DETERMINATION OF THE EQUATION OF STATE CONSTANTS FOR CARBON DIOXIDE

by

Elmer E. Selby, Jr.

Submitted in partial fulfillment of
the requirements for the degree of
Bachelor of Science
at the
Massachusetts Institute of Technology
September 1, 1953

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ABSTRACT

A semi-empirical equation of state proposed by Benedict, Webb, and Rubin for light hydrocarbons and their mixtures gives excellent results. The equation is:

$$P = RTd + (B_0RT - A_0 - C_0/T^2)d^2 + (bRT - a)d^3 + a\alpha d^6 + \frac{cd^3}{T^2}(1 + \gamma d^2)\exp(- \gamma d^2)$$

It was the object of this thesis to test the applicability of the equation to carbon dioxide, a substance slightly polar in nature.

The eight parameters of the equation were calculated from pressure-volume-temperature data for carbon dioxide. It was found that the Benedict-Webb-Rubin equation fits accurately the experimental pressure-volume-temperature data for carbon dioxide up to a density of 14.8 gm.-moles per liter.

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September 1, 1953

Professor Leicester F. Hamilton
Secretary of the Faculty
Massachusetts Institute of Technology
Cambridge 39, Massachusetts

Dear Sir:

The thesis entitled, "Determination of the Equation of State Constants for Carbon Dioxide", is hereby submitted in partial fulfillment of the requirements for the degree of Bachelor of Science in Chemical Engineering.

Respectfully submitted,

Signature redacted

Elmer E. Selby, Jr.

ACKNOWLEDGMENT

The author of this thesis would like to acknowledge the guidance and advice given by Professor Manson Benedict during the preparation of this thesis.

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SUMMARY

A semi-empirical equation of state proposed by Benedict, Webb, and Rubin for light hydrocarbons and their mixtures gives excellent results. This equation is:

$$P = RTd + (B_oRT - A_o - C_o/T^2)d^2 + (bRT - a)d^3 + a\alpha d^6 + \frac{cd^3(1 + \gamma d^2)\exp(-\gamma d^2)}{T^2} .$$

It was the object of this thesis to test the applicability of the equation to carbon dioxide, a substance slightly polar in nature.

This thesis shows that the Benedict-Webb-Rubin equation of state can be satisfactorily utilized to predict pressure-volume-temperature relations of carbon dioxide for densities up to 14.8 gm.-moles per liter, or 1.4 times the critical density. The following values of the eight parameters to be used with the equation were computed in this thesis:

B_o	0.0483000
A_o	2.64700
$C_o \times 10^{-5}$	1.41500
b	0.00396667
a	0.133333
$c \times 10^{-4}$	1.48148
$\alpha \times 10^{4}$	0.890000
γ	0.00557000

No attempt was made to adjust the above values of B_o, A_o, and C_o to fit vapor pressure data for carbon dioxide.

Pressures calculated using the Benedict-Webb-Rubin equation of state were compared with those calculated using the Beattie-Bridgeman equation of state and it was found on the whole that the Benedict-Webb-Rubin equation gave more accurate results. It was also found that the density range over which the Benedict-Webb-Rubin equation gave satisfactory results (up to 14.8 gm.-moles per liter) was greater than that over which the Beattie-Bridgeman equation was valid (up to 5.5 gm.-moles per liter).

It is recommended that an attempt be made to adjust the reported parameters to fit vapor pressure data for carbon dioxide and also that an attempt be made to extend the Benedict-Webb-Rubin equation to substances more polar in nature than carbon dioxide.

INTRODUCTION

An equation of state expresses the functional relationship between the pressure, volume, and temperature of a fluid. Such an equation is a concise summary of a large amount of experimental data and thus simplifies thermodynamic calculations.

Beginning with the perfect gas law of Boyle and Charles many equations of state have been proposed, such as the equations of van der Waals, Lorentz, Clausius, Dieterici, Keyes, and Beattie and Bridgeman. Each proposed equation has been an attempt to combine mathematical simplicity with an accurate representation of data over a wide temperature range. The present development of certain industrial processes, such as many met in the high pressure and fractionation process industries, requires accurate knowledge of the behavior of many gases. An equation of state which will satisfy this need must of necessity be more complex than previous approximations. Accurate knowledge of the behavior of gases is also valuable in the theoretical study of intermolecular forces.

The object of this thesis was the extension of the Benedict-Webb-Rubin equation of state to carbon dioxide, a substance which exhibits moderately polar properties.

Historical Summary

As an improvement on the perfect gas law of Boyle and Charles, van der Waals presented an equation of state (9),

$$P = \frac{RTd}{1 - bd} - ad^2, \qquad (1)$$

where P is the pressure in atmospheres, R is the gas constant, T is the absolute temperature, d is the molal density, and a and b are constants characteristic of each substance. Although this equation is mathematically simple the limitations involved in its use are very severe. If the same a and b are used over wide ranges of density, van der Waals pressures are sometimes in error more than ideal gas pressures (8).

