Distillation constants have been determined for many organic substances belonging to different groups. In homologous series the value of k increases with the lengthening of the carbon chain. This is obviously due to the decline in hydration as the molecular weight increases.

The effect of salts upon the steam distillation is powerful. Among the salts studied sodium chloride has in the greatest degree raised the value of k. The influence of anions is obviously much more intense than that of cations.

The effect of the salts upon the distillation of different substances is variable (Fig. 3). The curves indicating the dependency of k on salt concentration rise rather rectilinearly for those substances which dissolve indefinitely in salt solutions, while for those substances which do not dissolve indefinitely in water and which in part separate from water through the effect of salts, k rises with the increase in salt concentration so powerfully that the curve arches strongly upward.

The promoting effect of salts upon distillation is obviously due to the fact that they diminish the hydration of the substance, especially of undissociated molecules. The promoting effect of salts upon distillation can to a great extent be turned to advantage in distinguishing volatile from non-volatile compounds.

HELSINKI, FINLAND

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 207]

A NEW EQUATION OF STATE FOR FLUIDS. III. THE NORMAL DENSITIES AND THE COMPRESSIBILITIES OF SEVERAL GASES AT 0°

BY JAMES A. BEATTIE AND OSCAR C. BRIDGEMAN[1]

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The compressibility of gases at 0° and at pressures up to one atmosphere is of great importance in the determination of the atomic weights of the inert gases from density measurements and for the calculation of the normal densities of those gases whose molecular weights can be determined by chemical analysis. The experimental evaluation of the ratio of the pressure–volume product at 0° and at one atmosphere, p_1V_1, to the product at zero pressure, p_0V_0, is difficult, and it is believed that this ratio can be obtained for any gas for which there are extensive p–V–T data with as great an accuracy from the equation of state.

The relations between these quantities are given by the equations

$$p_0V_0/p_1V_1 = 1 + \lambda \tag{1}$$

$$p_0V_0 = (m/M)\, RT_0 \tag{2}$$

$$d_n = \frac{m}{V_1} = \frac{M(1 + \lambda)}{RT_0} \tag{3}$$

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[1] National Research Fellow in Chemistry.

where λ is a constant for a given gas, M is its molecular weight, R is the gas constant per mole and T_0 is the value of 0° on the Kelvin scale. In Equation 1 the ratio p_0V_0/p_1V_1 can refer to any quantity of gas, but in Equation 2 the product p_0V_0 is taken for m grams. Combination of these relations leads to Equation 3, in which d_n is the normal density of the gas, that is, the weight in grams of one liter of the gas at 0° and one atmosphere pressure.

Thus if RT_0 is known and a value of λ is available, the molecular weight of the gas can be calculated from the normal density. If, on the other hand, the molecular weight has been determined by chemical means, the normal density can be calculated.

Recently the authors have proposed a new equation of state[2]

$$p = \frac{RT\,(1-\epsilon)}{V^2}\,[V+B] - \frac{A}{V^2}$$

$$A = A_0(1 - a/V). \quad B = B_0(1 - b/V). \quad \epsilon = c/VT^3 \tag{4}$$

in which R is the gas constant and A_0, a, B_0, b and c are constants for each gas.

The values of these constants have been determined[3] for the ten gases helium, neon, argon, hydrogen, nitrogen, oxygen, air, carbon dioxide, methane and ether. The equation was found to reproduce the experimental pressure–volume–temperature data over wide ranges of temperature and density very satisfactorily. In the present article advantage is taken of this correlation to compute the values of p_0V_0/p_1V_1 and hence of λ for the nine of the above substances which are gases at 0° and one atmosphere; and then by use of Equation 3 to calculate the normal density of those gases for which the molecular weight can be determined by chemical means, and also to compute the molecular weights from the best values of the normal densities.

When working at constant temperature, it is more convenient to transform the Equation of state 4 into the virial form

$$\begin{aligned} pV &= RT + \beta/V + \gamma/V^2 + \delta/V^3 \\ \beta &= RTB_0 - A_0 - Rc/T^2 \\ \gamma &= -RTB_0b + A_0a - RB_0c/T^2 \\ \delta &= RB_0bc/T^2 \end{aligned} \tag{5}$$

For the gases under consideration at 0° and one atmosphere, the term δ/V^3 is negligible, and on the average γ/V^2 affects the calculated value of p_1V_1 by one part in 300,000, while β/V contributes one part in 600. In the least favorable case—carbon dioxide—these last two terms are about three times as large. Thus if β is known to only 1%, the uncertainty introduced into p_1V_1 is on the average 0.002%, while for carbon dioxide it is 0.007%.

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[2] Beattie and Bridgeman, This Journal, **49**, 1665 (1927).

[3] Beattie and Bridgeman, *ibid.*, **50**, 3133 (1928).

