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Review

Thermodynamic properties of regular interstitial solutions

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The thermodynamics of interstitial solutions are conceptually different from the thermodynamics of substitutional solutions because the state corresponding to pure solute is experimentally inaccessible for the interstitial solution. The thermodynamic functions for the ideal and regular interstitial solutions are given and expressions for the critical point, spinodal curve, solvus, two solid-phase equilibrium, and specific heat are derived for the regular interstitial solution.

1. Introduction

The concept of the regular solution has proven to be a useful one for the understanding of substitutional solid solutions because some features of their behaviour can be described by this simple model [1]. In the regular solution model the entropy of mixing is assumed to be ideal and the enthalpy of mixing for a binary substitutional solution is represented by some simple function of the mole fraction of one of the components. Essentially similar treatments have been employed for interstitial solutions without explicitly considering the treatments as regular interstitial solutions, for example, the early model for Pd–H given by Lacher [2]. The regular interstitial solution has been relatively successful for the description of some aspects of metal–H interstitial solutions because the H–H interaction, under free surface conditions, has been shown to arise from elastic interactions which are long-range [3] and may, therefore, be described by mean field theory. If each interstitial H interacts with all of the other interstitial H atoms, the interaction can be described by a dependence upon r^2, where r is the H-to-metal atom concentration ratio, which is similar to the dependence of the enthalpy of mixing upon composition for regular substitutional solutions. The configurational entropy change for H solution is ideal since, in the absence of blocking, one H atom can occupy one interstice. This model can also be referred to as a mean field–small hard core model. Small hard core model implies the absence of blocking whereas large hard core means that, although only one solute can occupy an interstice, the solute can block neighboring interstices for occupation. In the present thermodynamic discussion the model will be referred to as the regular interstitial solution model without specification of the nature of the solute–solute interaction.

The thermodynamic descriptions of interstitial solutions have employed mainly partial thermodynamic properties and a comprehensive, unified thermodynamic treatment, such as is available for substitutional solutions [1, 4, 5], is lacking. The difference between substitutional solutions and interstitial solutions is that in the former solution (binary) either pure component can serve as a reference state since both are physically realizable, but for interstitial solutions the state of pure interstitial solute is not physically realizable. For example, the state corresponding to pure hydrogen is not experimentally accessible for metal–hydrogen interstitial solutions. The purpose of this development is to present the thermodynamic formalism for the regular interstitial solution and

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no attempts will be made to make detailed comparisons of the resulting equations with experimental data. Besides the early work of Lacher [2], the regular interstitial solution model has been employed by many others, for example, Rudman [6] has employed it for metal–H systems and Hillert and Jarl for h c p systems [7]; McLellan [8] has also discussed this approximation. However, as mentioned above, a comprehensive, unified treatment is not available and, due to the great recent interest in interstitial solutions, it seems timely to present this compendium of the thermodynamics of regular interstitial solutions.

2. General aspects of the thermodynamic properties of interstitial solutions

Since the pure solute state is not generally accessible, the logical choice for a standard state for the interstitial solution is at infinite dilution. For this reason, a more convenient choice for the compositional variable is r or θ, where θ is the atom fraction of solute species to interstices (occupied and unoccupied). It is also convenient to express the integral quantities in ways other than per mole of total components. The following treatment will be limited to binary interstitial solutions.

The mole fraction of solute in the lattice of interstitial sites, X_l, will be defined by

$$X_l = \frac{n_I}{n_I + n_V} = \frac{n_I}{\beta n_M} = \frac{r}{\beta} = \theta, \tag{1}$$

where n_I, n_V and n_M are the number of moles of solute atoms in interstices, the number of moles of vacant interstices, and the number of moles of solvent (metal) atoms, respectively, and β is the number of interstices per metal atom. When defined in this manner, $X_l = \theta = 1$ is, in principle, accessible for the interstitial solution and, therefore, this modified definition of mole fraction is more analogous to that for the substitutional solution than would be the usual definition.

Integral thermodynamic parameters will be designated by subscripts which will also be used to designate the species. Some useful integral quantities for the general state function, Y, are:

$$Y_m = \frac{Y}{n_I + n_M}; \tag{2}$$

$$Y_s = \frac{Y}{n_M}; \tag{3}$$

$$Y_i = \frac{Y}{n_I}; \tag{4}$$

$$Y_l = \frac{Y}{\beta n_M}, \tag{5}$$

where m, s, i and l are defined by Equations 2 and 5. These integral quantities are related to each other using Equations 1 to 5 by

