The Application of Equations for the Chemical Potentials to Partially Miscible Solutions

BY GEORGE SCATCHARD AND WALTER J. HAMER

It has been shown[1] that an analytical expression for the thermodynamic functions is extremely valuable for the treatment of solutions containing more than two components. The method is equally valuable when the temperature varies with the composition, and is essential when one equilibrium relation is calculated from a quite different one. In the present paper this method is applied to the equilibrium between the two liquid or two solid phases of partially miscible solutions, and the results are used to calculate the liquid–vapor equilibrium when there are experimental measurements of the latter to serve as a check.

The liquid solutions which we discuss have at least one polar component, and should not be expected to obey the simple expression derived for non-polar mixtures,[2] that the free energy of mixing per mole, F_x^M, of a binary mixture is

$$F_x^M = RT (x_1 \ln x_1 + x_2 \ln x_2) + \beta V z_1 z_2 \quad (1)$$

in which x_1 and x_2 are the mole fractions of the two components, V is the volume of one mole of the mixture or $x_1 V_1 + x_2 V_2$, the z's are the volume fractions, $z_1 = x_1 V_1 / V$, and β is a parameter expressing the deviations from ideality, with the further relation that βV is independent of the temperature. However, the concentrations of the two phases in equilibrium, or the fact that the chemical potential of each component must have a horizontal inflection at the critical mixing point, permit the calculation of two parameters at each temperature. We have calculated them for equations of the form

$$F_x^M - RT(x_1 \ln x_1 + x_2 \ln x_2) = F_x^E = \beta V z_1 z_2 + \gamma z_1^2 z_2 = V z_1 z_2 [(\beta + \gamma/2) + \gamma(z - 1/2)] \quad (2)$$

and also of the form to which equation 2 reduces for components of equal molal volumes

$$F_x^E = B x_1 x_2 + C x_1^2 x_2 = x_1 x_2 [(B + C/2) + C(x - 1/2)] \quad (3)$$

(1) G. Scatchard and S. S. Prentiss, THIS JOURNAL, 56, 1486, 2314, 2320 (1934).

(2) G. Scatchard, Chem. Reviews, 8, 321 (1931); Kemisk Maanedsblad (Copenhagen), 13, 77 (1932); THIS JOURNAL, 56, 995 (1934). See also J. J. van Laar, Z. physik. Chem., 72, 723 (1910); 83, 599 (1913); J. H. Hildebrand and S. E. Wood, J. Chem. Phys., 1, 817 (1933).

F_x^E may be termed the excess free energy of mixing per mole.

The equations for the changes in chemical potential on mixing, μ_1^M and μ_2^M, and the excess chemical potentials, μ_1^E and μ_2^E, corresponding to equation 2 are

$$\mu_1^E = \mu_1^M - RT \ln x_1 = V_1(\beta + 2\gamma)z_2^2 - 2V_1\gamma z_2^3 \quad (4)$$

$$\mu_2^E = \mu_2^M - RT \ln x_2 = V_2(\beta - \gamma)z_2^2 + 2V_2\gamma z_1^3 \quad (5)$$

Those corresponding to equation 3 are

$$\mu_1^E = (B + 2C)x_2^2 - 2Cx_2^3 \quad (6)$$

$$\mu_2^E = (B - C)x_1^2 + 2Cx_1^3 \quad (7)$$

It will be noted that μ_1^M is RT times the natural logarithm of the activity of the first component, and μ_1^E is RT times the natural logarithm of the activity coefficient of that component.
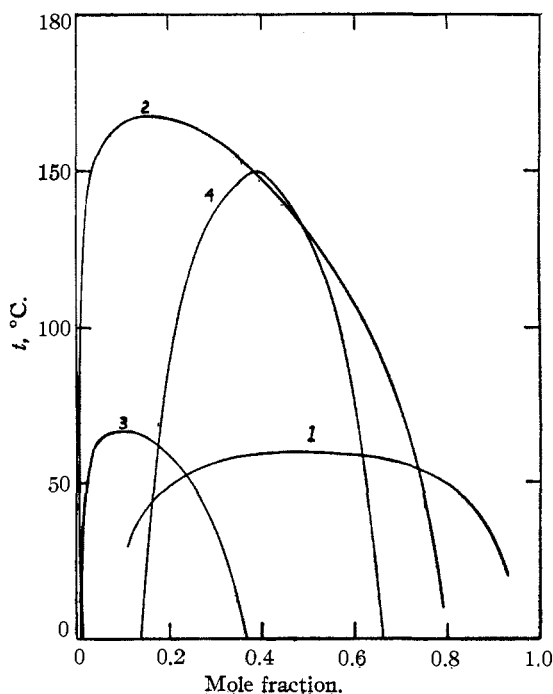

Fig. 1.—Equilibrium compositions: 1, aniline–hexane; 2, water–aniline; 3, water–phenol; 4, platinum–gold (add 1000° to t).

