[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE CARNEGIE INSTITUTE OF TECHNOLOGY]

Thermodynamics of Solid Solutions. II. Deviations from Raoult's Law

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In a recent publication[1] equations were derived for calculating the liquidus and solidus curves for binary systems which solidify with the formation of solid solutions, based on the assumption of perfect solution behavior in both phases. A general graphical method, applicable to non-ideal solutions, was also developed by which the phase equilibria could be established from experimental fugacity or activity values of the components in the liquid and solid phases. In the present paper, following this line of treatment, the forms of phase diagrams for binary systems which show complete solid miscibility will be considered in relation to the types of deviations from Raoult's law in the liquid and solid solutions. In such a continuous series of solid solutions it is doubtful that positive deviations from Raoult's law will ever occur; the general nature and properties of such solutions would probably give rise to negative deviations, as found experimentally by Wachter in the silver-gold system.[2] On this assumption three cases are to be considered.

(1) Positive Deviations in the Liquid—Negative in the Solid.—The most convenient graphical treatment is on the basis of activities, rather than fugacities, since activity values for metal systems can be determined by electromotive force measurements. Numerous examples of this procedure have appeared in the literature.[2,3] Either the pure solids or pure liquids can be taken as standard states for the calculation of activities and in this paper the former are used. With the pure solid phases as reference states (unit activity at every temperature), the pure liquids will have unit activity only at their freezing points. Above the melting point of the solid the pure liquid will have an activity less than unity, and below, a value greater than unity. As shown in the first paper of this series,[1] perfect solution behavior in both liquid and solid solutions gives rise to the familiar lens-shaped phase diagram. When the components in the liquid solutions show positive and in the solid solutions negative deviation from Raoult's law the phase diagram for the system will have a maximum, with the liquidus and solidus curves coincident at this point. Consider a system of two metals "A" and "B" with the melting point T_A lower than the melting point T_B. At a temperature between T_A and T_B the activity curves of the components are shown in Fig. 1, with a_A and a_B the activities of the component in the liquid solutions and a'_A and a'_B in the solid solutions. Above the activity curves another pair of curves is constructed on which are plotted for each component the difference between the abscissas of solid and liquid activity curves against the mole fraction of "B" in the liquid phase, calling this difference positive when the solid curve is to the right of the liquid curve. $\Delta N(A)$ is the curve for the "A" component and $\Delta N(B)$ for the "B" component. The intersection of these "difference curves" gives directly the equilibrium composition, N_B, of the liquidus curve at this temperature and by dropping a perpendicular to the liquid activity curves from this intersection and drawing horizontal lines to intersect the respective solid activity

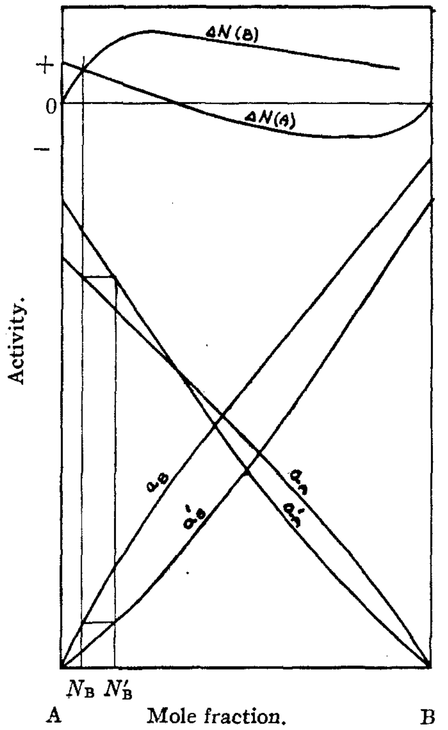

Fig. 1.

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[1] Seltz, THIS JOURNAL, **56**, 307 (1934).

[2] Wachter, *ibid.*, **54**, 4609 (1932).

[3] Hildebrand and Sharma, *ibid.*, **51**, 462 (1929).

curves the composition of the solidus equilibrium curve, N'_B, is determined.