$$Y_s = (1 + \beta\theta) Y_m; \tag{6}$$

$$Y_l = \left(\theta + \frac{1}{\beta}\right) Y_m; \tag{7}$$

$$Y_s = \beta Y_l; \tag{8}$$

$$Y_l = \theta Y_i. \tag{9}$$

The following general equations relating the integral and partial molar thermodynamic parameters which will be derived are valid for any thermodynamic state function, Y:

$$Y = n_I Y_I + n_M Y_M, \tag{10}$$

where

$$Y_I = (\partial Y/\partial n_I)_{T,p,n_M}$$

and

$$Y_M = (\partial Y/\partial n_M)_{T,p,n_I},$$

i.e., subscripts in capitals refer to partial molar quantities. When expressed per mole of interstices, Equation 10 becomes

$$Y_l = \theta Y_I + \frac{1}{\beta} Y_M. \tag{11}$$

The Gibbs–Duhem equation is

$$n_I \, dY_I + n_M \, dY_M = 0 \text{ at constant } p, T. \tag{12}$$

$$\int_0^r dY_M = -\int_0^r r \, dY_I \tag{13}$$

and

$$\frac{1}{\beta}\int_0^\theta dY_M = -\left(\theta Y_I - \int_0^\theta Y_I \, d\theta\right), \tag{14}$$

which gives

$$\frac{1}{\beta} Y_M = Y_l(\theta = 0) + \int_0^\theta Y_I \, d\theta - \theta Y_I \tag{15}$$

since $Y_M^0/\beta = Y_l(\theta = 0)$. Substitution of Equation 15 into Equation 11 gives

$$Y_l = Y_l(\theta = 0) + \int_0^\theta Y_I \, d\theta \tag{16}$$

from which it follows that

$$Y_{\mathrm{I}} = (\partial Y_{\mathrm{l}}/\partial\theta)_{T,p,n_{\mathrm{M}}} \tag{17}$$

and

$$\frac{1}{\beta}Y_{\mathrm{M}} = Y_{\mathrm{l}} - \theta(\partial Y_{\mathrm{l}}/\partial\theta)_{T,p,n_{\mathrm{M}}}. \tag{18}$$

Equations 17 and 18 are equivalent to the method of intercepts for evaluating partial molar quantities from integral quantities [1]. In a plot of Y_{l} against θ the tangent intercept if Y_{M} and Y_{I} is obtained from the tangent slope at θ.

The ideal interstitial solution is defined with respect to the ideal partial configurational entropy at a standard pressure p^0 and corresponding volume V^0, that is,

$$S_{\mathrm{I}}^{\mathrm{id}}(p^0, V^0, z_{\mathrm{I}}) = \lim_{z_{\mathrm{I}}\to 0,\, p\to p^0,\, V\to V^0} [S_{\mathrm{I}}(z_{\mathrm{I}}) + R\ln z_{\mathrm{I}}] - R\ln z_{\mathrm{I}}$$

$$= S_{\mathrm{I}}^0 - R\ln z_{\mathrm{I}}, \tag{19}$$

where $z_{\mathrm{I}} = \theta/(1-\theta)$. The corresponding ideal chemical potential is

$$\mu_{\mathrm{I}}^{\mathrm{id}}(p^0, V^0, z_{\mathrm{I}}) = \lim_{z_{\mathrm{I}}\to 0,\, p\to p^0,\, V\to V^0} [\mu_{\mathrm{I}}(z_{\mathrm{I}}) - RT\ln z_{\mathrm{I}}] + RT\ln z_{\mathrm{I}}$$

$$= \mu_{\mathrm{I}}^0 + RT\ln z_{\mathrm{I}}. \tag{20}$$

These definitions are valid under either conditions of constant pressure or constant volume [9]. It follows from Equation 20 that

$$V_{\mathrm{I}}^{\mathrm{id}} = 0, \tag{21}$$

which is consistent with the definition of an ideal solution. From Equation 15,

$$\frac{1}{\beta}S_{\mathrm{M}}^{\mathrm{id}} = \frac{1}{\beta}S_{\mathrm{M}}^0 - R\ln(1-\theta). \tag{22}$$

The integral ideal entropy per mole of interstices is

$$S_{\mathrm{l}}^{\mathrm{id}} = S_{\mathrm{l}}^{0,\mathrm{id}} - R\left[\theta\ln\frac{\theta}{(1-\theta)} + \ln(1-\theta)\right]$$

$$= S_{\mathrm{l}}^{0,\mathrm{id}} - R[\theta\ln\theta + (1-\theta)\ln(1-\theta)]. \tag{23}$$

The ideal chemical potential of the metal is given from Equations 15 and 20 as

$$\frac{1}{\beta}\mu_{\mathrm{M}}^{\mathrm{id}} = \frac{1}{\beta}\mu_{\mathrm{M}}^0 + RT\ln(1-\theta) \tag{24}$$

and the integral free energy, $G_{\mathrm{l}}^{\mathrm{id}}$, is obtained from Equations 11, 20 and 24

