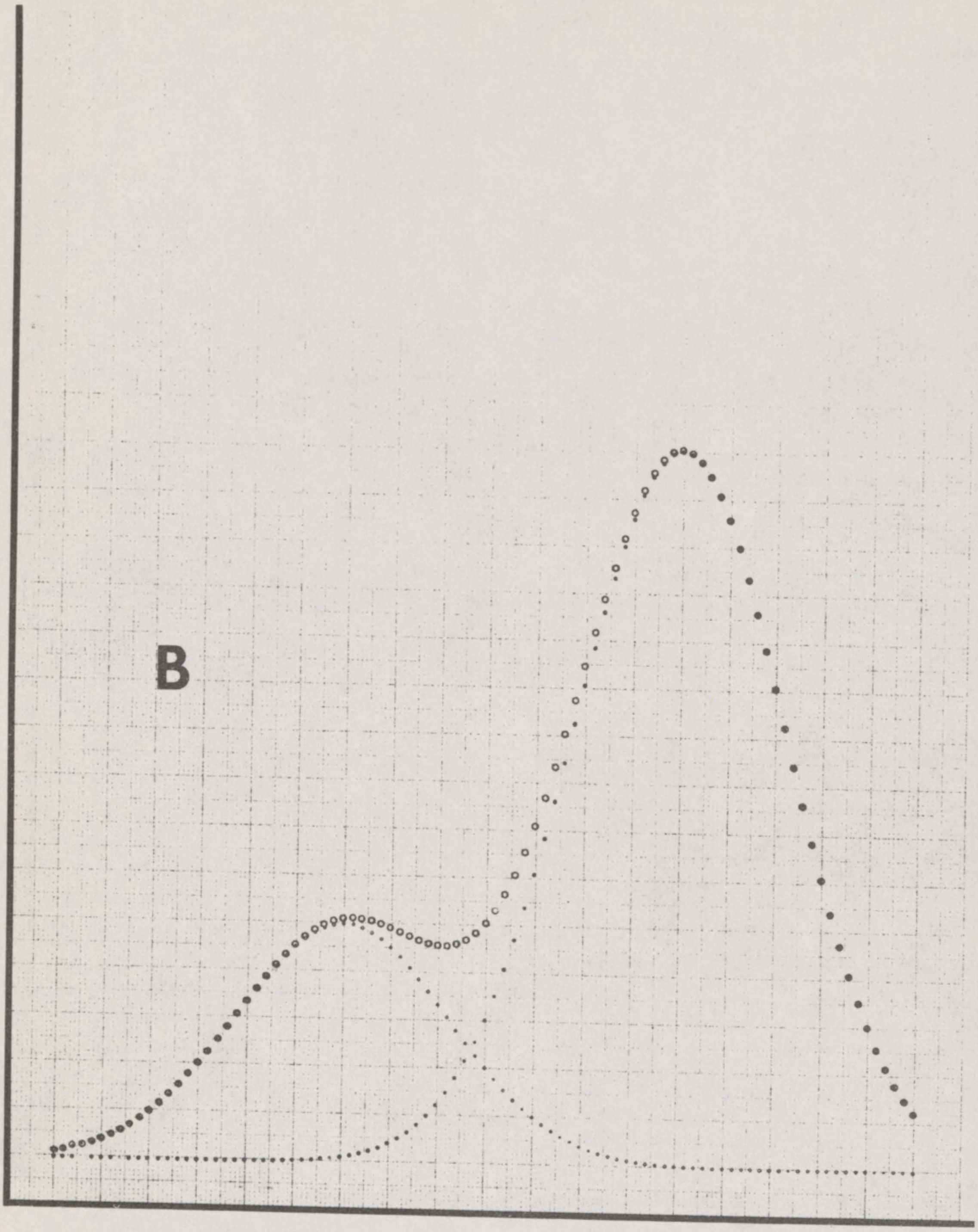


Figure 2-27

A-D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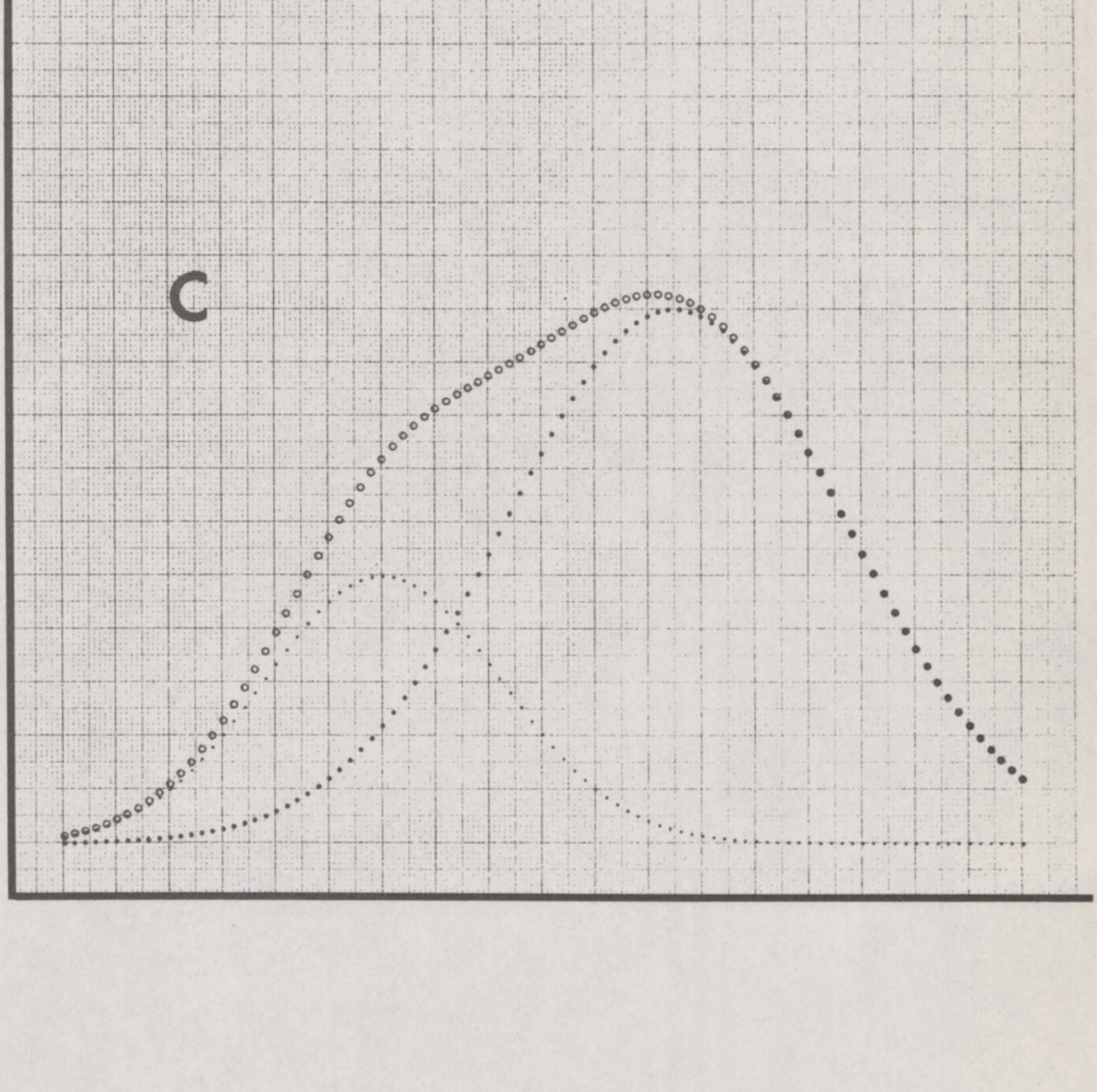
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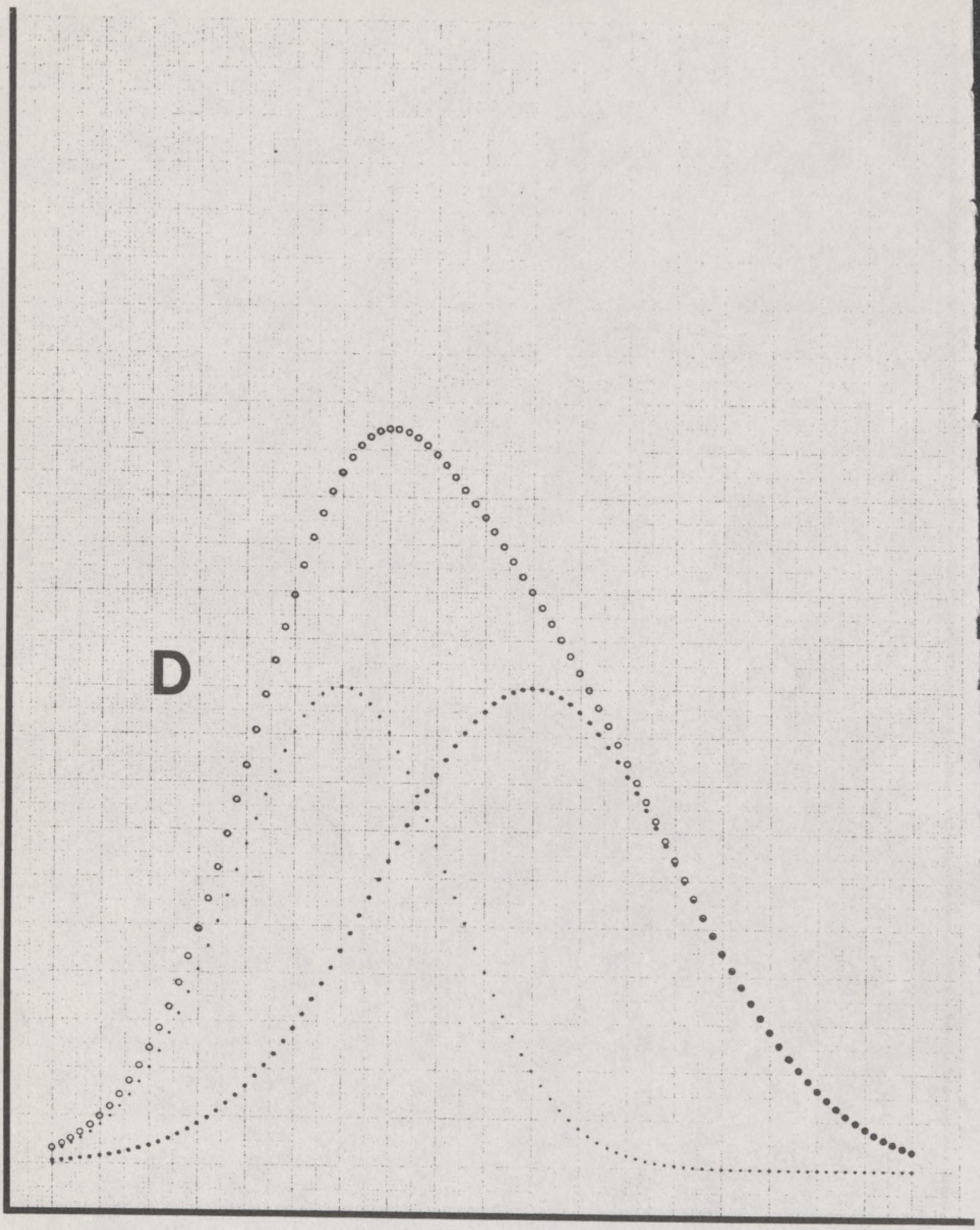

D

subject to considerable conceptual and mathematical uncertainty. Further complications occur in biological studies because of the frequent lack of closely spaced measurements. This problem is particularly important since the result frequently is a tendency on the part of various authors to ignore their own estimates of errors on each measurement, and draw grossly oversimplified and over-smoothed curves through meager sets of data points.

To "compose" - literally and figuratively - net curves showing distinct binodality or merely "shoulders", using simple arithmetic (or facilitated by the computer) is quite simple. The converse, however: to resolve a given curve into its possible components, is difficult and sometimes impossible. Resolution of the total curves requires an initial choice of nature of the type of curves into which the total net curve is to be made. An artificial restraint is introduced which may or may not be valid. Furthermore, the number of component curves into which the total curve to be resolved (two, three or many sub-curves) is a problem. This problem is one of current actuality in connection with the analysis of Raman and infra-red spectroscopic data (see the writings by Walrafen [1972].

Shortcomings in biological methodology have allowed the interpretation of thermal studies to be highly unrealistic, preventing the development of rigorous theory. The natural tendency is to accept an approach, based on the implicit notion of "maximum conceptual economy". Thus, rather than facing a notable complexity due to multiple, simultaneous phenomena, many investigators have chosen to assume only <u>one</u> major effect to be operating. Interpretation is forced accordingly. Mario Bunge (1963) has commented on this problem "...we cannot any longer believe in the scholastic

maxim, 'Simplex Sigillum veri' (simplicity is the seal of truth): because we know that all our constructions are defective, hence, corrigible, since deliberately or not, they involve the neglect of an unknown number of factors". The temptation to simplify is great, since it is frequently only through simplification that it becomes practicable to deal with such enormously complicated phenomena as cells. As the result, it is necessary to examine in detail large numbers of individual events but allowing for various options in the approach to interpretations. This, unfortunately, often leads to longiloquent and tedious presentations. Rephrasing Aldous Huxley (1958) one may observe, regarding brevity, that it is the soul of which "may become the very body of untruth".

G. Thermal Death Mechanisms

The problem of thermal death is of major ecological importance in connection with heated discharges from installations such as power plants. Yet, as observed by DeSylva (1969), "heat death" is seldom observed in nature, yet many organisms are killed at temperatures only slightly above those at which they normally live (Gunter, 1957; Kinne, 1963; Naylor, 1965). The cause of heat death in fishes has been extensively discussed by Brett (1956) and Fry (1957).