Among the equations of state which have been proposed as improvements of the van der Waals equation, that of Beattie and Bridgeman is probably the most accurate when applied to widely differing substances over a wide temperature range (10). The semi-empirical Beattie-Bridgeman equation is (1)

$$P = RTd + (B_oRT - A_o - Rc/T^2)d^2 + (-B_obRT + A_oa - RB_oc/T^2)d^3 + RB_obcd^4/T^2, \qquad (2)$$

where A_o, B_o, a, b, and c are constants characteristic of each substance. However, this equation does not correspond accurately with the pressure-volume-temperature properties of liquids or gases above the critical density. When used at temperatures above the critical and densities below the critical this equation permits the calculation of pressures which are accurate to within a few tenths of one per cent. The five constants of the equation have been determined by Beattie and his coworkers for a large number of gases (1).

Benedict-Webb-Rubin Equation of State

In 1940, M. Benedict, G. B. Webb, and L. C. Rubin proposed the following semi-empirical equation of state for hydrocarbons and their mixtures as a modification of the Beattie-Bridgeman equation (6)

$$P = RTd + (B_oRT - A_o - C_o/T^2)d^2 + (bRT - a)d^3 + a\alpha d^6 + \frac{cd^3(1 + \gamma d^2)\exp(-\gamma d^2)}{T^2} . \qquad (3)$$

In Eq. (3) A_o, B_o, C_o, a, b, c, α, and γ are constants characteristic of each substance. In the original article by Benedict, Webb, and Rubin (2) numerical values for the parameters of Eq. (3) were reported for methane, ethane, propane, and n-butane. The equation fits the experimental data very well up to about 1.8 times the critical density with temperatures well below the critical temperature. Over the density range below the critical density the average deviation of calculated pressures from observed pressures is slightly less than the average deviation from the Beattie-Bridgeman equation over the same range (2).

The original workers have fitted pressure-volume-temperature data for twelve or more light hydrocarbons and also for certain mixtures, while workers at the Carnegie Institute of Technology have determined the parameters for propylene vapor (5). At the Massachusetts Institute of Technology parameters were determined for the inert gases argon, krypton, and xenon by Chin, Galpern, and Walsh (3).

The purpose of this thesis was the extension of the Benedict-Webb-Rubin equation of state to a substance other than the light hydrocarbons, and specifically to test the accuracy of the equation when used to describe the pressure-volume-temperature properties of a slightly polar substance. Carbon dioxide, a substance which exhibits moderately polar properties, was selected for consideration.

There was available in the literature a sufficient quantity of pressure-volume-temperature data for carbon dioxide to permit determination of the parameters of the equation under consideration. The sources of the data which were utilized were Michels and Michels (6), Michels, Michels, and Wouters (7), and Kendall and Sage (4).

PROCEDURE

From the sources listed in the INTRODUCTION data were obtained at eight densities, the highest being approximately twice the critical density, and seven temperatures in the range 0°C to 237.78°C. Where necessary these data were converted to the units of the Benedict-Webb-Rubin equation and in the case of the data obtained from Kendall and Sage graphical interpolation was employed to obtain data at the densities previously selected. (For a complete tabulation of these data, see Table 2.)

The mathematical procedure used in the determination of the numerical values of the eight parameters from the experimental data is discussed in detail in Section A of the APPENDIX. The resulting provisional values were then used in combination with the Benedict-Webb-Rubin equation for the calculation of pressures at each of the experimental points utilized as data. The deviations of these calculated pressures from the observed pressures were determined, and it was observed that these deviations were satisfactorily small if the density did not exceed 14.8 gm.-moles per liter. Thus the provisional values of the parameters were accepted as final for densities not greater than 14.8 gm.-moles per liter.

RESULTS

The numerical values of the eight parameters for carbon dioxide are as follows:

B_o	0.0483000
A_o	2.64700
$C_o \times 10^{-5}$	1.41500
b	0.00396667
a	0.133333
$c \times 10^{-4}$	1.48148
$\alpha \times 10^{4}$	0.890000
γ	0.00557000

In the development of the equation of state the following values for the universal gas constant and the centigrade temperature of the ice point were used (2)

$$R = 0.08207$$

$$T(^{o}K) = t(^{o}C) + 273.13$$

and the units were atmospheres, liters, gm.-moles, and ^{o}K. These same values must therefore be used together with the above parameters in computing pressure-volume-temperature data by means of the Benedict-Webb-Rubin equation.

DISCUSSION OF RESULTS

The values of the eight parameters are given to six figures in the previous section. Although it is not possible to determine unique values accurate to six significant figures for the parameters, it has been shown that a simultaneous change of five per cent in all the constants does not seriously prejudice the calculated results (2). Four or five significant figures should be used when determining the properties of carbon dioxide by the use of the equation of state.

