

platinum has been measured at low mercury pressures. It has been found to approach unity as the temperature difference between the filament and wall approaches zero and to fall off about 0.08 for each 100° of this temperature difference. The data obtained in the measurements allow a calcu-

lation of the heat of vaporization of mercury. It is suggested that the method might be developed into a precise and convenient one of wide applicability for determining heats of vaporization and sublimation.

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Equation of State for Gases at High Pressures Involving Only Critical Constants

BY SAMUEL H. MARON AND DAVID TURNBULL

Several years ago F. G. Keyes,¹ starting with an equation of state involving PV as a linear function of pressure, deduced generalized equations for polar and non-polar gases at low pressures. More recently the authors,² using the principle of corresponding states, presented a method for estimating the Beattie-Bridgeman constants of any gas from those of a reference gas. The only supplementary data required were the critical pressures and temperatures of a gas and of the reference, for which nitrogen was taken. The success thus attained suggested that the pressure range over which calculations could be made could be extended appreciably provided an equation of state were available covering a wider range of pressures than that of Beattie-Bridgeman. Consequently an empirical equation of state for nitrogen was deduced, covering the temperature range of -70 to 600°, and for pressures up to 1000 atmospheres.³ The purpose of this paper is to show how this equation for nitrogen may be extended to other gases, and to present evidence for the validity of such an extension.

Derivation of Equation of State

The nitrogen compressibility data within the temperature and pressure ranges specified are represented with good reproducibility by the equation,³

$$PV = RT + \alpha_1'P + \alpha_2'P^2 + \alpha_3'P^3 + \alpha_4'P^4 \quad (1)$$

where the virial coefficients α_1' , α_2' , α_3' , α_4' are functions of the temperature only, and are given by

$$\alpha_1' = a_1 + \frac{a_2}{T} + \frac{a_3}{T^2} \quad (2)$$

$$\alpha_2' = \frac{b_1}{T^2} + \frac{b_2}{T^4} + \frac{b_3}{T^6} \quad (3)$$

$$\alpha_3' = \frac{c_1}{T^2} + \frac{c_2}{T^4} + \frac{c_3}{T^6} \quad (4)$$

$$\alpha_4' = \frac{d_1}{T^2} + \frac{d_2}{T^4} + \frac{d_3}{T^6} \quad (5)$$

$a_1, a_2, \dots, b_1, b_2, \dots, c_1, c_2, \dots, d_1, d_2, \dots$, etc., are constants independent of temperature and pressure. From (1) the expression for the compressibility coefficient, Z , of nitrogen follows as

$$Z = \frac{PV}{RT} = 1 + \frac{\alpha_1'P}{RT} + \frac{\alpha_2'P^2}{RT} + \frac{\alpha_3'P^3}{RT} + \frac{\alpha_4'P^4}{RT} = 1 + \left[\frac{\alpha_1'P_c'}{RT_c'} \right] \frac{P_r}{T_r} + \left[\frac{\alpha_2'(P_c')^2}{RT_c'} \right] \frac{P_r^2}{T_r} + \left[\frac{\alpha_3'(P_c')^3}{RT_c'} \right] \frac{P_r^3}{T_r} + \left[\frac{\alpha_4'(P_c')^4}{RT_c'} \right] \frac{P_r^4}{T_r} \quad (6)$$

where the substitutions $T = T_c'T_r$ and $P = P_c'P_r$ have been made for T and P . T_c' and P_c' are the critical constants of nitrogen, while T_r and P_r are the reduced temperature and pressure corresponding to T and P .

Now, the indications of various attempts at generalized correlation of compressibilities of gases^{4,5} are that Z is, to a fairly close approximation, a function of T_r and P_r only. If this statement be accepted provisionally, then it must follow that at any given values of T_r and P_r Z is the same for different gases, and hence the quantities in brackets in equation (6) must have the same values for all gases obeying the principle of corresponding states. Applying this identity condition to the first quantity in brackets in (6), we obtain for the relation between the primed quantities for nitrogen and the unprimed quantities for any other gas

$$\frac{\alpha_1'P_c'}{T_c'} = \frac{\alpha_1''P_c''}{T_c''} \\ \alpha_1'' = \left(\frac{\alpha_1'P_c'}{T_c'} \right) \frac{T_c''}{P_c''} \quad (7)$$

(1) Keyes, *THIS JOURNAL*, **60**, 1761 (1938).