Several detailed and specific suggestions have been made to account for thermal death. Among the possible causes in complex organisms are synaptic failure in the pacemaker, myoneural junctions, and smooth muscle peristalsis (see Fisher, 1958). Other authors have attributed the thermal death to denaturation of proteins in cells and to inactivation of enzymes such as choline-esterase. High levels of blood lactic acid concentrations have also been implicated presumably acting by lowering pH. Agersporg (1930) proposed partial coagulation of the blood in branchial capillaries. Mayer (1914) has suggested asphyxiation (simply insufficient oxygen level to support metabolic activity). Orr (1955) has suggested some type of neural failure. For the relatively few detailed suggestions for the mechanism of thermal death, very little is known with any degree of certainty. The point is again made here that although theoretical predictions are currently not possible with any degree of certainty, many of these proposed mechanisms - as well as countless others - may be related to the pecularities and intricacies of the water near interfaces (the vicinal water) and its structural transitions.

An excellent example of both the dramatic effects on physiology of temperature around 30 to 32°C, as well as evidence for the contention that

24-642 O - 73 - pt. 2 - 33

different types of phenomena play a role, respectively, above and below this temperature range, can be found in an article by Maynard-Smith (1958). Maynard-Smith exposed Drosophila to different temperatures, and determined survival times over a range of temperatures. The evidence for invoking different processes of senescence above and below the critical temperature range is summarized by the author: "At temperatures above 31°C, the expectation of life falls very rapidly to less than twenty-four hours at 33°. There are reasons for thinking that the changes which occur in individuals at temperatures above 31°C are different from those occurring below 31°C. Thus, if flies are exposed to 33°C for eight-hour periods, with intervening periods of sixteen hours at 20°C, their total survival time at 33° is much greater than the flies kept continuously at 33°C. In this sense, the changes occurring at 33°C are 'reversible', as are the changes which occur at still higher temperatures (Reference 3). In contrast, changes occurring at 30.5° are irreversible, in that the total survival time at this temperature is not increased by an intervening period of eight days at 20°C".

Clarke and Maynard-Smith (1961) had observed that between 15 and 30°C, it appeared that lifespan could be divided into two phases, consisting of an irreversible "aging" process, the rate of which was approximately independent of temperature from 15 to 30°C (but slower at 3°C) and a "dying" process which was initiated when aging has proceeded to a stage "at which the individual is no longer capable of maintaining a steady-state at the temperature at which it is living, although the same individual would be capable of maintaining a steady-state at some lower temperature". It is indeed unfortunate that these conclusions were based on measurements made at only 3, 15, 20, 26, 28.3, and 30°C, with no data for temperatures above 30°C, and with rather few measurements in the range from 3 to 26°C.

See also the more recent paper by Lamb (1968). In the paper by Lamb, data are reported supporting earlier studies by Hollingsworth (1968) which suggest that neither of the two theories for relating life expectancy to temperature - namely, the theory by Shaw and Bercaw (1962) nor of Clarke and Maynard-Smith (1961, see above) - are likely correct. Lamb concludes, "it is clear therefore that neither of these two theories provides a complete explanation of the effects of temperature on the lifespan of Drosophila". It seems obvious that these examples again represent cases where "theories" of temperature effects on living organisms appear primarily to be based on non-molecular, descriptive, pragmatic approaches, rather than in terms of underlying fundamental molecular events and processes. In the case of the papers mentioned briefly above, the main facet which is excluded is the specific role of the cellular water.

H. Low Temperature Death

Kinne (Marine Ecology, Section 3.31, p. 416, "Temperature Invertebrates") has emphasized that tolerance to cold is much more variable and far more difficult to determine than is heat tolerance. Furthermore, causes of cold death have been examined in a number of reviews (for references, see also Kinne, loco cit., p. 441). Significantly, it appears that not only are the causes of cold death complex, but the causes appear also to manifest themselves at different levels of organization. Elsewhere in this review, attention is called to the often far-less pronounced changes at lower temperatures; thus, for a large number of aquatic organisms, sharp upper thermal limits between 30 and 33°C appear to exist. However, exposure to low temperature - say, below 14 to 16°C, appears merely to influence or alter qualitative relationships rather than cause complete cessation of activity, or cold death (Drost-Hansen, 1971). Obviously, many organisms are subject to fluctuating temperatures, including very low temperatures at the higher latitudes. No discussion is presented in this review on the effects of freezing temperatures. However, the obvious inference is drawn that if the ambient temperature in a local, natural water system is increased by man-made energy input to establish a new level of ecological organization, the sudden stoppage of the "thermal enrichment" (such as due to shutdown of a power plant) may drop temperatures to the pre-plant operational level, with potential impact on the overall ecology. Whether or not such an effect would be noticeable or significant will depend on specific circumstances. However, the present author believes that if the operation of the power plant has increased the ambient local temperature for any significant length of time across one of the thermal transition regions (either the transition at approximately 14 to 16°C or at 30 to 33°C), ecological changes may be expected upon the return of the temperature to the pre-plant operational temperature level. This is certainly worth noting.

I. Neural Temperature-Sensitive Phenomena

Nerve conduction appears affected by temperature changes in a manner which suggests the participation of vicinal water structure changes.

In a recent study, Aubry and Posternak (1970) studied the differential effects of temperature and anesthetic agents on (A) α-fibers of the sciatic nerve from the frog (Rana ridibunda ridibunda). The authors found that sensory fibers are more susceptible to the effects of narcotics than motor fibers of same conduction velocity. However, the differential effects of the narcotics used (ethanol, 1-butanol, 3-butanol, hexanol and cocaine) on motor and sensory A α-fibers did not depend significantly on temperature shifts in the range from 0 to 38°C. The authors conclude that "it seems that [the differential effects] depend upon properties of both motor and sensory A α-fibers which are identically affected by temperature changes". This point, undoubtedly, is significant. A possible explanation would be that the "sensitive element" is indeed an agent common to both types of nerve fibers. This might, for instance, include the lipoproteins or lipids in bimolecular lipid membranes, or might be the water. Evidence for the water as the sensitive element may perhaps be inferred from the observation by Aubry and Posternak that the nerve conduction blockage caused by the narcotics is partially alleviated by increase in temperature from 0 to approximately 15°C. From 15°C to 38°C, the temperature increase reinforces the nerve blockage.

Latorre and Hidalgo (1969) have measured the effects of temperature on the resting potential of squid-axons. They reported a small linear decrease in the potential as a function of temperature in the range from approximately 3 to 23°C. A careful inspection of the data suggests an alternative interpretation. Allowing for some data scatter, it appears equally valid to describe the temperature dependence in terms of two separate, essentially

24-642 O - 73 - pt. 2 - 34

linear functions, respectively over the intervals 3 to 14°C, and 14 to 23°C. On this basis, the slopes become, respectively, 0.72 millivolt per degree, and 0.43 millivolt per degree (compared with the average value quoted by the authors of 0.53 millivolt per degree).

Chapman (1967) using the giant squid axon wanted to test the accuracy of the Hodgkin-Huxley theory of neural current velocity as a function of temperature. It is interesting that the agreement between theory and observed values was quite good in the range from approximately 5 to 25°C. However, above 25°C, a notable decrease occurred in the conduction velocity. At 30°C, the conduction velocity reaches a maximum, followed by a rather steep drop in the range between approximately 32 to 37°C. This drop is not predicted by the Hodgkin-Huxley theory (nor by any other current theory of neuroconduction). It therefore seems reasonable to infer that this notable deviation could be related to the structural changes in the vicinal water occurring at 30°C. The frequency of nerve impulses in the tarsal nerve of the cockroach has also been shown to decrease precipitously between approximately 0°C and 10°C, and increase with extreme rapidity above 35°C (Clarke, 1967).

Since the basis of axonal conduction and synaptic transmissions seems to be similar, similar effects of temperature might also be predicted for nerves in general.

PART 2

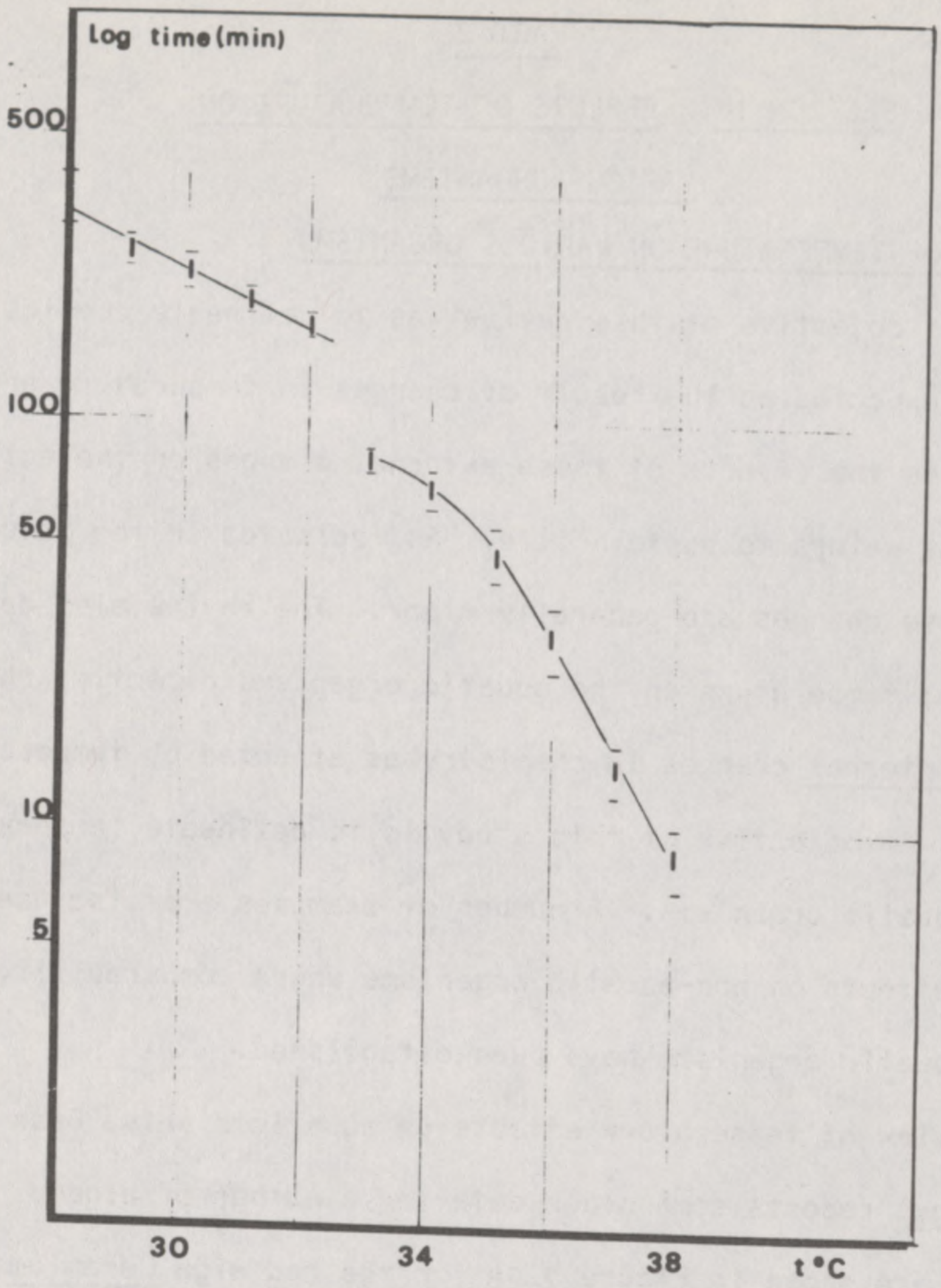
SECTION IV: EFFECTS OF TEMPERATURE ON VARIOUS ORGANISMS

IV. EFFECTS OF TEMPERATURE ON VARIOUS ORGANISMS

The first objective of this review was to delineate chemical changes which can be expected as the result of changes in temperature and, in turn, to assess the effects of these external changes on the suitability of the natural waters to sustain life. As indicated in the preceding sections, these changes are generally minor. The review also deals with the effects of temperature on the aquatic organisms directly; that is, through the internal changes in chemistry as affected by temperature variations. An objective of this study is to delineate temperature effects on aquatic organisms. A number of examples are also used of temperature effects on non-aquatic organisms where comparability to effects in aquatic organisms have been established.

In a review of temperature effects on aquatic plants, Gessner (Kinne, Marine Ecology) reports some older data for a number of algae. Data by Ayres (1916) are shown in Figure 2-28 for the red alga Ceramium tenuissimum. The length of survival (in minutes, usually a range of times), is given as a function of temperature. A graph of these data (Figure 2-28) shows an abrupt anomaly between 32 and 33°C. Essentially, below 32°C, the survival period increased exponentially with decreasing temperature (linearly in the log plot). Between 32 and 33°C, the survival period dropped by a factor of approximately 2 and decreased rapidly with increasing temperature.

Studies on the giant marine algal cell of genus Valonia, have provided some of the most extensive evidence for the concept of vicinal water structuring exerting a controlling influence on some cell biological functioning. Early measurements on the bioelectric potential of Valonia utricularis by Thorhaug (Drost-Hansen and Thorhaug, 1967) have shown abrupt changes in temperature coefficient at 15 and 31°C. Thorhaug recorded rather similar type



Length of survival time (in minutes) as a function of temperature for the red alga, Ceramium tenuissiumum. Note abrupt transition between 32 to 33°. Data by Ayres, quoted by Gessner, in Kinne, 1963).

