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University of California
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THE VAPOR PRESSURES OF
30 INORGANIC LIQUIDS BETWEEN ONE
ATMOSPHERE AND THE CRITICAL POINT

Livermore, California

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UNIVERSITY OF CALIFORNIA
Lawrence Radiation Laboratory
Livermore, California

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DAVID G. EDWARDS

June 17, 1964

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CONTENTS

Abstract	1
I. Introduction	3
A. Vapor Pressure Deviations from the Clausius-Clapeyron Equation	3
B. Experimental Data	12
C. Scope of this Work	16
II. Vapor Pressure Deviation Curves	17
A. Construction of Deviation Curves	17
B. Shape of Curves	18
C. Slope of Curve at Normal Boiling Point	19
D. Relation to Liquid and Vapor Densities Along Co-existence Envelope	22
E. Correspondence of Maxima and Minima	23
F. Correspondence of Data with Deviation Curve	24
III. Deviation Curves and Tables of Interpolated Vapor Pressures	27
A. Procedure	27
B. Summarized Critical Property and Vapor Pressure Values	28
C. Individual Substances	32
1. Hydrogen Isotopes	32
2. Neon	41
3. Nitrogen	44
4. Carbon Monoxide	48
5. Argon	51
6. Oxygen	54
7. Methane	57
8. Nitric Oxide	61
9. Krypton	64

CONTENTS (Continued)

10. Xenon		67
11. Silicon Tetrafluoride		71
12. Nitrous Oxide		74
13. Carbon Dioxide		78
14. Hydrogen Chloride		83
15. Hydrogen Bromide		86
16. Sulfur Hexafluoride		89
17. Hydrogen Sulfide		92
18. Hydrogen Iodide		96
19. Chlorine		99
20. Ammonia		102
21. Cyanogen		106
22. Sulfur Dioxide		110
23. Hydrogen Fluoride		115
24. Hydrogen Cyanide		118
25. Nitrogen Tetroxide		121
26. Bromine		125
27. Sulfur Trioxide		128
28. Carbon Tetrachloride		131
29. Tin Tetrachloride		134
30. Water		137
IV. Acknowledgments		139
V. References		140

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ABSTRACT

Literature values of the vapor pressures of H_2 , HD, D_2 , N_2 , O_2 , Ne, Ar, Kr, Xe, CO, NO, CH_4 , SiF_4 , N_2O , CO_2 , HCl, HBr, HI, SF_6 , H_2S , Cl_2 , Br_2 , NH_3 , C_2N_2 , SO_2 , SO_3 , HF, HCN, N_2O_4 , CCl_4 , and $SnCl_4$ have been compared with the Kirchhoff formula

$$\log P_K = -A/T + B$$

between the normal boiling point and the critical point, where A and B are determined for each liquid. Plots are presented of the deviations computed by the equation

$$d = P_K - P_{obs}.$$

Based on accurately determined curves for 17 of these substances, empirical hypotheses were developed to allow the prediction of the most probable course of the deviation curve in cases where the data appeared to be unreliable. In addition, where precise data were available, the possibility of the existence of fine-structure curvature has been demonstrated.

*Work performed under the auspices of the U. S. Atomic Energy Commission.

The deviation curves have been used to obtain tables of interpolated vapor-pressure values which are, in most cases, more accurate by one order of magnitude than any now in the literature, particularly where smoothed regression curves do not discriminate between random experimental errors and systematic deviations of an arbitrarily chosen formula from the real vapor-pressure curve. Since the deviation curve is invariably shown to approach the zero ordinate at the critical point with a large negative slope, the correspondence between the critical pressure and temperature is fixed with a high degree of confidence. A particular result of this work is that the critical pressure of NH_3 was shown to be about one atmosphere higher than the presently accepted value. Our values for the critical points of CH_4 , C_2N_2 , HCN , and Br_2 have also resolved differences existing between various authorities in the literature.

I. INTRODUCTION

A. VAPOR PRESSURE DEVIATIONS FROM THE CLAUSIUS- CLAPEYRON EQUATION

The approximate Clausius-Clapeyron relation (Eq. 3 below) predicts that the log of the vapor pressure P should vary linearly with the inverse of the absolute temperature T . Actually, the real vapor pressure deviates from this relationship, as shown in exaggerated form in Figure 1. The origin of these deviations can be seen from a consideration of the exact Clausius-Clapeyron equation

$$dP/dT = \Delta H/T (V_g - V_l), \quad (1)$$

where ΔH is the heat of vaporization at temperature T , and V_g and V_l are the vapor and liquid molar volumes, respectively. At pressures below one atmosphere, V_l is substantially zero and V_g is given quite closely by the ideal gas equation

$$V_g = RT/P. \quad (2)$$

Substituting Eq. 2 into 1, the familiar form of the approximate Clausius-Clapeyron equation is obtained:

$$\frac{d \ln P}{d(1/T)} = - \Delta H/R; \quad (3)$$

$\Delta H/R$ represents the slope of the line given by a plot of $\ln P$ vs $1/T$. The major deviation of the real vapor pressure from this line below the boiling point originates from the fact that ΔH is not a constant but varies with T according to a relation such as Eq. 4:

$$\Delta H = a + bT + cT^2, \quad (4)$$

where a , b , and c are constants. As T approaches the critical point, ΔH goes to zero; and above one atmosphere, the deviation of V_g from the ideal

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Fig. 1. The log P vs $1/T$ vapor-pressure curve exaggerated to show the various curvatures. (Adapted with permission from Industrial and Engineering Chemistry.)

gas equation becomes progressively greater; V_g also begins to increase significantly. At the critical point ΔV becomes zero; although $\Delta H/\Delta V$ is indeterminate at the critical point, it has a limiting value of approximately $7P_c$ (111).

Returning to an examination of Eq. 1, it is seen that the inflection point (shown between the boiling point and the critical temperature in Figure 1) arises from the necessity that the dew point line of the coexistence envelope change direction in order to attain closure at the critical point. This generally occurs for T/T_c between 0.75 and 0.85.

Thus the deviations of vapor pressure from ideal behavior are seen to be due to:

- (1) Departure of $d\Delta H/dT$ from linearity.
- (2) Deviation of V_g from ideal behavior.
- (3) An inflection point in $(dV_g/dT)_s$ at the saturated condition (denoted by the subscript s).

Although the vapor-pressure-temperature relationship could be exactly expressed by substituting a power series in T for ΔH , and a power series in $(1/T)P^n$ for ΔV (as discussed by Lewis and Randall (66)), it has been shown by Waring (111) that a four-constant equation of the form

$$\log P = A + B/T + CT + DT^2 \quad (5)$$

is adequate to describe the features of the real vapor-pressure curve illustrated in Figure 1. Indeed, Miller (78) has shown that for the region between one atmosphere and the critical point, which is the area of interest in this investigation, Eq. 5 could be fitted to the data for 23 of the compounds given by this work to within 1.54% average maximum error. Furthermore, according to Miller, even the simple Kirchhoff equation

$$\log P = -A/T + B \quad (6)$$

(where A and B are constants) fitted the same data with an average maximum error of only 3.20%. This close fit between the boiling point and the critical point is a consequence of the fact that for many substances a line of constant slope drawn between the boiling point and the critical point bisects the real vapor-pressure curve because of the existence of the inflection discussed above. In addition, it develops that the slope A in Eq. 6 is, for many of the substances investigated here, quite close to the slope at the boiling point, as is shown in Table I below; the arithmetic sum of the maximum positive and negative deviations of the vapor pressure from Eq. 6 for these substances is about 1 atm. or less, as is seen in Figures 2-5 below. The derivation of the modified Klein equation for predicting heats of vaporization (102) was based on a recognition of this condition.

Thus it is seen that while Eq. 5 adequately follows the real vapor-pressure curve, it may be in error by as much as 1.5% when the constants are derived from a correlation using T_b , P_c , and T_c (as shown by Miller (78)), or by a few tenths of a percent if fitted by a regression curve to the experimental vapor-pressure data between T_b and T_c , as done by many of the authors cited in this work. For critical pressures of 40 to 60 atm., errors of 1.5% amount to absolute errors of 0.6 to 0.8 atm. Even when fitted by regression-line treatment, the resulting equation fails markedly to fit the data to the same degree as the precision of the measurements in the region of high curvature between the inflection point and the critical point. This situation has been graphically demonstrated by Michels et al. (73-77). Furthermore, Friedman and White (31) have specifically stated that Eq. 5 cannot be made to give a good fit with the data for N_2 near both the boiling point and the critical point. This also has been recognized by Hoge (50), who fitted the data for oxygen to five separate equations of the type of Eq. 6, and by Osborne et al. (85, 86),

TABLE I
COMPARISON OF HEATS OF VAPORIZATION

Substance	ΔH_b cal./mole	ΔH_k cal./mole	$\Delta H_k - \Delta H_b$ cal./mole	$\Delta S_{k/b}$ cal./mole-°K.
n-H ₂	216	258	42	13
Ne	410	442	32	16.7
N ₂	1333	1353	20	18.0
CO	1444	1446	2	18.3
Ar	1558	1546	-12	18.3
O ₂	1630	1631	1	18.6
CH ₄	1955	1985	30	18.3
NO	3293	2988	-305	25.4
Kr	2158	2153	-5	18.5
Xe	3021	2995	-26	18.7
SiF ₄	4460	3945	-515	22.9
N ₂ O	3956	3768	-188	21.0
HCl	3860	3799	-65	20.8
HBr	4210	4090	-120	20.4
SF ₆	4080	3992	-88	20.1
H ₂ S	4463	4285	-178	20.7
HI	4724	4601	-123	19.9
Cl ₂	4878	4675	-326	20.2
NH ₃	5581	5340	-241	23.0
C ₂ N ₂	5576	5342	-234	21.9
SO ₂	5955	5677	-278	22.2
(HF) ₆	5020 ^a	6422	1402	22.6
HCN	6027	6478	451	22.3
N ₂ O ₄	7040 ^a	8203	1163	28.8
Br ₂	7030	6826	-204	21.2
SO ₃	9990	7639	-2351	24.8
CCl ₄	7170	6918	-252	20.4
SnCl ₄	8300	7794	-506	20.7
H ₂ O	9717	9147	-570	25.3

^aPerry, Chemical Engineers Handbook, Fourth Ed. p. 3-107, Ref. (91).

Fig. 2. Deviation curves for H_2 , D_2 , N_2 , CO , CO_2 , and SF_6 .

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Fig. 3. Deviation curves for Xe, Kr, CH₄, O₂, and Ar.

Fig. 4. Deviation curves for HBr, HCl, HI, Cl_2 , H_2S , Br_2 , N_2O , NH_3 , C_2N_2 , and SO_2 .

Fig. 5. Deviation curves for HF, N₂O₄, HCN, NO, Ne, CCl₄, and SnCl₄.

who fitted the data for the vapor pressure of H_2O with an equation utilizing exponential functions. Manifestly, then, the experimental determination of vapor pressure always will be capable of greater precision than can be obtained with simple equations containing up to four constants, and it is only with considerable effort that special equations have been developed that have sufficient flexibility to reliably smooth such high-precision data.

It appeared, therefore, that a deviation curve based on a relation as simple as Eq. 6 would:

- 1) Be capable of as great a degree of precision as more complicated equations.
 - 2) Conform more closely to the behavior of real vapor-pressure curves so as to more clearly define the magnitude of experimental errors.
 - 3) Establish precisely the value of dP/dT at any temperature.
 - 4) Establish precisely the value of the vapor pressure above one atmosphere relative to the boiling point as stated herein, and to the temperature scale used by the original investigator as transposed to an ice point of $273.15^\circ C$.
 - 5) Fix more precisely the correspondence between the critical pressure and the critical temperature (as recognized by Pickering (93)).
- The above points will be further amplified in the discussion below.

B. EXPERIMENTAL DATA

In considering the need for a comprehensive investigation of the data reported in the literature, the following points were weighed. The most accurate published correlations of vapor-pressure data above 1 atm., with the exception of NBS Circular 564 (84), dated back to the Landolt-Bornstein "Physikalisch-Chemisch Tabellen" (65), last revised in 1936, and the International Critical Tables (54), published in 1928. Stull's more recent (1947) results (108) based on Cox-Chart correlations had been shown by Miller (78) to be seriously in

error because the correlation used was such that the vapor-pressure curve was made to approach the critical point in the opposite direction from the real vapor-pressure curve shown in Figure 1. In addition, a considerable amount of new vapor-pressure data had been published.

A consideration of the data available indicated that initially our investigation would be well served if restricted to 30 or so inorganic substances. For half of these data of high precision had been reported; the remainder were of sufficient industrial and scientific importance to justify a careful re-examination of the data reported prior to 1947.

In addition to the works mentioned above, we would like to acknowledge our indebtedness to the bibliographic works of Kelley (59) and of Pickering (93); these have been of invaluable help in searching the literature. The original sources of all work relevant to the compounds considered by us have been studied, but we have cited only those containing data on which our results are based or those representing errors or omissions in the previous literature sources. Where the results of only the most recent investigators have been used, a thorough analysis of the work of the previous investigators has been given by one or more of the authors cited.

Since the details of the experimental work pertinent to the data used here are discussed by the original authors, only general comments need be given here regarding experimental methods. It is well recognized that the precision of vapor-pressure data will be governed by the following considerations: (1) purity of sample; (2) precision of pressure measurement; (3) precision of temperature measurements; and (4) adequate precision of temperature control and the design of the apparatus such as to insure the attainment of true liquid-vapor equilibrium.

Until the relatively recent advent of such powerful analytical tools as mass spectrography and gas chromatography, the methods available for determination of the purity of sample were restricted largely to simple measurements such as density, boiling point, and refractive index. In the early days, investigators making vapor-pressure measurements often pioneered in the synthesis of the material itself; in notable circumstances, as mentioned below, these vapor-pressure determinations have not been repeated even though the purity of the original material is manifestly suspect in the light of more recent synthetic work. Possibly the most remarkable case is that of arsine, for which no high-pressure measurements have been made since Faraday's work up to 13 atm., reported in 1845.

Since the development of the Keyes deadweight piston gage, for which the vapor pressure of CO_2 at 0°C . has been established as the standard calibration point, this instrument has been used either as the working gage or as the primary standard for all precision measurements above 2 or 3 atm. This gage is sensitive to 0.001 atm. at pressures up to 150 atm.

The temperature sensitivity corresponding to this degree of pressure sensitivity is 0.0007°C . in the neighborhood of the critical point, where dP/dT is about 1.5 atm./ $^\circ\text{C}$. This degree of sensitivity is attainable either with multi-junction thermocouples, which are to be generally preferred below 100°K ., or with platinum resistance thermometers above this temperature.

An important problem still unresolved is the fixing of the boiling points of many well known liquids on the International Temperature Scale. Until this has been done, the reported vapor-pressure values must be considered, at best, to be only internally consistent with the boiling point as determined by the investigator. Indeed, much of the confusion existing in the literature today has been caused by the historical fluctuation of the accepted value of the ice

point on the Kelvin scale and the impossibility of using a simple additive relationship to equate the many historic Kelvin scales which have been used.

Undoubtedly the greatest source of error — both in frequency and degree — to be found in vapor-pressure data has arisen from poor temperature control. Poor thermostating is generally the cause of error when the reported temperature does not correspond to the pressure measurement; this is particularly a cause of error near the critical point because of relatively sluggish attainment of liquid-vapor equilibrium. Where the heat of vaporization is relatively large at temperatures below the critical point, this heat exerts a self-correcting effect on measurements which tends to check temperature fluctuations. However, near the critical point, ΔH becomes smaller; in addition, the difference between the liquid and vapor density decreases markedly, thus increasing the difficulty in maintaining equilibrium.

Our examination of the deviation curves derived from the data convinced us that the interests of accuracy would be best served by:

- 1) Computing the deviations relative to the most accurate boiling point available in the literature.
- 2) Using the most accurate data to define a general behavior pattern for the deviation curve, including specifically a pattern for the location of the maximum and minimum and the relative slopes of the various portions of the deviation curve.
- 3) Estimating the accuracy of the data by their agreement with a smooth curve conforming to this generally established pattern.

Since there is a high conformity of the data to these requirements, we feel that the precision of the method has been positively demonstrated and the existence of situations where greater-than-normal errors had occurred could be distinguished. We feel these criteria are manifestly more reliable indicators of the

precision of the data than those claimed for the experimental apparatus by the original authors. The general accuracy of the best values given in this report relative to the International Temperature Scale is probably not better than $\pm 0.01^{\circ}\text{C}.$, with a corresponding pressure variation at the temperature in question. The absolute accuracy of the values is generally to one less decimal point than stated, but these values can be used for purposes of internal comparison (of dP/dT , for example) to the number of places quoted.

C. SCOPE OF THIS WORK

The usefulness of deviation curves to represent vapor-pressure data accurately from one atmosphere to the critical point is well recognized. There has been, however, no systematic effort to compare data for different substances with the same base function, each author adopting a mathematical function giving a preferred fit to his data. In many cases, deviations from the equations have not been plotted, and the problem of distinguishing between potentially real effects, systematic deviations from an assumed and perhaps inadequate empirical equation, and random deviations due to experimental error has generally been left to the reader. In cases where the precision of the data is within 0.001 atm. , and a corresponding temperature precision, this problem is obviated. However, where experimental errors and real effects are given equal weight in regression-curve treatment, the result is inevitably confused. Historically, then, the vapor-pressure deviation curve has been treated as a mathematical tool whose characteristics were imposed by the special conditions of each individual problem.

The objective of this work was to determine whether, if deviation curves for a large number of inorganic liquids were plotted on a single basis, any common characteristics could be established for substances whose vapor pressures were accurately known, and whether curves having these common

characteristics would give a reasonable fit for other substances whose reported vapor-pressure data were of questionable reliability.

In this work all data have been compared to the Kirchhoff equation

$$\log P_K = - \frac{A}{t^{\circ}\text{C} + 273.15} + B \quad (7)$$

and the deviation has been expressed as

$$d = P_K - P_{\text{obs}} \quad (8)$$

Temperatures expressed in the Kelvin scale were converted to degrees Celsius on the basis of the ice point used by the investigator, although we realized that these historic Kelvin scales were not strictly equivalent to the present 1954 Kelvin scale based on an ice point of 273.15°K. The A and B constants were evaluated using selected boiling points and critical points, and were expressed to six figures. The considerations governing the selection of these values will be discussed in more detail below. Equations 1 and 2 were combined and the deviations were computed on a IBM 650 machine. The deviations obtained were plotted to a scale consistent with the precision of the data, the most precise plots being readable to 0.001 atm. and a corresponding temperature precision.

