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NORMAL FREEZING OF IDEAL TERNARY SYSTEMS OF THE PSEUDOBINARY TYPE

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by

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ABSTRACT

Perfect liquid mixing but no solid diffusion is assumed in normal freezing. In addition, the molar compositions of the freezing solid and remaining liquid, respectively, follow the solidus and liquidus curves of the constitutional diagram. For the linear case, in which both the liquidus and solidus are perfectly straight lines, the normal freezing equation giving the fraction solidified at each melt temperature and the solute concentration profile in the frozen solid was determined as early as 1902, and has since been repeatedly published. Corresponding equations for quadratic, cubic or higher-degree liquidus and solidus lines have also been obtained. This memorandum gives the equation of normal freezing for ideal ternary liquid solutions solidified into ideal solid solutions of the pseudobinary type. Sample computations with the use of this new equation were made and are given for the Ga-Al-As system.

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INTRODUCTION

Perfect liquid mixing but no solid diffusion is assumed in normal freezing. In addition, the molar compositions of the freezing solid and remaining liquid, respectively, follow the solidus and liquidus curves of the constitutional diagram.

For the linear case, in which both the liquidus and solidus are perfectly straight lines, the normal freezing equation giving the fraction solidified at each melt temperature and the solute concentration profile in the frozen solid was determined as early as 1902 (Ref. 1), and has since been repeatedly published (Refs. 2-9). Corresponding equations for quadratic, cubic, or higher-degree liquidus and solidus lines have also been obtained (Refs. 10-12). A recent publication presents the normal freezing equation for ideal dilute solutions or alloys in which the liquidus and solidus are exponential functions of the reciprocal absolute melt temperature (Ref. 13). The logarithm of the mole fraction segregation coefficient k_m for the dilute component is, therefore, also a linear function of the reciprocal of the absolute temperature. Further, in such ideal solutions, the ratio of partial pressure of each component, p_A, to that of the pure component, p_A^o, equals the atomic fraction x_A, i.e., $x_A = p_A/p_A^o$. This last equation permits the computation of the solidification behavior of such solutions or alloys and the resultant solid concentration profiles from basic thermodynamic quantities without the use of phase diagrams.

THE PSEUDOBINARY SYSTEM

This memorandum gives the equation of normal freezing for ideal ternary liquid solutions of A, B, and C atoms (Fig. 1) solidified into ideal solid solutions of AB-AC compounds with A atoms on one sublattice and B or C atoms on the other. Such systems can be treated as pseudobinary systems. Account is taken of the entropy of mixing of the three atomic species to form the ideal liquid solutions along the pseudobinary.

