λ = heat of vaporization, joules/g.
ρ = density, g./cc.
σ = surface tension, dynes/cm.
μ = pressure, microns of mercury
χ = magnetic susceptibility, ergs/(gauss^2)(g.)

Subscripts

l = liquid
o = under reference conditions
v = vapor

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Thermodynamic Consistency Tests for Solid-Liquid Equilibria

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The technique of testing the validity of phase equilibria by applying thermodynamic consistency tests is highly developed for vapor-liquid equilibria. The application to solid-liquid equilibria, however, has been developed very little. The problems associated with thermodynamic consistency tests are discussed and a new technique for evaluating the validity of experimental data has been developed. Several possible test equations are presented and are applied to test the consistency of three sets of solid-liquid equilibrium data.

The use of thermodynamic consistency tests to evaluate the validity of experimental vapor-liquid equilibrium data is widespread. However, such tests are rarely, if ever, used for testing solid-liquid equilibria. The *need* for consistency tests is even greater for the solid-liquid case, because of the inherent difficulty in obtaining an equilibrium solid phase solution. Annealing times of months at or near the solidus temperature are sometimes required for equilibration of solid solutions.

The specific need for a thermodynamic consistency test arises in data taken by McNeely (3). There is substantial disagreement between data obtained by McNeely and those reported in the literature in the location of the solidus curve for the InSb-GaSb system. When such discrepancies arise in vapor-liquid equilibria, the usual procedure is to resolve the disagreement by testing the data for consistency with one of the forms of the Gibbs-Duhem equation. Usually one set of data will be thermodynamically inconsistent and the conclusion drawn that the data do not represent an equilibrium situation.

A search of the literature revealed no equivalent test of practical applicability for solid-liquid equilibria. The prime difficulty is in the fact that in vapor-liquid equilibria the nature of the vapor phase is sufficiently known that corresponding activities in the liquid phase can be calculated. For solid-liquid equilibria, however, neither phase is known to behave as an ideal solution in advance; thus, the activities of the two phases are not readily calculated. The purpose of this paper is to present a test for thermodynamic consistency in solid-liquid equilibria that surmounts this difficulty.

THEORY

The thermodynamic consistency tests for phase equilibria are generally based on the equation relating an infinitesimal change in free energy as

$$dF = -S_T dT + V_T dp + \Sigma \mu_i dn_i \qquad (1)$$

combined with a recognition that the total free energy of a system is given by $F = \Sigma \mu_i n_i$; thus

$$dF = \Sigma \mu_i dn_i + \Sigma n_i d\mu_i \qquad (2)$$

Equations (1) and (2) combined give

$$\Sigma n_i d\mu_i = - S_T dT + V_T dp$$

or when expressed as molar quantities

$$\Sigma x_i d\mu_i = - SdT + Vdp \tag{3}$$

Activity coefficients are generally defined as

$$\mu_i - \mu_i^{\circ} = RT\ln\gamma_i x_i \tag{4}$$

$$d(\mu_i - \mu_i^{\circ}) = RTd\ln\gamma_i x_i + R\ln\gamma_i x_i dT$$

or

$$(\Sigma x_i \ln\gamma_i x_i)dT + \mathrm{T}\,\Sigma x_i d(\ln\gamma_i x_i) = -\frac{S_M}{R}dT + \frac{V_M}{R}dp \tag{5}$$

Equation (5) is further reduced by recognizing that $\Sigma x_i d\ln x_i = \Sigma dx_i = 0$:

$$(\Sigma x_i \ln\gamma_i x_i)dT + T\,\Sigma x_i d(\ln\gamma_i) = -\frac{S_M}{R}dT + \frac{V_M}{R}dp \tag{6}$$

At this point in the development of vapor-liquid consistency tests, constant temperature and pressure are commonly assumed in deriving the Gibbs-Duhem equations

$$\Sigma x_i d\ln\gamma_i = 0 \tag{7}$$

These assumptions do not create much difficulty in the interpretation of vapor-liquid equilibria, since in most cases the data are isobaric, and, if there is a practical concern over the effect of activity coefficients, the temperature range is small. Vapor-liquid consistency tests do exist where the assumption of constant temperature is not used (*2*, *4*, *5*), these generally being applied at high pressures where the gas phase does not behave ideally.

