

OCT 29 1963



# Technical Note

No. 183

---

## A COMPARISON OF TWO MELTING-PRESSURE EQUATIONS CONSTRAINED TO THE TRIPLE POINT USING DATA FOR ELEVEN GASES AND THREE METALS

ROBERT D. GOODWIN AND LLOYD A. WEBER



---

U. S. DEPARTMENT OF COMMERCE  
NATIONAL BUREAU OF STANDARDS

## THE NATIONAL BUREAU OF STANDARDS

### Functions and Activities

The functions of the National Bureau of Standards are set forth in the Act of Congress, March 3, 1901, as amended by Congress in Public Law 619, 1950. These include the development and maintenance of the national standards of measurement and the provision of means and methods for making measurements consistent with these standards; the determination of physical constants and properties of materials; the development of methods and instruments for testing materials, devices, and structures; advisory services to government agencies on scientific and technical problems; invention and development of devices to serve special needs of the Government; and the development of standard practices, codes, and specifications. The work includes basic and applied research, development, engineering, instrumentation, testing, evaluation, calibration services, and various consultation and information services. Research projects are also performed for other government agencies when the work relates to and supplements the basic program of the Bureau or when the Bureau's unique competence is required. The scope of activities is suggested by the listing of divisions and sections on the inside of the back cover.

### Publications

The results of the Bureau's research are published either in the Bureau's own series of publications or in the journals of professional and scientific societies. The Bureau publishes three periodicals available from the Government Printing Office: The Journal of Research, published in four separate sections, presents complete scientific and technical papers; the Technical News Bulletin presents summary and preliminary reports on work in progress; and the Central Radio Propagation Laboratory Ionospheric Predictions provides data for determining the best frequencies to use for radio communications throughout the world. There are also five series of nonperiodical publications: Monographs, Applied Mathematics Series, Handbooks, Miscellaneous Publications, and Technical Notes.

A complete listing of the Bureau's publications can be found in National Bureau of Standards Circular 460, Publications of the National Bureau of Standards, 1901 to June 1947 (\$1.25), and the Supplement to National Bureau of Standards Circular 460, July 1947 to June 1957 (\$1.50), and Miscellaneous Publication 240, July 1957 to June 1960 (includes Titles of Papers Published in Outside Journals 1950 to 1959) (\$2.25); available from the Superintendent of Documents, Government Printing Office, Washington D.C. 20402.

# NATIONAL BUREAU OF STANDARDS

## *Technical Note 183*

Issued October 6, 1963

### A COMPARISON OF TWO MELTING-PRESSURE EQUATIONS CONSTRAINED TO THE TRIPLE POINT USING DATA FOR ELEVEN GASES AND THREE METALS

Robert D. Goodwin and Lloyd A. Weber  
Cryogenic Engineering Laboratory  
National Bureau of Standards  
Boulder, Colorado

NBS Technical Notes are designed to supplement the Bureau's regular publications program. They provide a means for making available scientific data that are of transient or limited interest. Technical Notes may be listed or referred to in the open literature.

---

For sale by the Superintendent of Documents, U. S. Government Printing Office  
Washington, D.C. 20402

PRICE

25 CENTS

#### IMPORTANT NOTICE

NATIONAL BUREAU OF STANDARDS REPORTS are usually preliminary or progress accounting documents intended for use within the Government. Before material in the reports is formally published it is subjected to additional evaluation and review. For this reason, the publication, reprinting, reproduction, or open-literature listing of this Report, either in whole or in part, is not authorized unless permission is obtained in writing from the Office of the Director, National Bureau of Standards, Washington 25, D. C. Such permission is not needed, however, by the Government agency for which the Report has been specifically prepared if that agency wishes to reproduce additional copies for its own use.

## CONTENTS

|    |                                         |   |
|----|-----------------------------------------|---|
| 1. | Introduction . . . . .                  | 1 |
| 2. | Data and Computational Method . . . . . | 3 |
| 3. | Results . . . . .                       | 5 |
| 4. | Summary and Conclusions . . . . .       | 7 |
| 5. | Acknowledgements . . . . .              | 8 |
| 6. | References . . . . .                    | 9 |



# A COMPARISON OF TWO MELTING-PRESSURE EQUATIONS CONSTRAINED TO THE TRIPLE POINT USING DATA FOR ELEVEN GASES AND THREE METALS

Robert D. Goodwin and Lloyd A. Weber

Parameters have been determined by a least-squares method for the reduced Simon equation and for a new, empirical melting equation using data for  $H_2$ ,  $D_2$ ,  $T_2$ , Ne, Ar, Kr, Xe,  $N_2$ ,  $O_2$ ,  $CO_2$ ,  $H_2O$ , Na, K, and Hg. The new equation,  $(P - P_t)/(T - T_t)^2 = A \exp(-\alpha/T) + BT$ , represents experimental data with essentially the same accuracy as the Simon equation. It provides a sensitive difference method for graphical examination of data.

## 1. Introduction

Experimental data for melting curves often have been represented by the original Simon equation [Simon and Glatzel, 1929; Simon, Ruhemann, and Edwards, 1930],

$$P = a + bT^c \quad (1-a)$$

with three parameters, omitting the triple-point datum. Since a number of triple-point determinations now are available, it is appropriate to establish the two parameters of the reduced Simon equation [Simon, 1937; 1953],

$$P - P_t = P_o \left[ (T/T_t)^c - 1 \right] \quad (1)$$



as constrained to the triple point (subscript  $t$ ), using a uniform computational method based on relative, rather than absolute deviations for all substances.

Whereas (1) has been derived with certain assumptions from modern theory of solids [Gilvarry, 1956; Glass, 1963; Salter, 1954; Voronel, 1948, 1959], real or apparent difficulties are encountered in the accurate empirical representation of some data, e. g. [Michels and Prins, 1962; Pistorius, Pistorius, Blakey, and Admiraal, 1963], and for some metals the theoretically derived relation

$$c = (6\gamma + 1)/(6\gamma - 2)$$

( $\gamma$  = Grueisen's constant) is not confirmed experimentally [Strong and Bundy, 1959].

In view of these difficulties, we have at the same time examined further the empirical equation recently used for interpolation near the triple point of hydrogen [Goodwin, 1962; Goodwin and Roder, 1963],

$$y = A \exp(-a/T) + BT, \quad (2)$$

where

$$y \equiv (P - P_t)/(T - T_t).$$

For this examination, substances other than low-boiling gases are included for which, however, the triple-points may not be accurately known. It is possible to deduce that (2) implies a temperature-dependence of the Grueisen constants, not found in the assumptions of the latter equation of state. Gilvarry, however, has concluded that a small temperature-dependence of these constants may be expected [Gilvarry, 1956]. Figure 1 illustrates behavior of the experimental function  $y$  with data for  $H_2$ ,  $D_2$ ,  $N_2$ , Ar, and  $CO_2$ . The small temperature-dependence of this function (as compared with the pressure



P) provides a direct method for graphical examination of the relative deviations or precision of a set of data, prior to the tedious iterative determination of parameters either for (1) or (2).

Concerning helium, for which no triple-point exists, we merely note, for example, that for  $(\alpha/T) \ll 0$  at very low temperatures, (2) may be reduced to

$$P = P_t - (BT_t) \cdot T + BT^2 \quad (2-a)$$

and that this form is the same as used by Mills, Grilly and Sydoriak (1961) near the melting pressure minimum for  $\text{He}^3$  in the range  $0.3 \leq T \leq 0.5^\circ\text{K}$ , namely,

$$P = 32.42 - 21.25 T + 32.20 T^2.$$

Equation (1), on the other hand, clearly is monotonic.

