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The probability function of Menke has been used as a basis for a statistical treatment of the intermolecular potentials in solutions of symmetrical molecules for which the entropy of mixing is the same as for an ideal solution of the same composition. The resulting expressions enable calculations to be made of the departure of iodine solutions from the ideal solution laws which agree satisfactorily with the observed departures.

THE senior author has called attention[1] to the existence of families of solubility curves for a single solute in a number of solvents where both components are comparatively nonpolar and the chemical effects of solvation, association and compound formation are absent. Such solutions have been called regular, and it has been suggested that the regularity is due to a completely random distribution of the component molecules resulting from thermal agitation, such as exists in ideal solutions. Such randomness cannot, of course, persist to indefinitely low temperatures in the presence of orienting or associating forces or unequal molecular fields. On lowering the temperature to the critical solution temperature, for example, the two species begin to unmix, giving a very different statistical distribution, and submicroscopic aggregates certainly form above this point; however, the range of temperature and concentration in which this aggregation occurs to any appreciable extent is certainly very small, as shown by theoretical and experimental studies of opalescence in this region.[2] Where this randomness exists, it suggests,

because of the well-known connection between entropy and probability, that the entropy of mixing for a regular solution should be the same as for an ideal solution of the same mole fraction. Writing the partial molal entropies of component X_1 in a regular and in an ideal solution as $\bar{S}_1{}^r$, and $\bar{S}_1{}^i$, respectively, the above conclusion can be expressed by the equation,

$$\bar{S}_1{}^r - \bar{S}_1{}^i = 0. \tag{1}$$

Since the corresponding partial molal free energies are related to the entropies by the equation, $\partial(\bar{F}_1{}^r - \bar{F}_1{}^i)/\partial T = -(\bar{S}_1{}^r - \bar{S}_1{}^i)$, we can integrate, and write

$$\bar{F}_1{}^r - \bar{F}_1{}^i = f(N), \tag{2}$$

where N denotes mole fraction. The form of $f(N)$ is the subject of this paper. It will be approached through the consideration of the energy of mixing. This is readily possible for regular solutions, since, when $\Delta S = 0$, $\Delta F = \Delta H$, and since, further, $\Delta H = \Delta E$ when $\Delta(PV)$ is negligible.

In order for a solution to be ideal, the potential of a given molecule must not alter when one species among the surrounding molecules is replaced by another. A solution will be regular even if this molecular potential varies, provided that the randomness of arrangement is still "ideal," i.e., complete. This can hardly be the case, in

[1] J. H. Hildebrand, J. Am. Chem. Soc. **51**, 66 (1929); also Proc. Nat. Acad. Sci. **13**, 267 (1927).

[2] Cf. M. v. Schmoluchowski, Ann. d. Physik [4] **25**, 205 (1908); A. Einstein, ibid. **33**, 1275 (1910); Wo. Ostwald, ibid. **36**, 848 (1911).

general, unless the molecules are symmetrical and nonpolar. (Isolated cases may be cited where a change of species, even with polar molecules, would probably not materially alter the arrangement, as with two isomeric esters.) We will assume equal molecular volumes, which allows a more satisfactory statistical treatment, before taking up the more difficult case of unequal volumes.

The form of $f(\text{N})$ has been deduced by van Laar,[3] from van der Waals theory, and by Heitler[4] by aid of the assumption that the liquid has a cubic lattice structure. The former treatment shares the unconvincing character of the van der Waals equation, and the latter depends upon a picture which cannot be true. Heitler failed, moreover, as shown by his chosen examples, to recognize the essential limitation to systems that we have called regular. The following derivation is, nevertheless, to be regarded as a refinement of his method.

The nature of liquid structure has been revealed by the studies of x-ray scattering made recently by H. Menke[5] in Debye's laboratory.