In the temperature range $0^{\circ}C$ to $238^{\circ}C$ and up to a density of 14.8 gm.-moles per liter the average deviation of calculated pressures from observed pressures is 0.140%. Comparison of these results with those reported by Beattie and Bridgeman (1) is made in Table 1. (For a complete comparison of the original data with calculated pressures, see Table 2.) It should be noted that the Beattie-Bridgeman parameters for carbon dioxide were determined from data obtained from different sources than those used in this thesis for the determination of the parameters of the Benedict-Webb-Rubin equation. The agreement of the observed and calculated pressures is slightly better for the Benedict-Webb-Rubin equation (0.127% deviation) than for the Beattie-Bridgeman equation (0.161% deviation) when the deviations are compared for the same range of temperature and density. It is therefore concluded the simpler Beattie-

TABLE 1

Comparison of Benedict-Webb-Rubin Equation with Beattie-Bridgeman Equation

Range		Average Deviation			
Temp. (°C)	Density $(\frac{\text{gm-moles}}{\text{liter}})$	Beattie-Bridgeman (atm.)	Benedict-Webb-Rubin (atm.)	Beattie-Bridgeman (%)	Benedict-Webb-Rubin (%)
0-100	2.0-5.0	0.105	0.089	0.161	0.127
0-100	0.5-5.5	0.128	---	0.203	---
0-238	2.0-5.0	---	0.100	---	0.110
0-238	2.0-14.8	---	0.294	---	0.140

Bridgeman equation should be used over this range unless the situation warrants slightly more accurate pressure-volume-temperature relations.

It is also observed from Table 1 that the Benedict-Webb-Rubin equation gives slightly smaller percentage deviations (0.140%) over the range 2.1 to 14.8 gm.-moles per liter and 0°C to 238°C than does the Beattie-Bridgeman equation (0.203%) over a much smaller range, 0.5 to 5.5 gm.-moles per liter and 0°C to 100°C. Thus the Benedict-Webb-Rubin equation can be utilized with accuracy under conditions for which the Beattie-Bridgeman equation is not valid.

In fitting the data to the equation of state large deviations from the observed pressure were obtained at densities greater than 14.8 gm.-moles per liter. The critical density for carbon dioxide is 10.45 gm.-moles per liter and so the equation was found valid within a reasonable limit of error to a density 1.4 times the critical density. In the case of the four original light hydrocarbons (2) it was found by Benedict, Webb, and Rubin that the equation of state fits the data well up to about 1.8 times the critical density. The discrepancy in range is probably due in part to the polar nature of carbon dioxide, though a similar discrepancy was noted when the equation of state was extended to the substances, argon, krypton, and xenon (3).

Modification of the parameters would be necessary for the extension of the equation to higher densities than

14.8 gm.-moles per liter. However, within the density range for which the given parameters are valid, they may be used at temperatures higher than 238°C with little loss in accuracy.

The results obtained in fitting pressure-volume-temperature data for carbon dioxide to the Benedict-Webb-Rubin equation of state give some indication that fairly good results can be expected should an attempt be made to extend the equation to substances more polar in nature than carbon dioxide. Though the density range, in terms of the critical density, within which the equation gives satisfactory results is smaller than that for the light hydrocarbons, it is greater than that found for argon by Chin, Galpern, and Walsh (3). In the case of argon the equation was valid up to about 1.2 times the critical density.

CONCLUSIONS AND RECOMMENDATIONS

Conclusions:

1. The empirically determined parameters reported in the section of RESULTS can be used with the Benedict-Webb-Rubin equation of state to calculate with high accuracy pressure-volume-temperature relationships within the specified range.

2. For densities not greater than 5.5 gm.-moles per liter the Beattie-Bridgeman equation is satisfactory for normal usage. For slightly more accuracy within this range and for all densities greater than 5.5 gm.-moles per liter the Benedict-Webb-Rubin equation should be used.

3. Within the specified density range the equation may be applied to temperatures higher than 238°C though large errors will be introduced if the equation is applied to densities greater than those specified.

Recommendations:

1. Because of its relative simplicity the Beattie-Bridgeman equation should be used for densities less than 5.5 gm.-moles per liter. The Benedict-Webb-Rubin equation should be used at higher densities.

2. An attempt should be made to adjust the values of the parameters B_o, A_o, and C_o determined in this thesis to fit vapor pressure data for carbon dioxide. It could thus be determined whether one set of parameters would fit both

vapor pressure and pressure-volume-temperature data for this substance.

3. An attempt should be made to extend the Benedict-Webb-Rubin equation to substances which are more polar in nature than carbon dioxide.

APPENDIX

A. Method for the Determination of the Numerical Values of the Parameters

Primary residuals, defined as $(P - RTd)/d^2$, were first determined, and at each density they were fitted by an equation of the form

$$(P - RTd)/d^2 = B(d)RT - A(d) - C(d)/T^2 \qquad \text{(B1)}$$

by the method of least squares, giving equal weight to each pressure. The values of B(d) so obtained were plotted against the density and a straight line was drawn through the points giving greater weight to the points at the higher densities. This straight line had the equation

$$B(d) = B_o + bd \qquad \text{(B2)}$$

where B_o and b are two of the equation of state parameters.