In solid-liquid equilibria it is usually conceded that pressure has little effect on phase diagrams in the range of practical importance; but the temperature range between melting points is often quite large. Thus, Equation (7) cannot be used. Equation (5), with constant pressure assumed, is valid

$$(\Sigma x_i \ln\gamma_i)dT + T\Sigma x_i d(\ln\gamma_i) = -\frac{S_M}{R}dT \tag{8}$$

A similar equation exists for the liquid phase

$$(\Sigma y_i \ln\Gamma_i y_i)dT + T\Sigma y_i d(\ln\Gamma_i) = -\frac{S_M'}{R}dT \tag{9}$$

For vapor-liquid equilibria the liquid phase activity coefficient can be calculated from

$$\Gamma_i = \frac{\pi z_i \Gamma_i'}{p_i^* y_i} \tag{10}$$

At low pressures Γ_i' is unity. At higher pressures it can be reasonably well estimated except near the critical point. This represents an enormous simplification since the Gibbs equation can be applied directly.

A similar equation to Equation (10) applies to solid-liquid equilibria

$$\gamma_i = \frac{\Gamma_i y_i}{\theta_i x_i} \tag{11}$$

The quantity θ_i is related to the change in free energy of the pure component as the solid temperature is raised to the melting point, the solid melted, and the liquid temperature is lowered to the system temperature. It is defined by

$$RT\ln\theta_i = \Delta F_i^{\circ}$$

where ΔF_i° is evaluated for the changes described. θ_i can be calculated by the equation

$$\theta_i = \exp\left\{\frac{1}{RT}\left[\Delta H_{fi}\left(1 - \frac{T}{T_i^*}\right) + \Delta C_i\left(T - T_i^* - T\ln\frac{T}{T_i^*}\right)\right]\right\}$$

if the heat of fusion ΔH_{fi} is evaluated at the melting point T_i^* and heat capacity difference between liquid and solid phases ΔC_i of the pure component *i* is assumed constant (*1*). The difficulty in using Equation (11) and the Gibbs equation is that neither Γ_i nor γ_i can generally be assumed unity or readily calculated.

One further modification of Equations (8) and (9) is possible, however, by evaluating the entropy of mixing as

$$S_M = S^R + S^E$$

where S^R is the *regular* solution entropy of mixing and S^E is the *excess* entropy of mixing. S^R is known:

$$S^R = - R\Sigma x_i \ln x_i$$

Thus

$$(\Sigma x_i \ln\gamma_i)dT + T\Sigma x_i d\ln\gamma_i - (\Sigma x_i \ln x_i)dT = \frac{-S^E}{R}\mathrm{dT}, \text{ and}$$

$$(\Sigma y_i \ln\Gamma_i y_i)dT + T\Sigma y_i d\ln\Gamma_i - (\Sigma y_i \ln y_i)dT = \frac{-S^{E\prime}}{R}dT \tag{12}$$

But, $\Sigma x_i \ln\gamma_i x_i = \Sigma x_i \ln\gamma_i + \Sigma x_i \ln x_i$; consequently

$$\Sigma x_i \ln\gamma_i dT + T\Sigma x_i d\ln\gamma_i = \frac{-S^E}{R}dT$$

or

$$\Sigma x_i d(T\ln\gamma_i) = \frac{-S^E}{R}dT$$

$$\Sigma y_i d(T\ln\Gamma_i) = \frac{-S^{E\prime}}{R}dT \tag{13}$$

For a regular solution these become

$$\Sigma x_i d(T\ln\gamma_i) = 0 \tag{14}$$

$$\Sigma y_i d(T\ln\Gamma_i) = 0$$

For constant temperature, they become the familiar Gibbs-Duhem equations

$$\Sigma x_i d\ln\gamma_i = 0$$

$$\Sigma y_i d\ln\Gamma_i = 0$$

Although further development of these consistency equations does not require a knowledge of the value of either γ_i or Γ_i, a knowledge of the *form* of the composition variation of *one* of these quantities is essential. Although equally valid consistency tests can be devised with other forms, the development herein assumes a binary system with the liquid phase obeying a Van Laar type of equation

$$\ln\Gamma_1 = A\left(\frac{By_2}{Ay_1 + By_2}\right)^2$$

$$\ln\Gamma_2 = B\left(\frac{Ay_1}{Ay_1 + By_2}\right)^2 \tag{15}$$

Since most, although not all, liquid solutions can be fitted to such equations if *A* and *B* are considered entirely empirical, this assumption does not represent a great restriction. The use of these equations for the liquid phase replaces the liquid phase equation of Equation (13). The solid phase equation can be written