The structure of a liquid is expressed by a probability function, W (designed W_r by Menke; the subscript is here omitted for the sake of simplicity) which is defined as follows. The probability that an element dV of a volume of liquid, V, will contain the center of a given molecule (e.g., the nucleus of a central atom) is dV/V. The probability that a given pair of molecules will occupy two such elements is $(dV/V)^2$, provided they are sufficiently far apart that they do not interfere with each other. When, however, the two elements of volume are very small, and their distance apart, r, is of the same order of magnitude as the molecular radius, the volume of the molecules themselves will help to determine their positions, and the probability must be expressed by $W(dV/V)^2$, where W is a function of r. Fig. 1A gives the plot of this function for mercury as determined by Menke from x-ray scattering.

It is possible to use W to calculate the number

[3] J. J. van Laar, Zeits. f. physik. Chemie A137, 421 (1928).

[4] Heitler, Ann. d. Physik [4] 80, 630 (1928). Cf. also J. H. Hildebrand and E. J. Salstrom, J. Am. Chem. Soc. 54, 4257 (1932).

[5] (a) H. Menke, Phys. Zeits. 33, 593 (1932); cf. further, (b) O. Kratky, ibid. 34, 482 (1933).
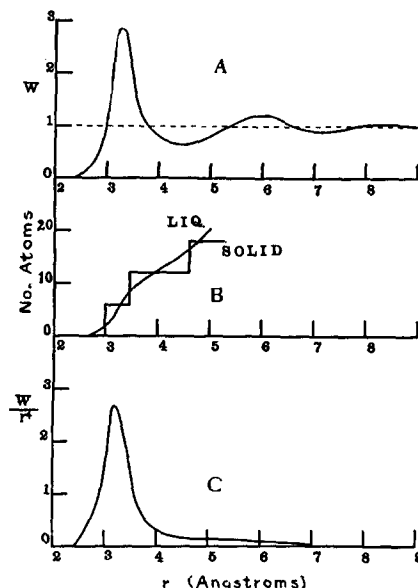
FIG. 1. A, Menke probability function for mercury; B, number of atoms within distance r of a central atom, for liquid and solid; C, potential function, area under which indicates small contribution to heat of vaporization of molecules beyond the "first layer."

of molecules (atoms in the case of mercury) surrounding a central one at various distances. The number of nuclei per cc in the liquid as a whole is N/v, where N is the Avogadro number and v the molal volume. The number of molecules in a large sphere of liquid would of course be $(N/\text{v})(4/3)\pi r^3$. In a small sphere, however, the number surrounding a central one is

$$(N/\text{v})\int_0^r 4\pi r^2 W dr.$$

Fig. 1B shows this number for various values of r calculated by graphic integration. The distribution for solid mercury is given for comparison (without correcting for the difference in density) and shows very strikingly how far the structure of the liquid differs from that of the solid.

The number in a spherical shell of radius r and thickness dr is $(4\pi N/\text{v})Wr^2 dr$. The number of molecules that can be regarded, in succession, as "central" to a shell is N, hence the total number of pairs at distance r from each other is $(2\pi N^2/\text{v})$ $Wr^2 dr$ (the numerical coefficient is changed from 4 to 2 to avoid counting each pair twice). If the potential of each pair is φ (a function of r) the potential of all the pairs at distance r is

$(2\pi N^2/v)\varphi Wr^2dr$, and the potential energy of the whole liquid, per mole, is

$$E^{0\prime} = (2\pi N^2/v)\int_0^\infty \varphi Wr^2dr. \qquad (3)$$

If we assume with London,[6] and others, that the attraction potential between molecules is given by $-k/r^6$, and neglect the repulsive potential, the potential energy of a mole of liquid would be

$$E^{0\prime} = (-2\pi N^2 k/v)\int_0^\infty (W/r^4)dr. \qquad (4)$$

Curve C, Fig. 1, shows the curve of W/r^4 plotted against r, the area under which represents the above integral. It is here given to illustrate how little is contributed by molecules beyond those immediately adjacent.