Secondary residuals, defined as

$$(P - RTd)/d^2 - (B_o + bd)RT,$$

were next calculated using the previously determined values of B_o and b and at each density they were fitted by an equation of the form

$$(P - RTd)/d^2 - (B_o + bd)RT = - \left[A'(d) + C'(d)/T^2\right] \qquad \text{(B3)}$$

giving equal weight to each pressure. By trial a value of γ was found such that when C'(d) was plotted against $d(1 + \gamma d^2)\exp(- \gamma d^2)$ the points fell on an approximately straight line. Giving greater weight to the points at the higher densities, a straight line having the equation

$$C'(d) = C_o - cd(1 + \gamma d^2)\exp(- \gamma d^2) \qquad \text{(B4)}$$

was passed through these points.

Tertiary residuals, defined as

$$(P - RTd)/d^2 - (B_o + bd)RT + \left[C_o - cd(1 + \gamma d^2)\exp(- \gamma d^2)\right]\frac{1}{T^2} ,$$

were next determined and they in turn determined A"(d) according to the equation

$$(P - RTd)/d^2 - (B_o + bd)RT + \left[C_o - cd(1 + \gamma d^2)\exp(- \gamma d^2)\right]\frac{1}{T^2} = - A''(d) \qquad \text{(B5)}$$

At densities near the critical, A"(d) was evaluated at the critical temperature, while at other densities an average value of A"(d) was determined. By trial a value of α was found such that when A"(d) was plotted against $d(1 - \alpha d^3)$ the points fell on an approximately straight line. Giving greatest weight to the points near the critical density, a straight line which had the equation

$$A''(d) = A_o + ad(1 - \alpha d^3) \qquad \text{(B6)}$$

was passed through these points.

By this method the provisional values for the eight parameters of the Benedict-Webb-Rubin equation were determined.

B. Summarized Data and Calculated Values

The data used for this thesis are presented in Table 2 along with calculated values of pressure and percentage deviations of the calculated values from observed data. The data of Michels *et al* (6, 7) were used at temperatures of 0°C, 49.712°C, 99.767°C, and 150.140°C while the data of Kendall and Sage (4) were used at temperatures of 104.44°C, 171.11°C, and 237.78°C.

TABLE 2

Summarized Data and Calculated Values

Density $(\frac{\text{gm-moles}}{\text{liter}})$		2.11660	5.03872	7.65544	10.1828	12.0270	14.7938	17.3709	20.5267
Temperature (^{o}C)		Pressure(atmospheres)							
0	obsd.	33.4202	---	---	---	---	---	---	---
	obsd.-calc.	0.0184							
	% dev.	0.055							
49.712	obsd.	44.9823	79.1582	94.0488	103.257	110.491	130.848	180.898	350.279
	obsd.-calc.	0.0284	0.2354	0.1118	-0.359	-0.320	-0.030	-6.665	-82.265
	% dev.	0.063	0.297	0.119	-0.347	-0.290	-0.023	-3.684	-23.49
99.767	obsd.	55.7976	110.947	149.054	184.991	216.386	286.180	403.553	691.824
	obsd.-calc.	-0.0806	0.083	0.098	-0.197	-0.099	-0.364	-10.213	-94.348
	% dev.	-0.145	0.075	0.066	-0.106	-0.046	-0.127	-2.530	-13.64
104.44	obsd.	56.80	113.8	154.0	192.5	225.0	300.7	423.6	---
	obsd.-calc.	-0.07	0.0	0.0	-0.3	-1.4	-0.4	-11.1	
	% dev.	-0.123	0.000	0.000	-0.156	-0.622	-0.133	-2.620	
150.140	obsd.	66.3704	141.534	202.746	266.859	324.034	444.846	628.422	1030.05
	obsd.-calc.	-0.1026	-0.088	-0.021	0.242	0.940	1.214	-9.769	-96.93
	% dev.	-0.155	-0.062	-0.010	0.091	0.290	0.273	-1.555	-9.41
171.11	obsd.	70.82	154.0	225.1	300.8	367.7	508.9	---	---
	obsd.-calc.	0.01	-0.2	0.2	0.4	-0.1	-0.2		
	% dev.	0.015	-0.130	0.089	0.133	-0.027	-0.039		
237.78	obsd.	84.57	193.5	294.0	406.2	508.2	---	---	---
	obsd.-calc.	0.18	-0.2	-0.4	-1.2	-0.7			
	% dev.	0.213	-0.103	-0.136	-0.295	-0.138			
	Average % dev.	0.110	0.111	0.070	0.188	0.236	0.119	2.597	15.51

C. Sample Calculations

The method for obtaining the eight parameters of the Benedict-Webb-Rubin equation of state was presented in Section A of the APPENDIX. The following calculations are made for a density of 10.1828 gm.-moles per liter and a temperature of 99.767°C, for which conditions the observed pressure was 184.991 atmospheres.

