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Thermal Expansion of Solids

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Thermal Expansion of Solids

by Peter Hidnert and Wilmer Souder

National Bureau of Standards Circular 486

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Preface

Thermal expansion is one of the fundamental properties of materials that is important in science and industry. The problems in which the thermal expansion of materials must be recognized are as varied as our industries.

This Circular is issued to supply a demand for information about various methods for determinations of thermal expansion of solids. Related topics such as relations between thermal expansion and chemical composition of materials are also discussed in the Circular.

Three types of thermostats (differential expansion, bimetallic flexure, and fluid expansion) used in various applications, are discussed.

At various times during the past four decades, this Bureau has published the results of investigations on the thermal expansion of various materials. A list of these publications will be sent free of charge to anyone interested, upon request.

E. U. Condon, *Director.*

Contents

Page

Preface ---- II

I. Introduction ---- 1

II. Types of Thermal-Expansion Apparatus ---- 2

  1. Precision micrometric method ---- 2
  2. Interference method ---- 4
  3. Fused-quartz tube and dial-indicator method ---- 5
  4. Autographic optical-lever method ---- 6
  5. Liquid-micrometer method ---- 7
  6. Induction-furnace and dial-indicator method ---- 8
  7. Capacitance method ---- 9
  8. X-ray method ---- 9
  9. Density method ---- 12
  10. Methods for determinations of volume changes in metals and alloys during casting ---- 13
    - (a) Liquid shrinkage ---- 14
    - (b) Solidification range ---- 14
    - (c) Solid shrinkage ---- 15
    - (d) Specific volume-temperature curves ---- 17
    - (e) Other methods ---- 18

III. Data on Thermal Expansion ---- 19

IV. Relations Between Thermal Expansion and Other Properties ---- 20

V. Applications of Thermal Expansion ---- 25

  1. Thermostats by differential expansion ---- 25
  2. Thermostats by bimetallic flexure ---- 26
  3. Thermostats by fluid expansion ---- 27

VI. References ---- 28

Thermal Expansion of Solids

by Peter Hidnert and Wilmer Souder

This Circular describes 10 methods for determinations of thermal expansion of solids. The procedures used in determining expansion equations and coefficients of expansion of materials are given. Relations between thermal expansion, temperature, chemical composition, density, compressibility, specific heat, melting point, atomic weight, and other properties of materials are indicated. The problems in which the thermal expansion of materials must be recognized are as varied as our industries. One of the important applications of thermal expansion is in thermostats that are described in the publication.

I. Introduction

One of the frequently measured physical properties of materials is thermal expansion. Practically all materials undergo a change of dimensions when they are heated or cooled. For isotropic bodies, the expansion or contraction is the same in all directions, but in anisotropic bodies the expansion or contraction is dependent on direction.

Determinations of dimensional changes of materials, of coefficients of linear and cubical expansion, and of the temperatures and magnitudes of dimensional changes during transformations at constant temperature and with slow or relatively rapid heating and cooling rates (including quenching) are important in science and industry. Dilatometric methods have an advantage over the thermal method (temperature-time cooling curves) in investigating transformations, for the temperatures may be passed through slowly or quickly or the sample may be held at a given temperature for any length of time in order to attain equilibrium and the heating or cooling then resumed. Various types of thermal-expansion apparatus are used for these determinations.

The change in length that takes place when a solid body is heated depends upon the original length of the body and the temperature range over which it is heated. The observation of this change is meaningless unless it is related to the length of the body and the temperature range. The relation between these factors known as the coefficient of linear thermal expansion has been defined in a number of ways.

The average coefficient of linear expansion is defined as

$$ {}_{t_1}a_{t_2}=\frac{L_2-L_1}{L_0(t_2-t_1)}=\frac{\Delta L}{L_0\cdot\Delta t}, \tag{1}$$

where ${}_{t_1}a_{t_2}$ is the average coefficient of expansion between temperatures t_1 and t_2, L_1 and L_2 are the lengths at t_1 and t_2, respectively, and L_0 is the length at a reference temperature. This reference temperature may be 0° C, room temperature, or any other convenient temperature. The authors prefer to use 0° C for the reference temperature. If it is not convenient to obtain the length at 0° C, the length at room temperature is used. The difference introduced in the latter case is negligible for the average coefficient of linear expansion.

The instantaneous coefficient of linear expansion or coefficient of expansion at any temperature, t, may be defined as

$$a_t=\lim_{t_1\to t_2}\frac{L_2-L_1}{L_0(t_2-t_1)}=\frac{dL}{L_0(dt)}, \tag{2}$$

where a_t is the instantaneous coefficient of linear expansion at temperature t.

If L_0 is the length of a solid body at 0° C, then its length at any temperature t° C may be represented by the empirical equation

$$L_t=L_0(1+at+bt^2+\ .\ .\ .), \tag{3}$$

where a and b are constants, depending upon the material. In most cases, these constants a and b are positive, for bodies usually expand at a faster rate as the temperature increases. For a short range of temperature, the equation $L_t=L_0(1+at)$ representing a straight line may be used instead of eq 3 representing a curve. When a molecular change (transformation) occurs on heating or cooling a body, its length may not be accurately represented by a first, second, or third degree equation. In such cases, it may be desirable to obtain two equations, one for the range below the transformation temperature or point of inflection, and the other equation for the range above the transformation temperature.

The instantaneous coefficient of linear expansion may also be derived by differentiation of eq 3, and represented as follows:

$$a_t=\frac{a+2bt+\ .\ .\ .}{L_0}, \tag{4}$$

where a and b are the same constants used in eq 3. The instantaneous coefficient of expansion at 0° C is a/L_0.

A change in volume that takes place when a solid body is heated may be treated in a similar manner. The following equations correspond to the previous equations relating to linear thermal expansion:

$${}_{t_1}\alpha_{t_2}=\frac{V_2-V_1}{V_0(t_2-t_1)}=\frac{\Delta V}{V_0(\Delta t)} \tag{5}$$

$$\alpha_t=\lim_{t_1\to t_2}\frac{V_2-V_1}{V_0(t_2-t_1)}=\frac{dV}{V_0(dt)} \tag{6}$$

$$V_t=V_0(1+\alpha t+\beta t^2+\ .\ .\ .) \tag{7}$$

$$\alpha_t=\frac{\alpha+2\beta t+\ .\ .\ .}{V_0}. \tag{8}$$

In eq 5 to 8

${}_{t_1}\alpha_{t_2}$=average coefficient of cubical thermal expansion between temperatures t_1 and t_2

V_1=volume at t_1

V_2=volume at t_2

V_0=volume at a reference temperature (In eq 7, volume at 0° C)

α_t=instantaneous coefficient of cubical thermal expansion at any temperature t°

V_t=volume at any temperature t°

α and β=constants depending upon the material.

The average coefficient of cubical thermal expansion of an isotropic body between t_1 and t_2, is represented by the equation

$${}_{t_1}\alpha_{t_2}=3\,{}_{t_1}a_{t_2}+3\,{}_{t_1}a^2_{t_2}(t_2+t_1)+{}_{t_1}a^3_{t_2}(t_2^2+t_2t_1+t_1^2) \tag{9}$$

When $t_1=0°$, eq 9 may be expressed as

$${}_0\alpha_t=3\,{}_0a_t+3\,{}_0a_t^2t+{}_0a_t^3t^2, \tag{10}$$

where ${}_0\alpha_t$ and ${}_0a_t$ represent the average coefficient of cubical expansion and the average coefficient of linear expansion, respectively, between 0° and t°. As the second and the third terms of eq 9 and 10 are usually negligible, they reduce to

$${}_{t_1}\alpha_{t_2}=3\,{}_{t_1}a_{t_2} \tag{11}$$

$${}_0\alpha_t=3\,{}_0a_t \tag{12}$$

II. Types of Thermal-Expansion Apparatus

Ten methods for measurement of thermal expansion are described in this Circular.

1. Precision Micrometric Method

The National Bureau of Standards uses micrometric thermal-expansion apparatus for the most precise work on the linear thermal expansion of solids between −150° C and +1,000° C. This apparatus is of two types: (1) The air-type heating chamber, shown at the left in figure 1, in which the sample is surrounded by air or an inert gas, and (2) the stirred-liquid bath, shown at the right in figure 1, in which the sample is surrounded by a suitable liquid.

In both types of apparatus electric heating is used. Thermocouples and a potentiometer are used for measuring temperatures. For determinations at low temperatures, cooling is secured in the stirred-liquid bath by expanding compressed air from a liquid-air interchanger through coils immersed in the bath.

The positions of the ends of the sample in the air chamber are indicated by fine wires (0.001 or 0.002 in. in diam) weighted and hanging vertically from the ends of the sample through slots in the bottom of the chamber. Two micrometer microscopes, mounted horizontally on a traveling comparator and separated by a lateral distance approximately equal to the length of the sample (10 to 50 cm), are used to measure the length changes, as indicated by the changes in separation of these wires. In the stirred liquid bath, tungsten wires (0.001 in. in diam) in contact with the ends of the sample, extend from a fixed horizontal bar above the sample to hinged fingers, inserted beneath the ends of the sample as indicated in figure 2. Here the length changes of the sample are proportional to the changes in the distances between the wires in the plane of the microscopes.

The sample is in the form of a straight rod or bar of uniform cross section. The usual length is 300 mm, and the diameter (or diagonal if the rod has a rectangular cross section) is 5 to 10 mm. The rod is prepared with cylindrical ends having radii of curvature equal to one-half the length of the rod, so that the measured length will not change for slight vertical rotations about its center. Provision has been made for handling samples of other lengths and diameters. The limits of length are the length of the furnace for long rods (50 cm) and the limit of contact approach of the two

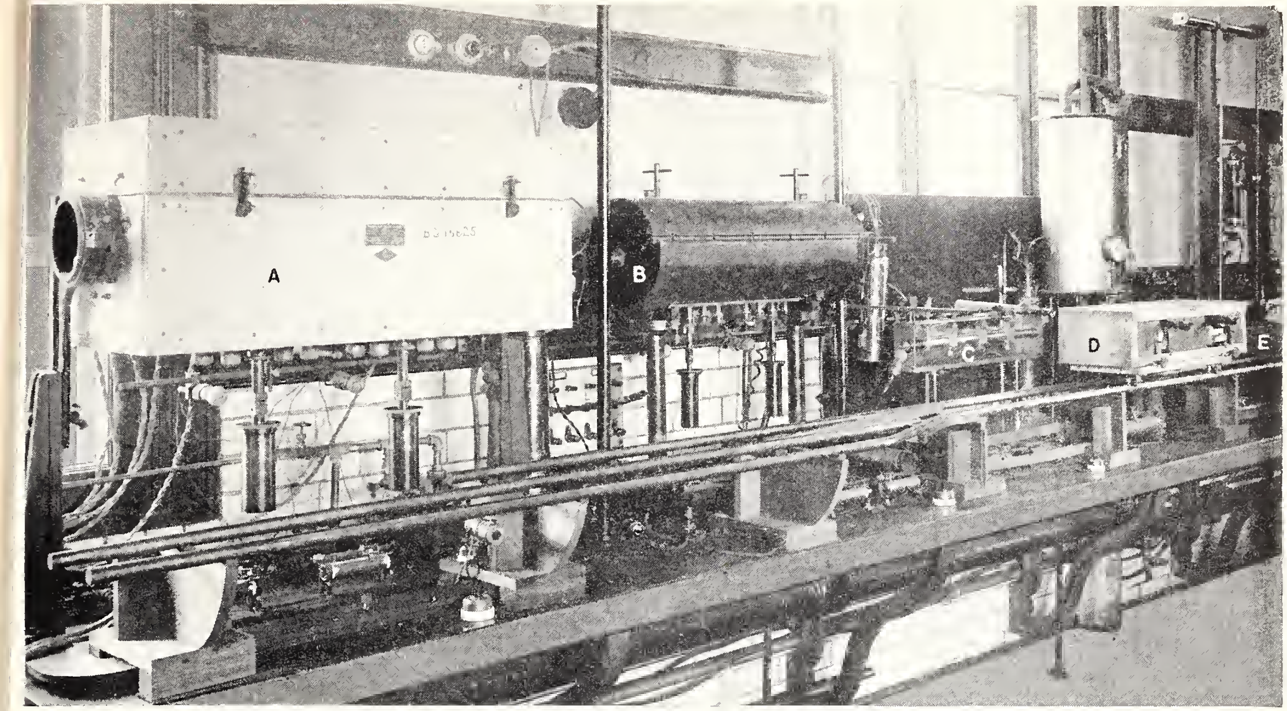

Figure 1. *Furnaces, standard bar and comparator of precision micrometric thermal-expansion apparatus.*

A, Furnace (20° to 1,000° C); *B*, furnace (20° to 600° C); *C*, standard bar; *D*, microscope comparator; *E*, bath (−150° to +300° C).

micrometer microscopes for short rods (10 cm).

When a sample must be heated in the air furnace to a temperature at which oxidation or scaling is expected, the furnace may be filled with an inert gas. When such gas is not available, it is possible to minimize the effects of oxidation or scaling by placing the observation wires in sharp V-grooves cut around the rod near each end.

A vane (5 to 25 g), attached to the bottom of each observation wire in the air-type heating chamber, is suspended in oil to damp out vibrations from the building and surroundings. The wires are annealed before observations are started by passing sufficient electric current to heat them to a visible glow. For determinations below 700° C, 0.001- or 0.002-in. diameter Chromel wires may be used. For determinations from 20° to 1,000° C, platinum-osmium, platinum-rhodium or platinum-ruthenium wires 0.002 in. in diameter may be used.

With the air furnace it is possible to make measurements between 20° and 1,000° C. The stirred liquid bath is used for temperatures between −150° and +300° C. The stirred liquid bath, by reason of the circulation and intimate contact of the heated or cooled liquid, permits more rapid observations than the air furnace. Observations are recorded when the sample has reached the temperature of the furnace. This condition may be established by waiting until the observation wires show no movement in the microscopes. After readings are completed the heating current is adjusted for the next temperature. The immersion of samples in the liquid bath is limited to those samples not attacked by the liquids used. The usual practice is to use a light engine oil (Esstic 42) for the temperature range 20° to 300° C. For the range −65° to +60° C Dow Corning Fluid No. 500 (kinematic viscosity 2.0 centistokes at 25° C) is used, and 2-methylpentane is used at low temperatures to about −150° C. A water coil in the liquid bath is used to hasten cooling between 300° and 20° C.

The observation wires on which microscope settings are made are illuminated by 10-watt frosted spherical lamp bulbs placed behind them. Resistances in the lamp circuit are used to reduce the illumination to a satisfactory intensity. An excellent arrangement for high-precision measurements is secured by the parallel spider lines on the

Figure 2. *Sample, sample holder, and hinged fingers for wires in liquid bath.*

reticle frames moved by the microscope micrometers.

The air furnace has control rheostats for each side and end of the heating chamber. The external heat loss from these rheostats is reduced by using a transformer for the lower temperatures.

With these types of apparatus it is essential that the position of the samples be maintained horizontally during the determinations. A further requirement for the stirred liquid bath is that the readings be made at a known distance above each end of the sample, and that the ratio of distances (level of observation to upper supports of wires, and ends of sample to upper supports of wires) be known and maintained.