II. VAPOR PRESSURE DEVIATION CURVES

A. CONSTRUCTION OF DEVIATION CURVES

In order to fully define the deviation curve using eqs. 1 and 2, the following information was required:

1. The boiling point, T_b ;
2. The critical temperature, T_c ;
3. The critical pressure, P_c ;
4. Vapor-pressure data between T_b and T_c .

Satisfactory boiling point values based on accurate, low pressure work were found in the literature for most of the substances. In a few cases, the boiling point used was determined by us from the high-pressure deviation curve presented in this report.

By passing the linear Kirchhoff equation through the boiling point and critical point, the value of d is necessarily 0 at one atmosphere and at the critical pressure. In some cases minor corrections in P_c have been made by adjusting d_c rather than by recalculating the constants in eq. 1. (See tables in Part III.)

In cases where the critical point was established by accurate PVT determinations of the coexistence envelope, in conjunction with adequate vapor pressure measurements between T_b and T_c , no problem was found in constructing a deviation curve.

In other cases a lack of correspondence between P_c and the vapor pressure predicted by the deviation curve at T_c was revealed by a gross discontinuity in the deviation curve at the critical point. Here the prime criterion which we used was the necessity for a general correspondence of the maximum and minimum of the deviation curve with those for similar substances. Then, since only two data are necessary among items 2, 3, and 4, the choice of either T_c or P_c fixed the other. The considerations involved in the choices of T_c and P_c will be discussed below in connection with the specific compounds involved.

B. SHAPE OF CURVES

For the generalized comparison of the deviation curves, the temperature range between the boiling point and the critical point was normalized on a $1/T$ basis and expressed as percent, where

$$\%(1/T) = 100 \left(\frac{1/T_b - 1/T}{1/T_b - 1/T_c} \right). \quad (9)$$

The curves are presented for each liquid individually in Part III of this report but for the purposes of the generalized discussion, are variously grouped in Figures 1-5. It should be noted that in each of Figures 1-5, some curves shown are determined from experimental data of a high degree of precision. Specifically, the well defined curves are those for H_2 , HD, D_2 , N_2 , CO, Ne, Ar, O_2 , CH_4 , Kr, Xe, N_2O , CO_2 , NH_3 , SO_2 , SO_3 , HF, N_2O_4 , and CCl_4 . Curves for which empirical considerations were involved, to varying degrees, in fixing their positions were SiF_4 , Cl_2 , C_2N_2 , Br_2 , $SnCl_4$, NO, HCl, HBr, SF_6 , H_2S , HI, and HCN.

Referring to Figures 2-6, it can be seen that the curves fall into two general classes, as further illustrated in Figure 7, where various points have been designated by the letters b, j, h, k, and c. The distinction between Class I and Class II is not fundamental but results from the arbitrary choice of the normal boiling point as the lower terminus of the curve. If a lower temperature were to be taken so as to increase the bj distance in curve I, the Class II curve would be obtained.

C. SLOPE OF CURVE AT NORMAL BOILING POINT

Comparison of eq. 6 with the exact Clausius-Clapeyron equation

$$\frac{Rd (\ln P)}{d(1/T)} = - \frac{\Delta H}{\Delta Z} \quad (10)$$

shows that

$$(4.5758)(\Delta Z)(A) = \Delta H_k, \quad (11)$$

where ΔH_k is the heat of vaporization at the boiling point corresponding to a constant $d (\log P)/d(1/T)$ slope, A, between T_b and T_c ; and ΔZ is the difference between the liquid and vapor compressibility. According to Miller (78) an average ΔZ for inorganic liquids at the boiling point is 0.97. Substituting this value for ΔZ in eq. 5, ΔH_k 's have been calculated and are given in Table I, along with ΔH_b values from NBS Circular 500 (83) and Perry (91).

Fig. 6. Deviation curves for SiF₄ and SO₃.

Class I curve

Class II curve

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Fig. 7. Classes of deviation curves.

It can be seen from the above that the difference, $\Delta H_k - \Delta H_b$, should indicate whether the slope of the deviation curve at the boiling point will be positive or negative. Comparison of Column 4 in Table I with the deviation curves given in Part III indicates that this criterion is quantitatively obeyed in that, in 27 out of 30 cases, the sign of the slope is correctly predicted. The quantitative disparity of some of the ΔH differences as compared with the slopes of the deviation curves leads us to observe, however, that because of curvature of the vapor pressure temperature function at the boiling point, this difference may only be quantitatively obeyed for a few degrees above the boiling point. In addition, it is probably true that in some cases our average value for ΔZ is not accurate and that in some cases the value used for ΔH_b may be inaccurate.

Table I also gives values of 4.5758 B, a psuedo-entropy term, i. e. , $\Delta S_{k/b}$ cal. per degree per mole of vapor. As can be seen from the Table, values of $\Delta S_{k/b}$ above 21.0 are generally found with associated liquids.

D. RELATION TO LIQUID AND VAPOR DENSITIES ALONG COEXISTENCE ENVELOPE

The upturn of the deviation curve at b in Class I and at j in Class II curves is probably most closely related to large percentage changes which are beginning to occur in the liquid density along the bubble-point line. No correlation of this point with coexistence data has been made, but it should be pointed out as a matter of experimental procedure that adequate and reliable vapor-pressure data in this region are a prime requisite for accurately defining the deviation curve. As the heat of vaporization and the difference between liquid and vapor volumes become rapidly smaller, the problems of maintaining temperature and pressure equilibrium are aggravated. However, the problems are considerably less at this point than at temperatures above point

k, and any effort expended in getting accurate measurements in this region pay dividends toward minimizing the effect of uncertainties encountered in the kc region. The inflection point at h appears to be due to the inflection point in the vapor density along the dew-point line as mentioned previously.

It is of interest to comment on the evidence for fine-structure effects demonstrated in the precisely determined curves. In examining the bjh region of the curves for accurately known substances, it is found in all 15 cases that in this region the curve may be composed of two, three, or four nearly straight sections joined by relatively sharp curves. These straight sections were particularly evident for the Class I curves having no negative deviations; i. e., H_2 , N_2 , CO, Ar, O_2 , CH_4 , Kr, Xe, and HF and are strikingly illustrated in the cases of N_2 and CH_4 , for which large-scale plots are provided below. Although in most cases the data shown could be almost as well fitted with smoother curves, and although four points cannot be said to conclusively establish a straight line, it would be equally presumptuous to conclude, a priori, that deviation curves must demonstrate a low-order curvature, data points notwithstanding.

E. CORRESPONDENCE OF MAXIMA AND MINIMA

Empirically, it appears that on the scales plotted in Figures 2-6 the peak k of the jhkc loop is located so that the angle formed by the straight section of hk with the vertical is for Class I curves from 60 to 80° and for Class II curves from 20 to 40°; the angle generally formed by kc is about half as great; and furthermore that the d ordinate values for j and k for similar substances do exhibit a general degree of correspondence as shown in Figures 1-5. Thus the $d = 0$ requirement at P_c fixes P_c within relatively narrow limits. Because the high dP/dT slope of the deviation curve at the critical point is superimposed on the contribution of the Kirchhoff equation, dP/dT may vary

between 1.0 and 2.0 atm./°C. For a dP/dT of 1.5 atm./deg., for example, a pressure difference of 0.01 atm. is equivalent to a 0.0067°C. temperature difference. Thus it can be seen that the pressure is an especially sensitive function of temperature at the critical point. This means, of course, that random temperature errors near the critical region represent the highest degree of pressure dispersion on the deviation plot. Complementing this, however, is the magnification of the precision with which the pressure is fixed by a well defined deviation curve. If the necessity is assumed for the k height to correspond to a uniform pattern for similar substances to at least within ± 0.05 atm. as discussed above, P_c is fixed certainly within these limits and correspondingly T_c is fixed to within about $\pm 0.03^\circ\text{C}$.

F. CORRESPONDENCE OF DATA WITH DEVIATION CURVE

The following section presents general considerations involved in selecting the preferred deviation-curve location for situations where the vapor pressure data were ambiguous.

In Figure 2, the accurately known curves were those of H_2 , D_2 , N_2 , CO , and CO_2 .

In the case of SF_6 the only consistent data were those of one investigator in the kc region. The data in the bjh region were badly scattered and one investigator's data in the kc region demonstrated a low-pressure "nose" between k and c . Other examples of this "nose" effect have been found in the course of this study, and, without exception, they have been found to be spurious when compared with precise measurements. We have discounted these points, therefore. The curve derived from the average of the scattered points in the bjh region also was suspect in that this curve was not in harmony with the preferred hkc data. Furthermore, this curve differed markedly from that of CO_2 , a compound with a similar coexistence line. In this region therefore,

our preferred curve was derived from the normalized CO_2 curve as described below. To support this judgment it can be pointed out that N_2 and CO , whose molecular similarity are well recognized (47), show practically identical deviation curves in Figure 2.

In Figure 3 all curves are well defined by the data. In Figure 4, the accurately known curves are NH_3 , N_2O , and SO_2 . Three general problems were encountered in locating the other curves in regions of poorly determined data. In the case of Br_2 and C_2N_2 , where relatively good data were available in the bjh region, the problem was to choose a critical pressure corresponding to the accepted T_c so that the bjh portion of the curves would form a mutually symmetrical pattern. This was done by adjusting the j and k peaks to be in mutual correspondence with the other curves shown. In the cases of HCl and H_2S , no data were available in the bjh region, and in the case of Cl_2 , the bj data departed markedly from the general slope. The course adopted here was to draw the curves to harmonize both with the hjk points and the other bjh curves shown in Figure 4. In the case of Br_2 no data were available in the kc region, so this curve was drawn to be in mutual harmony with Cl_2 .

The third problem in Figure 4 with Cl_2 , HBr , and HI was that these data exhibited excessive scatter overall. The preferred curves were therefore drawn so as to best approach the points giving curves matching the pattern established by HCl and H_2S . Points deviating from this pattern by more than the normal confidence limits were neglected. It can be seen by examining the individual curves given below for these substances that a reasonable degree of agreement with the data has been obtained in the jhk region where there is less difficulty in attaining equilibrium conditions.

In the case of NH_3 , a choice was made in the kc region between the data of Beattie (8) and of Keyes (60). The data of Beattie were used because a

deviation curve following Keyes' points indicated a critical pressure 0.5 atm. lower than Beattie's. Basing the deviation curve on A and B constants calculated from Keyes' indicated P_c would have not only lowered the k point below that for C_2N_2 but would also have lowered the j point to -0.55 atm., or 0.15 atm. below any other compound shown in Figure 4. It was believed that Keyes' data were in error here and critical values were chosen to correspond with Beattie's points so that the deviation curve harmonized as shown in Figure 3. A similar situation is also discussed below in Section III. C.7 on CH_4 .

In Figure 5 the curves were plotted on different pressure scales for convenience in comparing shapes. For Ne, CCl_4 , and $SnCl_4$, the d ordinate is 0.1 atm./division, for NO and HCN 0.2 atm./division, and for HF and N_2O_4 0.4 atm./division. The curves for HF, N_2O_4 , Ne, CCl_4 , and $SnCl_4$ were well determined by the data. The curve for HCN was found to fit the few observed data well when matched with that for N_2O_4 . The curve shown for NO was drawn so as to best fit the few points that seemed to indicate a reasonable curve and so as to harmonize with the other curves as shown.

Figure 6 presents the deviation curves for SiF_4 and SO_3 . These curves do not conform to those in the previous figures since the d's are not zero at the boiling point and in the case of SO_3 , also at the critical point. By means of this change, the deviation curves were able to be presented on a scale comparable to those of Figures 1-4 without excessively large negative values for the j minimum. It should be noted that the data for SO_3 in the kc region were ambiguous but that the kc height shown was drawn to conform to that of SO_2 , which appeared to be reasonable.

In the kc region we have noted that the prevailing disagreements with the most accurate data appear to be in the direction of lower pressures. This has been found to be true in the cases of Ne, Ar, CH_4 , HCl, H_2S , SF_6 , NH_3 ,

N_2O_4 , and SnCl_4 . In the cases of HBr and HI , where deviation curves were located so as to correspond to curves for other substances determined by accurate data, data which matched the curve in question in the jhk region were low in the kc region. We are unable to advance any firm reasons for expecting experimental errors to prevail in this direction; however, the relative absence of scatter in the other direction tends to suggest that this is a systematic error. Hence, in the absence of consistently reliable data in this region, we have located the curve so as to be symmetrical with similar substances having approximately the same k coordinates and have avoided points to the right of k which would flatten the peak and require a drastic increase in kc curvature and slope. Substances for which reliable data were completely unavailable in the jhkc region have not been considered in this study. It should be emphasized that the utility sought for a hypothesis of the general behavior of the deviation curve is that in the face of contradictory data, it more closely approximates the probable position of the deviation curve than does regression line treatment.

III. DEVIATION CURVES AND TABLES OF INTERPOLATED VAPOR PRESSURES

A. PROCEDURE

Deviation curves were prepared as described above and are given in this Part in connection with each specific substance. The text accompanying each curve below cites the sources of the data used and discusses the considerations involved in locating the preferred position of the curve. Rather than attempt to reproduce the large-scale deviation plots, deviation values read from these plots have been included in the Tables of Interpolated Vapor Pressures. The first column of the Tables of Interpolated Vapor Pressure gives the temperature in $^{\circ}\text{C}.$, the second column gives the interpolated vapor pressure calculated by the equation

$$P_i = P_K - d, \quad (12)$$

and the third and fourth columns give P_K and d , respectively. The reliability of the last figure given for P_i is generally questionable. In the cases of hydrogen, nitrogen, oxygen, methane, and carbon dioxide, reduced size figures of the original large-scale plots of d against $^{\circ}\text{C}$. are also presented. This has been done to show for these substances the basis for our judgment as to most probable position of the deviation curve where the results of several investigators are in disagreement, and to exemplify the nature of "fine-structure" effects which have been generally brought out by high-precision measurements. The other substances, for which only small-scale graphs are presented, fall into one of two categories: either the precision of the data of several investigators is adequately represented by the small scale used, or the data of a single investigator is considered to be of superior reliability and earlier results have been rejected on the bases mentioned above. Comparisons with these other data have usually been presented by the authors cited.

B. SUMMARIZED CRITICAL PROPERTY AND VAPOR PRESSURE VALUES

In addition to the individual tables of vapor pressures, Table II is presented showing the comparison of our preferred critical values with those selected by Stull (108) and Kobe and Lynn (63). In general, these two authorities' values correspond with Pickering (93) and with other authorities in the International Critical Tables (54).

Our interpolated vapor pressure tables giving the vapor pressures for even temperature values may be compared directly with the International Critical Tables. For comparison with Stull's values, we have prepared Table III giving temperature values for even pressure values.

TABLE II
SUMMARY OF SELECTED DATA COMPARED WITH LITERATURE

Substance	b p °C	Stull (108)		Critical Properties Kobe and Lynn (63)		This Work	
		T _c °C	P _c atm	T _c °C	P _c atm	T _c °C	P _c atm
eq-H ₂	-252 88	--	--	-240 22	12 77	-240 17 ^a	12 76 ^a
n-H ₂	-252 77	-240 0	12 80	-239 9	12 80	-239 92 ^a	12 80 ^a
HD	-251 02	--	--	-237 25	14 645	-237 25 ^a	14 645 ^a
eq-D ₂	-249.52	--	--	-234 90	16 282	-234 90 ^a	16 28 ^a
n D ₂	-249 49	--	--	-234 81	16 432	-234 82 ^a	16 42 ^a
Ne	-246 06	-228 3	26 90	-228 7	26 9	-228 75 ^a	26 19 ^a
N ₂	-195 78	-147 2	33 5	-147 0	33 5	-146 93 ^b	33 54 ^a
CO	-191 48	-138 7	34 6	-140	34 5	-140 23 ^a	34 53 ^a
Ar	-185 91	-122 0	48 0	-122	48 0	-122 29 ^a	48 34 ^a
O ₂	-182 97	-118 9	49 7	-118 4	50 1	-118 38 ^a	50 14 ^a
CH ₄	-161 49	-82 1	45 8	-82 1	45 8	-82 61 ^a	45 49 ^b
NO	-151 74	-92 9	64 6	-93	64	-92 9 ^a	64 6 ^a
Kr	-153 40	-63	54	-63 8	54 3	-63 77 ^a	54 31 ^b
Xe	-108 12	--	--	16 59	58 0	16 59 ^a	57 64 ^a
SiF ₄	-90 2 ^c	-14 2	36 7	-14 1	36 7	-14 17 ^a	36 66 ^a
N ₂ O	-88 46	36 5	71 7	36 5	71 7	36 43 ^a	71 60 ^a
CO ₂	-56 57 ^c	31 1	73 0	31 0	72 9	31 04 ^a	72 84 ^a
HCl	85 03	51 4	81 6	51 4	81 5	51 54 ^a	82 07 ^b
HBr	66 72	90 0	84 4	90 0	84 0	90 0 ^a	84 5 ^b
SF ₆	-51 ^c	--	--	45 55	37 11	45 64 ^a	37 19 ^a
H ₂ S	-60 19	100 3	88 9	100 4	88 9	99 9 ^a	88 26 ^a
HI	-35 35	151	82	150	81	150 7 ^a	81 9 ^b
Cl ₂	-34 05	144	76 1	144	76 1	144 1 ^b	76 1 ^a
NH ₃	-33 35	132 4	111 5	132 3	111 3	132 50 ^a	112 53 ^b
C ₂ N ₂	-21 15	126 6	58 2	127	59	128 30 ^a	59 98 ^b
SO ₂	-10 02	157 2	77 7	157 5	77 8	157 50 ^a	77 81 ^a
HF	19 5	--	--	--	--	188 ^a	64 07 ^a
HCN	25 70	183 5	50 0	183 5	53 2	183 5 ^a	48 89 ^b
N ₂ O ₄	21 0	158	99	158	100	158 2 ^a	99 66 ^b
Br ₂	58 2	302 2	121	311	102	311 ^a	102 ^a
SO ₃	44 55	218 3	83 6	218 2	83 8	217 7 ^a	81 44 ^b
CCl ₄	76 7	283 1	45 0	283 2	45 0	283 15 ^a	44 97 ^a
SnCl ₄	114 1	318 7	37 9	318 7	36 95	318 7 ^a	36 95 ^a