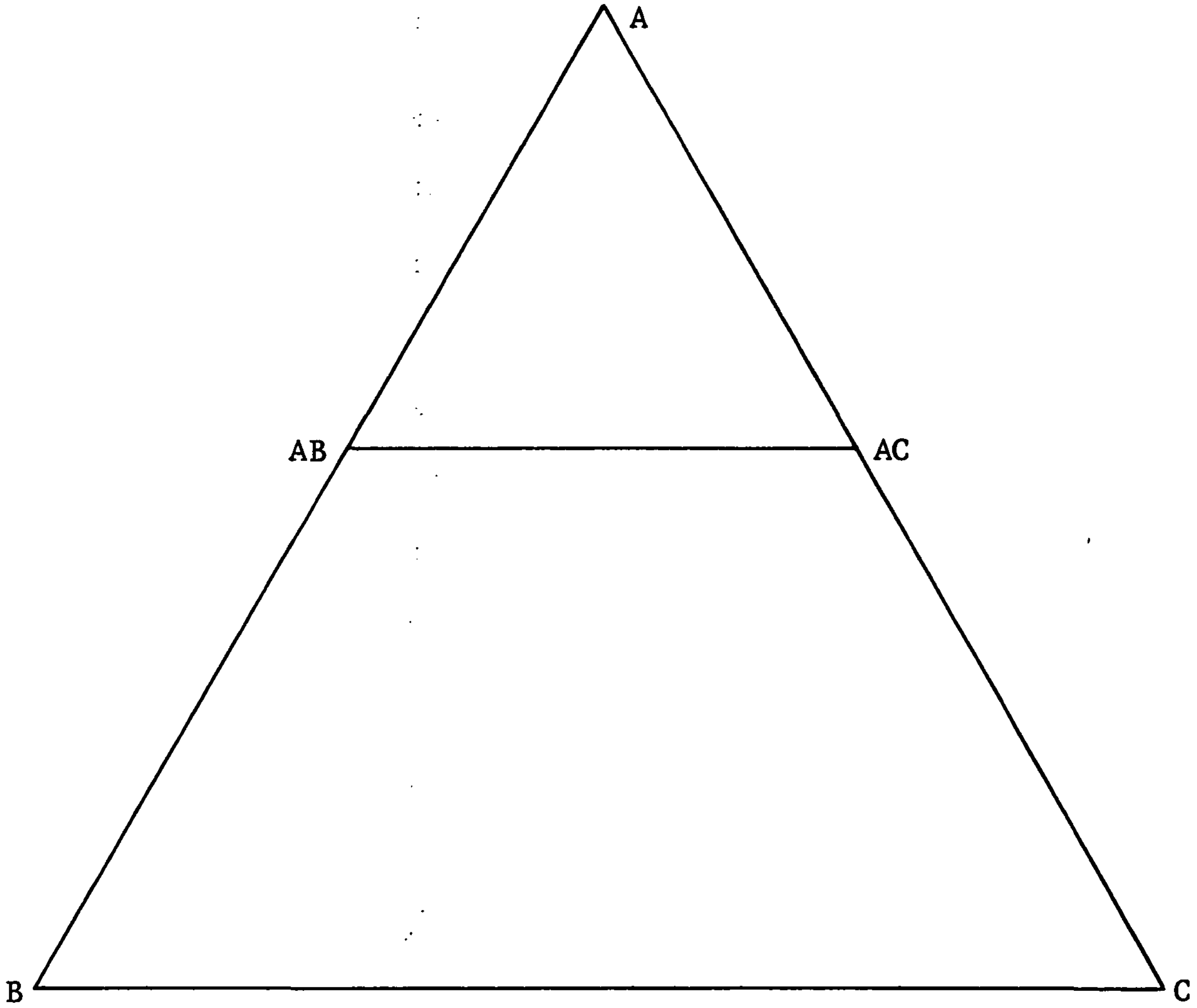

Fig. 1 Constitutional Diagram for a Ternary System of the Pseudobinary Type

For the compound AB, we have

$$AB(s) = A(l) + B(l) \quad . \qquad (1)$$

The equilibrium constant for the reaction is

$$K = \frac{x_A^l \cdot x_B^l}{x_{AB}^s} \qquad (2)$$

and the standard free energy ΔF_{AB}^o and the free energy of formation ΔF_{AB}^f are related to K at temperature T by

$$-\Delta F_{AB}^o + \Delta F_{AB}^f = RT \ln K \quad . \qquad (3)$$

For the compound AB, the free energy of formation, ΔF_{AB}^f, is related to the free energy of melting, ΔF_{AB}^m, and the heat of melting, ΔH_{AB}^m, at the melting point T_{AB}^m by

$$\Delta F_{AB}^m = \Delta H_{AB}^m \, (1 - T/T_{AB}^m) = -\Delta F_{AB}^f - RT \ln 4 \quad . \qquad (4)$$

It has been assumed that the difference in heat capacity between the liquid and solid is negligible. The $-RT \cdot \ln 4$ term is the ideal entropy of mixing to form the stoichiometric liquid phase. Hence,

$$-RT \ln 4 \cdot \frac{x_A^l \cdot x_B^l}{x_{AB}^s} = \Delta H_{AB}^m \, (1 - T/T_{AB}^m) \quad . \qquad (5)$$

Similarly, for the compound AC, we have

$$-RT \ln 4 \cdot \frac{x_A^l \cdot x_C^l}{x_{AC}^s} = \Delta H_{AC}^m \; (1 - T/T_{AC}^m) \quad , \qquad (6)$$

where ΔH_{AC}^m is the heat of formation of the compound AC, assumed constant; and T_{AC}^m is the melting point of AC.