The arrangement of the furnaces, standard bar, and comparator is shown in figure 1. The air type heating chamber, or furnace, is shown at the extreme left of the figure. A smaller air furnace is shown at the right of the large furnace. The standard bar of fused quartz and the micrometer comparator appear in front of the window. The interchanger and stirred liquid bath are partially visible near the right margin of figure 1. Vacuum bottles filled with melting ice for maintaining the temperature of the cold junctions at 0° C appear at the right of the two furnaces in this figure. Connections to the potentiometer are made through lead-covered cables and a selector switch. Triple-junction thermocouples are placed in the air furnaces. A single thermocouple junction in the stirred liquid bath is sufficient. The forced circulation of the bath liquid by a motor and a propeller maintains uniformity of temperature. Platinum platinum-rhodium thermocouples are used for the 1,000° C air furnace. For the smaller air furnace (600° C), gold-palladium platinum-rhodium thermoaouples are used. A copper-constan9an thermocouple is employed in the stirred liquid bath. The interchanger is of the regular air-liquefying type. The cooled air, compressed to about 2,500 lb/in.^{2}, is expanded through coils in the stirred liquid bath, when temperatures between +20° and −150° C are required.

This method for determining linear thermal expansion is believed to be the most precise known. Under most favorable conditions, measurements of coefficients of expansion accurate to 0.1 percent are possible.

Additional information about this equipment is given in publications by Hidnert [1] [1] and Souder and Hidnert [2]. Blueprints giving details of construction are on file at the National Bureau of Standards and may be borrowed upon request.

2. Interference Method

When only small samples of material (about 10 mm or less in length) are available, the Fizeau-Pulfrich interference method is especially useful for determinations of linear thermal expansion. The method is also useful for determinations of the linear thermal expansion of crystals or other solids in different directions. The sample is placed vertically between two transparent fused-quartz plates, each about 4 mm thick and reasonably free from bubbles and other imperfections. The surfaces of each plate should be flat within one-fifth of a fringe, and should be inclined to each other at an angle of about 20′ of arc. The sample with the two fused-quartz plates is set in an electric furnace or cooling chamber for heating or cooling. When the plates are illuminated normally with monochromatic light, a set of interference fringes is produced by the interference of the light reflected between the lower surface of the upper plate and the upper surface of the lower plate, when the angle between these surfaces is slight. The fringes are observed by means of a viewing device. Changing the temperature of the sample brings about a change in length, which causes the distance between the plates to change with a corresponding movement of the interference fringes past a reference mark on the lower surface of the upper plate. From the observed displacement of the fringes, the change in length, or linear thermal expansion, can be determined. The temperature of the sample is determined with a thermocouple, resistance thermometer, or interference thermometer [3]. This method may be used at low temperatures and at elevated temperatures to about 1,000° C.

If the sample is maintained in a vacuum during the determinations, the linear thermal expansion per unit length for a given temperature interval is computed from the equation

$$\frac{\Delta L}{L}=\frac{\lambda N}{2L}, \tag{13}$$

where L is the initial length of the sample, ΔL is the change in length or linear thermal expansion, λ is the wave length of monochromatic light, and N is the number of fringes that passed the reference mark. If the sample is heated or cooled in air, the following equation should be used:

$$\frac{\Delta L}{L}=\frac{\lambda N}{2L}+\frac{A}{L}, \tag{14}$$

where A is the "air correction". This correction varies with the pressure and the temperature of the air. Tables 2 and 3 of Merritt's publication [4] give values of A/L in microns per centimeter for 760 mm atmospheric pressure, and for various temperatures between −194° and +1,100° C. The average coefficient of expansion is computed by dividing $\Delta L/L$ by the change in temperature.

Austin [5] stated that the maximum errors of the interference method with his vacuum furnace

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[1] Figures in brackets indicate the literature references at the end of this Circular.

should not be greater than 1 percent at 300° C or 0.7 percent at 600° C, and the probable errors will be much less than these values. When the sample is heated in an air furnace, the errors may be greater as a result of the uncertainty caused by the presence of an air film between the sample and the interferometer plate and the oxidation or scaling of the sample.

Additional information about the interference method has been published by Peters and Cragoe [6], Merritt [4], and Saunders [7].

Trowbridge [8], Arnulf [9], Sinden [10], Nix and MacNair [11], and Saunders [12] described methods of photographing fringes.

In 1916 Meggers [13] indicated how the determination of the exact order of interference or the optical measurement of length can be made with the aid of certain wavelengths of neon radiation. In 1919 Peters [14] described the use of the interferometer in the measurement of small dilations by observing fractional orders due to several wavelengths by the method described by Meggers. Willey and Fink [15] have recently used this method in determinations of coefficients of expansion of aluminum alloys. The constant attention of the observer and the counting of the interference fringes that pass the reference mark during heating or cooling, or the photographing of fringes are not required. The method has been used for many years at the National Bureau of Standards for determinations of the lengths of gage blocks at room temperature.

3. Fused-Quartz Tube and Dial-Indicator Method

A fused-quartz-tube thermal-expansion apparatus may be used for determinations of linear thermal expansion for various temperature ranges between −190° and +1,000° C. This type of apparatus, as improved by Hidnert and Sweeney [16] over a similar type used abroad, is recommended for commercial laboratories where data of the highest precision are not required. With the apparatus it is possible to obtain an accuracy of 2 percent.

Figure 3 shows a fused-quartz tube closed at the bottom, with a sample (20 cm) in the tube ready for heating or cooling. A movable fused-quartz rod rests on top of the sample and extends above the open end of the tube. The bottoms of the tube and the movable rod are ground concave and the ends of the sample, convex, in order to secure satisfactory contacts. The top of the movable rod, on which a dial indicator rests, is flat. Heating is effected by placing the tube containing the sample in a water or oil bath, or in an electric furnace (fig. 4) extending well above the top of the sample. Low temperatures are secured by using a cooling cabinet or suitable cooling baths, such as liquid air, solid carbon dioxide in a mixture of equal parts of carbon tetrachloride and chloroform, ice and sodium chloride, and melting ice. A thermocouple, placed inside the fused-quartz tube near the center

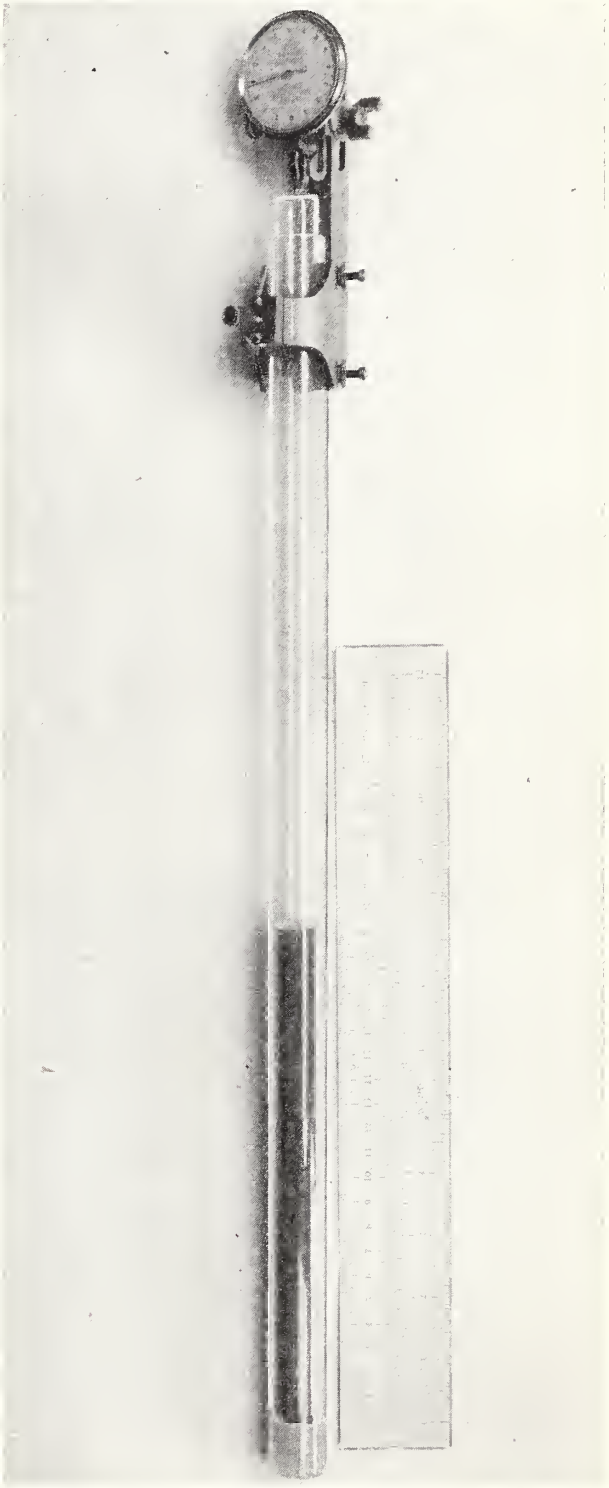

Figure 3. *Fused-quartz tube, dial indicator, and sample.*

FIGURE 4. *Fused-quartz tube and dial indicator thermal-expansion apparatus.*

of the sample, indicates the temperature. A dial indicator, fastened near the top of the tube, registers the differential expansion between the sample and an equivalent length (20 cm) of fused quartz. A small correction for the linear expansion of fused quartz is made. Prints showing details of this apparatus may be secured from the National Bureau of Standards.

Modifications of the fused-quartz-tube thermal-expansion apparatus for use with shorter samples or with a load on the samples, have been described by Hidnert [17] and by Hidnert and Dickson [18].

Walters and Gensamer [19] modified this type of apparatus so that the expansion of a sample can be determined in a vacuum or an inert gas between −200° and +1,000° C. Kingston [20] modified the apparatus to a recording dilatometer by means of a contact mechanism, transmission shaft, recorder and electronic relay. He also made provision for the use of various atmospheres.

4. Autographic Optical-Lever Method

Souder, Hidnert, and Fox [21] designed and constructed an autographic optical-lever thermal-expansion apparatus for use in commercial laboratories. It was found to give more accurate results than previous apparatus of similar type. With this apparatus it is possible to obtain expansion curves photographically or to observe points on the expansion curves of materials during the progress of the test.

A general view of the autographic expansion apparatus is shown in figure 5. The apparatus consists essentially of a furnace, *F*, mounted on a common base with a camera box, *C*, and a source of illumination, *I*. The back of the camera is provided with a hinged bookform plate holder for 8- by 10-in. photographic plates, films, sensitized paper, or a ground-glass screen for photographic or visual observations. The over-all length of the apparatus is approximately 64 in., height 19 in., and width 14 in.

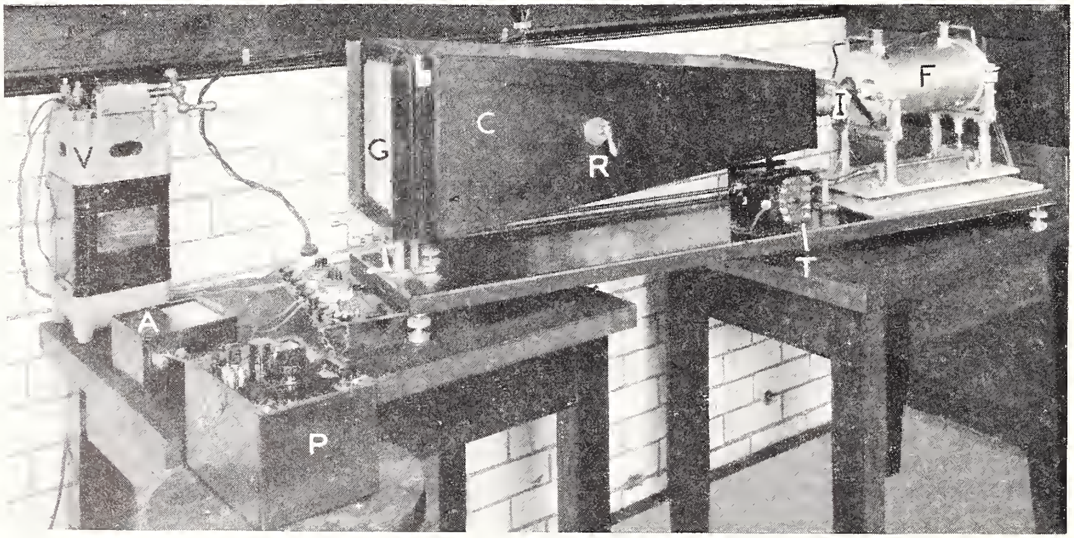

FIGURE 5. *Autographic expansion apparatus.*

A, Ammeter; *C*, camera box; *F*, furnace; *G*, glass screen; *I* illumination; *P*, potentiometer indicator; *R*, internal reflecting mirror; *T*, transformer; *V*, induction voltage regulator.

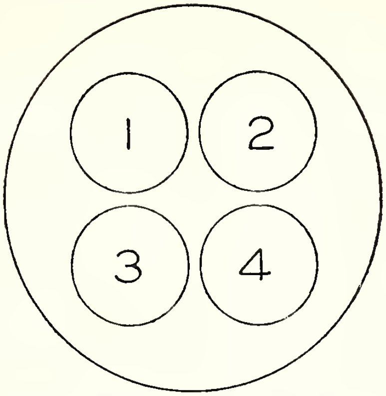

FIGURE 6. *Cross section of alundum cylinder in furnace indicating the holes and the positions of "stationary" axis, temperature axis, sample, and thermocouple.*

1, "Stationary" axis; 2, temperature axis; 3, sample (expansion axis); 4, thermocouple.
The observer is located at the glass screen, *G*, of the camera box (fig. 5) and is looking toward the furnace.

The following materials are inserted in the four horizontal holes of the furnace (fig. 6):

Hole 1—A long, fused-quartz rod, which represents a "stationary" axis.

Hole 2—A rod of Chromel *A* having uniform rate of expansion, 150 mm in length, which represents a temperature axis.

Hole 3—A sample 150 mm in length.

Hole 4—A Chromel-Alumel thermocouple with 3 junctions, 1 near the center of the sample in hole 3, and the other junctions near the ends of the sample.

The ends of the rod of Chromel and the sample in holes 2 and 3, respectively, are pointed. The angle at each pointed end is about 80°.

A fused-quartz plug is in contact with each end of the Chromel rod (temperature axis) and of the sample. The pointed ends of these 4 plugs and of the long, fused-quartz rod ("stationary" axis) extend beyond the ends of the furnace. The rear of the mirror *M* (fig. 7), held in position by means of a spring, is in contact with the fused-quartz plugs and the "stationary" axis (fused-quartz rod) extending from the left face of the furnace.

Fused-quartz plugs are in contact with the right ends of the Chromel rod and the sample. At each end of these plugs there is a 90° pivot bearing. One end of each of these plugs and one end (90° pivot bearing) of the "stationary" axis extend beyond the right face of the furnace. Each of these ends is held against an adjustable screw.

When the furnace is heated, the sample and the Chromel rod (temperature axis) expand. The mirror which is in contact with the plugs extending from the sample, Chromel rod (temperature axis) and "stationary" axis therefore moves. The expansion of the sample causes the bottom of the mirror to move and deflect the spot of light upward. The expansion of the Chromel rod (temperature axis) causes one side of the mirror to move and deflect the spot horizontally. The expansion of the fused-quartz plugs, extending on each side of the sample, should balance the expansion of the fused-quartz plugs extending on each side of the Chromel rod (temperature axis), and also the expansion of an equivalent length of the "stationary" axis. A spot of light focused on the mirror and reflected on a glass screen, *G*, or photographic plate, indicates the expansion both of the sample and of the Chromel rod and describes a curve, the resultant of these two expansions vertically and horizontally. The abscissas indicate the expansion of the Chromel rod and may be evaluated to represent temperature. The ordinates represent the expansion of the sample. The curve therefore represents the expansion of the sample versus temperature.