We will next consider a solution of n_1+n_2 moles of species X_1 and X_2, whose molal volumes are identical, v, and which mix without volume change. The number of molecular centers of both species per cc is the same as for the pure substance, i.e., N/v; the probability function should be the same for both species, hence the total number of molecules of both kinds at distance r from a central molecule is $(4\pi N/v)Wr^2dr$, and since there are $(n_1+n_2)N$ possible central molecules, the total number of pairs at distance r from each other is $(2\pi N^2/v)(n_1+n_2)Wr^2dr$. The chances that these pairs are of the respective species X_1X_1, X_2X_2 and X_1X_2 are $n_1^2/(n_1+n_2)^2$, $n_2^2/(n_1+n_2)^2$ and $2n_1n_2/(n_1+n_2)^2$, hence the number of pairs of each kind are, respectively

$$\frac{2\pi N^2}{v}\cdot\frac{n_1^2}{n_1+n_2}\cdot Wr^2dr,\quad \frac{2\pi N^2}{v}\cdot\frac{n_2^2}{n_1+n_2}\cdot Wr^2dr$$

and

$$\frac{4\pi N^2}{v}\cdot\frac{n_1n_2}{n_1+n_2}\cdot Wr^2dr.$$

The potentials of single pairs are functions of r of the same form, designated by φ_{11}, φ_{22} and φ_{12}, where the subscripts denote the species forming the pair. The potential of all the X_1X_1 pairs at distance r is then $(2\pi N^2/v)\cdot[n_1^2/(n_1+n_2)]\cdot\varphi_{11}Wr^2dr$, and the potential of all X_1X_1 pairs

[6] F. London, Zeits. f. Physik **63**, 245 (1930).

throughout the liquid is $(2\pi N^2/v)\cdot[n_1^2/(n_1+n_2)]$ $\cdot\int_0^\infty \varphi_{11}Wr^2dr$, and similarly for the X_2X_2 and X_1X_2 pairs. Adding these gives the potential energy of the entire liquid of n_1+n_2 moles, designated by E'. The partial molal energy of X_1 in this solution is $\bar E_1 = (\partial E'/\partial n_1)_{n_2}$, which gives

$$\bar E_1' = \frac{2\pi N^2}{v}\cdot\frac{1}{(n_1+n_2)^2}\Bigg[(n_1^2+2n_1n_2)$$

$$\times\int_0^\infty \varphi_{11}Wr^2dr - n_2^2\int_0^\infty \varphi_{22}Wr^2dr$$

$$+2n_2^2\int_0^\infty \varphi_{12}Wr^2dr\Bigg]. \qquad (5)$$

Subtracting $E_1^{0\prime}$ for a mole of the pure X_1, setting $\bar E_1' - E_1^{0\prime} = \bar E_1 - E_1^0$, the difference in potential energy equal to the difference in total energy, and collecting yields

$$\bar E_1 - E_1^0 = (2\pi N^2 N_2^2/v)\Bigg[2\int_0^\infty \varphi_{12}Wr^2dr$$

$$-\int_0^\infty \varphi_{11}Wr^2dr - \int_0^\infty \varphi_{22}Wr^2dr\Bigg]. \qquad (6)$$

If we set $\varphi_{11} = -k_{11}/r^6$, etc., we obtain an approximation formula

$$\bar E_1 - E_1^0 = \frac{2\pi N^2 N_2^2}{v}(k_{11}+k_{22}-2k_{12})\int_0^\infty \frac{W}{r^4}dr. \qquad (7)$$

If, as has been frequently assumed, $k_{12} = (k_{11}k_{22})^{\frac12}$, then

$$k_{11}+k_{22}-2k_{12}=[(k_{11})^{\frac12}-(k_{22})^{\frac12}]^2. \qquad (8)$$

By setting up the equations in the form of Eq. (3) for both pure components it can be seen that Eq. (7) can be transformed into

$$\bar E_1 - E_1^0 = [(E_1^0)^{\frac12} - (E_2^0)^{\frac12}]^2 N_2^2. \qquad (9)$$