^aLiterature value cited in text

^bValue determined from deviation curve in this work

^cTriple pt above 1 atm

TABLE III

TEMPERATURE AT SELECTED VAPOR PRESSURE VALUES

Substance	Temperature, °C															I _c	P _c
	1 atm.	2 atm	5 atm.	10 atm.	20 atm	30 atm.	40 atm	50 atm	60 atm	70 atm	80 atm	90 atm	100 atm	110 atm			
nH ₂	-252.77	-250.15	-245.78	-241.60												-239.92	12.80
nD ₂	-249.49	-246.87	-242.50	-238.33												-234.82	16.42
Ne	-246.06	-243.55	-239.43	-235.54	-230.81											-228.75	26.19
N ₂	-195.78	-189.38	-179.08	-169.27	-157.36	-149.30										-146.93	33.54
CO	-191.48	-184.90	-174.11	-163.97	-151.64	-143.30										-140.23	34.53
Ar	-185.91	-178.78	-167.22	-156.36	-143.15	-134.13	-127.13									-122.29	48.34
O ₂	-182.97	-175.77	-164.16	-153.29	-140.12	-131.14	-124.16	-118.45								-118.38	50.14
CH ₄	-161.49	-152.39	-137.68	-123.79	-107.01	-95.53	-86.71									-82.61	45.49
NO	-151.74	-145.4	-135.0	-125.1	-114.0	-107.1	-102.0	-97.8	-94.3							-92.9	64.6
Kr	-153.40	-143.76	-128.24	-113.67	-96.04	-83.93	-74.51	-66.71								-63.77	54.31
Xe	-108.12	-95.06	-73.92	-54.19	-30.19	-13.76	-0.92	9.68								16.59	57.64
SiF ₄	--	-88.32	-72.1	-55.4	-34.5	-20.9										-14.17	36.66
N ₂ O	-88.46	-76.03	-56.20	-37.90	-15.98	-1.10	10.48	20.06	28.25	35.39						36.43	71.60
CO ₂	--	--	--	-39.78	-19.07	-5.07	5.82	14.84	22.56	29.29						31.04	72.84
HCl	-85.03	-71.96	-51.23	-32.29	-9.53	5.92	17.84	27.70	36.20	43.67	50.27					51.54	82.07
HBr	-66.72	-52.16	-29.15	-7.71	18.51	36.12	49.69	60.94	70.66	79.24	86.85					90.0	84.5
SF ₆			-29.98	-8.08	18.35	35.92										45.64	37.19
H ₂ S	-60.19	-45.46	-22.13	-0.64	25.22	42.77	56.46	67.85	77.69	86.36	94.10					99.9	88.26
HI	-35.35	-18.25	9.19	34.64	65.50	86.86	103.6	117.4	129.3	139.8	149.0					150.7	81.9
Cl ₂	-34.05	-17.00	10.33	35.60	66.16	87.10	103.3	116.8	128.4	138.6						144.1	76.1
NH ₃	-33.35	-18.56	4.52	25.34	49.86	66.27	78.98	89.50	98.52	106.46	113.59	120.01	125.87	131.22		132.50	112.53
C ₂ N ₂	-21.15	-4.84	20.88	44.43	72.40	91.40	106.25	118.45								128.30	59.98
SO ₂	-10.02	6.71	32.91	56.81	85.32	104.45	119.21	131.40	141.85	151.03						157.50	77.81
HF	19.5	40.03	71.06	98.51	129.02	148.54	163.40	175.05	184.59							188.0	64.07
HCN	25.70	45.53	77.25	105.48	136.95	157.37	172.73									183.5	48.89
N ₂ O ₄	21.0	36.78	59.71	79.13	100.44	113.87	123.85	131.85	138.54	144.32	149.44	154.08				158.2	99.66
Br ₂	58.2	80.72	116.4	148.5	186.9	213.0	233.3	250.2	264.7	277.5	289.1	299.6	309.2			311	102
SO ₃	44.55	59.88	84.76	108.74	138.37	158.90	174.59	187.54	198.61	208.29	216.62					217.7	81.44
CCl ₄	76.7	101.52	141.10	177.73	221.88	251.30	273.82									283.15	44.97
SnCl ₄	114.1	140.65	183.37	222.85	270.07	301.50										318.7	36.95

An additional, more meaningful comparison between our deviation curve and the Stull and ICT values was made by us by comparing the deviations of these values with our deviation curve. It appears that Cragoe's calculated values in the International Critical Tables agree fairly well with our values. Stull's values, however, invariably show large negative deviations and no positive deviations. This is to be expected from the nature of the Cox Chart correlation method used by him which always approaches the critical point from the negative rather than the positive deviation side.

While the choice of a location for the deviation curve in the absence of reliable data is difficult, especially in cases where apparently reliable data are in conflict, it is believed that the procedures which have been used have resulted in the closest possible approach to the true vapor pressure. This is based on the demonstration by this study of a high degree of consistency in the general shape of the deviation curve. For several different materials the curves are almost identical; for instance, the groups N_2 and CO ; HF and N_2O_4 ; O_2 , Ar , Xe , Kr , and CH_4 show this trait. The demonstration of conformity of the deviation curve behavior with the results of published studies on vapor pressure and heats of vaporization also supports this procedure. On this basis the reasons for rejecting data which are in radical disagreement with this behavior appear justified.

It is worth noting that in addition to NO no reliable high pressure data are available in the literature for such common substances as CF_4 , CS_2 , COS , $COCl_2$, SiH_4 , PH_3 , AsH_3 , H_2Se , N_2H_4 , BCl_3 , BF_3 , $SiCl_4$, and $GeCl_4$.

It is hoped that this study has sufficiently demonstrated the utility of the deviation curve method as to encourage its future use to demonstrate the consistency and reliability of experimental data.

C. INDIVIDUAL SUBSTANCES

1. Hydrogen Isotopes

Deviation curves have been computed for the following hydrogen isotopes: eq-H₂, n-H₂, HD, eq-D₂, and n-D₂. The curves plotted on a $\%(1/T)$ basis are shown in Figure 8. It appears that on this basis the curves for the ortho and para forms coincide with each other both for H₂ and D₂ but that contrary to Friedman, White, and Johnston (33) the curves for the H₂ and D₂ isotopes are separated from each other by about 5 to 6% in the b-k region, with HD falling between H₂ and D₂. Plotting the curves on a reduced-temperature basis as was done by Friedman, White, and Johnston does not appreciably reduce this separation, since the reduced boiling points do not differ by more than 1%.

The boiling points quoted in Table II are due to the following authors: n-H₂ (118); eq-H₂; HD, and eq-D₂ (51); and n-D₂ (43).

The sources of critical constants used for deriving the Kirchhoff equations were: n-H₂ (117); eq-H₂ (100); HD and eq-D₂ (52); and n-D₂ (32).

The vapor-pressure data from the various investigations of the NBS (51, 112, 42) and Grilly (43) show good precision and are in good agreement. Friedman, White, and Johnston's data on n-D₂ (32) are in agreement with Hoge's data and with the deviation curves in Figure 8 above point k. In the b-k region, Friedman, White, and Johnston's results agree after their temperatures in this region are adjusted to agree with Grilly's boiling point. In the case of n-H₂ neither White, Friedman, and Johnston (116) nor Cath and Kammerlingh Onnes (20) agree precisely with Grilly, as can be seen from Figure 9. The deviation curve shown in Figure 9 was obtained by projecting a curve based on Grilly's results and coinciding with the deviation curve for eq-H₂ shown in Figure 8.

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- (33) Friedman, A. S., White, D., and Johnston, H. L., J. Chem. Phys. 19, 126 (1951).
- (118) Wooley, H. W., Scott, R. B., and Brickwedde, F. G., J. Res. Natl. Bur. Std. 41, 379 (1948).
- (51) Hoge, H. J., and Arnold, R. D., J. Res. Natl. Bur. Std. 47, 63 (1951).
- (43) Grilly, E. R., J. Am. Chem. Soc. 73, 843 (1951).
- (117) White, D., Friedman, A. S., and Johnston, H. L., J. Am. Chem. Soc. 72, 3565 (1950).
- (100) Roder, H. M., Diller, D. E., Weber, L. A., and Goodwin, R. D., Cryogenics 3, 16 (1963).
- (52) Hoge, H. J., and Lassiter, J. W., J. Res. Natl. Bur. Std. 47, 75 (1951).
- (32) Friedman, A. S., White, D., and Johnston, H. L., J. Am. Chem. Soc. 73, 1310 (1951).
- (112) Weber, L. A., Diller, D. E., Roder, H. M., and Goodwin, R. D., Cryogenics 2, 236 (1962).
- (42) Goodwin, R. D., Diller, D. E., Roder, H. M., and Weber, L. A., J. Res. Natl. Bur. Std. 67A, 173 (1963).
- (116) White, D., Friedman, A. S., and Johnston, H. L., J. Am. Chem. Soc. 72, 3927 (1950).
- (20) Cath, P. G., and Kammerlingh Onnes, H., Koninkl. Ned. Akad. Wetenschap. Proc. Ser. B 26, 490 (1917) Leiden Comm. No. 152a.

Fig. 8. Deviation curves for H isotopes.

Fig. 9. Deviation curve for n-H₂ vs t °C.

TABLE IV
VAPOR PRESSURE OF eq-H₂

$$\log P_K = -58.1591/T + 2.86950$$

t, °C.	P _i , atm.	P _K , atm.	d, atm.
-252.882	1.000	1.000	.000
252.50	1.116	1.130	.014
252.0	1.284	1.317	.033
251.5	1.472	1.525	.053
251.0	1.677	1.753	.076
250.5	1.901	2.003	.102
250.0	2.144	2.276	.132
249.5	2.410	2.572	.162
249.0	2.698	2.892	.194
248.5	3.012	3.237	.225
248.0	3.350	3.606	.256
247.5	3.713	4.000	.287
247.0	4.102	4.420	.318
246.5	4.518	4.866	.348
246.0	4.961	5.338	.377
245.5	5.435	5.836	.401
245.0	5.943	6.360	.417
244.5	6.486	6.911	.425
244.0	7.060	7.487	.427
243.5	7.670	8.091	.421
243.0	8.303	8.720	.417
242.5	8.998	9.375	.377
242.0	9.722	10.056	.334
241.5	10.489	10.763	.274
241.0	11.299	11.495	.196
240.5	12.164	12.252	.088
240.174	12.759	12.759	.000

TABLE V
VAPOR PRESSURE OF n-H₂

$$\log P_K = -58.3365/T + 2.86244$$

t, °C.	P _i , atm.	P _K , atm.	d, atm.
-252.77	1.000	1.000	.000
252.50	1.080	1.090	.010
252.00	1.241	1.271	.030
251.50	1.421	1.472	.051
251.00	1.620	1.693	.073
250.50	1.838	1.936	.098
250.00	2.075	2.200	.125
249.50	2.334	2.488	.154
249.00	2.616	2.798	.182
248.50	2.920	3.132	.212
248.00	3.244	3.491	.247
247.50	3.597	3.874	.277
247.00	3.974	4.282	.308
246.50	4.375	4.715	.340
246.00	4.803	5.173	.370
245.50	5.260	5.657	.397
245.00	5.749	6.167	.418
244.50	6.273	6.703	.430
244.00	6.830	7.264	.434
243.50	7.423	7.851	.428
243.00	8.048	8.464	.410
242.50	8.705	9.102	.397
242.00	9.403	9.765	.362
241.50	10.146	10.454	.308
241.00	10.927	11.167	.240
240.50	11.765	11.905	.140
240.00	12.641	12.667	.020
239.916	12.797	12.797	.000

TABLE VI
VAPOR PRESSURE OF HD

$$\log P_K = -67.2848/T + 3.04002$$

t, °C.	P _i , atm.	P _K , atm.	d, atm.
-251.017	1.000	1.000	.000
250.5	1.159	1.173	.014
250.0	1.331	1.360	.029
249.5	1.522	1.567	.045
249.0	1.732	1.794	.062
248.5	1.960	2.044	.084
248.0	2.208	2.316	.108
247.5	2.477	2.611	.134
247.0	2.769	2.931	.162
246.5	3.085	3.275	.190
246.0	3.428	3.646	.218
245.5	3.796	4.042	.246
245.0	4.191	4.465	.274
244.5	4.613	4.915	.302
244.0	5.064	5.394	.330
243.5	5.543	5.898	.355
243.0	6.054	6.432	.378
242.5	6.596	6.994	.398
242.0	7.172	7.586	.414
241.5	7.784	8.206	.422
241.0	8.431	8.855	.424
240.5	9.117	9.533	.416
240.0	9.841	10.240	.399
239.5	10.609	10.977	.368
239.0	11.420	11.742	.322
238.5	12.280	12.536	.256
238.0	13.187	13.360	.173
237.5	14.152	14.212	.060
237.252	14.645	14.645	.000

TABLE VII
VAPOR PRESSURE OF eq-D₂

$$\log P_K = -74.8801/T + 3.16926$$

t, °C.	P ₁ , atm.	P _K , atm.	d, atm.
-249.523	1.000	1.000	.000
249.5	1.005	1.007	.002
249.0	1.159	1.171	.012
248.5	1.329	1.354	.025
248.0	1.518	1.556	.038
247.5	1.724	1.778	.054
247.0	1.951	2.022	.071
246.5	2.198	2.288	.090
246.0	2.468	2.578	.110
245.5	2.757	2.891	.134
245.0	3.070	3.230	.160
244.5	3.406	3.595	.189
244.0	3.742	3.958	.216
243.5	4.159	4.403	.244
243.0	4.577	4.849	.272
242.5	5.023	5.323	.300
242.0	5.498	5.826	.328
241.5	6.005	6.359	.354
241.0	6.545	6.921	.376
240.5	7.117	7.513	.396
240.0	7.726	8.136	.410
239.5	8.370	8.790	.420
239.0	9.054	9.475	.421
238.5	9.775	10.191	.416
238.0	10.536	10.939	.403
237.5	11.335	11.718	.383
237.0	12.180	12.528	.348
236.5	13.074	13.370	.296
236.0	14.017	14.244	.227
235.5	15.015	15.150	.135
235.0	16.059	16.087	.028
234.898	16.282	16.282	.000

TABLE VIII

VAPOR PRESSURE OF n-D₂

$$\log P_K = -75.1357/T + 3.17564$$

t, °C.	P _i , atm.	P _K , atm.	d, atm.
-249.49	1.000	1.000	.000
249.0	1.149	1.160	.011
248.5	1.318	1.341	.023
248.0	1.506	1.542	.036
247.5	1.713	1.763	.050
247.0	1.938	2.006	.068
246.5	2.185	2.271	.086
246.0	2.450	2.560	.110
245.5	2.739	2.872	.133
245.0	3.051	3.210	.159
244.5	3.388	3.574	.186
244.0	3.750	3.964	.214
243.5	4.138	4.381	.243
243.0	4.554	4.826	.272
242.5	5.000	5.300	.300
242.0	5.475	5.802	.327
241.5	5.981	6.334	.353
241.0	6.518	6.896	.378
240.5	7.089	7.488	.399
240.0	7.695	8.112	.417
239.5	8.338	8.766	.428
239.0	9.018	9.451	.433
238.5	9.740	10.168	.428
238.0	10.502	10.916	.414
237.5	11.308	11.696	.388
237.0	12.157	12.508	.351
236.5	13.054	13.352	.298
236.0	13.991	14.228	.237
235.5	14.986	15.136	.150
235.0	16.034	16.075	.041
234.82	16.421	16.421	.000

2. Neon

The boiling point and critical-point data used in computing the deviation curve for neon were taken from Grilly (44). The vapor-pressure data used in computing the deviation curve were kindly supplied to us in a private communication by Dr. Grilly. Grilly's data agree with the deviation curve to ± 0.001 atm. in the low pressure region and ± 0.01 atm. at pressures above 10 atm. The deviation curve for neon is given in Figure 10.

(44) Grilly, E. R., Cryogenics 2, 226 (1962).

GLL-637-1703

Fig. 10. Deviation curve for Ne.

3. Nitrogen

Since 1926 several investigators (12, 27, 30, 74, 94) have measured the vapor pressure of nitrogen above 1 atm., and the disagreement between them shown by Figure 11 is not as serious as reported by Michels. Moreover, Friedman and White's critical point values (31) are in good agreement with his vapor-pressure data and also with Michels' results. Therefore, we have selected a critical temperature of $-146.93^{\circ}\text{C}.$ to fit the critical pressure of 33.54 atm. as given by Friedman and White (31). A boiling point of $-195.78^{\circ}\text{C}.$ has been selected as best fitting our deviation curve. This is in good agreement with the results of Dodge and Giauque and Clayton (36). Armstrong (5) has reported a value of $-195.796^{\circ}\text{C}.$

In view of the demonstrated over-all high precision of Michels' measurements, and since his points most closely fit the expected course of the deviation curve, we have used his data to locate our curve. In addition, his results appear to represent a good mean value. The precision of Friedman's points appears to be equally good, with a systematic difference of about -0.04 atm. between -180 and $-158^{\circ}\text{C}.$ Friedman's point at $-147.63^{\circ}\text{C}.$ is apparently in error, as are Dodge's data in the neighborhood of $-151^{\circ}\text{C}.$

(12) Bloomer, O. T., and Parent, J. D., Inst. Gas. Techn. Tes. Bull. 17, (1952).

(27) Dodge, B. F., and Davis, H. N., J. Am. Chem. Soc. 49, 610 (1927).

(30) Friedman, A. S., and White, D., J. Am. Chem. Soc. 72, 3931 (1950).

(74) Michels, A., Wassenaar, T., DeGraaf, W., and Prins., Chr., Physica 19, 26 (1953).

TABLE IX
VAPOR PRESSURE OF Ne

$$\log P_K = -98.5614/T + 3.63803$$

t, °C	P _l , atm.	P _K , atm.	d, atm.
-246.058	1.000	1.000	.000
246.0	1.017	1.018	.001
245.5	1.178	1.184	.006
245.0	1.359	1.370	.011
244.5	1.559	1.577	.018
244.0	1.780	1.806	.026
243.5	2.023	2.060	.037
243.0	2.290	2.339	.049
242.5	2.583	2.644	.061
242.0	2.903	2.978	.075
241.5	3.251	3.341	.090
241.0	3.626	3.736	.110
240.5	4.028	4.162	.134
240.0	4.463	4.622	.159
239.5	4.929	5.117	.188
239.0	5.432	5.648	.216
238.5	5.971	6.216	.245
238.0	6.550	6.824	.274
237.5	7.168	7.470	.302
237.0	7.827	8.158	.331
236.5	8.527	8.887	.360
236.0	9.272	9.660	.388
235.5	10.062	10.476	.414
235.0	10.899	11.337	.438
234.5	11.786	12.244	.458
234.0	12.725	13.198	.473
233.5	13.716	14.198	.482
233.0	14.760	15.248	.488
232.5	15.857	16.345	.488
232.0	17.009	17.493	.484
231.5	18.222	18.690	.468
231.0	19.501	19.938	.437
230.5	20.853	21.237	.384
230.0	22.284	22.588	.304
229.5	23.796	23.990	.194
229.0	25.375	25.445	.070
228.75	26.193	26.193	.000

- (94) Porter, F., and Perry, J. H., J. Am. Chem. Soc. 48, 2059 (1926).
- (31) Friedman, A. S., and White, D., J. Am. Chem. Soc. 73, 5713 (1951).
- (36) Giaque, W. F., and Clayton, J. O., J. Am. Chem. Soc. 55, 4875 (1933).
- (5) Armstrong, G. T., J. Res. Natl. Bur. Std. 53, 263 (1954).