$$\Sigma x_i d\left(T\ln\frac{\Gamma_i y_i}{\theta_i x_i}\right) = \frac{-S^E}{R}dT$$

or

$$\Sigma x_i \left\{ d(T\ln\Gamma_i) + d\left(T\ln\frac{y_i}{\theta_i}\right) - d(T\ln x_i) \right\} = \frac{-S^E}{R}\,dT$$

or

$$\Sigma x_i d(T\ln\Gamma_i) + \Sigma x_i d\left(T\ln\frac{y_i}{\theta_i}\right) - \Sigma x_i d(T\ln x_i) = \frac{-S^E}{R}\,dT \tag{16}$$

But

$$\Sigma x_i d(T\ln x_i) = T\Sigma x_i d\ln x_i + (\Sigma x_i \ln x_i)dT$$
$$= (\Sigma x_i \ln x_i)dT$$

Thus

$$\Sigma x_i d(T\ln\Gamma_i) + \Sigma x_i d\left(T\ln\frac{y_i}{\theta_i}\right) = \left(\frac{-S^E}{R} + \Sigma x_i \ln x_i\right) dT$$

Equation (15) may be differentiated to give

$$d\ln\Gamma_1 = \frac{-2A^2B^2}{(Ay_1 + By_2)^3}\, y_2 dy_1 \tag{18}$$

$$d\ln\Gamma_2 = \frac{-2A^2B^2}{(Ay_1 + By_2)^3}\, y_1 dy_2 \tag{18}$$

From Equation (18), after some simplification

$$\Sigma x_i d\ln\Gamma_i = \frac{2\left(\frac{A}{B}\right)^2 B}{\left(\frac{A}{B}\frac{y_1}{y_2} + 1\right)^3}\,\frac{(y_1 - x_1)}{y_2^3}\,dy_1 \tag{19}$$

From Equation (15)

$$\Sigma x_i \ln\Gamma_i = \frac{B\left(\frac{A}{B}\right)\left\{ x_1 + \frac{A}{B}x_2\left(\frac{y_1}{y_2}\right)^2 \right\}}{\left(\frac{A}{B}\frac{y_1}{y_2} + 1\right)^2} \tag{20}$$

But $\Sigma x_i d(T\ln\Gamma_i) = T\Sigma x_i d\ln\Gamma_i + (\Sigma x_i \ln\Gamma_i)dT$; therefore, Equation (17) becomes

$$\int \frac{2\left(\frac{A}{B}\right)^2 BT\,(y_1 - x_1)}{\left(1 + \frac{A}{B}\frac{y_1}{y_2}\right)^3 y_2^3}\,dy_1 + \int \frac{B\left(\frac{A}{B}\right)\left\{ x_1 + \frac{A}{B}x_2\left(\frac{y_1}{y_2}\right)^2 \right\} dT}{\left(1 + \frac{A}{B}\frac{y_1}{y_2}\right)^2}$$
$$= \int \left(\frac{-S^E}{R} + x_1\ln x_1 + x_2\ln x_1\right) dT - \int x_1 d\left(T\ln\frac{y_1}{\theta_2}\right) - \int x_2 d\left(T\ln\frac{y_2}{\theta_1}\right) \tag{21}$$

where the data are integrated over appropriate corresponding limits. Solving for B

$$B = \frac{\int \left(\frac{-S^E}{R} + x_1\ln x_1 + x_2\ln x_2\right) dT - \int x_1 d\left(T\ln\frac{y_1}{\theta_1}\right) - \int x_2 d\left(T\ln\frac{y_2}{\theta_2}\right)}{2\left(\frac{A}{B}\right)^2 \int \frac{T(y_1 - x_1)}{\left(1 + \frac{A}{B}\frac{y_1}{y_2}\right)^3 y_2^3}\,dy_1 + \frac{A}{B}\int \frac{x_1 + \frac{A}{B}x_2\left(\frac{y_1}{y_2}\right)^2}{\left(1 + \frac{A}{B}\frac{y_1}{y_2}\right)^2}\,dT} \tag{22}$$

Simplifications of Equation (22) are readily made by incorporating various assumptions. A few of these follow