In the determination of the equation of state constants from the pressure–volume–temperature data, the values of R and T_0 used were 0.08206 and 273.13 in units of international atmospheres for pressure, liters per mole for volume, and degrees Kelvin for temperature.[4] These give 22.4131 for RT_0, which is in good agreement with the value 22.4133 recently found by Baxter and Starkweather,[5] based on their determinations of the density of oxygen.

In Table I are listed the values at 0° of the parameters β, γ and δ calculated from the equation of state constants by means of the relations (5). It should be noted that these values are based on the correlation of the pressure–volume–temperature data of different investigators for each gas, over the whole temperature range and a wide density range, thus tending to eliminate both constant and accidental errors.

Table I

Virial Coefficients at 0° Computed from the Equation of State

R = 0.08206; T_0 = 273.13; RT_0 = 22.4131 (g = 980.665). Units: international atmospheres, liters per mole, degrees Kelvin.

Gas	β	$\gamma \times 10^3$	$\delta \times 10^5$	Gas	β	$\gamma \times 10^3$	$\delta \times 10^5$
He	0.29214	1.292	....	N*	−0.23870	33.345	−42.7
Ne	.24810	4.644	....	O_2	− .50752	31.399	10.3
A	− .47553	27.457	....	CO_2	−3.38451	111.131	5502.6
H_2	.27172	19.467	−0.5	CH_4	−1.16581	54.224	−125.1
N_2	− .25974	40.669	−16.1	Air	−0.31547	34.303	−24.2

N* denotes values of the constants obtained from a consideration of the data of Smith and Taylor alone.

In Table II are given the details of the calculation of the ratio p_0V_0/p_1V_1 from the coefficients of Table I, by means of the relation

$$\frac{p_0V_0}{p_1V_1} = \frac{RT_0}{RT_0 + \beta/V_1 + \gamma/V_1^2 + \delta/V_1^3} = 1 + \lambda \qquad (6)$$

In the second column of this table are listed values of $p_1V_1 - RT_0$, that is, $\beta/V_1 + \gamma/V_1^2 + \delta/V_1^3$, which indicates the magnitude of the quantity which is obtained from the equation of state. In the third are given values of p_1V_1 calculated by use of Equation 5. Since the volume is contained implicitly in this relation, the perfect gas value, 22.41, was assumed for the first approximation. The convergence was very rapid, the next approximation giving the final value of p_1V_1. In the last two columns are listed the values of λ calculated from Equation 6 and those

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[4] This value of R is used in the "International Critical Tables" and was derived by Keyes, *Amer. Soc. Refrig. Eng. J.*, **8**, 505 (1922); the value of T_0 was determined by Buckingham, *Bull. Bureau Standards,* **3**, 237 (1907), and has been used for many years in this Laboratory.

[5] Baxter and Starkweather, *Proc. Nat. Acad. Sci.*, **10**, 479 (1924); *ibid.*, **12**, 699 (1926), give the value 22.4144 using 980.616 for g, and this was reduced to the international gravity, 980.665.

selected by Pickering.[6] It should be noted that the variations of the measured values obtained by different observers are large.

TABLE II

RATIO AT 0° OF THE pV PRODUCTS AT 0 AND 1 ATMOSPHERE

$RT_0 = 22.4131$ ($g = 980.665$)

Gas	$p_1V_1 - RT_0$	p_1V_1	$1 + \lambda$	$\lambda \times 10^3$, calcd.	$\lambda \times 10^3$, obs.[a]
He	0.01303	22.4261	0.99942	−0.58	-0.4_6
Ne	.01107	22.4242	.99950	− .50	$-0._4$
A	− .02118	22.3919	1.00095	+ .95	$+ .9_0$
H_2	.01216	22.4253	0.99946	− .54	$- .6_1$
N_2	− .01151	22.4016	1.00051	+ .51	$+ .4_7$
N*	− .01059	22.4025	1.00047	+ .47	
O_2	− .02260	22.3905	1.00101	+1.01	$+ .9_4$
CO_2	− .15181	22.2613	1.00682	+6.82	$+7.0_6$
CH_4	− .05203	22.3611	1.00233	+2.33	+2.4
Air	− .01402	22.3991	1.00063	+0.63	$+0.6_1$

[a] Observed values are those given in "International Critical Tables," Vol. III, p. 3.