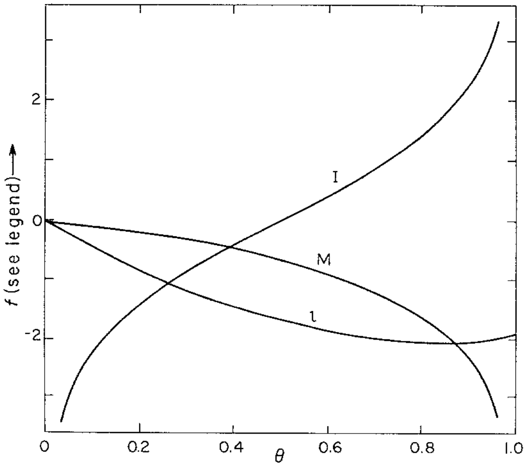

Figure 1 Ideal interstitial solution behaviour: $f = (\mu_{\mathrm{I}}^{\mathrm{id}} - \mu_{\mathrm{I}}^0)/RT$ for Curve I; $f = (\mu_{\mathrm{M}}^{\mathrm{id}} - \mu_{\mathrm{M}}^{\mathrm{id}})/\beta RT$ for Curve M; $f = (G_{\mathrm{l}}^{\mathrm{id}} - G_{\mathrm{l}}^0)/RT$ for Curve l. $G_{\mathrm{l}}^0 = \mu_{\mathrm{I}}^0/RT$ has been chosen as -2 and β has been chosen as 1.

$$G_{\mathrm{l}}^{\mathrm{id}} = \theta\mu_{\mathrm{I}}^{\mathrm{id}} + \frac{1}{\beta}\mu_{\mathrm{M}}^{\mathrm{id}} =$$

$$\left(\theta\mu_{\mathrm{I}}^0 + \frac{1}{\beta}\mu_{\mathrm{M}}^0\right) + RT[\theta\ln\theta + (1-\theta)\ln(1-\theta)]. \tag{25}$$

Fig. 1 shows plots of $(\mu_{\mathrm{I}}^{\mathrm{id}} - \mu_{\mathrm{I}}^0)/RT$, $(\mu_{\mathrm{M}}^{\mathrm{id}} - \mu_{\mathrm{M}}^0)/\beta RT$ and $(G_{\mathrm{l}}^{\mathrm{id}} - G_{\mathrm{l}}^0)/RT$, where $G_{\mathrm{l}}^0 = (1/\beta)\mu_{\mathrm{M}}^0$, and μ_{I}^0/RT has been chosen as -2.

3. The thermodynamics of the regular interstitial solution

For regular binary substitutional solutions the relative enthalpy of mixing is expressed as

$$\Delta H_{\mathrm{mix}} = \lambda X_1(1-X_1), \tag{26}$$

where λ is a constant, X_1 is the mole fraction of one of the components and ΔH_{mix} refers to one mole of solution. This definition for the enthalpic component of the regular substitutional solution results from the consideration of nearest neighbour constant interaction energies of pairing [1]. It follows from Equation 26 that

$$(\partial\Delta H_{\mathrm{mix}}/\partial X_1)_{T,p} = \lambda(1-2X_1), \tag{27}$$

which has the same dependence upon the compositional variable as the following equation,

$$H_{\mathrm{I}} = H_{\mathrm{I}}^0 + \theta H_{\mathrm{II}}, \tag{28}$$

where H_{II} is an interaction enthalpy coefficient. Equation 28 will be used to describe the enthalpic component of the regular interstitial solution.

From Equations 15 and 28

$$\frac{1}{\beta}H_\mathrm{M} = -\frac{\theta^2}{2}H_\mathrm{II} + \frac{H_\mathrm{M}^0}{\beta} \tag{29}$$

is obtained, and, from Equations 16 and 28 this gives

$$H_l = \theta H_\mathrm{I}^0 + \frac{H_\mathrm{M}^0}{\beta} + \frac{\theta^2}{2}H_\mathrm{II}. \tag{30}$$

Equations for the chemical potentials and free energy of the regular interstitial solution can be obtained from the above equations for the enthalpies and from the ideal entropies (Equations 19, 22 and 23)

$$\mu_\mathrm{I} = \mu_\mathrm{I}^0 + \theta H_\mathrm{II} + RT\ln\frac{\theta}{(1-\theta)}, \tag{31}$$

$$\frac{1}{\beta}\mu_\mathrm{M} = \frac{1}{\beta}\mu_\mathrm{M}^0 - \frac{\theta^2}{2}H_\mathrm{II} + RT\ln(1-\theta) \tag{32}$$

and

$$G_l = \left(\theta\mu_\mathrm{I}^0 + \frac{1}{\beta}\mu_\mathrm{M}^0\right) + \frac{\theta^2}{2}H_\mathrm{II} + RT\{\theta\ln\theta + (1-\theta)\ln(1-\theta)\}. \tag{33}$$