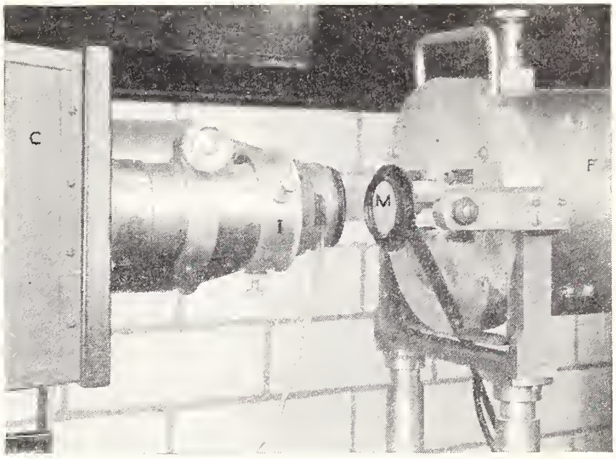

FIGURE 7. *Stellite mirror in contact with the fused quartz rods and the "stationary" axis extending from the left face of the furnace.*

C, Camera box; *F*, furnace; *I*, illuminator; *M*, optical lever mirror.

For materials having coefficients of expansion approximately equal to those for ordinary steel, the error of the autographic expansion apparatus is about 6 percent for the range from 20° to 100° C, and about 3 percent for the range from 20° to 500° C. The apparatus is not sufficiently sensitive for tests on low-expanding materials. It is not satisfactory at temperatures where softening occurs in the sample or for materials that bend at elevated temperatures.

Chevenard [22] and other investigators used other forms of the optical lever method for determinations of the linear thermal expansion of materials.

5. Liquid-Micrometer Method

A liquid-micrometer method for determining linear thermal expansion of solids has been described by Andrew, Rippon, Miller, and Wragg

[23]. The sample (in the form of a hollow cylinder 2 in. long, ¾ in. in diameter with a ⅜-in. hole through the center) is placed horizontally in a silica tube of 1-in. internal diameter. The heating coil consists of a platinum wire wound around the silica tube over a length of 9 in. On the ends of the sample, which have been ground parallel and polished, two silica disks (also accurately ground) are placed. These disks are pressed against the ends of the sample by means of two silica tubes, which transmit changes in the length of the sample. One of the latter silica tubes is butted up against a heavy cast-iron block, and the other silica tube is pressed against a measuring device butted to a large lead block.

The relative movement of the silica tube is measured by a hydraulic device. This consists of a thick steel disk 8 in. in diameter, having a saucer-like depression on its face over which is clamped a thin disk of saw steel. The space so enclosed is filled with colored water. A pipe runs through the back of the steel disk, connecting this liquid with a horizontal glass tube to which a scale is attached. A small reservoir with a stopcock is also fitted for adjusting the amount of liquid in the system. This liquid micrometer is bolted to the lead block, so that the thin steel disk is vertical. A steel disk with a flat surface 1 in. in diameter transmits the movement of the silica tube to the thin steel diaphragm. With a glass tube of about 2-mm bore, the movement of the meniscus magnifies the displacement of the silica tube two thousand times. The temperature of the sample is measured by means of a thermocouple placed at the center of the sample. Figure 8 shows a diagrammatic sketch of the apparatus.

A flexible gas-tight joint is made by means of tubes of thin rubber fixed on the ends of the furnace tubes and then wired to the moving silica tubes. Through holes drilled in these two silica tubes, gas may be circulated around the sample to prevent oxidation.

It is necessary to calibrate this apparatus with samples of known expansion.

The apparatus was modified by Haughton and Griffiths [24], the changes being the method of rendering the apparatus autographic, the method of mounting so as to enable adjustment of zero and resetting to be easily performed, and various minor modifications which simplify its arrangement and use. With this modified dilatometer, using a 2-in. sample, it is possible to record changes of the order of 10^{-6} in., although neither the sensitivity nor the accuracy is normally as high as this.

Because it is under pressure both in the original apparatus and in that modified by Haughton and Griffiths, the sample is likely to become deformed at high temperatures.

6. Induction-Furnace and Dial-Indicator Method

A high-frequency induction furnace was used by Heindl [25] for determinations of the linear thermal expansion of refractories between 20° and 1,800° C. The heat was generated through the medium of a cylindrical graphite muffle, 12 in. long, 6 in. in diameter, and having a wall ½ in. thick. A dial indicator, independent of the furnace, was supported by a framework with fused-quartz tubes for legs.

The arrangement of the sample (about 6 in. in length) is indicated in figure 9. This set-up formed a continuous system which expanded and contracted, independently of the furnace. Tungsten plates, ⅞ in. square and 0.015 in. thick were placed between the sample and the graphite parts in a reducing atmosphere. The sample was placed within a muffle prepared from zirconium silicate.

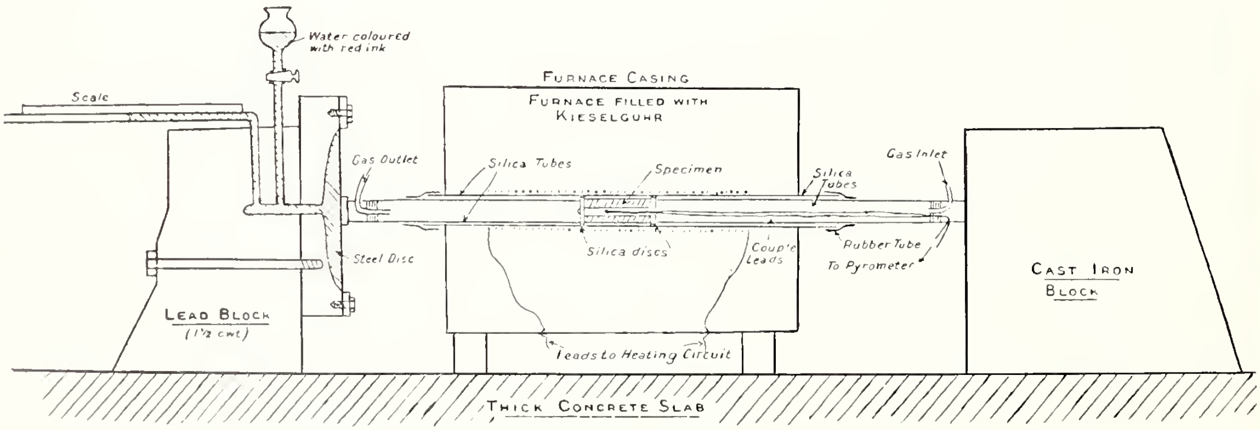

Figure 8. *Diagrammatic sketch of liquid-micrometer dilatometer (Andrew, Rippon, Miller, and Wragg).*

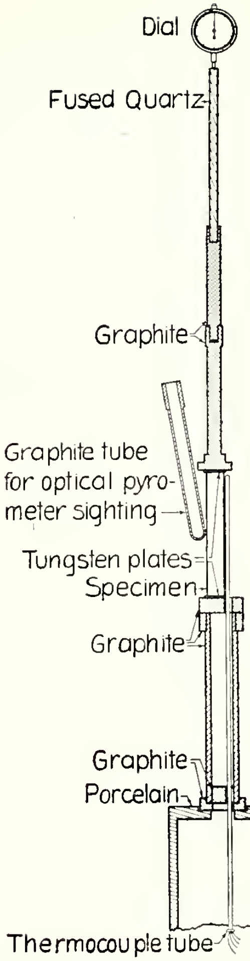

FIGURE 9. *Specimen, specimen support, and the system transmitting the expansion in the induction furnace (Heindl).*

The fused-quartz rod does not extend into the furnace.

Temperatures were measured with two platinum platinum-rhodium thermocouples up to about 1,500° C. Then the couples were removed from the apparatus and higher temperatures observed with an optical pyrometer.

From a comparison of dial readings, with this apparatus, on a bar of artificial graphite between 20° and 1,800° C and on a bar of fused quartz of known expansion between 20° and 1,000° C, a curve was derived which gives corrections to be applied to the apparent expansion of a sample at various temperatures between 20° and 1,800° C. The portion of the correction curve from 1,000° to 1,800° C was extrapolated, since the apparent expansion of artificial graphite showed no irregularities between 1,000° and 1,800° C.

7. Capacitance Method

A capacitance dilatometer was developed by Prytherch [26] for use in the Metallurgy Department of the National Physical Laboratory. An oscillatory circuit is used and the sample (about 2 cm in length) is made to actuate the moving plate of a small capacitor, which constitutes part of the series grid capacitance of the circuit. Small changes in this capacitance bring about relatively large changes in the mean steady plate current of the tube. A continuous record of the plate current of the tube is made on a recorder, which also simultaneously records the temperature of the sample. The length changes of the sample are correlated with temperature. Haughton and Adcock [27] altered this apparatus somewhat to examine samples at temperatures up to 1,300° C in an inert atmosphere. The circuit arrangements of the oscillator are those described by Prytherch, but Haughton and Adcock found it advantageous to screen the oscillator completely by means of a copper-lined box.

8. X-Ray Method

With the X-ray method it is possible to determine the coefficients of expansion of crystals in different directions over large temperature ranges. A very small amount of material is sufficient for a sample.

When a crystal is heated, the perpendicular distance between its atomic planes parallel to its crystal face generally increases. This distance d at any temperature may be determined by an X-ray method from Bragg's law [28]

$$n\lambda = 2d\ \sin\Theta, \tag{15}$$

where λ is the wavelength of a monochromatic beam of X-rays incident upon the cleavage face of the crystal, Θ is the angle between the incident X-ray beam and the atomic reflecting plane or the angle between the reflected beam and the same plane, and n is a small integral number that represents the order of reflection. From eq 15, the following equation may be obtained for the average coefficient of linear thermal expansion for a temperature range from 0° to t°:

$${}_0a_t = \frac{\sin\Theta_0 - \sin\Theta_t}{t\ \sin\Theta_t}, \tag{16}$$

where ${}_0a_t$ is the average coefficient of linear expansion between 0° and t°, and Θ_0 and Θ_t are the angles indicated previously, at temperatures 0° and t°, respectively. From eq 16 it will be noted that it is not necessary to know the value of λ.

Hull [29] and Debye and Scherrer [30] modified Bragg's method so that a polycrystalline material (thin sheet or powder) can be used. Some of the crystals in this sample will be oriented so that when monochromatic X-rays are normally incident, they will be reflected from every plane

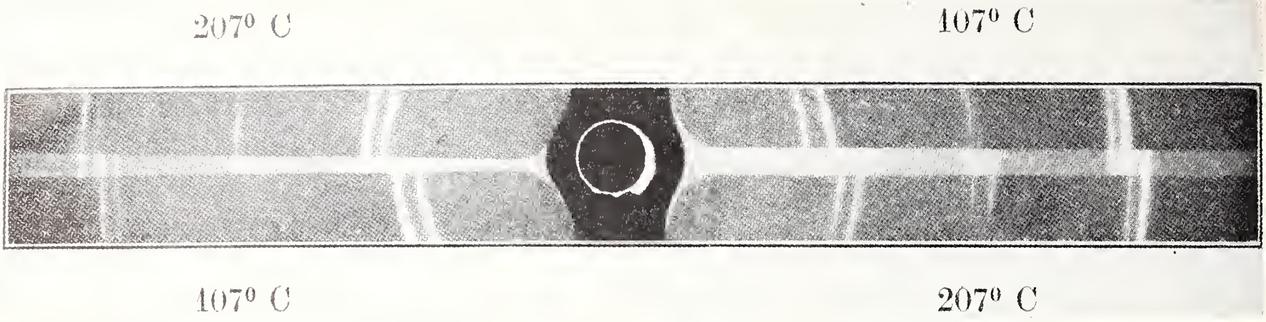

FIGURE 10. *Shifts of the Hull-Debye-Scherrer rings of the reflections (114) and (103) of magnesium,* FeK *radiation (Hanawalt and Frevel).*

set that is characteristic of the crystal. A diffraction pattern consisting of concentric circles may be obtained by placing a photographic plate in back of the sample. The innermost circle is caused by those crystals presenting the plane set having the largest lattice constant at the proper angle for reflection. When the sample is heated, the change in d will cause a corresponding reciprocal change in $\sin\theta$ (see eq 15), and hence in the diameter of the circle.

If the sample consists of a speck of powder, it may be supported by a fine wire and rotated so that complete lines are obtained on a cylindrical photographic film when the X-rays passing through a slit system are diffracted from the sample. The shift in the position of the lines at different temperatures indicates the change in the distance d, from which the linear thermal expansion may be computed.

Figure 10 shows the shifts of the Hull-Debye-Scherrer rings of the reflection (114) and (105) of magnesium (FeK radiation), obtained by Hanawalt and Frevel [31] at 107° and 207° C. The sample consisted of a thin disk of magnesium which was mounted in an electric furnace heated by storage batteries. The X-ray beam penetrated an aluminum foil covering that served as a window for the heating chamber. An iron-constantan thermocouple was attched to the surface of the sample. Two strips of lead covered the quadrants 1 and 3 of the film during the low temperature exposure, and quadrants 2 and 4 during the high temperature exposure. The films were measured on a comparator and the data used to evaluate the coefficients of expansion of magnesium, parallel to and perpendicular to the c-axis.

The X-ray tube used by Shinoda [32] and shown in figure 11, was designed to take Hull-Debye-Scherrer photographs with a large angle of reflection. The body of the X-ray tube made from a brass block 5.5 by 5.5 by 8 cm is shown in figure 12. A hole, F, 3.4 cm in diameter, was bored from one end of the block to the central part of the flat surface at the other end. The anticathode shown by b, and A, in figure 12, was made from a flat copper or iron block 4.5 by 5.5 by 0.7 cm, having a slightly raised part on one side. This anticathode fits on the flat end of the body of the X-ray tube and the raised part of the anticathode enters hole F. As the electrons emitted from the hot cathode are focused on the center of hole F, the raised part of the anticathode becomes the source of X-rays. A narrow groove extends from hole F and forms a slit for the X-ray beam. A cellophane window covers the slit. The sample, S, is placed very close to this window, as shown in figure 12. The distance between the sample and the source of the X-ray beam is about 2.5 cm. The specimen holder is made from a copper block 1 by 1 by 0.5 cm, and the sample, usually a foil, is attached on one surface and covered with layers of cellophane and paper. The other surfaces of the specimen holder are covered with asbestos. For determinations at 100° C, steam is introduced through an opening in the specimen holder.

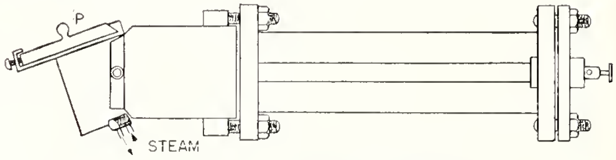

FIGURE 11. *X-ray tube (Shinoda).*

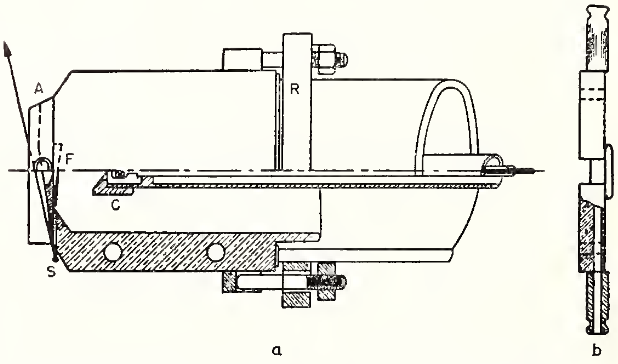

FIGURE 12. *Body of X-ray tube a, and anticathode b (Shinoda).*

The cathode is an ordinary hot cathode with a ungsten filament covered by a cap, *C*. This cap serves as a focusing device. Its anticathode side s V-shaped to secure a sharp line-focus. Insulation between the cathode and the body of the X-ray tube is attained by a glass tube 17.5 cm in length and 5 cm in diameter. This glass tube is connected to the cathode and the body by bolts and nuts through the brass ring *R*, with rubber rings used as packing.

The plate holder *P* in figure 11 can move up and down so that four photographs can be taken in succession. With this apparatus, an exposure of 3 to 5 min is sufficient for each photograph. The X-rays are excited by 5 to 7 ma and 40 kv.

