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.

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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

$$F_x^M = RT(x_1 \ln x_1 + x_2 \ln x_2) + Bx_1x_2 \qquad (1)$$

$$\mu_1^M = RT \ln x_1 + Bx_2^2 \qquad (2)$$

$$\mu_2^M = RT \ln x_2 + Bx_1^2 \qquad (3)$$

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.

$$F_x^{M'} = x_1L_1(T/T_1 - 1) + x_2L_2(T/T_2 - 1) + RT(x_1 \ln x_1 + x_2 \ln x_2) + B'x_1x_2 \qquad (4)$$

$$\mu_1^{M'} = L_1(T/T_1 - 1) + RT \ln x_1 + B'x_2^2 \qquad (5)$$

$$\mu_2^{M'} = L_2(T/T_2 - 1) + RT \ln x_2 + B'x_1^2 \qquad (6)$$

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(1) H. Seltz, THIS JOURNAL, **56**, 307 (1934); *ibid.*, **57**, 391 (1935).

(2) G. Scatchard and W. J. Hamer, *ibid.*, **57**, 1805 (1935).

For approximate work we have found the method of Gibbs[3] more convenient than that of Seltz, although the latter would be preferable for exact calculations. Gibbs' method is to plot F_x^M and $F_x^{M'}$ against x_2 at each temperature, draw the common tangent and read the points of tangency as the composition of the respective phases. It is necessary to determine the two parameters by trial and error, so that some general conclusions may be noted. If $B = B'$ the liquidus and solidus will each approach asymptotically at each end the corresponding curve for ideal solutions, but they will deviate from the ideal curves in the middle unless B and B' are zero: if the parameters are positive the curves will spread outside (liquidus above, solidus below) the ideal curves; if the parameters are negative both curves will lie between the two ideal curves. If the parameters are unequal both curves will be displaced from the ideal toward the region which has the more positive parameter: if B' is more positive than B, the curves will be lowered and may give a minimum if the difference is great enough; if B' is more negative both curves will be raised and may give a maximum. The separation of the two curves will increase as the average of B and B' becomes more positive. The application of the method is illustrated for two systems.

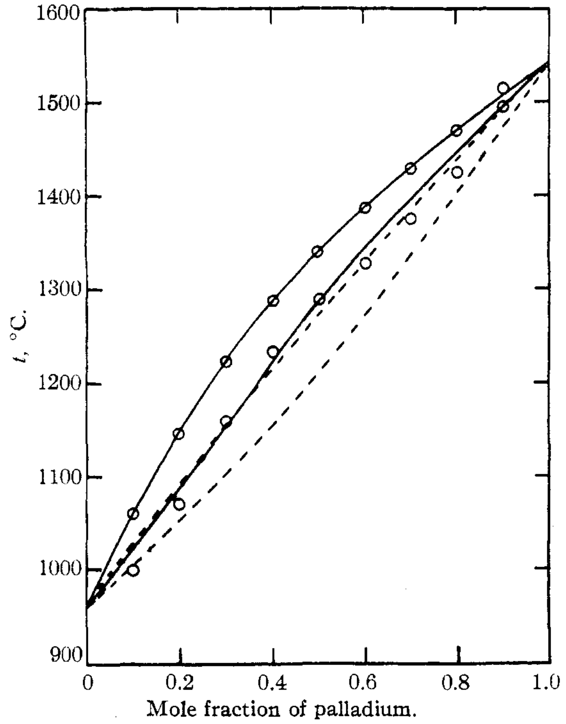

Fig. 1.—Silver-palladium equilibrium compositions: broken line, ideal; full line, equations 1 and 4; circles, observed.

Figure 1 shows the silver-palladium system, calculated with 2628 and 3822 cal. per mole for the heats of fusion of silver and palladium, respectively, and $B/2.3R = +83.93$; $B'/2.3R = -52.85$. The agreement with the liquidus is excellent. The parameters were chosen to fit the solidus near the middle of the temperature range, and miss some of the points as much as 25°. They obviously could have been chosen to give a better average fit over the whole curve, but it is not at all certain that the solidus curve is determined experimentally any more accurately than the present agreement. The figure shows definitely that a much more complicated equation would be required to give as pronounced a hump in the solidus curve as the experimental results indicate. The broken lines are the ideal curves.