Fig. 2 shows plots of $(\mu_\mathrm{I}-\mu_\mathrm{I}^0)/RT$, $(\mu_\mathrm{M}-\mu_\mathrm{M}^0)/\beta RT$ and $(G_l - G_l^0)/RT$, where $G_l^0 = (1/\beta)\mu_\mathrm{M}^0$ and H_II/RT is chosen as -10 and μ_I^0/RT is chosen as -2 with $\beta = 1$. It can be seen that there is an extensive range where phase separation occurs for the solute and this is reflected in values of μ_M which also show an instability range when plotted against θ^{-1}. The rule of equal areas can be employed for $(\mu_\mathrm{I}-\mu_\mathrm{I}^0)/RT$ in order to determine the value of this function for the two-phase coexistence region; alternatively, the rule of equal areas can be used in plots of $(\mu_\mathrm{M}-\mu_\mathrm{M}^0)/RT$ against θ^{-1} to determine the value of this function for the two-phase coexistence region. The phase boundaries may be located, as shown in Fig. 2, by values of θ corresponding to equal tangents to the G_l plot.

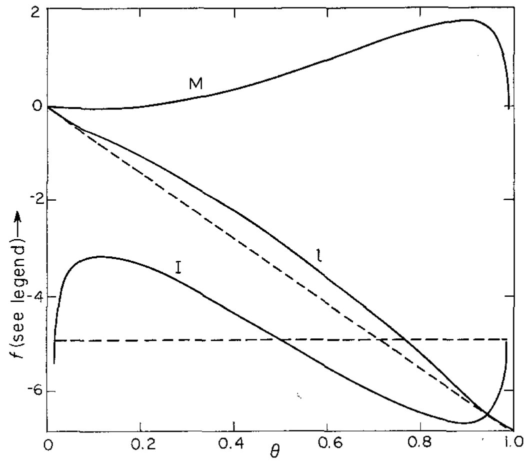

Figure 2 Regular interstitial solution behaviour where: $f = (\mu_\mathrm{I} = \mu_\mathrm{I}^0)/RT$ for Curve I; $f = (\mu_\mathrm{M}-\mu_\mathrm{M}^0)/\beta RT$ for Curve M; $f = (G_l - G_l^0)/RT$ for Curve l. $G_l^0 = \mu_\mathrm{M}^0/\beta$, μ_I^0/RT has been chosen as -2, H_II/RT has been chosen as -10 and β has been chosen as 1. The broken horizontal line has been drawn by the rule of equal areas and its location determined the value of $(\mu_\mathrm{I}-\mu_\mathrm{I}^0)/RT$ for the two-phase coexistence region. The location of the equal tangents to Curve l determines the coexisting phase compositions.

In contrast to some substitutional solutions where ΔV_mix can be zero, for interstitial solutions it is clear that ΔV_l must be finite when solute is "mixed" with metal atoms. It will be assumed in our definition of the regular interstitial solution that the solute has a finite partial molar volume which is independent of θ, i.e., $V_\mathrm{I} = V_\mathrm{I}^0$. From Equation 11, we have

$$V_l = \theta V_\mathrm{I}^0 + \frac{1}{\beta}V_\mathrm{M} \tag{34}$$

or

$$V_\mathrm{s} = rV_\mathrm{I}^0 + V_\mathrm{M}, \tag{35}$$

and it follows from a development analogous to that which leads to Equation 15 that

$$\frac{1}{\beta}V_\mathrm{M} = \frac{1}{\beta}V_\mathrm{M}^0 + \int_0^\theta V_\mathrm{I}^0\,\mathrm{d}\theta - \theta V_\mathrm{I}^0 = \frac{1}{\beta}V_\mathrm{M}^0. \tag{36}$$

Therefore, according to this definition of the regular interstitial solution, where V_I is assumed to be independent of θ, V_M must also be independent of θ. Thus Vegard's law applies if the limiting compositions are considered to be $\theta = 0$ and $\theta = 1$; the latter limit is analogous to a mole fraction of unity for a binary substitutional solution.

