[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BROWN UNIVERSITY]

Influence of Dipole Fields between Solute Molecules. III. Thermodynamic Properties of Non-Electrolytes

BY RAYMOND M. FUOSS

It is well known that the freezing point depression of practically all real solutions is never equal to that corresponding to an ideal solution of the same concentration. Leaving strong electrolytes out of consideration, the deviation between actual and ideal depressions is usually proportional to concentration, at least in the limit of low concentrations. One of the following two explanations is possible: either the solute is associated to form clusters containing at least two molecules, or else the effect is simply due to intermolecular forces, which, while they furnish a contribution to free energy and hence appear in the thermodynamic properties, do not actually cause the formation of stable configurations containing several molecules. Very similar possibilities are found in the case of electrolytes, of course; in solvents of low dielectric constant, the Coulomb potential is high enough to render ion clusters stable to thermal impact, while in solvents of high dielectric constant, only the long range effects of the Coulomb forces appear. Every real molecule has a certain polarizability, and most molecules have permanent quadruple or dipole moments, so that one always has to reckon with intermolecular forces, even in the case of non-electrolytes, and forces between particles obviously mean non-ideal solutions. Because dipole molecules include so large a fraction of the known chemical compounds, and because a dipole is the next highest electrical singularity after a point charge, it seems worth while to consider the properties of such solutions.

In a previous paper[1] the osmotic properties of solutions of molecules which contain large dipole moments were calculated in terms of a parameter

$$x = \mu^2/a^3DkT \qquad (1)$$

When $x \gg 1$, the main contribution to the free energy arises from configurations where the molecules are in actual contact, and here it seems proper to speak of association. But when x is of the order of unity, appreciable contributions are given by molecule-pairs which have not yet approached to contact, so that we have here the simple case when intermolecular forces produce deviations from ideal behavior, without their being strong enough to cause association, if the latter is defined to mean pairwise grouping of individual molecules whose mutual energy is large compared to kT.

When $x = O(1)$, the previous asymptotic expansion cannot be used, of course. It is the purpose of the present paper to derive the thermodynamic properties of solutes whose molecules may be represented as spheres containing point dipoles at the center.[2]

In the limit of low concentrations,[3] we have

$$(p_i - p)/p_i = NI/2V \qquad (2)$$

where

$$I = \int_a^\infty (e^{-u/kT} - 1)\mathrm{d}V \qquad (3)$$

Here u is the potential energy of two dipole molecules as a function of their relative coördinates; the other symbols have the meaning given in the first reference and will not be redefined here. In terms of the Lewis and Randall j-function, we then have

$$(dj/dm)_{m=0} = NdI/2000 \qquad (4)$$

as the limiting slope on a j-m plot. For the spherical model, we shall show that

$$I = (\mu^2/DkT)\cdot 2\theta(x)$$

where $\theta(x)$ is the function of the parameter x defined by (13) and for which Table II gives numerical values. Then

$$\left(\frac{dj}{dm}\right)_0 = \frac{Nd}{1000}\,\frac{\mu^2}{DkT}\,\theta(x) \qquad (5)$$

If benzene is used as the solvent for the freezing point determinations, (5) and (1) become

$$(dj/dm)_0 = 6.25 \times 10^{-3}\mu_D{}^2\theta(x) \qquad (6)$$

---

[1] Fuoss, THIS JOURNAL, **56**, 1027 (1934).

[2] This is the case treated by Debye, "Handbuch der Radiologie (Marx)," Leipzig, 1925, p. 636 ff. The present result differs from Debye's by a factor of 5/4 in the leading term. As will be shown later, Debye's earlier result appears to be incorrectly computed. The writer takes this opportunity to thank Professor Debye for looking over the present calculation.

Also, in accordance with the request of one of the referees for this paper, another reference to earlier work seems proper. Keesom [*Physik. Z.*, **22**, 129, 643 (1921)] treated the problem of the equation of state of dipole gases, as was mentioned in footnote 7 of the first paper of this series. Kirkwood [*J. Chem. Phys.*, **2**, 351 (1934)] suggested that Keesom's method could be applied to the case of zwitterion interaction, which is closely related to the dipole–dipole case. The first paper of this series was in the Editor's hands before Kirkwood's paper was published; the author is not interested in asserting any priority claims, but merely wishes to state that his work was independent, and that the present paper is a logical continuation of the previous work, particularly because experimental work in this Laboratory on the problems concerned has been under way for some time.

[3] Ref. 1, Eq. 6.

and

$$x = 11.52\mu_D^2/\delta^3 \tag{7}$$

where μ_D is the moment in Debye units and δ is the molecular diameter in Ångström units.

