pendence of heat capacity on concentration in some cases.

Summary

For the case of solute molecules which may be represented as spheres containing a point dipole, it is shown that a linear relationship exists in the limit of low concentrations (1) between the osmotic deviation function j of Lewis and Randall and the concentration and (2) between the partial molar heat capacity and the concentration. Explicit values of the corresponding coefficients are given, in terms of the moment and size of the solute molecule and the dielectric constant and temperature of the solvent.

[CONTRIBUTION FROM VALENCIA HIGH SCHOOL]

A General Equation of State

BY GEORGE WOOLSEY

Ever since van der Waals introduced his equation of state, a tremendous amount of work has been done in an effort to find an equation which would represent more nearly than his the behavior of fluids over wide ranges of temperature and pressure. It is clearly evident that the constants of van der Waals' reduced equation

$$\left(P + \frac{3}{V^2}\right)\left(V - \frac{1}{3}\right) = \frac{8}{3}T$$

are determined by the mathematical fact that the equation is cubic in V and has three real roots at the critical point. Consequently, these constants can have little physical significance.

Since the value of $Rt_c/P_cV_c = n$ varies considerably for different substances (from 3.26 for helium to 4.98 for acetic acid), any general equation of state must allow for this variation.

Recently the attempt to obtain a general equation of state has been more or less abandoned as impossible because it has been noticed that reduced vapor pressure curves for different substances do not coincide. For instance, at $T = 0.95$ the vapor pressure of methane is 0.730 and that of methyl alcohol is 0.637, and the corresponding values of PV/T for the vapor are 2.07 and 2.53, respectively. This seems at first to indicate that a general equation is impossible, until it is recalled that no consideration has been given to the differences in the values of n and to the fact that the vapor pressure curve is not an isothermal line. It might be possible that isothermal lines for all substances coincide but that the vapor pressure curves for different substances cross the isotherms at slightly different points, depending upon the value of n.

The Beattie–Bridgeman equation of state fits any given substance as accurately as desired but its constants must be determined anew for each new material. Consequently, it seems that there is still a place for a general equation which, though possibly not fitting as closely as the Beattie–Bridgeman equation, can be used as a guide to the behavior of all pure, non-associating, and non-dissociating substances in the gaseous and liquid states.

In order to find out whether or not a general equation of state is possible, some means must be found to plot the isotherms of all substances on a comparable basis. The simplest method of doing this seems to be to plot reduced values of PV/T against reduced values of P. On such a graph the critical point is at (1,1) and the equation for the gas at such low pressures and high temperatures that it acts like an ideal gas would be represented by the line $PV/T = n$. This is easily shown to be true by multiplying the perfect gas equation, $pv/t = R$, by $t_c/P_cV_c = n/R$. Since n is different for different substances some means must be used to make the different ideal gas lines coincide. This can be done if the space from $PV/T = 0$ to $PV/T = 1$ is undisturbed and the space above $PV/T = 1$ is stretched or compressed so that all the $PV/T = n$ lines coincide at some arbitrary line $PV/T = n_0$. The equation for such a stretch is

$$\left(\frac{PV}{T} - 1\right)\frac{n_0 - 1}{n - 1} = \frac{PV'}{T} - 1 \text{ or}$$

$$\frac{PV'}{T} = \frac{PV}{T}\frac{n_0 - 1}{n - 1} + \frac{n - n_0}{n - 1}$$

where PV'/T is the value of PV/T on the stretched plot. When PV'/T values for points above $PV/T = 1$ and PV/T values for points

below $PV/T = 1$ for hydrogen, nitrogen, carbon monoxide, carbon dioxide, methane, and ethylene were plotted together they formed a single series of isothermal lines everywhere consistent with each other to within a few per cent.

To find an equation to fit this series of isotherms it was thought simplest first to find an equation for the critical isotherm. The values of four points on the critical isotherm when $n = n_0 = 3.25$ were selected for this purpose. These points were $P = 1$, $PV = 1$; $P = 0.5$, $PV = 2.7$; $P = 10$, $PV = 4$; and $P = 20$, $PV = 7.2$.

