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Perfect Ternary Solid Solutions

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In this paper equations are developed for calculating the solidus and liquidus surfaces, with tie-lines, for ternary systems showing complete solid solubility, based on the assumption that both liquid and solid solutions are perfect. The forms of the liquidus and solidus isotherms predicted by these equations are considered for an hypothetical example. The ternary system of gold, copper and nickel is shown to deviate markedly from ideal behavior at low mol fractions of gold, even though the copper-nickel system is practically ideal in its binary behavior.

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. For a system of two components "A" and "B" melting at T_A and T_B respectively the mol fraction of "B," N_B, of the liquidus at a temperature T was given by the equation,

$$N_B=(1-k_Ae^{\Delta H_A/RT})/(k_Be^{\Delta H_B/RT}-k_Ae^{\Delta H_A/RT}) \quad (1)$$

and for the equilibrium solidus at this temperature, the mol fraction N_B' was given by the relation,

$$N_B'=N_Bk_Be^{\Delta H_B/RT}, \quad (2)$$

where ΔH_A and ΔH_B are the heats of fusion of the pure components and $k_A=e^{-\Delta H_A/RT_A}$ and $k_B=e^{-\Delta H_B/RT_B}$. The system copper-nickel was shown to be almost ideal and recently the liquidus curve for the system[2] H_2O-D_2O has been shown to agree with Eq. (1).

In this paper equations are derived for calculating the liquidus and solidus surfaces for a three-component system showing complete solid miscibility, again assuming that Raoult's law is obeyed by the three components over the entire composition range in both liquid and solid solutions.

DERIVATION OF THE EQUATIONS

Following the treatment used for the binary system,[1] the necessary equations are here derived from a consideration of the fugacities of the components in the two phases. If Raoult's law is obeyed, then at every temperature and composition,

$$f_A=N_Af_A^\circ, \quad f_B=N_Bf_B^\circ, \quad f_C=N_Cf_C^\circ \quad (3)$$

where f_A is the fugacity of component "A" in a solution containing a mol fraction N_A of that component, and where f_A° is the fugacity of pure liquid A at the temperature in question. Similarly, f_B and f_C are the fugacities of the "B" and "C" components. For the solid phase also,

$$f_A'=N_A'f_A^{\circ\prime}, \quad f_B'=N_B'f_B^{\circ\prime}, \quad f_C'=N_C'f_C^{\circ\prime} \quad (4)$$

with the primes denoting the corresponding terms for the solid state. At any temperature between the melting points of the highest and lowest melting components an isothermal section of the ternary diagram will show two curves, one for the liquidus and one for the solidus, with tie-lines connecting the phases in equilibrium. An infinite number of such equilibrium pairs exist, but for a given pair, $f_A=f_A'$, $f_B=f_B'$ and $f_C=f_C'$ and from Eqs. (3) and (4), $N_A'=N_Af_A^\circ/f_A^{\circ\prime}$, $N_B'=N_Bf_B^\circ/f_B^{\circ\prime}$ and $N_C'=N_Cf_C^\circ/f_C^{\circ\prime}$. Furthermore, as shown in the previous paper,[1] neglecting the change in the heats of fusion with change of temperature,

$$f_A^\circ/f_A^{\circ\prime}=k_Ae^{\Delta H_A/RT}, \quad f_B^\circ/f_B^{\circ\prime}=k_Be^{\Delta H_B/RT},$$
$$f_C^\circ/f_C^{\circ\prime}=k_Ce^{\Delta H_C/RT}$$

whence

$$N_A'=N_Ak_Ae^{\Delta H_A/RT}, \quad N_B'=N_Bk_Be^{\Delta H_B/RT},$$
$$N_C'=N_Ck_Ce^{\Delta H_C/RT}. \quad (5)$$

These equations must be satisfied simultaneously for a condition of equilibrium. At the same time,

$$N_A+N_B+N_C=1, \quad N_A'+N_B'+N_C'=1. \quad (6)$$

[1] Seltz, J. Am. Chem. Soc. **56**, 307 (1934).
[2] La Mer and Baker, J. Am. Chem. Soc. **56**, 2641 (1934).

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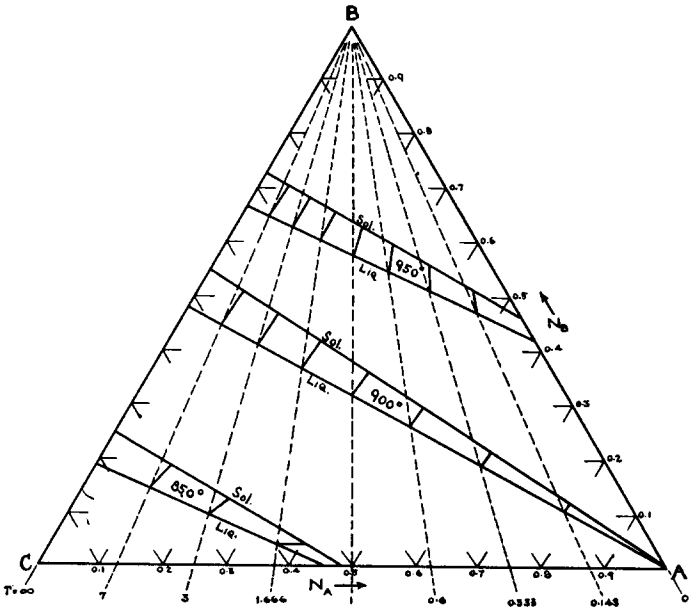

FIG. 1. Isotherms for an ideal ternary system.