At higher temperatures N_B and N'_B will move toward the right until the melting point of "B" is reached. The activity curves will then appear as shown in Fig. 2. At this temperature pure liquid and solid "B" are of course in equilibrium, but the intersection of the ΔN curves shows that, at the same temperature, liquid and solid solutions of composition N_B and N'_B are also in equilibrium. At a temperature above T_B, Fig. 3, two intersections of the ΔN curves (one positive and one negative) give two sets of liquid–solid equilibria, the first pair at N_B and N'_B and the second pair at (N'_B) and (N_B). At still higher temperatures the two intersections of the ΔN curves will approach each other with a corresponding decrease in the spread of the liquidus–solidus equilibria until a temperature is reached, Fig. 4, where the "A" and "B" activity curves intersect at the same composition. The ΔN curves pass through zero at this point tangent to each other. This is the maximum point on the phase diagram and liquidus and solidus curves coincide. Above this temperature only the liquid phase can exist, since the ΔN curves do not intersect at any point.

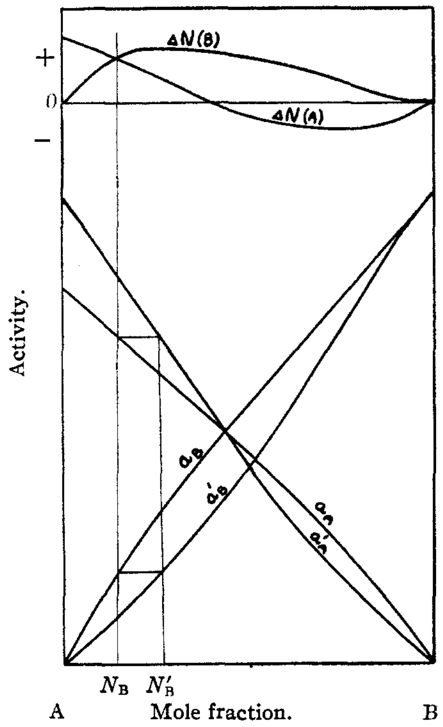

Fig. 2.

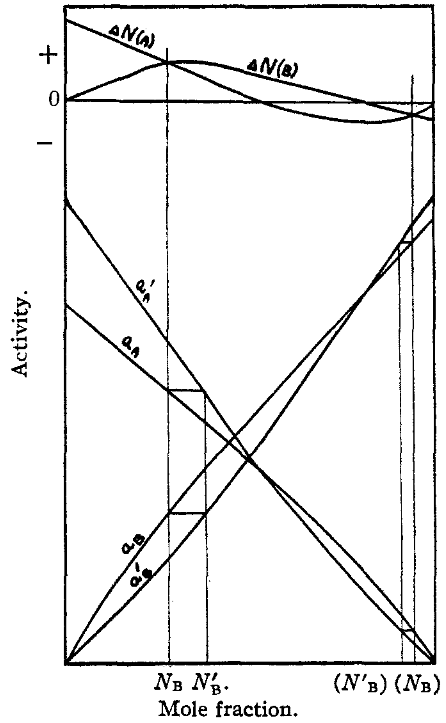

Fig. 3.

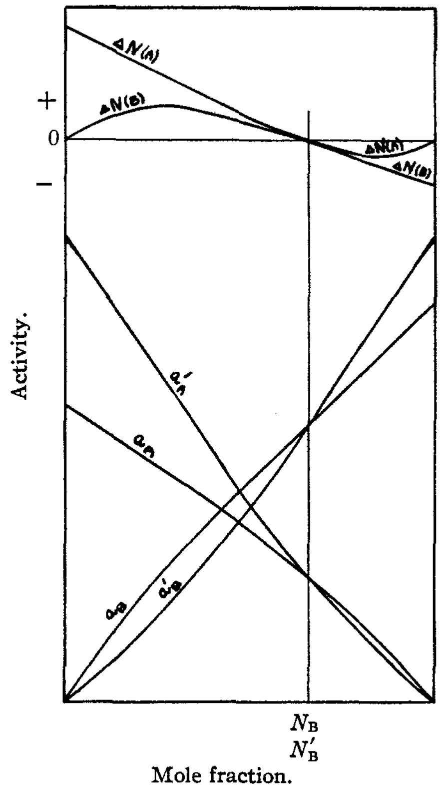

Fig. 4.