(1) Determination of B_o and b:

The primary residual was determined as follows:

$$\frac{P - RTd}{d^2} = \frac{184.991 - (0.08207)(372.897)(10.1828)}{(10.1828)^2}$$

$$= -1.22134$$

All the data points were then utilized by the method of least squares to determine the value of B(d), A(d), and C(d) which best fitted the equation

$$(P - RTd)/d^2 = B(d)RT - A(d) - C(d)/T^2. \qquad \text{(B7)}$$

Equations (B8), (B9), and (B10) were used for the method of least squares, and the summations were taken over all temperatures at the specified density.

$$\Sigma\left[(P - RTd)/d^2\right]\left[T\right] = B(d)\Sigma(RT^2) - A(d)\Sigma(T) - C(d)\Sigma(\tfrac{1}{T}) \qquad \text{(B8)}$$

$$\Sigma\left[(P - RTd)/d^2\right] = B(d)\Sigma(RT) - A(d)\Sigma(\text{points}) - C(d)\Sigma(\tfrac{1}{T}2) \qquad \text{(B9)}$$

$$\Sigma\left[(P- RTd)/d^2\right]_2\left[\frac{1}{T^2}\right] = B(d)\Sigma\left(\frac{R}{T}\right) - A(d)\Sigma\left(\frac{1}{T^2}\right) - C(d)\Sigma\left(\frac{1}{T^2}\right) \qquad (B10)$$

For the density under consideration the equations of the method of least squares took the following form:

$$-2180.77 = (83988.3)B(d) - (2451.73)A(d) - (0.0149986)C(d)$$

$$-5.73162 = (201.213)B(d) - (6)A(d) - (3.82805 \times 10^{-5})C(d)$$

$$-4.14035 \times 10^{-5} = (1.23093 \times 10^{-3})B(d) - (3.82805 \times 10^{-5})A(d) - (2.64485 \times 10^{-10})C(d).$$

The value of B(d) and the provisional values of A(d) and C(d) obtained from these equations were

$$B(d) = 0.0851999$$

$$A(d) = 3.70700$$

$$C(d) = 16536.3$$

Table 3 presents the complete set of determined values of B(d), A(d), and C(d). The values of B(d) were plotted against the density (Fig. 1) and a straight line was drawn through the points using the densities from 2.11660 gm.-moles per liter to 14.7938 gm.-moles per liter inclusive. From the equation of this line,

$$B(d) = B_o + bd, \qquad (B11)$$

values of B_o and b were determined.