The magnitude of γ relative to $(\beta + \gamma/2)$ indicates the extent of the failure of equation 1 to represent the dependence on the concentration; and the change of $(\beta + \gamma/2)$ with the temperature

TABLE I
COMPOSITION OF EQUILIBRIUM SOLUTIONS AND PARAMETERS

t	x_2'	x_2''	z_2'	z_2''	$\dfrac{\beta + \gamma/2}{2.3R}$	$\dfrac{\gamma}{2.3R}$	$\dfrac{B + C/2}{2.3R}$	$\dfrac{C}{2.3R}$
			Aniline (91.06)–Hexane (130.47)					
59.6	0.4994	0.4994	0.5884	0.5884	2.511	−1.017	289.0	0.5
58	.3371	.6420	.4215	.7199	2.621	−0.943	292.5	17.9
55	.2669	.7257	.3428	.7913	2.726	−1.033	308.0	3.7
50	.2064	.7825	.2715	.8375	2.859	−1.000	320.4	6.7
40	.1412	.8691	.1906	.9049	3.113	−1.278	345.4	− 9.0
30	.1115	.9068	.1524	.9330	3.258	−1.440	359.5	−20.7
			Water (18.07)–Aniline (91.06)					
167.5	0.1424	0.1424	0.4555	0.4555	6.942	−2.010	− 858.7	1503.8
165	.0786	.2385	.3008	.6122	7.226	−2.149	− 714.3	1452.7
160	.0573	.3021	.2345	.6857	7.568	−2.422	− 525.0	1331.4
140	.0296	.4458	.1331	.8021	8.453	−3.085	− 147.5	1083.9
120	.0191	.5432	.0895	.8570	9.089	−3.691	+ 59.7	929.0
100	.0148	.6277	.0702	.8947	9.585	−4.629	+ 213.6	766.0
80	.0113	.6886	.0546	.9177	9.906	−5.214	+ 290.8	677.9
60	.0088	.7326	.0430	.9325	10.048	−5.543	+ 331.8	620.9
40	.0077	.7617	.0374	.9416	9.919	−5.733	+ 347.8	565.9
20	.0070	.7838	.0341	.9481	9.646	−5.820	+ 350.8	514.1
			Water (18.07)–Phenol (87.78)					
68.5	0.0880	0.0880	0.3192	0.3192	4.645	1.043	−2985	3163
66	.0898	.0898	.3241	.3241	4.670	0.923	−2807	3013
65	.0568	.1393	.2262	.4402	4.831	.837	−2523	2822
60	.0372	.1903	.1582	.5332	5.047	.839	−2152	2593
50	.0250	.2428	.1107	.6090	5.270	.827	−1737	2322
40	.0199	.2782	.0899	.6519	5.392	.748	−1430	2094
30	.0180	.3079	.0819	.6837	5.474	.513	−1130	1834
20	.0168	.3311	.0767	.7063	5.482	.326	− 925	1642
10	.0157	.3511	.0720	.7244	5.450	.190	− 775	1496
0	.0146	.3699	.0673	.7404	5.400	.081	− 655	1374
			Platinum (91.9)–Gold (101.2)					
1150	0.395	0.395					1174	379
1100	.218	.567					1177	449
1050	.170	.622					1175	479
1000	.138	.660					1167	509
950	.116	.686					1153	532
900	.098	.706					1133	560
850	.082	.722					1109	596
800	.066	.738					1088	646

shows how far the solution is from regular in the sense of Hildebrand.[3] Figure 1 shows the equilibrium compositions for liquid solutions of aniline–hexane,[4] water–aniline[4] and water–phenol,[4] and for solid solutions of platinum–gold[5] (for which 1000° must be added to the temperature scale). Table I gives the mole fractions and volume fractions of the larger component in the two equilibrium solutions, and the parameters computed from them. The figures in parentheses after the names of the substances are the molal volumes in

cubic centimeters at 20 or at 25°, the values used in equations 2, 4 and 5.

For aniline–hexane, equation 3 gives a much smaller asymmetry term than equation 2, but for the solutions containing water, equation 3 leads to so great asymmetry that the excess free energy of mixing is negative over a large part of the range even though the solutions are not completely miscible. Equation 2 gives about the same degree of asymmetry for each of the three liquid solutions, and the constants decrease with increasing temperature as should be expected with polar components. For platinum–gold solid solutions, the volumes are so nearly equal and are

(3) J. H. Hildebrand, THIS JOURNAL, **51**, 66 (1929).