For the ternary liquid phase of the pseudobinary,

$$\begin{aligned} x_A^l &= \tfrac{1}{2} \quad , \\ x_B^l + x_C^l &= \tfrac{1}{2} \quad . \end{aligned} \qquad (7)$$

Hence,

$$-RT \ln 4 \cdot \tfrac{1}{2} \cdot x_B^l / x_{AB}^s = \Delta H_{AB}^m \; (1 - T/T_{AB}^m) \quad , \qquad (8)$$

and

$$-RT \ln 4 \cdot \tfrac{1}{2} \cdot (\tfrac{1}{2} - x_B^l)/(1 - x_{AB}^s) = \Delta H_{AC}^m \; (1 - T/T_{AC}^m) \quad . \qquad (9)$$

Equations (8) and (9) are essentially the same as those previously given (Refs. 14,15). From these equations,

$$\begin{aligned} 2 \cdot x_B^l &= x_{AB}^s \cdot \exp\left(- \frac{\Delta H_{AB}^m}{R} \left[1/T - 1/T_{AC}^m \right] \right) \\ &= x_{AB}^s \cdot \exp(a + b/T) = x_{AB}^s \cdot U \end{aligned} \qquad (10)$$

$$\begin{aligned} 1 - 2 \cdot x_B^l &= (1 - x_{AB}^s) \cdot \exp\left(- \frac{\Delta H_{AC}^m}{R} \left[1/T - 1/T_{AC}^m \right] \right) \\ &= (1 - x_{AB}^s) \cdot \exp(f + g/T) = (1 - x_{AB}^s) \cdot V \end{aligned} \qquad (11)$$

where

$$b = -\Delta H^m_{AB}/R \quad , \quad a = -b/T^m_{AB} \quad , \quad g = -\Delta H^m_{AC}/R \quad , \quad \text{and} \quad f = -g/T^m_{AC} \qquad (12)$$

are constants for a given ternary system of the type shown in Fig. 1, while the temperature-dependent variables

$$U = \exp(a + b/T) \quad \text{and} \quad V = \exp(f + g/T) \quad . \qquad (13)$$

Equations (10) and (11) yield the solidus equation for the compound AB

$$1 - x^s_{AB} \cdot U = (1 - x^s_{AB}) \cdot V \quad . \qquad (14)$$

Hence,

$$x^s_{AB} = (1 - V)/(U - V) \quad . \qquad (15)$$

The value of x^s_{AB} can be as small as zero when, according to Eqs. (15) and (13), $V = 1 = \exp(f + g/T)$, i.e., when $T = -g/f = T^m_{AC}$ and $x^l_B = x^s_{AB}/2 = 0$ [Eq. (11)], as expected. The value of x^s_{AB} can also be as large as 1 when $U = 1 = \exp(a + b/T)$ in accordance with Eqs. (15) and (13), i.e., when $T = -b/a = T^m_{AB}$ and $x^l_B = x^s_{AB}/2 = \frac{1}{2}$ [Eq. (10)], also as expected.

Notice that there are no AB or AC compounds in the melt, while in the solid there are only compounds AB and/or AC, but no individual elements A, B, and C. Hence, the thermodynamic molar concentrations x^s_{AB}, x^s_{AC}, x^l_A, x^l_B, x^l_C.

Considering the ternary liquid or solid solutions as a whole, and, without regard to crystallographic lattice arrangements, we can define the chemical molar concentrations m_A, m_B, and m_C. Evidently,

$$\left.\begin{aligned} & m_A^s = m_A^l = \tfrac{1}{2} \quad , \\ & m_B^l + m_C^l = m_B^s + m_C^s = \tfrac{1}{2} \quad , \\ & m_B^l = x_B^l \quad , \quad \text{and} \\ & m_B^s = \tfrac{1}{2}\, x_{AB}^s \quad . \end{aligned}\right\} \qquad (16)$$

THE NORMAL FREEZING EQUATION

We can now balance the amount of component B in the remaining liquid by its chemical molar concentrations m_B^l and m_B^s, and then obtain the usual differential equation for normal freezing (Refs. 9, 11-13) as follows

$$\frac{dm_B^l}{m_B^l - m_B^s} = \frac{dp}{1 - p} \tag{17}$$

where p is the fraction solidified.

Substituting into the normal freezing differential equation results in

$$-d \ln(1 - p) = \frac{V(b[1 - v] - g[1 - U])}{(1 - U)(1 - V)(1 - V/U)} d(1/T)$$

$$= \left[\frac{\alpha}{(1 - U)} + \frac{\beta}{(1 - V)} + \frac{\gamma}{(1 - V/U)}\right] d(\frac{1}{T})$$

where

$$\left.\begin{aligned} \alpha &= \frac{q}{q - 1} \\ \beta &= \frac{1}{1 - s} \\ \gamma &= \frac{r}{1 - r} \end{aligned}\right\} , \tag{18}$$