$$B_o = 0.0483000$$

$$b = 0.00396667$$

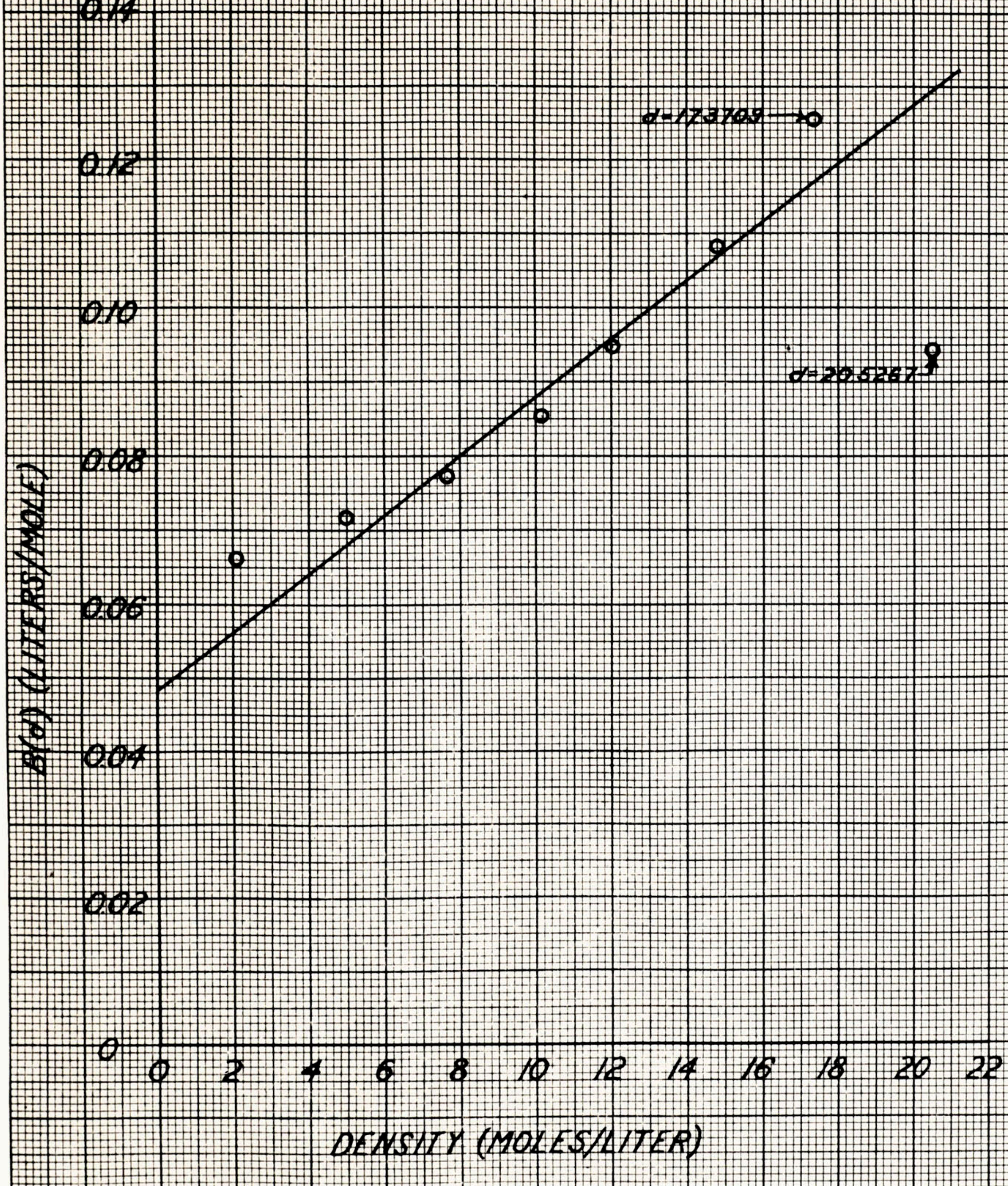
TABLE 3

Values of B(d), A(d), and C(d) at Various Densities

d (gm.-moles/liter)	B(d)	A(d)	C(d) x 10^{-4}
2.11660	0.0660696	3.35415	9.31944
5.03872	0.0718383	3.49639	5.68944
7.65544	0.0771286	3.55542	3.59898
10.1828	0.0851999	3.70700	1.65363
12.0270	0.0947893	3.94033	0.131220
14.7938	0.108109	4.10011	-0.438337
17.3709	0.125506	4.31311	-0.646282
20.5267	0.0941931	1.92628	1.08534

FIBURE 1

CALCULATION OF B_0 & b



(2) Determination of C_o, c, and γ:

For the data point under consideration the secondary residual was then determined as follows:

$$(P - RTd)/d^2 - (B_o + bd)RT = -1.22134 - [0.0483000 + (0.0039667)(10.1828)](0.08207)(372.897) = -3.93563.$$

At each density the secondary residuals were plotted against $(1/T^2)$ and the best straight line was drawn through the points. The slope of each line was accepted as the best value of $C'(d)$ at that density for the equation

$$(P - RTd)/d^2 - (B_o + bd)RT = -[A'(d) + C'(d)/T^2]. \quad (B12)$$

For a density of 10.1828 gm.-moles per liter $C'(d) = -8190.00$. Table 4 presents the complete set of determined values of $C'(d)$. The values of $C'(d)$ obtained at each density were plotted against $d(1 + \gamma d^2)\exp(-\gamma d^2)$ (Figure 2) where γ was determined by trial as that value which gave the straight line relation

$$C'(d) = C_o - cd(1 + \gamma d^2)\exp(-\gamma d^2). \quad (B13)$$

Thus values of C_o, c and γ were determined.

$$C_o = 1.41500 \times 10^5$$

$$c = 1.48148 \times 10^4$$

$$\gamma = 0.00557000$$

(3) Determination of A_o, a, and α:

For the data point under consideration the tertiary residual was determined as follows:

$$(P - RTd)/d^2 - (B_o + bd)RT + [C_o - cd(1 + \gamma d^2)\exp(-\gamma d^2)]\frac{1}{T^2} = -A''(d). \quad (B14)$$

TABLE 4

Values of C'(d) at Various Densities

d (gm.-moles/liter)	C'(d) x 10^{-4}	$d(1+\gamma d^2)e^{-\gamma d^2}$
2.11660	11.1	2.1158
5.03872	6.73	4.9927
7.65544	3.25	7.3315
10.1828	0.819	9.0199
12.0270	-0.225	9.7032
14.7938	-0.243	9.7171
17.3709	0.831	8.6614
20.5267	2.93	6.5678