(2) Maron and Turnbull, *Ind. Eng. Chem.*, **33**, 408 (1941).

(3) Maron and Turnbull, *THIS JOURNAL*, **64**, 44 (1942).

(4) Dodge, *Ind. Eng. Chem.*, **24**, 1353 (1932).

(5) Lewis, *ibid.*, **28**, 257 (1936).

Substituting now $T = T_c' T_r$ for T in (2), and inserting the result in (7), we find for α_1

$$\alpha_1 = \frac{T_c}{P_c} \left\{ \left[\frac{a_1 P_c'}{T_c'} \right] + \left[\frac{a_2 P_c'}{(T_c')^2} \right] \frac{1}{T_r} + \left[\frac{a_3 P_c'}{(T_c')^4} \right] \frac{1}{T_r^3} \right\} \\ = \frac{T_c}{P_c} \left[\beta_1 + \frac{\beta_2}{T_r} + \frac{\beta_3}{T_r^3} \right] \quad (8)$$

where β_1 , β_2 and β_3 are constants given by the quantities in brackets involving the a 's and the critical pressure and temperature for nitrogen.

By extending this procedure to the other α 's, it can readily be shown that

$$\alpha_2 = \frac{T_c}{P_c^2} \left\{ \left[\frac{b_1 (P_c')^2}{(T_c')^3} \right] \frac{1}{T_r^2} + \left[\frac{b_2 (P_c')^2}{(T_c')^5} \right] \frac{1}{T_r^4} + \left[\frac{b_3 (P_c')^2}{(T_c')^7} \right] \frac{1}{T_r^6} \right\} \\ = \frac{T_c}{P_c^2} \left[\frac{\beta_4}{T_r^2} + \frac{\beta_5}{T_r^4} + \frac{\beta_6}{T_r^6} \right] \quad (9)$$

$$\alpha_3 = \frac{T_c}{P_c^3} \left\{ \left[\frac{c_1 (P_c')^3}{(T_c')^3} \right] \frac{1}{T_r^3} + \left[\frac{c_2 (P_c')^3}{(T_c')^5} \right] \frac{1}{T_r^5} + \left[\frac{c_3 (P_c')^3}{(T_c')^7} \right] \frac{1}{T_r^7} \right\} \\ = \frac{T_c}{P_c^3} \left[\frac{\beta_7}{T_r^3} + \frac{\beta_8}{T_r^5} + \frac{\beta_9}{T_r^7} \right] \quad (10)$$

$$\alpha_4 = \frac{T_c}{P_c^4} \left\{ \left[\frac{d_1 (P_c')^4}{(T_c')^3} \right] \frac{1}{T_r^3} + \left[\frac{d_2 (P_c')^4}{(T_c')^5} \right] \frac{1}{T_r^5} + \left[\frac{d_3 (P_c')^4}{(T_c')^7} \right] \frac{1}{T_r^7} \right\} \\ = \frac{T_c}{P_c^4} \left[\frac{\beta_{10}}{T_r^3} + \frac{\beta_{11}}{T_r^5} + \frac{\beta_{12}}{T_r^7} \right] \quad (11)$$

If the above considerations are valid, equations (8), (9), (10), and (11) should give the α 's for any gas in terms of the constants for nitrogen as they appear in the β 's, and the critical pressure and temperature of the gas in question. These α 's, then, when substituted in equation (1) for the α 's for nitrogen should permit a calculation of the compressibility of various gases from a knowledge of their critical constants and the β 's for nitrogen. In other words, the equations for the α 's should give the virials of any gas whose PV behavior as a function of P is represented by equation (1).