To find the form of the equation a start was made from van der Waals' equation with terms added in such a way as not to increase the degree of the equation beyond that of a cubic in V.

$$\left(P + \frac{A}{V^2 + CV + D}\right)(V - B) = n_0 T = n_0 = 3.25$$

A could not be a function of V of the type $A_0 + aV + bV^2$, etc., for the equation must reduce to $PV = nT$ for large values of V. It could be the type $A_0 + \dfrac{a}{V} + \dfrac{b}{V^2}$, etc., but this would increase the degree of the equation beyond that of a cubic. Consequently A was treated as a true constant. B was also considered to be a true constant because the $(PV/T,P)$ isothermal lines are linear at high pressures. (In the case of helium this is true up to $P = 440$.) If B were not a constant the slopes of these lines would become less with increasing pressure. One of the constants C or D had to be introduced because of the presence of n in the equation. Therefore two points, $(1,1)$ and any other point on the critical isotherm, are sufficient to determine the values of the constants A, B, C and D. This equation, however, could not be made to follow the isotherm over its entire range.

Two other terms were then added so that the equation read

$$\left(P + \frac{A}{V^2 + CV + D}\right)(V - B) =$$
$$3.25 + KP + q \log\left(\frac{1}{V} + 1\right)$$

The four points above mentioned were required *to evaluate the constants of this equation*, but though the curve for this equation could be made to pass through these four points it did not follow the critical isotherm at intermediate points. The equation was then changed to

$$\left(P + \frac{A}{V^2 + CV + D}\right)(V - B) =$$
$$3.25 + KP + q \log(P + 1)$$

This equation was found perfectly satisfactory, though it could not be made to follow the critical isotherm if its constants were evaluated with any of them set equal to zero. The constants of the equation as it stands were evaluated as follows.

Making the equation a perfect cubic in V at $P = 1$, $V = 1$ gave the values

$$A = C^2 + 3C + 3 - D$$
$$AB = 1 - 3D - CD$$
$$B + K = C - 0.25 - 0.30103q$$

Substituting these values and $P = 20$, $V = 0.36$ into the equation gave

$$q = 4.0439\left(\frac{0.36C^2 - 0.09C + CD - 0.61D - 0.065259}{0.1296 + 0.36C + D}\right)$$

Substituting these values and in turn $P = 0.5$, $V = 5.4$ and $P = 10$, $V = 0.4$ gave two simultaneous equations, cubic in C and quadratic in D. Various values of C were tried until both equations gave the same value of D. The equation with the solved values of the constants is

$$\left(P + \frac{5.145}{V^2 + 0.9054V + 1.3907}\right)(V + 0.8611) =$$
$$3.25 + 1.1478P + 1.2247 \log(P + 1)$$

or in the more familiar appearing form

$$\left(P + \frac{5.145}{V^2 + 0.9054V + 1.3907}\right)(V - 0.2867) =$$
$$3.25 - \frac{5.906}{V^2 + 0.9054V + 1.3907} + 1.2247 \log(P + 1)$$

or in the more usable form

$$PV + \frac{5.145V + 4.431}{V^2 + 0.9054V + 1.3907} = 3.25 + 0.2867P +$$
$$1.2247 \log(P + 1)$$

To show how well this equation follows the critical isotherm

V	10	2.0556	0.55	0.454	0.3767
P, calcd.	0.30−	0.89+	1.94	4.95	14.6+
P, experimental	0.3	0.9	2	5	15

Attention was next turned to the vapor pressure curve, and to PV/T for the liquid in equilibrium with the vapor and PV'/T for the vapor, both at the same values of P. Here it was found that these curves cut the isotherms in such a way as to give a continuous variation with values of n. Using values for methane, ethane, ethyl ether, normal heptane, propyl alcohol and methyl alcohol it was found that at $T = 0.7$, $PV'/T = 3.025 \pm 0.51\%$; at $T = 0.85$, $PV'/T = 2.567 \pm 0.49\%$; and at $T = 0.95$, $PV'/T = 1.967 \pm 0.25\%$; and at $T = 0.85$, the vapor pressure, $P = 0.7713 - 0.1221n$, while at $T = 0.95$, $P = 1.008 - 0.0834n$. The last two equations were used for calculating molecular weights by using

$$M \text{ (calcd.)} = Rt_c d_c / p_c n \text{ (calcd.)}$$

and it was found that the probable error of the molecular weight determinations made at $T = 0.85$ was 3.75% and that at $T = 0.95$ it was 1.78%. Likewise for the liquid in equilibrium with the vapor it was found that at $T = 0.85$, $PV/T = 0.4761 - 0.08n$.