The values of λ calculated from the equation of state can be used to compute the normal density of those gases whose molecular weights can be determined by chemical means. The method of carrying out the calculation is evident from a consideration of Equation 3 and the results are given in Table III. The atomic weights given in "International Critical Tables," Vol. I, were used, and the resultant weights of a normal liter are compared with those selected by Blanchard and Pickering.[7]

TABLE III

COMPARISON OF OBSERVED AND CALCULATED WEIGHTS OF ONE LITER FOR SEVERAL GASES AT 0° AND 1 ATMOSPHERE

Gas	Int. crit. tables Mol. wt.	p_1V_1 (from Table II)	Wt. of liter, calcd.	Wt. of liter, obs.[a]
H_2	2.0154	22.4253	0.08987	0.08988
N_2	28.016	22.4016	1.25062	1.2505_7
N*	28.016	22.4025	1.25057	
O_2	32.000	22.3905	1.42918	1.4290_4
CO_2	44.000	22.2613	1.97652	1.9769
CH_4	16.0308	22.3611	0.71691	0.716_8

[a] Observed values are those given in "International Critical Tables."

Recently Baxter and Starkweather[8] have determined the normal densities of helium, neon, argon, nitrogen and oxygen. These differ in some cases from the values selected by Blanchard and Pickering. In Table IV

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[6] Pickering, "International Critical Tables," McGraw-Hill Book Company, New York, **1928**, Vol. III, p. 3.

[7] Blanchard and Pickering, *U. S. Bureau of Standards Scientific Paper*, No. 529, 1926; see also Pickering, "International Critical Tables," Vol. III, p. 3, 1928.

[8] Baxter and Starkweather, ref. 5; *Proc. Nat. Acad. Sci.*, **11**, 231 (1925); *ibid.*, **12**, 20, 703 (1926); *ibid.*, **14**, 50, 57 (1928).

the measured values of Baxter and Starkweather (reduced to $g = 980.665$), and the selected values of Blanchard and Pickering (which only in the case of helium and oxygen include a consideration of the measurements of the former) are used in the computation of the molecular weights of the various gases. The results are compared with the values given in the "International Critical Tables," Vol. I. For those gases whose molecular weights can be determined by chemical analysis, this comparison is given as an indication of the consistency of the *measured* normal density and *calculated* λ, with the molecular weight. The agreement in general is excellent.

TABLE IV

COMPUTATION OF THE MOLECULAR WEIGHT FROM THE WEIGHT OF A NORMAL LITER

Gas	Reference[a]	Exp. wt. of a normal liter	p_1V_1 (from Table II)	Mol. wt., calcd.,	Mol. wt., (Int. Crit. Tables)
He	B. and P.	0.1785	22.4261	4.003	4.00
He	B. and S.	.17847		4.002	
Ne	B. and P.	$.900_2$	22.4242	20.186	20.2
Ne	B. and S.	.89994		20.180	
A	B. and P.	1.7825	22.3919	39.914	39.91
A	B. and S.	1.78373		39.941	
H_2	B. and P.	0.08988	22.4253	2.0156	2.0154
N_2	B. and P.	1.2505_7	22.4016	28.015	28.016
N_2	B. and S.	1.25042		28.011	
O_2	B. and P.	1.4290_4	22.3905	31.997	32
O_2	B. and S.	1.42904		31.997	
Air	B. and P.	1.2929	22.3991	28.960	
CO_2	B. and P.	1.9769	22.2613	44.008	44.000
CH_4	B. and P.	0.716_8	22.3611	16.028	16.0308

[a] B. and P. = Blanchard and Pickering; B. and S. = Baxter and Starkweather.

The calculated values of λ depend only on the equation of state constants of the various gases and the value of RT_0, and small errors in the latter evidently tend to cancel. The deviations between the observed and calculated values of λ and of the normal densities and molecular weights shown in Tables II to IV are well within the variations between the determinations of different observers except for the gas oxygen. Thus, for instance, Moles[9] gives 1.25062 as the normal density of nitrogen, while the review of the normal densities of gases given by Blanchard and Pickering shows a rather wide variation in the experimental determinations. In the case of oxygen, however, the value of λ calculated from the equation of state seems to be too large, which gives too large a value for the normal density. The equation of state of oxygen reproduces the experimental compressibility data quite satisfactorily in the neighborhood of 0°. Moreover, since the values of λ calculated for other gases from the equation of state agree well with the experimental values, it seems reasonable to assume

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[9] Moles, *Gazz. chim. ital.*, **56**, 915 (1926). The value was reduced to $g = 980.665$.

that the discrepancy in the case of oxygen is due to an inconsistency between the compressibility and the normal density data.

The value of λ and the weight of a normal liter have been determined experimentally for carbon monoxide and nitrous oxide, but the compressibility data on these gases are too fragmentary to allow of the evaluation of their equation of state constants. Langmuir[10] has pointed out that the physical properties of CO and N_2O are very similar to those of N_2 and CO_2, respectively. He has postulated that the external arrangements of the electrons are the same in CO and N_2, and in N_2O and CO_2; and thus in each pair the electrical fields are quite similar. The constants of the equation of state are probably due largely to the external electrical fields and hence the constants of CO and N_2O should be close to those of N_2 and CO_2. In Table V the experimentally determined values of λ and of the weight of a normal liter of CO and N_2O selected by Blanchard and Pickering[7] are compared with those calculated from the equation of state, using the values of the constants of N_2 and CO_2, respectively. The agreement is good and indicates that at moderate pressures and at temperatures which are not too near the critical temperature, the thermodynamic properties of CO and N_2O can be calculated by use of the equation of state constants for N_2 and CO_2.