(4) "I. C. T.," Vol. III, pp. 397, 389.

(5) C. H. Johansson and J. O. Linde, Ann. Physik, [5], **5**, 762 (1930).

measured at a temperature so far from those of the equilibrium measurements that no attempt was made to use equation 2. We note that its use would reduce the asymmetry, but by only a small amount. For this system $(B + C/2)$ is independent of the temperature over a large range, and the change at lower temperatures may well be within the experimental error. The simple theory would predict this behavior for non-polar components. Equation 3 might be expected to give the variation with composition for two isomorphous solids. The asymmetry may arise from the fact that a foreign molecule which is too large distorts a crystal lattice more than one which is too small.

Keyes and Hildebrand[6] obtain 290 mm. for the vapor pressure of hexane and 277 mm. for the vapor pressure of the two-liquid system at 40°. Using the former figure and 1 mm. for the vapor pressure of aniline, we obtain 262 mm. for the two-liquid system by equation 2, and 263 mm. by equation 3, assuming the vapors to be perfect gases. Since the vapor pressure of hexane is 15 mm. higher than that accepted for the "International Critical Tables," it is not certain that the discrepancy should be attributed to our calculations.

For water–aniline, the "International Critical Tables" give values for the composition of the vapor in equilibrium with two liquid phases from 40 to 90°, and the vapor composition and pressure for several compositions of the water-rich phase at 75°. Figure 2 shows the comparison of the first (circles) with calculations from equation 2
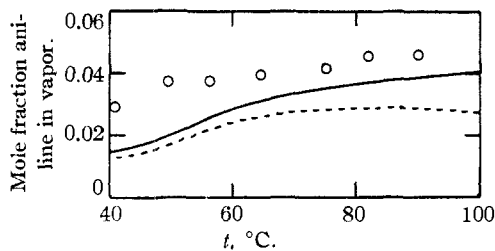

Fig. 2.—Water–aniline, two liquids: full line, equation 2; broken line, equation 3; circles, observed.

(full line) and from equation 3 (broken line), using the parameters determined from the liquid–liquid equilibrium. For equation 2 the discrepancy varies from 50% at 41.5° to 7% at 90°; for equation 3 the discrepancies are somewhat larger.

(6) D. B. Keyes and J. H. Hildebrand, THIS JOURNAL, 39, 2126 (1917).

Figure 3 shows the vapor pressure and the vapor composition at 75° as a function of the liquid composition, with calculations from equation 2 only. The agreement of the vapor compositions is excellent, except for the saturated solution. The calculated pressures are consistently 2% lower than the measured values. It should be noted that the condensate is two-phase in almost all these measurements, and that the experimenter (Schreinemakers) claimed no great accuracy.
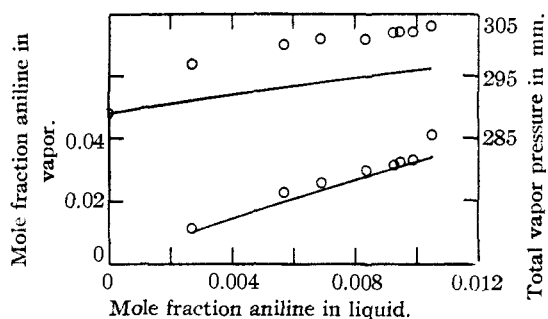

Fig. 3.—Water–aniline, 75°: above, total vapor pressure; below, mole fraction aniline in vapor.

For water–phenol there are measurements of the composition and pressure of the vapor in equilibrium with two liquid phases from 15 to 68.5°, and measurements over the whole composition range at 56.3[7] and at 58.4°.[8] The calculations require the vapor pressure of liquid phenol (supercooled through much of the range) and no measurements were found. The values found were obtained by extrapolating the "I. C. T." equation valid from 116 to 180°. Figure 4 shows the vapor composition and pressure of the two-liquid system as a function of the temperature. The agreement of equation 2 is apparently well within the uncertainty in the vapor pressure of phenol. Equation 3 leads, however, to absurd results for this system, as might be expected from the large values of the parameters.

The vapor compositions and pressures were calculated at 57.5°, and compared with the measured values at the two neighboring temperatures. For this comparison the measured pressures were multiplied by the ratio of the vapor pressure of water at 57.5° to its vapor pressure at the temperature of the measurements. The vapor composition is shown as the logarithm of the "relative volatility," α.

$$\log \alpha = \log (y_2 x_1 / y_1 x_2) = \frac{(\mu_2^E - \mu_1^E)}{2.3RT} + \log (P_2/P_1) \quad (8)$$

(7) F. A. H. Schreinemakers, Z. physik. Chem., 35, 459 (1900).