Figure 2-28

of results for Valonia ventricosa and Valonia microphysa (see Thorhaug, 1971a,b).

Thorhaug (1969) also measured the mean potassium concentration of the vacuolar sap of Valonia macrophysa as a function of temperature from approximately 6 to 37°C. The curve shows a remarkably broad concentration below 13 and above 34°C. Conversely, the average sodium concentration in the vacuolar sap of Valonia macrophysa over the same temperature range showed a very distinct, broad minimum between approximately 13 and 33°C.

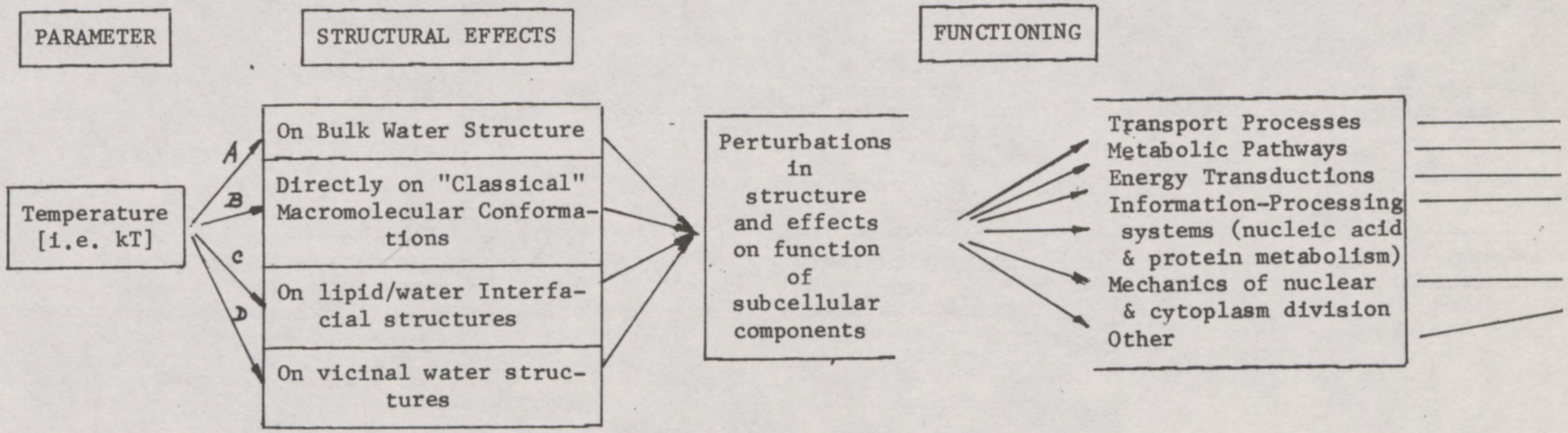
Perhaps one of the best examples of dramatic changes at the temperatures of the thermal anomalies observed by Thorhaug was the degree of irreversible plasmolysis in the Valonia macrophysa, exposed for three days to a temperature range from approximately 8 to 37°C. Nearly exactly 0% plasmolysis was observed between 14.5 and 31°C with very close to 95% plasmolysis below 14 and above 34°C. Similar results were obtained for Valonia utricularis.

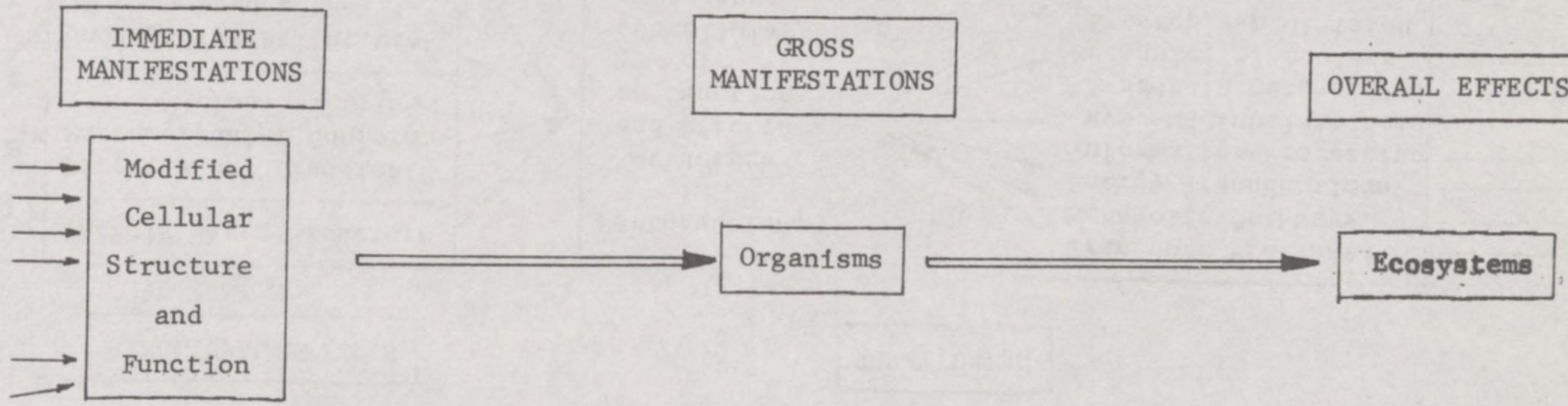
These general water structure effects were not restricted to Valonia. Thorhaug has reported very similar results for the abrupt plasmolysis of representatives of genera Nitella and Chara.

Table 2-2 shows an attempt to connect conceptually variations in temperature with overall effects in ecological systems. The scheme is highly simplified, but may, nonetheless, serve to indicate some significant features. The environmental parameters of reasonably direct importance are temperature and pressure. While other possible factors include light intensity (and, in general, electromagnetic fields of any type), gravitational forces, etc., only temperature will be considered. (For some molecular, physiological and adaptive problems related to hydrostatic pressure, see the volumes edited by Sleigh and MacDonald (1972), by Zimmerman (1970), and by Kinne (1963).

One central point of this review is the possible role of vicinal water structures among the various possible structural effects. Most standard treatments of the structure and functioning of subcellular components have been related to "classical" macromolecular conformational changes. Obviously, such play an enormous role. However, it seems that intrinsic changes due to vicinal water structures and/or "minor" conformational changes of macromolecules imposed by the vicinal water structures, must also be carefully considered. Thus, in addition to the "traditional" three pathways indicated (A, B, and C), vicinal water structure effects are shown here in Pathway D: the effects of vicinal water structure may play a role in many (or all) of the individual, functional attributes on which classical macromolecular conformational changes are presumed to exert an effect.

Table 2-2


PARAMETER
STRUCTURAL EFFECTS
FUNCTIONING
Temperature [i.e. kT]
A
B
C
D
On Bulk Water Structure
Directly on "Classical" Macromolecular Conformations
On lipid/water Interfacial structures
On vicinal water structures
Perturbations in structure and effects on function of subcellular components
Transport Processes
Metabolic Pathways
Energy Transductions
Information-Processing systems (nucleic acid & protein metabolism)
Mechanics of nuclear & cytoplasm division
Other


IMMEDIATE MANIFESTATIONS
GROSS MANIFESTATIONS
OVERALL EFFECTS
Modified Cellular Structure and Function
Organisms
Ecosystems

Gessner also reports some maximum temperatures "tolerated after gradual warmup" (based on data by Vilhelm, 1927). Green, brown and red algae were studied. Of seventeen species reported, all but four (i.e., a total of 76%) died at 45 ± 2°C (with two species dying at 39°C, one at 40°C, and one at 42°C).

Kasturi Bai, et al. (1969) have studied the effect of temperature on the ciliated protozoan, Blephrisma intermedium. They observed that temperatures ranging from 27 to 30°C did not markedly affect size, shape, activity or color of the organism. However, the size decreased apparently abruptly at 31°C. Further increase in temperature led to continued decrease in size and at 38°C, the shape was changed from nearly symmetrically oval to pear shaped. The size range had decreased from an initial range of 200 to 480 microns in length, to a lower range of 200 to 250 microns in length. At 34°C, movement became sluggish, and the color faded, while no movement was observed at 38°C or above. Kasturi Bai, et al. also studied the nuclear apparatus, and specifically determined the fission rate. This quantity shows a sharp maximum at approximately 28°C (increasing from zero at 24°C) and decreased by about 40% at 30°C. Above 30°C, the rate of fission decreases relatively slowly until approximately 35°C. No fission was observed at 38°C. Perhaps the most interesting and dramatic effect is the change in rate of fission at 30°C, which decreases by more than an order of magnitude.

A. D. Brown (1957) has studied the effects of temperature on some properties of a psychrophilic pseudomonad, and particularly the rate of utilization of glucose by this organism and by Pseudomonas aeruginosa. Particularly interesting are his results for the effect of temperature on the duration of the lag phase and on the growth rate. For both the psychrophilic and Pseudomonas aeruginosa, rather sharp maxima were obtained for the growth rate

near 30°C. The psychrophilic strain showed a relatively sharp maximum in the reciprocal lag phase near 25°C, with an abrupt decrease at 30°C; for Pseudomonas aeruginosa a steep S-shaped curve with an inflection point at 30°C was observed.

Garibaldi (1971) has studied the influence of temperature on the iron metabolism of a pseudomonad. In the absence of hydroxamate-iron-transport-compound(s), the growth rate, even in the presence of up to ten micrograms of iron per liter, was practically nil at temperatures of 31°C; the rate of growth differed relatively little between 20 and 28°C. In the absence of an iron transport compound, the amount of cell growth dropped precipitously between 28 and 30°C.

Gerber, et al. (1973) have studied the rate of polymerization ("reconstitution") of flagellin and the rate of breakdown of flagellin at neutral pH (from flagella isolated from three different Salmonella strains). In general, abrupt changes in the rate of polymerization of flagellin occurred at 28 to 30°C; thus, the relative rates of polymerization for flagellin from all three strains of Salmonella showed sharp maxima near 30°C followed by precipitous drops between 30 and approximately 37°C.

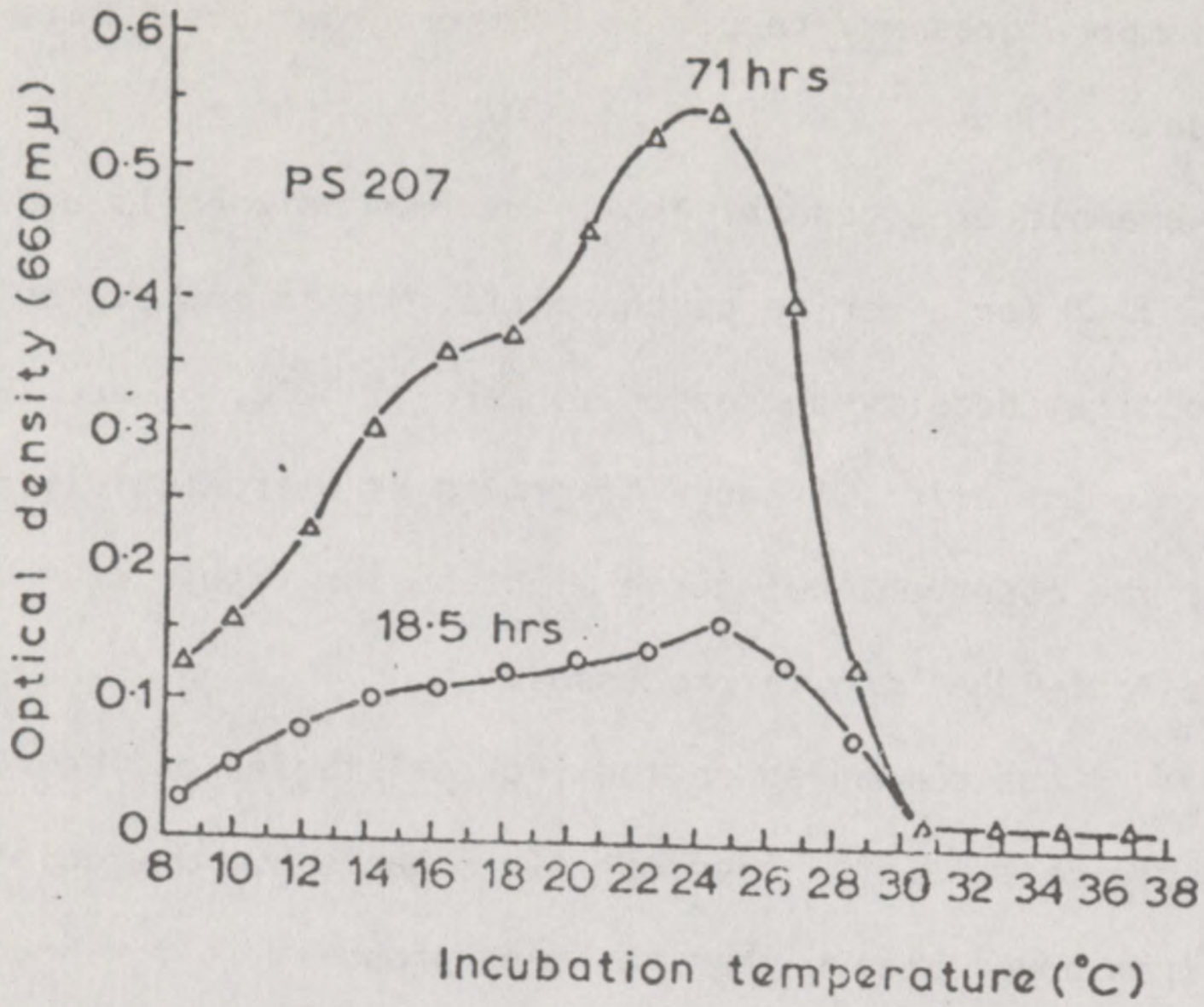
Shaw, et al. (1971) made an accurate determination of the minimal temperature for growth of Escherichia coli. They point out that minimal temperatures are very rarely well defined, and a few experiments were carried out in general to determine this quantity. The authors define minimal temperature for growth as the lowest temperature which will permit sustained growth. Thus, as an example, the authors observe for E. coli a minimal temperature for growth between 7.5 and 7.8°C (in a glucose minimal medium). In agreement with the definition used by these authors, transfer

to subminimal temperatures may result in further growth, but this growth is not sustained.

