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An Approximate Relation Between Surface Tension and Concentration for Regular Solutions

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An equation for the variation of surface tension with concentration in regular solutions is derived using Hildebrand's model and calculating the work per unit interfacial area required to separate a body of liquid reversibly into two infinitely removed parts. Spherical symmetry in shape and molecular field of both components is assumed. Values of a factor of deviation from the geometric mean relationship for intermolecular attraction between unlike non-polar molecular species are calculated both from surface tension and vapor pressure data. Values of the factor calculated from these two independent sources for a number of systems are in reasonable agreement. The linearity of surface tension with volume fraction in ideal systems is predicted, in agreement with experiment.

I. INTRODUCTION

HILDEBRAND¹ has derived an equation for partial molal heats of solution in non-polar binary systems on the assumptions of spherical symmetry of the two molecular species, geometric mean interaction between unlike molecules, and neglect of repulsion potentials. The same relation has also been obtained from different postulates.^{2,3}

In this paper equations for the variation of surface tension with concentration will be derived using Hildebrand's model and the calculation by Margenau⁴ of the "total surface energy" of a pure liquid. Margenau's result is considered by Kassel and Muskat⁵ to represent more nearly the free surface energy or surface tension.

If a column of liquid is reversibly separated into two parts, the work per unit interfacial area necessary to accomplish the separation of the parts to infinity is equal to twice the free surface energy, while the sum of the work required and the heat absorbed per unit interfacial area during this process is equal to twice the total surface energy.

Kassel and Muskat⁵ calculated the potential energy of one-half of an infinite body of liquid with respect to the other half and considered this

to be the increase in total surface energy when the two parts were separated to infinity. This corresponds to the work done in an irreversible separation, and as they admitted, all that can be rigorously stated about the quantity calculated in this manner is that it is greater than the surface tension and less than the total surface energy. However, arguments were advanced to show that it corresponded more nearly to the total surface energy than to the free surface energy.

Margenau,⁴ on the other hand, calculated the force exerted by one-half of the liquid upon the other as a function of the distance of separation between halves and formed $\int_0^\infty Fx dx$ to obtain the work required in the separation. According to Kassel and Muskat this represents an approach to an equilibrium process and the quantity obtained should be very nearly equal to twice the surface tension.

In the following calculations, emphasis should be placed on the fact that the validity of the relationships deduced does not depend on the equality of Margenau's equation to the surface tension, but only upon its proportionality, provided the constants of proportionality are the same for the mixture and both components. In addition to the postulates of Hildebrand, the effect of the vapor phase is neglected, as well as that of differences in bulk and surface concentration, on the force of attraction between halves during separation. The neglect of the vapor phase should not affect the form of the relationship

¹ J. H. Hildebrand, *Solubility* (Reinhold Publishing Company, New York, 1936), second edition, pp. 69-73.

² J. J. Van Laar, *Zeits. f. physik. Chemie* **A137**, 421 (1928).

³ G. Scatchard, *Chem. Rev.* **8**, 321 (1931).

⁴ H. Margenau, *Phys. Rev.* **38**, 365 (1931).

⁵ L. S. Kassel and M. Muskat, *Phys. Rev.* **40**, 627 (1932).

Therefore, from (4),

$$\gamma = \pi \left(\frac{N}{V} \right)^2 \int_0^\infty \int_x^\infty \int_y^\infty \int_r^\infty r \left[n_1^2 W_{11} \left(\frac{\partial E_{11}}{\partial z} \right) + n_2^2 W_{22} \left(\frac{\partial E_{22}}{\partial z} \right) + 2n_1 n_2 W_{12} \left(\frac{\partial E_{12}}{\partial z} \right) \right] dz dr dy dx. \quad (6)$$

Now for either pure component it can be shown in a similar manner that

$$\gamma_{1,2} = \pi \left(\frac{N}{V_{1,2}} \right)^2 \int_0^\infty \int_x^\infty \int_y^\infty \int_r^\infty r W_{11,22} \times \left(\frac{\partial E_{11,22}}{\partial z} \right) dz dr dy dx. \quad (7)$$

V_1 and V_2 are the molal volumes of the pure components. Substituting (7) into (6) gives the following relation:

$$\gamma = \frac{n_1^2 V_1^2 \gamma_1}{V^2} + \frac{n_2^2 V_2^2 \gamma_2}{V^2} + \frac{c' n_1 n_2}{V^2}. \quad (8)$$

The quantity C' in the last term contains the function W_{12} which on the basis of Hildebrand's postulates is independent of concentration. This factor should therefore be a constant at constant temperature, and could also be written

$$C' = C V_1 V_2. \quad (9)$$

Equation (8) then becomes

$$\gamma = v_1^2 \gamma_1 + v_2^2 \gamma_2 + c v_1 v_2, \quad (10)$$

where v_1 and v_2 are fractions by volume, provided the volume of the solution is additive from the volumes of the constituents. This is very nearly the case for the mixtures considered.