## 2. Data and Computational Method

For each substance, the self-consistent data of but one investigator have been selected for present purposes. Original, unpublished data on hydrogen, deuterium, tritium, neon, nitrogen, and oxygen were generously given to us by Edward R. Grilly [Mills and Grilly, 1955; Mills and Grilly, 1956]. Argon, on the other hand, has been selected for illustration using data of three investigators over a wide range of pressures [Bridgman, 1935; Lahr, and Eversole, 1962; and Michels and Prins, 1962]. Further references to experimental data are given by authors cited here. Triple-point constants used for the present computations are given in table 1. All pressures are in atmospheres [Hilsenrath, 1955]. Absolute temperatures below  $80^\circ\text{K}$  are on the NBS 1955 low-temperature scale [Goodwin and Roder, 1963].

Since relative, rather than absolute, error is roughly constant in the experimental determination of melting pressures, the least-squares method (with trial variation of one parameter) has been applied to constant or nearly constant forms of the above equations,

$$(P-P_t)/(T/T_t)^c - 1 = P_o, \quad (1-b)$$

$$(P-P_t)/(T-T_t) T = AT^{-1} e^{-a/T} + B. \quad (2-b)$$

In (2-b), all three constants have been treated as adjustable parameters, in contrast to the earlier treatment for hydrogen isotopes [Goodwin, 1962].

Computational results include the root mean square (r. m. s.) absolute deviation in atm, and the r. m. s. relative deviation in percent, defined respectively by

$$D \equiv \left[ \sum (\Delta P)^2/n \right]^{1/2}, \quad (3-a)$$

$$\Delta \equiv \left[ \sum \delta^2/n \right]^{1/2}, \quad (3-b)$$

where

$$\delta \equiv 100 (P_{\text{calc}} - P)/P \quad (3-c)$$

for a number  $\underline{n}$  of datum points, and where  $\Delta P$  is the difference between calculated and experimental values. The form of (3-a) is the same as used by Mills and Grilly [1956]. Minima in  $D$  and  $\Delta$ , however, generally do not occur for the same set of parameters. Those corresponding to the minimum relative deviation,  $\Delta$ , are given in the following results, in contrast to those for a minimum in  $D$  given by Mills and Grilly [1956]. To examine detailed behavior

near the triple point, the average of absolute values of deviations from the first six data of each investigator at the lowest pressures are given in percent in table 2 under the symbol  $\bar{\delta}$ .

### 3. Results

Table 2 presents the sources of data and the number of points,  $n$ , used in the least-squares determination of parameters, and the maximum pressure of these data. There follow the parameters and deviations for each equation. For hydrogen on lines 1 and 2, two different sets of data are compared. Argon is examined with various data. Line 6 is for the mutually consistent data of Michels and Prins [1962] and of Bridgman [1935]. On line 7 (2) has been fitted to synthetic data computed by (1), line 6. Line 8 includes, also, the data of Lahr and Eversole to 18,000 atm [Lahr and Eversole, 1962], whereas line 9 employs the latter data only.

A comparison of relative deviations,  $\Delta$ , in table 2 shows in general that (2) represents the data as well as, or, for some substances, somewhat better than (1). The improvement is clear for the hydrogen data on line 1, for argon on line 6, for xenon, and for water.

Equation (2) contains a term which may be compared with the internal pressure,  $P_o$ , of (1) at  $T = T_t$ . The ratio of these terms for the gases through  $O_2$  in table 2 is found to be

$$(AT_t/P_o) \exp (-a/T_t) = 1.2 \pm 0.1$$

with the exception of xenon for which the ratio is 1.70.

For xenon, in table 3, the comparison of equations is given at all points, since Michels and Prins found it necessary to fit the data by (1-a), independently, in two regions [Michels and Prins, 1962].

Whereas (2) gives a better average representation than (1), it does not overcome the systematic deviation seen in this table.

Some of the results for argon are presented graphically. The ordinate of the figure 2 logarithmic plot was computed with the internal pressure of Michels and Prins for (1-a), while the slope of the extrapolated straight line corresponds to their values of  $\underline{c}$  [Michels and Prins, 1962]. Included for comparison are data of Bridgman [1935], of Lahr and Eversole [1962], and of Robinson [1954]. As compared to the pressure at 360°K (near 18,000 atm.), given by (1), line 6 of table 2, the smoothed function of Lahr and Eversole yields a value 7.0% lower, and (2), line 6 of table 2, yields a value 3.5% higher, the latter equation being shown by the dashed curve of figure 1.

Figure 3 for argon is derived from (2), using parameters from line 6 of table 2. The straight line represents (2). The dashed line represents (1). Datum points are the same as on figure 2. Figure 4 is similar, except that all constants are from line 8 of table 2. This type of difference plot provides a highly sensitive method for graphical examination of the precision of experimental data.

Table 4 for argon presents relative deviations of both equations from the data of Bridgman [1935]; Lahr and Eversole [1962]; and Michels and Prins [1962], line 8 of table 2 to 18,000 atmospheres. It is seen that the two equations give comparable representations of these combined data to 18,000 atm.

Table 5 for argon compares first derivatives,  $s \equiv dP/dT$ , of the two equations in terms of percent difference,  $100(s_2 - s_1)/s_1$ , in which subscripts refer to the equations. Under heading (a) are given results for the consistent data of line 6 of table 2, whereas, under (b), the results correspond to the apparently less consistent data of line 8



of table 2. For each case, it is seen that the first derivatives of the two equations are comparable over the range of the data.

Table 6 presents a comparison of the Simon constants recently determined by S. E. Babb, Jr. [1963], by a method of absolute deviations, with those determined in the present report by a method of relative deviations.

Since importance has been attached to the fact that (1) is a "reduced" form [Simon, 1937], the reduced constants for (2) are examined in table 7. The following ranges of values are found for the gases  $H_2$  through  $N_2$  of table 2,

$$\begin{array}{ccc} \frac{a/T_t}{0.04 \rightarrow 0.4} & \frac{AT_t P_t}{(3 \rightarrow 17) \cdot 10^3} & \frac{BT_t/P_t}{(0.1 \rightarrow 1.3) \cdot 10^2} \end{array} .$$

#### 4. Summary and Conclusions

The two parameters of the reduced Simon equation have been determined for a number of gases and some metals by a uniform method which assumes that relative rather than absolute uncertainties are roughly constant in the experimental pressures.

Some current empirical and theoretical difficulties with the Simon equation, already mentioned, have led to examination of a new, empirical equation with three parameters. The latter equation is presented as a result of the remarkable equivalence to the Simon equation found here in the empirical representation of data, even though no simple mathematical equivalence between the equations is apparent.

It may be concluded that (1) will be preferred to (2) for its simplicity and qualitative theoretical support, except where the latter gives improved empirical representation of data, or until such time as it receives some theoretical interpretation. Equation (2), however, provides a sensitive difference method for graphical examination of the precision of data.

### 5. Acknowledgements

We are indebted to Roger M. Gallet of NBS for suggesting this examination of the reduced form of the Simon equation and for pointing out Lahr and Eversole, [1962], and to John W. Stewart of The University of Virginia for a relation between (2) and the Gruneisen constants. Robert J. Corruccini of this laboratory kindly brought to our attention Strong and Bundy, [1959]. The work has been supported in part by the National Aeronautics and Space Administration.