A typical example of a general growth maximum between 15 and 30°C is shown in Figure 2-29 for a marine psychrophile (Morita and Burton, 1963). Note that the optical density decreases to zero at 30°C. There is a distinct inflection point after 71 hours of growth at approximately 18°C, suggesting that the observed, net curve might be the result of the superposition of two individual growth processes.

Brock (1970) has commented on the lack of studies on the rate of digestion of waste materials by thermophilic organisms. One potential use of waste heat from power plants that has been proposed is to increase the rate and efficiency of the activated sludge process by heating the sludge tanks during periods of low air temperature. Brock refers to the early work by Viehl and Meissner, who had measured the effects of temperatures over a wide range (between 1.5 and 55°C) on the rate of oxidation of organic matter and ammonia (the process of nitrification). According to Brock, the observed rate of reduction of biochemical oxygen demand was roughly constant between 8 and 35°C, but decreased at 45 to 55°C. A sharp optimum occurred in the nitrification at around 26°C with no nitrification at 45°C or higher temperatures. No organisms were found at 55°C, and only one species of small amoeba observed at 45°C. By far the largest number of species were found at 26 to 29°C.

Smayda (1969) has studied the effects of light, temperature and salinity on the cell division of the marine diatom, Detonula confervacea. The diatom is an arctic species, producing two or more spores per cell. It is particularly abundant near West Greenland. The diatom has been reported from various fjords in Denmark and Norway, and in the Gulf of Maine. The optimum for growth appears to be at about 10°C with survival, but no growth, at 15°C.



Typical Growth Curve for Marine Psychrophile (PS207) as a Function of Temperature. Note Development of "Shoulder" around 15-18° and Precipitous Drop Between 27 and 30°. (After Morita and Burton, 1963, Quoted by Oppenheimer in Kinne, 1963, page 357).

Figure 2-29

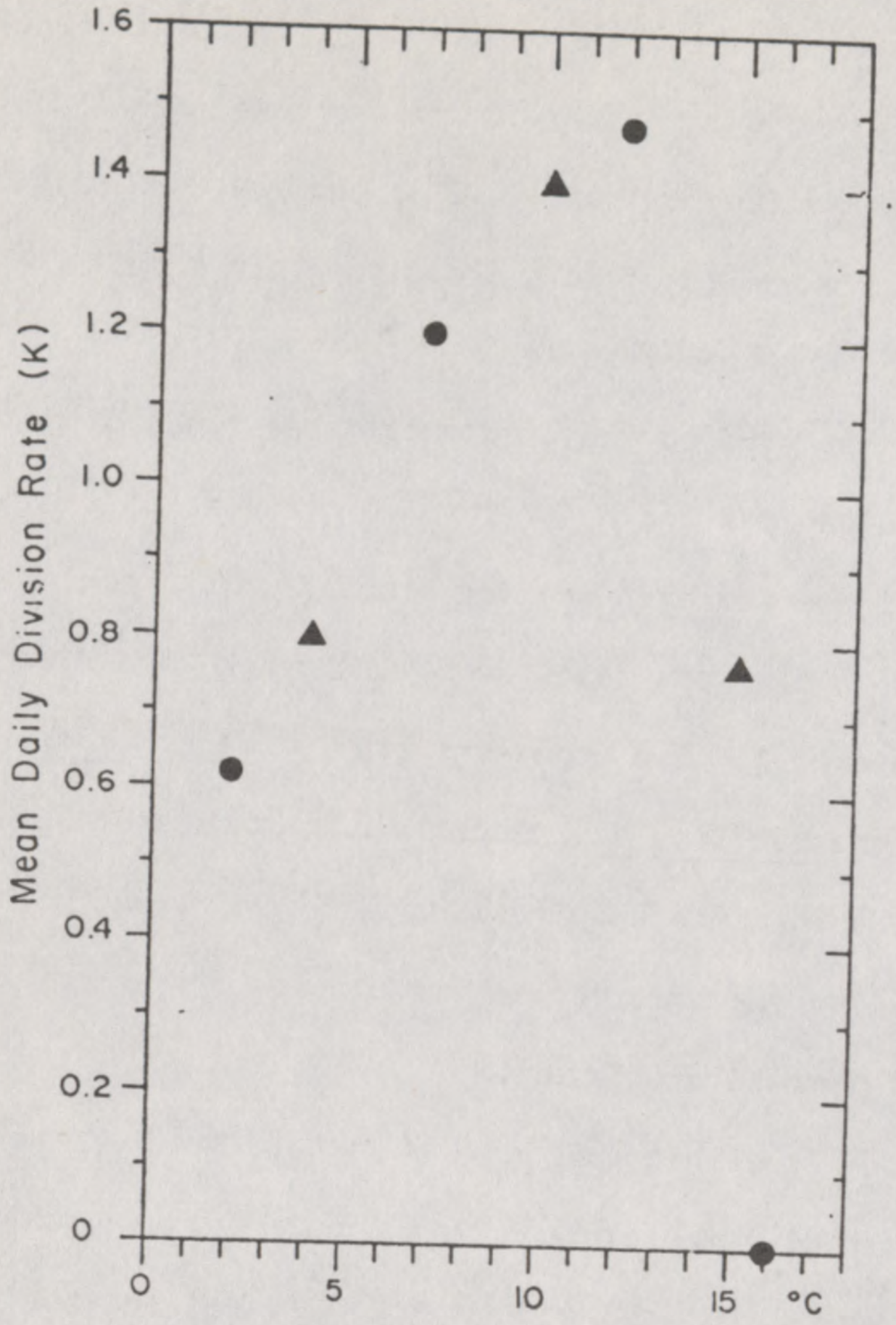
The decrease in rate of cell division as a function of temperature is shown in Figure 2-30. Note the extremely abrupt decrease in cell division rate between the optimum (at approximately 12°C) and the zero rate of cell division at 16°C. More examples of this are given in the paper by Patrick, Vannote and Bott in this report series.

Nakae (1971) has studied the growth of three types of bacteria grown on a yeast-glucose-peptone broth (or in skim milk) as a function of temperature. Nakae presented evidence for binodal growth curves and, particularly, curves with distinct "shoulders" (in other words, curves suggesting considerable complexity). The organisms studied were: Lactobacillus casei; Pseudomonas sp.; and Bacillus sp. Results are in general agreement with previous studies by Oppenheimer and Drost-Hansen (1960), and Nakae has implicated the possibility that microorganisms utilize different metabolic pathways in different temperature intervals.

Heinzelmann, Kraepelin and Bogen (1972) have studied the growth of yeast as a function of temperature on a glucose-peptone-yeast medium. These authors observed that the cell-free (filtered) supernatant solutions exhibited distinct, reproducible anomalies in surface tension at approximately 15, 27, 43 and 61°C. Furthermore, the rates of growth for the two types of yeast studied (Saccharomyces cerevisiae and Candida curiosa) both showed temperature dependent anomalies at 17 and 27°C. For Candida curiosa, the growth rate showed a (remarkable) minimum near 16°C. These authors discussed their findings in terms of the structural anomalies of water at the "cell/aqueous medium interface" as described by the present author.

Interesting temperature effects on fungi have been recorded by many authors. A few are mentioned here.

Eugenio, et al. (1970) have studied temperature effects on the produc-



Temperature Effects on Mean Daily Division Rate in the Marine Diatom, Detonula confervacea. Composite Graph of Two Sets of Data (Smayda, 1969). Note Extremely Abrupt Drop Between 12 and 16° C).

Figure 2-30

tion of F-2 microtoxin on corn, in response to isolates from Fusarium roseum. A sharp maximum was obtained around 15°C, with practically no production of microtoxin below 4°C or above 37°C.

McCracken (1970) has studied the rates of spore production in the fungus Hericium erinaceus (an organism causing butt rot in bottom-land hardwoods). The number of spores discharged when studied in a controlled environment chamber, showed a gently increasing number of spores liberated for temperatures ranging from 0 to approximately 27°C, and a precipitous drop between 27°C and 31°C. No spores were produced above approximately 32°C.

Rotem, et al. (1971) have studied the effects of temperature on the infection of potato leaves by Phytophora infestans. The authors concluded that the optimum range (while depending somewhat on the degree of wetting) frequently showed a narrow optimum, usually at 15°C. In the presence of longer wetting periods, broader optimum ranges were found. However, a notable drop occurred in the incidence of disease at 28°C, suggesting the complete absence of infection at temperatures higher than 28°C.

A number of fungi show an extremely abrupt change in germination properties with temperature. Thus, Chang and Chu (1969) have determined the rate of germination of a common southeast Asian mushroom (the edible straw mushroom, Volvariella volvacea). The authors observed that the rate of spore germination on a complete medium showed a sharp change at 30°C, a sharp maximum at 40°C, and an abrupt decrease (to 0% germination) at 45°C. On a potato dextrose agar medium, somewhat slower germination was observed, being zero at 30 and 45°C, with a maximum near 40°C.

Examples of the effects of temperature on the growth and sporulation of fungi have been reported in an extensive literature review by Rao (1970). The data shown by Rao for Phytophora palmivora is remarkable in showing a

very sharp change in growth rate at 15°C; a relatively broad optimum of growth between approximately 18°C and 28°C and a precipitous drop in growth rate between 29 and 35°C (with no growth at 5° nor at 35°).

Hirayama and Kusano (1972) have studied various fundamental aspects of the growth of rotifers in mass culture. Among the parameters measured were time intervals for 50% survival, time to reach peak of fecundity, intrinsic rate of increase, net reproduction rate, and the mean generation time. The intrinsic rate appears to go through a sharp maximum at 27°C. Hirayama and Kusano suggest that 27°C would be close to the most desirable temperature. However, the other indices reported suggest that 27°C is uncomfortably close to the upper thermal limit. Thus, all the parameters mentioned above tend to decrease markedly as the temperature approaches 30°C - particularly the net reproduction rate.

Strong and Sheldahl (1970) have studied the effect of temperature on longevity and fecundity in the insect, Lygus hesperus (Hemiptera). The authors reported values of "intrinsic rate of increase" (r_c), pre-oviposition time and total number of eggs produced. In all three cases, extrema were observed: for r_c and total eggs produced, extremely sharp maxima were obtained near 30 to 32°C, while the pre-oviposition times showed a relatively sharp minimum near 30°C. In all three cases, semi-logarithmic plots were employed, and the line segments above and below 30°C were remarkably straight. The degree of abruptness of the change near 30°C is indeed striking.

Ali (1970) has studied the effects of temperature on the filtration rate of unicellular algae by a common bivalve (Higtella arctica). The filtration rate depends on the density of food cells available as well as temperature. The filtration rate, using one algal species, showed a sharp

maximum between 15 and 17°C. The rate further decreased to essentially zero at 25°C. Regarding the type of results obtained, Ali concluded "The curves obtained ... are similar to those obtained for many other types of activity curves in poikilotherms, showing an exponential rise as temperature increases, reaching a maximum and then falling rather more abruptly beyond the maximum".

Another example which strongly suggests that molecular aspects of the cellular water must be taken into account is apparent from the data by Percy and Aldrich (1971). These authors have studied the possible temperature independence of metabolic rate for various mollusk tissues (gill, mantle and adductor muscle). Their data suggests abrupt changes in the vicinity of 15°C for the respiration rate of the adductor muscle of Crassosteria virginica (American oyster) and for the foot retractor muscle of Mytilus edulis (data by Glaister and Kerly,). Respiration rates of the adductor muscle and the mantle also show distinct decreases at temperatures above 30°C.

Licht and Brown (1967) have studied various aspects of behavioral thermal regulation and the role of temperature selection in the ecology of the red-bellied Newt, Taricha rivularis. The aquatic larvae exhibit distinct thermal preferences between 20 to 26°C (within one week after hatching). The authors observe that heat resistance varies with age, and with the previous thermal history, but note that the thermal preference is relatively invariant. Licht and Brown also call attention to the earlier claims of Brattstrom (1963) who concluded that salamanders do not seem to possess a preferred temperature, but are willing to accept the temperature available (within their respective limits of tolerance). This appears not to apply to Newts, which indeed do seek specific thermal conditions.

24-642 O - 73 - pt. 2 - 35

Another interesting aspect of this study, although not stressed by the authors, is the nearly complete avoidance of temperatures between 28 to 30°C (and above).

Cocking (1959) has studied the effects of high temperature on the roach (Rutilus rutilus). Using a clever "set-up" the fish could be subjected to increasing temperatures at different constant rates of temperature increase, ranging from 0.05 to 0.08°C/hour for periods ranging up to two weeks. A total of five different rates of temperature increase were utilized. The times were recorded for death and the temperature as well as the time at which the fish died. At very low rates of temperature increase (0.05°C/hour) the average thermal death point was 32.9°C). For rates between 0.1 and 0.8°C/hour, the thermal death point varied only slightly between 31.4 and 32.4°C. Cocking also noticed a characteristic stage of "predistress" behavior which appeared "well below the temperature at which the fish became distressed and disappearing again as the temperature rose". The reader is referred to the interesting details in the paper by Cocking.