(2) Negative Deviations in both Phases—More Marked in the Solid than in the Liquid.—

There are two possibilities with these activity conditions. Continuing with the same nomenclature, if the curve for a_A does not fall completely below the curve for a'_A when the melting point of "B" is reached, the phase diagram will show a maximum as in Case 1.

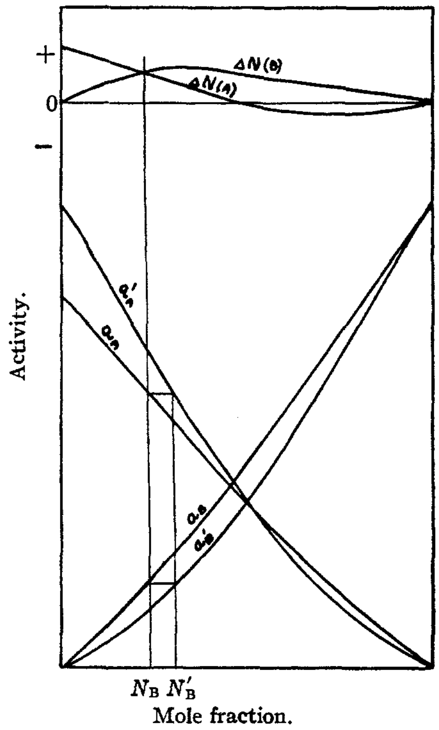

Fig. 5.

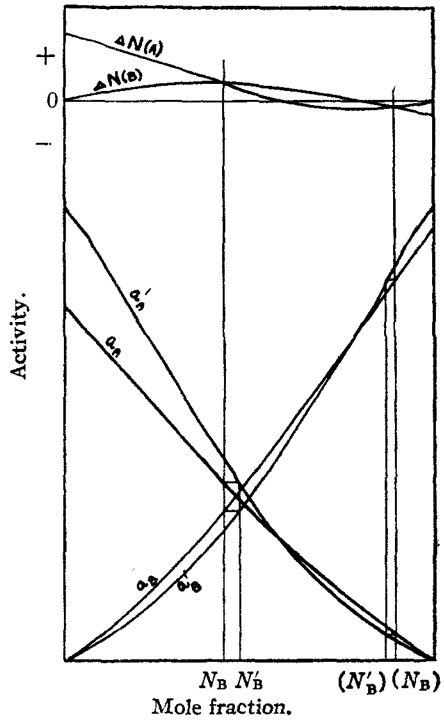

Fig. 6.

This is illustrated in Figs. 5, 6 and 7. Figure 5 is at T_B; Fig. 6 is at a temperature between T_B and the maximum; Fig. 7 corresponds to the maximum point.

On the other hand, if the a_A curve falls below the a'_A curve before T_B is reached, no maximum will appear. All the points on the liquidus and solidus curves will lie between T_A and T_B. The resulting phase diagram, however, will have both curves displaced above the curves calculated on the basis of perfect solution behavior, that is, the N_B and N'_B points will be displaced toward the side of the lower melting component. Figure 8 shows this relationship at a temperature between T_A and T_B. The dotted lines are for perfect solution behavior, giving a liquidus point at N_{B_i} and a solidus at N'_{B_i}.

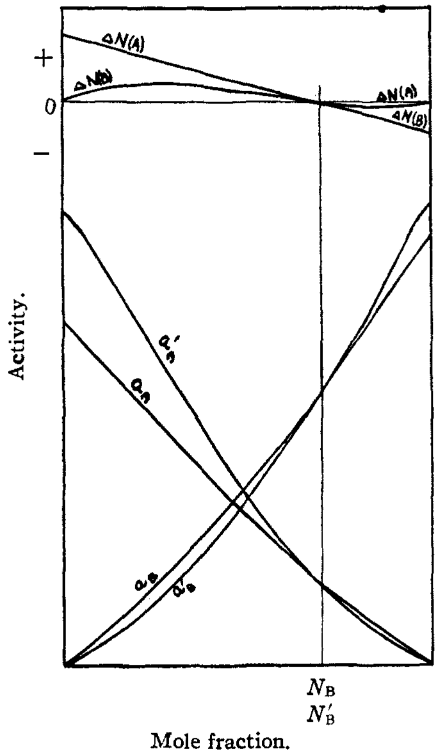

Fig. 7.