3.1. Critical point, spinodal and equation of state for the regular interstitial solution

At the spinodal, $[\partial(\mu_\mathrm{I}/T)/\partial\theta)]_{T_\mathrm{s}} = 0$ and, therefore, from Equation 31

$$[\partial(\mu_{\rm I}/T)/\partial\theta]_{T_{\rm s}} = \frac{H_{\rm II}}{T_{\rm s}} + R\left(\frac{1}{\theta_{\rm s}} + \frac{1}{(1-\theta_{\rm s})}\right)$$

$$= 0 \qquad (37)$$

and, therefore,

$$\frac{H_{\rm II}}{RT_{\rm s}} = -\frac{1}{\theta_{\rm s}(1-\theta_{\rm s})}, \qquad (38)$$

where θ_s as a function of T_s can be obtained by solving Equation 38, that is

$$\theta_{\rm s} = \frac{1}{2} \pm \left[\frac{1}{4} + \frac{RT_{\rm s}}{H_{\rm II}}\right]^{1/2}. \qquad (39)$$

At the critical point,

$$\frac{\partial^2(\mu_{\rm I}/T)}{\partial\theta^2} = 0 = -R\left[\frac{1}{\theta_{\rm c}^2} - \frac{1}{(1-\theta_{\rm c})^2}\right] = 0 \qquad (40)$$

and $\theta_c = \frac{1}{2}$. From Equation 38 at $T_s = T_c$ and $\theta_c = \frac{1}{2}$ we obtain

$$H_{\rm II} = -4RT_{\rm c}. \qquad (41)$$

Substitution of Equation 41 into Equation 39 gives

$$\theta_{\rm s} = \frac{1}{2} \pm \frac{1}{2}\left(1 - \frac{T_{\rm s}}{T_{\rm c}}\right)^{1/2}. \qquad (42)$$

Since both the spinodal and binodal are symmetrical about $\theta = \frac{1}{2}$, it follows that $\theta_a + \theta_b = 1$ where a and b indicate the phase boundaries and $\theta_b > \theta_a$. (Lacher [2] has shown that the binodal must be symmetrical about $\frac{1}{2}$ and it follows from Equation 39 that the spinodal must also be symmetric about $\frac{1}{2}$.) At the binodal the chemical potentials of each component must be equal and, therefore, from Equations 31 and 32 we have

$$\theta_{\rm a}H_{\rm II} + RT\ln(\theta_{\rm a}/(1-\theta_{\rm a}))$$

$$= \theta_{\rm b}H_{\rm II} + RT\ln\theta_{\rm b}/(1-\theta_{\rm b}) \qquad (43)$$

and

$$-\frac{\theta_{\rm a}^2}{2}H_{\rm II} + RT\ln(1-\theta_{\rm a})$$

$$= -\frac{\theta_{\rm b}^2}{2}H_{\rm II} + RT\ln(1-\theta_{\rm b}). \qquad (44)$$

From Equations 43 and 44 we obtain

$$(\theta_{\rm b} - \theta_{\rm a})\frac{H_{\rm II}}{2RT} = \ln(\theta_{\rm a}/\theta_{\rm b}) \qquad (45)$$

and, employing equation 41, gives

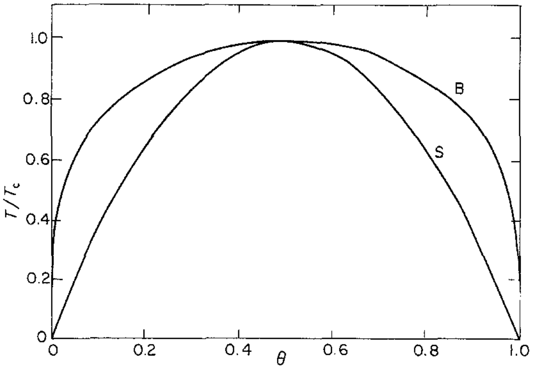

Figure 3 Spinodal and binodal curves for the regular interstitial solution using the same parameters as for Fig. 2. B = binodal curve and S = spinodal curve.

$$T/T_{\rm c} = 2(2\theta_{\rm a} - 1)/\ln[\theta_{\rm a}/(1-\theta_{\rm a})]. \qquad (46)$$

Fig. 3 shows the spinodal curve (Equation 39) and the binodal curve (Equation 46) for the regular interstitial solution.

Equation 45 has been earlier derived by Alefield [10] in a different manner and given in the form

$$M = \tanh(-H_{\rm II}M/4RT), \qquad (47)$$

where M is analogous to an order parameter and is defined as $(\theta_b - \theta_a)$.