Fig. 11. Deviation curve for N_2 vs t °C.

TABLE X

VAPOR PRESSURE OF N₂

$$\log P_K = -304.913/T + 3.94097$$

t, °C.	P _i , atm.	P _K , atm.	d, atm
-195.78	1.000	1.000	.0
194	1.226	1.226	.0
192	1.526	1.526	.0
190	1.879	1.879	.0
188	2.291	2.291	.0
186	2.769	2.769	.0
184	3.317	3.317	.0
182	3.943	3.943	.0
180	4.651	4.652	+0.001
178	5.435	5.450	.015
176	6.306	6.344	.038
174	7.276	7.340	.064
172	8.352	8.443	.091
170	9.540	9.659	.119
168	10.844	10.994	.150
166	12.269	12.454	.185
164	13.822	14.043	.221
162	15.510	15.766	.256
160	17.342	17.628	.286
158	19.326	19.634	.308
156	21.471	21.788	.317
154	23.790	24.094	.304
152	26.295	26.555	.260
150	28.999	29.176	.177
149	30.426	30.547	.121
148	31.905	31.959	+0.054
147	33.432	33.412	-0.020
146.93	33.542	33.515	-0.027

4. Carbon Monoxide

The deviation curve for carbon monoxide shown in Figure 12 is based on the data of Michels et al. (76). The curve agrees with the data to within 0.001 atm. The boiling point is taken as -191.48°C . as determined by Giaque and Clayton (35). The deviation curve appears to be in excellent agreement with the critical data of Mathias and Crommelin (68).

-
- (76) Michels, A., Wassenaar, T., and Zwietering, Th. N. Physica 18, 160 (1952).
- (35) Giaque, W. F., and Clayton, J. O., J. Am. Chem. Soc. 54, 2610 (1932).
- (68) Mathias, E., and Crommelin, O. A., Ann. Phys. 5, 137 (1936).

GIL-637-1705

Fig. 12. Deviation curve for CO.

TABLE XI

VAPOR PRESSURE OF CO

$$\log P_K = -325.813/T + 3.98938$$

t, °C.	P _i , atm.	P _K , atm.	d, atm.
-191.48	1.000	1.000	.0
190	1.183	1.178	-0.005
188	1.466	1.456	.010
186	1.798	1.782	.016
184	2.179	2.161	.018
182	2.620	2.600	.020
180	3.120	3.102	.018
178	3.686	3.674	.012
176	4.324	4.322	-0.002
174	5.042	5.050	+0.008
172	5.845	5.865	.020
170	6.734	6.772	.038
168	7.716	7.777	.061
166	8.797	8.885	.088
164	9.982	10.101	.119
162	11.280	11.431	.151
160	12.692	12.880	.188
158	14.228	14.452	.224
156	15.892	16.152	.260
154	17.692	17.985	.293
152	19.634	19.955	.321
150	21.727	22.066	.339
148	23.981	24.322	.341
146	26.413	26.727	.314
144	29.034	29.284	.250
143	30.416	30.621	.205
142	31.853	31.996	.143
141	33.346	33.412	.066
140.23	34.529	34.529	.0

5. Argon

The deviation curves shown in Figure 13 are based on the measurements of Michels and Levelt (72) and Michels, Wassenaar and Zwietering (21) and on measurements by Clark, Din and Robb also reported in reference (21). The boiling point of -185.91°C. is reported by Michels (21) and the critical point of -122.29°C. and 48.34 atm. is reported by Michels (72). Michels' vapor-pressure data (72) from 10 atm. to the critical point lie between his data (72) and Clark's data (21) with a variation of about 0.01 atm. We have harmonized Michels' later high-pressure data with his earlier results to obtain our preferred vapor pressures given in Table XII. Michels' critical constants are in good agreement with the deviation curve. Crommelin (26) has reported the critical point to be -122.44°C. and 47.996 atm.

(72) Michels, A., and Levelt, J. M., Physica 24, 659 (1958).

(21) Clark, A. M., Din, F., Robb, J., Michels, A., Wassenaar, T., and Zwietering, Th. N., Physica 17, 876 (1951).

(26) Crommelin, C. A., Koninkl. Ned. Akad. Wetenschap. Proc. Ser. B 22, 1212 (1913) Leiden Comm. Nos. 115a, 138c, 140a.

Fig. 13. Deviation curve for Ar.

TABLE XII

VAPOR PRESSURE OF Ar

$$\log P_K = -348.432/T + 3.99395$$

t, °C.	P _i , atm.	P _K , atm.	d, atm.
-185.91	1.000	1.000	.0
184	1.218	1.218	.0
182	1.484	1.484	.0
180	1.790	1.792	.002
178	2.144	2.148	.004
176	2.545	2.555	.010
174	3.000	3.018	.018
172	3.513	3.542	.029
170	4.087	4.131	.044
168	4.729	4.789	.060
166	5.444	5.522	.078
164	6.232	6.334	.102
162	7.099	7.230	.131
160	8.049	8.214	.165
158	9.085	9.291	.206
156	10.212	10.464	.252
154	11.438	11.739	.301
152	12.766	13.119	.353
150	14.201	14.609	.408
148	15.749	16.212	.463
146	17.415	17.932	.517
144	19.204	19.773	.569
142	21.119	21.737	.618
140	23.169	23.829	.660
138	25.357	26.052	.695
136	27.687	28.407	.720
134	30.169	30.899	.730
132	32.818	33.530	.712
130	35.638	36.301	.663
128	38.631	39.215	.584
126	41.821	42.275	.454
125	43.493	43.859	.366
124	45.227	45.481	.254
123	47.020	47.140	.120
-122.29	48.340	48.340	.0

6. Oxygen

The work of Hoge (50) is considered to be definitive. We have, however, prepared a deviation curve based on an ice point of 273.15°K. as compared to his ice point of 273.16°K. Hoge has mathematically fitted his data very well by connecting separate equations for each of five temperature regions. Our deviation curve shown in Figure 14 represents an accuracy within 0.001 atm. For a critical discussion of other measurements on oxygen see Hoge's paper.

(50) Hoge, H. J., J. Res. Natl. Bur. Std. 44, 321 (1950).

Fig. 14. Deviation curve for O_2 vs $t^\circ C$.

TABLE XIII

VAPOR PRESSURE OF O₂

$$\log P_K = -367.390/T + 4.07396$$

t, °C.	P _i , atm.	P _K , atm.	d, atm.
-182.97	1.000	1.000	.0
182	1.105	1.105	.0
180	1.350	1.349	-0.001
178	1.633	1.632	-0.001
176	1.960	1.960	.0
174	2.334	2.336	+0.002
172	2.760	2.766	.006
170	3.241	3.253	.012
168	3.780	3.802	.022
166	4.384	4.418	.034
164	5.055	5.106	.051
162	5.800	5.870	.070
160	6.623	6.715	.092
158	7.526	7.646	.120
156	8.514	8.668	.154
154	9.594	9.784	.190
152	10.771	11.001	.230
150	12.049	12.322	.273
148	13.431	13.752	.321
146	14.923	15.295	.372
144	16.528	16.954	.426
142	18.255	18.735	.480
140	20.111	20.641	.530
138	22.098	22.676	.578
136	24.224	24.844	.620
134	26.492	27.147	.655
132	28.911	29.589	.678
130	31.486	32.173	.687
128	34.228	34.902	.674
126	37.147	37.779	.632
124	40.255	40.807	.552
122	43.562	43.987	.425
121	45.300	45.636	.336
120	47.091	47.323	.232
119	48.951	49.049	+0.098
118.38	50.140	50.139	-0.001

7. Methane

The vapor-pressure data reported up to 1955 have been correlated by Armstrong, Brickwedde, and Scott (6). Since then Hestermans and White (47) have made additional measurements. Along with Armstrong, Brickwedde, and Scott's smoothed values, we have presented in Figure 15 the experimental measurements of Keyes, Taylor, and Smith (61), Bloomer and Parents (12), and Hestermans and White. Bennewitz and Andreev (9) have determined only the critical point. Between -162 and -96°C . Bloomer and Parent's results are in good agreement with Armstrong's correlation and with Armstrong's boiling point value of -161.49°C . We have given preference to Bloomer's data in drawing the deviation curve because they follow the common fine-structure pattern. Hesterman's and White's values generally parallel those of Bloomer and Parent with a pressure difference of -0.04 atm.

Keyes, Taylor, and Smith's data tend to corroborate Armstrong's and Bloomer's values at lower temperatures, but between -96°C . and the critical point, the situation is confused. Here Armstrong's correlation diverges considerably from the experimental measurements of Bloomer and of Hestermans. This is due mostly to the fact that Armstrong has used Keyes' data, which appear to be inaccurate in this region, and possibly partly to the fact that his type of equation was not sufficiently flexible to produce the curvature required to reach the critical point. Armstrong has recognized in his paper that his correlation in the kc region did not fit the accepted critical value, but Bloomer and Parent's data were not available at the time of Armstrong's publication. Three experimental measurements of the critical temperature are in fairly good agreement, as shown in Figure 15; those of Keyes, Bloomer, and Bennewitz. It appears to us that Bloomer's critical temperature of -82.61°C . and the corresponding pressure of 45.49 atm. as indicated by the deviation

curve is a good value for the critical point. Bloomer's critical pressure is 45.47 atm. In the light of Hestermans' and Bloomer's data, Kobe and Lynn's (63) selected value of -82.1°C . and 45.8 atm., which is based on Keyes' calculated pressure value, is not well founded and indeed confuses the matter, in spite of a seeming numerical similarity, since in reality, this pressure is 0.40 atm. low at the stated temperature.

This point is worth emphasizing since, had Hestermans' and Bloomer's measurements not been available, a deviation curve based on Keyes' vapor-pressure measurements would be so radically different as to class methane with nitrogen and carbon monoxide instead of with oxygen and the noble gases.

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- (6) Armstrong, G. T. Brickwedde, F. G., and Scott, R. B., J. Res. Natl. Bur. Std. 55, 39 (1955).
- (47) Hestermans, P., and White, D., J. Phys. Chem. 65, 362 (1961).
- (61) Keyes, F. G., Taylor, R. S., and Smith, L. B., J. Math. Phys. 1, 211 (1922).
- (12) Bloomer, O. T., and Parent, J. D., Inst. Gas. Techn. Res. Bull. 17 (1952).
- (9) Bennewitz, K., and Andreev, N., Z. Physik Chem., A142, 37 (1929).
- (63) Kobe, K. A., and Lynn, R. E., Jr., Chem. Rev. 52, 117 (1953).

GLL-633-444B

Fig. 15. Deviation curve for CH₄ vs t°C.

TABLE XIV
VAPOR PRESSURE OF CH₄

$\log P_K = -447.259/T + 4.00554$			
t, °C.	P _i , atm.	P _K , atm.	d, atm.
-161.49	1.000	1.000	.0
160	1.129	1.129	.0
158	1.322	1.322	.0
156	1.541	1.541	.0
154	1.786	1.786	.0
152	2.054	2.059	.005
150	2.353	2.364	.011
148	2.686	2.702	.016
146	3.054	3.076	.022
144	3.459	3.487	.028
142	3.904	3.938	.034
140	4.391	4.431	.040
138	4.915	4.968	.053
136	5.474	5.552	.078
134	6.079	6.185	.106
132	6.734	6.868	.134
130	7.445	7.606	.161
128	8.210	8.398	.188
126	9.032	9.248	.216
124	9.906	10.158	.252
122	10.838	11.130	.292
120	11.836	12.166	.330
118	12.898	13.267	.369
116	14.029	14.437	.408
114	15.229	15.676	.447
112	16.501	16.987	.486
110	17.847	18.371	.524
108	19.268	19.831	.563
106	20.760	21.367	.607
104	22.334	22.982	.648
102	23.994	24.676	.682
100	25.744	26.452	.708
98	27.588	28.312	.724
96	29.527	30.255	.728
94	31.591	32.283	.692
92	33.723	34.399	.676
90	35.992	36.602	.610
89	37.171	37.737	.566
88	38.382	38.894	.512
87	39.629	40.074	.445
86	40.904	41.276	.372
85	42.213	42.501	.288
84	43.557	43.749	.192
83	44.938	45.020	.082
82.61	45.490	45.522	.032

8. Nitric Oxide

No high-pressure measurements have been made on nitric oxide since Adwentowski's (2) work in 1909. This is surprising, since analysis of his results indicates that this work fails seriously to meet modern standards of precision for purity of sample, measurement of temperature and pressure, and attainment of pressure and temperature equilibrium. Our deviation curve shown in Figure 16 is based on Johnston and Giauque's (56) determination of the boiling point and Adwentowski's value for the critical point. Adwentowski's data can in no sense be said to determine the deviation curve since almost 60% of them do not exhibit any expected consistent behavior. Nevertheless, a deviation curve consistent with his critical point can be reasonably drawn through some of his data, this has been done in Figure 16. No conclusions can be drawn as to the accuracy of our proposed vapor-pressure values or Adwentowski's reported critical point, and certainly the need for a redetermination of this vapor pressure is dictated.

(2) Adwentowski, K., Intern. Bull. Acad. Sci. Cracovie II 1909, 742.

(56) Johnston, H. L., and Giauque, W. F., J. Am. Chem. Soc. 51, 3194 (1929).

Fig. 16. Deviation curve for NO.

TABLE XV
VAPOR PRESSURE OF NO

$$\log P_K = .673.273/T + 5.54545$$

t, °C.	P _i , atm.	P _K , atm.	d, atm.
-151.74	1.00	1.00	.0
150	1.23	1.20	-0.03
145	2.09	1.96	.13
140	3.33	3.08	.25
135	5.00	4.70	.30
130	7.18	6.95	.23
125	10.04	10.02	-0.02
120	13.81	14.10	+0.29
115	18.84	19.42	.58
110	25.41	26.23	.82
105	33.86	34.79	.93
100	44.53	45.40	.87
95	57.97	58.37	.40
92.9	64.60	64.60	0

9. Krypton

The vapor-pressure deviation curve for krypton shown in Figure 17 is based on the work of Michels, Wassenaar, and Zwietering (75). The data agree with the deviation curve to within 0.001 atm. The critical temperature of Meihuizen and Crommelin (69) of -63.77°C . is taken, and the critical pressure corresponding to this temperature is 54.31 atm. This is in good agreement with Meihuizen's value of 54.270 atm. The boiling point is due to Michels (75).

(75) Michels, A., Wassenaar, T., and Zwietering, Th. N., Physica 18 63 (1952).

(69) Meihuizen, J. J., and Crommelin, C. A. Physica 4, 1 (1937).

GLL-637-1710

Fig. 17. Deviation curve for Kr.

TABLE XVI
VAPOR PRESSURE OF Kr

t, °C.	$\log P_K = -4885.128/T + 4.05201$		
	P_i , atm.	P_K , atm.	d, atm
-153.40	1.000	1.000	.0
152	1.114	1.114	.0
150	1.294	1.294	.0
148	1.496	1.496	.0
146	1.720	1.721	.001
144	1.969	1.972	.003
142	2.245	2.250	.005
140	2.549	2.557	.008
138	2.883	2.895	.012
136	3.249	3.266	.017
134	3.649	3.672	.023
132	4.084	4.115	.031
130	4.554	4.596	.042
128	5.062	5.118	.056
126	5.611	5.682	.071
124	6.203	6.291	.088
122	6.838	6.946	.108
120	7.521	7.651	.130
118	8.247	8.405	.158
116	9.024	9.212	.188
114	9.857	10.073	.216
112	10.745	10.989	.244
110	11.690	11.964	.274
108	12.695	12.999	.304
106	13.754	14.095	.341
104	14.876	15.254	.378
102	16.062	16.478	.416
100	17.319	17.769	.450
98	18.639	19.127	.488
96	20.028	20.556	.528
94	21.485	22.055	.570
92	23.017	23.627	.610
90	24.625	25.273	.648
88	26.313	26.995	.682
86	28.080	28.793	.713
84	29.934	30.669	.735
82	31.877	32.624	.747
80	33.915	34.660	.745
78	36.047	36.777	.730
76	38.274	38.976	.702
74	40.603	41.259	.656
72	43.034	43.626	.592
70	45.577	46.078	.501
68	48.226	48.616	.390
67	49.599	49.917	.318
66	51.015	51.240	.225
65	52.473	52.585	+0.112
64	53.960	53.952	-0.008
63.77	54.306	54.270	-0.036

10. Xenon

The deviation curve for xenon shown in Fig. 18 is based on the data of Michels and Wassenaar (73). The data agree with the curve within 0.001 atm. Patterson, Cripps, and Whytlaw-Gray (89), and Weinberger and Schneider (113) have both found the critical temperature to be 16.59°C. The corresponding vapor pressure from our curve is 57.64 atm. Habgood and Schneider (45) have reported the critical pressure to be 57.636 atm. The boiling point is due to Michels (73).

-
- (73) Michels, A., and Wassenaar, T., Physica 16, 253 (1950).
- (89) Patterson, H. S., Cripps, R. S., and Whytlaw-Gray, R., Proc. Roy. Soc. (London) A86, 579 (1912).
- (113) Weinberger, M. A., and Schneider, W. G., Can. J. Chem. 30, 422 (1952).
- (45) Habgood, H. W., and Schneider, W. G., Can. J. Chem. 32, 98 (1954).

Fig. 18. Deviation curve for Xe.