Becker [33], Jay [34], and Wilson [35] described X-ray cameras used in determinations of the coefficients of linear thermal expansion of materials. The X-ray camera and auxiliary equipment used by Wilson are shown in figure 13. This camera consists of two circular brass plates, the upper (*A* in fig. 13) about 19 cm in diameter, the lower (*B*) somewhat larger containing a groove to receive the cover *C*. The plates are held about 1.1 cm apart by two brass V-blocks *D* and *E*. Each V-block carries a pair of stainless steel knife-edges that mark out definitely the length of film exposed to the X-rays. The film, backed by a sheet of black paper, is held firmly against the upper plate and the boss of the lower plate by two strips of steel ribbon on each side. The strips are attached to the back V-block, *D*, and are clipped firmly to the front V-block, *E*, by phosphor-bronze springs. The lower diagram of figure 13 shows, on the left side of the camera, the film, paper and steel strips lying loosely; on the right side it shows them clipped to the front V-block.

Each plate contains two water-cooling channels, *F*, and *G*, about 1-cm^2 section. The water enters through one of four tubes, *H*, at the back of the camera, passes through V-block *D*, to the upper plate, where it flows half-way round the outer channel until it meets a baffle, through U-tube *J* to the inner channel, where it flows completely round and through another U-tube to the other half of the outer channel and finally emerges through another of the tubes, *H*. The circulation in the lower plate is similar.

The furnace consists of two bobbins, *K* and *L* (fig. 13), made of oxidation-resistant steel. The windings are of platinum insulated from the bobbins by mica. The bobbins are fastened by screws in two soapstone members held to the plates of the camera by circular brass clamps *M* and *N*. The leads from the furnace are taken to small Bakelite terminal boards on the clamps. The lower clamp, *N*, supports a platinum platinum-rhodium thermocouple, *P*. The upper clamp, *M*, contains a ball-race carrying a device, *Q*, for centering the sample. The sample is contained in a thin-walled silica tube that is mounted in a brass rod screwed into a small brass block. This contains two mutually perpendicular grooves into which fit small disks on the ends of two screws. The sample is easily brought into the axis of rotation of the camera by adjusting these screws. A third screw clamps the block in position after centering. The sample is turned four times a minute by a small synchronous motor, *R*, that can be swung back out of the way, when it is necessary to remove the specimen holder. The leads from the motor and the upper half of the furnace pass out of the camera through four holes in the front V-block, E.

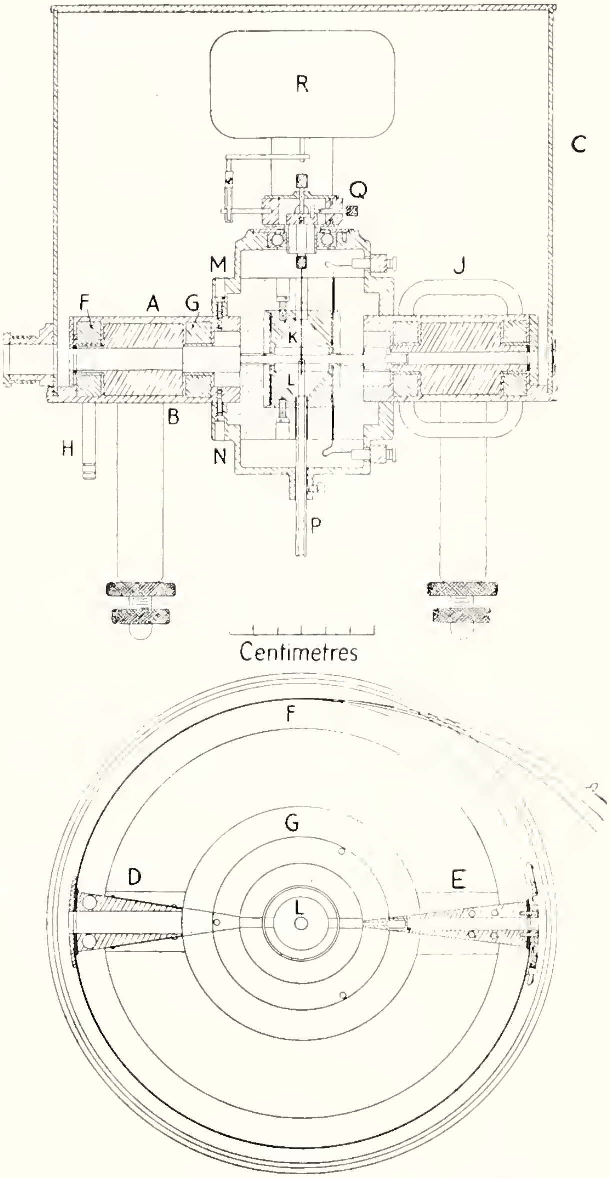

FIGURE 13. *X-ray camera and auxiliary equipment (Wilson).*

The X-rays enter the camera (fig. 13) through a small hole in the front of the cover. Filters are placed in a small pocket on the outside of the cover when necessary. The X-rays pass through a hole in the block, E, and strike the slit system, a small removable brass block fitting the inner end of the hole. The slit itself, about 0.8 by 3 mm, is at the outer end of this block; the wider part toward the center of the camera prevents rays scattered by the edges of the slit from striking the film. The rays then pass out of the camera through a hole in block D larger than that in block E. Two strips fastened to the outside of D prevent any rays scattered by it from striking the film.

The heating currents in the two furnace bobbins, K and L (fig. 13), can be varied independently. At high temperatures it is necessary to place an opaque screen between the furnace and the film to prevent fogging by the light emitted.

From Bragg's law, Shinoda [36] derived the following equation for a sample placed at the center of a circular film:

$$\frac{\Delta d}{d}=\frac{1}{2r}(\cot \Theta)\Delta l \tag{17}$$

where Δd is a small variation of d, r is the radius of the film, and Δl is the displacement of the line (l is the distance between the line and the zero position). If a plate perpendicular to the X-ray beam is substituted for a circular film, eq 17 becomes

$$\frac{\Delta d}{d}=\frac{1}{r}\cot \Theta\,\frac{1}{1+\left(\frac{l}{r}\right)^2}\,\Delta l \tag{18}$$

The coefficient of linear expansion of a cubic crystal may be obtained by dividing $\Delta d/d$ by the change in temperature. Shinoda gives the following relations for other crystals:

For tetragonal

$$\frac{\Delta d}{d}=\frac{1}{1+(h_1c_1)^2}\left[\frac{\Delta a}{a}\,(h_1c_1)^2+\frac{\Delta c}{c}\right], \tag{19}$$

where $c_1=\frac{c}{a}$, $h_1^2=\frac{h^2+k^2}{l^2}$ and h, k, l are indices of planes.

For rhombic

$$\frac{\Delta d}{d}=\frac{1}{\frac{h^2}{a^2}+\frac{k^2}{b^2}+\frac{l^2}{c^2}}\left[\frac{h^2}{a^2}\frac{\Delta a}{a}+\frac{k^2}{b^2}\frac{\Delta b}{b}+\frac{l^2}{c^2}\frac{\Delta c}{c}\right]. \tag{20}$$

For hexagonal

$$\frac{\Delta d}{d}=\frac{1}{1+(h_1c_1)^2}\left[\frac{\Delta a}{a}\,(h_1c_1)^2+\frac{\Delta c}{c}\right], \tag{21}$$

where $c_1=\frac{c}{a}$ and $h_1^2=\frac{4}{3}\left(\frac{h^2+hk+k^2}{l^2}\right)$.

From the values of $\Delta d/d$ in the preceding equations, it is possible to calculate $\Delta a/a$, $\Delta b/b$ and $\Delta c/c$ that correspond to the linear expansion of the a-, b-, and c-axis, respectively. The coefficients of expansion for these axes may be obtained by dividing $\Delta a/a$, $\Delta b/b$, and $\Delta c/c$ by the temperature change.

Becker [33] determined the coefficients of linear thermal expansion of materials from measurements of the angle Θ at room temperature, and at elevated temperatures up to 2,200° C. Table 1 gives an example of his data and derived values for silicon. The following equation was used in computing the average coefficient of expansion:

$$1+a\,(t_2-t_1)=\frac{\sin\frac{\Theta_1}{2}}{\sin\frac{\Theta_2}{2}}, \tag{22}$$

where a is the average coefficient of linear thermal expansion between temperatures t_1 and t_2, Θ_1 is the angle at t_1, and Θ_2 is the angle at t_2.

Table 1. *Data and derived values for silicon*

(hkl)	18° C		950° C			$1+a(t_2-t_1)$
	$\frac{\Theta_1}{2}$	$\sin\frac{\Theta_1}{2}$	$\frac{\Delta\Theta}{2}$	$\frac{\Theta_2}{2}$	$\sin\frac{\Theta_2}{2}$	
111	21° 30′	0.3665	0° 5′	21°25′	0.3651	1.0038
220	36 40′	.5972	9	36 31	.5951	1.0035
311	44 25	.6999	10	44 15	.6978	1.0030
400	57 40	.8450	17	57 23	.8423	1.0032
420	71 0	.9455	31	70 29	.9425	1.0032
					Avg	1.0033

The average coefficient of linear expansion between 18° and 950° C is

$$a=\frac{1.0033-1}{950-18}=3.5\times10^{-6}\text{ per deg C.}$$

Becker stated that the accuracy of his determinations is 8 percent for electrically conducting materials and 15 percent for nonconducting materials. Wilson [35] found that the systematic and random errors of his determinations of d are each about 0.0001 A, and that the errors of the coefficients of expansion are from 1 to 2 percent.

9. Density Method

The density method has been used for determinations of the coefficients of cubical expansion. If the densities of a sample are determined by weighing it in a liquid of known density at two temperatures, 0° and t°, the average coefficient of cubical expansion may be computed from the equation

$$_0\alpha_t=\frac{D_0-D_t}{D_t t}, \tag{23}$$

where ${}_0\alpha_t$ is the average coefficient of cubical expansion between 0° and t°, and D_0 and D_t are the densities of the sample at 0° and t°, respectively. If the sample is isotropic, the coefficient of linear expansion may be taken equal to one-third the coefficient of cubical expansion.

If the volumes of the sample at 0° and t° are obtained during the density determinations or by another method, the average coefficient of cubical expansion may be calculated from the equation

$$ {}_0\alpha_t = \frac{V_t - V_0}{V_0 t}, \qquad (24) $$

where V_0 and V_t are the volumes of the sample at 0° and t°, respectively.

The density method has been used previously by Matthiessen [37, 38] and Dewar [39], for determinations of the coefficients of cubical expansion of various materials. By this method it is possible to make determinations with small irregular pieces of materials.

The methods used in determinations of the densities of materials are given in Bureau Circular 487.

10. Methods for Determinations of Volume Changes in Metals and Alloys During Casting

The foundryman, in producing a satisfactory casting, has a threefold interest in the shrinkage problem—first, he must make the dimensions of his pattern greater than the dimensions of the desired casting; second, he must employ all possible means to attain the maximum density in the casting and to produce a metal free from porosity, piping, and gas holes; and third, he must consider the design of his casting in its relation to the tendency of the casting to crack in the mold, as a result of stresses set up by differential shrinkage, particularly at sharp angles or abrupt changes in cross section. Determinations of volume changes of metals and alloys during casting are therefore important in design, pattern making, and foundry practice.

When a molten metal or alloy is cooled to room temperature, a change of volume takes place. This change is the algebraic sum of three consecutive volume changes that may be defined as follows:

1. Liquid shrinkage is the volume contraction of a metal or alloy on cooling from any temperature in the liquid state to the freezing point of a metal, or to the beginning of the freezing range of an alloy.

2. Solidification shrinkage (or expansion) is the volume contraction (or expansion) of a metal or alloy on passing from the liquid state at the freezing point to the solid state at the melting point. In the case of a pure metal, the freezing point and the melting point occur at the same temperature. When an alloy solidifies over a freezing range, the solidification shrinkage (or expansion) is the volume contraction (or expansion) that occurs from the beginning to the end of freezing. The solidification shrinkage of a eutectic or an intermetallic compound, which freezes at a constant temperature, is similar to that of a pure metal.

3. Solid shrinkage is the volume contraction of a metal or alloy on cooling from the melting point in the solid state to any lower temperature, usually room temperature.

Liquid shrinkage is a definite physical property of a metal or alloy. Solidification shrinkage is essentially a constant for a pure metal, eutectic, or intermetallic compound. However, in alloys of the solid-solution type, the solidification shrinkage is complicated due to the fact that the solid that separates from the melt during freezing continually changes in composition. During this selective crystallization stresses may be set up on account of different coefficients of expansion. Solid shrinkage of a metal or alloy may also be variable. Stresses may exist in a cast alloy of the solid-solution type as a result of progressive solidification and structural transformations after solidification. Such stresses may also be due partly to temperature gradients set up during cooling.

As a result of these stresses in a cast alloy, the observed linear contraction of a bar, designated as patternmaker's shrinkage, may differ from that calculated from available data on linear thermal expansion of the alloy. Another factor which influences the difference between the linear thermal expansion of a metal or alloy and the patternmaker's shrinkage, is the apparent failure of a casting to register the true shrinkage taking place at and slightly below the melting point. The cause of this may possibly be due to the fact that material at the grain boundaries does not possess sufficient rigidity to register the actual contraction of the grains or crystallites.

The contraction of liquid metal as it cools and solidifies is distributed between external pipe and internal voids. Except where conditions are such that a completely rigid shell is formed about a cooling mass of molten metal before the interior has reached the freezing temperature, the shrinkage caused by contraction of the liquid interior will result in a depression in the upper surface (external pipe). Shrinkage that takes place during the change of state may contribute largely to the production of internal voids, when such tendency is exhibited by the metal or alloy.

The distribution of the shrinkage, or contraction, during solidification, in the form of an external pipe, internal pipe, or small cavities (porosity) throughout the casting, will depend largely on the following factors: (a) The magnitude of the shrinkage during solidification, (b) the freezing temperature of the metal, (c) type of metal, whether it is pure, eutectic, intermetallic compound, solid solution, or any combination of these, (d) fluidity of the metal, (e) thermal conductivity, heat capacity, and pouring temperature of the metal, (f) location and design of gates and risers, (g) ratio of surface area to volume, and (h) heat capacity, thermal conductivity, and initial temperature of the mold material.

In 1932 Saeger and Ash [40] described a method for determining the volume changes occurring when a molten metal is cooled to room temperature. They obtained data from which specific volume[2]-temperature curves could be constructed for the range from the molten state to room temperature.

In figure 14, V_a-V_b represents the change in specific volume with change in temperature of a metal in the liquid state as it cools from some temperature, *a*, to the freezing temperature, *b*. The interval V_b-V_c represents the change in specific volume of a metal in passing from the liquid state at temperature *b*, to the solid state at temperature *c*. The interval V_c-V_d represents the change in specific volume of the solid metal as it cools from the melting point *c*, to room temperature, *d*. The change in volume, in percent, for any interval can be calculated from the difference in specific volume for the interval; thus $100(V_a-V_b)/V_a$ represents this change on cooling the metal from temperature *a* to temperature *b*.

(a) Liquid Shrinkage

Saeger and Ash [40] devised an apparatus for determining the specific volumes of molten metals and alloys over a wide range of temperatures. The apparatus is shown in figures 15 and 16. It is essentially a picnometer, but is designated a "crucible immersion apparatus." The crucible, lid, and supporting rods were made of Acheson graphite.

Graphite is unsatisfactory for the sampling of cast iron because of the reaction between the iron and the graphite, which changes not only the dimensions of the crucible but also the composition of the iron. It was found, however, that graphite can be protected from the action of molten cast iron by surfacing it with a refractory "wash." Zirconium-oxide powder to which had been added a small amount of colloidal clay for bond and mixed with water to a "consistency of cream" was found to be satisfactory.