Since an infinite number of tie-lines exist at a given temperature, another condition must be fixed before these equations can be solved. The most satisfactory treatment is to derive an equation for the mol fraction of one component with a fixed ratio of the mol fractions of the other two. Thus, in deriving an equation for N_B we shall assume a fixed value r for N_C/N_A, whence,

$$N_C = rN_A, \quad N_B + N_A + rN_A = 1. \tag{7}$$

From Eqs. (5) and (6)

$$N_B k_B e^{\Delta H_B/RT} = 1 - N_A' - N_C'$$

and

$$N_B k_B e^{\Delta H_B/RT} = 1 - N_A k_A e^{\Delta H_A/RT} - N_C k_C e^{\Delta H_C/RT}$$

and with Eqs. (7)

$$N_B = \frac{(1+r) - k_A e^{\Delta H_A/RT} - rk_C e^{\Delta H_C/RT}}{(1+r)k_B e^{\Delta H_B/RT} - k_A e^{\Delta H_A/RT} - rk_C e^{\Delta H_C/RT}}. \tag{8}$$

Introducing convenient values of r, the mol fractions of "B" for the liquidus surface can be calculated for the temperature range of the system. It will be noted that when r is set equal to 0 or ∞, corresponding to the binary systems $B-A$ and $B-C$, Eq. (8) reduces to the form of Eq. (1). To fix the composition of the solid phase in equilibrium with this liquid phase of mol fraction N_B and ratio r at the temperature T, the mol fractions of two components must be calculated, since in general the solidus will not lie on the same ratio line as the liquidus.

These values are readily calculated, however, from Eqs. (5) and (7), whence,

$$N_B' = N_B k_B e^{\Delta H_B/RT},$$
$$N_A' = ((1-N_B)/(1+r))k_A e^{\Delta H_A/RT}. \tag{9}$$

It is obvious that Eqs. (8) and (9), calculating along a series of convenient constant ratio lines, will serve to establish liquidus and solidus surfaces over the entire range of temperature and to fix the tie-line for each liquid-solid equilibrium.

TABLE I.

A	B	C
$\Delta H_A = 2500$	$\Delta H_B = 3000$	$\Delta H_C = 2000$
$T_A = 900$	$T_B = 1000$	$T_C = 800$
$k_A = 0.2478$	$k_B = 0.2213$	$k_C = 0.2848$

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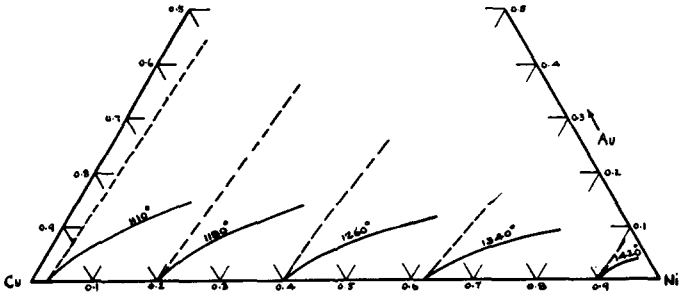

FIG. 2. Liquidus isotherms for the Ni–Cu–Au system. Dotted line, ideal; solid line, experimental.

These equations can be applied to an hypothetical example to illustrate the forms of isothermal sections for an ideal system. We shall assume the following data (Table I) for the components A, B and C, in which the heats of fusion are in calories/mol and the melting points in degrees absolute.

In Table II the calculated values of N_B, N_B' and N_A' are shown for various "r" values at three temperatures, and in Fig. 1 the corresponding liquidus and solidus curves and tie-lines are shown on the usual type of ternary diagram section.

TABLE II.

$r = N_C/N_A$	∞	7	3	1.666	1.0	0.6	0.333	0.1428	0
950°K									
N_B	0.662	0.643	0.622	0.597	0.573	0.543	0.504	0.466	0.420
N_B'	0.722	0.700	0.678	0.651	0.625	0.592	0.550	0.508	0.457
N_A'	—	0.042	0.088	0.141	0.200	0.267	0.349	0.437	0.543
900°K									
N_B	0.480	0.447	0.409	0.364	0.316	0.257	0.185	0.102	0
N_B'	0.548	0.510	0.466	0.416	0.361	0.293	0.212	0.117	0
N_A'	—	0.069	0.148	0.238	0.342	0.464	0.612	0.786	1
850°K									
N_B	0.189	0.144	0.095	0.038	—	—	—	—	—
N_B'	0.247	0.188	0.123	0.039	—	—	—	—	—
N_A'	—	0.116	0.246	0.392	—	—	—	—	—

THE COPPER-NICKEL-GOLD SYSTEM

The binary system of copper and nickel, as previously shown,[1] gives practically an ideal liquidus curve. It is of interest to consider the departure from ideal behavior on the addition of a third component. The liquidus isotherms for the ternary system of copper, nickel and gold have been determined.[3] These results have been recalculated to a mol fraction basis and are plotted as full lines at several temperatures in Fig. 2. The dotted lines are the ideal liquidus curves calculated from Eqs. (8) and (9), with the melting points of Ni, Cu and Au, 1450°C, 1083°C and 1065°C, and the heats of fusion per gram atom, 4280 cals., 2655 cals., and 3130 cals., respectively. It is apparent that marked deviations occur at relatively low mol fractions of gold, as would be anticipated, since the gold-nickel system shows partial miscibility in the solid state and the gold-copper system, though completely miscible in the solid state, shows a minimum in its phase diagram.

[3] De Cesaris, Gazetta Chemica Italiana **44**, 1, 27, 14.

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