Results and Discussion

Table I gives the β values calculated from the constants of equations (2) to (5) as published,³ and from the critical constants of nitrogen, $T_c' = 126.0^\circ\text{K}$. and $P_c' = 33.5$ atmospheres. From these β 's and the appropriate critical constants α 's were determined for a number of gases at various reduced temperatures, and these, in turn, were employed with equation (1) to estimate the volumes of these gases at various temperatures and pressures. In line with Newton,⁶ the critical

TABLE I

β VALUES FOR EQUATIONS (8) TO (12)^a

$\beta_1 = 1.01961 \times 10^{-2}$	$\beta_7 = -1.2516 \times 10^{-4}$
$\beta_2 = -2.1420 \times 10^{-2}$	$\beta_8 = 4.6408 \times 10^{-4}$
$\beta_3 = -3.2548 \times 10^{-2}$	$\beta_9 = -1.5573 \times 10^{-3}$
$\beta_4 = 3.6991 \times 10^{-3}$	$\beta_{10} = 1.7019 \times 10^{-6}$
$\beta_5 = -4.3022 \times 10^{-3}$	$\beta_{11} = -1.1221 \times 10^{-5}$
$\beta_6 = 1.8289 \times 10^{-2}$	$\beta_{12} = 3.2830 \times 10^{-5}$

^a These constants are for V in liters, P in atmospheres, and $T = (t^\circ\text{C} + 273.18)^\circ\text{K}$.

temperatures for hydrogen and helium were taken as $T_c + 8$, with the critical pressures as $P_c + 8$, since these definitions for the critical constants were found necessary to generalize the thermodynamic behavior of these gases. The results thus obtained with nine gases are summarized in Table II. Column 1 gives the temperature in $^\circ\text{C}$., column 2 the corresponding reduced temperature, while column 3 the maximum pressure to which the calculations were extended. Finally, columns 4 and 5 give, respectively, the maximum and average percentage deviation of the volumes calculated in this manner from the observed.

Before considering these results it should be pointed out that the equation for nitrogen, from which the more general equation presented here is derived, was set up from data which cover the reduced temperature interval 1.61-7 and up to $P_r = 30$. Therefore, in extending this equation through the principle of corresponding states to other gases, it is to be anticipated that the proposed equation will be strictly applicable over the same reduced temperature and pressure interval. Actually it has been found that the equation may be extended to T_r values lower than 1.6 although in such extension the maximum and average deviations which appear are higher than within the specified interval.

The results in Table II indicate that within the range of equations, compressibilities of various gases can be calculated with a maximum deviation no greater than about 4%, and an average deviation less than 2%, up to pressures of 1000 atmospheres in many instances. The reason for not extending all calculations to this pressure is lack of data for comparison. However, in the case of helium, where data are available, the limitation is the high reduced pressure, which is already 58.5 at 600 atmospheres. Any attempts to carry the calculations beyond this large P_r extrapolation result in an appreciable decrease in concordance with observed data.

(6) Newton, *Ind. Eng. Chem.*, **27**, 302 (1935).