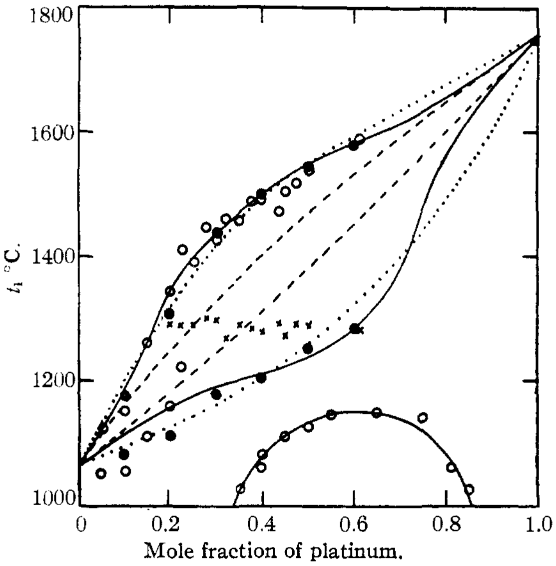

Fig. 2.—Gold-platinum equilibrium compositions: – – –, ideal; . . . ., customary curves ——, equations 1 and 4; ●, Doerinckel; ○, Grigorjew (liquidus and solidus); ×, Grigorjew (three phase); lower curve and circles, solid-solid equilibrium.

Figure 2 shows the gold-platinum system, calculated with 3130 and 5250 cal. per mole for the latent heats of fusion of gold and platinum, respectively, and $B/2.3R = +1155.5$; $B'/2.3R = +1164.6$. The top of the solid-solid equilibrium curve is also shown. The broken lines are those calculated for ideal solutions, and the dotted lines are the lens shaped pair usually drawn

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[3] J. W. Gibbs, "Collected Works," Longmans, Green, and Co., New York, 1906, p. 118.

from the measurements of Doerinckel,[4] which are represented by the black circles. The open circles represent the measurements of Grigorjew[5] of the liquidus and solidus, and the crosses represent his supposed equilibrium between two solids and a liquid. Our curves (full line) fit the liquidus and solidus at least as well as the usual curves. (Failure to obtain equilibrium should give too low a solidus.) They probably explain also the observations of Grigorjew, whose own explanation is certainly wrong.[6] The solidus curve is so flat from 1300 to 1200° that most of the remaining liquid solidifies in so small a temperature range that he interpreted it as an isothermal transition.

Since $B'/2R = 1340$, it indicates partial miscibility below 1340°A. or 1067°C., with the critical mixing composition fixed at the equimolal mixture by the nature of the equation. The experimentally observed critical mixing point is at 1150° and 60 mole per cent. platinum. Those forces, neglected in our equations, which displace this point from 50 to 60 mole per cent., might well raise the temperature 5 or 6%. The agreement may be considered a very good confirmation of the approximate accuracy of our treatment.

We attempted to apply the same method to the manganese–cobalt system, which shows a minimum melting point. In equilibria between two different states of aggregation, the temperature of a minimum or maximum gives only the difference between B and B', and the composition at the minimum or maximum is determined from the transition temperatures and heats of the components. Unless the heats of fusion in the literature are in error by more than their rather wide scattering, $B-B'$ for this system decreases rapidly with increasing temperature, or with increasing cobalt concentration, and our equations are quite inadequate.

Seltz believed that "A phase diagram with liquidus curve displaced above the ideal and with solidus displaced below is shown to require the existence of very unusual activity curves," but we have reproduced such a diagram for the gold–platinum system accurately with equations corresponding to the simplest form of non-ideal curves. The discrepancy arises because Seltz makes the comparison between the deviations of the two components in each solution rather than between the deviations of each component in the two solutions. Such a phase diagram may result if the deviation of the higher melting component is more positive in the liquid than in the solid, and the deviation of the lower melting component is more positive in the solid than in the liquid. Since the solid solution is at every temperature richer in the higher melting component and poorer in the lower melting component than the liquid, this criterion is not hard to satisfy if the deviations are all positive.

Summary

Simple equations for the change in chemical potentials on mixing are applied to the equilibria between solid and liquid solutions of the silver–palladium and the gold–platinum systems, and some general conclusions are noted.

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(4) Fr. Doerinckel, *Z. anorg. Chem.*, **54**, 345 (1907).

(5) A. T. Grigorjew, *ibid.*, **178**, 97 (1929).

(6) C. H. Johansson and J. O. Linde, *Ann. Physik*, [5] **5**, 762 (1930); W. Stengel and J. Weerts, *Siebert Festschr.*, 300–308 (1931).