(8) H. D. Sims, Chem. Eng. Thesis, M.I.T., 1933.

in which y_1 and y_2 are the mole fractions in the vapor, and P_1 and P_2 the vapor pressures of the pure components. The comparison is shown in
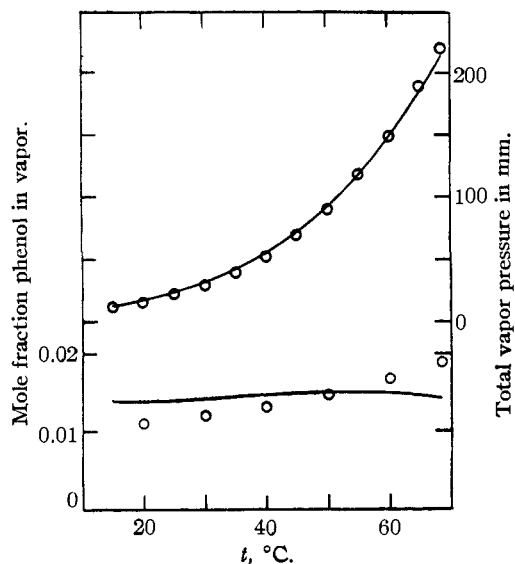

Fig. 4.—Water–phenol, two liquids: above, total vapor pressure; below, vapor composition.

Fig. 5, with the liquid composition expressed as weight fraction, rather than mole fraction, to give a better distribution of the points. The broken line for log α is that obtained by increasing log
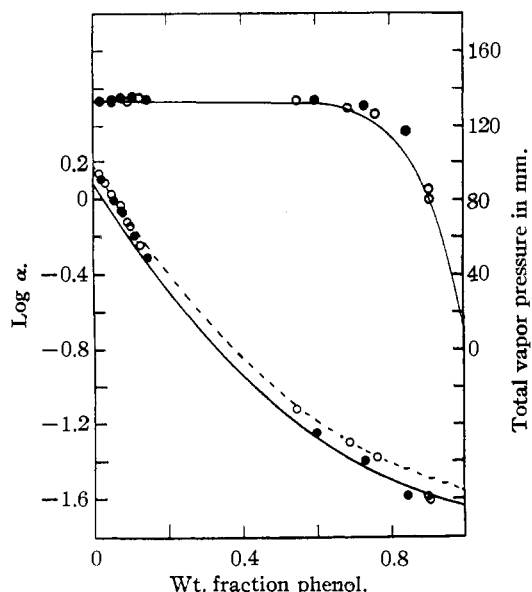

Fig. 5.—Water–phenol, 57.5°: above, total vapor pressure; below, log α; ●, Schreinemakers; ○, Sims.

P_2 by 0.1. The agreement with the experiments appears to be within this range, which is probably smaller than the experimental error.

Recently Guggenheim[9] has criticized the use of such equations, particularly that to which equation 1 reduces when the molal volumes are equal

$$F_x^E = Bx_1x_2 \qquad (9)$$

for solutions which deviate so widely from ideality as to be only partially miscible on the ground that these equations neglect the deviations from random distribution. There is no doubt about the basis of his criticism, but there is reason to believe that the equations used in this paper agree better with the behavior of actual systems than the approximate treatment offered by Guggenheim (equation 21). We may compare this equation with equation 9 if we assume that each molecule is in contact with twelve others, as in closely packed crystals. The upper curves in Fig. 6 show the equilibrium temperature divided
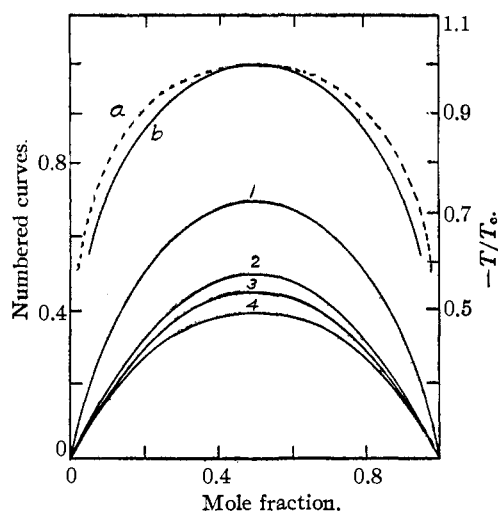