and

$$\left.\begin{aligned} q &= \exp(f - ga/b) \\ r &= \exp \frac{ag - bf}{g - b} \\ s &= \exp \frac{bf - ag}{g} \\ U_o &= \exp(f + g/T_o) \\ V_o &= \exp(a + b/T_o) \end{aligned}\right\} , \qquad (19)$$

and

$$p = 1 - \left[\frac{1 - U_o}{1 - U}\right]^{\alpha} \cdot \left[\frac{1 - V_o}{1 - V}\right]^{\beta} \cdot \left[\frac{1 - V_o/U_o}{1 - V/U}\right]^{\gamma} \qquad (20)$$

where T_o is the initial freezing temperature and can be determined from the pseudoliquidus line on substituting for x^l_{AB} the initial melt composition, $x^l_{AB,o} = 2 \cdot x^l_{B,o}$.

THE Ga-Al-As SYSTEM

This ternary system can be considered as a GaAs-AlAs pseudo-binary. In the liquid melt, we have

$$x_A^l = x_{As}^l = m_{As}^l = 0.5$$

$$x_B^l + x_C^l = x_{Ga}^l + x_{Al}^l = m_B^l + m_C^l = m_{Ga}^l + m_{Al}^l = 0.5 \quad .$$

In the GaAs-AlAs mixed crystal, we have

$$x_{GaAs}^s = 2m_{Ga}^s$$

$$x_{AlAs}^s = 2m_{Al}^s$$

$$x_{GaAs}^s + x_{AlAs}^s = 2(m_{Ga}^s + m_{Al}^s) = 1.0 \quad .$$

To determine the phase diagram [i.e., liquidus and solidus, Eqs. (8)-(15)] and, in addition, to compute the normal freezing behavior according to Eqs. (18)-(20), the following four thermodynamic constants are required (Ref. 14 gives the values of these constants):

• Melting point of GaAs	1511 K
• Melting point of AlAs	2013 K
• Heat of formation of GaAs	16.64 Kcal/mol
• Heat of formation of AlAs	22.8 Kcal/mol .

Hence, $a = 5.700$, $b = -11{,}470$, $f = 5.542$, $g = -8{,}374$, $q = 3.983$, $r = 0.1505$, $s = 166.5$, $\alpha = -1.335$, $\beta = 0.1772$, and $\gamma = 1.006$.

Table 1 summarizes the solidification behavior of the Ga-Al-As system, treated as a pseudobinary. The first three columns describe the phase diagram, i.e., the concentration of aluminum in the liquid melt x^{l}_{Al} and that of AlAs in the solid crystal x^{s}_{AlAs} at temperatures from 1720°C down to 1238°C at 20°C intervals. The next two columns, obtained from the first three, show that the segregation coefficient k for Al, i.e., $k_{Al} = x^{s}_{AlAs}/2x^{l}_{Al}$, always exceeds unity while that of Ga, i.e., $k_{Ga} = (1 - x^{s}_{AlAs})/(1 - 2x^{l}_{Al})$, never does so except at 1238°C. Both of these segregation coefficients, however, are widely variable, increasing with decreasing melt temperature, by factors of over 6.3 in the case of k_{Al} and of over 3.7 in the case of k_{Ga}. Thus, for this system, as well as for many others, the linear normal freezing equations (Refs. 1-9) involving constant segregation coefficients are generally not applicable.

These phase diagram data can, of course, be obtained also by means of the equations of Ilegems and Pearson (Ref. 14), or those of Steininger (Ref. 15). The direct computation of the normal freezing data from basic thermodynamic constants, however, appears to have never been attempted or published. By means of Eqs. (18) and (19) of this memorandum, these normal freezing data are calculated and given as the last nine columns. Here, the fraction