TABLE XVII
VAPOR PRESSURE OF Xe

$$\log P_K = -674.974/T + 4.09000$$

t, °C.	P _i , atm.	P _K , atm.	d, atm.
-108.12	1.000	1.000	.0
108	1.007	1.007	.0
106	1.128	1.127	-0.001
104	1.260	1.258	.002
102	1.403	1.400	.003
100	1.559	1.555	.004
98	1.728	1.723	.005
96	1.910	1.905	.005
94	2.106	2.101	.005
92	2.317	2.312	.005
90	2.541	2.539	-0.002
88	2.783	2.783	.000
86	3.041	3.044	+0.003
84	3.316	3.323	.007
82	3.609	3.621	.012
80	3.922	3.940	.018
78	4.254	4.278	.024
76	4.608	4.638	.030
74	4.984	5.020	.036
72	5.381	5.425	.044
70	5.801	5.854	.053
68	6.243	6.307	.064
66	6.710	6.786	.076
64	7.203	7.291	.088
62	7.720	7.822	.102
60	8.265	8.382	.117
58	8.836	8.970	.134
56	9.435	9.587	.152
54	10.062	10.234	.172
52	10.720	10.912	.192
50	11.407	11.621	.214
48	12.125	12.363	.238
46	12.874	13.137	.263
44	13.658	13.946	.288
42	14.475	14.789	.314
40	15.323	15.667	.344

TABLE XVII (Continued)

t, °C.	P ₁ , atm.	P _K , atm.	d, atm.
-38	16.205	16.581	376
30	17.119	17.501	112
34	18.074	18.519	445
32	19.067	19.544	477
30	20.099	20.608	.509
28	21.170	21.711	54
26	22.282	22.854	572
24	23.434	24.038	604
22	24.626	25.262	636
20	25.861	26.528	667
18	27.140	27.836	696
16	28.464	29.186	.722
14	29.836	30.580	.744
12	31.255	32.017	.762
10	32.722	33.498	.776
8	34.236	35.024	.788
6	35.801	36.595	.794
4	37.416	38.212	.796
-2	39.082	39.875	.793
0	40.802	41.584	782
+2	42.584	43.340	.756
4	44.425	45.143	.718
5	45.367	46.062	.695
6	46.326	46.994	.668
7	47.299	47.937	638
8	48.288	48.892	.604
9	49.295	49.859	.564
10	50.325	50.839	514
11	51.372	51.830	.458
12	52.450	52.834	384
13	53.546	53.850	304
14	54.660	54.878	.218
15	55.793	55.919	.126
16	56.950	56.972	+0.022
16.59	57.639	57.599	-0.040

11. Silicon Tetrafluoride

The deviation curve in Figure 19 for silicon tetrafluoride is based on the data of Patnode and Papish (88), and Booth and Swinehart (13). The triple point and critical properties are due to these authors. Patnode and Papish's points appear to be fairly consistent although not of the highest precision. Only about half of Booth and Swinehart's data approach the expected deviation curve, and, in addition, no data are available for the center portion of the curve between -75 and -40°C . The reliability of the vapor-pressure values above -75°C . is, therefore, probably not better than ± 0.05 atm.

(88) Patnode, W. I., and Papish, J., J. Phys. Chem. 34, 1494 (1930).

(13) Booth, H. S., and Swinehart, C. F., J. Am. Chem. Soc. 57, 1337 (1935).

Fig. 19. Deviation curve for SiF_4 .

TABLE XVIII

VAPOR PRESSURE OF SiF_4

$$\log P_K = -888.743/T + 4.99589$$

t, °C.	P_i , atm.	P_K , atm.	d, atm.
-90.2	1.756	2.076	+0.320
90	1.781	2.098	.317
85	2.500	2.720	.220
80	3.351	3.479	.128
75	4.35	4.396	+0.047
70	5.52	5.490	-0.027
65	6.86	6.783	.080
60	8.40	8.299	.100
55	10.14	10.059	.082
50	12.12	12.089	-0.028
45	14.35	14.411	+0.062
40	16.87	17.051	.179
35	19.72	20.032	.310
30	22.94	23.380	.442
25	26.60	27.116	.512
20	30.80	31.267	.465
15	35.72	35.854	.100
14.17	36.66	36.660	0

12. Nitrous Oxide

The vapor-pressure data of Hoge (49) and Couch and Kobe (24) have been used to derive the deviation curve shown in Figure 20. Our deviation curve was drawn to a precision of 0.001 atm. and appears to agree quite well with the data except for Couch's point at 35.5°C., which is high. The boiling point and critical point values quoted are the above authors' experimental values.

(49) Hoge, H. J., J. Res. Natl. Bur. Std. 34, 281 (1945).

(24) Couch, E. J., and Kobe, K. A., J. Chem. Eng. Data 6, 229 (1961).

Fig. 20. Deviation curve for N_2O .

TABLE XIX
VAPOR PRESSURE OF N₂O

$$\log P_K = -849.122/T + 4.59767$$

t, °C.	P ₁ , atm.	P _K , atm.	d, atm.
-88.465	1.000	1.000	.0
88	1.028	1.027	-0.001
86	1.156	1.150	.006
84	1.297	1.284	.013
82	1.452	1.431	.021
80	1.620	1.590	.030
78	1.804	1.764	.040
76	2.003	1.953	.050
74	2.217	2.157	.060
72	2.451	2.379	.072
70	2.702	2.618	.084
68	2.971	2.875	.096
66	3.260	3.152	.108
64	3.571	3.450	.121
62	3.903	3.769	.134
60	4.258	4.111	.147
58	4.637	4.477	.160
56	5.042	4.868	.174
54	5.472	5.285	.187
52	5.929	5.729	.200
50	6.414	6.202	.212
48	6.928	6.704	.224
46	7.470	7.236	.234
44	8.045	7.801	.244
42	8.651	8.399	.252
40	9.291	9.031	.260
38	9.965	9.698	.267
36	10.675	10.403	.272
34	11.421	11.145	.276
32	12.207	11.927	.280
30	13.031	12.750	.281
28	13.894	13.614	.280
26	14.800	14.522	.278
24	15.746	15.474	.272
22	16.738	16.472	.266
20	17.774	17.516	.258

TABLE XIX (Continued)

t, °C.	P _i , atm.	P _K , atm.	d, atm.
-18	18.857	18.610	-0.247
16	19.986	19.752	.234
14	21.163	20.946	.217
12	22.388	22.192	.196
10	23.663	23.491	.172
8	24.995	24.846	.149
6	26.378	26.256	.122
4	27.815	27.723	.092
-2	29.309	29.249	.060
0	30.861	30.835	-0.026
+2	32.474	32.482	+0.008
4	34.147	34.191	.044
6	35.883	35.963	.080
8	37.682	37.800	.118
10	39.545	39.703	.158
12	41.474	41.674	.200
14	43.474	43.712	.238
16	45.550	45.820	.270
18	47.704	47.999	.295
20	49.934	50.249	.315
22	52.242	52.572	.330
24	54.629	54.969	.340
26	57.101	57.441	.340
28	59.661	59.989	.328
30	62.311	62.614	.303
31	63.671	63.956	.285
32	65.064	65.318	.254
33	66.483	66.699	.216
34	67.936	68.100	.164
35	69.418	69.522	.104
36	70.931	70.964	.033
36.434	71.596	71.596	.0

13. Carbon Dioxide

The most reliable and consistent measurements of CO_2 are those of Michels, Wassenaar, Zwietering, and Smits (77) and Meyers and Van Dusen (70).

The triple-point value of -56.573°C . and 5.116 atm. is due to Michels. Meyers' value of -56.60°C . and 5.112 atm. differs from Michels' pressure of 5.110 atm. at -56.60°C . by +0.002 atm. Between the triple point and $+3^\circ\text{C}$., Michels' and Meyers' data are in good agreement. From this point to the critical point, the data of Michels, Blaisse, and Michels (71), determined in 1936, are in radical disagreement both with Meyers' results and with their later work cited above. Unfortunately, Michels' later paper does not resolve this contradiction. The measurements of Roebuck, Murrell, and Miller (101) in the range from -20°C . to the critical, while not to as high a degree of accuracy as the work of Meyers, well support his data, as compared to those of Michels, Blaisse, and Michels. Because, as is shown in Table XX, Wentorf's (114) measurement of the critical point excellently confirms Michels' values, we have adjusted the deviation curve between 20°C . and the critical point to conform to this value rather than Meyers' value.

The values in Table XX were obtained from the large-scale plot of the region between 20.0 and 31.1°C . drawn in Figure 21. It can be seen from Figure 21 that Michels' reported pressure of 72.85 atm. at 31.04°C . is higher than that obtained from a smooth curve through his points at 29.929 , 30.409 , and 31.013°C . From this curve, we obtained a pressure of 72.842 atm. as compared to Wentorf's reported value of 72.839 atm. Meyers' value of 72.800 atm. is also seen from the plot to be about 0.005 atm. below the mean of his values through the critical region. Additional critical data (106, 67, 3) are also given in Table XX. Figure 22 is a plot of the deviation curve on a $\% (1/T)$ basis.

- (77) Michels, A., Wassenaar, T., Zwietering, Th. N., and Smits, P., Physica 16, 501 (1950).
- (70) Meyers, C. H., and Van Dusen, M. S., J. Res. Natl. Bur. Std. 10, 381 (1933).
- (71) Michels, A., Blaisse, B., and Michels, C., Proc. Roy. Soc. (London) A160, 358 (1937).
- (101) Roebuck, J. R., Murrell, T. A., and Miller, E. E., J. Am. Chem. Soc. 64, 400 (1942).
- (114) Wentorf, R. H., Jr., J. Chem. Phys. 24, 607 (1956).
- (106) Schmidt, E., and Thomas, W., Forsch. Gebeite. Ingenieurw 20B, 161 (1954).
- (67) Lorentzen, H. C., Acta Chem. Scand. 7, 1335 (1953).
- (3) Ambrose, D., Trans Faraday Soc. 52, 772 (1956).

TABLE XX
CRITICAL PROPERTIES OF CO₂ AS MEASURED BY
VARIOUS INVESTIGATORS

Observer	Reported		From deviation curve plot	
	T _c	P _c	T _c	P _c
Meyers	31.00	72.80	31.00	72.805
			31.04	72.872
Michels	31.04	72.85	31.04	72.842
Wentorf	31.04	72.839		
Schmidt and Thomas	31.01	72.50		
Lorentzen	31.04			
Ambrose	31.01

Fig. 21. Deviation curve for CO₂ vs t°C. from 20°C. to the critical point.

Fig. 22. Deviation curve for CO₂ vs % (1/T).

TABLE XXI
VAPOR PRESSURE OF CO₂

$\log P_K = -867.295/T + 4.71346$			
t, °C	P _L , atm.	P _K , atm.	d, atm.
-56.573	5.116	5.118	+0.002
54	5.711	5.703	-0.008
52	6.210	6.193	.017
50	6.740	6.715	.025
48	7.302	7.270	.032
46	7.901	7.861	.040
44	8.536	8.488	.048
42	9.209	9.153	.056
40	9.918	9.857	.061
38	10.668	10.602	.066
36	11.457	11.389	.068
34	12.290	12.220	.070
32	13.166	13.096	.070
30	14.089	14.019	.070
28	15.059	14.990	.069
26	16.078	16.012	.066
24	17.146	17.085	.061
22	18.265	18.211	.054
20	19.436	19.391	.045
18	20.662	20.628	.034
16	21.944	21.923	.021
14	23.283	23.277	-0.006
12	24.679	24.692	+0.013
10	26.135	26.169	.034
8	27.655	27.711	.056
6	29.239	29.318	.079
4	30.890	30.993	.103
-2	32.606	32.736	.130
0	34.392	34.550	.158
+2	36.249	36.435	.186
4	38.179	38.395	.216
6	40.184	40.429	.245
8	42.265	42.539	.274
10	44.427	44.728	.301
12	46.671	46.996	.325
14	48.999	49.345	.346
16	51.414	51.777	.363
18	53.920	54.292	.372
20	56.521	56.893	.372
22	59.221	59.581	.360
24	62.024	62.357	.333
26	64.936	65.222	.286
27	66.439	66.689	.250
28	67.972	68.179	.207
29	69.537	69.692	.155
30	71.138	71.228	.090
31	72.773	72.787	.014
31.04	72.840	72.850	.010

14. Hydrogen Chloride

The data of Thomas (109a) and of Cardoso and Germann (19), between -30 and 50°C. appear to be in disagreement by a constant systematic error as seen in Figure 23. The deviation curve has been located to correspond to Thomas' data because his work is more recent and appears to give the most consistent agreement with the other hydrogen halide curves shown in Figure 3. Thomas has measured a critical temperature of 51.54°C. and calculated a critical-pressure of 81.97 atm. from his vapor-pressure equation. We have found a critical pressure value of 82.07 to be in better agreement with our deviation curve. This difference is attributed to the inability of Thomas' equation to follow the curvature of the vapor-pressure curve near the critical point. Cardoso and Germann (18) reported critical point values of 51.4°C. and 81.55 atm. Kopper (64) has measured a value of 51.0°C. for the critical temperature. Giaque and Wiebe's (39) measurements have been used to locate the deviation curve in the vicinity of the boiling point.

(109a) Thomas, W., Prog. Intern. Res. Thermodynamic Transport Properties ASME Second Symposium, 1962.

(19) Cardoso, E., and Germann, A. F. O., J. Chim. Phys. 11, 632 (1913).

(18) Cardoso, E., and Germann, A. F. O., J. Chim. Phys. 10, 517 (1912).

(64) Kopper, H., Z. Physik. Chem. A175, 469 (1936).

(39) Giaque, W. F., and Wiebe, R., J. Am. Chem. Soc. 50, 101 (1928).

GLL-637-1715A

Fig. 23. Deviation curve for HCl.

TABLE XXII

VAPOR PRESSURE OF HCl

$$\log P_K = -856.120/T + 4.55093$$

t, °C	P _i , atm.	P _K , atm.	d, atm.
-85.03	1.00	1.000	.000
85	1.00	1.002	.000
80	1.32	1.314	-0.008
75	1.72	1.700	.018
70	2.20	2.171	.025
65	2.78	2.741	.038
60	3.47	3.423	.050
55	4.29	4.231	.060
50	5.25	5.181	.070
45	6.37	6.288	.078
40	7.65	7.568	.080
35	9.12	9.038	.080
30	10.79	10.714	.075
25	12.68	12.616	.060
20	14.79	14.759	-0.032
15	17.15	17.162	+0.015
10	19.74	19.842	.100
-5	22.62	22.816	.200
0	25.80	26.102	.305
+5	29.31	29.718	.405
10	33.18	33.680	.500
15	37.42	38.005	.590
20	42.05	42.708	.660
25	47.09	47.807	.714
30	52.57	53.315	.744
35	58.50	59.248	.747
40	64.91	65.619	.710
45	71.91	72.443	.530
50	79.56	79.732	.170
51.54	82.07	82.073	.0

15. Hydrogen Bromide

The only data available for HBr are those of Drozdowski and Pietrzak (28), whose measurements on HCl are in very poor agreement with our curve for HCl. Nevertheless, the points shown for HBr appear to agree fairly well with the projected curve shown in Figure 24 and Giauque and Wiebe's boiling point value (40). The critical temperature determined by Kopper (64) is 89.9°C., by Moles (81) 89.8°C, and by Drozdowski and Pietrzak 90.0°C. We have used 90.0°C. and found the corresponding pressure to be 84.5 atm., which is in good agreement with Drozdowski's value of 84.44 atm.

(28) Drozdowski, E., and Pietrzak, J., Bull. Intern. Acad. Sci. Cracovie
A1913, 219.

(40) Giauque, W. F., and Wiebe, R., J. Am. Chem. Soc. 50, 2193 (1928).

(64) Kopper, H., Z. Physik. Chem. A175, 469 (1936).

(81) Moles, E., J. Chim. Phys. 17, 415 (1919).

GLL-637-1716A

Fig. 24. Deviation curve for HBr.

TABLE XXIII
VAPOR PRESSURE OF HBr

$$\log P_K = -921.687/T + 4.46489$$

t, °C.	P _i , atm.	P _K , atm.	d, atm.
-66.72	1.000	1.000	.0
65	1.09	1.089	.0
60	1.39	1.383	-0.010
55	1.76	1.737	.020
50	2.20	2.160	.035
45	2.72	2.661	.055
40	3.32	3.249	.075
35	4.03	3.933	.100
30	4.85	4.724	.125
25	5.78	5.632	.150
20	6.84	6.668	.170
15	8.02	7.844	.180
10	9.35	9.170	.180
-5	10.81	10.658	.155
0	12.44	12.320	.120
+5	14.23	14.166	-0.060
10	16.20	16.210	+0.010
15	18.36	18.461	.105
20	20.73	20.932	.200
25	23.33	23.634	.300
30	26.18	26.578	.400
35	29.27	29.775	.502
40	32.64	33.236	.600
45	36.30	36.972	.675
50	40.25	40.992	.740
55	44.51	45.306	.796
60	49.10	49.924	.823
65	54.02	54.855	.840
70	59.28	60.108	.828
75	64.91	65.691	.785
80	70.94	71.612	.670
85	77.43	77.880	.450
90.0	84.50	84.500	.0

16. Sulfur Hexafluoride

The deviation curve for SF_6 shown in Figure 25 is based on the triple point of 2.20 atm. at -51°C . determined by Miller, Verdelli, and Gall (79) and a critical point of 37.193 atm. at 45.642°C . determined by Wentorf (114). Unfortunately, there are no data of comparable reliability between these two temperatures. The average of Miller's liquid vapor-pressure measurements from -50 to 0°C . does not show the expected negative region for the deviation curve and does not match Clegg, Rowlinson, and Sutton's (23) 0 and 10°C . points. Because of the similarity of its coexistence line with that of SF_6 , it was expected that the normalized CO_2 curve might well represent the SF_6 data; and, as shown in Figure 25, it indeed fits Clegg's data fairly well. On this basis we have used this curve for SF_6 in the -51 to 30°C . region as shown in Figure 1 above. Otto and Thomas' (87) data are suspect between 0 and 20°C . because they do not predict a negative deviation region below 0°C . and are evidently in error above 30°C ., where they exhibit a "nose" effect in disagreement with Clegg's data. Near the critical point the measurements of both Otto and Clegg agree with Wentorf's critical point.

(79) Miller, H. C., Verdelli, L. S., and Gall, J. F., Ind. Eng. Chem. 43 1126 (1951).

(114) Wentorf, R. H., Jr. J. Chem. Phys. 24, 607 (1956).

(23) Clegg, H. P., Rowlinson, J. S., and Sutton, J. R., Trans. Faraday Soc. 51, 1325 (1955).

(87) Otto, J., and Thomas, W., Z. Physik. Chem. (Frankfurt) 23, 84 (1960).

GLL-637-1717A

Fig. 25. Deviation curve for SF_6 .

TABLE XXIV
VAPOR PRESSURE OF SF₆

$$\log P_K = -899.335/T + 4.39153$$

t, °C.	P _i , atm.	P _K , atm.	d, atm.
-51	2.20	2.204	.000
50	2.30	2.298	-0.004
45	2.84	2.816	.022
40	3.46	3.421	.038
35	4.18	4.123	.053
30	5.00	4.930	.066
25	5.93	5.853	.073
20	6.97	6.902	.072
15	8.15	8.086	.062
10	9.46	9.418	.042
-5	10.92	10.906	-0.010
0	12.53	12.562	+0.032
+5	14.32	14.396	.080
10	16.28	16.419	.138
15	18.43	18.641	.208
20	20.80	21.072	.273
25	23.40	23.722	.324
30	26.26	26.601	.343
35	29.39	29.719	.330
40	32.82	33.085	.265
45	36.64	36.708	.070
45.64	37.19	37.191	.0

17. Hydrogen Sulfide

The high-pressure data for H_2S in the literature do not extend below $0^\circ C$. The measurements of Reamer, Sage, and Lacey (95) and Kay and Rambosek (58) agree to better than 0.1 atm. below $70^\circ C$., as shown in Figure 26. Above $70^\circ C$. Reamer's points represent vapor pressures which are lower by 0.2 to 0.3 atm. Most of Cardoso's (15) measurements are systematically lower by 0.5 atm. than those of Reamer and of Kay. Figure 23 shows a similar difference between Cardoso's and Thomas' data for HCl . We have based our deviation curve on Kay and Rambosek's data because they are more complete than Reamer's in the jhk region and because Reamer's measurements in the kc region appear to exhibit a "nose" effect. Reamer's points shown in Figure 26 are comprised of three published experimental points and three others kindly supplied to us by him. We have not used any of Reamer's published smoothed points since he has stated that they are of poorer precision. It is remarkable that our vapor pressure values shown in Table XXV agree within 0.1 atm. with Cragoe's (54) smoothed points published in 1928.