The temperature of the molten metal is measured by means of a platinum platinum-rhodium thermocouple within a glazed-porcelain protection tube placed inside a graphite tube 1 in. in diameter. The graphite tube is treated with the refractory coating described previously, when it is to be immersed in cast iron.

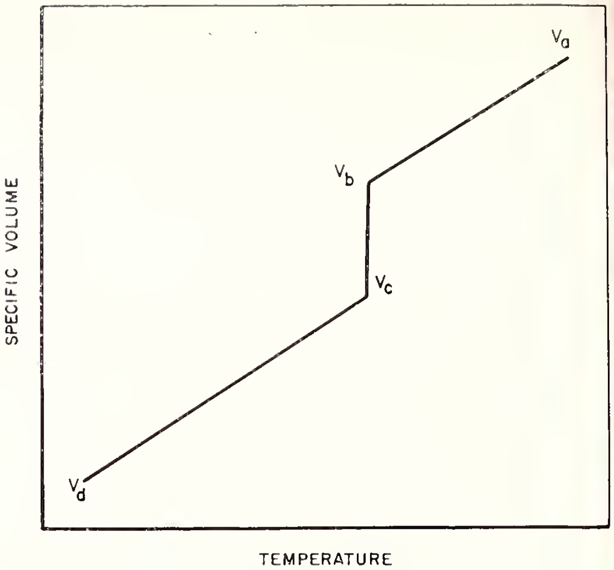

FIGURE 14. *Typical specific volume-temperature curve of a metal (Saeger and Ash).*

(b) Solidification Range

For alloys that solidify over a freezing range, it is necessary to determine the freezing point (the temperature at which incipient crystals form on cooling) and the melting point (the temperature at which incipient fusion begins on heating). These temperatures may be determined by a thermal-analysis method. The interval between the freezing point and the melting point is the solidification range.

With this apparatus it is possible to isolate a known volume of liquid metal at a definite and predetermined temperature from a ladle of molten metal. The procedure is as follows: The crucible is filled by immersing it in a ladle of molten metal and sufficient time is allowed for the crucible to come to the temperature of the surrounding metal, or to allow both crucible and metal to cool to the temperature at which it is desired to obtain a sample. When the desired temperature is reached the lid is pressed down firmly on the crucible, and the whole assembly removed from the ladle of metal.

The sample of metal thus obtained is allowed to freeze within the crucible and to cool to room temperature. Obviously the mass of the metal does not change on cooling. The resulting ingot is weighed at room temperature. The specific volume of the metal at the temperature of sampling is calculated by dividing the volume of the crucible at that temperature by the weight of the ingot.

The volume of the crucible at room temperature was determined by weighing the mercury required to fill it, when the lid was pressed down firmly. The volumes of the graphite crucible at elevated temperatures were calculated from data on linear thermal expansion of graphite.

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[2] Specific volume is the reciprocal of the density, or the volume in milliliters per gram.

Saeger and Ash [40] used cast samples 5 in. long and 1½ in. in diameter to determine the solidification range. A ⅜-in. hole, 4 in. long, was drilled along the longitudinal axis of the cylindrical sample into which was inserted a platinum platinum-rhodium thermocouple protected by means of a glazed-porcelain tube. The sample was mounted in a 4-in. coil of a high-frequency induction furnace and the intervening space filled with zircon sand. The electromotive force developed by the thermocouple was measured by means of a potentiometer. The time in seconds required for each successive change of 0.1 mv was recorded, and inverse-rate heating and cooling curves of the sample were obtained. The freezing point was taken as that temperature at which the first break occurred in the cooling curve, and the melting point as the first break in the heating curve.

(c) Solid Shrinkage

In addition to determining the specific volume-temperature curve for the liquid metal, it is necessary to determine a similar curve for the metal on cooling in the solid state. Thermal-expansion data for many metals are available in the literature, and can be used for calculating the specific volume-temperature relations for solid metals. In the case of gray cast iron, however, thermal-expansion data obtained by heating a gray-iron casting will not answer the purpose because heating causes permanent growth as indicated in figure 17. It is necessary, therefore, to obtain data on the contraction of gray cast iron as it cools from the melt.

The dimensional changes occurring during the cooling of cast iron are affected by the separation of graphite. On freezing and during cooling, the cementite undergoes a partial transformation to ferrite and graphite. As the specific volume of graphite is about three times that of cementite, the transformation results in an increase in volume. This increase varies with the amount of cementite decomposed and therefore is dependent on the composition of the cast iron, particularly the carbon, silicon, and manganese contents, and on the rate of cooling. The dimensional changes

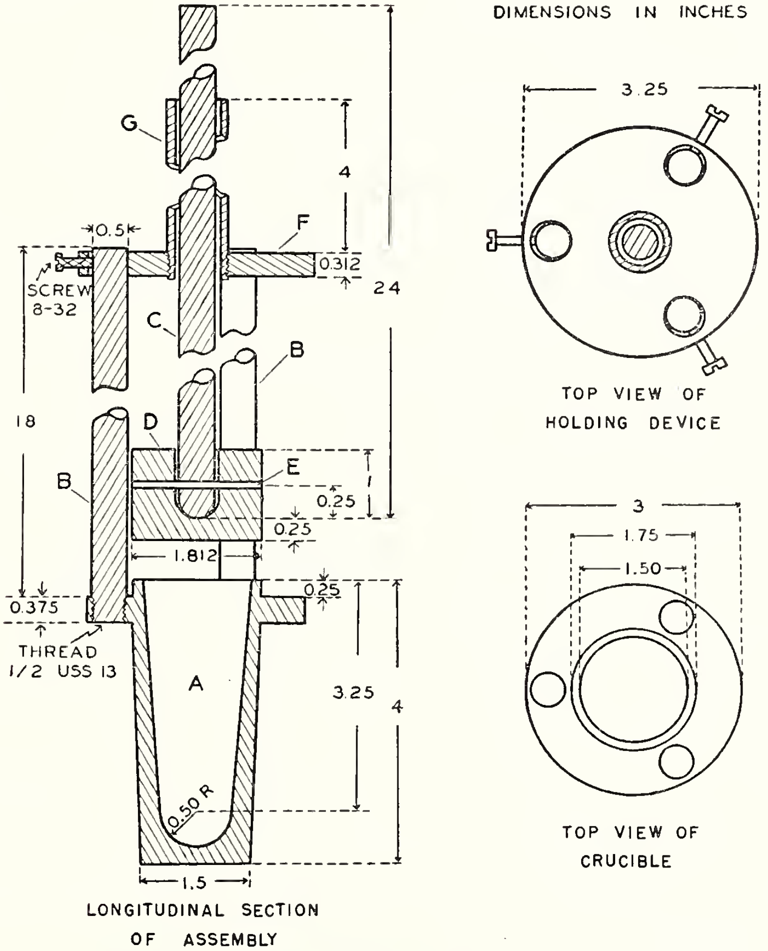

Figure 15. *Crucible immersion apparatus (Saeger and Ash).*

A, Crucible; *B*, support rods; *C*, control rod; *D*, lid; *E*, sustaining pin (4-mm carbon arc rod); *F*, metal base; *G*, metal handle.

Figure 16. *Crucible immersion apparatus and ingot (Saeger and Ash).*

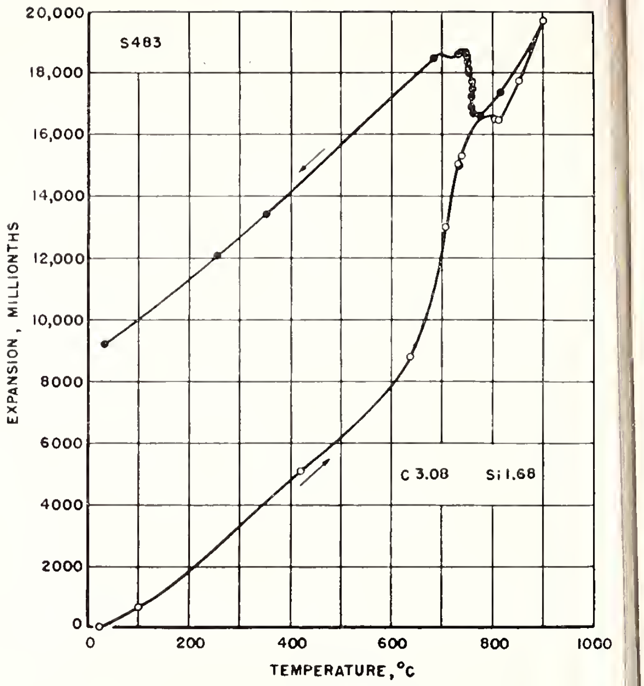

Figure 17. *Curve showing linear thermal expansion and growth of cast iron.*

resulting from the graphite separation are affected by factors that affect the cooling rate, such as pouring temperature, thermal conductivity of the mold and metal, temperature of the mold, size of casting (total heat content), and thickness of cross section.

Figure 18 is a sketch of the apparatus used by Saeger and Ash [40] for determining the linear contraction of cast metals and alloys. The portion of the cast bar beyond the fixed pin can be of any convenient length, and the cross section can be made to any convenient dimensions.

A fused-quartz rod was used to indicate the linear movement of the cast bar on cooling. The rod was allowed to project into the mold cavity about ⅛ in. to insure that it would be firmly gripped by the metal on casting. The small movement of the cast bar as transmitted through the fused-quartz rod was measured by means of a microscope mounted on a micrometer slide.

It was essential that the average temperature of the cast bar be obtained. In order to secure this, three thermocouples were located in the 12-in. cast bar at distances 1½, 6, and 10½ in., respectively, from the free end of the bar. Saeger and Ash assumed that an average of the three temperatures measured in this manner represented the average temperature of the bar. In practice, the three thermocouples, all of the same length and size, were joined in parallel, and the average temperature of all three was obtained by one

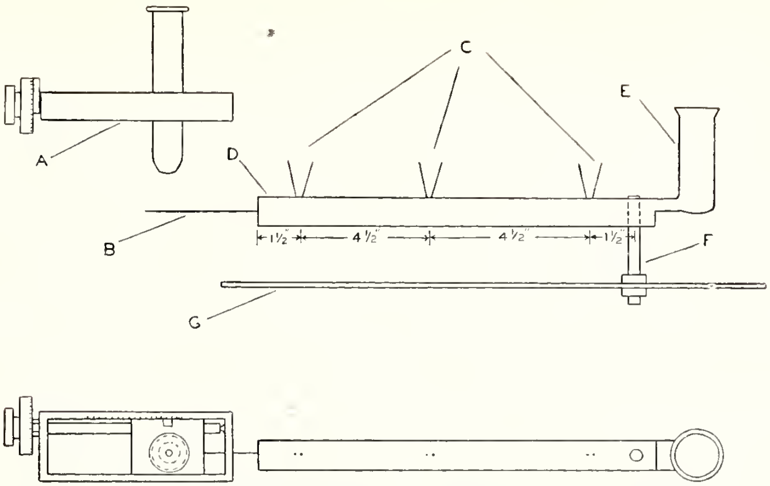

FIGURE 18. *Sketch of apparatus for determining linear contraction of metals and alloys (Saeger and Ash).*

A, Micrometer slide and microscope; *B*, fused-quartz rod; *C*, thermocouples; *D*, shrinkage bar; *E*, pouring gate; *F*, fixed steel pin; *G*, steel plate.

reading of the instrument. Chromel-alumel thermocouples and a portable potentiometer indicator were used to indicate temperatures. The wires of the thermocouples were insulated from each other and from the molten metal by means of a sodium silicate silica-flour cement. The welded tip of each thermocouple extended into the mold cavity to one-half the thickness of the resulting bar.

The procedure was as follows: A shrinkage bar was cast by pouring molten metal from a ladle into a green-sand mold. The temperatures of the cast bar were read simultaneously with observations on the movement of the fused-quartz rod. The contraction curve was obtained from these data.

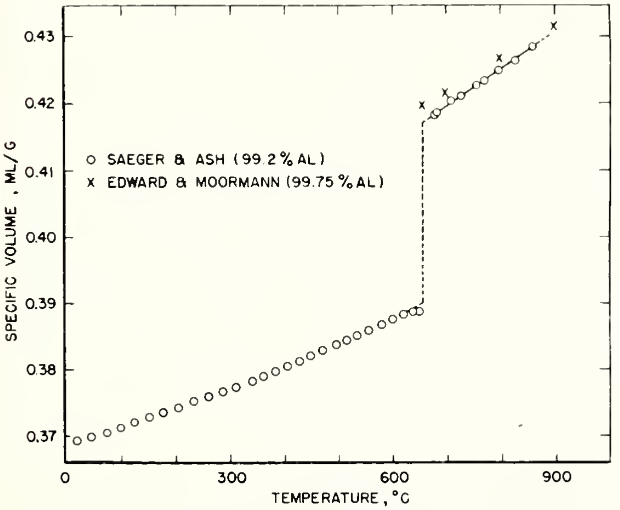

FIGURE 19. *Specific volume-temperature curve for aluminum (Saeger and Ash).*

Solidification shrinkage 6.6 percent; solid shrinkage (658° to 25° C) 5.5 percent.

(d) Specific Volume-Temperature Curves

Saeger and Ash [40] determined the specific volume-temperature curves for some nonferrous metals and cast irons. The procedure used in obtaining the specific volume-temperature curve for aluminum will be briefly indicated as an example.

The specific volume of liquid aluminum at 770° C was calculated as follows from experimental data obtained with the crucible immersion apparatus:

Specific volume of aluminum at 770° C

$$=\frac{\text{Volume of liquid aluminum sample at } 770^\circ\text{ C}}{\text{Weight of liquid aluminum sample at } 770^\circ\text{ C}}$$

$$=\frac{\text{Volume of graphite crucible at } 770^\circ\text{ C}}{\text{Weight of aluminum ingot at room temperature}}$$

$$=\frac{68.18}{160.99}=0.4235\text{ ml/g.}$$

In a similar manner, the specific volume of liquid aluminum was determined at other sampling temperatures. By plotting these values, the upper portion of the curve in figure 19 was obtained. This portion of the curve represents the specific volume of liquid aluminum at various temperatures.

Measurements of changes of length with temperature were made on a 1-in. square bar of aluminum of 99.2 percent purity during the period of cooling from its melting point (658° C) to room temperature. As may be observed from the lower portion of the curve in figure 19, the solid specific volume-temperature curve tends to flatten out just below the melting point, as the cast bar may not have been sufficiently rigid at this high temperature to register the true contraction taking place. This condition was overcome by extrapolating the main portion of the curve to the melting point. The observed linear contraction of the bar (12 in. long at the casting temperature) from the melting point to room temperature was 0.213 in. (1.78 percent) and as corrected for the extrapolated portion, 0.222 in., or 1.85 percent.

The cubical contraction was taken as three times the linear contraction. The value 5.55 percent (3 · 1.85 percent) represents the decrease in volume undergone by aluminum in cooling from the melting point to room temperature, and agrees closely with the value 5.57 percent for the cubical contraction of aluminum of the same purity calculated, by extrapolation from linear thermal-expansion data given by Hidnert [41].

The specific volume of a sample cut from this cast bar of aluminum, after forging at 400° C and annealing at 450° C, was determined as 0.3683 ml/g at 20° C. The corresponding specific volume of aluminum in the solid state at 658° C is 0.3899 ml/g, computed on the basis of the specific volume of the metal at 20° C and the cubical contraction of 5.55 percent on cooling from 658° to 20° C.