Table 1

SOLIDIFICATION OF Ga-Al-As SYSTEMS

T, °C	x_{Al}^{1}	x_{AlAs}^{s}	k_{Al}	k_{Ga}	$x_{Al,o}^{1}$ = 0.05	0.10	0.15	0.20	0.25	0.30	0.35	0.40	0.45
1720	0.4633	0.9808	1.058	0.2617									---
1700	0.4281	0.9607	1.122	0.2731								---	0.4156
1680	0.3946	0.9399	1.191	0.2852				Fraction Solidified, p				0.0809	0.6776
1660	0.3627	0.9181	1.266	0.2982							---	0.4072	0.7921
1640	0.3325	0.8955	1.346	0.3120							0.1805	0.5839	0.8541
1620	0.3038	0.8718	1.435	0.3267						---	0.3935	0.6921	0.8920
1600	0.2767	0.8470	1.530	0.3425						0.2029	0.5349	0.7638	0.9172
1580	0.2510	0.8210	1.635	0.3595					---	0.3728	0.6340	0.8142	0.9348
1560	0.2268	0.7937	1.749	0.3776					0.1904	0.4971	0.7066	0.8510	0.9477
1540	0.2040	0.7649	1.874	0.3972				---	0.3415	0.5910	0.7613	0.8788	0.9575
1520	0.1826	0.7345	2.012	0.4182				0.1470	0.4585	0.6637	0.8037	0.9004	0.9650
1500	0.1624	0.7024	2.162	0.4408			---	0.2926	0.5510	0.7211	0.8372	0.9174	0.9710
1480	0.1436	0.6684	2.328	0.4652			0.0604	0.4096	0.6252	0.7672	0.8642	0.9310	0.9758
1460	0.1259	0.6323	2.510	0.4915			0.2120	0.5049	0.6857	0.8048	0.8861	0.9422	0.9797
1440	0.1095	0.5938	2.712	0.5200		---	0.3369	0.5834	0.7355	0.8357	0.9041	0.9513	0.9829
1420	0.0942	0.5528	2.935	0.5510		0.0641	0.4408	0.6486	0.7769	0.8614	0.9192	0.9590	0.9856
1400	0.0799	0.5089	3.183	0.5845		0.2101	0.5280	0.7034	0.8117	0.8831	0.9318	0.9654	0.9878
1380	0.0668	0.4619	3.458	0.6210		0.3335	0.6018	0.7498	0.8411	0.9013	0.9424	0.9708	0.9897
1360	0.0546	0.4115	3.765	0.6607	---	0.4386	0.6646	0.7892	0.8662	0.9169	0.9515	0.9754	0.9914
1340	0.0435	0.3571	4.108	0.7041	0.0995	0.5289	0.7185	0.8231	0.8877	0.9302	0.9593	0.9793	0.9928
1320	0.0332	0.2985	4.492	0.7515	0.2489	0.6070	0.7652	0.8525	0.9063	0.9418	0.9660	0.9828	0.9940
1300	0.0239	0.2348	4.922	0.8034	0.3801	0.6757	0.8062	0.8782	0.9227	0.9520	0.9720	0.9858	0.9950
1280	0.0153	0.1660	5.407	0.8604	0.4982	0.7375	0.8431	0.9014	0.9374	0.9611	0.9773	0.9885	0.9960
1260	0.0076	0.0909	5.954	0.9232	0.6120	0.7970	0.8787	0.9238	0.9516	0.9699	0.9825	0.9911	0.9969
1240	0.0007	0.0091	6.573	0.9923	0.7782	0.8839	0.9306	0.9564	0.9723	0.9828	0.9900	0.9949	0.9982
1238	0.0000	0.0000	6.643	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000

Basic thermodynamic constants used in the computation:

ΔH_{GaAs} = 16.64 Kcal/mol $\quad$ T_{GaAs} = 1511 K

ΔH_{AlAs} = 22.8 Kcal/mol $\quad$ T_{AlAs} = 2013 K solidified, p, is given as a function of both the melt temperature, T, and the Al concentration in the original liquid melt, $x^{l}_{Al,o}$. The concentration profile can be obtained by plotting the concentration of AlAs in the solid crystal, x^{s}_{AlAs}, against the fraction solidified, p, for the appropriate initial Al concentration in the melt, $x^{l}_{Al,o}$.

OTHER SYSTEMS

Many other ternary systems can also be treated as pseudobinaries. The necessary thermodynamic constants are usually available in the literature. Steininger (Ref. 15), for example, has examined a number of important systems and given the necessary thermodynamic constants required to compute the solidification behaviors and the phase diagrams. These systems include: InAs-GaAs, InSb-InAs, InSb-GaSb, GaSb-AlSb, InSb-AlSb, CdTe-ZnTe, CdTe-CdSe, HgTe-CdTe, GeTe-MnTe, $PbBr_2$-$PbCl_2$, InAs-InP, SnTe-PbTe, PbTe-PbSe, HgTe-HgSe, ZnTe-ZnSe, and HgTe-ZnTe. For the first 13 systems, his calculated solidus curves are in good to excellent agreement with the published experimental values. These systems can, therefore, be considered ideal. One can thus compute with some confidence their normal freezing behaviors according to Eqs. (18)-(20) of this memorandum.

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