Giauque and Blue (34) and Clark, Cockett, and Eisner (22) report boiling points of -60.33 and $-60.19^\circ C$., respectively. Kopper (64) has determined a critical temperature of $100.1^\circ C$. and Cardoso reports a critical point of $100.4^\circ C$. and 88.90 atm. Kay and Rambosek's critical point of $99.92^\circ C$. and 88.26 atm. agrees well with our deviation curve.

(95) Reamer, H. H., Sage, B. H., and Lacey, W. N., Ind. Eng. Chem. 42, 140 (1950).

(58) Kay, W. B., and Rambosek, G. M., Ind. Eng. Chem. 221 (1953).

(15) Cardoso, E., Gazz. Chim. Ital. 51, 1 (1921).

- (54) "International Critical Tables," Vol. III, McGraw-Hill Book Company, Inc., New York, 1928, pp. 201-249.
- (34) Giaque, W. F., and Blue, R. W., J. Am. Chem. Soc. 58, 831 (1936).
- (22) Clark, A. M., Cockett, A. H., and Eisner, H. S., Proc. Roy. Soc. (London) A209, 408 (1951).
- (64) Kopper, H., Z. Physik. Chem. A175, 469 (1936).

Fig. 26. Deviation curve for H_2S .

TABLE XXV
VAPOR PRESSURE OF H₂S

$$\log P_K = -965.518 + 4.53380$$

t, °C.	P _i , atm.	P _K , atm.	d, atm.
-60.19	1.00	1.000	.0
60	1.01	1.009	-0.001
55	1.38	1.282	.010
50	1.64	1.611	.025
45	2.04	2.004	.040
40	2.53	2.470	.060
35	3.10	3.017	.080
30	3.76	3.655	.100
25	4.52	4.395	.120
20	5.38	5.245	.140
15	6.38	6.218	.160
10	7.50	7.324	.180
-5	8.77	7.573	.200
0	10.19	9.978	.210
+5	11.77	11.550	.220
10	13.52	13.301	.220
15	15.45	15.242	.210
20	17.57	17.386	.185
25	19.89	19.744	.150
30	22.44	22.328	.110
35	25.21	25.149	-0.060
40	28.22	28.220	.000
45	31.49	31.551	+0.065
50	35.01	35.153	.140
55	38.83	39.038	.210
60	42.94	43.217	.280
65	47.35	47.698	.350
70	52.07	52.494	.420
75	57.13	57.613	.480
80	62.55	63.064	.510
85	68.34	68.858	.510
90	74.56	75.001	.440
95	81.22	81.504	.280
99.92	88.26	88.260	.000

18. Hydrogen Iodide

As is the case of HBr, the only data for HI have been determined by Drozdowski and Pietrzak (28). The deviation curve shown in Figure 27 is drawn to fit Giaque and Wiebe's boiling point (41) and matches the deviation curve patterns shown in Figure 3. Drozdowski's points in the k region of the curve are much too low to fit the curve and have been discarded. The critical temperature used, 150.7°C., is that of Kopper (64). The corresponding pressure is 81.9 atm. Drozdowski and Pietrzak's critical values are 150.0°C. and 80.8 atm.

(28) Drozdowski, E., and Pietrzak, J., Bull. Intern. Acad. Sci. Cracovie
A1913, 219.

(41) Giaque, W. F., and Wiebe, R., J. Am. Chem. Soc. 51, 1441 (1929).

(64) Kopper, H., Z. Physik. Chem. A175, 469 (1936).

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Fig. 27. Deviation curve for HI.

TABLE XXVI
VAPOR PRESSURE OF HI

$$\log P_K = -1036.51/T + 4.35875$$

t, °C.	P _i , atm.	P _K , atm.	d, atm.
-35.35	1.00	1.000	.0
35	1.02	1.015	.0
30	1.26	1.247	-0.010
25	1.54	1.520	.020
20	1.87	1.838	.035
15	2.26	2.206	.050
10	2.70	2.630	.065
-5	3.19	3.114	.080
0	3.76	3.665	.100
+5	4.41	4.288	.120
10	5.12	4.990	.135
15	5.93	5.776	.150
20	6.82	6.652	.165
25	7.81	7.626	.180
30	8.90	8.702	.195
35	10.09	9.887	.205
40	11.40	11.189	.215
45	12.83	12.613	.220
50	14.38	14.165	.220
55	16.06	15.852	.205
60	17.86	17.681	.180
65	19.80	19.656	.140
70	21.88	21.785	.090
75	24.10	24.074	-0.025
80	26.48	26.528	+0.050
85	29.01	29.152	.140
90	31.72	31.954	.230
95	34.61	34.937	.330
100	37.69	38.107	.420
105	40.96	41.470	.510
110	44.45	45.031	.581
115	48.15	48.793	.640
120	52.09	52.761	.670
125	56.25	56.941	.690
130	60.64	61.335	.691
135	65.28	65.949	.665
140	70.19	70.785	.595
145	75.46	75.847	.385
150	81.09	81.139	.045
150.7	81.90	81.898	.0

19. Chlorine

Knietsch (62) and Pellaton (90) have both measured the vapor pressure of Cl_2 between the boiling point and the critical point. Knietsch's results are considered to be generally unreliable since below 0°C . they show a high pressure "nose" and above 40°C . they diverge steeply in the high pressure direction. Pellaton's values are fragmentary and not too consistent between 80 and 100°C . However, in general they fit the projected curve fairly well. Giauque and Powell's value (37) has been used for the boiling point. The deviation curve for Cl_2 is shown in Fig. 28.

(62) Knietsch, Ann. Chem. 259, 100 (1890).

(90) Pellaton, M., J. Chim. Phys. 13, 426 (1915).

(37) Giauque, W. F., and Powell, T. M., J. Am. Chem. Soc. 61, 1970 (1939).

Fig. 28. Deviation curve for Cl_2 .

TABLE XXVII
VAPOR PRESSURE OF Cl₂

$$\log P_K = -1053.45/T + 4.40590$$

t, °C.	P _i , atm.	P _K , atm.	d, atm.
-34.05	1.00	1.000	0.000
30	1.19	1.184	-0.010
25	1.47	1.448	.019
20	1.79	1.756	.029
15	2.15	2.114	.040
10	2.58	2.527	.053
-5	3.07	3.001	.067
0	3.62	3.542	.080
+5	4.25	4.155	.095
10	4.95	4.846	.106
15	5.74	5.623	.115
20	6.61	6.492	.120
25	7.59	7.458	.128
30	8.66	8.529	.132
35	9.85	9.711	.135
40	11.15	11.012	.137
45	12.57	12.437	.130
50	14.11	13.994	.119
55	15.78	15.690	.092
60	17.58	17.531	.052
65	19.53	19.524	-0.003
70	21.62	21.675	+0.060
75	23.86	23.991	.130
80	26.28	26.478	.203
85	28.86	29.143	.285
90	31.63	31.991	.362
95	34.59	35.029	.435
100	37.76	38.262	.500
105	41.14	41.697	.555
110	44.74	45.337	.600
115	48.56	49.189	.630
120	52.62	53.258	.640
125	56.92	57.549	.630
130	61.49	62.066	.576
135	66.34	66.813	.470
140	71.52	71.796	+0.280
144.12	76.10	76.081	-0.019

20. Ammonia

The deviation curve for ammonia shown in Figure 29 is constructed from the data of Cragoe, Meyers, and Taylor (25) and Beattie and Lawrence (8). The data of Cragoe are in excellent agreement with those of Beattie up to 40°C. At 70°C., which is the highest temperature measured by Cragoe, his results are about 0.03 atm. lower than those of Beattie. The results of Keyes and Brownlee (60) are also shown in Figure 29. Keyes and Brownlee's results at low temperatures are about 0.10 atm. higher than those of Beattie and Lawrence, while converging with those of Beattie at higher temperatures. Above 110°C., however, Keyes' values drop considerably below those of Beattie. Section III. F discusses the considerations involved in further detail. Our deviation curve agrees with Beattie's data to within 0.001 atm., except at high temperatures, where Beattie did not report his pressures to the third decimal place. Kopper's (64) value of 132.5°C. for the critical temperature was used, and the critical pressure corresponding to this temperature is 112.53 atm. These critical constants are much more consistent with Beattie's vapor-pressure data than those given in the literature by other authorities whose critical pressure is about 1 atm. lower. Armstrong also arrived at the same conclusion in his unpublished report (4) in which a critical point of 132.4°C. and 112.4 atm. was selected.

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- (25) Cragoe, C. S., Meyers, C. H., and Taylor, C. S., Natl. Bur. Std. Sci. and Tech. Papers 16, 1 (1920) and J. Am. Chem. Soc. 42, 206 (1920).
(8) Beattie, J. A., and Lawrence, C. K., J. Am. Chem. Soc. 52, 6 (1930).
(60) Keyes, F. G., and Brownlee, R. B., J. Am. Chem. Soc. 40, 25 (1918).
(64) Kopper, H., Z. Physik. Chem. A175, 469 (1936).
(4) Armstrong, G. T., Natl. Bur. Std. Rept. 2626 (1953).

Fig. 29. Deviation curve for NH_3 .

TABLE XXVIII
VAPOR PRESSURE OF NH_3

$\log P_K = -1203.05/T + 5.01689$			
t, °C.	P_i , atm.	P_K , atm.	d, atm.
-33.35	1.000	1.000	.0
32	1.070	1.067	-0.003
30	1.180	1.172	.008
28	1.301	1.287	.014
26	1.430	1.410	.020
24	1.569	1.543	.026
22	1.717	1.685	.032
20	1.878	1.839	.039
18	2.050	2.004	.046
16	2.234	2.180	.054
14	2.432	2.369	.063
12	2.643	2.571	.072
10	2.869	2.787	.082
8	3.110	3.017	.093
6	3.367	3.263	.104
4	3.640	3.524	.116
-2	3.930	3.802	.128
0	4.238	4.098	.140
+2	4.563	4.411	.152
4	4.908	4.744	.164
6	5.273	5.096	.177
8	5.659	5.468	.191
10	6.068	5.862	.206
12	6.499	6.279	.220
14	6.952	6.718	.234
16	7.429	7.182	.247
18	7.931	7.670	.261
20	8.459	8.185	.274
22	9.013	8.726	.287
24	9.594	9.295	.299
26	10.204	9.893	.311
28	10.842	10.520	.322
30	11.512	11.179	.333
32	12.213	11.869	.344
34	12.945	12.591	.354
36	13.711	13.348	.363
38	14.510	14.139	.371
40	15.344	14.966	.378
42	16.215	15.831	.384
44	17.122	16.733	.389
46	18.066	17.674	.392
48	19.052	18.656	.396
50	20.075	19.679	.396
52	21.137	20.745	.392
54	22.241	21.854	.387
56	23.389	23.008	.381

TABLE XXVIII (Continued)

t, °C.	P ₁ , atm.	P _K , atm.	d, atm.
58	24.580	24.207	-0.373
60	25.817	25.454	.363
62	27.100	26.749	.351
64	28.430	28.093	.337
66	29.809	29.488	.321
68	31.236	30.934	.302
70	32.714	32.433	.281
72	34.244	33.986	.258
74	35.826	35.595	.231
76	37.459	37.259	.200
78	39.148	38.982	.166
80	40.894	40.763	.131
82	42.699	42.604	.095
84	44.563	44.506	.057
86	46.488	46.470	-0.018
88	48.474	48.498	+0.024
90	50.523	50.591	.068
92	52.637	52.749	.112
94	54.819	54.975	.156
96	57.070	57.269	.199
98	59.390	59.632	.242
100	61.780	62.066	.286
102	64.241	64.571	.330
104	66.776	67.150	.374
106	69.385	69.802	.417
108	72.070	72.530	.460
110	74.830	75.335	.505
112	77.676	78.217	.541
114	80.612	81.178	.566
116	83.643	84.219	.576
118	86.762	87.340	.578
120	89.978	90.544	.566
122	93.293	93.832	.539
124	96.705	97.203	.498
125	98.450	98.921	.471
126	100.221	100.661	.440
127	102.020	102.422	.402
128	103.848	104.205	.357
129	105.715	106.009	.294
130	107.622	107.836	.214
131	109.567	109.685	.118
132	111.535	111.557	+0.022
132.50	112.526	112.501	-0.025

21. Cyanogen

Measurements of vapor pressure of C_2N_2 have been reported by Perry and Bardwell (92) and by Terwen (109). The results of both investigators are in good agreement, and our curve shown in Figure 30 indicates a good fit in the jhkc region. Terwen's value of the critical temperature $126.55^\circ C.$ does not fit well with the deviation curve and Cardoso and Baume's (16) value of $128.3^\circ C.$ is preferred. The corresponding critical pressure is 59.98 atm. compared to 58.20 atm. and 59.75 atm. reported by Terwen and Cardoso and Baume, respectively. Ruehrwein and Giaque's (99) value of the boiling point is in good agreement with the deviation curve.

(92) Perry, J. H., and Bardwell, D. C., J. Am. Chem. Soc. 47, 2629 (1925).

(109) Terwen, J. W., Z. Physik. Chem. 91, 469 (1916).

(16) Cardoso, E., and Baume, G., J. Chim. Phys. 10, 509 (1912).

(99) Ruehrwein, R. A., and Giaque, W. F., J. Am. Chem. Soc. 61,
2940 (1939).

Fig. 30. Deviation curve for C_2N_2 .

TABLE XXIX
VAPOR PRESSURE OF C₂N₂

$$\log P_K = -1203.57/T + 4.77607$$

t, °C.	P _i , atm.	P _K , atm.	d, atm.
-21.15	1.000	1.000	.0
20	1.052	1.051	-0.001
18	1.151	1.145	.006
16	1.258	1.246	.012
14	1.373	1.354	.019
12	1.494	1.470	.024
10	1.624	1.594	.030
8	1.763	1.725	.038
6	1.911	1.866	.045
4	2.066	2.015	.051
-2	2.234	2.174	.060
0	2.413	2.343	.070
+2	2.603	2.523	.080
4	2.803	2.713	.090
6	3.014	2.914	.100
8	3.237	3.127	.110
10	3.473	3.353	.120
12	3.723	3.591	.122
14	3.986	3.843	.143
16	4.263	4.108	.155
18	4.554	4.388	.166
20	4.860	4.682	.178
22	5.182	4.992	.190
24	5.518	5.317	.201
26	5.872	5.659	.213
28	6.244	6.019	.225
30	6.631	6.395	.236
32	7.038	6.790	.248
34	7.463	7.204	.259
36	7.906	7.637	.269
38	8.370	8.090	.280
40	8.853	8.563	.290
42	9.358	9.058	.300
44	9.883	9.574	.309
46	10.432	10.113	.319
48	11.002	10.675	.327
50	11.595	11.261	.334
52	12.211	11.871	.340

TABLE XXIX (Continued)

t, °C.	P _i , atm.	P _K , atm.	d, atm.
54	12.852	12.506	-0.346
56	13.518	13.166	.352
58	14.210	13.853	.357
60	14.928	14.567	.361
62	15.674	15.308	.366
64	16.447	16.078	.369
66	17.247	16.877	.370
68	18.076	17.705	.371
70	18.932	18.563	.369
72	19.820	19.453	.367
74	20.734	20.374	.360
76	21.679	21.327	.352
78	22.653	22.313	.340
80	23.658	23.333	.325
82	24.693	24.387	.306
84	25.761	25.477	.284
86	26.860	26.602	.258
88	27.993	27.763	.230
90	29.161	28.961	.200
92	30.368	30.198	.170
94	31.606	31.472	.134
96	32.880	32.786	.094
98	34.189	34.139	.050
100	35.536	35.533	-0.003
102	36.92	36.969	+0.046
104	38.35	38.446	.099
106	39.82	39.965	.150
108	41.33	41.528	.202
110	42.88	43.134	.254
112	44.48	44.785	.304
114	46.13	46.481	.352
116	47.83	48.223	.393
118	49.59	50.011	.420
120	51.42	51.846	.426
122	53.33	53.730	.396
124	55.33	55.661	.330
125	56.36	56.645	.281
126	57.43	57.642	.216
127	58.52	58.651	.133
128	59.64	59.672	.033
128.30	59.98	59.981	.001

22. Sulfur Dioxide

Although a great many measurements of the vapor pressure of SO_2 have been made, the data are in poor agreement above 30°C . Between the boiling point and 30°C ., Hirth, as quoted in reference (57) (which contains data obtained independently by Hirth, Kang, and Hellwig) and Riedel (98) are in excellent agreement. Riedel's boiling point value of -10.01°C . has been used by us. Between 30 and 95°C . Hirth's and Kang's data quoted in reference (57) are in radical disagreement with each other. Unfortunately their paper does not resolve this question, and no other data of comparable precision are available for confirmation of the true pressures. Toriumi and Hara's (110) measurements shown in Figure 31 generally support Hirth's results. The data of Regnault (96) and Cardoso and Fiorentino (17) not shown in Figure 31, are quite scattered in this region. This mean of Regnault's data appears to support Hirth, while the data of Cardoso and Fiorentino are closer to those of Kang and Hellwig quoted in reference (57). Pending definitive measurements, we have chosen Hirth's data for the location of the deviation curve in the 30 - 95°C . range, since his measurements are in good agreement with precise measurements above and below these temperatures, and a deviation curve through his data harmonizes best with other curves in Figure 3. From 95 to 135°C . Kang's points have been used to locate the deviation curve. From 135°C . to the critical point Kang's data are inconsistent and indicate an inflection point in the kc region which is considered to be spurious. Our deviation curve has been drawn in the kc region to harmonize with Kang's data in the jh region and with other deviation curves in Figure 3.

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- (57) Kang, T. L., Hirth, L. J., Kobe, K. A., and McKetta, J. J., J. Chem. Eng. Data 6, 220 (1961).
- (98) Riedel, L., Bull. Intern. Inst. Refrig. 20, No. 4, Annex No. 5, B1 (1939).
- (110) Toriumi, T., and Hara, R., J. Soc. Chem. Ind. (Japan) 47, 502 (1944).
- (96) Regnault, H. V., Mem. De Paris 26, (1862).
- (17) Cardoso, E., and Fiorentino, U., J. Chim. Phys. 23, 841 (1926).