## 6. References

- [ 1 ] Babb, S. E., Jr., (1963), Parameters in the Simon equation relating pressure and melting temperature, *Rev. Modern Phys.* 35, 400.
- [ 2 ] Babb, S. E., Jr., (1963), Values of the Simon constants, *Rev. Modern Phys.* 38, 2743.
- [ 3 ] Bridgman, P. W., (1914); (1926), Change of phase under pressure, *Phys. Rev.* 3, 153, (1914); 27, 68 (1926).
- [ 4 ] Bridgman, P. W., (1935), The melting curves and compressibilities of nitrogen and argon, *Proc. Am. Acad. Arts. Sci.* 70, 1.
- [ 5 ] Danon, F., and K. S. Pitzer, (1962), Corresponding states theory for argon and xenon, *J. Phys. Chem.* 66, 583.
- [ 6 ] Gilvarry, J. J., (1956), Equation of the fusion curve, *Phys. Rev.* 102 (2), 325-31.
- [ 7 ] Glass, Solomon J., (1963), The Gruneisen equation of state Simon melting equation, Private communication.
- [ 8 ] Goodwin, Robert D., (Dec. 1962), Melting-pressure equation for the hydrogens, *Cryogenics* 2, 353.
- [ 9 ] Goodwin, R. D., and H. M. Roder, (Mar. 1963), Pressure-density-temperature relations of freezing liquid para-hydrogen to 350 atm., *Cryogenics*, 3(1), 12.
- [ 10 ] Grilly, E. R., (1951), The vapor pressures of hydrogen, deuterium and tritium up to three atmospheres, *J. Am. Chem. Soc.* 73, 843.
- [ 11 ] Grilly, E. R., (June, 1962), The vapor pressure of solid and liquid neon, *Cryogenics* 2, 226.
- [ 12 ] Hilsenrath, Joseph, editor, (1955), Tables of thermal properties of gases, NBS Circular 564.



- [13] Hoge, Harold J., (1950), Vapor pressure and fixed points of oxygen and heat capacity in the critical region, J. Res. 44, 321.
- [14] Lahr, P. H., and W. G. Eversole, (1962), Compression isotherms of argon, krypton, and xenon through the freezing zone, J. Chem. and Eng. Data, 7(1), 42.
- [15] Michels, A., B. Blaisse, and J. Hoogschagen, (1942), The melting curve of CO<sub>2</sub> to 2800 atmospheres, Physica 9, 565.
- [16] Michels, A., T. Wassenaar, and B. Blaisse, (1942), The melting curve of Hg to 3000 atmospheres, Physica 9, 574.
- [17] Michels, A., T. Wassenaar, Th. Sluyters, and W. DeGraaff, (1957), The triple points of carbon dioxide and of argon as fixed points for the calibration of thermometers, Physica 23, 89.
- [18] Michels, A., and C. Prins (1962), The melting lines of argon, krypton, and xenon up to 1500 atm; representation of the results by a law of corresponding states, Physica 28, 101.
- [19] Mills, R. L., and E. R. Grilly, (1955), Melting curves of He<sup>3</sup>, He<sup>4</sup>, H<sub>2</sub>, D<sub>2</sub>, Ne, N<sub>2</sub> and O<sub>2</sub> up to 3500 Kg/cm<sup>2</sup>, Phys. Rev. 99, 480.
- [20] Mills, R. L., and E. R. Grilly, (1956), Melting curves of H<sub>2</sub>, D<sub>2</sub> and T<sub>2</sub> up to 3500 Kg/cm<sup>2</sup>, Phys. Rev. 101, 1246.
- [21] Mills, R. L., E. R. Grilly, and G. Sydoriak (1961), Anomalous melting properties of He<sup>3</sup>, Annals of Physics 12, 41.
- [22] Pistorius, C. W. F. T., M. C. Pistorius, J. P. Blakey, and L. J. Admiraal, (1963), Melting curve of ice VII to 200 k bar, J. Chem. Phys. 38(3), 600-602.
- [23] Robinson, D. W., (1954), An experimental determination of the melting curves of argon and nitrogen into the 10,000 atm. region, Proc. Roy. Soc. (London) A225, 393.
- [24] Salter, L., (1954), The Simon melting equation, Phil. Mag. (7) 45, 369.

- [ 25 ] Simon, Franz E., and G. Glatzel, (1929), Remarks on melting-pressure curves, Z. Anorg. Allgem. Chem. 178, 309.
- [ 26 ] Simon, F. E., M. Ruhemann, and W. A. M. Edwards, (1930), The melting curves of hydrogen, neon, nitrogen, and argon, Z. Phys. Chem. B6, 331.
- [ 27 ] Simon, F., (1937), On the range of stability of the fluid state, Trans. Faraday Soc. 33, 65.
- [ 28 ] Simon, F., (1953), The melting of iron at high pressures, Nature 172, 746.
- [ 29 ] Strong, H. M., and F. P. Bundy, (1959), Fusion curves of four group VIII metals to 100,000 atmospheres, Phys. Rev. 115, 278.
- [ 30 ] Voronel', A. V., (1948); (1959), On the equation of the melting curve, Zh. tekhn. Fiz. 28(11), 2630-4 (1948), in Russian; Physics Abstracts 62, 10941 (1959).
- [ 31 ] Woolley, H. W., R. B. Scott, and F. G. Brickwedde, (1948), Compilation of thermal properties of hydrogen in its various isotopic and ortho-para modifications, J. Res. 41, 379.

Table 1. Triple-point constants used.

| Substance        | $T_t, ^\circ\text{K}$ | $P_t, \text{atm.}$ | Reference  |
|------------------|-----------------------|--------------------|------------|
| n-H <sub>2</sub> | 13.947                | 0.071              | [ 31 ]     |
| n-D <sub>2</sub> | 18.72                 | 0.169              | [ 10 ]     |
| n-T <sub>2</sub> | 20.61                 | 0.213              | [ 10 ]     |
| Ne               | 24.544                | 0.427              | [ 11 ]     |
| Ar               | 83.812                | 0.685              | [ 17, 18 ] |
| Kr               | 115.745               | 0.724              | [ 18 ]     |
| Xe               | 161.364               | 0.806              | [ 18 ]     |
| N <sub>2</sub>   | 63.146                | 0.124              | [ 12 ]     |
| O <sub>2</sub>   | 54.353                | 0.0015             | [ 13 ]     |
| CO <sub>2</sub>  | 216.577               | 5.11               | [ 17, 12 ] |
| H <sub>2</sub> O | 354.75*               | 21,260.*           | [ 22 ]     |
| Na               | 370.75†               | 0.9684†            | [ 3 ]      |
| K                | 335.65†               | 0.9684†            | [ 3 ]      |
| Hg               | 234.32†               | 0.0                | [ 17 ]     |

\* Triple-point ice VI + ice VII + liquid.

† The melting-point of original data.