This, unlike 6, can hardly be a rigid equation on account of the additional assumptions involved, especially Eq. (8), and it is not our purpose to subject it to a searching experimental test at this juncture. One illustration only will be given. Iodine and carbon disulfide have nearly identical molal volumes, 59.0 cc and 60.7 cc, respectively, at 25°C. Both have zero dipole moment. The solubility of iodine in carbon disulfide agrees closely[1] with the equation $\ln N_1^i/N_1 = bN_2^2/RT$,

where b is a constant. This corresponds to the relation $\bar{F}_1{}^r - \bar{F}_1{}^i = b N_2{}^2$. The value of b calculated from solubility is 870 cal. The energies of vaporization at 25° are, respectively, 11,300 cal. and 5970 cal., from which we calculate $[(E_1{}^0)^{\frac{1}{2}} - (E_2{}^0)^{\frac{1}{2}}]^2 = 840$ cal., a sufficiently good agreement.

Eq. (6), at any rate, should correspond well for systems conforming to the conditions postulated. The function, W, should depend chiefly on the molecular radius, for symmetrical molecules, and be relatively independent of the species of molecule. It should flatten out as the temperature increases and the departure from hexagonal close packing[5b] becomes greater.

Let us now consider a solution of two species whose molecular volumes are different, and where a single common probability function can not suffice. Consider a spherical shell of thickness dr, at a distance r, from the center of a central molecule. The volume of this shell is $dV = 4\pi r^2 dr$. The number of X_1 molecules whose centers are in 1 cc of liquid is $n_1 N/V$, where V is the total volume of the solution. The shell under consideration would contain $n_1 N dV/V$ molecular centers of X_1 if there were no interference due to the size of the central molecule, but since such interference exists a probability function will have to be introduced for each combination of species. This will be designated by subscripts, W_{11} for the $X_1 X_1$ combination, etc.

The total number of molecules in the solution, each able to play the rôle of "central" molecule, is $(n_1 + n_2)N$. The number of central molecules of X_1 is $n_1 N$. The number of X_1 molecules in the shell surrounding each is $n_1 N W_{11} dV/V$. The number of $X_1 X_1$ "pairs" throughout the solution at distance r is $\frac{1}{2} n_1{}^2 N^2 W_{11} dV/V$. (The $\frac{1}{2}$ is introduced to avoid counting each pair twice.) The potential of each $X_1 X_1$ pair is φ_{11}, hence the potential of all such pairs at distance r is $(2\pi n_1{}^2 N^2/V) \cdot \varphi_{11} W_{11} r^2$, and the potential of all $X_1 X_1$ pairs throughout the liquid at all distances, is $(2\pi N^2 n_1{}^2/V) \int_0^\infty \varphi_{11} W_{11} r^2 dr$. We will abbreviate this expression by writing for the integral the symbol $\mathcal{f}(11)$, giving $(2\pi N^2 n_1{}^2/V) \mathcal{f}(11)$. For the $X_2 X_2$ we get the corresponding expression,

$(2N^2 n_2{}^2/V) \mathcal{f}(22)$ and for the $X_1 X_2$ and $X_2 X_1$ pairs, which are identical, $(4\pi N^2 n_1 n_2/V) \mathcal{f}(12)$.

We will pause here to consider the probability functions, W_{11}, W_{22}, W_{12} and W_{21}. It would seem that the position of the first maximum, as shown in Fig. 1A, should be the same for the solution as for the pure substance, since it depends chiefly on the sum of the two molecular radii, increased somewhat by thermal agitation. The position of the second maximum would, however, be different, for, if X_2 is thought of as smaller than X_1, two molecules of X_1 might be separated by an X_2 instead of another X_1. The frequency of this separation would depend upon the proportion of X_2 molecules, hence W_{11} for the solution would be a function of the composition beyond the first maximum. A quantitative formulation of this dependence seems very difficult and we shall, for the present, take refuge in the fact that the potential is but little affected by the course of W much beyond the first maximum, as illustrated by the area under the curve in Fig. 1C, permitting us to set W_{11} for solution and pure X_1 equal to each other as a first approximation. We are undertaking an experimental study of these functions.