Fig. 31. Deviation curve for SO₂.

TABLE XXX
VAPOR PRESSURE OF SO₂

$\log P_K = -1279.15/T + 4.86128$			
t, °C.	P _i , atm.	P _K , atm.	d, atm.
-10.01	1.000	1.000	.0
10.00	1.001	1.001	.0
8	1.092	1.089	-0.003
6	1.190	1.183	.007
4	1.296	1.284	.012
-2	1.410	1.392	.018
0	1.532	1.508	.024
+2	1.661	1.631	.030
4	1.799	1.762	.037
6	1.946	1.901	.045
8	2.102	2.049	.053
10	2.267	2.206	.061
12	2.444	2.374	.070
14	2.631	2.551	.080
16	2.828	2.738	.090
18	3.037	2.936	.101
20	3.258	3.146	.112
22	3.492	3.368	.124
24	3.738	3.602	.136
26	3.997	3.849	.148
28	4.269	4.108	.161
30	4.557	4.383	.174
32	4.858	4.671	.187
34	5.174	4.974	.200
36	5.507	5.293	.214
38	5.854	5.626	.228
40	6.219	5.977	.242
42	6.600	6.345	.255
44	6.998	6.730	.268
46	7.415	7.133	.282
48	7.851	7.555	.296
50	8.305	7.996	.309
52	8.780	8.458	.322
54	9.272	8.939	.333
56	9.786	9.442	.344
58	10.318	9.966	.352
60	10.873	10.513	.360
62	11.447	11.082	.365
64	12.045	11.675	.370
66	12.667	12.293	.374
68	13.311	12.935	.376
70	13.980	13.602	.378
72	14.676	14.296	.380

TABLE XXX (Continued)

t, °C	P _L , atm.	P _K , atm.	d, atm.
74	15.397	15.016	-0.381
76	16.145	15.764	.381
78	16.920	16.540	.380
80	17.725	17.345	.380
82	18.556	18.179	.377
84	19.417	19.043	.374
86	20.308	19.938	.370
88	21.228	20.864	.364
90	22.178	21.822	.356
92	23.160	22.814	.346
94	24.172	23.839	.333
96	25.217	24.898	.319
98	26.293	25.991	.302
100	27.405	27.121	.284
102	28.544	28.282	.262
104	29.729	29.489	.240
106	30.949	30.729	.220
108	32.206	32.008	.198
110	33.502	33.325	.177
112	34.838	34.682	.156
114	36.215	36.080	.135
116	37.633	37.518	.115
118	39.095	38.999	.096
120	40.598	40.522	.076
122	42.144	42.088	.056
124	43.734	43.698	.036
126	45.366	45.352	-0.014
128	47.043	47.051	+0.008
130	48.765	48.797	.032
132	50.533	50.589	.056
134	52.356	52.428	.072
136	54.227	54.315	.088
138	56.151	56.251	.100
140	58.126	58.236	.110
142	60.154	60.270	.116
144	62.236	62.356	.120
146	64.374	64.492	.118
148	66.569	66.681	.112
150	68.822	68.922	.100
151	69.968	70.062	.094
152	71.132	71.216	.084
154	73.504	73.564	.060
156	75.939	75.966	.027
157	77.181	77.188	+0.007
157.50	77.810	77.804	-0.006

23. Hydrogen Fluoride

The data of Jarry and Davis (55) and Franck and Spalthoff (29) are in good agreement and appear to have good precision. Franck and Spalthoff are to be commended for the care taken in adequately defining the kc region of the curve. We note, however, in comparing in Figure 4 the deviation curve for HF with that obtained for N_2O_4 , that the HF curve lies somewhat to the right of the N_2O_4 curve in the kc region. In drawing the N_2O_4 curve, we have preferred the data of Schlenger and Sage over that of Sheffer and Treub, whose points seem to exhibit a typical low-pressure defect in this region. It is possible, then, that Franck and Spalthoff's data may be slightly low in this region also. Kelley's (59) boiling point of $19.5^\circ C$. appears to agree with the above data.

(55) Jarry, R. L., and Davis, W., Jr., J. Phys. Chem. 57, 600 (1953)
and Am. Doc. 4069.

(29) Franck, E. V., and Spalthoff, W., Z. Elektrochem. 61, 348 (1957).

(59) Kelley, K. K., U. S. Bur. Mines Bull. 383 (1935).

Fig. 32. Deviation curve for HF.

TABLE XXXI
VAPOR PRESSURE OF HF

$$\log P_K = -1446.97/T + 4.94437$$

t, °C.	P _j , atm.	P _K , atm.	d, atm.
19.5	1.000	1.000	0
20	1.018	1.020	.002
25	1.208	1.234	.026
30	1.433	1.483	.050
35	1.697	1.773	.076
40	1.998	2.107	.109
45	2.366	2.490	.124
50	2.729	2.929	.200
55	3.199	3.427	.228
60	3.672	3.991	.319
65	4.237	4.627	.390
70	4.861	5.341	.480
75	5.540	6.140	.600
80	6.299	7.031	.732
85	7.158	8.021	.863
90	8.12	9.12	1.00
95	9.19	10.33	1.14
100	10.36	11.66	1.30
105	11.68	13.12	1.44
110	13.07	14.72	1.60
115	14.64	16.46	1.81
120	16.38	18.36	1.98
125	18.31	20.42	2.11
130	20.43	22.66	2.23
135	22.72	25.07	2.35
140	25.23	27.67	2.44
145	27.95	30.48	2.53
150	30.88	33.48	2.60
155	34.07	36.71	2.64
160	37.50	40.16	2.66
165	41.22	43.84	2.62
170	45.23	47.72	2.49
172	47.10	49.41	2.31
174	48.99	51.10	2.11
176	50.92	52.82	1.90
178	52.92	54.58	1.66
180	54.97	56.39	1.42
182	57.10	58.24	1.14
184	59.32	60.14	.82
186	61.64	62.08	.44
188.0	64.06	64.06	.0

24. Hydrogen Cyanide

Giauque and Ruhrwein's (38) boiling point is in good agreement with the pressure measurements of Hara and Sinozaki (46) and Bredig and Teichman (14). Above 50°C. the data of Bredig and Teichman shown in Figure 33 are sparse but show a reasonably accurate fit to a curve based on our N_2O_4 curve. Bredig and Teichman's critical pressure (53.2 atm.) is in very poor agreement with their critical temperature and we have selected a critical pressure of 48.89 atm.

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- (38) Giauque, W. F., and Ruhrwein, R. A., J. Am. Chem. Soc. 61, 2626 (1939).
- (46) Hara, R., and Sinozaki, H., Tech. Repts. Tohoku Imp. Univ. 4, 145 (1924).
- (14) Bredig, G., and Teichman, L., Z. Elektrochem. 31, 449 (1925).

Fig. 33. Deviation curve for HCN.

TABLE XXXII
VAPOR PRESSURE OF HCN

$$\log P_K = -1459.42/T + 4.88345$$

t, °C.	P _i , atm.	P _K , atm.	d, atm.
25.7	1.000	1.000	.0
30	1.17	1.17	.0
35	1.40	1.40	.0
40	1.66	1.67	.01
45	1.97	1.98	.01
50	2.31	2.33	.02
55	2.70	2.73	.03
60	3.13	3.18	.05
65	3.61	3.69	.08
70	4.14	4.27	.13
75	4.72	4.92	.20
80	5.36	5.63	.27
85	6.08	6.43	.35
90	6.89	7.32	.43
95	7.79	8.30	.51
100	8.78	9.38	.60
105	9.89	10.57	.68
110	11.11	11.87	.76
115	12.45	13.29	.84
120	13.92	14.84	.92
125	15.53	16.51	.98
130	17.29	18.34	1.05
135	19.21	20.31	1.10
140	21.29	22.44	1.15
145	23.55	24.73	1.18
150	26.01	27.20	1.19
155	28.66	29.84	1.18
160	31.54	32.67	1.13
165	34.65	35.69	1.04
170	38.02	38.92	.90
174	40.95	41.65	.70
176	42.51	43.07	.56
177	43.32	43.79	.47
178	44.14	44.52	.38
179	44.98	45.26	.28
180	45.82	46.00	.18
181	46.69	46.76	.07
182	47.50	47.53	+0.03
183	48.45	48.31	-0.14
183.5	48.89	48.70	-0.19

25. Nitrogen Tetroxide

Vapor-pressure measurements have been made by Baume and Robert (7) up to 38°C. and 2 atm.; by Mittasch, Kuss, and Schlueter (80) up to 60°C. and 5 atm.; by Schlinger and Sage (105) up to 149°C. and 79 atm.; and by Scheffer and Treub (103) up to the critical temperature of 158.2°C. Bennewitz and Windisch (10) report a critical temperature value of 158.4°C. The critical pressure of N_2O_4 has never been experimentally determined.

Critical values of 158.0°C. and 99 atm., which are attributed by Kobe and Lynn (63) to Baume and Robert, appear in reality to be due to Cragoe's calculated values given in the International Critical Tables (54). The results of all investigators are in good agreement up to 130°C., as shown in Figure 34. Above this temperature some of Sheffer and Treub's data exhibit a low-pressure "nose," and since Schlinger and Sage's data show the most consistent precision, we have chosen to extrapolate their data to the observed critical temperature where we find fair agreement with Sheffer and Treub. The critical pressure determined by the deviation curve is 99.66 atm. Kelley's (59) boiling point of 21.0°C. appears to agree well with these data.

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- (7) Baume, G., and Robert, M., Compt. Rend. 168, 1199 (1919).
- (80) Mittasch, A., Kuss, E., and Schlueter, H., Z. Anorg. Allgem. Chem. 159, 1 (1926).
- (105) Schlinger, W. G., and Sage, B. H., Ind. Eng. Chem. 42, 2158 (1950).
- (103) Scheffer, F. E. C., and Treub, J. P., Z. Physik. Chem. 81, 308 (1913).
- (10) Bennewitz, K., and Windisch, J. J., Z. Physik. Chem. A166, 401 (1933).
- (63) Kobe, K. A., and Lynn, R. E., Jr., Chem. Rev. 52, 117 (1953).
- (54) "International Critical Tables," Vol. III, McGraw-Hill Book Company, Inc., New York, 1928, pp. 201-249.
- (59) Kelley, K. K., U. S. Bur. Mines Bull. 383 (1935).

Fig. 34. Deviation curve for N_2O_4 .

TABLE XXXIII
VAPOR PRESSURE OF N_2O_4
 $\log P_K = -1848.20/T + 6.28320$

t, °C.	P_i , atm.	P_K , atm.	d, atm.
21	1.000	1.000	.000
22	1.046	1.050	.004
24	1.144	1.157	.013
26	1.251	1.274	.023
28	1.368	1.400	.032
30	1.494	1.535	.042
32	1.630	1.685	.055
34	1.775	1.845	.069
36	1.934	2.018	.084
38	2.106	2.204	.098
40	2.290	2.406	.116
42	2.489	2.622	.133
44	2.704	2.855	.151
46	2.933	3.106	.173
48	3.179	3.375	.196
50	3.444	3.663	.219
52	3.727	3.972	.245
54	4.027	4.303	.275
56	4.347	4.657	.310
58	4.689	5.036	.347
60	5.054	5.439	.385
62	5.443	5.870	.427
64	5.858	6.329	.471
66	6.300	6.818	.518
68	6.772	7.339	.567
70	7.274	7.892	.618
72	7.810	8.481	.671
74	8.378	9.105	.727
76	8.982	9.767	.785
78	9.622	10.469	.847
80	10.299	11.213	.914
82	11.020	12.000	.980
84	11.782	12.833	1.051
86	12.593	13.714	1.121
88	13.448	14.644	1.196
90	14.356	15.626	1.270
92	15.314	16.662	1.348

TABLE XXXIII (Continued)

t, °C.	P _i , atm.	P _K , atm.	d, atm.
94	16.328	17.754	1.426
96	17.402	18.904	1.502
98	18.533	20.116	1.583
100	19.728	21.391	1.663
102	20.988	22.732	1.744
104	22.317	24.141	1.824
106	23.714	25.622	1.908
108	25.185	27.176	1.991
110	26.741	28.807	2.066
112	28.382	30.518	2.136
114	30.111	32.310	2.199
116	31.933	34.188	2.255
118	33.846	36.154	2.308
120	35.856	38.212	2.356
122	37.961	40.364	2.403
124	40.169	42.613	2.444
126	42.491	44.964	2.473
128	44.941	47.418	2.477
130	47.511	49.981	2.470
132	50.21	52.654	2.443
134	53.05	55.442	2.391
136	56.02	58.348	2.324
138	59.14	61.377	2.239
140	62.41	64.530	2.124
142	65.83	67.813	1.987
144	69.41	71.229	1.822
146	73.16	74.783	1.621
148	77.08	78.476	1.400
150	81.16	82.316	1.158
151	83.27	84.291	1.025
152	85.41	86.303	.891
153	87.60	88.356	.757
154	89.83	90.445	.615
155	92.10	92.574	.469
156	94.42	94.743	.324
157	96.78	96.952	.176
158	99.18	99.203	+0.027
158.2	99.66	99.658	-0.002

26. Bromine

The only high-pressure measurements on bromine have been made by Scheffer and Voogd (104). Their results are in agreement with our deviation curve shown in Figure 35; however, no data were taken above 200 °C. Beyond this point, the curve is projected so as to correspond with other curves shown in Figure 4. Scheffer and Voogd did determine the critical temperature to be 311 °C. and calculated a corresponding critical pressure of 102 atm. This value is in good agreement with our deviation curve and is definitely to be preferred over Stull's value of 121 atm. (108) calculated from Nadejine's (82) critical temperature of 302 °C. Stull's boiling point (108) has been used.

(104) Scheffer, F. E. C., and Voogd, M., Rec. Trav. Chim. 45, 214 (1926).

(108) Stull, D. R., Ind. Eng. Chem. 39, 517 1684 (1947).

(82) Nadejine, Bull. Acad. Imp. Sci. St. Petersburg 30, 327 (1886).

GLL-637-1728A

Fig. 35. Deviation curve for Br_2 .

TABLE XXXIV

VAPOR PRESSURE OF Br₂

$$\log P_K = -1537.90/T + 4.64132$$

t, °C.	P _i , atm.	P _K , atm.	d, atm.
58.2	1.00	1.000	.0
60	1.06	1.059	-0.002
70	1.45	1.444	.012
80	1.96	1.934	.022
90	2.58	2.549	.034
100	3.36	3.311	.049
110	4.30	4.241	.062
120	5.44	5.365	.080
130	6.81	6.708	.102
140	8.42	8.297	.120
150	10.30	10.160	.135
160	12.47	12.326	.145
170	15.97	14.823	.150
180	17.83	17.682	.145
190	21.06	20.931	.125
200	24.67	24.602	-0.070
210	28.72	28.724	.000
220	33.22	33.32	+0.10
230	38.22	38.44	.22
240	43.75	44.09	.34
250	49.87	50.31	.44
260	56.61	57.12	.51
270	63.98	64.54	.56
280	72.04	72.62	.58
290	80.80	81.36	.56
300	90.38	90.80	.42
305	95.50	95.79	.29
311.0	102.00	102.00	.00

27. Sulfur Trioxide

The deviation curve for SO_3 was calculated from original data kindly supplied by Dr. P. F. Tiley (1). We have computed a boiling point of 44.55°C . from our deviation curve. Hyne and Tiley (53) have reported a boiling point of $44.45 \pm 0.15^\circ\text{C}$. Tiley (1) has determined the critical point to be $217.7^\circ\text{C} \pm 0.2^\circ\text{C}$. and calculated the critical pressure to be 80.8 atm. We have calculated a P_c of 81.44 atm. from our deviation curve, estimating a kc peak height equivalent to that for SO_2 in absence of precise data in this region. The results of Smits and Schoenmaker (107) and Berthoud (11) are in good agreement at the boiling point and Berthoud's data are in fair agreement near the critical point. Berthoud's critical point is 218.2°C . and 83.8 atm.

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- (1) Abercomby, D. C., and Tiley, P. F., J. Chem. Soc. (London) 1963, 4902.
(53) Hyne, R. A., Tiley, P. F., J. Chem. Soc. (London) 1961, 2348.
(107) Smits, A., and Schoenmaker, P., J. Chem. Soc. (London) 1926, 1108.
(11) Berthoud, A., Helv. Chim. Acta 5, 513 (1922).

GLL-637-1729

Fig. 36. Deviation curve for SO_3 .

TABLE XXXV
VAPOR PRESSURE OF SO₃
 $\log P_K = -1623.87/T + 5.22851$

t, °C.	P _i , atm.	P _K , atm.	d, atm.
44.55	1.00	1.31	+0.31
45	1.02	1.33	.31
50	1.30	1.60	.30
55	1.63	1.91	.28
60	2.01	2.26	.25
65	2.46	2.67	.21
70	2.98	3.14	.16
75	3.58	3.67	.09
80	4.26	4.27	+0.01
85	5.04	4.95	-0.09
90	5.90	5.71	.19
95	6.86	6.57	.29
100	7.91	7.53	.38
105	9.07	8.60	.47
110	10.33	9.78	.55
115	11.72	11.09	.63
120	13.22	12.53	.69
125	14.86	14.12	.74
130	16.67	15.87	.80
135	18.61	17.78	.83
140	20.70	19.86	.84
145	22.91	22.13	.78
150	25.29	24.60	.69
155	27.84	27.27	.57
160	30.62	30.17	.45
165	33.61	33.29	.32
170	36.83	36.65	.18
175	40.29	40.27	-0.02
180	43.97	44.16	+0.19
185	47.90	48.32	.42
190	52.10	52.77	.67
195	56.58	57.52	.94
200	61.35	62.58	1.23
205	66.44	67.98	1.54
210	71.89	73.71	1.82
212	74.22	76.10	1.88
214	76.64	78.54	1.90
216	79.18	81.04	1.86
217	80.50	82.32	1.82
217.7	81.44	83.22	1.78

28. Carbon Tetrachloride

The data of Young (119) and Wertheimer (115) shown in Figure 37 are in good agreement and give a well defined deviation curve. Young's critical point value of 283.15°C. and 44.97 atm. is well confirmed by the deviation curve. Hildenbrand and McDonald's (48) boiling point of 76.73°C. is used.

(119) Young, S., J. Chem. Soc. 59, 911 (1891).

(115) Wertheimer, E., Ber. Deut. Physik. Ges. 21, 435 (1919).

(48) Hildenbrand, D. L., and McDonald, R. A., J. Phys. Chem. 63, 1521 (1959).