3.2. Equation of state of the regular interstitial solute

The equation of state of the regular interstitial solute will be derived; it is first necessary to introduce the specific volume occupied by the interstitial solute which is given by the reciprocal of the lattice ratio,

$$V_{\rm I}^* = \theta^{-1} \qquad (48)$$

Note that V_I^* differs from V_I. The latter is the partial molar volume of the solute in the solution (Equations 34 and 35) and the former is a dimensionless quantity, the reciprocal of the lattice ratio. At constant temperature:

$$d\mu_{\rm I} = V_{\rm I}^*\,dp^* = \theta^{-1}\,dp^*, \qquad (49)$$

where p^* is the "pressure" for the regular interstitial solute and it has units of $\text{J mol}^{-1}\ \text{solute}^{-1}$. This quantity is the three-dimensional analogue of the spreading pressure [11] which has units of J m^{-2}. From Equation 49 we obtain

$$(\partial\mu_\mathrm{I}/\partial\theta)_{T,p} = \frac{1}{\theta}(\partial p^*/\partial\theta)_{T,p}$$
$$= (K^*)^{-1}/\theta^2, \qquad (50)$$

where K^* is the compressibility of the regular interstitial solute. From Equation 31

$$(\partial\mu_\mathrm{I}/\partial\theta)_{T,p} = H_\mathrm{II} + RT\frac{1}{\theta(1-\theta)}$$
$$= \frac{1}{\theta}(\partial p^*/\partial\theta)_{T,p}. \qquad (51)$$

From integration of Equation 51 we obtain an expression for p^*, the equation of state,

$$p^* = \tfrac{1}{2}H_\mathrm{II}\theta^2 - RT\ln(1-\theta). \qquad (52)$$

At small values of θ Equation 52 reduces to an equation of the form of the ideal gas law, and the compressibility from Equations 50 and 51 is

$$(K^*)^{-1} = H_\mathrm{II}\theta^2 + RT\theta/(1-\theta); \qquad (53)$$

as $\theta \to 0$, $K^* \to \infty$ and as $\theta \to 1$, $K^* \to 0$. At T_c, $K^* = 4/H_\mathrm{II}$. An equation similar to Equation 53 has been derived for metal–H systems [12].

From Equation 32 it can be seen that

$$\frac{1}{\beta}(\mu_\mathrm{M} - \mu_\mathrm{M}^0) = -p^*. \qquad (54)$$

Equation 54 also follows from the Gibbs–Duhem relation and Equation 49, that is,

$$\frac{\mathrm{d}\mu_\mathrm{M}}{\beta} = -\theta\,\mathrm{d}\mu_\mathrm{I} = -\mathrm{d}p^*. \qquad (55)$$

The chemical potential of the metal is, therefore, related to the "pressure" of the interstitial solute within the metallic matrix.

3.3. The phase change reaction

With reference to Fig. 2 the phase change represents the appearance of the condensed phase from the dilute phase without addition of solute. This cannot be realized experimentally under isothermal conditions but, nonetheless, the following equations describe such a hypothetical first-order phase transition:

$$\Delta H(\mathrm{a}\to\mathrm{b}) = H_\mathrm{I}^\mathrm{b} - H_\mathrm{I}^\mathrm{a}$$
$$= (\theta_\mathrm{b} - \theta_\mathrm{a})(H_\mathrm{I}^0 + \tfrac{1}{2}H_\mathrm{II}); \qquad (56)$$

$$\Delta S(\mathrm{a}\to\mathrm{b}) = (\theta_\mathrm{b} - \theta_\mathrm{a})S_\mathrm{I}^0; \qquad (57)$$

$$\Delta G(\mathrm{a}\to\mathrm{b}) = (\theta_\mathrm{b} - \theta_\mathrm{a})(H_\mathrm{I}^0 + \tfrac{1}{2}H_\mathrm{II} - TS_\mathrm{I}^0); \qquad (58)$$

and from Equations 34 and 35

$$\Delta V(\mathrm{a}\to\mathrm{b}) = (\theta_\mathrm{b} - \theta_\mathrm{a})V_\mathrm{I}^0. \qquad (59)$$

At the critical point all of these quantities vanish, as expected for a first-order phase transition, but it should be noted that when the phase change occurs *via* reaction with one mole of solute, these quantities do not vanish at the critical point.

The phase change occurs experimentally under isothermal conditions *via* reaction with the pure solute species which is generally a diatomic gas, for example, H_2, O_2 and N_2. The thermodynamics of of the phase change *via* reaction with solute will be illustrated with metal–H_2 systems, but this treatment is applicable to other regular interstitial solutions. The reaction of H_2 to form a hydride phase from the H-saturated solution is represented by

$$\tfrac{1}{2}H_2(\mathrm{g, 1\,atm}) + \frac{MH_\mathrm{a}}{(b-a)} \to \frac{MH_\mathrm{b}}{(b-a)} \qquad (60)$$