Fig. 6.—Comparison with Guggenheim's equation: a, equilibrium compositions by Guggenheim's Equation 21; b, equilibrium compositions by Equation 9; (1) $-[x_1 \ln x_1 + x_2 \ln x_2]$; (2) $F_x^E = H_x^M$ at T_c, Equation 9; (3) F_x^E at T_c. Guggenheim's Equation 21; (4) H_x^M at T_c. Guggenheim's Equation 21.

by the critical mixing temperature as a function of the composition for a regular solution obeying equation 9 (B independent of the temperature) as a full line, and for Guggenheim's equation 21 as a broken line. The lower curves in this figure show, as functions of the composition, $-[x_1 \ln x_1 + x_2 \ln x_2]$; $F_x^E = H_x^M$ for the critical mixing isotherm according to equation 9; F_x^E according to Guggenheim; and H_x^M according to Guggenheim.

(9) E. A. Guggenheim, Proc. Roy. Soc., (London), A148, 304 (1935).

F_x^M is given by the difference between the second, or third, curve and the first.

From the upper curves we see that Guggenheim's equation fits most partially miscible liquids better than equation 9 in that it is somewhat flatter, but there is no assurance that this is not a coincidence and that B should not actually decrease with increasing temperature because of polarity, giving rise to a flatter curve than that corresponding to equation 9. The platinum–gold system, which should correspond closely to the model used by Guggenheim, shows little or no flattening. In any case most systems deviate from equation 9 much more seriously through their lack of symmetry than through their flatter maxima.

The lower curves show that the difference between the two treatments is not very great, and that the modification introduced by Guggenheim is probably in the wrong direction, for the second curve is independent of the temperature but the third and fourth increase with increasing temperature with the second curve as limit at infinite temperature. Experimentally it is found, even with non-polar mixtures, that when any variation of F_x^E with temperature can be detected it is a decrease and not an increase, and that whenever F_x^E and H_x^M have both been measured the second is larger than the first. We believe that Guggenheim's approximation, in addition to its failure to represent the asymmetry of most real systems, gives much too large an effect of the deviation from random distribution.

Summary

Equations for the free energy of mixing are computed from the mutual solubilities of partially miscible substances, and the vapor compositions and pressures computed from these equations are compared with the experimental measurements with good agreement.

Guggenheim's treatment is discussed and found less satisfactory than the simpler one given here.

The Application of Equations for the Chemical Potentials to Equilibria between Solid Solution and Liquid Solution

By George Scatchard and Walter J. Hamer

The method of determining the composition of liquid and solid phases in equilibrium at each temperature from the melting points and heats of fusion of the components when both solutions are ideal, or when the activity coefficients are known, has been developed by Seltz.[1] His treatment of the activity coefficients is, however, completely qualitative. Analytical expressions for the chemical potentials[2] permit a consistent treatment of such equilibria. From the compositions of the two phases at equilibrium it is possible to calculate two parameters, one of which may be attributed to each solution. The accuracy of the experimental measurements, which are carried out at constant composition and not at constant temperature, does not warrant the calculation of these constants at each temperature, but the solutions may be treated as regular and the parameters calculated at one temperature may be used to compute the equilibrium compositions at other temperatures. Since the molal volumes of the metals at the equilibrium temperatures are not well known and are not very different, we have expressed the excess free energies of mixing in terms of mole fractions rather than volume fractions.

For the liquid solution the changes on mixing of the free energy per mole and of the molal chemical potentials are

$$F_x^M = RT(x_1 \ln x_1 + x_2 \ln x_2) + Bx_1x_2 \quad (1)$$
$$\mu_1^M = RT \ln x_1 + Bx_2^2 \quad (2)$$
$$\mu_2^M = RT \ln x_2 + Bx_1^2 \quad (3)$$

Similar equations would apply to the solid solutions, but we need the change in these functions in going from the two liquid components to the solid solutions, which functions we shall designate with primes.

$$F_x^{M'} = x_1L_1(T/T_1 - 1) + x_2L_2(T/T_2 - 1) + RT(x_1 \ln x_1 + x_2 \ln x_2) + B'x_1x_2 \quad (4)$$
$$\mu_1^{M'} = L_1(T/T_1 - 1) + RT \ln x_1 + B'x_2^2 \quad (5)$$
$$\mu_2^{M'} = L_2(T/T_2 - 1) + RT \ln x_2 + B'x_1^2 \quad (6)$$

(1) H. Seltz, This Journal, 56, 307 (1934); ibid., 57, 391 (1935).
(2) G. Scatchard and W. J. Hamer, ibid., 57, 1805 (1935).