We should note, further, that although W_{12} and W_{21} might appear to be different, the number of $X_1 X_2$ and $X_2 X_1$ pairs is the same, hence $\mathcal{f}(12) = \mathcal{f}(21)$. We are now prepared to write for the total potential energy of $n_1 + n_2$ moles of solution,

$$E' = (2\pi N^2/V)\left[n_1{}^2 \int (11) + n_2{}^2 \int (22) \right.$$
$$\left. + 2n_1 n_2 \int (12) \right]. \quad (10)$$

The partial molal energy of X_1, i.e., $\bar{E}_1'$, is obtained, as before by differentiating with respect to n_1 at constant n_2, remembering that $V = n_1 v_1 + n_2 v_2$, approximately. We should write, more strictly, $V = n_1 \bar{v}_1 + n_2 \bar{v}_2$, where $\bar{v}_1$ and $\bar{v}_2$ are the partial molal volumes, but this could hardly be worth the added labor in view of the other approximations involved. Carrying out this differentiation and subtracting the value of $E_1{}^{0'}$ from Eq. (3) gives

$$\bar{E}_1 - E_1{}^0 = 2\pi N^2 \left(\frac{n_2 v_2}{n_1 v_1 + n_2 v_2} \right)^2 \cdot v_1 \left[\frac{2}{v_1 v_2} \int (12) - \frac{1}{v_1{}^2} \int (11) - \frac{1}{v_2{}^2} \int (22) \right]. \quad (11)$$

We may regard this equation as valid for any system of the sort here considered. To apply it rigidly will, however, require more data than we now have concerning probability functions and intermolecular potentials. Indeed, one of its principal uses is likely to be the throwing of light upon the latter question. In the meantime we may derive from it an approximation formula which may be tested by the aid of solubility data now at hand.

First, we will neglect the repulsive potential and write for the attractive potential simply $= -k/r^6$. This may make an appreciable error in dealing with mercury at ordinary temperatures,[7] which is not much expanded over its volume at $0°K$. Fig. 1B shows the average number of molecules in the liquid which are closer together than in the solid. For substances at temperatures nearer their boiling points the effect of repulsion would be less.

Next, we will assume, by analogy with Eq. (8), that

$$\int (12) = \int^{\frac{1}{2}} (11) \times \int^{\frac{1}{2}} (22). \qquad (12)$$

The physical significance of this is as follows. Since the form of the function, W, is the result of a thermally disturbed close packed arrangement, it may be assumed to be, for all spherical molecules, approximately the same function of the molecular domain. This could hardly be strictly true, for even the curve for a pure liquid will surely flatten with increasing thermal agitation, hence curves for different liquids must be, in general, slightly different. However, if we neglect differences in flattening as an effect of higher order, we may express the different W's as the same function of the position of the first maximum, $\mathbf{r}$, for each, i.e., $W = f(r/\mathbf{r})$. The curves obtained by Menke for mercury and gallium, when plotted against $r/\mathbf{r}$, agree very closely, probably within the limit of error. We will therefore assume that the integral $k \int_0^\infty (W/r^4) dr$, if transformed into

$$\frac{k}{\mathbf{r}^3} \int_0^\infty \left(\frac{\mathbf{r}}{r}\right)^4 f\left(\frac{r}{\mathbf{r}}\right) d\left(\frac{r}{\mathbf{r}}\right),$$

would be the same for all substances so far as the

[7] J. H. Hildebrand, Phys. Rev. 34, 984 (1929).

integrand is concerned. Introducing this, with subscripts appropriate to each combination, into Eq. (12), and cancelling out the integrand, leaves

$$k_{12}/\mathbf{r}_{12}^3 = (k_{11}k_{22}/\mathbf{r}_{11}^3\mathbf{r}_{22}^3)^{\frac{1}{2}}. \qquad (13)$$

If we write $\mathbf{r}_{12} = \frac{1}{2}(\mathbf{r}_{11} + \mathbf{r}_{22})$, which should be very nearly true, Eq. (13) becomes

$$k_{12} = \frac{(\mathbf{r}_{11} + \mathbf{r}_{22})^3}{8\mathbf{r}_{11}^3\mathbf{r}_{22}^3} (k_{11}k_{22})^{\frac{1}{2}}. \qquad (14)$$