TABLE II
COMPARISON OF CALCULATED AND OBSERVED VOLUMES
FOR SOME GASES^a

$t, ^\circ\text{C.}$	T_r	Max. press., atm.	% Dev. max.	% \pm Dev. av.
Hydrogen— $T_c = 41.28, P_c = 20.8$				
-175	2.378	75	-0.55	0.22
-100	4.195	100	0.10	.06
- 50	5.406	1000	2.00	.60
0	6.617	1000	2.10	.33
100	9.040	1000	2.55	.36
300	13.885	1000	1.30	.24
500	18.730	1000	2.43	.53
Methane— $T_c = 190.68, P_c = 45.8$				
0	1.432	1000	7.12	3.60
25	1.563	1000	3.70	1.71
50	1.694	1000	2.89	1.21
100	1.957	1000	3.28	1.02
150	2.219	1000	3.14	1.32
200	2.481	1000	2.99	1.42
Helium— $T_c = 13.28, P_c = 10.26$				
- 70	15.299	600	1.84	0.70
0	20.570	600	2.12	0.88
200	35.631	600	2.64	1.46
Propane— $T_c = 369.99, P_c = 42.01$				
225	1.346	104.2	4.83	2.17
250	1.414	266.06	3.13	1.53
275	1.481	303.03	1.90	0.79
Ethane— $T_c = 305.28, P_c = 48.8$				
125	1.304	111.46	9.45	4.05
175	1.468	222.44	3.05	0.88
225	1.631	311.09	3.10	1.12
250	1.713	345.38	2.99	1.17
275	1.795	345.30	2.32	1.63
Carbon Dioxide— $T_c = 304.28, P_c = 73.0$				
137	1.348	225	4.85	2.01
198	1.548	1000	4.35	2.30
258	1.745	400	-2.91	1.18
Nitric Oxide— $T_c = 179.18, P_c = 65$				
9	1.574	160	3.27	1.80
Ethylene— $T_c = 282.88, P_c = 50.9$				
137.5	1.451	500	3.13	1.43
198.5	1.667	900	2.82	1.24
Oxygen— $T_c = 154.38, P_c = 49.7$				
0	1.77	1000	2.30	0.85
99.5	2.41	1000	1.10	0.41
199.5	3.06	900	2.10	1.14
Carbon Monoxide— $T_c = 134.18, P_c = 35.0$				
- 70	1.51	800	4.4	1.75
- 50	1.66	1000	4.2	1.75
- 25	1.85	1000	2.9	1.18
0	2.04	1000	3.2	0.86
100	2.78	1000	1.0	.27
200	3.53	1000	1.1	.52

^a Sources of P - V - T data: hydrogen—Otto and Holborn, *Z. Physik*, **33**, 1 (1925); Bartlett, Cupples and Tremearne, *THIS JOURNAL*, **50**, 1275 (1928); methane—

Kvalnes and Gaddy, *ibid.*, **53**, 394 (1931); helium—Wiebe, Gaddy and Heins, *ibid.*, **53**, 1721 (1931); propane—Beattie, Kay and Kaminsky, *ibid.*, **59**, 1589 (1937); ethane—Beattie, Hadlock and Poffenberger, *J. Chem. Physics*, **3**, 93 (1935); carbon dioxide—Amagat, *Ann. chim. phys.*, **29**, 68 (1893); nitric oxide—Briner, Biedermann and Rother, *Helv. chim. acta*, **8**, 923 (1925); ethylene—Amagat, *Ann. chim. phys.*, **29**, 68 (1893); oxygen—*ibid.*; carbon monoxide—Bartlett, Hetherington, Kvalnes and Tremearne, *THIS JOURNAL*, **52**, 1374 (1930).

The results for hydrogen and helium indicate that the equation is suitable for extrapolation to values of T_r much higher than seven. In fact, the agreement for hydrogen at $T_r = 18.7$ and helium at $T_r = 35.6$ is not very much worse than at the lower T_r 's. On the other hand, the calculations do indicate that extrapolation to values of T_r lower than 1.6 cannot be made as freely. With some sacrifice in accuracy the equation may be applied to T_r values as low as 1.3, although in such cases it is found necessary to decrease the pressure range to be covered. All things considered, it does not seem advisable to recommend the equation for its full pressure range below $T_r = 1.55$. At $T_r = 1.3$ the equation should be used only up to pressures of 100 atmospheres, with progressive increase in pressure range up to $P_r = 30$ as T_r approaches 1.55. Above $T_r = 1.55$ the equation seems to hold very well even at pressures considerably higher than the reduced pressure range for which the original nitrogen equation was deduced.

To show the superiority of the equation proposed here over a simple equation of state such as van der Waals, Table III gives a comparison of PV 's observed and calculated by means of the two equations. Throughout the equation proposed here reproduces the observed compressibility data with a much higher fidelity than does the van der Waals equation. Further, when extended to pressures beyond the upper limits given in the table the van der Waals equation gives deviations which are above 15% and which reach 200–300% as the pressures approach 1000 atmospheres, whereas the equation of this paper still reproduces the data within a few per cent. A further comparison of the present equation with those of van der Waals, Dieterici, and Berthelot with data on hydrogen and oxygen at 0°⁷ also shows that up to 1000 atmospheres our equation reproduces much more satisfactorily the data for these gases than do the other equations.

(7) Maron and Turnbull, *Ind. Eng. Chem.*, **34**, 544 (1942).