By extrapolating that portion of the curve (fig. 19) representing the specific volume of liquid aluminum, to the freezing point (658° C), the specific volume of liquid aluminum at the freezing point was found to be 0.4173 ml/g. The difference between the specific volumes of liquid and solid aluminum at 658° C, the change in the specific volume caused by solidification shrinkage, is equal to 0.4173−0.3899=0.0274 ml/g. This is equivalent to 6.6 percent, based on the specific volume of the liquid at the freezing point.

The specific volume-temperature curve of aluminum from about 900° C to room temperature is shown in figure 19. Several values reported by Edwards and Moormann [42] were also plotted in this figure for comparison.

The linear contraction of commercial aluminum in the solid state, reported by Anderson [43] is appreciably less than the value calculated from data on linear thermal expansion. He found that his results for the linear contraction of aluminum and many of its alloys varied as follows: other conditions being equal, (a) the smaller the cross section of a cast bar of given length, the less the contraction, (b) the greater the length for a given cross section, the less the contraction, and (c) the contraction was less in chill molds than in sand-cast molds.

(e) Other Methods

Coleman [44] found a linear casting shrinkage of 1.25 percent for a gold-copper alloy containing 10 percent of copper, whereas the linear contraction of the solid alloy from the melting point to 20° C, computed from thermal expansion data, was 1.62 percent. The apparatus used for measuring the linear casting shrinkage is shown in figure 20. The procedure was as follows: The large caps were screwed tightly into the ends of the flask, and the small hollow plugs screwed into the caps and locked in position with lock nuts. A metal rod, inserted through and supported by the hollow plugs, served as the pattern. The sprue was attached to the pattern with wax, the crucible former placed in position and the flask filled with dental investment. After the investment had set, the crucible former, sprue, and pattern rod were removed. The hollow plugs were replaced with the solid plugs, thus forming a mold, the length of which is determined solely by the distance between the inside

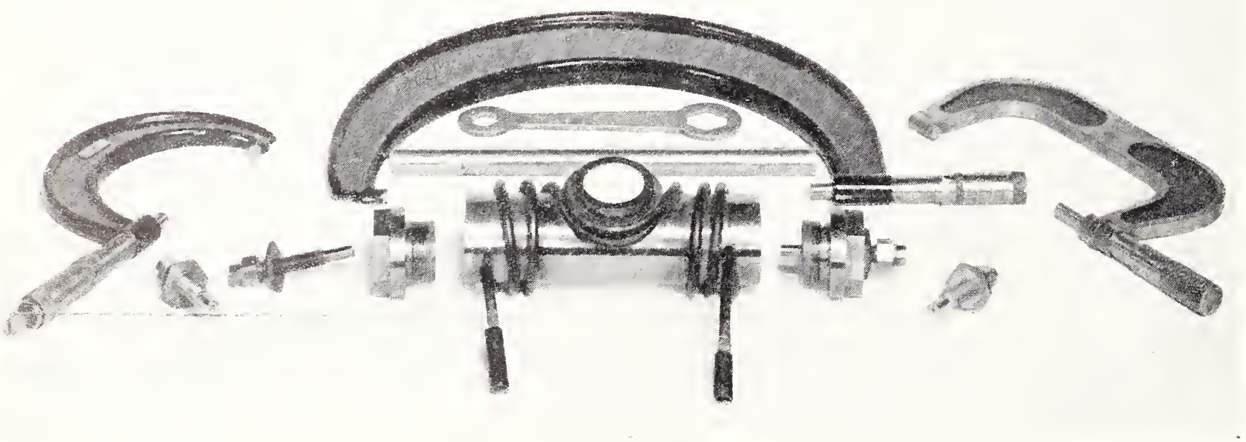

Figure 20. *Apparatus for determining the linear casting shrinkage of gold alloys (Coleman).*

faces of the solid plugs. The flask was then placed in an oven and "burned out" at the desired temperature. Castings approximately 3¼-in. long and 0.12 in. in diameter, were made with an air-pressure machine.

The metal parts of the apparatus are of an oxidation-resisting steel, the coefficient of linear thermal expansion of which is known. The temperatures of various parts of the flask were measured with small thermocouples and a potentiometer. The length, at room temperature, of each of the solid plugs was determined accurately. The distance between the outside faces of the solid plugs was measured with a micrometer. From these values the distance between the inside faces of the solid plugs, or the length of the mold, was computed.

Two possible explanations of the difference between the observed linear casting shrinkage of the gold alloy, and the calculated linear contraction from thermal-expansion data were suggested by Coleman [44]: (1) There may be sufficient friction or interlocking between the casting and the walls of the mold to hold and stretch the casting while it is cooling through that range of temperature within which the metal is very soft or weak, thus preventing the full normal shrinkage, and (2) the compensation of part of the total shrinkage of the solid metal may be dependent upon a difference in the rates of cooling of different parts of the casting. If part of the metal in the mold solidifies and cools to some temperature below the melting point before the metal in the sprue freezes, the shrinkage caused by the cooling of this solid metal may be compensated by the addition of metal from the crucible.

Other methods that have been employed for measuring the volume changes undergone by a metal in cooling from the liquid state to room temperature have been reviewed by Saeger and Ash [40] under four headings—dilatometric; buoyancy; picnometer; sand-cast sphere, cone, or cylinder.

III. Data on Thermal Expansion

From observations on the linear thermal expansion of a sample of material it is possible to derive an empirical equation showing the relation between linear expansion and temperature. For example, the following second-degree equation was derived for molybdenum (fig. 21) by the method of least squares:

$$\Delta L=4.090(t+142.5)10^{-6}+0.00226(t+142.5)^2 10^{-6}, \tag{25}$$

where ΔL represents the change per unit length from the length at the initial temperature −142.5° C, and t represents any temperature between −142.5° and +305° C. The probable error per unit length of molybdenum was found to be $\pm 8.3\times 10^{-6}$. This value may be affected by the departure of the expansion curve from the assumed parabolic law.

The first derivative of eq 25 gives

$$\frac{d}{dt}[\Delta L]=4.090\times 10^{-6}+0.00452(t+142.5)10^{-6} \tag{26}$$

and represents the tangent or instantaneous coefficient of expansion a_t, at any temperature t, between −142.5° and +305° C.

Eq 25 can be transformed into the following form:

$$L_t=L_0[1+(4.73t+0.00226t^2)10^{-6}], \tag{27}$$

where L_t is the length of the sample at any temperature t, between −142.5° and +305° C, and L_0 the length at 0° C. In this equation, 4.73×10^{-6} represents the instantaneous coefficient of expansion at 0° C.

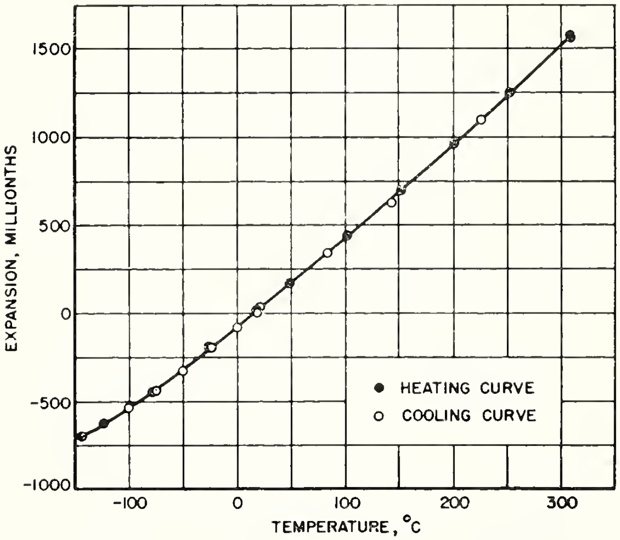

Figure 21. *Linear thermal expansion of molybdenum.*

From observations with the initial temperature at any temperature (usually room temperature), Souder [45] in 1918 derived two normal equations from which it is possible to compute directly two constants of a second-degree equation in terms of L_0, the length of a sample at 0° C. These normal equations are

$$a\Sigma(\Delta t)^2+b\Sigma\Delta t^2\Delta t=\Sigma e\Delta t \tag{28}$$

$$a\Sigma\Delta t^2\Delta t+b\Sigma(\Delta t^2)^2=\Sigma e\Delta t^2, \tag{29}$$

where a and b are constants, $\Delta t = t_n - t_1$, or the change in observed temperature from the initial temperature t_1, $\Delta t^2 = t^2_n - t^2_1$, or the change in the square of the observed temperature from the square of the initial temperature t_1, and e is the corresponding observed linear expansion per unit length from the initial temperature.

The constants a and b may be obtained by solving these normal equations by determinants. This method gives

$$a = \frac{\Sigma(\Delta t^2)^2 \Sigma e \Delta t - \Sigma \Delta t^2 \Delta t \Sigma e \Delta t^2}{\Sigma(\Delta t^2)^2 \Sigma(\Delta t)^2 - [\Sigma \Delta t^2 \Delta t]^2} \tag{30}$$

and

$$b = \frac{\Sigma(\Delta t)^2 \Sigma e \Delta t^2 - \Sigma \Delta t^2 \Delta t \Sigma e \Delta t}{\Sigma(\Delta t^2)^2 \Sigma(\Delta t)^2 - [\Sigma \Delta t^2 \Delta t]^2}. \tag{31}$$

The values computed for a and b may then be substituted in eq 3.

Coefficients of expansion of various materials are given in the following publications:

International Critical Tables.
Landolt-Börnstein Physikalisch-Chemische Tabellen.
Smithsonian Physical Tables.
National Bureau of Standards Circular C447, Mechanical Properties of Metals and Alloys.
Handbooks.

A chart indicating the linear thermal expansion of 18 materials on heating from 0° to 100° C is shown in figure 22.

IV. Relations between Thermal Expansion and Other Properties

From the data obtained on a sample by means of one of the dilatometric methods, it is possible to plot a curve which shows the relationship between expansion and temperature, on heating and cooling. The curve on cooling may or may not coincide with the curve on heating, depending on the nature and the previous treatment of the sample. From the expansion curve it is possible to compute average coefficients of expansion for various temperature ranges, or an empirical equation may be derived from the original data.

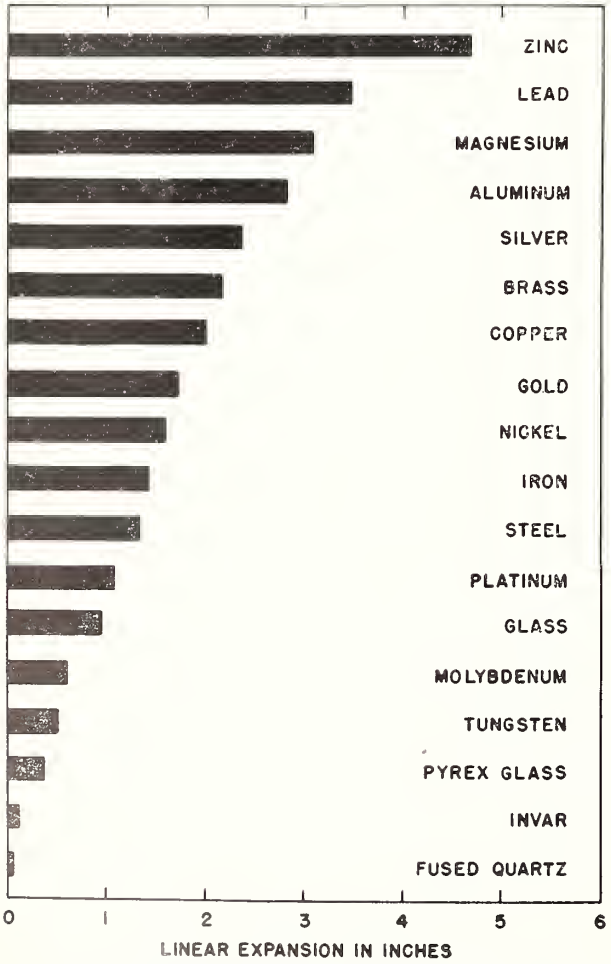

FIGURE 22. *Linear thermal expansion of 100 feet of various materials from 0° to 100° C.*

Dilatometric methods permit the investigation of slow or rapid reactions, and a quantitative description of transformations. These changes observed during the heating and cooling of a sample are caused by transformations of the constituents (allotropic phase transformations, anomalous transformations without change of phase, and decomposition of phases) and by the reactions between phases. Iron is an example of a metal which undergoes a transformation with change of phase. When alpha iron (body-centered cubic crystal structure) is heated, it undergoes an allotropic transformation $\alpha \rightarrow \gamma$ at about 910° C, with a contraction for several degrees higher. On being further heated above this temperature (Ac_3), gamma iron (face-centered cubic crystal structure) expands. On cooling, gamma iron undergoes an allotropic transformation $\gamma \rightarrow \alpha$ at about 900° C with an expansion. On further cooling below this temperature (Ar_3), alpha iron contracts.

Figure 23 shows the linear expansion of a carbon steel on heating and cooling between 20° and 900° C. This steel expanded regularly to 729° C (Ac_1) and then contracted to 759° C (Ac_3). During this range from 729° to 759° C, alpha iron transformed to gamma iron, and iron carbide went into solution in gamma iron. At 759° C, the steel resumed its expansion at higher temperatures. On cooling, the steel contracted regularly to 685° C (Ar_3), when expansion started with a transformation to alpha iron. The expansion continued on cooling to 659° C (Ar_1). On further cooling to 20° C, the steel contracted in a normal manner.

Dilatometric data may be used not only for obtaining relationships between thermal expansion and temperature, and for investigations of the constitution of metals and alloys, of dimensional changes on hardening steels, aging phenomena of alloys and steels, kinetics of transformations of austenite during cooling of steels and during isothermal holding below the eutectoid temperature, and of graphitization of cast iron; but also for obtaining relationships between thermal expansion, chemical composition, thermal and mechanical treatments of materials, and the like. For example, the following equation shows the relationship between linear thermal expansion and chemical composition of cold-rolled copper-zinc alloys:

$$a_{50}=(22.923-0.06833X+0.0000695X^2)10^{-6} \quad (32)$$

where a_{50} is the instantaneous coefficient of expansion at 50° C, and X is the copper content between 62 and 97 percent by weight.

Grüneisen's law [46], first deduced empirically in 1908, states that for a metal the ratio of the coefficient of linear expansion to its specific heat at constant pressure is constant at all temperatures. Various theories of the solid state lead to the relation

$$3a=dbkc\ , \quad (33)$$

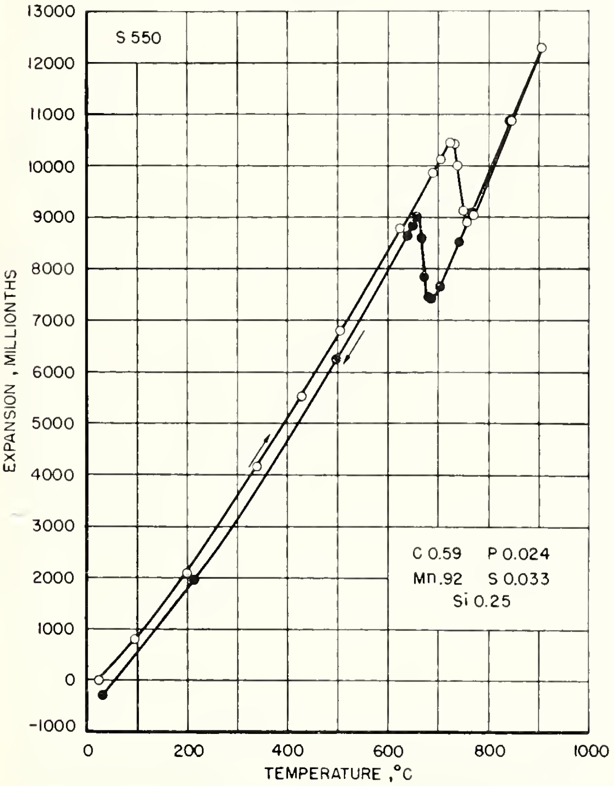

FIGURE 23. *Linear thermal expansion and transformations of steel.*

where a is the coefficient of linear expansion, d is the density, b is the compressibility, k is approximately a constant, and c_v is the heat capacity at constant volume. Wilson [35] showed that this relation may be derived by a method which is thermodynamical, except for the assumption of the Debye or some similar expression for c_V. Neither Grüneisen's law or eq 33 is well obeyed at high temperatures.