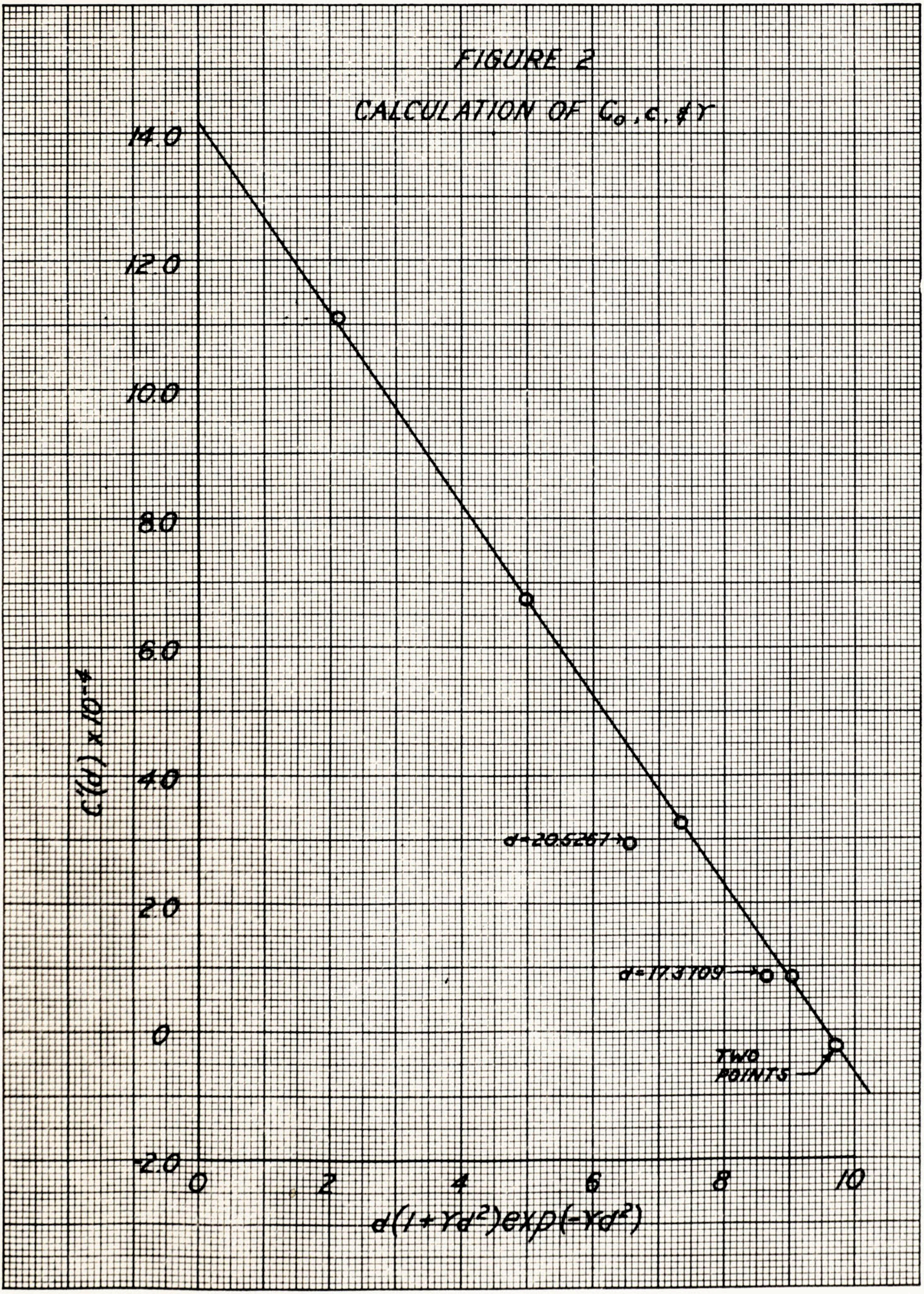


FIGURE 2

CALCULATION OF C_o, c, & γ

Evaluating:

$$-A''(d) = -3.93563 + \left[1.41500 \times 10^5 - (1.48148 \times 10^4)(10.1828)(1 + 0.00557000 \times 10.1828^2)\exp(-0.0557000 \times 10.1828^2)\right] \frac{1}{(372.897)^2} = -3.87901.$$

At each density an average value of $A''(d)$ was calculated (Table 5) and these average values were plotted versus $d(1 - \alpha d^3)$(Fig. 3). By trial α was determined such that a straight line resulted having the equation

$$A''(d) = A_o + ad(1 - \alpha d^3). \qquad \text{(B15)}$$

From the equation values of A_o and a were determined corresponding to the α already selected.

$$A_o = 2.64700$$
$$a = 0.133333$$
$$\alpha = 0.890000 \times 10^{-4}$$

(4) Deviation between observed and calculated pressures:

The use of Eq. (2) of the INTRODUCTION with the values of the parameters listed above results in a calculated pressure of 185.188 atmospheres. Thus the deviation from the observed pressure is

Observed - Calculated = 184.991 - 185.188 = - 0.197 atm.

This corresponds to a deviation of - 0.106%.