TABLE III
COMPARISON OF OBSERVED AND CALCULATED PV 'S

Gas	Pressure range, ^a atm.	Reduced temp., T_r	PV van der Waals		PV this paper	
			% Max. dev.	% Av. dev.	% Max. dev.	% Av. dev.
Methane	30-300	1.694	7.67	3.66	2.14	0.96
Ethane	38.64-311.09	1.631	- 8.43	4.81	-3.10	1.12
Propane	41.23-303.03	1.481	14.05	6.07	-1.90	0.79
Ethylene	50-300	1.667	- 6.44	4.10	-1.57	0.61
Carbon monoxide	25-200	1.663	- 7.16	4.54	-2.57	0.90
Carbon dioxide	75-500	1.548	11.33	6.26	-3.64	2.17

^a Above the upper limits of pressure indicated the van der Waals equation gives deviations which are 15% or higher, and which reach 200-300% at pressures approaching 1000 atmospheres.

From the equations given in this paper it is readily possible to derive a generalized equation for the compressibility coefficients of gases obeying the principle of corresponding states. If the values of the α 's given by equations (8) to (11) be substituted into equation (1), and Z solved for, the result is

$$Z = 1 + \left[\frac{\beta_1}{T_r} + \frac{\beta_2}{T_r^2} + \frac{\beta_3}{T_r^3} \right] \frac{P_r}{R} + \left[\frac{\beta_4}{T_r^3} + \frac{\beta_5}{T_r^5} + \frac{\beta_6}{T_r^7} \right] \frac{P_r^2}{R} + \left[\frac{\beta_7}{T_r^5} + \frac{\beta_8}{T_r^7} + \frac{\beta_9}{T_r^9} \right] \frac{P_r^3}{R} + \left[\frac{\beta_{10}}{T_r^7} + \frac{\beta_{11}}{T_r^9} + \frac{\beta_{12}}{T_r^{11}} \right] \frac{P_r^4}{R} \quad (12)$$

This equation should reproduce the generalized compressibility coefficient curves deduced empirically by various authors within the ranges specified. That it will do so is evidenced by the comparisons of calculated and observed volumes given in this paper.

Summary

1. Employing the principle of corresponding states, an equation of state for gases is deduced requiring only the critical temperature and pressure of a gas.

2. The equation is shown to be applicable to pressures as high as 1000 atmospheres and reduced temperatures of $T_r = 1.55$ and above.

3. Below $T_r = 1.55$ the equation proposed is applicable down to $T_r = 1.30$ provided the pressure interval covered is reduced to 100 atmospheres at the lower temperature.

4. A comparison of the proposed equation with several other common equations of state shows the present equation to be superior to these.

5. A generalized equation for compressibility coefficients of gases is deduced.

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[CONTRIBUTION FROM THE MORLEY CHEMICAL LABORATORY, WESTERN RESERVE UNIVERSITY]

Systems with Boron Trifluoride¹

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The boron atom of boron trifluoride has been found to be an acceptor to form a large number of coördinate compounds. The number of donor atoms has been found so far to be quite small, being confined to the seven elements carbon, nitrogen, oxygen, fluorine, phosphorus, sulfur and argon.

One of the best procedures for the identification of these coördinate compounds is thermal analysis, particularly as applied to liquefied gases. The object of the present investigation was to extend our knowledge of the coördinate compounds of boron

trifluoride and various gases by means of thermal analysis.

Apparatus and Procedure

The apparatus shown in Fig. 1 is similar in principle and operation to that described in detail by Germann and Booth,² save for the following features.

1. Boron trifluoride³ from the cylinder B was purified by fractional distillation in the fractionating column⁴ LH and stored in ampoule T_2 separated by the mercury cut-off MC to prevent contamination from stopcock grease or from leakage.

(2) Germann and Booth, *J. Phys. Chem.*, **30**, 389 (1926).

(3) Obtained through the kindness of the Harshaw Chemical Company.

(4) Booth and Bozarth, *Ind. Eng. Chem.*, **29**, 470 (1937).

(1) From a part of a thesis submitted by Donald Ray Martin to the Graduate Faculty of Western Reserve University, May, 1941, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.