Hume-Rothery [47] adopted the following modification of Grüneisen's relation used by Simon and Vohsen [48]:

$$\frac{V_T-V_0}{V_0}=\frac{E_T}{Q_0-kE_T}, \quad (34)$$

where

V_0=volume at absolute zero

V_T=volume at $T°K$

$$E_T=\int_0^T c_v dT$$

$Q_0=\frac{c_p}{3a}+2kE_T$ (where c_p and a are the values of the specific heat and coefficient of expansion at room temperature)

$$k=\text{constant}=\gamma+\frac{2}{3},$$

where

$$\gamma=\frac{-V\dfrac{\partial V}{\partial T}}{c_v\dfrac{\partial V}{\partial p}}.$$

Hume-Rothery stated that for most metals Q_0 is of the order 10^4 to 10^5 cal, k is a small number of the order 1 to 3, and E_T is of the order 1,000 at room temperature and increases by about 600 for each 100 deg rise of temperature. He found very good agreement between the observed and calculated changes in volume of the cubic metals silver, copper, and aluminum between absolute zero and a temperature of the order two-thirds of the melting point on the absolute scale, but for iron he found good agreement only up to the temperature at which the magnetic transformation begins.

Carnelley [49] and Lémeray [50] showed an approximate relation between the coefficients of linear expansion and the melting points of the chemical elements. Available coefficients of linear thermal expansion of the chemical elements at room temperature or for the range from 20° to 100° C versus their melting points (° K) are plotted in figure 24. The hyperbolic curve was derived from data on body-centered cubic and face-centered cubic elements, except manganese and the alkali metals. The curve indicates that the coeffi-

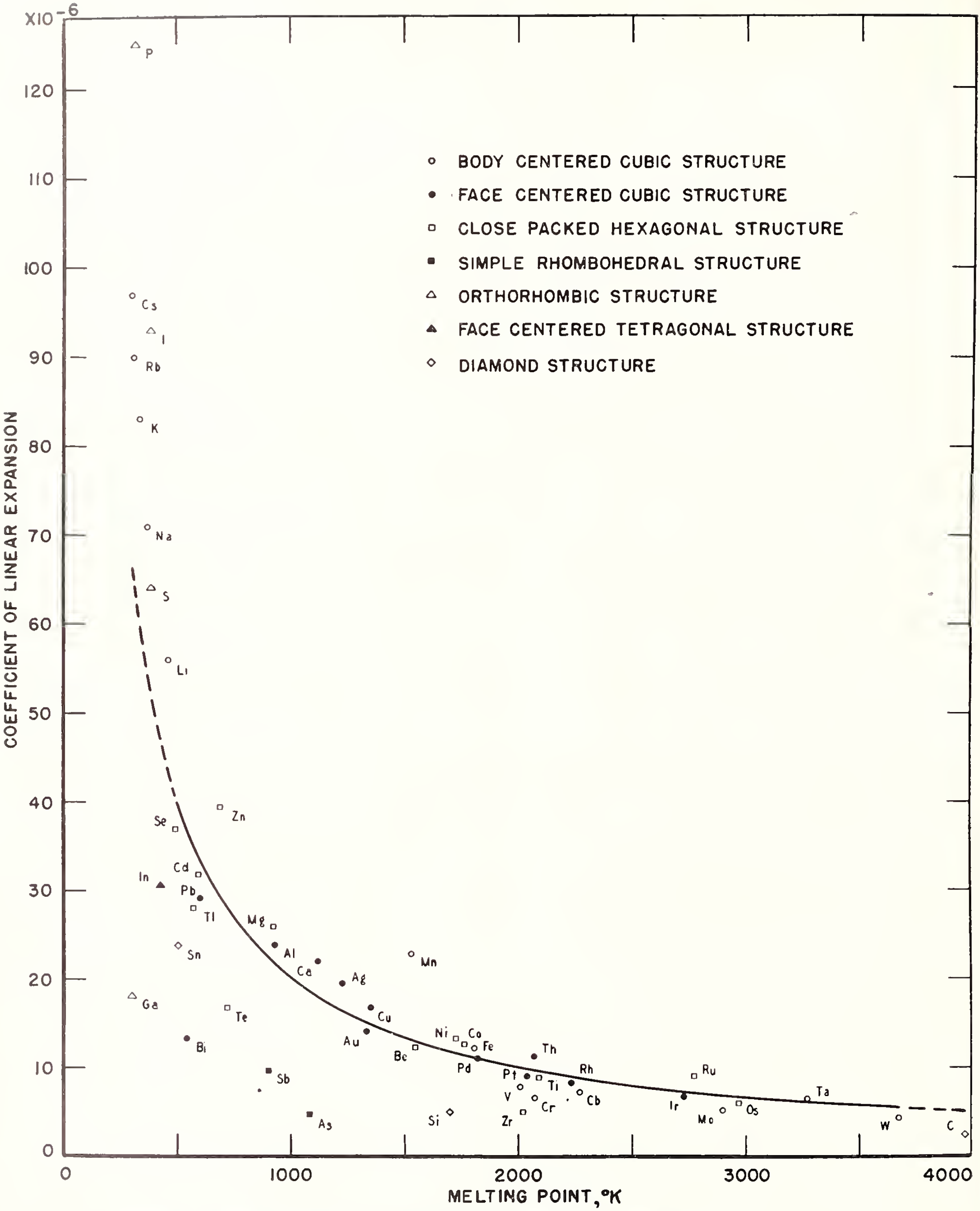

Figure 24. *Relation between coefficients of linear thermal expansion (at room temperature or for the range from 20° to 100° C) and melting points of chemical elements.*

Curve derived from data on body-centered cubic and face-centered cubic elements, except manganese and the alkali metals.

cients of linear expansion of the elements decrease as their melting points increase. The coefficients of expansion of the low-melting elements are relatively very large compared to those of the high-melting elements. Most of the elements having body-centered cubic, face-centered cubic or close-packed hexagonal structures lie close to the curve. The elements In, Sn, Ga, Bi, Te, Sb, As, and Si lie appreciably below the curve. Most of the elements that do not lie close to the curve have melting points below 1,000° K. The curve may be represented by the equation

$$a=\frac{0.020}{T}, \tag{35}$$

where a is the coefficient of linear expansion of a chemical element and T is its melting point (° K).

Wiebe [51] found the following relation between the coefficients of cubical expansion, specific heats, melting points, and atomic weights of the chemical elements that crystallize in the regular system:

$$\alpha=\frac{1}{2.6AcT}, \tag{36}$$

where α is the coefficient of cubical expansion, A is the atomic weight, c is the specific heat, and T is the melting point (° K). Since the coefficient of cubical expansion is three times the coefficient of linear expansion,

$$a=\frac{1}{7.8AcT}. \tag{37}$$

Table 2 gives a comparison of the observed and computed coefficients of linear expansion of 28 chemical elements that showed a difference of less than 6×10^{-6}. These elements have body-centered cubic, face-centered cubic, or hexagonal crystal structures (only one exception). The average difference between the observed and computed coefficients of expansion of these elements is $\pm2.1\times10^{-6}$. The differences for other chemical elements on which data (atomic weight, specific heat, melting point, and coefficient of expansion) are available are considerably greater than the differences indicated in the last column of table 2.

With the aid of the law of Petit and Dulong [52], which states that the product of the atomic weight and the specific heat of an element is approximately constant, Wiebe [53] transformed eq 36 into

$$\alpha=\frac{1}{16.6T}, \tag{38}$$

where α is the coefficient of cubical expansion, and T is the melting point (°K).

TABLE 2. *Comparison of observed and computed (eq 37) coefficients of linear expansion of 28 elements*

Element	Crystal structure [a]	Observed coefficient of linear expansion, 20° to 100° C	Computed coefficient of linear expansion $\left(a=\frac{1}{7.8AcT}\right)^{b}$	Difference
		$\times10^{-6}$	$\times10^{-6}$	$\times10^{-6}$
Aluminum	F	23.8	22.5	+1.3
Cadmium	H	31.8	34.9	−3.1
Calcium	F (H)	[c] 22	18	+4
Chromium	B (H)	6.6	9.9	−3.3
Cobalt	H (F)	12.6	12.5	+0.1
Copper	F	[d] 16.8	16.2	+.6
Gold	F	14.1	15.7	−1.6
Iridium	F	6.8	7.6	−0.8
Iron	B (F)	12.2	11.8	+.4
Lead	F	29.1	34.4	−5.3
Lithium	B	56	51	+5
Magnesium	H	26.0	22.9	+3.1
Molybdenum	B	5.2	7.1	−1.9
Nickel	H (F)	13.3	11.3	+2.0
Osmium	H	[c] 6.1	7.3	−1.2
Palladium	F	11.1	11.1	0.0
Platinum	F	9.1	10.0	−.9
Rhodium	F	8.3	9.3	−1.0
Ruthenium	H	[c] 9.1	7.5	+1.6
Selenium	H	[c] 37	39	−2
Silver	F	19.6	17.2	+2.4
Sulfur	O	[c] 64	59	+5
Tantalum	B	6.6	6.0	+0.6
Thorium	F	11.3	9.5	+1.8
Titanium	H (B)	8.8	9.0	−0.2
Tungsten	B	4.3	5.6	−1.3
Vanadium	B	[c] 7.8	10.9	−3.1
Zirconium	H (B)	5	10.5	−5.5

[a] B=body-centered cubic; F=face-centered cubic; H=close-packed hexagonal; O=orthorhombic. The designation in parenthesis indicates a modification at higher temperatures.

[b] In this equation, a=coefficient of linear expansion, A=atomic weight, c=specific heat, and T=melting point (° K). Specific heats at room temperature were used in computing the values given in this column.

[c] At 20° C.

[d] From 25° to 100° C.

If the coefficients of linear expansion (at room temperature or for the range from 20° to 100° C) versus the atomic numbers of the chemical elements are plotted, the periodic curve shown in figure 25 is obtained. Lithium, sodium, phosphorus, potassium, rubidium, iodine, and cesium appear at the maxima of the curve. Carbon, silicon, chromium, molybdenum, and tungsten are some of the elements that appear at the minima of the curve. A similar relationship is obtained if the products of the atomic volumes [3] and the coefficients of linear expansion versus the atomic numbers are plotted.

Cork [54] gives an equation for the difference of the specific heats of solids at constant pressure and constant volume. This equation may be written as follows:

$$a=\frac{1}{3}\sqrt{\frac{(C_p-C_v)J}{cVT}}, \tag{39}$$

where a is the coefficient of linear expansion at $T°K$, C_p is the specific heat at constant pressure, C_v is the specific heat at constant volume, J is

---

[3] The atomic volume of a chemical element is equal to its atomic weight divided by its density.

the mechanical equivalent of heat, e is the coefficient of volume elasticity or bulk modulus, and V is the volume occupied by a gram or a gram-mole of the material (depending whether the specific heat at constant pressure is per gram or per gram-mole).

From available data on eight metals, Pictet [55] in 1879 derived a relation between thermal expansion, melting point, density, and atomic weight. The following equation was derived in 1947 from available data on the body-centered cubic and face-centered cubic elements except the alkali metals:

$$a=\frac{0.0465\sqrt[3]{\frac{d}{A}}}{T}, \qquad (40)$$

where a is the coefficient of linear expansion, d is the density (g/cm ^{3}), A is the atomic weight, and T is the melting point (°K). Table 3 gives a comparison of the observed and computed coefficients of linear expansion of these body-centered and face-centered cubic elements. Calcium, chromium, and manganese show large differences between the observed and computed coefficients of expansion. The average difference between the observed and computed coefficients of expansion of the 19 elements is $\pm 2.5\times 10^{-6}$.

In connection with an investigation of bonding between plastics and metals, Turner [56] developed the following formula for the coefficient of cubical expansion, α_r, of a mixture in terms of the coefficients of cubical expansion, α, fraction

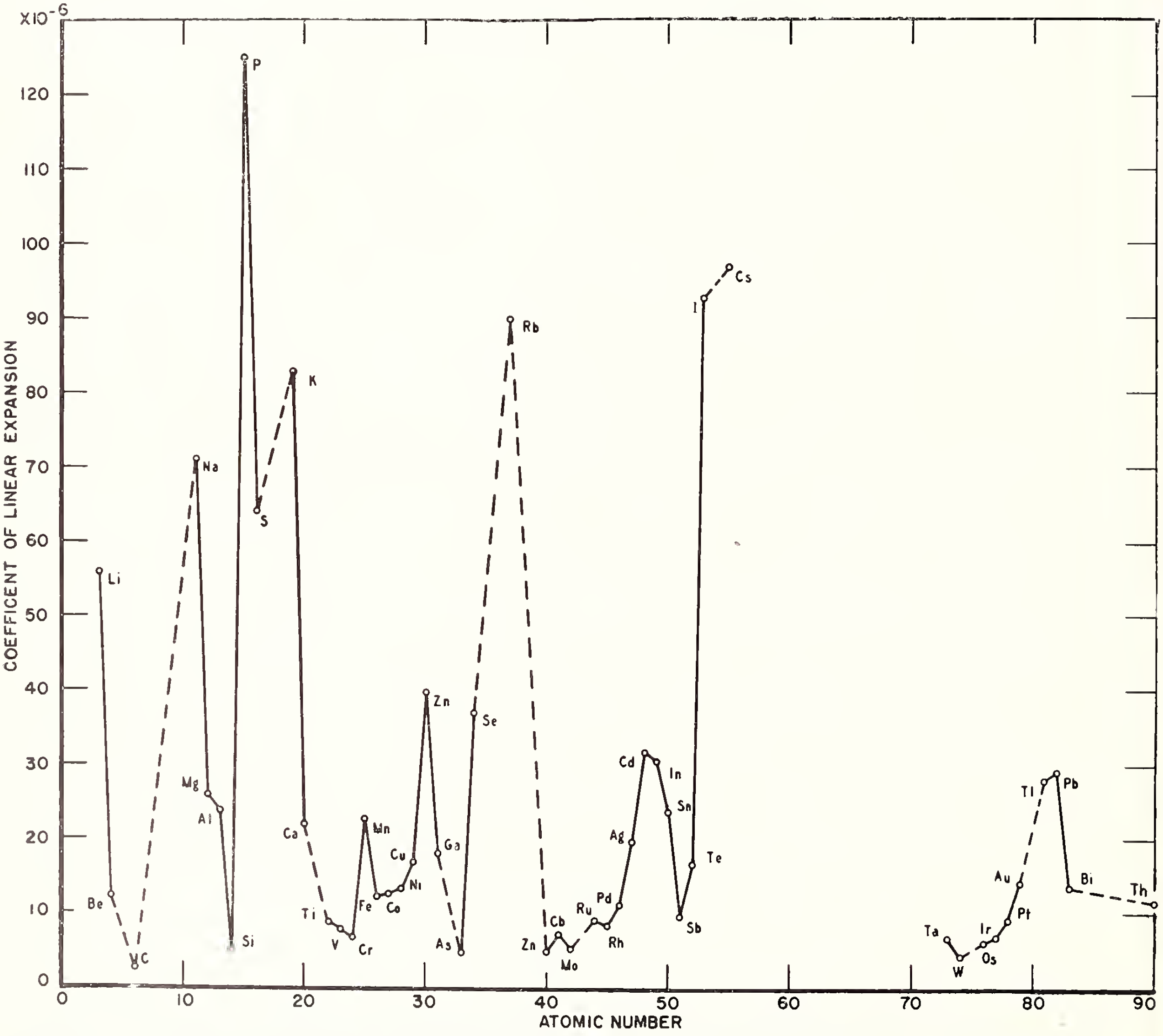

FIGURE 25. *Relation between coefficients of linear thermal expansion (at room temperature or for the range from 20° to 100° C) and atomic numbers of chemical elements.*

Table 3. *Comparison of observed and computed (eq 40) coefficients of body-centered cubic and face-centered cubic elements (except alkali metals)*

Element	Crystal structure [a]	Observed coefficient of linear expansion, 20° to 100° C	Computed coefficient of linear expansion $\left(a=\frac{0.0465\sqrt[3]{\frac{d}{A}}}{T}\right)^{b}$	Difference
		$\times 10^{-6}$	$\times 10^{-6}$	$\times 10^{-6}$
Aluminum	F	23.8	23.1	+0.7
Calcium	F(H)	[c] 22	14.0	+8.0
Chromium	B(H)	6.6	11.6	−5.0
Columbium	B	[d] 7.2	9.2	−2.0
Copper	F	[e] 16.8	17.8	−1.0
Gold	F	14.1	16.0	−1.9
Iridium	F	6.8	8.3	−1.5
Iron	B(F)	12.2	13.4	−1.2
Lead	F	29.1	29.4	−0.3
Manganese	B(T)	22.8	15.6	+7.2
Molybdenum	B	5.2	7.6	−2.4
Palladium	F	11.1	12.3	−1.2
Platinum	F	9.1	10.9	−1.8
Rhodium	F	8.3	10.3	−2.0
Silver	F	19.6	17.3	+2.3
Tantalum	B	6.6	6.4	+0.2
Thorium	F	11.3	8.2	+3.1
Tungsten	B	4.3	6.0	−1.7
Vanadium	B	[c] 7.8	11.1	−3.3

[a] B=body-centered cubic; F=face-centered cubic; H=close-packed hexagonal: T=face-centered tetragonal. The designation in parentheses indicates a modification at higher temperatures.