A similar relation was proposed by Poisson:⁷

$$h\rho = (h\rho)_1 v_1^2 + (h\rho)_2 v_2^2 + f v_1 v_2, \quad (10a)$$

where h is the capillary rise and ρ the density and f is a constant. This is identical with (10) only when the angles of contact for both components and the solution are equal.

⁷ S. D. Poisson, *Theorie de l'action capillaire* (Paris, 1831). See W. H. Whatmough, *Zeits. f. physik. Chemie* **39**, 129 (1902).

By making use of certain simplifying assumptions, it is possible to evaluate roughly the constant C in terms of other properties of the mixture under consideration.

Returning to Eq. (6), it can be seen that C is equal to

$$\frac{2\pi N^2}{V_1 V_2} \int_0^\infty \int_x^\infty \int_y^\infty \int_r^\infty r W_{12} \left(\frac{\partial E_{12}}{\partial z} \right) dz dr dy dx. \quad (11)$$

It can also be shown by repeated integration that

$$\gamma_{1,2} = \frac{\pi}{8} \left(\frac{N}{V_{1,2}} \right)^2 \int_0^\infty z^4 \left(\frac{\partial E_{11,22}}{\partial z} \right) W_{11,22} dz. \quad (12)$$

If it is assumed that $E(Z) = -k/z^6$ (neglecting the repulsion potential), (12) becomes

$$\gamma_{1,2} = \frac{3}{4} \left(\frac{N}{V_{1,2}} \right)^2 k_{1,2} \int_0^\infty \frac{W_{11,22}}{z^3} dz. \quad (12a)$$

By assuming with Hildebrand⁸ that all the W functions are the same functions of that value of z at which their first maximum occurs the integrals for the pure components (12a) may be transformed to (13), where the integrand is the same for both components.

$$\frac{3}{4} \left(\frac{N}{V_{1,2}} \right)^2 \frac{\pi k_{1,2}}{z_{1,2}^2} \int_0^\infty \left(\frac{z_{1,2}}{z} \right)^3 f \left(\frac{z}{z_{1,2}} \right) d \left(\frac{z}{z_{1,2}} \right). \quad (13)$$

z_1 or z_2 and k_1 or k_2 are the above-mentioned values of z and the force constants k for the components.

This is equivalent to assuming that the structure of each pure component liquid is essentially the same except for differences in molecular size. How nearly justified this is for actual non-polar liquids is a debatable question. However, mercury and gallium⁸ obey this assumption very closely, as would be expected, since they are spherical molecules.

Putting the expression (11) for C into the form (13) we have

$$C = \frac{3}{4} \frac{\pi N^2 k_{12}}{z_{12}^2 V_1 V_2} \int_0^\infty \left(\frac{z_{12}}{z} \right)^3 f \left(\frac{z}{z_{12}} \right) d \left(\frac{z}{z_{12}} \right), \quad (14)$$

where z_{12} is the value of z at which the function

⁸ J. H. Hildebrand, *Solubility*, second edition, p. 72.

W_{12} has its first maximum and k_{12} is the force constant for the potential function between unlike molecules [$E_{12}(Z) = -k_{12}/Z^6$ neglecting the repulsion potential as before].

Hildebrand assumed that $k_{12} = (k_1 k_2)^{1/2}$. This expression was derived from wave mechanical considerations⁹ and represents the upper limit for the dispersion effect between unlike molecules. In general, $k_{12} < (k_1 k_2)^{1/2}$. We shall write

$$k_{12} = s(k_1 k_2)^{1/2}, \quad (15)$$

where $s < 1$ and is a property of the system under consideration.