In order to find the way in which T enters the condition equation, the values of P and of PV/T for the liquid and of PV'/T for the vapor were determined from the above equations at $T = 0.85$ and $n = 3.25$.

Then, using

P	1	20	0.3745	0.3745
V	1	0.36	5.8264	.49048
T	1	1	0.85	.85

and the equation

$$\left(P + \frac{A}{T^x V^2 + T^y CV + T^z D}\right)(V - B) = 3.25T + KP + q \log (P + 1)$$

various values of x, y and z were used, the constants determined, and computed values were compared with actual values at four widely differing points. The development of this work is tabulated.

x	y	z	$B + K$	q	A	$-AB$	D	C
0	0	0	0.444	−1.908	2.775	0.866	0.598	0.1195
0	0	−1	.352	−0.0954	4.287	1.725	0.763	.5735
0	0	−1.5	.281	1.300	5.441	3.629	1.180	.923
0.5	0	−1.5	.266	1.712	4.965	7.83	2.191	1.031
.5	0.5	−1.5	.277	1.434	4.646	7.516	2.151	0.957
.5	1	−1.5	.292	1.183	4.389	7.227	2.111	.898
.5	0.67	−1.5	.2837	1.343	4.555	7.427	2.140	.9382

P (calculated) at

| $V =$ | | | 4 | 1.56 | 0.91 | 5.4 |
| $T =$ | | | 1 | 8 | 4 | 1 |
x	y	z	$P = 10$	20	20	0.5
0	0	0	Impossible	19.6	17.9	0.499
0	0	−1	4.2	19.3	16.5	.492
0	0	−1.5	10.2	19.2	15.6	.498
0.5	0	−1.5	12.0	20.5	17.0	.51
.5	0.5	−1.5	10.5	20.7	18.5	.51
.5	1	−1.5	9.7	21.1	20.06	.513
.5	0.67	−1.5	10.2	20.9	19.0	.510

Other trial solutions not tabulated showed that x could not possibly be $+1$ or -1. The probable error for $y = 1$ is slightly less than for $y = {}^2/_3$, being 2.6 and 2.8%, respectively, but a comparison with the constants as determined by the critical isotherm, together with a theoretical consideration to be discussed later in this paper, indicates that $y = {}^2/_3$ is the better value.

First comparing the constants as determined

from the critical isotherm and from the vapor pressure, orthobaric densities data

	$B + K$	q	A	$-AB$	D	C
Critical isotherm	0.2867	1.225	5.145	4.431	1.391	0.9054
Vapor pressure	.2837	1.343	4.555	7.427	2.140	.9382

it is seen that there is a fair general agreement and that there is a remarkably good agreement between the values for $B + K$ which probably is a simple function of the volume occupied by the molecules. Next following the reasoning of van der Waals, it is probably true that the backward force on a molecule as it strikes a boundary is inversely proportional to the square of the volume. However, the loss of pressure would not be proportional to this force, as assumed by van der Waals, but it would be equal to $\int f dt$ during the time the force was acting. This time would be inversely proportional to the square root of the temperature. This reasoning seems to give a valid theoretical reason for the $T^{1/2}V^2$ term which was found empirically. It is also interesting to note that this term lies between the V^2 term of van der Waals and the TV^2 term of Clausius, Berthelot, Wohl and possibly others.

This term does not take into consideration any surface condensation or film. Possibly the $T^{2/3}V$ term is due to that effect. T is proportional to V, and the equations of Eötvös and of Ramsay and Shields show the product of surface tension and of $V^{2/3}$ to be a linear function of the temperature. Finally, the $D T^{-3/2}$ term may possibly be considered a term to account for the increased blocking effect of each molecule in the surface film at higher temperatures.