TABLE V

COMPARISON OF OBSERVED AND CALCULATED VALUES OF λ AND OF THE WEIGHT OF A NORMAL LITER OF CO AND N_2O

Gas	Mol. wt., I. C. T.	$\lambda \times 10^3$ (calcd.)	$\lambda \times 10^3$ (obs.)	Wt. of liter (calcd.)	Wt. of liter (obs.)
CO	28.000	+0.51	+0.5	1.2499	1.250_4
N_2O	44.016	+6.82	+7.4	1.9772	1.977_8

Calculated values are obtained by use of the equation of state constants for N_2 and CO_2, the isosteres of CO and N_2O. Observed values are those given in "International Critical Tables."

Summary

The equation of state proposed by the authors is used to calculate values of the ratio at 0° of the pV products at one atmosphere and at zero pressure for several gases, and a brief discussion is given concerning the merits of this particular method and its accuracy. These ratios are then employed to compute the weights of a normal liter of hydrogen, oxygen, nitrogen, carbon dioxide and methane, whose molecular weights can be determined by chemical means, and a good agreement is obtained with accepted values. The molecular weights of the gases named above and of helium, neon, argon and air are calculated from the normal densities, and the agreement with the "International Critical Tables" values is very good. The agreement obtained in these calculations indicates that the

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[10] Langmuir, THIS JOURNAL, **41**, 868, 1543 (1919).

equation of state extrapolates to low pressures with a high degree of accuracy.

The values at 0° of the ratio of the pV product at one atmosphere to that at zero pressure, and the weights of a normal liter of CO and N_2O are calculated from their molecular weights and the values of the constants of the equation of state of their isosteres, namely N_2 and CO_2. The agreement with the observed values is very good, and indicates that for many thermodynamic calculations the constants of N_2 and CO_2 can be used for CO and N_2O, respectively.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY OF THE UNIVERSITY OF PENNSYLVANIA]

THE IONIC CONCENTRATIONS AND ACTIVITY COEFFICIENTS OF WEAK ELECTROLYTES IN CERTAIN SALT SOLUTIONS

BY HERBERT S. HARNED AND ROBERT A. ROBINSON[1]

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The electromotive forces of cells of the types

$$\mathrm{Ag} \mid \mathrm{AgX} \mid \mathrm{HX}(m_0),\ \mathrm{MX}(m) \mid \mathrm{H_2} \mid \mathrm{HX}(m_0) \mid \mathrm{AgX} \mid \mathrm{Ag}$$

and

$$\mathrm{H_2} \mid \mathrm{MOH}(m_0),\ \mathrm{MX}(m) \mid \mathrm{M_xHg} \mid \mathrm{MOH}(m_0) \mid \mathrm{H_2}$$

have proved very useful in determining the activity coefficients of some strong acids and hydroxides in certain salt solutions.[2] In the cases so far considered, this method has been applied to the class of strong acids and hydroxides. The question naturally arises as to whether measurements of this kind cannot be extended so as to determine the activity coefficients of weak acids and hydroxides in salt solutions of varying strengths as well as the hydrogen and hydroxyl ion concentrations of weak acids and hydroxides in these solutions.

It is the purpose of this study to show that this information may be acquired by measurements of cells without liquid junction potentials. Furthermore, this result can be accomplished with cells which contain easily reproducible electrodes such as the hydrogen and silver–silver chloride electrodes. The limitations of the method are for the most part experimental and depend on the difficulty of obtaining the reversible electro-

[1] Commonwealth Fund Fellow, 1927–1929.

[2] (a) Harned, THIS JOURNAL, **38**, 1986 (1916); (b) **42**, 1808 (1920); (c) **47**, 684 (1925); (d) **48**, 326 (1926); (e) Loomis, Essex and Meacham, *ibid.*, **39**, 1133 (1917); (f) Chow, *ibid.*, **42**, 497 (1920); (g) Harned and Brumbaugh, *ibid.*, **44**, 2729 (1922); (h) Åkerlöf, *ibid.*, **48**, 1160 (1926); (i) Harned and Swindells, *ibid.*, **48**, 126 (1926); (j) Harned and James, *J. Phys. Chem.*, **30**, 1060 (1926); (k) Harned and Åkerlöf, *Physik. Z.*, **27**, 411 (1926); (l) Güntelberg, *Z. physik. Chem.*, **123**, 199 (1926); (m) Randall and Breckenridge, THIS JOURNAL, **49**, 1435 (1927).