(1) Regular solution in solid phase

$$B = \frac{\int (x_1\ln x_1 + x_2\ln x_2)\, dT - \int x_1 d\left(T\ln\frac{y_1}{\theta_1}\right) - \int x_2 d\left(T\ln\frac{y_2}{\theta_2}\right)}{2\left(\frac{A}{B}\right)^2 \int \frac{T(y_1 - x_1)}{\left(1 + \frac{A}{B}\frac{y_1}{y_2}\right)^3 y_2^3}\,dy_1 + \frac{A}{B}\int \frac{x_1 + \frac{A}{B}x_2\left(\frac{y_1}{y_2}\right)^2}{\left(1 + \frac{A}{B}\frac{y_1}{y_2}\right)^2}\,dT} \tag{23}$$

(2) Regular solution, symmetrical system in liquid phase

$$B = \frac{\int (x_1\ln x_1 + x_2\ln x_2)\, dT - \int x_1 d\left(T\ln\frac{y_1}{\theta_1}\right) - \int x_2 d\left(T\ln\frac{y_2}{\theta_2}\right)}{2\int \frac{T(y_1 - x_1)}{\left(1 + \frac{y_1}{y_2}\right)^3 y_2^3}\,dy_1 + \int \frac{x_1 + x_2\left(\frac{y_1}{y_2}\right)^2}{\left(1 + \frac{y_1}{y_2}\right)^2}\,dT} \tag{24}$$

(3) Constant temperature

$$B = -\frac{\int x_1 d\ln\frac{y_1}{\theta_1} + \int x_2 d\ln\frac{y_2}{\theta_2}}{2\left(\frac{A}{B}\right)^2 \int \frac{(y_1 - x_1)}{\left(1 + \frac{A}{B}\frac{y_1}{y_2}\right)^3 y_2^3}\,dy_1} \tag{25}$$

(4) Regular solid phase solution, ideal liquid solution

$$\int x_1 d\left(T\ln\frac{y_1}{\theta_1}\right) + \int x_2 d\left(T\ln\frac{y_2}{\theta_2}\right) =$$

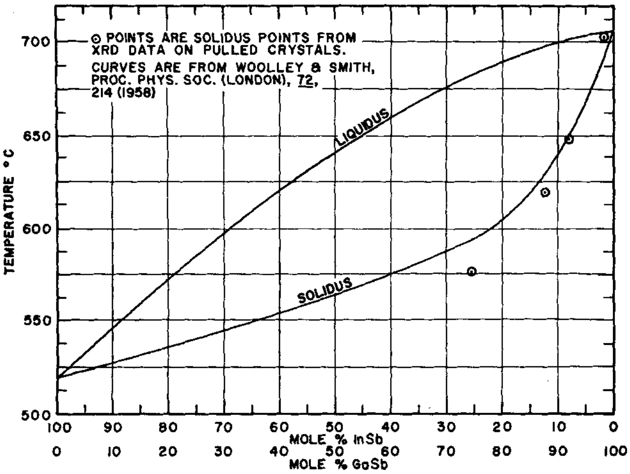

Fig. 1. Phase diagram for InSb-GaSb system.

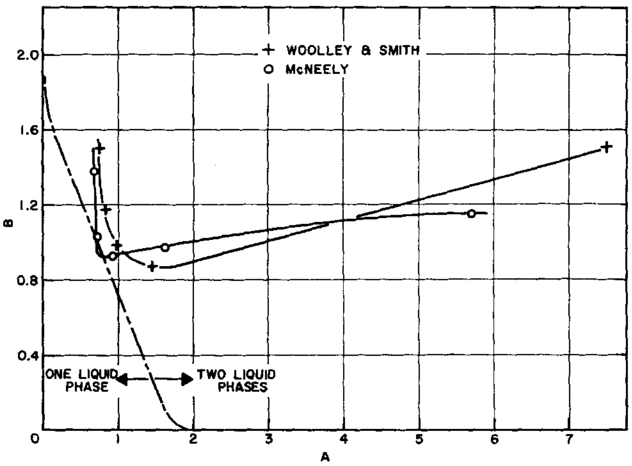

Fig. 2. Consistency test for InSb-GaSb system.

$$\int (x_1 \ln x_1 + x_2 \ln x_2)\, dT \tag{26}$$

(5) Constant temperature, ideal liquid solution

$$\int x_1 d\ln \frac{y_1}{\theta_1} + \int x_2 d\ln \frac{y_2}{\theta_2} = 0 \tag{27}$$

Equations (23) through (27) are all equally valid in terms of common logarithms, provided Equation (15) is expressed in common logarithms. The integrations indicated in Equations (22) through (27) may be made between any set of limits, providing, of course, that the limits of all the integrals correspond as a set.