(3) Negative Deviations in both Phases—More Marked in the Liquid than the Solid.—Here again there are two possibilities. If at T_A (the melting point of the *lower* melting component) the activity curve a_B does not fall completely above the curve a'_B, then the phase diagram will show a minimum. Figure 9 is at

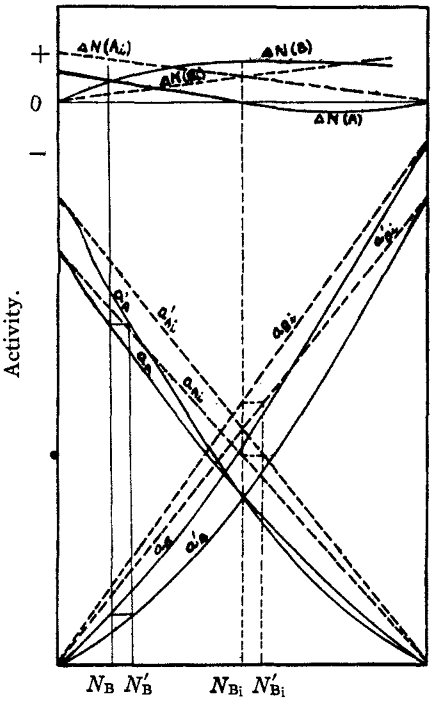

Fig. 8.

the melting point T_A, where, besides the equilibrium between the two pure phases, liquid and solid solutions of compositions N_B and N'_B can also exist in equilibrium. Below this temperature two pairs of liquid–solid points appear, converging to the minimum at still lower temperatures.

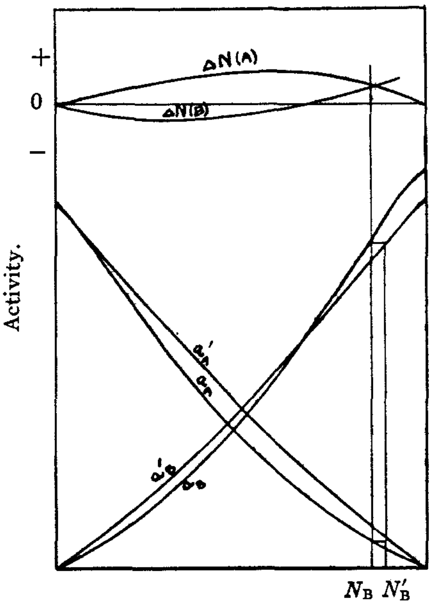

Fig. 9.

The other possibility for deviations of this type is that the activity curve a_B falls completely above the curve a'_B at the melting point T_A. It can be readily shown that this gives rise to liquidus and solidus curves lying entirely between T_A and T_B, but displaced *below* the curves for perfect solution behavior.

(4) Possibility of Displacement of the Liquidus Curve above and the Solidus below the Ideal Curves.—Figure 10 reproduces the gold–platinum phase diagram as determined by Doerinckel,[4] in which the liquidus curve lies entirely *above* the calculated ideal curve and the solidus curve lies entirely *below* the ideal curve.

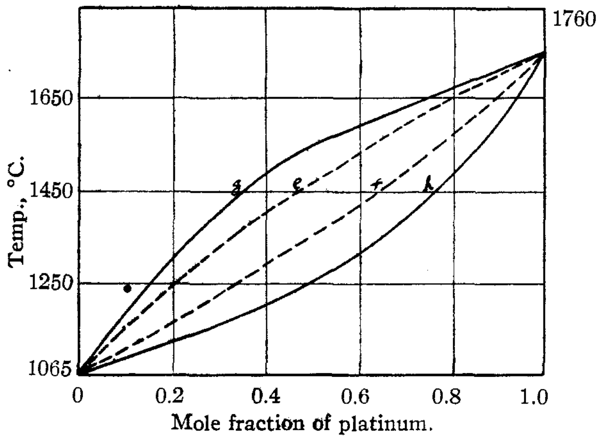

Fig. 10.—Solidus and liquidus curves for the gold–platinum system: ——, observed; – – – –, ideal.