In summary, the examples discussed in this section demonstrate the remarkable degree of abruptness of change near certain critical temperatures, usually centered around 14 to 16°C, 29 to 32°C and 44 to 46°C. This temperature range (44 to 46°C) is outside the usual range of natural water bodies. However, the examples have been included for two reasons. First, where local heating near a power plant may be excessive, such temperature could conceivably be reached in tropical or subtropical regions. Furthermore, the examples clearly demonstrate yet another set of anomalously abrupt and likely strongly cooperative changes manifested in properties and behavior of individual organisms. It is emphasized

that although "classical" macromolecular transformational changes are real and do indeed affect the responses of many types of biological systems, other types of cooperative phase transitions, such as those that are likely due to the hydration-associated parameters ("water of hydration") of the systems of organisms considered, might play an equally significant role.

PART 2

SECTION V: ECOLOGICAL ASPECTS

V. ECOLOGICAL ASPECTS

A. Introduction

Whatever its mode of action, temperature is, undoubtedly, one of the most important environmental factors, and because of the ease with which temperature studies can be made, an overwhelming amount of such data exists. Unfortunately, these studies too often suffer from lack of closely spaced temperature measurements.

Suppose an aquatic organism is sensitive to or dependent on the activity of a certain ionic species in solution. Increasing the temperature of the water will change the ion's activity. In addition, the temperature will change a complex multitude of internal reactions in the organism. It is proposed (without offering any "proof") that one may estimate the direct effect of a change in ion activity (due to temperature increase) by simply transferring the organism isothermally to an otherwise identical solution of slightly different concentration. Thus, in effect, the separate occurrence of an ion activity change due to a temperature change is evaluated isothermally. As is fairly obvious, dramatic changes are not to be expected on this basis with most ordinary ionic solutes. Estimates of the changes in ion activities can be obtained to various degrees of approximation from suitable tables or use of different types of Debye-Huckel type expressions for ionic activity.

Table 2-3 shows the activity coefficient of sodium chloride in one molar concentration, calculated from the equation given by Robinson and Stokes (1959, p. 212):

$$\log \gamma = 11.4326 - 535.45 \cdot \frac{1}{T} - 3.9679 \log T$$

It is seen that a temperature increase of 10°C (from 15 to 25°C) results in

Table 2-3

Activity Coefficient of Sodium Chloride at 1 M Calculated from:

$$\log \gamma = 11{\cdot}4326 - 535{\cdot}45/T - 3.9679 \log T$$

Temperature	$\gamma_{obs.}$	$\gamma_{calc.}$
Freezing Point	0·639	0·634
0°	0·638	0·638
15°	0·654	0·653
25°	0·658	0·658
40°	0·655	0·660
60°	0·655	0.654
70°	0·648	0·648
80°	0·641	0·640
90°	0·632	0·631
100°	0·622	0·621

a difference in the observed activity coefficient, corresponding to an increase of 0.004, or roughly 0.6%. (The calculated value is more nearly 0.8%).

An increase in the activity coefficient of 0.004 corresponds to an increase of approximately 25% in the concentration of sodium chloride, at I molar. Near 0.5 molar, an increase in the activity coefficient of 0.004 corresponds more nearly to an increase in concentration of electrolyte by about 10%. Thus, the effect of a 10°C temperature increase on the activity coefficient of sodium chloride for approximately 1/2 molar solution (roughly 30 0/00 seawater) corresponds merely to an increase in salt concentration by 10% (under "equivalent isothermal conditions"). Very few organisms are critically dependent on the total salinity and it may probably safely be concluded therefore that the "direct chemical effects" of a 10°C increase - exerted via the external chemistry - is probably of only minimal importance to the overall ecology. At least dramatic or catastrophic changes are not apt to be expected on this basis.

However, abrupt changes with temperature are indeed observed in ecological systems, notwithstanding the general insensitivity of the individual organisms in the ecological network to small changes in the external chemistry. It appears, therefore, that the cause of such changes must be sought in areas not related to the details of the external chemistry. It is proposed that the sensitive, critical element of the organism is the overall chemical and biophysical change effected through changes in the internal water structure. Particularly susceptible are water structures near interfaces such as those associated with cell membranes or the "hydration complexes" of biomacromolecules.

B. Fluctuating Temperatures

In connection with the effects of increased temperature in natural waters, one must take into account natural fluctuations not often simulated in the laboratory. The relative time spent in the different environments - that is, at high and low temperatures - compared to the average temperature, may have profound effects above a certain temperature range; the fluctuations may exceed the critical temperatures; this exposure in each cycle may be sufficiently short not to be lethal, but still enough to severely reduce activity. Thus, the natural fluctuations must be considered in combination with the overall temperature level, increased through thermal discharge. This, in turn, implies that a larger fraction of the time may be spent above the critical point: in a sinusoidal temperature field, relatively more time is spent at the low and at the high temperatures than near the average value.

The problem of varying temperatures is exceedingly complex on the cellular level. Unfortunately, the bulk of available data on temperature effects in biological systems have been obtained under laboratory conditions where temperatures are usually maintained (unreasonably) constant. This, obviously, is a heritage from the physio-chemical approach to the analysis of equilibrium thermodynamics or steady-state kinetics.

Short term exposure to elevated temperatures must result in effects which depend on a number of macroscopic parameters. Lee (19 73) has commented on the maximum possible deleterious effects on a fish swimming through a hot plume in the discharge from a power plant. The effects were assessed to be minimal, given "average, normal" swimming speeds, metabolic rates, etc. However, another problem involves the passage of plankton and other microorganisms through heat exchangers. Obviously, the smaller the organism, the more rapidly it will assume the temperature of the

environment. For multicellular organisms, the size, the surface-to-volume ratio, and similar factors will determine the degree to which a transient passage through a heated region will affect the functioning of the organism. Although possibly only a second-order effect, attention is called to the fact that the more structured the intracellular water, the higher its thermal conductivity may be. Likewise, the specific heat capacity of the intracellular water is different from that of bulk water.

Regarding the rate with which temperature changes may be experienced, Trueman and Lowe (1971) have studied the effects on heart rate of temperature on a bivalve mollusk (Isognomon alatus). They observe that changes in the temperature of the water result in immediate increase or decrease in heart rate. As an example, these authors observed that, subjected to a temperature change of 8.5°C, the heart rate increased from 16 to 25 beats per minute, and after three minutes, reached 30 beats per minute. The authors concluded that the rapidity and sensitivity of this reaction must reflect a neural mechanism at which therman receptors in the inhaled region of the mantle cavity determine the heart rate, rather than the overall average temperature of the mollusk.

C. Multivariant Analysis

Alderdice (Kinne, editor, "Marine Ecology", Vol. I, Part 3, p. 1659) has described some of the methods used in response surface analysis of the complex interrelationships between biological responses and the various physical and chemical environmental influences acting simultaneously. The approach used in the present review follows the approach which Alderdice refers to as the "dismemberment of a complex phenomenon" through an examination of the recognized components by "univariable techniques". It is obvious that this approach, which in many respects simulates the laboratory approach, "leads to a lack of confidence in the ability to interpret ecological phenomena through inductive 'inference' ". However, as Alderdice pointed out, the "complexities inherent in the field approach lead to a suspicion that interpretation of ecological phenomena may be constrained by the natural limits of human deductive capabilities". Granted that the univariable ("laboratory") approach may imply significant restrictions on our ability to extrapolate to overall ecological aspects (by inductive inferences), the advantage of the "dismemberment" is that it appears, at the present, to be the only reasonable way of elucidating phenomena in the complex world of realities in terms of individual, molecular events. Qualitatively speaking, then, the "univariable technique" is aimed at producing and understanding - (even if relatively limited in its predictive values and its gross descriptive aspects) - in terms of fundamentals rather than merely a more or less complete descriptive accounting of a natural system. There is little doubt that a thorough descriptive assessment is as necessary as molecular insight. However, in view of the fact that far more effort is currently directed toward the systematic, thorough, qualitative descriptions, the present author has chosen to approach the

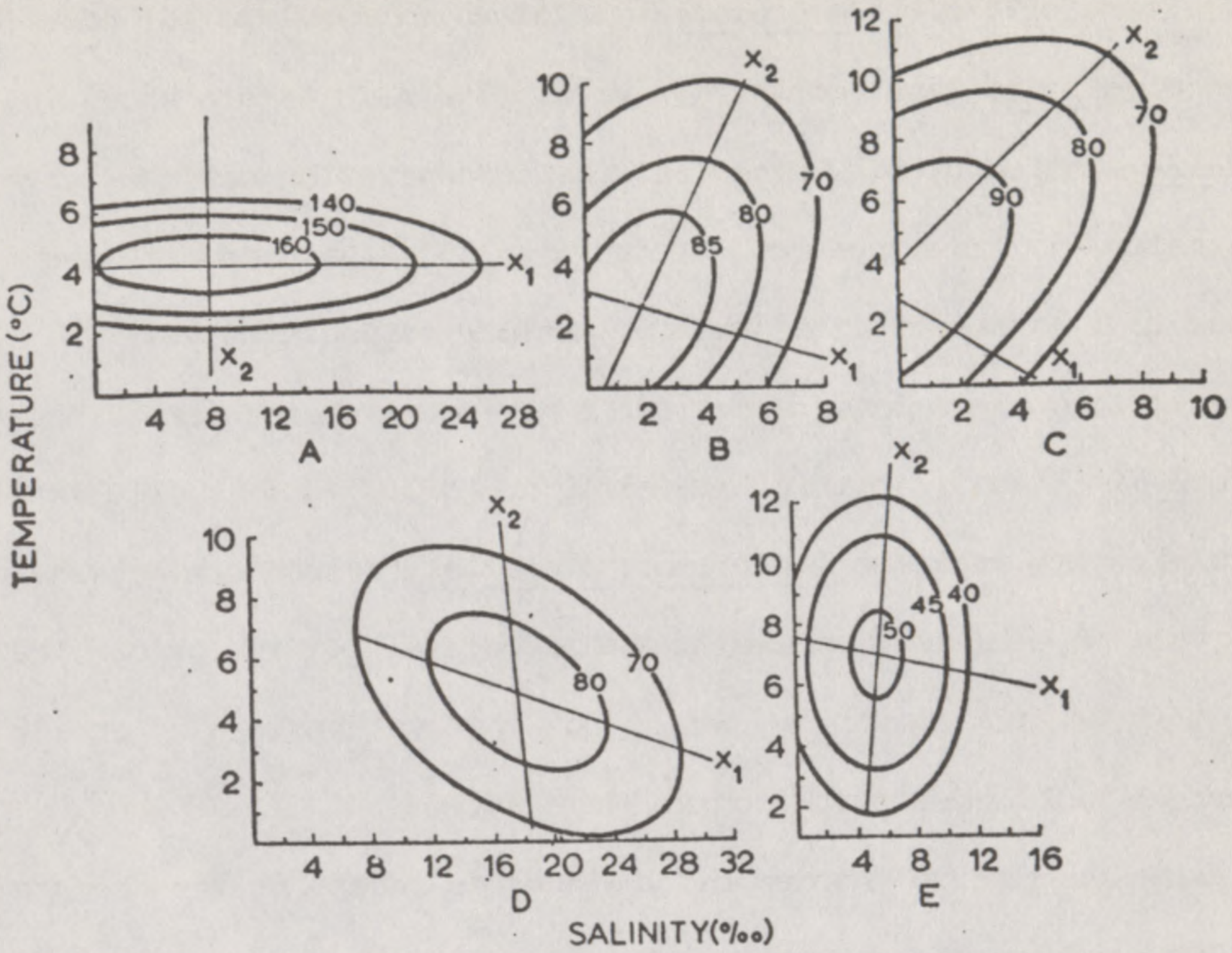
subject in terms of "molecular happenings" as elucidated through the standard techniques of physical chemistry and chemical physics.

Alderdice has eloquently argued for a multivariable approach: "Aspects of changes in tolerance and capacity, plasticity of response, and interaction of environmental variables are best appreciated by employing a multivariable approach; the nature of these phenomena can be described by examining response surfaces". As a specific example, the examination by Alderdice of the response surface for the juvenile Coho salmon - exposed to sodium pentachlorophenate as a function of salinity and temperature is shown in Figure 2-31.

Alderdice has called attention to the possible utility of multivariable techniques to delineate multidimensional response curves for problems in pollution ecology.

The toxic effects of a man-made additive to the natural environment depends on the temperature and salinity as well as on the stage of development of the organism. Not only may the stage, and age of the organism play a role, but possibly also the intrinsic size of each individual. Alderdice concludes (p. 1685): "In attempting to set maximum permissible concentrations of water-borne pollutants, consideration must be given to sensitivity of the species comprising the biota, the variations in tolerance of organisms related to size, season or state of physiological development, and the range or field of combinations of levels of natural variables under which the biota will experience such changes in water quality ...".

An excellent example of a "response surface" was reported by Precht, et al. (1955, loco cit., p. 265, based on data by S. Emerson, "Growth Responses of a Sulphonamide-Requiring Strain of Neurospora",



Five response surfaces for juvenile Coho salmon (Oncorhynchus kisutch) as a function of salinity and temperature in the presence of 3 parts per million sodium pentachlorophenate. The contour lines show median resistance times (in minutes) for five different age groups of the fish (fry, smolt and three post-smolt stages) .