[b] In this equation, a=coefficient of linear expansion, d=density, A=atomic weight, and T=melting point (°K).

[c] At 20° C.

[d] From 0° to 100° C.

[e] From 25° to 100° C.

or percentage by weight, P, bulk modulus, K, and density, d, of the individual components:

$$\alpha_r=\frac{\frac{\alpha_1 P_1 K_1}{d_1}+\frac{\alpha_2 P_2 K_2}{d_2}+\;\cdots\;+\frac{\alpha_n P_n K_n}{d_n}}{\frac{P_1 K_1}{d_1}+\frac{P_2 K_2}{d_2}+\;\cdots\;+\frac{P_n K_n}{d_n}}. \qquad (41)$$

If the coefficients of cubical expansion of all components are equal to the same constant times their coefficients of linear expansion, then a can be substituted for α in eq 41 to obtain

$$a_r=\frac{\frac{a_1 P_1 K_1}{d_1}+\frac{a_2 P_2 K_2}{d_2}+\;\cdots\;+\frac{a_n P_n K_n}{d_n}}{\frac{P_1 K_1}{d_1}+\frac{P_2 K_2}{d_2}+\;\cdots\;+\frac{P_n K_n}{d_n}}, \qquad (42)$$

where a is the coefficient of linear expansion.

Equation 41, based on stress equilibrium, reduces to a percentage by volume calculation if the ingredients have the same bulk moduli. If the ingredients have the same modulus to weight ratios, the calculation amounts to a percentage by weight interpolation.

The size and shape of the filler particles in plastic mixtures have an effect on the resultant coefficient of expansion of the mixture. Equations 41 and 42 do not take this phenomenon into consideration. Difficulty is also encountered because the bulk moduli of some materials are not available. To solve these problems, eq 41 and 42 may be modified by substituting an empirically determined constant C for K/d for each material. Constant C is interpreted as proportional to the modulus-density ratio rather than being equal to it.

For a mixture with components having nearly equal values of Poisson's ratio the bulk moduli are nearly proportional to the corresponding Young's moduli. For such mixtures Young's modulus, E, may therefore be substituted for bulk modulus in eq 42 to yield the following expression for the coefficient of linear expansion of a mixture:

$$a_r=\frac{\frac{a_1 P_1 E_1}{d_1}+\frac{a_2 P_2 E_2}{d_2}+\;\cdots\;+\frac{a_n P_n E_n}{d_n}}{\frac{P_1 E_1}{d_1}+\frac{P_2 E_2}{d_2}+\;\cdots\;+\frac{P_n E_n}{d_n}}. \qquad (43)$$

Thus, in many cases where the bulk moduli are not available, eq 43 may be used instead of eq 42.

V. Applications of Thermal Expansion

The problems in which the thermal expansion of materials must be recognized are as varied as our industries. The precision chronometer is useless without proper temperature compensation. The elaborate suspension bridge carrying thousands of tons of traffic hourly would be unsafe if in its design and construction provisions for changes in dimensions of its members incident to temperature changes had not been made. Precision instruments such as indicators for measuring lengths, composed of parts having differing expansivities may give erratic indications unless the temperature is maintained constant.

One of the most important uses of thermal expansion is in thermostats of various types (differential expansion, bimetallic flexure, and fluid expansion). Thermostats may be used in actuating circuit controllers for electrical devices such as electric furnaces, electric irons, electric refrigerators, vulcanizers, alarm devices, and stack controls, in the operation of mechanical controls such as means for regulating the flow of gas to gas ovens, and in pyrometers for indicating temperatures.

1. Thermostats by Differential Expansion

A large differential thermal expansion between two materials offers a basis for controlling and indicating temperature over a useful temperature range. For example, the change may be linear by placing one material within the other, as an aluminum rod within a fused-quartz tube. If the two materials are attached at one end and heated or cooled, a differential motion is obtained at the other end. The linear motion may be converted into angular movement that may be magnified mechanically, if necessary.

2. Thermostats by Bimetallic Flexure

Thermostat metal (or bimetal) may be prepared from two strips of metals or alloys having widely different coefficients of expansion, by welding the strips throughout their entire length. Heating or cooling a thermostat metal produces a change of curvature of the thermostat metal, as indicated in figure 26. Heating a straight narrow piece of thermostat metal will cause it to bend and form an arc of a circle with the low-expanding metal on the inner side. Conversely, if the straight narrow piece of thermostat metal is cooled, the high-expanding metal will be on the inner side of the arc of a circle. The action caused by the change of curvature of thermostat metal can be converted into a linear or angular movement.

Commercial types of thermostat metals are available for various temperature ranges between −50° and +1,200° F (−46° and +649° C). These thermostat metals may be classified as "low-temperature" and "high-temperature" types. The low-temperature group includes invar in combination with brass or bronze. The high-temperature group includes all those thermostat metals that can be used at higher temperatures than those using brass or bronze. For high-temperature use, brass or bronze has been replaced by stronger alloys such as nickel-copper alloys and nickel-chromium stainless alloys, to increase the temperature range of uniform deflection. It is desirable that the thermal expansion and contraction of the metals or alloys selected for use in a thermostat metal, should be reversible on heating and cooling in the temperature range in which the thermostat metal can be subjected in use, in shipment, and in the process of mounting by welding, soldering, or brazing. Thermostat metal should be properly heat treated in order to relieve internal stresses set up during the working and forming of the metal.

The fundamental relation between the properties of the two metals or alloys (elements 1 and 2) of a narrow [4] thermostat metal when heated or cooled, may be expressed by the equation [5]

$$\frac{1}{R}=\frac{6(\Delta a)(\Delta T)(t_1+t_2)t_1t_2E_1E_2}{3(t_1+t_2)^2t_1t_2E_1E_2+(t_1E_1+t_2E_2)(t_1^3E_1+t_2^3E_2)}, \tag{44}$$

where

R = radius of curvature of thermostat metal
Δa = difference in coefficients of expansion of elements 1 and 2
ΔT = difference in temperature
t_1 = thickness of element 1
t_2 = thickness of element 2
E_1 = elastic modulus of element 1
E_2 = elastic modulus of element 2.

When the elastic moduli are equal, eq (44) reduces to

$$\frac{1}{R}=\frac{6(\Delta a)(\Delta T)t_1t_2}{(t_1+t_2)^3}. \tag{45}$$

When the elastic moduli are equal and $t_1=t_2$, eq 44 reduces to

$$\frac{1}{R}=\frac{3(\Delta a)(\Delta T)}{2t}, \tag{46}$$

where t is the total thickness of the thermostat metal.

The coefficients of thermal expansion and the elastic moduli of most materials are not uniform over wide temperature ranges. For a limited temperature range the curvature can be expressed by the equation

$$\frac{1}{R}=\frac{2k(\Delta T)}{t}, \tag{47}$$

where k is a constant depending on the difference in the coefficients of thermal expansion and on the ratio of the elastic moduli of the two elements.

For a narrow straight strip of thermostat metal fastened at one end and free to move at the other end, the deflection or distance moved by the free end may be represented approximately by

$$d=\frac{L^2}{2R}, \tag{48}$$

where d is the deflection and L is the effective length of the strip. If the value of $\frac{1}{R}$ from eq 47 is substituted in eq 48, the following equation is obtained for the deflection:

$$d=\frac{k(\Delta T)L^2}{t}. \tag{49}$$

If the narrow strip of thermostat metal is shaped in the form of a U with arms of equal length, the deflection of the free end is given by

$$d=\frac{k(\Delta T)L^2}{2t}, \tag{50}$$

where L is the developed length of the strip.

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[4] A flat, wide strip of thermostat metal when heated or cooled will assume the shape of a portion of a curved tube.

[5] The equations in this subsection were obtained from catalog (1935 edition) by the H. A. Wilson Co., Newark, N. J. and publication by Hood [57].

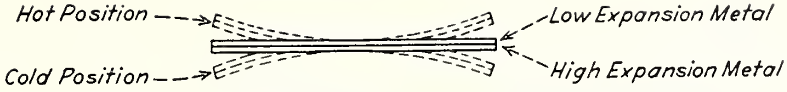


Figure 26. *Effect of heating and cooling thermostat metal (Hood).*

For thermostat metal shaped in the form of a circular ring, the deflection of the free end is

$$d=\frac{k(\Delta T)L^2}{\pi t}, \tag{51}$$

where L is the developed length of the ring. This shape is used for restricted spaces in which auxiliary arms or levers are employed to obtain additional motion.

The force exerted at the end of a straight strip of thermostat metal fastened at one end and touching a stop at the other end may be represented by

$$P=\frac{k(\Delta T)wt^2E}{4L}, \tag{52}$$

where P is the force, and w is the width of the strip.

For a thermostat metal in the form of a helix or spiral, the angular rotation between the ends may be obtained approximately from the following equation:

$$\Theta=\frac{360k(\Delta T)L}{\pi t}, \tag{53}$$

where Θ is the angular rotation in degrees. The torque of a coil is

$$M=\frac{k(\Delta T)wt^2E}{6}, \tag{54}$$

where M is the torque.

Thermostat metal is also used in the form of a round disk pressed into a concave or convex shape so that on heating or cooling, the disk will buckle from one side to the other.

Figure 27 shows some of the shapes of thermostat metals. Additional information about these materials may be obtained from manufacturers of thermostat metals.

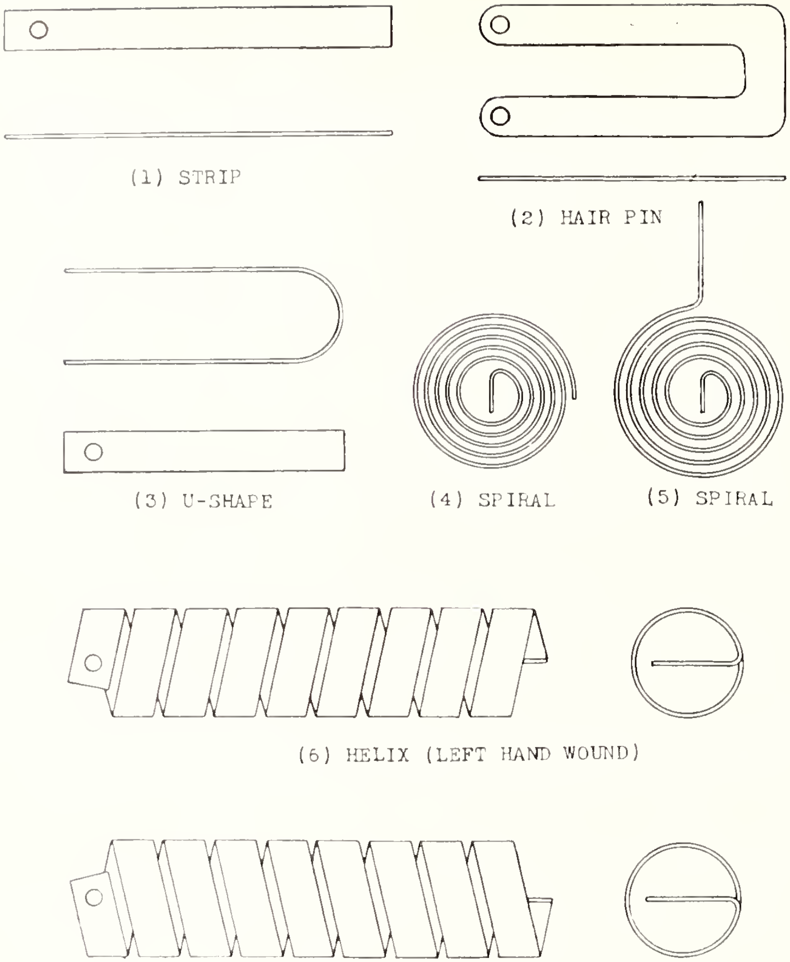
Methods of testing thermostat metals have been published by American Society for Testing Materials [58].

3. Thermostats by Fluid Expansion

The large cubical thermal expansion of some liquids and gases has been applied for thermostats and for pyrometers. In the mercurial thermostat the contact is made by the mercury column, which rises when heated and contacts electric wires embedded in the glass and projecting into the capillary tube. Another type of liquid thermostat consists of a bulb, capillary tube, and bellows filled with a suitable liquid. The expansion or contraction of the liquid on heating or cooling actuates the bellows. The mercurial thermometer is the most common application for indicating temperature. The tin pyrometer is another application in which a chemical element in the liquid state has been used in the measurement of high temperatures.

Gas-filled thermostats have wider application than liquid-filled thermostats on account of the greater temperature range of the former. The sensitive bulb may be connected by capillary tubing to a Bourdon tube spring wound into the form of a helix. When the thermostat is heated, the gas expands and exerts a pressure that causes the spring to unwind. In some fire-alarm systems, the operation depends on the expansion of air from the heat of the fire or air within a vent-compensated system, which deflects diaphragms forming one side of connected air cells to make an electrical contact instrumental in sounding the alarm. The operating pressure and vent are so adjusted that pressures built up from ordinary temperature changes will not cause false operation of the system. The air volume concerned can be contained in long runs of fine tubing or can be consolidated in clusters of tubing or in bulbs of relatively large volume.

A thermostat using ether vapor in a balanced mercury column system, similar to that described by Green and Loring [59] is used in the gage block constant-temperature room of the National Bureau of Standards and has been found to be highly sensitive. Green and Loring's thermostat bulb has been replaced by a spiral to increase the sensitivity. A displacement of ½ in. corresponds to a change of about 1° C.


(1) STRIP

(2) HAIR PIN

(3) U-SHAPE

(4) SPIRAL

(5) SPIRAL

(6) HELIX (LEFT HAND WOUND)

(7) HELIX (RIGHT HAND WOUND)

FIGURE 27. *Typical shapes of thermostat metal (Catalog, W. M. Chace Co., 1934).*

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