The coefficient of $k_{11}k_{22}$ does not differ much from unity, even when $\mathbf{r}_{11}$ and $\mathbf{r}_{22}$ differ considerably; for example, it is only 1.06 when $\mathbf{r}_{11}$ and $\mathbf{r}_{22}$ differ by 50 percent. Eq. (14) is therefore nearly identical with Eq. (8), which is generally regarded as approximately true. We are therefore encouraged to try the effect of combining Eq. (12) with Eq. (11), and then combine the result with Eq. (3) applied to each pure component. The final result is

$$\bar{E}_1 - E_1^0$$
$$= \left(\frac{n_2V_2}{n_1V_1 + n_2V_2}\right)^2 V_1\left[\left(\frac{E_1^0}{V_1}\right)^{\frac{1}{2}} - \left(\frac{E_2^0}{V_2}\right)^{\frac{1}{2}}\right]^2. \qquad (15)$$

The equation derived by van Laar[3] with the aid of the van der Waals equation reduces to this under the conditions herein postulated. The same equation has been given by Scatchard[8] by the aid of some of the same assumptions as here employed, plus the arbitrary one that the cohesive energy of a mole of mixture is given by the expression

$$\frac{a_{11}V_1^2n_1^2 + 2a_{12}V_1V_2n_1n_2 + a_{22}V_2^2n_2^2}{(n_1V_1 + n_2V_2)^2},$$

where the a's are regarded as constants (equivalent to the van der Waals constants.)

Experimental data now being obtained in this laboratory upon tetrahalides and their solutions will enable us to make a more searching test of the laws of regular solutions than is now possible. In the meantime we may cite certain iodine solutions as most nearly conforming to the requirements. We have data for the solubility of iodine[9]

[8] Geo. Scatchard, Chem. Rev. 8, 321 (1931).

[9] J. H. Hildebrand and C. A. Jenks, J. Am. Chem. Soc. 42, 2080 (1920); G. R. Negishi, L. H. Donnally and J. H. Hildebrand, ibid. Nov. (1933); cf. also reference 1.

in the tetrachlorides of carbon, silicon and titanium, all very symmetrical molecules with zero electric moment. To these we shall add the solutions in carbon disulfide. Table I gives values of $\bar{F}_2{}^r - \bar{F}_2{}^i$ for iodine, calculated from the experimental data by the expression $RT \ln (N_2{}^i/N_2)$, in comparison with values of $\bar{E}_2{}^r - E_2{}^0$, calculated from Eq. (12). The values of v_1, v_2, $E_1{}^0$ and $E_2{}^0$ used are indicated in Table I. They are taken from the usual sources which need not here be elaborated, since the purpose is merely illustrative. The values are given for 25° only, since the uncertainty regarding the change of the heat of vaporization with temperature hardly makes it worth while to attempt to check the small temperature trend.

The agreement between the figures in the last two columns may be regarded as very satisfactory, indicating that the solubility of iodine could be calculated by the aid of Eq. (12) without serious error.

TABLE I. *Test of Eq. (12) by means of solubility data for iodine at 25°C.*

Solvent	v cc per mole	E^0 cal.	Mole percent I_2 in soln.	$\bar{F}_2 - \bar{F}_2{}^i$ cal.	$\bar{E}_2 - E_2{}^0$ cal.
TiCl$_4$	110.5	8370	2.150	1365	1535
SiCl$_4$	115.4	6610	0.499	2220	2320
CCl$_4$	97.1	7088	1.594	1725	1635
CS$_2$	60.7	6070	5.76	770	815
Iodine	59.0	11330			

The solubility data for sulfur and for stannic iodide might also be used, but uncertainties regarding heats of vaporization at the temperatures in question diminish the significance of the comparisons, and they are here omitted.

One of the most important uses for the equations here derived will doubtless be to throw light upon the important question of the potential functions for pairs of like and unlike molecules. We expect to be able to report upon this in the near future.