We now proceed to the evaluation of $\theta(x)$. Starting with our previous result, and simplifying to the case of spherical molecules, we have

$$I = \frac{2\pi}{\sqrt{3}} \int_1^2 \frac{\xi a \xi}{\sqrt{\xi^2 - 1}} \int_a^\infty r^2 \mathrm{d}r \left(\frac{e^{Z\xi} - e^{-Z\xi}}{Z\xi} - 2 \right) \tag{8}$$

Expanding the hyperbolic sine as a series and integrating over r, we find

$$I = \frac{2\pi a^3}{3\sqrt{3}} \sum_1^\infty \frac{x^{2n}}{(2n+1)!\,(2n-1)} \int_1^4 \frac{z^n\,\mathrm{d}z}{\sqrt{z-1}} \tag{9}$$

For simplification, we introduce the abbreviation

$$j_n = \int_1^4 z^n \mathrm{d}z/\sqrt{z-1}$$

where the j_n's satisfy the recursion formula

$$j_n = 2(4^n\sqrt{3} + nj_{n-1})/(2n+1) \tag{10}$$
$$j_0 = 2\sqrt{3}$$

If we substitute in (9), we have

$$I = \frac{\mu^2}{DkT} \frac{4\pi x}{9} \sum_1^\infty \beta_n x^{2n-2} \tag{11}$$

where

$$\frac{\beta_n}{\beta_{n-1}} = \frac{j_n}{j_{n-1}} \frac{2n-3}{(2n-1)(2n)(2n+1)} \tag{12}$$

For $\theta(x)$, we finally obtain

$$\theta(x) = \frac{2\pi x}{9}\left(1 + \frac{1}{25}x^2 + \frac{29}{18375}x^4 + \ldots\right) \tag{13}$$

The first 10 coefficients are given in Table I and suffice for the computation of $\theta(x)$ for $0 \leqslant x \leqslant 5$; the function (13) is tabulated in Table II.

TABLE I

COEFFICIENTS OF $\theta(x)$

n	β_n	n	β_n
1	1.0000	6	1.9042×10^{-8}
2	0.0400	7	2.6436×10^{-10}
3	1.5782×10^{-3}	8	2.9604×10^{-12}
4	4.7511×10^{-5}	9	2.7251×10^{-14}
5	1.0828×10^{-6}	10	2.0960×10^{-16}

TABLE II

VALUES OF $\theta(x)$

x	$\theta(x)$	x	$\theta(x)$
0.1	0.0698	1.0	0.7272
.2	.1398	2.0	1.6596
.3	.2102	3.0	3.206
.4	.2810	3.5	4.508
.5	.3526	4.0	6.520
.6	.4250	4.4	9.007
.7	.4985	4.7	11.694
.8	.5731	5.0	15.448
.9	.6493	6.0	44.35

The leading term in $\theta(x)$ as derived above is $2\pi x/9$, while the leading term in Debye's function[2] is $8\pi x/45$. Apparently, Debye obtained his result by applying a charging process in his treatment of the problem; at least the analog of the method used in his treatment of electrolytes gives $8\pi x/45$ as the leading term. But it hardly seems necessary to use this method for the case of dipoles, because the short range of dipole forces permits explicit calculation of the integral I, without meeting the convergence difficulties which beset the electrolytes problem.

It would be very interesting to calculate the c^2 term in (2), in order to see how soon the freezing point curve should deviate from linearity, but the mathematical difficulties are enormous. It would be perhaps simple enough to calculate another term in the pairwise interaction, but this term would be of the same order as the leading term from triple interactions of dipoles, and both are needed in order to estimate the c^2 term. It will, therefore, be necessary to decide the importance of higher terms from an examination of experimental data; at present there are none available in the literature of sufficient accuracy to justify a theoretical study. Experimental work on the problem is in progress in this Laboratory; preliminary results indicate that equation (5) is the correct limiting law for the case under consideration.

The dependence on concentration of the partial molal heat capacity of a dipole solute can also be obtained by the general method used in the papers of this series. We have, as a first approximation for the free energy

$$-\psi = RT \ln V + kT \ln\left(1 + N^2 I/2V\right) \tag{14}$$

where I is the integral defined by (3). By application of the Gibbs-Helmholtz equation to (14) and differentiation with respect to the temperature and concentration, we obtain

$$\left(\frac{\partial C_v}{\partial c}\right)_{c=0} = \frac{NR}{1000}\frac{\mu^2}{DkT}\varphi(x) \tag{15}$$

where

$$\varphi(x) = \frac{4\pi}{75}x^3\left(1 + \frac{58}{441}x^2 + \frac{11}{1323}x^4 + \ldots\right) \tag{16}$$

Experimental work on this problem is in active progress in this Laboratory. Gucker[4] states that he has already found experimentally a linear de-

---

[4] Gucker, Abstract of Papers to be presented before the Division of Physical and Inorganic Chemistry, Kansas City, Mo., week of April 12, 1936, p. 20, paper 69.

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.

PROVIDENCE, R. I. RECEIVED MARCH 28, 1936

[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