This reaction can be written as

$$\Delta G(\tfrac{1}{2}H_2 + \mathrm{a}\to\mathrm{b}) =$$
$$\Delta H(\tfrac{1}{2}H_2 + \mathrm{a}\to\mathrm{b}) - T\Delta S(\tfrac{1}{2}H_2 + \mathrm{a}\to\mathrm{b})$$
$$= RT\ln p_{\mathrm{H}_2}^{1/2}\ \text{(equilibrium)}, \qquad (61)$$

where $\tfrac{1}{2}H_2 + \mathrm{a}\to\mathrm{b}$ represents Reaction 60. For the reactions:

$$M + \frac{a}{2}H_2 \to MH_\mathrm{a} \qquad (62)$$

and

$$M + \frac{b}{2}H_2 \to MH_\mathrm{b} \qquad (63)$$

the free energy changes are $\beta\Delta G_\mathrm{I}^\mathrm{a}$ and $\beta\Delta G_\mathrm{I}^\mathrm{b}$, respectively. By subtracting the free energy change for Reaction 62 from that of Reaction 63, an expression for the free energy change of Reaction 60 can be obtained,

$$\Delta G(\tfrac{1}{2}H_2 + \mathrm{a}\to\mathrm{b}) = \frac{\Delta G_\mathrm{I}^\mathrm{b}}{(\theta_\mathrm{b} - \theta_\mathrm{a})} - \frac{\Delta G_\mathrm{I}^\mathrm{a}}{(\theta_\mathrm{b} - \theta_\mathrm{a})}$$
$$= \frac{1}{(\theta_\mathrm{b} - \theta_\mathrm{a})}\int_{\theta_\mathrm{a}}^{\theta_\mathrm{b}} \Delta G_\mathrm{H}\,\mathrm{d}\theta \qquad (64)$$

and for the enthalpy and entropy changes, from Equations 19 and 28 and Reactions 62 and 63, we have

$$\Delta H(\tfrac{1}{2}H_2 + \mathrm{a} \rightarrow \mathrm{b}) = \frac{1}{(\theta_\mathrm{b} - \theta_\mathrm{a})} \int_{\theta_\mathrm{a}}^{\theta_\mathrm{b}} \Delta H_\mathrm{H}\, \mathrm{d}\theta = \Delta H^0_\mathrm{H} + \tfrac{1}{2} H_\mathrm{HH} \tag{65}$$

and

$$\Delta S(\tfrac{1}{2}H_2 + \mathrm{a} \rightarrow \mathrm{b}) = \frac{1}{(\theta_\mathrm{b} - \theta_\mathrm{a})} \int_{\theta_\mathrm{a}}^{\theta_\mathrm{b}} \Delta S_\mathrm{H}\, \mathrm{d}\theta = \Delta S^0_\mathrm{H}. \tag{66}$$

Aside from the fact that values given in Equations 64 to 66 are relative to $\frac{1}{2}H_2$ (g, 1 atm) and those in Equations 56 to 58 are not, the former differ from the latter only by the multiplicative term $(\theta_\mathrm{b} - \theta_\mathrm{a})^{-1}$, that is, the presence of this term prevents the values in Equations 64 to 66 from going to zero at the critical point. The constancy of values of $\Delta H(\frac{1}{2}H_2 + \mathrm{a} \rightarrow \mathrm{b})$ often observed for metal–H systems over an extended temperature range [6, 13] follows from Equation 65 provided that the change in heat capacity ΔC_p, is nil and provided that the regular interstitial solution is a good approximation for the metal–H system.

For Reaction 60 the change of volume is given by

$$\Delta V(\tfrac{1}{2}H_2 + \mathrm{a} \rightarrow \mathrm{b}) = V^0_\mathrm{H} - \tfrac{1}{2} V^0_{\mathrm{H}_2}\ (1\ \mathrm{atm}, T). \tag{67}$$

3.4. Solvus line for a regular interstitial solution

The solvus line is defined as the line relating the solute concentrations at which a new phase first appears to the temperature. This temperature dependence is described by plots of $\ln a$ versus T^{-1} where a is the r-value for the solute-saturated solution at which the new phase first appears. Experimental data for solvus lines are generally given in terms of a instead of θ_a so this nomenclature will be used here. At equilibrium in the region of coexistence of two condensed phases for a metal–H solution

$$[\mathrm{d}(\Delta\mu_\mathrm{H}/T)/\mathrm{d}(1/T)]_\mathrm{a} = [\mathrm{d}(\Delta\mu_\mathrm{H}/T)/\mathrm{d}(1/T)]_\mathrm{b} = \Delta H(\tfrac{1}{2}H_2 + \mathrm{a} \rightarrow \mathrm{b}), \tag{68}$$

where $\Delta\mu_\mathrm{H}$ is the chemical potential of the solute relative to a standard state of solute removed from the solution. Since the phase compositions are functions of temperature, we can write for the a boundary:

$$\begin{aligned}[\mathrm{d}(\Delta\mu_\mathrm{H}/T)/\mathrm{d}(1/T)]_\mathrm{a} &= [\partial(\Delta\mu_\mathrm{H}/T)/\partial(1/T)]_\mathrm{a} \\ &\quad + [\partial(\Delta\mu_\mathrm{H}/T)/\partial r]_\mathrm{T}\, [\mathrm{d}r/\mathrm{d}(T^{-1})] \\ &= \Delta H(\tfrac{1}{2}H_2 + \mathrm{a} \rightarrow \mathrm{b}).\end{aligned} \tag{69}$$