Table 2. Constants and deviations for the two equations

| Line | Sub-<br>stance   | Data      |    | $P_{\max}$ | Equation 1 |          |        |                |          | Equation 2 |           |         |       |                |          |
|------|------------------|-----------|----|------------|------------|----------|--------|----------------|----------|------------|-----------|---------|-------|----------------|----------|
|      |                  | Reference | n  |            | c          | $P_o$    | D      | $\bar{\delta}$ | $\Delta$ | a          | A         | B       | D     | $\bar{\delta}$ | $\Delta$ |
| 1    | n-H <sub>2</sub> | [31]      | 15 | 608        | 1.930      | 216.72   | 2.7    | 0.52           | 0.75     | 6.2        | 32.859    | .60768  | 0.8   | 0.50           | 0.43     |
| 2    | n-H <sub>2</sub> | [20]      | 26 | 3,600      | 1.795      | 244.89   | 15.7   | 2.06           | 1.41     | 4.1        | 28.803    | .67444  | 10.4  | 2.43           | 1.45     |
| 3    | n-D <sub>2</sub> | [20]      | 23 | 3,500      | 1.815      | 406.07   | 7.7    | 0.56           | 0.49     | 4.4        | 33.055    | .67890  | 4.6   | 0.65           | 0.44     |
| 4    | n-T <sub>2</sub> | [20]      | 15 | 3,000      | 1.780      | 509.88   | 3.6    | 1.32           | 1.14     | 1.0        | 30.869    | .72807  | 6.5   | 1.34           | 1.16     |
| 5    | Ne               | [19]      | 36 | 3,400      | 1.630      | 985.06   | 6.2    | 0.47           | 0.46     | 4.0        | 59.334    | .59879  | 5.7   | 0.46           | 0.47     |
| 6.   | Ar               | [4,18]    | 16 | 5,800      | 1.594      | 2,087.7  | 3.3    | 0.03           | 0.09     | 7.2        | 33.275    | .10971  | 1.0   | 0.03           | 0.05     |
| 7.   | Ar               | ---       | 16 | 5,800      | -----      | -----    | ---    | ---            | ---      | 9.0        | 34.294    | .10596  | 1.32  | 0.03           | 0.04     |
| 8    | Ar               | [4,14,18] | 30 | 18,000     | 1.521      | 2,213.3  | 89.9   | 0.75           | 1.47     | 24.0       | 45.413    | .06264  | 75.0  | 0.39           | 1.33     |
| 9    | Ar               | [14]      | 14 | 18,000     | 1.510      | 2,242.2  | 108.1  | 1.95           | 1.80     | 48.0       | 56.334    | .04234  | 119.2 | 1.66           | 1.57     |
| 10   | Kr               | [18]      | 14 | 1,500      | 1.615      | 2,349.0  | 0.1    | 0.12           | 0.11     | 5.0        | 24.949    | .07680  | 0.2   | 0.12           | 0.11     |
| 11   | Xe               | [18]      | 19 | 1,500      | 1.710      | 2,352.3  | 2.1    | 0.46           | 0.42     | 71.0       | 38.580    | 0.0     | 1.0   | 0.29           | 0.26     |
| 12   | N <sub>2</sub>   | [19]      | 24 | 3,500      | 1.790      | 1,586.2  | 2.1    | 0.30           | 0.22     | 7.0        | 33.133    | .24087  | 2.0   | 0.31           | 0.21     |
| 13   | O <sub>2</sub>   | [19]      | 16 | 3,500      | 1.755      | 2,666.8  | 5.1    | 0.60           | 0.47     | 14.0       | 83.374    | .38743  | 5.4   | 0.59           | 0.44     |
| 14   | CO <sub>2</sub>  | [15]      | 25 | 2,800      | 3.1        | 3,178.3  | 5.4    | 2.48           | 1.65     | 0.0        | - 7.05304 | .242083 | 4.9   | 2.55           | 1.64     |
| 15   | H <sub>2</sub> O | [22]      | 26 | 196,000    | 4.8        | 6,048.3  | 4370.0 | 2.30           | 5.13     | 450.       | -5546.02  | 4.80652 | 3005. | 2.30           | 3.58     |
| 16   | Na               | [3]       | 12 | 11,600     | 3.6        | 11,409.0 | 22.1   | 0.76           | 0.74     | 380.       | -1530.54  | 1.78578 | 26.2  | 0.74           | 0.62     |
| 17   | K                | [3]       | 12 | 11,600     | 4.4        | 4,224.4  | 31.3   | 0.37           | 0.44     | 280.       | - 503.249 | .815969 | 39.4  | 0.35           | 0.49     |
| 18   | Hg               | [16]      | 13 | 3,000      | 0.76       | 59,249.  | 3.6    | 0.99           | 0.94     | 260.       | -8872.22  | 13.3083 | 2.4   | 0.94           | 0.88     |



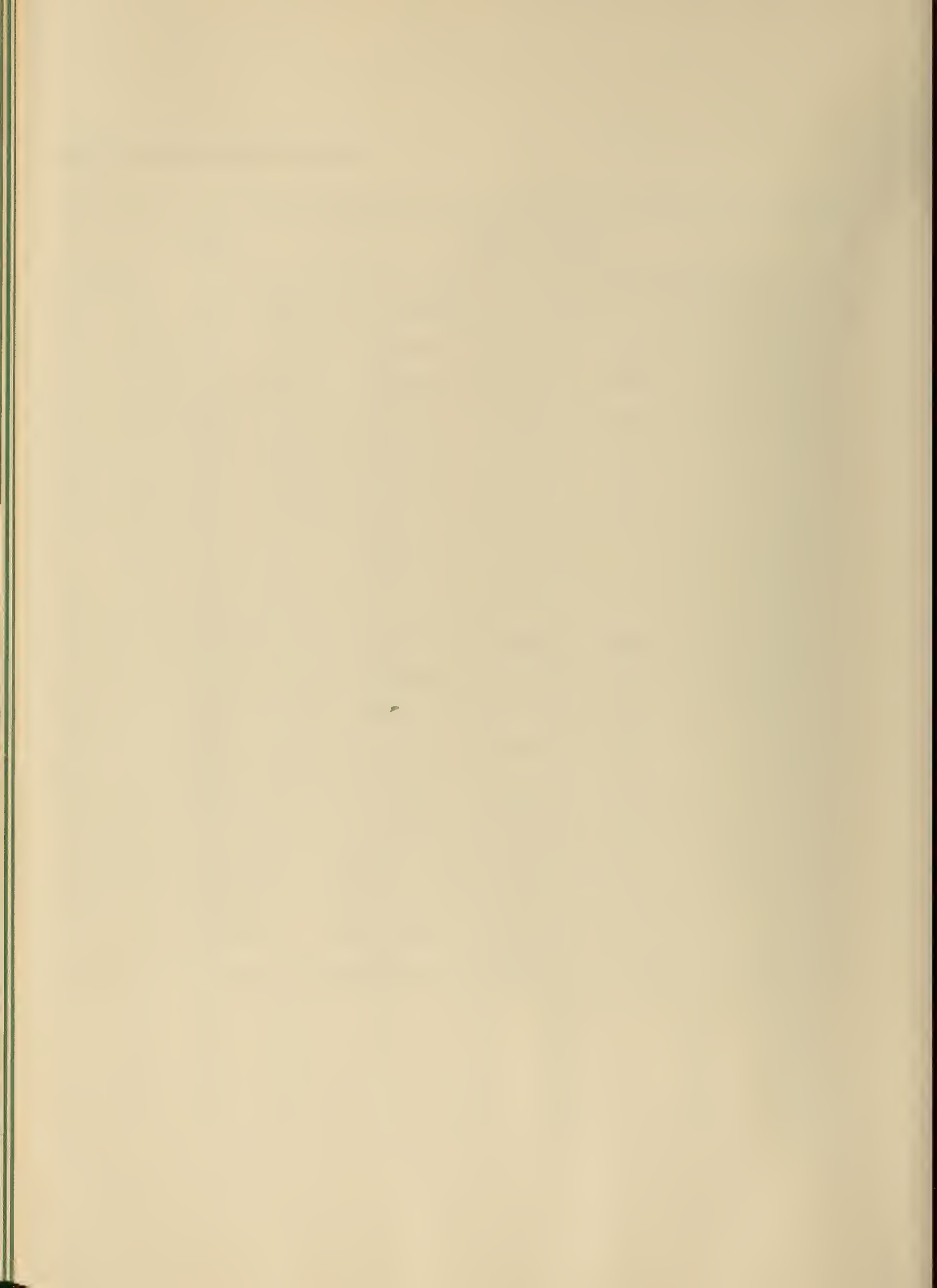


Table 3. Comparison of (1) and (2) for Xenon

| <u>T</u> | <u>P</u> | <u><math>\delta_1</math></u> | <u><math>\delta_2</math></u> |
|----------|----------|------------------------------|------------------------------|
| 161.554  | 5.53     | 0.33                         | 0.00                         |
| 162.439  | 27.49    | 0.66                         | 0.39                         |
| 163.375  | 50.82    | 0.67                         | 0.45                         |
| 164.171  | 70.95    | 0.37                         | 0.19                         |
| 167.154  | 147.31   | -0.23                        | -0.28                        |
| 171.455  | 259.23   | -0.51                        | -0.42                        |
| 176.978  | 405.89   | -0.64                        | -0.42                        |
| 184.004  | 596.25   | -0.56                        | -0.26                        |
| 191.144  | 794.08   | -0.39                        | -0.09                        |
| 197.868  | 984.49   | -0.22                        | 0.02                         |
| 203.000  | 1132.20  | -0.06                        | 0.09                         |
| 207.205  | 1255.18  | 0.05                         | 0.10                         |
| 211.142  | 1371.51  | 0.17                         | 0.11                         |
| 215.264  | 1494.53  | 0.30                         | 0.11                         |
|          |          | <u>0.37</u>                  | <u>0.21</u>                  |