If the limits of integration are set across the entire composition range of a binary solution (that is from $x_1 = 0$ to $x_1 = 1$), some desirable modifications can be made through integration by parts. In Equations (22), (23), (24), and (26)

$$\int_{x_1=0}^{x_1=1} x_1 d\left(T\ln \frac{y_1}{\theta_1} \right) + \int_{x_1=0}^{x_1=1} x_2 d\left(T\ln \frac{y_2}{\theta_2} \right)$$

$$= \int_0^1 T\ln \frac{y_2\theta_1}{y_1\theta_2}\, dx_1 \tag{28}$$

In Equations (25) and (27)

$$\int_{x_1=0}^{x_1=1} x_1 d\ln \frac{y_1}{\theta_1} + \int_{x_1=0}^{x_1=1} x_2 d\ln \frac{y_2}{\theta_2} = \int_0^1 \ln \frac{y_2\theta_1}{y_1\theta_2}\, dx_1 \tag{29}$$

Equations (22) through (29) show that, unless one may assume an ideal liquid phase solution, testing for thermodynamic consistency is not as straightforward as in vapor-liquid equilibria. One does not obtain a simple yes or no answer to the problem in any of the equations except (26) and (27). What can be obtained is a locus of corresponding values of A and B for which the y-x-T data can be thermodynamically consistent. These values must then be examined to determine whether they are compatible with the type of liquidus obtained.

Two examples of the application of the foregoing thermodynamic consistency tests will now be described.

Table 1. Equilibrium Data Calculated from Sodium Carbonate–Sodium Sulfate Phase Diagram of Gitleson and Motzfeldt

T (°C.)	x_1	y_1	θ_1	θ_2	T (°K.)
884	0.	0.	0.8889	1.	1,157
880	0.028	0.037	0.9042	0.9927	1,153
870	0.090	0.120	0.9461	0.9754	1,143
860	0.150	0.200	0.9907	0.9587	1,133
850	0.222	0.286	1.0382	0.9424	1,123
840	0.316	0.394	1.0885	0.9257	1,113
830	0.478	0.532	1.1416	0.9109	1,103
826	0.622	0.622	1.1640	0.9049	1,099
830	0.800	0.734	1.1416	0.9109	1,103
840	0.910	0.852	1.0885	0.9257	1,113
850	0.963	0.934	1.0382	0.9424	1,123
858	1.	1.	1.	0.9554	1,131

APPLICATION

The first application to be illustrated is the phase diagram for the sodium sulfate–sodium carbonate system reported by Gitleson and Motzfeldt (*1*). Values of heat of fusion and Δc used in Equation (11) are

Component	Heat of fusion, cal./g.-mole	Heat capacity difference, cal./(g.-mole)(°K.)
1. Sodium carbonate	7,300	−2
2. Sodium sulfate	5,670	+ 4.5

Tabulated values of x, y, θ, and T are given in Table 1. Inasmuch as the temperature range of the data is fairly small (58°C.), it seems reasonable to test these data according to Equation (27). The appropriate integrals were evaluated graphically, and, in terms of an arbitrary planimeter count, are

$$\int x_1 d\log \frac{y_1}{\theta_1} = \quad 0.939$$

$$\int x_2 d\log \frac{y_2}{\theta} = -0.856$$

$$\text{Net area} = \quad 0.083$$

Considering the total absolute value of the areas measured, the net area 0.083 justifies the conclusion that these data are consistent thermodynamically.

The data for this system give the simplest type of test, although it should be noted that the system does form an eutectic. Such straightforward applications of the consistency tests are the exception rather than the rule.