The next point of interest was to find the variation of the constants of the equation, and particularly of $(B + K)$ with varying values of n.

The same four points on the critical isotherm were redetermined by means of the stretch formula to other values of n and the constants of the

equation were determined as before. The following values were found:

n	$B + K$	q	A	$-AB$	D	C
3	0.2519	1.096	4.285	1.862	0.799	0.5818
3.25	.2867	1.225	5.145	4.431	1.391	0.9054
4.375	.4492	1.208	8.792	27.836	5.558	2.1878

This shows that the differences between the constants from the two computations for $n = 3.25$ can be considered to be due to a slight uncertainty in the value of n.

This entire discussion, then, would seem to indicate that the P-V-T relationships between all pure, non-associating and non-dissociating substances are very similar when proper allowance is made for the size of the molecules and the attractive forces between them. The equation given here

$$PV + \frac{4.555V + 7.427}{T^{1/2}V^2 + 0.9382T^{2/3}V + 2.140/(T^{3/2})} =$$
$$3.25T + 0.2837P + 1.343 \log (P + 1)$$

is probably as correct in form as can be obtained without going to higher degree in V than the cube, though the values of the constants could probably be improved by a method of choosing points for their determination other than the more or less random one employed here for that purpose. A marked deviation from it on the part of any substance should be rather definite evidence of association or dissociation.

The Ionization Constant of Glycolic Acid from 0 to 50°

BY LESLIE FREDERICK NIMS

Recently Harned and co-workers[1,2] have developed a method for the precise determination of the thermodynamic ionization constant of a weak electrolyte at different temperatures. This method was used in obtaining results reported here for glycolic acid, the first member of the homologous series of α-hydroxy acids.

Method and Results

Lithium, potassium and barium glycolates, prepared by neutralizing an aqueous solution of glycolic acid with the respective c. p. carbonates, were recrystallized three times from water, dried and analyzed by conversion to the sulfates. Stock buffer solutions were made by dissolving weighed amounts of the purified salts in the requisite weight of a carefully analyzed hydrochloric acid solution. The buffer solutions were then analyzed by titration with standard sodium hydroxide and evaporation with sulfuric acid. The concentrations of acid and salt determined by these two independent methods agreed to within $\pm 0.1\%$.

Solutions obtained from the stock solutions by weight dilution were used as electrolytes in the cell Pt, H_2/Buffer solution/AgCl/Ag and the electromotive force of the cell was determined at several temperatures. The relation of the electromotive force of such a cell to the ionization constant of the weak acid present is expressed by the equation

$$pK - \log \frac{\gamma_{Cl^-}\gamma_{HG}}{\gamma_{G^-}} =$$
$$\frac{(E - E_0)F}{2.303RT} - \log \left(\frac{\nu m_2}{m_1 - m_H} - 1\right) + \log m_1 \quad (1)$$

where m_1 is the molality of hydrochloric acid, m_2 the molality of the salt of the weak electrolyte and ν is the valence of the cation of the salt. The other terms have their usual significance. Inspection of equation (1) reveals that the right-hand side consists of known or measured quantities with the exception of m_H, which occurs as a small correction term and may be estimated with sufficient accuracy by a simple approximation. Therefore, at any temperature, if the right-hand side is plotted as a function of the ionic strength, the intercept at zero ionic strength will be the negative logarithm of the ionization constant. Derivations of equations similar to equation (1) as well as a complete description of the experimental technique have been given in former papers.[3,4] Values of E_0 for the cell used in the measurements have been determined by Harned and Ehlers.[5]

The electromotive forces at the indicated tem-

(1) Harned and Owen, THIS JOURNAL, **52**, 5079 (1930).

(2) Harned and Ehlers, ibid., **54**, 1350 (1932).

(3) Nims, ibid., **55**, 1946 (1933).

(4) Nims and Smith, J. Biol. Chem., **101**, 401 (1933).

(5) Harned and Ehlers, THIS JOURNAL, **55**, 2179 (1933).