TABLE 2. COMPARISON OF EQUIS. (1) AND (2) FOR ARGON.

| T                 | P       | $\delta_1$ | $\delta_2$ |
|-------------------|---------|------------|------------|
| Michels and Prins |         |            |            |
| 85.532            | 69.39   | 1.07       | -.71       |
| 87.458            | 147.46  | .89        | -.65       |
| 89.110            | 215.06  | .88        | -.47       |
| 93.543            | 400.40  | .69        | -.20       |
| 98.129            | 597.46  | .54        | .06        |
| 102.587           | 794.12  | .41        | .25        |
| 106.796           | 984.49  | .28        | .37        |
| 109.921           | 1129.13 | .14        | .39        |
| 112.526           | 1251.52 | .03        | .41        |
| 115.095           | 1373.85 | -.06       | .41        |
| 117.649           | 1497.02 | -.16       | .41        |
| Bridgman          |         |            |            |
| 106.4             | 967.8   | .14        | .21        |
| 144.9             | 2903.5  | .92        | .08        |
| 161.9             | 3871.4  | -1.52      | -.55       |
| 177.8             | 4839.2  | -2.15      | -1.29      |
| 192.9             | 5807.0  | -2.67      | -1.96      |

| T                 | P     | $\delta_1$  | $\delta_2$  |
|-------------------|-------|-------------|-------------|
| Lahr and Eversole |       |             |             |
| 137               | 2389  | 3.01        | 3.99        |
| 182               | 4972  | .29         | 1.13        |
| 188               | 5417  | -1.23       | -.46        |
| 197               | 6249  | -5.46       | -4.82       |
| 226               | 7690  | 1.35        | 1.69        |
| 245               | 9100  | .02         | .13         |
| 262               | 10250 | .65         | .57         |
| 278               | 11366 | 1.17        | .93         |
| 284               | 11898 | .45         | .16         |
| 288               | 12236 | .16         | -.17        |
| 291               | 12440 | .37         | .01         |
| 299               | 12960 | 1.12        | .69         |
| 317               | 14413 | .81         | .25         |
| 360               | 18040 | .35         | -.43        |
|                   |       | <u>0.97</u> | <u>0.80</u> |

\* Constants from line 8 of table 2.

Table 5. Comparisons of  $s \equiv dP/dT$  for Argon

| T      | $100 (s_2 - s_1)/s_1$ |       |
|--------|-----------------------|-------|
|        | (a)                   | (b)   |
| 83.812 | + .06                 | -2.02 |
| 83.900 | + .07                 | -2.00 |
| 84.000 | + .07                 | -1.97 |
| 84.500 | + .06                 | -1.83 |
| 85.000 | + .06                 | -1.70 |
| 86     | + .06                 | -1.44 |
| 87     | + .06                 | -1.21 |
| 88     | + .05                 | - .98 |
| 90     | + .04                 | - .58 |
| 100    | - .06                 | + .80 |
| 110    | - .15                 | +1.42 |
| 120    | - .21                 | +1.61 |
| 140    | - .13                 | +1.34 |
| 160    | + .18                 | +0.74 |
| 180    | + .69                 | +0.10 |
| 200    | +1.35                 | -0.47 |
| 240    | -----                 | -1.30 |
| 280    | -----                 | -1.71 |
| 320    | -----                 | -1.76 |
| 360    | -----                 | -1.54 |

(a) Constants from line 6 of table 2.

(b) Constants from line 8 of table 2.

Table 6. Comparison of Simon Constants  
of S. E. Babb, Jr. [1963] with those of table 2.

| Substance         | $(P_o)_{\text{Babb}} / (P_o)_{\text{table 2}}$ | $(c)_{\text{Babb}} / (c)_{\text{table 2}}$ |
|-------------------|------------------------------------------------|--------------------------------------------|
| n-H <sub>2</sub>  | 1.1051                                         | 0.9716                                     |
| n-D <sub>2</sub>  | 1.0443                                         | 0.9847                                     |
| n-T <sub>2</sub>  | 1.0258                                         | 0.9911                                     |
| Ne                | 1.0395                                         | 0.9815                                     |
| Ar                | 0.9992                                         | 0.9994                                     |
| Kr                | 0.9983                                         | 1.0012                                     |
| Xe                | 1.0951                                         | 0.9294                                     |
| N <sub>2</sub>    | 0.9996                                         | 1.0006                                     |
| O <sub>2</sub>    | 1.0114                                         | 0.9929                                     |
| CO <sub>2</sub> * | 1.2421                                         | 0.8387                                     |
| H <sub>2</sub> O* | 2.1180                                         | 0.6479                                     |
| Na                | 1.0355                                         | 0.9814                                     |
| K                 | 0.9975                                         | 1.0091                                     |
| Hg*               | 0.6366                                         | 1.5487                                     |

\* Different data used by respective authors.

Table 7. Approximate reduced constants for equation (2)

| Line* | Substance        | $\alpha/T_t$ | $(AT_t/P_t) \cdot 10^{-3}$ | $(BT_t/P_t) \cdot 10^{-2}$ |
|-------|------------------|--------------|----------------------------|----------------------------|
| 1     | H <sub>2</sub>   | 0.445        | 6.45                       | 1.194                      |
| 2     | H <sub>2</sub>   | 0.294        | 5.66                       | 1.325                      |
| 3     | D <sub>2</sub>   | 0.235        | 3.66                       | 0.752                      |
| 4     | T <sub>2</sub>   | 0.049        | 2.99                       | 0.704                      |
| 5     | Ne               | 0.163        | 3.41                       | 0.344                      |
| 6     | Ar               | 0.086        | 4.07                       | 0.134                      |
| 7     | Ar               | 0.107        | 4.20                       | 0.130                      |
| 8     | Ar               | 0.286        | 5.56                       | 0.076                      |
| 9     | Ar               | 0.573        | 6.89                       | 0.052                      |
| 10    | Kr               | 0.043        | 3.89                       | 0.120                      |
| 11    | Xe               | 0.440        | 7.72                       | 0                          |
| 12    | N <sub>2</sub>   | 0.111        | 16.87                      | 1.227                      |
| 13    | O <sub>2</sub>   | 0.258        | 3021.                      | 140.                       |
| 14    | CO <sub>2</sub>  | 0            | -0.30                      | 0.103                      |
| 15    | H <sub>2</sub> O | 1.27         | -0.09                      | .0008                      |
| 16    | Na               | 1.03         | -586.                      | 6.84                       |
| 17    | K                | 0.83         | -175.                      | 2.83                       |

\* Lines correspond to table 2.