From (14), (15), and the expressions for the pure components (13), and remembering that all the integrands should be equal, we obtain

$$C = 2s(\gamma_1 \gamma_2)^{1/2} \left(\frac{z_1 z_2}{z_{12}^2} \right). \quad (16)$$

The expression involving the z 's is only slightly different from unity even when the respective values differ by as much as 50 percent. Therefore, it would be expected that C would be equal to or less than $2(\gamma_1 \gamma_2)^{1/2}$ since $S \leq 1$. This is in agreement with experiment.

It would also be expected that the greater the deviation from the value $2(\gamma_1 \gamma_2)^{1/2}$ the greater would be the deviation of the constant

$$D^2 = \left[\left(\frac{\Delta E}{V} \right)_1 - \left(\frac{\Delta E}{V} \right)_2 \right]^2 \quad (17)$$

in the Van Laar-Scatchard-Hildebrand equation for activity coefficients of regular solutions from its value calculated from vapor pressure data. This follows from the fact that k_{12} was assumed to be equal to $(k_1 k_2)^{1/2}$ in obtaining the constant D^2 in this form. Any departure from this leads to a difference in the values obtained from vapor pressures and those calculated from (17).

The relationship between C and D^2 will now be put in a semiquantitative form. The internal latent heat of vaporization of a non-polar liquid is

$$\Delta E = \frac{2\pi N^2 k}{V} \int_0^\infty E(z) W z^2 dz \quad (18)$$

without regard to sign.

⁹ R. Eisenschitz and F. London, *Zeits. f. Physik* **60**, 491 (1930). F. London, *ibid.* **63**, 245 (1930); *Zeits. f. physik. Chemie* **B11**, 222 (1930).

Making the assumptions in (12a) through (15), applying them to (18), and having also the relation¹⁰

$$D^2 = 2\pi N^2 \left[\frac{2k_{12}}{V_1 V_2} \int_0^\infty \frac{W_{12}}{z^4} dz - \frac{k_1}{V_1^2} \int_0^\infty \frac{W_{11}}{z^4} dz - \frac{k_2}{V_2^2} \int_0^\infty \frac{W_{22}}{z^4} dz \right], \quad (19)$$

we obtain

$$D_p^2 = \left\{ \left(\frac{\Delta E}{V} \right)_1 + \left(\frac{\Delta E}{V} \right)_2 - 2s \left(\frac{[z_1^3 z_2^3]}{z_{12}^3} \right) \left[\left(\frac{\Delta E}{V} \right)_1 \left(\frac{\Delta E}{V} \right)_2 \right]^{1/2} \right\}, \quad (20)$$

where D_p^2 should now be equal to the value obtained from vapor pressures since deviations of k_{12} from $(k_1 k_2)^{1/2}$ have been taken into account. The s factor, naturally, should be the same as in Eq. (16). The factor involving the z 's is also always fairly close to unity, although not equal to that in (16). Lumping this factor together with s , (16) and (20) can be rewritten

$$C = 2S_\gamma (\gamma_1 \gamma_2)^{1/2}, \quad (16a)$$

$$D_p^2 = \left\{ \left(\frac{\Delta E}{V} \right)_1 + \left(\frac{\Delta E}{V} \right)_2 - 2S_p \left[\left(\frac{\Delta E}{V} \right)_1 \left(\frac{\Delta E}{V} \right)_2 \right]^{1/2} \right\}, \quad (20a)$$

where S_γ and S_p should be nearly equal, or at least of the same order of magnitude and both equal to or less than unity. In view of the approximations involved, it seems rash to predict whether one or the other will be greater, on the basis of the z terms.

III. IDEAL SOLUTIONS

Some conclusions can be drawn from (16a) and (20a) with regard to the surface tension—concentration relationship in ideal solutions.

For all the systems of the type discussed, γ_1 and γ_2 are near enough together so that $2(\gamma_1 \gamma_2)^{1/2} = \gamma_1 + \gamma_2$ without appreciable error. (See experimental data and calculations.) When $C = \gamma_1 + \gamma_2$, Eq. (10) reduces to

$$\gamma = v_1 \gamma_1 + v_2 \gamma_2. \quad (21)$$

¹⁰ J. H. Hildebrand, *Solubility*, second edition, p. 71.