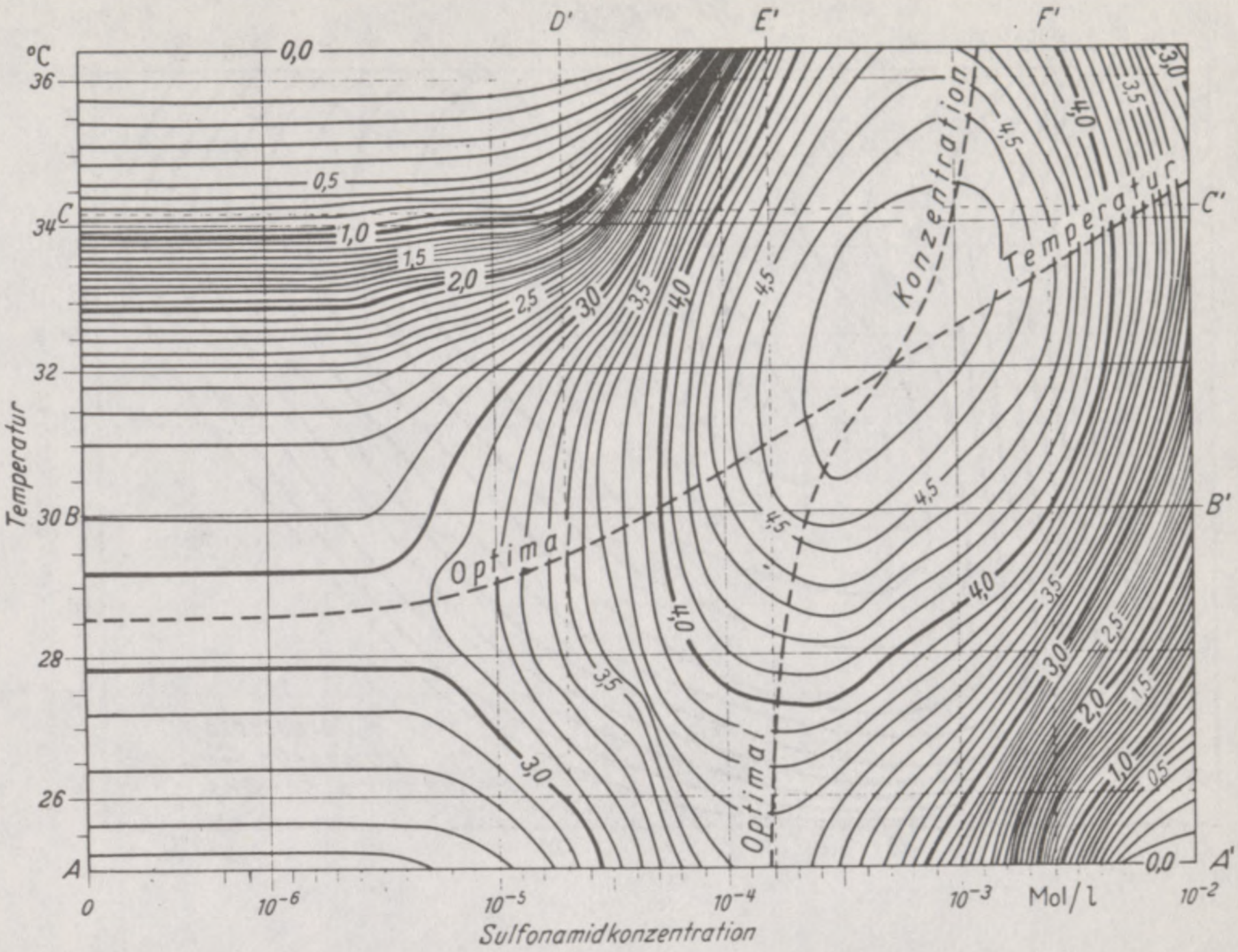
(Illustration from Alderdice in Kinne, 1972).

Figure 2-31

1947). A Neurospora mutant which required sulphonamide in order to grow was utilized in this work. The results are shown in Figure 2-32. Notice in this case that the concentration optimum curve and temperature optima curve are neither straight lines nor orthogonal at the point of intersection of the two maximal response curves.

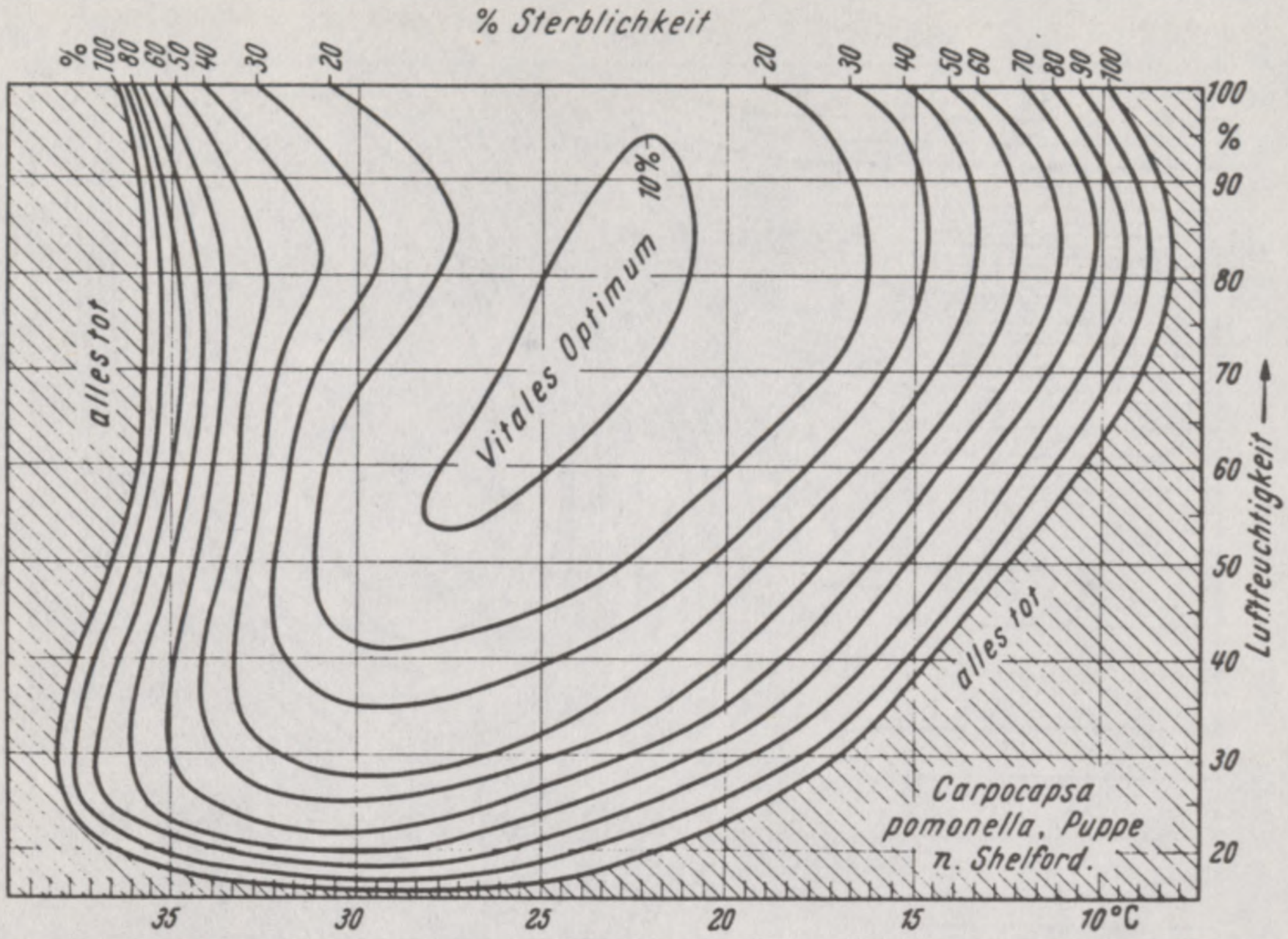
Another type of response curve for a non-aquatic organism is shown in Figure 2-33 (Precht, et al., loco cit., p. 107). In this illustration the mortality of the insect Carpocapsa pomonella (Lepidoptera) is shown as a function of relative humidity and temperature. It is obvious that the optmum of "vitality" occurs in a narrow interval between 23 and 28°C (for relative humidities ranging from 54 to 94%).

We quote the general statement by Alderdice regarding the need to define specifically various domains of environmental parameters as related to environmental pollution problems (p. 1685): "In studying biological problems arising from water pollution, it has been common practice to describe maximum permissible concentration limits of a given pollutant as a function of thresholds of acute (lethal) response. In such cases, ancillary variables (e.g., temperature, dissolved oxygen) are usually constrained to specific levels, largely as a matter of operational convenience. Developments in this field of inquiry would suggest, however, that for a given species, a specific set of levels of those ancillary variables known or suspected to be of importance should be adopted as a background requirement for biological assays of tolerance to a suggested pollutional substance. Furthermore, it is suggested that this set of levels might be pre-determined as that providing the greatest potential for development and survival, for the species and stage considered, in terms of some objective measure or measures of biological capacity. Conversely, it is



Detailed Response Surface Showing Growth Rate as a Function of Temperature of a Mutant of Neurospora, Requiring Sulfanamide. (Precht et al., 1955, page 265, Based on a Study by Emerson).

Figure 2-32



Response Surface of Pupae of the Codling Moth (Carpocapsa pomonella). The mortality is Shown as a Function of the Humidity and Temperature. Note the very limited Minimum Mortality (i.e., "vital optimum"). (Data by Weber, 1954, quoted by Precht et al., 1955, page 107).

Figure 2-33

suggested that the operation of ancillary environmental variables (e.g., temperature, dissolved oxygen) on the response to a pollutional substance, should be investigated by multivariable techniques to insure that threshold levels of these substances would apply to the organism over all environmental loading conditions. The range of loading conditions would be determined by the ranges of the ancillary variables and combinations of their levels normally found in the environment under investigation" (Alderdice, 1967).

The above quote from Alderdice sets forth the overwhelmingly large task facing those who must make decisions regarding pollution levels. For each organism, in each stage of development, at various ages, body weights, etc., and for a whole host of ancillary conditions (such as temperature, salinity, oxygen tension, light conditions, etc.), the biological responses must be determined. Myriad data would thus be required in each case, including detailed histories of previous acclimatization. While the fact that multivariant response surface analysis may facilitate the analysis of the data, does not lessen the necessary labor to gather the phenomenally large amount of needed data. It is for these reasons that it is imperative to seek an understanding on the molecular level, rather than on the operational, pragmatic descriptive level.

D. Specific Examples

We review finally some of the types of response surfaces reported by Alderdice (sometimes based on data by other authors). The locomotory activity of Homarus americanus (lobster) suggests that lethal temperatures approach 30 to 31°C, corresponding to acclimatization temperatures between 25 and 30°C (with some extraordinary degree of extrapolation). Conversely, cold lethal temperatures approach 12 to 13°C.

Somewhat similar types of data are available for the cruising speed of goldfish (Carassius auratus). Here the preferred temperatures fall distinctly below 30°C (approximately 27 to 28°C). Of interest to note is that the cruising speed for animals acclimated at the test temperature goes through a relatively well defined maximum at 23°C, with a rather rapid falloff between 30 and 34°C.

Another interesting response surface is reported by Alderdice for the viability of developing eggs of the marine bony fish Parophrys vetulus. This result shows a very well defined maximum for "normal hatch" located at approximately 27 parts per thousand (ppt) salinity and 9°C. Various major developmental anomalies occurred frequently for extreme salinities (say, below 17 ppt, or above 34 ppt). At the same time, 12°C appears to be an upper limit for the majority of larvae which hatched normally while a "closed contour" may possibly be interpolated in the range from low to high salinities going from "curvature of body" to "collapsing eggs" with a maximum near 14 to 16°C.

Hedgpeth and Gonor (1969) reviewed some of the effects of temperature on the dominant microflora in Narragansett Bay, as reported by Sieburth (1967) for the period December 1960 through November 1961. It appears from this illustration that very little growth occurs at temperatures above 30°C; and none reported above 33°C. This is somewhat similar to the findings reported by McIntyre and Be (see Kinne, Section 3.2, p. 403) for which the maximum and particularly optimum temperature ranges for placolith and cyrtolith species in the Atlantic Ocean are all found below 29°C - and usually above 13°C (with the exception of Coceolithus pelagicus which exhibits an optimum around 8 to 10°C).

E. Cytoecology

Professor Troshin (1967) called attention to "cytoecology" as a new "disciplinary interface between cytology and ecology". Troshin went on to describe that the primary objective in this field is to gain an understanding of cellular and molecular processes of adaptation of organisms, and secondly, to study the cellular adaptations per se. "Particular attention has been paid by cytologists to environmental temperature factors, and this is not surprising. A temperature factor is an unavoidable and obligatory condition of existence for any living organism. It is one of the universal factors for all processes taking place and living systems are under its influence. Furthermore, it is a directly acting factor, since in many living organisms, it has particular influence on the rate and characteristic of life processes. It is of particular importance to the influence of the environmental temperature that has led to its choice as a principle subject of this Symposium".

Reviewing the Symposium Proceedings, a physical chemist - at least one concerned primarily with aqueous systems - observes the absence of discussions of aqueous electrolyte chemistry in general, as well as discussion of biological water structure in particular.

Denko determined the temperature at which protoplasmic streaming ceased in the aquatic plant Cabomba aquatica. Lower epidermal cells were used for this study. The samples were subjected to 17-hour exposures to different temperatures from 3 to 36°C. (The plants had originally been grown at about 20°C).