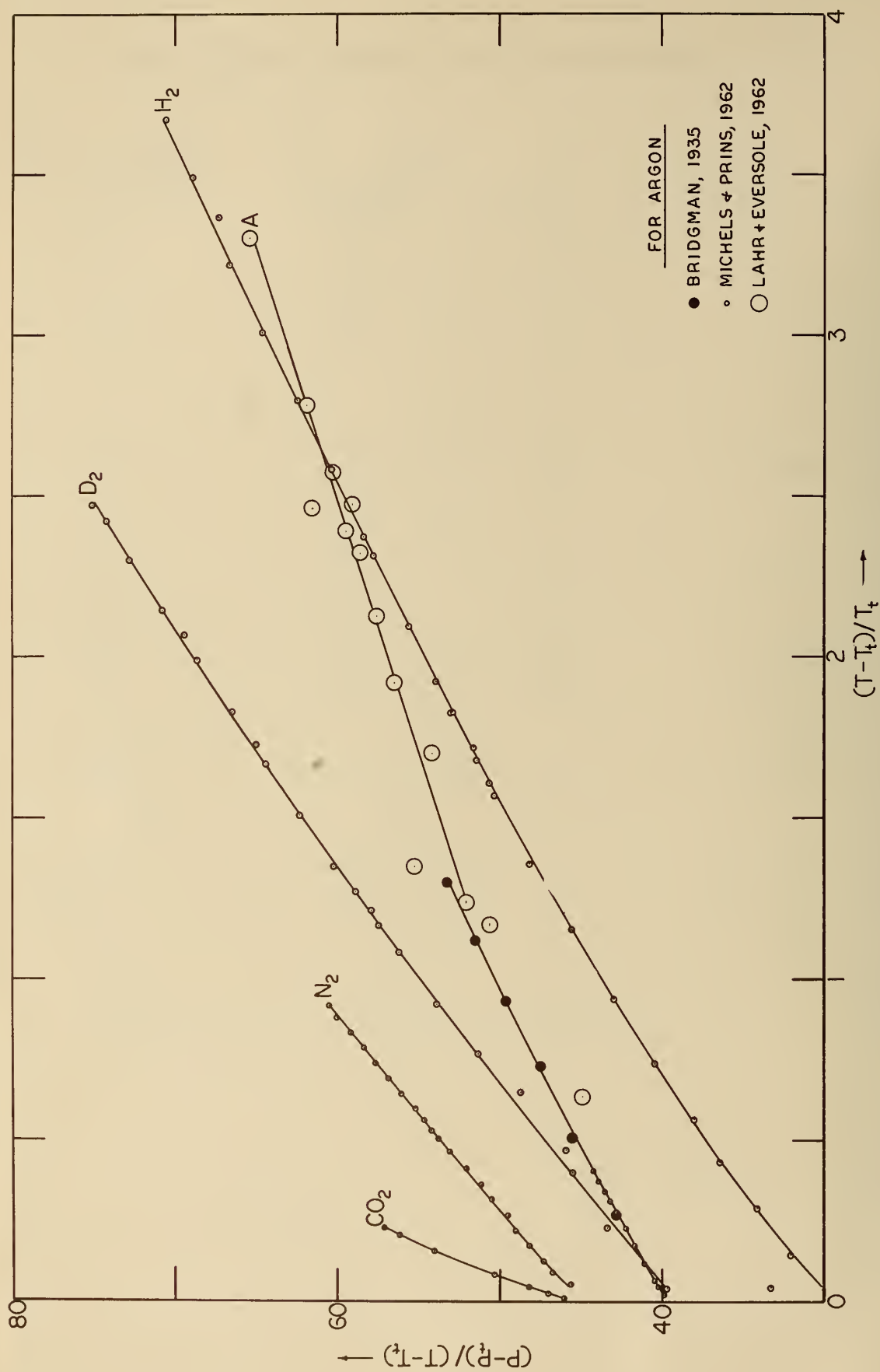


Figure 1. The function  $(P-P_t)/(T-T_t)$  vs.  $(T-T_t)/T_t$ .

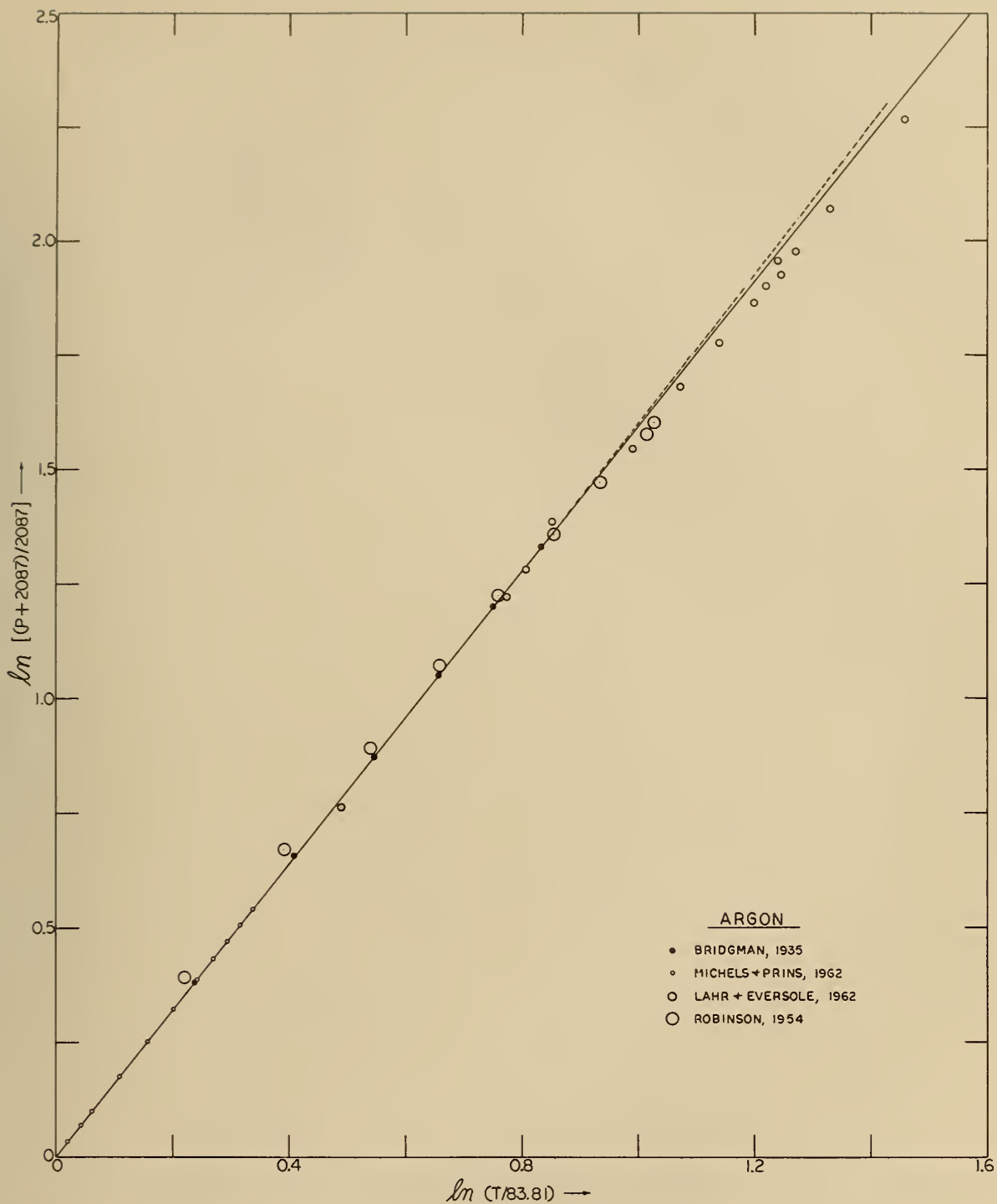


Figure 2. Logarithmic plot of equation (1) for argon using the value  $P_o = 2087$  atm.