TABLE I.*

System	S_γ	S_p	Int. pressure	$t^\circ\text{C}$	D^2 Vapor pressure	$t^\circ\text{C}$
CCl_4 -benzene 50°C	0.96	0.994 ^a	0.22	25°C	0.92	50°C
Benzene-cyclohexane 25°C	0.95-0.98	0.986 ^b	0.96	79°C	2.19	79°C
Benzene-ethylene chloride 17°C	0.96-0.98	1.00 ^c	0.07	25°C	0	—
50°C	1.00	1.00	—	—	—	—
CS_2 -benzene 20°C	0.85-0.92	{0.99} ^d	{1.0	25°C	{3.24	25°C}
CS_2 -benzene 30°C	0.86-0.81	{0.99}	{1.0	25°C	{3.24	25°C}
Benzene-naphthalene 79.5°	1.00	1.00 ^e	0.36	25°C	0	79.5°C
Benzene-toluene 10.8°	1.00	1.00 ^f	0.35	25°C	0	80°C

* All internal pressures were taken from Hildebrand, *Solubility*, second edition, pp. 104-105.^a J. V. Zawidzki, *Zeits. f. physik. Chemie* 35, 129 (1900).^b J. H. Hildebrand, *Solubility*, second edition, p. 124.^c See reference 17.^d J. Sameshima, *J. Am. Chem. Soc.* 40, 1503 (1918).^e A. N. Campbell, *Can. J. Research* B19, 143 (1941).^f See reference 16.TABLE II. Tabulated data and calculations. All values of γ in dynes/cm. Benzene-ethylene dichloride.*

Vol. % ethylene chloride	γ 17°C	C Calc. 17°C	Calc. γ 17°C C=59.5	Calc. γ 17°C linear relation	γ 50°C	Calc. γ 50°C linear relation
0	29.17	—	—	—	24.08	—
10	29.33	59.9	29.30	29.42	24.38	24.38
20	29.50	59.8	29.46	29.67	24.66	24.67
30	29.61	59.3	29.64	29.92	24.98	24.99
50	30.05	59.4	30.09	30.42	25.56	25.56
70	30.53	59.0	30.64	30.93	26.16	26.16
90	31.21	58.5	31.30	31.42	26.75	26.75
100	31.68	—	—	—	27.05	—
		$\gamma_1 + \gamma_2$ at 17°C = 60.9		$2(\gamma_1\gamma_2)^{1/2} = 60.8$		
		C=59.5				

* Yajnik, Sharma, and Bharadway, *Quart. J. Ind. Chem. Soc.* 3, 63 (1926). Volume fractions calculated by the authors.

TABLE III. Carbon tetrachloride-benzene 50°C.*

Mole % benzene	Vol. % benzene	γ	C	γ calc. C=47.0
0	0	22.98	—	—
20.19	20.28	23.21	46.8	23.23
35.32	33.75	23.47	47.2	23.45
52.88	51.15	23.78	47.0	23.78
67.85	66.30	24.09	47.0	24.09
81.85	80.80	24.39	46.6	24.45
100.00	100.00	24.98	—	—
		Densities—Benzene=0.8372	$\gamma_1 + \gamma_2 = 48.0$	
		Carbon tetrachloride=1.537	$2(\gamma_1\gamma_2)^{1/2} = 48.0$	
		C=47.0		

* J. W. Belton, *Trans. Faraday Soc.* 31, 1642 (1935).

This relation was proposed by Volkmann.¹¹ In other words, when $S_\gamma = 1$, Eq. (21) would be expected to hold.

It is an experimental fact that when for non-polar liquids, $(\Delta E/V)_1 = (\Delta E/V)_2$ the mixture is ideal, and $D_p^2 = 0$. In this case, from Eq. (20a) it is obvious that $S_p = 1$. Now, since $S_\gamma \leq S_p$ it is

highly probable that Eq. (21) will hold, although it is possible that S_γ may be slightly less than unity, leading to negative deviations of the surface tension from this linear relation. In other words, when vapor pressure is linear in mole fraction, surface tension can reasonably be expected to be linear in volume fraction. This subject will be discussed at greater length in the next section.

¹¹ Volkmann, *Ann. d. Physik* [3] 16, 321 (1882).