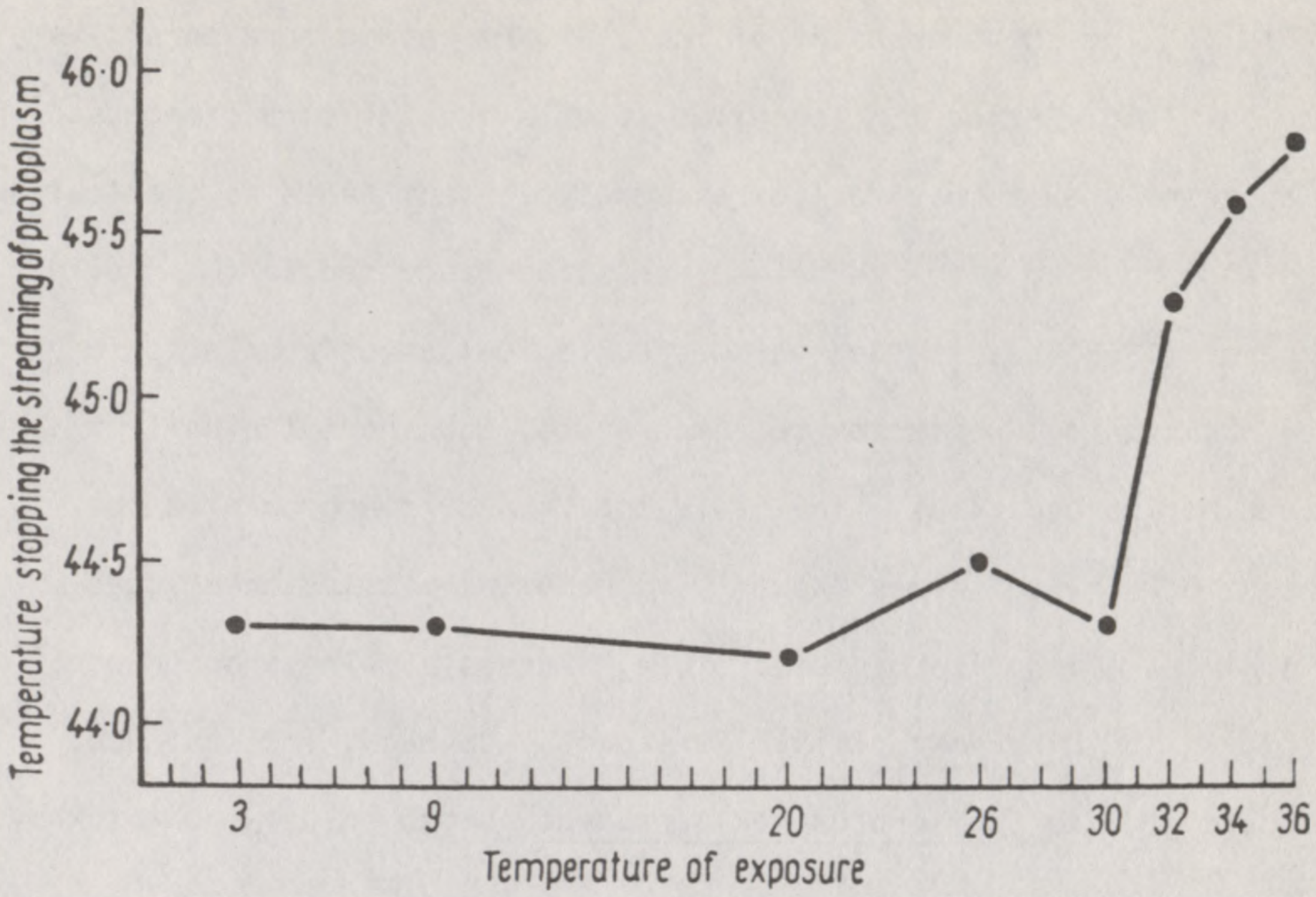
Over the range of exposure from 3 to 30°C, the temperature at which protoplasmic streaming ceased remained essentially unchanged at 44.4 ± 0.2°C. Exposure to environmental temperatures above 30°C (32, 34, 36°C) resulted in changes in the temperature at which the protoplasmic streaming ceases; the

24-642 O - 73 - pt. 2 - 36

increase, however, was small, as temperatures of cessation rose only to approximately 45.7°C (see Figure 2-34). Note in this experiment both the criticality of the event at 30 (to 32°C) and the fact that protoplasmic streaming ceased somewhere between 44 to 46°C. Alexandrov, in the same Symposium (edited by Troshin, 1967, loco cit., p. 142, see particularly p. 144) reported likewise on the heat resistance as measured by the duration of retention of protoplasmic streaming as a function of temperature. For four of the plants studied (all of the gramineae), the streaming essentially lasted less than 5 minutes at temperatures ranging from 43.5 to 46°C with a number of plants maintaining streaming for 5 minutes at temperatures of 48 to 49.5°C.

Denko (1967) also observed that small but distinct increases in the heat resistance of C. aquatica as the result of low temperature stress. Lower plants, as pointed out by Denko, usually suffer a decrease in heat resistance. For C. aquatica the resistance to ethanol as well as the resistance to high hydrostatic pressures also increased as the result of low temperature stress and the resistance to these stresses (ethanol and pressure) also increased as the result of short term high temperature stress.

Lomagin, Antropova and Ilmete (1967, Troshin Symposium) studied the influence of heat-hardening on the ability of plant cells to resist damage by various injurious agents. The authors found that heat hardening increased the cellular resistance of the epidermis (of Tradescantia fluminensis vell.) to heating and as well to ethyl alcohol, acetic acid and high pressures. Also, it increased the resistance to the deleterious action of ether, potassium rhodanate and cadmium chloride (these materials all being denaturants of native proteins). On the other hand, heat hardening did not increase the cell resistance to 2,4-dinitrophenol, nor to sodium azide. In fact,



Heat resistance of cells of the aquatic plant Cabomba aquatica after short exposure to different environmental temperature. Ordinate: temperature at which streaming of the protoplasm ceased in the leaves. Note that the (short-term) exposure to temperatures above 30° increases the maximum tolerated temperature for protoplasmic streaming by only 1.5°. (Denko in Troshin, page 162).

Figure 2-34

some cells (during photoreduction of the 2,4-DNP) became more sensitive to this inhibitor. Attention is called to this type of study, because of the apparently extremely varied responses of plant cells to chemical stresses when coupled with thermal stresses, as discussed in this review.

Ushakov (1968) has studied various ecological aspects related to cellular resistance, adaptation to temperature, and thermal stability of various marine organisms. The basis for Ushakov's approach is the measurement of survival times (usually in minutes) plotted on a logarithmic scale as a function of temperature. Curves showing pronounced binodality in the "thermostability" is shown by Ushakov, for instance, for the caraugid fish, Trachurus mediterraneus (based on data by Altukhov, 1963).

It is unfortunate that Ushakov has based nearly all his studies on rather limited measurements of survival time with relatively little consideration for adaptation, rate of heating, and other variables (see Section 2-III of this review). This is particularly unfortunate because of the extensive use to which Ushakov has subsequently put his data. The main conceptual contribution by Ushakov is the claim that the thermal stabilities of organisms may be related to interspecific differences in the protein thermal stabilities. These, in turn, were claimed to be describably in terms of linear equations.

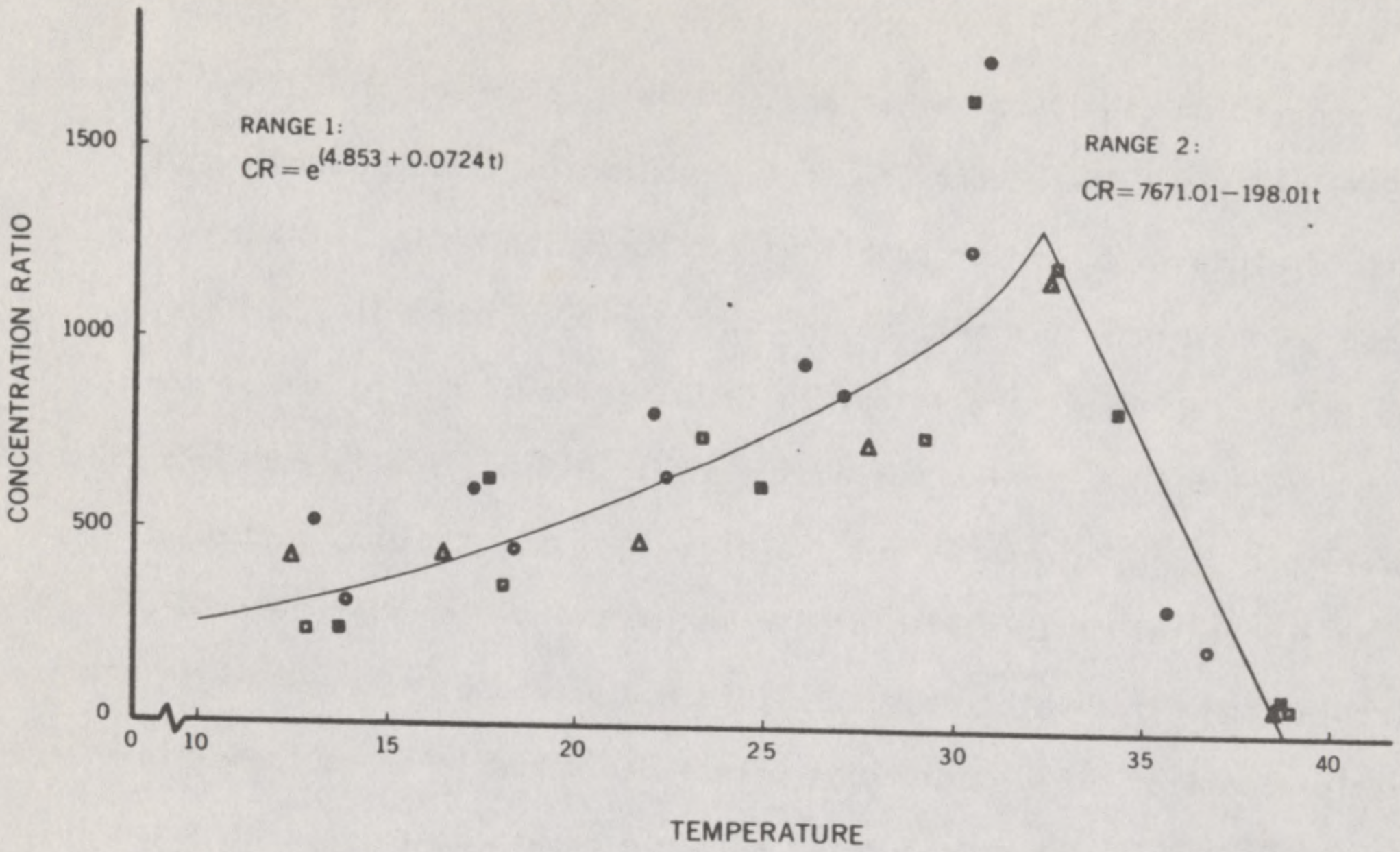
The approach used by Ushakov has attracted considerable attention, particularly in Russia. Many examples of the use of the concept and methodology for measuring thermal stability are discussed in the volume edited by Troshin (1967).

An excellent - although uncritical - summary of the studies by Ushakov, Ushakov and co-workers, and a number of other Russian authors has been given by Kinne (Marine Ecology, 1970, 1971, 1972).

It is interesting that over a period of a year, multiple optima in the population density of algae are sometimes observed. Thus, Skullberg (1964) has shown the occurrence of two maxima in the total numbers of various algae in the water supply of two Norwegian cities. Obviously a number of physical phenomena may account for such temporal binodality. One is the fact that stratification is only present during the summer with circulation occurring during the winter. Specifically for Lake Borrevannet, the data show that the algae respond rapidly to changes in environmental factors with growth maxima coinciding with periods of circulation of the water masses. It is now proposed, however, that multiple optima in hydrodynamically less-disturbed lakes may possibly exist due to temperature regulated multiple growth optima, as discussed for various microorganisms by Oppenheimer and Drost-Hansen (1960) and, more recently reviewed by the present author (1965, 1971), and mentioned in this review, Section 2-III-F.

A number of ecologically interesting examples of abrupt changes in biological functioning near various critical temperatures are summarized below. The reader is referred for details to the original contributions.

Waldman (1967) has studied the effects of temperature on the rate of uptake of iodide-131 by the marine alga Enteromorpha flexuosa. The study is interesting in demonstrating a distinct and rather abrupt maximum in iodide uptake at about 31°C (see Figure 2-35). This finding may be singularly important ecologically suggesting that the rate and amount of other trace compounds incorporated possibly including radioactive waste materials, may be critically dependent on temperature. This aspect is particularly important because temperature may indeed exert a critical influence on both the internal chemistry - as suggested above - and on the external chemistry.



CONCENTRATION RATIO AS A FUNCTION OF TEMPERATURE.

Concentration of incorporated (radioactive) iodide as a function of temperature in the marine alga, Enteromorpha flexuosa (Waldmann, 1967).

Figure 2-35

The distribution of a trace of ion such as Th^{4+} in the environment will be determined by what may be highly temperature-dependent adsorption effects on mineral grains and the equally (or even more) temperature-dependent incorporation into cellular organisms!

See the discussion of the effects of temperature and toxicity, by Dr. Cairns in another paper in this series.

Richards (1965) has determined the thermal response of two species of aquatic snails. The species employed were Australorbis glabratus, which is indigenous to relatively warm tropical breeding sites, and the temperate water snail, Lymnaea stagnalis. It is noteworthy that in both cases, the growth rates show indications of changes in slope around 15°C, and drops sharply above 30°C.

Davis and Calabrese (1969) have studied the survival and growth of larvae of the European oyster (Ostrea edulis) as a function of temperature. The measurements are expressed as percent of increase in mean length of survival over the range from 10 to 32.5°C. Particularly noteworthy is the broad optimum in the mean length increase between approximately 17 and 30°C and the precipitous drop (from 82% to approximately 25%) going from 30 to 32.5°C (see Figure 2-36). The "optimum conditions" for these organisms, as defined by the authors, are delineated in double-lines in Figure 2-36. 5, 50 and 6% increases are shown as (lighter) contours (estimated by the present author). Note in all cases the abrupt decreases between 30 and 32.5°C, especially for the higher salinities.