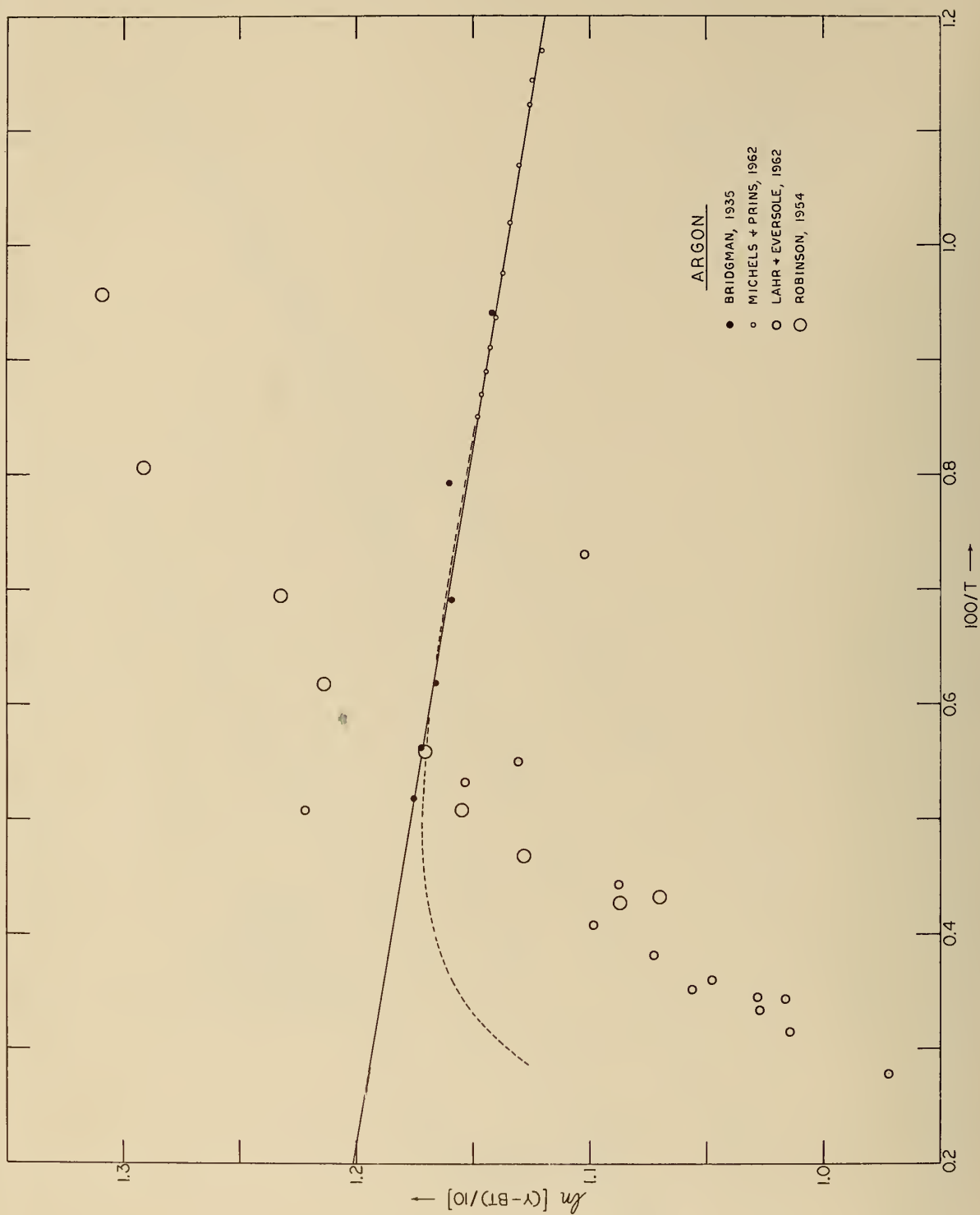


Figure 3. Logarithmic plot of equation (2) for argon using the value  $B = 0.10971 \text{ atm deg}^{-2}$

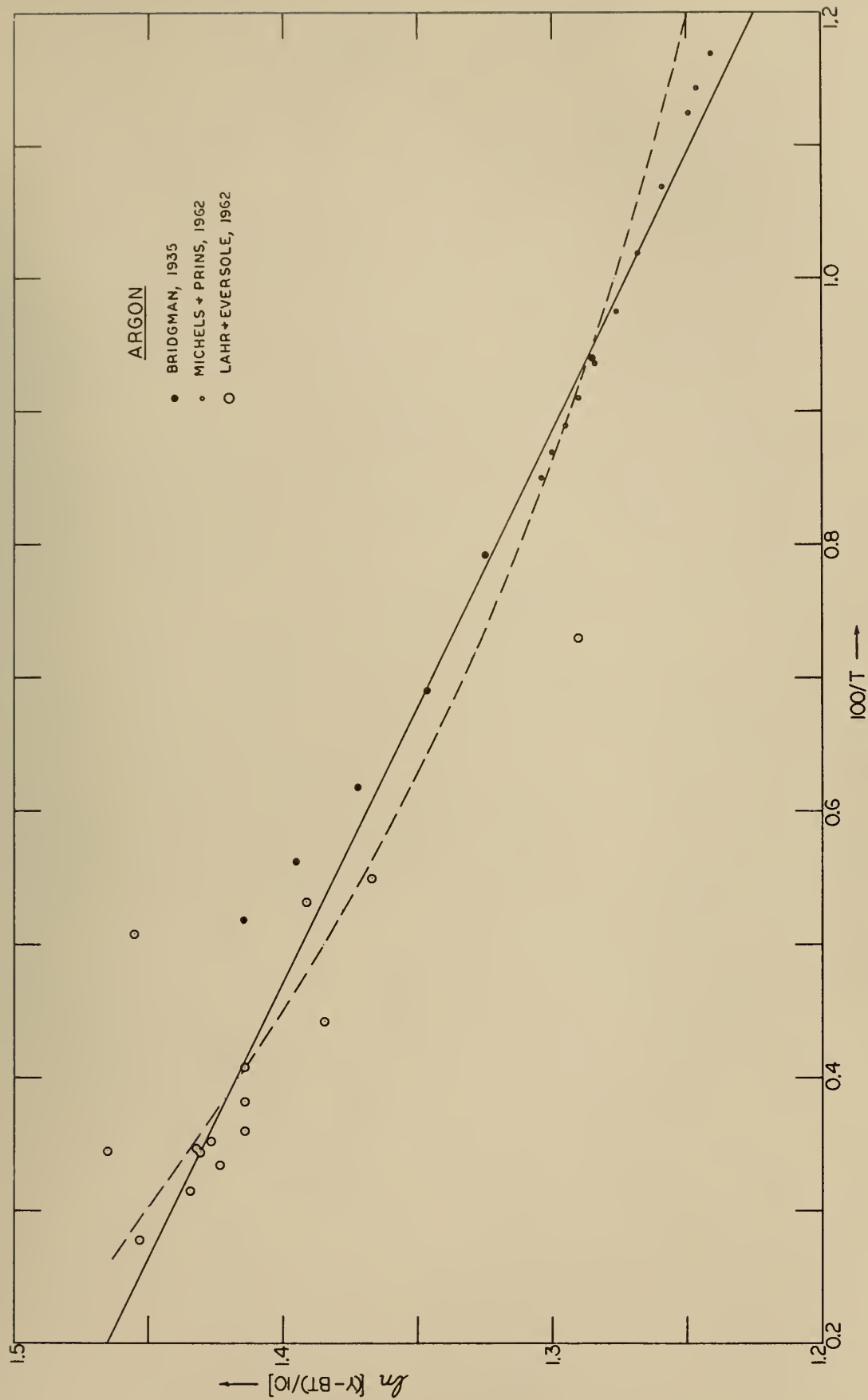
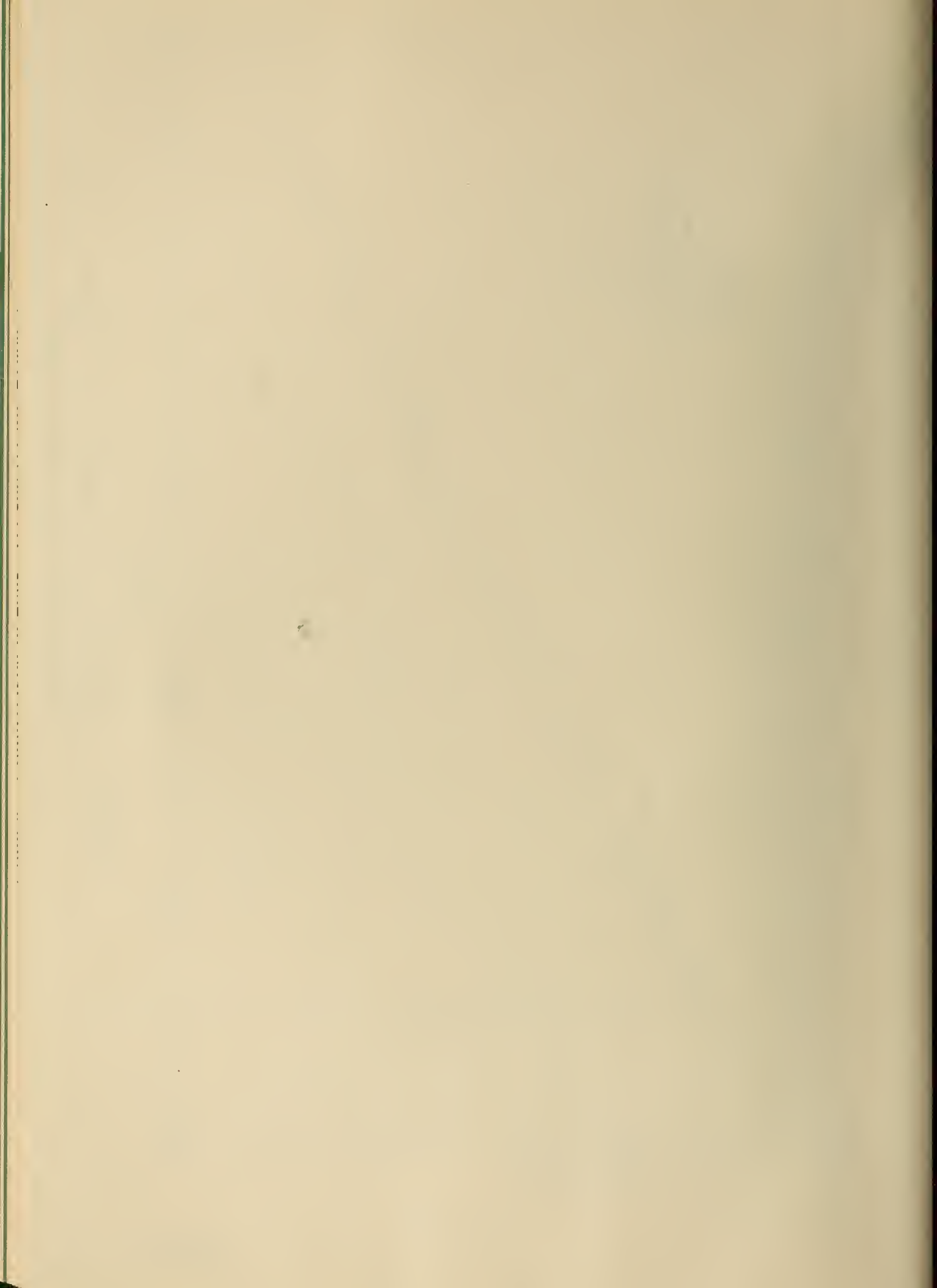