Fig. 37. Deviation curve for CCl₄.

TABLE XXXVI
VAPOR PRESSURE OF CCl_4

$$\log P_K = -1558.62/T + 4.45472$$

t, °C.	P_i , atm.	P_K , atm.	d, atm.
76.73	1.00	1.000	.0
80	1.10	1.10	-0.003
85	1.28	1.267	.009
90	1.47	1.455	.015
95	1.68	1.664	.021
100	1.92	1.896	.027
105	2.19	2.153	.033
110	2.48	2.437	.040
115	2.80	2.749	.047
120	3.15	3.092	.054
125	3.53	3.468	.060
130	3.94	3.878	.066
135	4.40	4.325	.072
140	4.89	4.810	.077
145	5.42	5.337	.082
150	5.99	5.907	.085
155	6.61	6.522	.087
160	7.27	7.184	.086
165	7.98	7.897	.084
170	8.74	8.661	.076
175	9.54	9.480	.060
180	10.39	10.356	.038
185	11.30	11.291	-0.012
190	12.27	12.287	+0.017
195	13.30	13.348	.047
200	14.40	14.474	.077
205	15.56	15.669	.110
210	16.79	16.934	.145
215	18.09	18.273	.182
220	19.46	19.687	.223
225	20.91	21.179	.268
230	22.44	22.751	.306
235	24.07	24.405	.336
240	25.78	26.143	.362
245	27.59	27.969	.380
250	29.49	29.883	.393
255	31.49	31.888	.400
260	33.59	33.986	.393
265	35.81	36.180	.368
270	38.14	38.470	.330
275	40.59	40.860	.270
280	43.15	43.351	.202
283.15	44.97	44.974	.0

29. Tin Tetrachloride

Young (119) and Werthimer (115) have measured the vapor pressure of SnCl_4 , and their data are in agreement on a boiling point of 114.1°C . Above 280°C . Young's data that are not shown in Figure 38 are evidently inaccurate and we have used Wertheimer's data to the critical point. The critical-point values of 318.7°C . and 36.95 atm. are reported by Wertheimer but appear to be based on Young's calculated T_c of 318.7°C ., corresponding to his observed critical pressure of 36.95 atm. (120).

(119) Young, S., J. Chem. Soc. 59, 911 (1891).

(115) Wertheimer, E., Ber. Deut. Physik. Ges. 21, 435 (1919).

(120) Young, S., Sci. Proc. Roy. Dublin Soc. 12, 374 (1909).

Fig. 38. Deviation curve for SnCl₄.

TABLE XXXVII
VAPOR PRESSURE OF SnCl_4

$$\log P_K = -1756.05/T + 4.53467$$

t, °C.	P_i , atm.	P_K , atm.	d, atm.
114.1	1.00	1.000	.000
115	1.02	1.024	-0.001
120	1.18	1.170	.008
125	1.35	1.331	.017
130	1.54	1.510	.025
135	1.74	1.707	.033
140	1.97	1.924	.042
145	2.21	2.163	.050
150	2.48	2.425	.060
155	2.78	2.711	.069
160	3.10	3.024	.079
165	3.45	3.364	.089
170	3.83	3.733	.100
175	4.24	4.133	.109
180	4.68	4.565	.118
185	5.16	5.032	.126
190	5.67	5.535	.133
195	6.21	6.076	.138
200	6.80	6.657	.140
205	7.42	7.279	.141
210	8.08	7.945	.140
215	8.79	8.656	.138
220	9.55	9.414	.134
225	10.35	10.222	.126
230	11.20	11.080	.115
235	12.10	11.992	.103
240	13.04	12.959	.087
245	14.05	13.983	.069
250	15.12	15.066	.049
255	16.24	16.209	.027
260	17.42	17.415	-0.003
265	18.66	18.687	+0.022
270	19.98	20.026	.045
275	21.37	21.433	.067
280	22.82	22.910	.085
285	24.36	24.461	.100
290	24.97	26.086	.112
295	27.67	27.787	.118
300	29.45	29.567	.118
305	31.32	31.427	.109
310	33.28	33.370	.088
315	35.34	35.396	.052
318.7	36.95	36.950	.0

30. Water

The deviation curve for H_2O taken from the tables of Osborne, Stimson, and Ginnings (86), is presented in Figure 39 for the purpose of comparison with the other curves in this report. The fact that water is highly associated is responsible for the disproportionate length of the bj section of the curve. It should be noted, however, that the sum of the j and k peaks of 1.22 atm. is only slightly higher than that of HCl , H_2S , HBr , and HI and less than that for HF , N_2O_4 , and SO_3 .

(86) Osborne, N. S., Stimson, H. F., and Ginnings, D. C., J. Res. Natl. Bur. Std. 23, 261 (1939).

Fig. 39. Deviation curve for H_2O .

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V. REFERENCES

- (1) Abercomby, D. C., and Tiley, P. F., J. Chem. Soc. (London) 1963, 4902.
- (2) Adwentowski, K., Intern. Bull. Acad. Sci. Cracovie II 1909, 742.
- (3) Ambrose, D., Trans. Faraday Soc. 52, 772 (1956).
- (4) Armstrong, G. T., Natl. Bur. Std. Rept. 2626 (1953).
- (5) Armstrong, G. T., J. Res. Natl. Bur. Std. 53, 263 (1954).
- (6) Armstrong, G. T., Brickwedde, F. G., and Scott, R. B., J. Res. Natl. Bur. Std. 55, 39 (1955).
- (7) Baume, G., and Robert, M., Compt. Rend. 168, 1199 (1919).
- (8) Beattie, J. A., and Lawrence, C. K., J. Am. Chem. Soc. 52, 6 (1930).
- (9) Bennewitz, K., and Andreev, N., Z. Physik. Chem. A142, 37 (1929).
- (10) Bennewitz, K., and Windish, J. J., Z. Physik. Chem. A166, 401 (1933).
- (11) Berthoud, A., Helv. Chim. Acta 5, 513 (1922).
- (12) Bloomer, O. T., and Parent, J. D., Inst. Gas Techn. Res. Bull. 17 (1952).
- (13) Booth, H. S., and Swinehart, C. F., J. Am. Chem. Soc. 57, 1337 (1935).
- (14) Bredig, G., and Teichman, L., Elektrochem. 31, 449 (1925).
- (15) Cardoso, E., Gazz. Chim. Ital. 51, 1 (1921).
- (16) Cardoso, E., and Baume, G., J. Chim. Phys. 10, 509 (1912).
- (17) Cardoso, E., and Fiorentino, U., J. Chim. Phys. 23, 841 (1926).
- (18) Cardoso, E., and Germann, A. F. O., J. Chim. Phys. 10, 517 (1912).
- (19) Cardoso, E., and Germann, A. F. O., J. Chim. Phys. 11, 632 (1913).
- (20) Cath, P. G., and Kammerlingh Onnes, H., Koninkl. Ned. Akad. Wetenschap. Proc. Ser. B. 26, 490 (1917) Leiden Comm. No. 152a.
- (21) Clark, A. M., Din, F., Robb, J., Michels, A., Wassenaar, T., and Zwietering, Th. N., Physica 17, 876 (1951).

- (22) Clark, A. M., Cockett, A. H., and Eisner, H. S., Proc. Roy. Soc. (London) A209, 408 (1951).
- (23) Clegg, H. P., Rowlinson, J. S., and Sutton, J. R., Trans. Faraday Soc. 51, 1325 (1955).
- (24) Couch, E. J., and Kobe, K. A., J. Chem. Eng. Data 6, 229 (1961).
- (25) Cragoe, C. S., Meyers, C. H., and Taylor, C. S., Natl. Bur. Std. Sci. and Tech. Papers 16, 1 (1920) and J. Am. Chem. Soc. 42, 206 (1920).
- (26) Crommelin, C. A., Koninkl. Ned. Akad. Wetenschap. Proc. Ser. B 22, 1212 (1913) Leiden Comm. Nos. 115a, 138c, 140a.
- (27) Dodge, B. F., and Davis, H. N., J. Am. Chem. Soc. 49, 610 (1927).
- (28) Drozdowski, E., and Pietrzak, J., Bull. Intern. Acad. Sci. Cracovie A 1913, 219.
- (29) Franck, E. V., and Spalthoff, W., Z. Elektrochem. 61, 348 (1957).
- (30) Friedman, A. S., and White, D., J. Am. Chem. Soc. 72, 3931 (1950).
- (31) Friedman, A. S., and White, D., J. Am. Chem. Soc. 73, 5713 (1951).
- (32) Friedman, A. S., White, D., and Johnston, H. L., J. Am. Chem. Soc. 73, 1310 (1951).
- (33) Friedman, A. S., White, D., and Johnston, H. L., J. Chem. Phys. 19, 126 (1951).
- (34) Giaque, W. F., and Blue, R. W., J. Am. Chem. Soc. 58, 831 (1936).
- (35) Giaque, W. F., and Clayton, J. O., J. Am. Chem. Soc. 54, 2610 (1932).
- (36) Giaque, W. F., and Clayton, J. O., J. Am. Chem. Soc. 55, 4875 (1933).
- (37) Giaque, W. F., and Powell, T. M., J. Am. Chem. Soc. 61, 1970 (1939).

- (38) Giauque, W. F., and Ruhrwein, R. A., J. Am. Chem. Soc. 61, 2626 (1939).
- (39) Giauque, W. F., and Wiebe, R., J. Am. Chem. Soc. 50, 101 (1928).
- (40) Giauque, W. F., and Wiebe, R., J. Am. Chem. Soc. 50, 2193 (1928).
- (41) Giauque, W. F., and Wiebe, R., J. Am. Chem. Soc. 51, 1441 (1929).
- (42) Goodwin, R. D., Diller, D. E., Roder, H. M., and Weber, L. A., J. Res. Natl. Bur. Std. 67A, 173 (1963).
- (43) Grilly, E. R., J. Am. Chem. Soc. 73, 843 (1951).
- (44) Grilly, E. R., Cryogenics 2, 226 (1962).
- (45) Habgood, H. W., and Schneider, W. G., Can. J. Chem. 32, 98 (1954).
- (46) Hara, R., and Sinozaki, H., Tech. Repts. Tohoku Imp. Univ. 4, 145 (1924).
- (47) Hestermans, P., and White, D., J. Phys. Chem. 65, 362 (1961).
- (48) Hildenbrand, D. L., and McDonald, R. A., J. Phys. Chem. 63, 1521 (1959).
- (49) Hoge, H. J., J. Res. Natl. Bur. Std. 34, 281 (1945).
- (50) Hoge, H. J., J. Res. Natl. Bur. Std. 44, 321 (1950).
- (51) Hoge, H. J., and Arnold, R. D., J. Res. Natl. Bur. Std. 47, 63 (1951).
- (52) Hoge, H. J., and Lassiter, J. W., J. Res. Natl. Bur. Std. 47, 75 (1951).
- (53) Hyne, R. A., and Tiley, P. F., J. Chem. Soc. (London) 1961, 2348.
- (54) "International Critical Tables," Vol. III, McGraw-Hill Book Company, Inc., New York, 1928, pp. 201-249.
- (55) Jarry, R. L., and Davis, W., Jr., J. Phys. Chem. 57, 600 (1953) and Am. Doc. 4069.
- (56) Johnston, H. L., and Giauque, W. F., J. Am. Chem. Soc. 51, 3194 (1929).

- (57) Kang, T. L., Hirth, L. J., Kobe, K. A., and McKetta, J. J., J. Chem. Eng. Data 6, 220 (1961).
- (58) Kay, W. B., and Rambosek, G. M., Ind. Eng. Chem. 22, 1 (1953).
- (59) Kelley, K. K., U. S. Bur. Mines Bull. 383 (1935).
- (60) Keyes, F. G., and Brownlee, R. B., J. Am. Chem. Soc. 40, 25 (1918).
- (61) Keyes, F. G., Taylor, R. S., and Smith, L. B., J. Math. Phys. 1, 211 (1922).
- (62) Knietsch, Ann. Chem. 259, 100 (1890).
- (63) Kobe, K. A., and Lynn, R. E., Jr., Chem. Rev. 52, 117 (1953).
- (64) Kopper, H., Z. Physik. Chem. A175, 469 (1936).
- (65) Landolt-Bornstein, "Physikalisch-Chemische Tabellen," Verlag von Julius Springer, Berlin, 1923-36, HW 1332-77, IE 721-42, IIE 1290-1310, III E 2430-62.
- (66) Lewis, G. N., and Randall, M., "Thermodynamics," Second Ed. (Revised by Pitzer and Brewer) McGraw-Hill Book Co., Inc., New York, 1961.
- (67) Lorentzen, H. C., Acta Chem. Scand. 7, 1335 (1953).
- (68) Mathias, E., and Crommelin, C. A., Ann. Phys. 5, 137 (1936).
- (69) Meihuizen, J. J., and Crommelin, C. A., Physica 4, 1 (1937).
- (70) Meyers, C. H., and Van Dusen, M. S., J. Res. Natl. Bur. Std. 10, 381 (1933).
- (71) Michels, A., Blaisse, B., and Michels, C., Proc. Roy. Soc. (London) A160, 358 (1937).
- (72) Michels, A., and Levelt, J. M., Physica 24, 659 (1958).
- (73) Michels, A., and Wassenaar, T., Physica 16, 253 (1950).
- (74) Michels, A., Wassenaar, T., DeGraaf, W., and Prins, Chr., Physica 19, 26 (1953).

- (75) Michels, A., Wassenaar, T., and Zwietering, Th. N., Physica 18, 63 (1952).
- (76) Michels, A., Wassenaar, T., and Zwietering, Th. N., Physica 18, 160 (1952).
- (77) Michels, A., Wassenaar, T., Zwietering, Th. N., and Smits, P., Physica 16, 501 (1950).
- (78) Miller, D. G., Ind. Eng. Chem. 56, 46 (1964).
- (79) Miller, H. C., Verdelli, L. S., and Gall, J. F., Ind. Eng. Chem. 43, 1126 (1951).
- (80) Mittasch, A., Kuss, E., and Schlueter, H., Z. Anorg. Allgem. Chem. 159, 1 (1926).
- (81) Moles, E., J. Chim. Phys. 17, 415 (1919).
- (82) Nadejine, Bull. Acad. Imp. Sci. St. Petersburg 30, 327 (1886).
- (83) U. S. Natl. Bur. Std. Circ. 500 (1952).
- (84) Natl. Bur. Std. Circ. 564 (1955).
- (85) Osborne, N. S., and Meyers, C. H., J. Res. Natl. Bur. Std. 13, 1 (1934).
- (86) Osborne, N. S., Stimson, H. F., and Ginnings, D. C., J. Res. Natl. Bur. Std. 23, 261 (1939).
- (87) Otto, J., and Thomas, W., Z. Physik. Chem. (Frankfurt) 23, 84 (1960).
- (88) Patnode, W. I., and Papish, J., J. Phys. Chem. 34, 1494 (1930).
- (89) Patterson, H. S., Cripps, R. S., and Whytlaw-Gray, R., Proc. Roy. Soc. (London) A86, 579 (1912).
- (90) Pellaton, M., J. Chim. Phys. 13, 426 (1915).
- (91) Perry, J. H., "Chemical Engineers Handbook," Fourth Ed., McGraw-Hill Book Company, Inc., New York, 1963, pp. 3-107.
- (92) Perry, J. H., and Bardwell, D. C., J. Am. Chem. Soc. 47, 2629 (1925).

- (93) Pickering, S. F., J. Phys. Chem. 28, 97 (1924) and Natl. Bur. Std. Sci. and Tech. Papers 21, 597 (1926).
- (94) Porter, F., and Perry, J. H., J. Am. Chem. Soc. 48, 2059 (1926).
- (95) Reamer, H. H., Sage, B. H., and Lacey, W. N., Ind. Eng. Chem. 42, 140 (1950).
- (96) Regnault, H. V., Mem. de Paris 26, (1862).
- (97) Richardson, J. W., and Smith, P. R., "Electron Density Shifts During Chemical Bond Formation," presented at the 145th Meeting of the American Chemical Society, New York, 1963.
- (98) Riedel, L., Bull. Intern. Inst. Refrig. 20, No. 4, Annex No. 5, B1 (1939).
- (99) Ruehrwein, R. A., and Giaque, W. F., J. Am. Chem. Soc. 61, 2940 (1939).
- (100) Roder, H. M., Diller, D. E., Weber, L. A., and Goodwin, R. D., Cryogenics 3, 16 (1963).
- (101) Roebuck, J. R., Murrell, T. A., and Miller, E. E., J. Am. Chem. Soc. 64, 400 (1942).
- (102) Sama, D. A., M. S. Thesis, Chemical Engineering, Massachusetts Institute of Technology, 1955.
- (103) Scheffer, F. E. C., and Treub, J. P., Z. Physik. Chem. 81, 308 (1913).
- (104) Scheffer, F. E. C., and Voogd, M., Rec. Trav. Chim. 45, 214 (1926).
- (105) Schlinger, W. G., and Sage, B. H., Ind. Eng. Chem. 42, 2158 (1950).
- (106) Schmidt, E., and Thomas, W., Forsch. Gebeite. Ingenieurw 20B, 161 (1954).
- (107) Smits, A., and Schoenmaker, P., J. Chem. Soc. (London) 1926, 1108.
- (108) Stull, D. R., Ind. Eng. Chem. 39, 517, 1684 (1947).

- (109) Terwen, J. W., Z. Physik. Chem. 91, 469 (1916).
- (109a) Thomas, W., Prog. Intern. Res. Thermodynamic Transport Properties ASME Second Symposium, 1962.
- (110) Toriumi, T., and Hara, R., J. Soc. Chem. Ind. (Japan) 47, 502 (1944).
- (111) Waring, W., Ind. Eng. Chem. 46, 762 (1954).
- (112) Weber, L. A., Diller, D. E., Roder, H. M., and Goodwin, R. D., Cryogenics 2, 236 (1962).
- (113) Weinberger, M. A., and Schneider, W. G., Can. J. Chem. 30, 422 (1952).
- (114) Wentorf, R. H., Jr., J. Chem. Phys. 24, 607 (1956).
- (115) Wertheimer, E., Ber. Deut. Physik. Ges. 21, 435 (1919).
- (116) White, D., Friedman, A. S., and Johnston, H. L., J. Am. Chem. Soc. 72, 3927 (1950).
- (117) White, D., Friedman, A. S., and Johnston, H. L., J. Am. Chem. Soc. 72, 3565 (1950).
- (118) Wooley, H. W., Scott, R. B., and Brickwedde, F. G., J. Res. Natl. Bur. Std. 41, 379 (1948).
- (119) Young, S., J. Chem. Soc. 59, 911 (1891).
- (120) Young, S., Sci. Proc. Roy. Dublin Soc. 12, 374 (1909).

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