Salinity (‰)	12·5	15·0	17·5	20·0	22·5	25·0	27·5	30·0	32·5	
12·5	0	0	0	0	0	2	0	0	0	
15·0	0	<1	3	9	20	31	17	12	0	5%
17·5	<1	5	21	36	59	66	68	63	15	
20·0	5	17	39	60	80	82	87	85	54	50%
22·5	12	25	48	68	83	88	85	91	61	
27·0	16	30	53	71	83	93	83	98	65	65%

Survival of larvae of European oyster (Ostrea edulis). Data by Davis and Calabrese (1969).

Figure 2-36

F. Various Ecological Examples

Olla and Studholme (1971) have studied the effects of temperature on the physiology and activity of the blue fish (Pomatomus saltatrix L.). The criteria used to describe the behavior of the fish were swimming speed and schooling behavior. The conclusions reached by Olla and Studholme are interesting. They conclude that the blue fish responds to thermal stresses with increased responsiveness. Both high and low temperature stresses may serve to move the animals away from the areas adversely affected by unusual temperatures. The authors also quote Lunde and Maltezos who noted that when the water temperature falls below 15°C, the adult blue fish begins its fall migration. This parallels the findings by Olla and Studholme of high swimming speeds at temperatures below 15°C. Finally, the daily rhythmic activities became less defined as the fish were subject to thermal stress, but that (within limits) this decrease in normal daily rhythmic activity could be reversed upon returning to more normal temperature regimes.

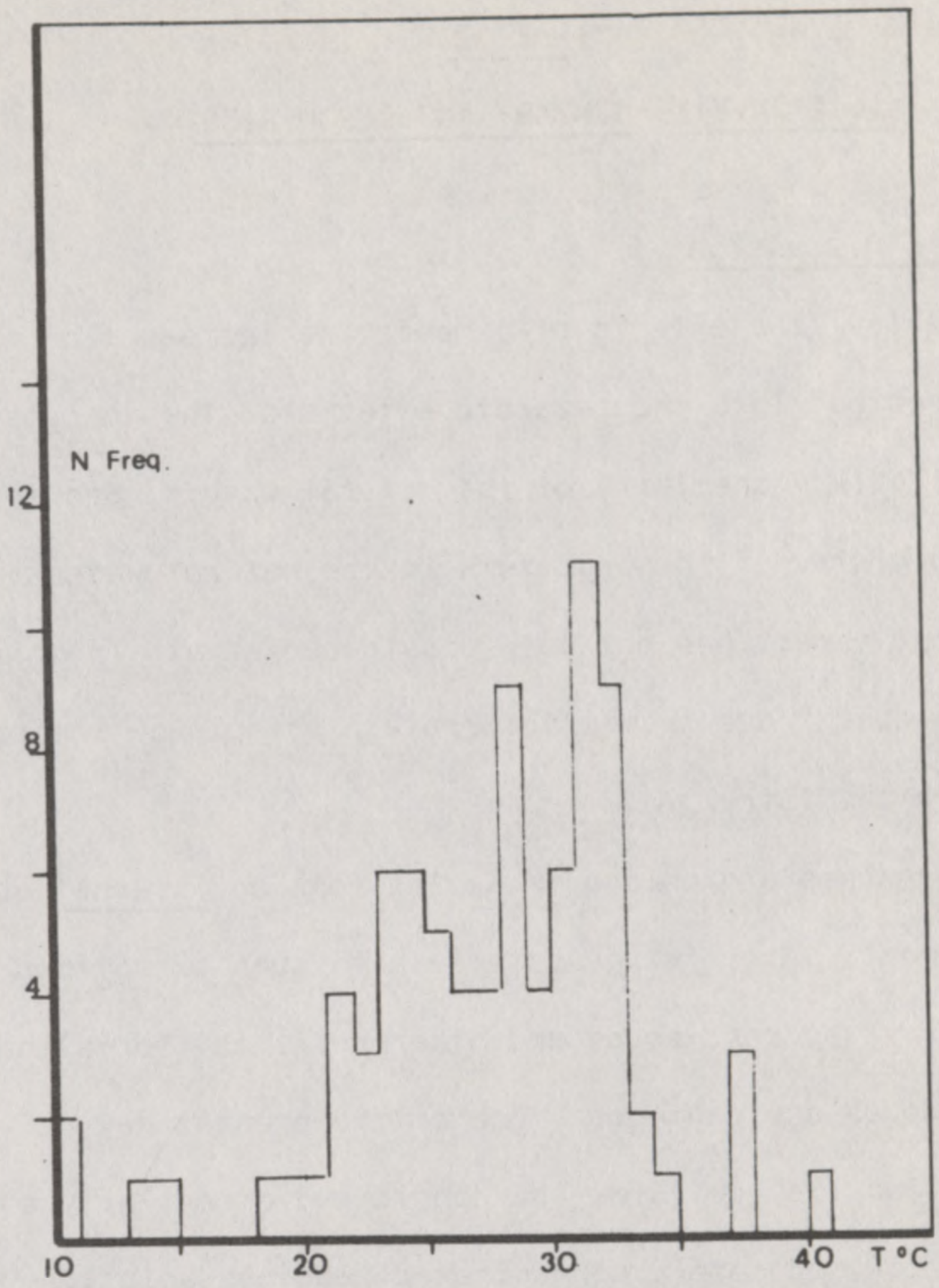
An interesting example of a rather pronounced change in physiological functioning has been reported by Meuwis and Heuts (1957). These authors measured the breathing rate, temperature relationship for carp (Cyprinus carpio), ranging in weight from 20 g to 2000 g, and in age from 3 months to 4 years. The important finding by Meuwis and Heuts is that log plots (vs. temperature) of breathing rate show abrupt and pronounced changes in slope near two critical temperature regions. The extremes of these thermal regions are, respectively, 12.3 to 19°C, and the higher one between 32 to 34.5°C. An inspection of their data shows that more frequently the lower temperature transition occurs quite close to 15°C, particularly for younger specimens. The fish were always transferred from a lower temperature to a

higher temperature, and the rate of acclimatization was studied in a few cases. Steady-state breathing rate was usually achieved within three to four days. The authors note that the acclimatization is generally the shortest between 16 and 30°C.

In his study of upper temperature tolerances (as reported from laboratory experiments) of marine and estuarine fishes, DeSylva (see Krenkel and Parker, 1969, pp. 236-238) reported several "tolerance limits". A graph of frequency of occurrence (see Figure 2-37) as a function of temperature reveals a fairly distinct maximum around 29-30°C with a pronounced "shoulder" near 23°C. Unfortunately, the data do not suffice to determine with any degree of certainty whether or not an actual binodal distribution exists.

An inspection of the water quality criteria for European freshwater fish (Water Research, loco cit., pp. 652-653, 1969) indicates a number of lethal temperatures for various trouts and Coregonids. An inspection of these lethal temperatures reveal that the values generally fall around 30°C within ± 2°C, with a few notable exceptions (such as Coregonus albula lugoga; 23°C, or Cyprinus carpio, from a heated lake in Poland, for which the temperature was observed to be 40.6°C. Depending on the duration and temperature of acclimatization, temperatures for Cyprinus carpio up to 39°C have been observed). In general, however, the distribution of lethal temperatures is quite narrow, between 29 and 32°C.

The implications of water structure changes are far reaching in their applications to ecological systems. A few different examples will be mentioned briefly.



Frequency of Occurrence of Upper Temperature Tolerances (Reported in Laboratory Experiments) for Marine and Estuarine Fishes). (DeSylva in Krenkel and Parker, 1969, page 236-238).

Figure 2-37

PART 2

SECTION VI: SUMMARY AND DISCUSSION

VI. Summary and Discussion

In this review, the effects of temperature increases on natural waters have been "dissected" into the separate effects on the changes in the overall, external ("bulk") chemistry of the natural waters, and the changes in the internal chemistry of the organisms in the natural waters. (One extremely important aspect has not been considered at all in this review, namely, the "feedback" due to the temperature effects on the organisms on the overall bulk chemistry).

Aquatic organisms are unique in having both an internal and external aqueous environment. All living systems (with such exceptions as severely "dehydrated" cysts, spores, seeds and other resistant forms) have some kind of internal, aqueous environment. Much of the present day cell biology is based on the notion that cells may be considered essentially as "membranous bags" of dilute (or moderately concentrated) aqueous solutions (Mazur, 1970). Such an approach has the advantage that it permits the use of classical techniques of physical chemistry and phase equilibria to explain the various properties of cellular functioning, but the approach neglects the fact that biological systems have very large surface-to-volume ratio systems. Because of the large interfacial area between the water and the constituents of the cell (ranging from complex organelles to membranes to dissolved macromolecules), interfacial phenomena play an important and sometimes dominant role. These aspects have only rarely been stressed. The reason for this omission can be understood in that the structure of pure, bulk, unadulterated liquid water is not yet understood or fully described. Less is known with certainty about the structure of dilute (let alone concentrated) aqueous solutions. Further, complications which arise from interactions between an interface and the aqueous phase do not have a detailed

theoretical description at present. Cell physiologists have, for lack of any theoretical models, tended to ignore the problem. At this time, no profound molecular theory exists to account for the nature and properties of water as influenced by a variety of interfaces. However, instead of ignoring these interfacial interactions, the present approach is based on trying to determine some possible results of interfacial structuring of water in cellular systems.

Only rarely have attempts been made to present generalizations in the form of mathematical models, in which the effects of temperature on organisms, singly or in communities, are related to events on the molecular level. Reasons for this lack of a quantitative treatment are obvious: the enormous complexity of the problem and relatively meager understanding of the structure and properties of water, the kinetics of the incredible number of possible chemical reactions in the aquatic medium. Some answers may come from a more thorough understanding of macromolecular conformational changes as functions of temperature; from a detailed understanding of lipid/water interactions (see particularly the extensive writings by Chapman, 1968) from studies of the nature of the hydration of biological macromolecules and the state of water in general in cellular systems. It appears at this time necessary to attempt descriptions of temperature effects on living systems - from the characteristics of an individual unicellular organism to the biotic levels of communities and ecosystems - in terms of underlying molecular concepts and probably particularly in terms of the compound water.

In summary, one cannot help notice the remarkable frequency with which anomalies and frequently abrupt changes in biological systems occur over rather narrow, specific temperature ranges, notably 29 to 32°C and 14 to 16°C. These changes are not readily interpreted in terms of "conventional wisdom" of cell biology, but may often be related directly to the suspected structural changes in the internal aqueous environments of the organisms.

Semantics Note

The study of water and aqueous solutions is beset with a number of semantics problems. The classical example is the difficulties which have arisen from the phrase "icebergs", coined by Professor Frank who apparently had no intention whatever of implying the development or enhancement of water structures with all the attributes of Ice-Ih. Other difficulties have been introduced through use of the terms structure-makers and structure-breakers. The latter phrase is fairly obvious, but the former is ambiguous. Thus, does a structure-maker make some "new" type of water structure around a solute, or does it enhance the intrinsic structure of the water as it exists (unaffected by the presence of any solute)? The innumerable problems derived from the use of the ghastly phrase "bound water" in connection with biological systems were discussed, for instance, by Merryman (1966) and the present author (1971).

In the study of the properties of water near interfaces, thermal anomalies occur at a number of different, discrete temperatures. The temperature at which transitions occur have sometimes been referred to as "critical temperatures" while the standard use of the phrase "critical temperature", of course, refers to the phase diagram and the termination of a liquid/gas equilibrium.*

In studies of entropy-enthalpy relationships, a "critical temperature" is introduced as an extra thermodynamic parameter, in connection with entropy-enthalpy plots.

*For a brief, historical note on the introduction of the phrase "critical temperature" in the study of phasetransformations, see the article by Domb (1971).

In addition to these uses, "critical temperatures" are often used loosely regarding biological systems; the phrase has been used to denote maximum temperature; temperature of an abrupt change; occasionally the temperature for minimal activity; or lethal temperatures.

In view of the many different uses of the phrase "critical temperatures" which have thus been employed, it is suggested that the phrase be used with utmost caution (and perhaps primarily reserved for those thermal phenomena which genuinely refer to a "critical state") - in the thermodynamic sense.

Another matter of semantics deserves brief mentioning. Damadian and co-workers (1971) have suggested the word "QUERP WATER" for water in biological systems with unique properties. The authors correctly point out that the literature currently contains such diverse and ill-defined phrases for cell water as "ice-like", "crystalline", "adsorbed", or "ordered" (or "bound"). This obviously is a source of confusion. Hence, Damadian suggests QUERP WATER for such water, derived from "quick, endocytic, relaxing pulse", referring to the rapid relaxation times, T_1 and T_2, observed in biological tissues. Damadian goes on to form a verb from this noun with the suggestion that the name would communicate something about the current knowledge of the state of the water - namely, the NMR behavior - "while remaining non-committal with respect to the physical model for its form". The present author feels that a notation based on the results attainable by a single, specific instrumental methodology is unnecessarily restrictive and advocates instead the use of the previously introduced phrase, "vicinal water". This phrase is equally non-committal as regards the state of ordering as is the phrase QUERP WATER but it does not imply conceptual or specifically instrumental limitations. Furthermore,

it seems slightly more aesthetic (from an etimological point of view) to use a familiar concept (neighboring), expressed in a classical language, compared to an acronym which, anyway, certainly does not readily transliterate into other languages.

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