TABLE 5

Values of A"(d) at Various Densities

d (gm.-moles/liter)	A"(d) avg.	d(1 - αd^3)
2.11660	2.92947	2.11481
5.03872	3.30941	4.98135
7.65544	3.62680	7.34976
10.1828	3.87937	9.22592
12.0270	4.00390	10.1648
14.7938	4.05092	10.5309
17.3709	3.91390	9.26728
20.5267	3.49359	4.72636

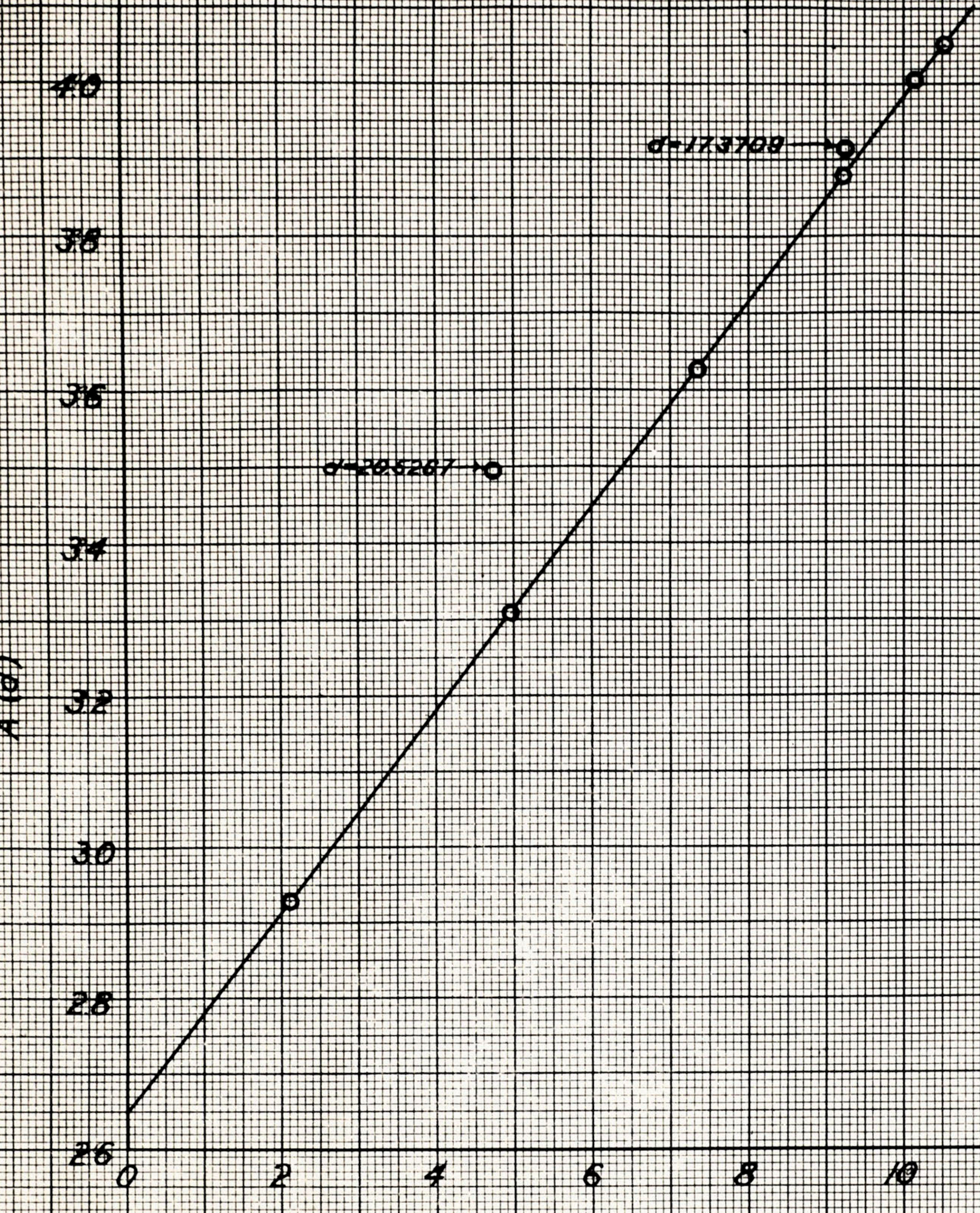


FIGURE 3

CALCULATION OF A_0, a, & α

D. Table of Nomenclature

A_o - Constant, Eqs. (2), (3), (B6), (B15)

A(d) - Defined by Eq. (B6)

a - Constant, Eqs. (1), (2), (3), (B6), (B15)

B_o - Constant, Eqs. (2), (3), (B2), (B3), (B5), (B11), (B12), (B14)

B(d) - Defined by Eq. (B11)

b - Constant, Eqs. (1), (2), (3), (B2), (B3), (B5), (B11), (B12), (B14)

C_o - Constant, Eqs. (3), (4), (B5), (B13), (14)

C(d) - Defined by Eq. (B4)

c - Constant, Eqs. (3), (B4), (B5), (B13), (B14)

d - Density, gm.-moles per liter

P - Pressure, atmospheres

R - Universal gas constant, 0.08207 liter atmospheres per gm.-mole ^{o}K

T - Temperature, ^{o}K

α - Constant, Eqs. (3), (B6), (B15)

γ - Constant, Eqs. (3), (B4), (B5), (B13), (B14)

Σ - Summation sign (summations taken over all temperatures at each density)

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