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CHEMISTRY

CALCULATED AND EXPERIMENTAL PHASE DIAGRAMS OF THE SIMPLEST BINARY SYSTEMS (E/T)

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The position of the curves representing the decomposition of solutions on the phase diagrams of binary systems may be calculated /1-4/ from ~~xtxxx~~ : a) ~~by~~ the melting points T_A and T_B of the pure components, ~~and~~ b) ~~by~~ their heats of fusion Q_A and Q_B, and ~~xxxbyxthe~~ also c) from the value of the so-called energies of mixing in different phases (U_0^I in the liquid, U_0^{II} ~~xaxxthe~~, U_0^{III}, etc. in the solid phases). Theory has as yet only been compared with experiment /4/ for four binary systems having diagrams of the same type, viz. diagrams with a eutectic point and ~~with~~ complete insolubility in the solid phases. In this paper we present a comparison with twenty experimental diagrams of three different types.

1. Diagram of the "Cigar" Type. The conditions for the formation of this type of diagram, according to calculation, are the following :

a) The system should be two-phase (both components ~~in the solid~~

should have the same type of crystal lattice in the solid phase ; on the approximation taken for the calculation, this corresponds to having the same change in entropy for the two components on melting, ... , in which k is Botzmann's constant and q is the change in entropy referred to one particle).

Fig. 1. Cu-Ni. 1) Experimental curve ; 2) ..... ; 3) .....erg/particle.

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b) The following inequalities should be satisfied :

..... R.p. 387 (1)(2)

where x and y are the concentrations of the liquid and solid solutions.

The latter inequalities may in practice be written /4/ in the form:

.....R.p. 387 (2a)

since the products $x(1 - x)$ and $y(1 - y)$ are always..... . The equations of the lines $x = x(T)$ and $y = y(T)$ bounding the region of phase separation

.....R.p. 387 (3)

may approximately be represented (after expanding the logarithms of the denominators into series in powers of.....and....., where .....and.....)in the form

.....R.p. 388 (4a) (4b)

For.....these correspond to ~~the~~ a "cigar" symmetrical with respect to the straight line joining the melting points of the components :

.....R.p. 388

(5)

The calculated diagram for the copper-nickel system obtained from equation (5) is shown in Fig. 1.

Fig. 2. ..... .

In the nickel-cobalt system it is known experimentally that the width of the region of phase separation is practically zero over the whole range of concentrations. If we take....., then the calculated width of the region of phase separation in this system, as calculated from formula (5), is ~~x~~ no greater than....., which agrees with the experimental results.

The two diagrams mentioned correspond to symmetrical "cigars". When.....and inequalities (4) and (2) are satisfied, the region of phase separation, according to formula (4), should have the form of an unsymmetrical "bent cigar", in which the ~~line~~ median line of the "cigar", i.e., ..., is convex to the x axis for..... and concave for..... .

By using experimentally-established diagrams and drawing the lines.....on these, we may verify the agreement between these lines and formula (4b) and also determine the value of..... ~~from~~ by reference to the deviation from the linear relationship.

The values of..... in ergs/particle are 0.57 for Ag-Pd, 0.05 for Ag-Au, and 0.54 for Cu-Pd.

For all three systems criterion (1) is satisfied and the calculated curve.....agrees closely with the experimental, which may be regarded as evidence that the difference in the energy of mixing does not depend on the concentration (i.e., that the approximation on which the calculation was based is valid). Figure 2 shows the diagrams of the three systems in question.

Fig. 3. ..... .

Data relating to the equilibrium phase diagram of the gold-palladium system were published in /5/ ; here the decomposition curves of the solutions also formed an "asymmetric cigar". Calculation of the quantity..... based on the deviation of the .....curve from a straight line gives .....erg/particle for this system ; criterion (1) is not, however, satisfied. The equation..... is valid, from which it follows that the diagram should contain a point of equal concentrations (see below) at y = x = 0.905. It is easy to establish from the experimental diagram that in the present case the discrepancy may be explained by measuring inaccuracies, since the region of phase separation near x = 1 is very narrow. In Fig. 3 the continuous line gives the experimental diagram and the broken line the calculated one. In the experimental diagram, in the range of concentrations close to unity, no region of phase separation is in general given ; in the range of concentrations around 15% the solid and liquid solutions are contiguous along a line, which is well known to be impossible.

<u>2. Diagrams with a Point of Equal Concentrations.</u> It follows

from equations (3) that at the point of equal concentrations

.....R.p. 389 (6)

The criterion for the formation of a diagram of this type is

.....R.p. 389 (7)

(together with the satisfaction of inequalities (2) or (2a)).

Table 1

Key

1) System

2) calc.

3) expt.

According to (6), at the point of equal concentrations

.....R.p. 389 (8)

In this relation between T_m and x_o there are no unknown energies of mixing ; hence the validity of the calculation may be verified primarily ~~from~~ by reference to the satisfaction of relation (8).

Data for ten binary systems forming diagrams with points of equal concentrations are given in Table 1 (the calculated T_m were determined from (8) by means of experimental values of x_o).

The calculated and experimental values of T_m agree closely for all the systems considered except two : gold-copper and gold-nickel, which are characterized by the greatest difference ~~in~~ between the atomic radii of the components, so that the "lattice-distortion energy" is a maximum /2/. The deviations from relation (8) for the Au-Cu and Au-Ni systems qualitatively agree with those expected ~~from~~ after ~~calculation~~ considering the energy of distortion.

3. Diagrams with a Eutectic Point. These are in general three-phase systems (for example, one liquid phase, and two solid crystalline phases with different symmetries), and are described by four equations (equations (17) in /3/). In the complete ab-

Fig. 4. a) Sn-Ga, $U_s = 0.85.10^{-13}$ erg/particle ; b) Cd-Tl, $U_o = 1.28.10^{-13}$ erg/particle. 1) Experimental ~~pax~~ curve ; 2) calculated curve ; 3) $U_o = 0$.

sence of solubility in the crystal phases, the "liquidus" lines are described by the equations

.....R.p. 390 (9)

Table 2

Key
1) System
2) erg/particle

We checked the agreement between equations (9) and experimental data for four systems * : tin-gallium, aluminum-germanium, cadmium-thallium, and gold-antimony (see Fig. 4). Table 2 contains data relating to the energies of mixing.

* In calculating the cadmium-thallium diagram we neglected the solubility of cadmium in thallium ; in the gold-antimony diagram we only calculated the left-hand branch of the "liquidus" and the position of the eutectic point.

The agreement between calculation and experiment may be regarded as satisfactory. Table 2 shows that the criterion.....is satisfied.

LITERATURE CITED

/1/ B. Ya. Pines, ZhÉTF.....

/2/ B. Ya. Pines, Izv. sektora fi.z-khim. analiza, 16, No. 1, (1943).

/3/ B. Ya. Pines, ZhFKh.....

/4/ V. I. Danilov and D. S. Kamenetskaya, ZhFKh.....

/5/ M. Hansen, Constitution of Binary Alloys /Russian translation/, Moscow-Leningrad, 1941.