TABLE IV. Benzene-naphthalene 79.5°C.*

Wt. % naphthalene	Molal volume of mixture cc	Vol. % naphthalene	γ	Linear relation ^a
0	95.7	0.00	27.80 ^b	—
10	98.3	8.41	29.20	29.08
20	100.9	17.15	30.44	30.40
30	103.4	26.10	31.70	31.70
40	105.9	35.50	33.00	33.06

* A. N. Campbell, Can. J. Research **B19**, 143 (1941).^a Read off a straight line through the experimental points on a plot of γ versus v .^b There is obviously an error of method here. The I.C.T. value at 80° is 21.26 dynes/cm.

TABLE V. Benzene-cyclohexane 25°C.*

Mole % benzene	Vol. % benzene	γ	C	γ calc. $C=51.0$	
0.00	0.00	24.35 ^a	—	—	
37.03	32.92	25.36	51.5	25.27	$\gamma_1 + \gamma_2 = 52.7$
47.60	42.77	25.65	51.0	25.65	$2(\gamma_1\gamma_2)^{\frac{1}{2}} = 52.6$
54.92	50.06	25.84	50.7	25.91	$C \leq 51.0$
70.37	66.15	26.41	50.2	26.60	
100.00	100.00	28.32	—	—	
Densities—Benzene 0.8734					
Cyclohexane 0.7743					

* D. L. Hammick and L. W. Andrew, J. Chem. Soc. **132**, 754 (1929).^a Interpolated value from the data of M. Hennaut-Roland and L. Lek, Bull. Soc. Chim. Belg. **40**, 177 (1931). See *Annual Tables of Physical Constants*, Section 700(c), p. 4 (1941).

TABLE VI. Benzene-toluene 10.8°C.*

Mole % benzene	γ	Vol. % benzene	γ from linear relation
0	29.61	0	—
24.98	29.76	24.7	29.74
50.07	29.85	49.5	29.86
75.06	30.02	74.6	29.98
100.00	30.11	100.0	—
Densities—Benzene 0.8885			
Toluene 0.8742			

* J. L. R. Morgan and M. A. Griggs, J. Am. Chem. Soc. **39**, 2261 (1917). See also *International Critical Tables*, first edition, Vol. IV, p. 473 (1928).

TABLE VII. Carbon disulfide-benzene.*

Mole % benzene	γ 20°C	γ 30°C	Vol. % benzene	C Calc. 20°C	C Calc. 30°C	γ 20°C $C=55.0$ Calc.	Calc. γ 30°C $C=50.0$
0	32.38	30.91	0	—	—	—	—
7.89	31.04	29.69	11.21	52.0	50.1	31.36	29.69
16.84	30.20	28.82	22.99	53.4	51.0	30.48	28.62
28.23	29.56	283.6	36.69	54.5	52.8	29.56	27.75
46.47	29.04	27.75	56.39	55.6	48.8	28.90	26.96
63.81	28.94	27.55	72.20	56.6	47.0	28.64	26.80
100.00	28.89	27.52	100.00	—	—	—	—
Densities—Benzene = 0.8794				Densities—Benzene = 0.8678			
20°C carbon disulfide = 1.263				30°C carbon disulfide = 1.248			
20° $\gamma_1 + \gamma_2 = 61.3$				30° $\gamma_1 + \gamma_2 = 58.4$			
$2(\gamma_1\gamma_2)^{\frac{1}{2}} = 61.2$				$2(\gamma_1\gamma_2)^{\frac{1}{2}} = 58.3$			

* J. W. Belton, Trans. Faraday Soc. **31**, 1642 (1935).

TABLE VIII. Carbon disulfide-chloroform 18°C.*

Wt. % chloroform	Vol. % chloroform	γ	C	γ calc. $C=55.5$	
0	0	32.24	—	—	
20	17.49	30.59	54.0	30.81	$\gamma_1 + \gamma_2 = 59.5$
40	36.13	29.53	55.5	29.53	$2(\gamma_1 \gamma_2)^{\frac{1}{2}} = 59.4$
60	55.99	28.42	55.3	28.47	$C \leq 55.5$
80	77.25	27.78	55.7	27.74	
100	100.00	27.33	—	—	

Densities—Chloroform 1.493
Carbon disulfide 1.266

* W. H. Whatmough, *Zeits. f. physik. Chemie* **39**, 129 (1902).