The second system to be tested is InSb-GaSb, where the data of Woolley and Smith (*6*) conflict with data of McNeely. Figure 1 shows the phase diagram reported by

TABLE 2. EQUILIBRIUM DATA FOR INSB-GASB SYSTEM

	x_1 (m.f. InSb)				
T (°K.)	McNeely	Woolley & Smith	y_1	θ_1	θ_2
979	0.015	0.003	0.05	0.2568	1.006
930	0.070	0.070	0.409	0.3478	1.393
892	0.120	0.145	0.599	0.4503	1.837
849	0.253	0.373	0.791	0.6201	2.588

TABLE 3. LOCI OF A AND B FOR INSB-GASB SYSTEM

McNeely data		Woolley and Smith data	
A	B	A	B
5.71	1.142	7.49	1.498
1.619	0.973	1.462	0.877
0.924	0.924	0.977	0.977
0.734	1.028	0.834	1.168
0.689	1.379	0.752	1.504

Woolley and Smith with the data of McNeely superimposed. Table 2 lists the x-y-T-θ data for the two sets of points. Heats of fusion of 11.2 kcal./g.-mole and 12 kcal./g.-mole were used for InSb and GaSb, respectively. Since heat capacity data were not available, $\Delta c = 0$ was assumed for both components.

A test by Equation (26) was attempted first, but the values for both sets of data gave strong negative tests. With McNeely's data, over the range of the data

$$\int x_1 d\left(T \log \frac{y_1}{\theta_1}\right) = + \ 4.84°\text{K.}$$

$$\int x_2 d\left(T \log \frac{y_2}{\theta_2}\right) = - \ 34.25°\text{K.}$$

$$\text{Net} = - \ 29.31°\text{K.}$$

$$\int (x_1 \log x_1 + x_2 \log x_2)\ dT = + \ 1.56°\text{K.}$$

These results merely indicate that the liquid phase cannot be an ideal solution and be consistent with the phase data.

The data were then tested by Equation (23). The procedure was to assume a value for A/B, perform the indicated integrations of the data to obtain B, from which a corresponding value of A was then calculated. Base 10 logarithms were used. The values of A and B thus found are given in Table 3.

Figure 1 shows the above data plotted as B vs. A. Also shown in Figure 2 is a locus of B, A values that indicate the formation of two liquid phases. Since the liquidus of Figure 1 indicates a single liquid phase for all compositions, only points lying in the one liquid phase region of Figure 2 are valid. The A, B locus of McNeely's data lies partially within the one liquid phase region, whereas the locus from the Woolley and Smith data does not.

The conclusion implied by this test is that, within the limitations of the Van Laar form for the liquid phase, McNeely's data can be consistent with the assumption of a regular solution in the solid phase, whereas those of Woolley and Smith cannot. Beyond this, no further conclusion can be reached without an independent estimation of the entropy of mixing.

CONCLUSION

A set of thermodynamic consistency tests for solid-liquid equilibrium in binary systems, based on reasonable assumptions regarding liquid phase behavior, has been derived.

On application these tests have been shown to be useful in interpreting and choosing between sets of experimental data.

The tests require considerably more judgment in interpretation than do corresponding tests for vapor-liquid equilibria. If the nature of the liquid phase behavior were as well known as is gas phase behavior, however, the tests would be identical.

These tests, through further development and more extensive application, could be valuable tools not only for testing, but also for interpreting, or even predicting, the thermodynamic behavior of solid solutions.

NOTATION

A,B = constants of the Van Laar equation
ΔC_i = difference between liquid and solid phase molal heat capacity of component i
ΔH_{fi} = heat of fusion of component i
F = Gibbs free energy
n_i = number of moles of component i
p_i^* = vapor pressure of component i
p = pressure
R = gas constant
S = molal entropy
S_T = total entropy
S_M = entropy of mixing
S^R = regular solution entropy of mixing
S^E = excess entropy of mixing
T = absolute temperature
T_i^* = melting temperature of component i
V = molal volume
V_T = total volume
V_m = volume change on mixing
x_i = mole fraction component i in solid phase
y_i = mole fraction component i in liquid phase
z_i = mole fraction component i in vapor phase

Greek Letters

γ_i = activity coefficient of component i in the solid phase
Γ_i = activity coefficient of component i in the liquid phase
Γ_i' = product of vapor phase activity coefficient and fugacity ratio of component i
μ_i = chemical potential of component i
θ_i = defined by equation

$$= \exp\left\{\frac{1}{RT}\left[\Delta H_f\left(1 - \frac{T}{T_i^*}\right) + \Delta C_i\left(T - T_i^* - T\ln\frac{T}{T_i^*}\right)\right]\right\}$$

π = total pressure

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