Figure 4. Logarithmic plot of equation (2) for argon using the value  $B = 0.06264 \text{ atm deg}^{-2}$ .



U. S. DEPARTMENT OF COMMERCE

Luther H. Hodges, *Secretary*

NATIONAL BUREAU OF STANDARDS

A. V. Astin, *Director*



## THE NATIONAL BUREAU OF STANDARDS

The scope of activities of the National Bureau of Standards at its major laboratories in Washington, D.C., and Boulder, Colorado, is suggested in the following listing of the divisions and sections engaged in technical work. In general, each section carries out specialized research, development, and engineering in the field indicated by its title. A brief description of the activities, and of the resultant publications, appears on the inside of the front cover.

### WASHINGTON, D. C.

**Electricity.** Resistance and Reactance. Electrochemistry. Electrical Instruments. Magnetic Measurements. Dielectrics. High Voltage. Absolute Electrical Measurements.

**Metrology.** Photometry and Colorimetry. Refractometry. Photographic Research. Length. Engineering Metrology. Mass and Volume.

**Heat.** Temperature Physics. Heat Measurements. Cryogenic Physics. Equation of State. Statistical Physics. **Radiation Physics.** X-ray. Radioactivity. Radiation Theory. High Energy Radiation. Radiological Equipment. **Nuclear Instrumentation.** Neutron Physics.

**Analytical and Inorganic Chemistry.** Pure Substances. Spectrochemistry. Solution Chemistry. Standard Reference Materials. Applied Analytical Research. Crystal Chemistry.

**Mechanics.** Sound. Pressure and Vacuum. Fluid Mechanics. Engineering Mechanics. Rheology. Combustion Controls.

**Polymers.** Macromolecules: Synthesis and Structure. Polymer Chemistry. Polymer Physics. Polymer Characterization. Polymer Evaluation and Testing. Applied Polymer Standards and Research. Dental Research.

**Metallurgy.** Engineering Metallurgy. Metal Reactions. Metal Physics. Electrolysis and Metal Deposition. **Inorganic Solids.** Engineering Ceramics. Glass. Solid State Chemistry. Crystal Growth. Physical Properties. Crystallography.

**Building Research.** Structural Engineering. Fire Research. Mechanical Systems. Organic Building Materials. Codes and Safety Standards. Heat Transfer. Inorganic Building Materials. Metallic Building Materials.

**Applied Mathematics.** Numerical Analysis. Computation. Statistical Engineering. Mathematical Physics. Operations Research.

**Data Processing Systems.** Components and Techniques. Computer Technology. Measurements Automation. Engineering Applications. Systems Analysis.

**Atomic Physics.** Spectroscopy. Infrared Spectroscopy. Far Ultraviolet Physics. Solid State Physics. Electron Physics. Atomic Physics. Plasma Spectroscopy.

**Instrumentation.** Engineering Electronics. Electron Devices. Electronic Instrumentation. Mechanical Instruments. Basic Instrumentation.

**Physical Chemistry.** Thermochemistry. Surface Chemistry. Organic Chemistry. Molecular Spectroscopy. Elementary Processes. Mass Spectrometry. Photochemistry and Radiation Chemistry.

Office of Weights and Measures.

### BOULDER, COLO.

#### CRYOGENIC ENGINEERING LABORATORY

Cryogenic Processes. Cryogenic Properties of Solids. Cryogenic Technical Services. Properties of Cryogenic Fluids.

#### CENTRAL RADIO PROPAGATION LABORATORY

**Ionosphere Research and Propagation.** Low Frequency and Very Low Frequency Research. Ionosphere Research. Prediction Services. Sun-Earth Relationships. Field Engineering. Radio Warning Services. Vertical Soundings Research.

**Troposphere and Space Telecommunications.** Data Reduction Instrumentation. Radio Noise. Tropospheric Measurements. Tropospheric Analysis. Spectrum Utilization Research. Radio-Meteorology. Lower Atmosphere Physics.

**Radio Systems.** Applied Electromagnetic Theory. High Frequency and Very High Frequency Research. Frequency Utilization. Modulation Research. Antenna Research. Radiodetermination.

**Upper Atmosphere and Space Physics.** Upper Atmosphere and Plasma Physics. High Latitude Ionosphere Physics. Ionosphere and Exosphere Scatter. Airglow and Aurora. Ionospheric Radio Astronomy.

#### RADIO STANDARDS LABORATORY

**Radio Standards Physics.** Frequency and Time Disseminations. Radio and Microwave Materials. Atomic Frequency and Time-Interval Standards. Radio Plasma. Microwave Physics.

**Radio Standards Engineering.** High Frequency Electrical Standards. High Frequency Calibration Services. High Frequency Impedance Standards. Microwave Calibration Services. Microwave Circuit Standards. Low Frequency Calibration Services.

Joint Institute for Laboratory Astrophysics-NBS Group (Univ. of Colo.).