IV. COMPARISON OF CALCULATED AND EXPERIMENTAL RESULTS

To sum up the preceding deductions, it has been shown that the surface tension of a regular solution would be expected to obey the equation

$$\gamma = v_1^2 \gamma_1 + v_2^2 \gamma_2 + C v_1 v_2. \quad (10)$$

The constant C would be expected to vary with each specific system, being in general $\leq 2(\gamma_1 \gamma_2)^{\frac{1}{2}}$. This would give either zero or negative deviations of the surface tension from the linear relation

$$\gamma = v_1 \gamma_1 + v_2 \gamma_2, \quad (21)$$

this relation holding for ideal systems. These conclusions are in agreement with experiment. It has been observed¹²⁻¹⁴ that when the system is ideal the surface tension is linear in volume fraction and when the vapor pressure shows positive deviations from Raoult's law, the surface tension shows negative deviations from Eq. (21), and vice versa. Since all regular solutions show positive deviations from ideality, the theoretical relations are in harmony with these facts. The case of negative deviations from Raoult's law does not pertain to the theory developed, but positive deviations from the linear surface tension relation would be expected since $C > 2(\gamma_1 \gamma_2)^{\frac{1}{2}}$ due to chemical bonding or strong dipole at-

traction. Naturally Eq. (10) would not hold, with C varying with concentration.

Quantitatively, all the surface tension-concentration data found in the literature by the author for regular solutions can be fitted by Eqs. (10) or (21), with the exception of that for carbon disulfide-benzene. Equation (10) gives a minimum which does not exist. This error may be caused by a neglect of the difference between surface and bulk concentration in the derivation, but is probably due to orientation of the asymmetric CS_2 molecules in the interface. This system agrees with the vapor pressure equation for regular solutions fairly well.¹⁵ In all cases for the non-ideal systems the constant C varies slightly with concentration. Nearly always there is a definite slight drift, but not enough to invalidate the equation except for CS_2 -benzene.

For the ideal systems benzene-naphthalene and benzene-toluene the surface tension is linear in volume fraction, as would be expected.

For ethylene dichloride-benzene at 50°C, surface tension is linear in volume fraction. At 17°C, it shows slight negative deviations. This system behaves ideally over this range.¹⁶ The behavior at 17°C is theoretically possible from differences in S_γ and S_p .

Some objection might be raised as to whether this system constitutes a legitimate test of the theory, on account of the dipole moment of ethylene dichloride. However, the internal pressures of benzene and ethylene dichloride are, respectively, 80.9 and 82.3 cal./cc at 25°C¹⁷ at which temperature the mixture is ideal, in agree-

* A relation of similar form might also hold for non-regular non-polar mixtures (i.e., one or both components a normal long chain hydrocarbon) with modifications, considering each "submolecule" in the chain as a molecule. However, this discussion is concerned only with regular solutions and it would be beyond the scope of this paper to discuss this possibility.

¹² R. P. Worley, *J. Chem. Soc.* **105**, 273 (1914).

¹³ Yajnik, Sharma, and Bharadway, *Quart. J. Ind. Chem. Soc.* **3**, 63 (1926).

¹⁴ O. Faust, *Zeits. f. anorg. allgem. Chemie* **54**, 61 (1926).

¹⁵ J. H. Hildebrand, *Solubility*, second edition, p. 125.

¹⁶ *International Critical Tables*, first edition, Vol. III, p. 287 (1928).

¹⁷ Hildebrand, *Solubility*, "Table of internal pressure," second edition, p. 105.

ment with D^2 calculated from these values. Apparently the dipole effect is very small compared with the dispersion effect in its contribution to intermolecular attraction. The system carbon disulfide-chloroform also has a polar component, but behaves at least in qualitative accord with internal pressure differences.¹⁸ This system was included because of this and the paucity of data available. There are more results in the literature for surface tensions of non-polar mixtures than are given here, but they were not used since they gave "shotgun curves" when plotted against concentration.

With regard to the factors S_γ and S_p , the values calculated from surface tension data and those from vapor pressures do not differ a great deal. The vapor pressure values are the larger. Values obtained where data were available are

tabulated below (see Tables I-VIII). In calculating S_p values of internal pressures at the temperature in the fourth column and values of D^2 at the temperature in the sixth column were used.

In calculating volume fractions in all cases except where otherwise shown, the densities used were obtained from the equations of the *International Critical Tables*.¹⁹

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¹⁸ Hildebrand, *Solubility*, second edition, p. 127.

¹⁹ *International Critical Tables*, first edition, Vol. III, p. 28 (1928).