The dotted ideal curves are calculated as previously described.[1] From a graphical treatment this system seems to require the existence of very unusual activity curves for the components of the liquid and solid solutions. In Fig. 11 the dotted lines a'_{A_i} and a'_{B_i} represent the ideal activity curves for gold and platinum, respectively, in the solid solutions and a_{A_i} and a_{B_i} are the corresponding liquid curves at 1450°. N_{B_i} and N'_{B_i} are taken from the ideal liquidus and solidus compositions (*e* and *f* of Fig. 10), so that the a_{A_i} and a_{B_i} curves are correctly located relative to the a'_{A_i} and a'_{B_i} curves. N_B and N'_B are the compositions of the experimental liquidus and solidus curves at this temperature (*g* and *h* of Fig. 18). Thus the actual activity curves must be so located that the a_B and a'_B curves for platinum intersect the N_B and N'_B isopleths at the same activity, and that a_A and a'_A curves for the gold behave in a similar manner. The locations of these inter-

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[4] Doerinckel, *Z. anorg. Chem.*, **54**, 333 (1907).

sections are restricted by the Duhem equation relating the activities of the two components in a binary solution. If one component shows negative deviations over the entire range of composition, the other cannot show positive deviations over the entire range. A possible location of the various activity curves is thus shown by the heavy sections in Fig. 11, labeled a'_A, a'_B, a_A and a_B. At other temperatures the graphical treatment shows deviations of similar nature. It is apparent that a system of this type can result from activity curves which show more pronounced deviations for the B component than for the A component in the solid phase and more pronounced deviations for the A component than for the B component in the liquid phase at every temperature and hence at every composition. If positive deviations are assumed in place of negative deviations, it can readily be shown that these abnormalities would merely be reversed. It seems doubtful that such curves would comply with the Duhem equation. Unfortunately no actual activity values (and partial molal relative heat contents) are available for either liquid or solid phases of this system; furthermore, it does not seem possible to obtain such values experimentally by electromotive force methods owing to the nature of the two metals.

It is of interest, however, that gold and platinum are the only two metals thus far investigated which form a continuous series of solid solutions showing this type of deviation from the ideal liquidus and solidus curves.

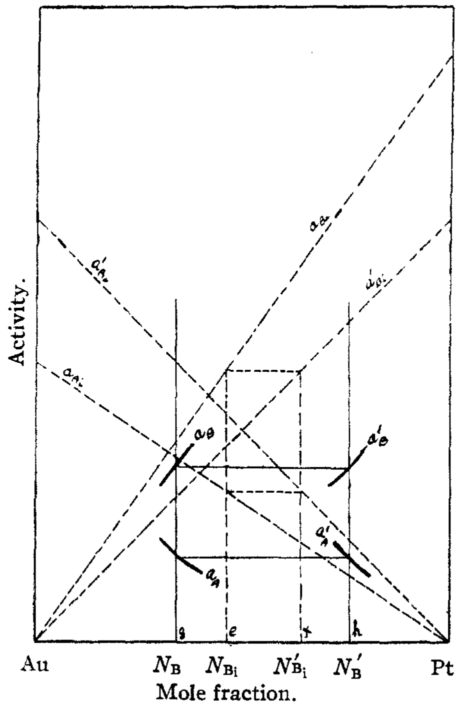

Fig. 11.

Summary

1. Employing a graphical method previously developed, the forms of phase diagrams for binary systems which show complete solid miscibility are considered in relation to the types of deviations from Raoult's law in the liquid and solid solutions.

2. Positive deviations in the liquid phase with negative deviations in the solid phase give rise to diagrams showing a maximum.

3. The types of diagrams resulting from negative deviations in both phases depend on the relative magnitude of these deviations. The various possibilities are considered.

4. A phase diagram with liquidus curve displaced above the ideal and with the solidus displaced below is shown to require the existence of very unusual activity curves.

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