Since $[\partial(\Delta\mu_\mathrm{H}/T)/\partial(1/T)]_\mathrm{a} = \Delta H_\mathrm{H}$ (at a), we can solve for the solvus line slope

$$-R\,\mathrm{d}\ln a/\mathrm{d}(T^{-1}) = \frac{-\Delta H(\tfrac{1}{2}H_2 + \mathrm{a} \rightarrow \mathrm{b}) + \Delta H_\mathrm{H}\ (\text{at a})}{\frac{a}{R}\,[\partial(\Delta\mu_\mathrm{H}/T)/\partial r]_T} = \Delta H_\mathrm{sol}. \tag{70}$$

It has been shown by the authors [14] that for metal–H systems only in the limit as a → 0 does ΔH_sol correspond to the decomposition of one mole of H in the hydride phase to form one mole of H in the H-saturated metal.

For the regular interstitial solution Equation 70 can be reduced to

$$\Delta H_\mathrm{sol} = \frac{-\Delta H(\tfrac{1}{2}\mathrm{H}_2 + \mathrm{a} \rightarrow \mathrm{b}) + \Delta H^0_\mathrm{H} + H_\mathrm{HH}a/\beta}{\dfrac{\beta}{\beta - a} + \dfrac{H_\mathrm{HH}a/\beta}{RT}} = \frac{H_\mathrm{HH}(\theta_\mathrm{a} - \tfrac{1}{2})}{\dfrac{1}{1-\theta_\mathrm{a}} + \dfrac{H_\mathrm{HH}\theta_\mathrm{a}}{RT}}; \tag{71}$$

in the limit as $\theta_\mathrm{a} \rightarrow 0$ Equation 71 reduces to $-\frac{1}{2}H_\mathrm{HH}$. Thus, in the limit of $\theta_\mathrm{a} \rightarrow 0$ for a regular interstitial solution the enthalpy change for decomposition of one mole of H in the condensed phase to one mole of H in the solute-saturated solution is $-\frac{1}{2}H_\mathrm{HH}$.

Since, at equilibrium the chemical potential of the solute must be equal in the hydride phase and saturated dilute phase, $\Delta G_\mathrm{sol} = 0$. On the other hand, the temperature derivative of a solvus free energy, $\mathrm{d}(\Delta G^\mathrm{E}_\mathrm{sol}/T)/\mathrm{d}T^{-1}$, has been employed to determine ΔH_sol (Equation 70, where, more exactly, $\Delta G^\mathrm{E}_\mathrm{sol} = -RT\ln(a/\beta - a)$ instead of $-RT\ln a$. It can be shown that this is an excess solvus free energy [15].

$$\Delta G^\mathrm{E}_\mathrm{sol} = \Delta G_\mathrm{sol} - \Delta G^\mathrm{id}_\mathrm{sol}, \tag{72}$$

where $\Delta G^\mathrm{id}_\mathrm{sol}$ is the ideal solvus free energy. The expression for $\Delta G^\mathrm{id}_\mathrm{sol}$ can be obtained from the free energy change for the solvus process of decomposition of one mole of H in the hydride phase to one mole of H in the saturated solution. This is obtained from the sum of the free energy changes for the reverse of Reaction 60, $-\Delta\mu_{\mathrm{H}}^{0}$, where this value results from Equations 65 and 66, because the H_{HH} term is omitted for the ideal change, and from Equation 20, i.e., $\Delta\mu_{\mathrm{H}}^{0} + RT \ln Z_{\mathrm{H}}$, where $Z_{\mathrm{H}} = a/\beta$ as $a \to 0$. Therefore,

$$\Delta G_{\mathrm{sol}}^{\mathrm{E}} = -RT \ln a/\beta. \qquad (73)$$

The excess solvus entropy is given by differentiation of Equation 73 with respect to temperature:

$$\begin{aligned} -(\partial \Delta G_{\mathrm{sol}}^{\mathrm{E}}/\partial T)_p &= \Delta S_{\mathrm{sol}}^{\mathrm{E}} \\ &= R \ln a/\beta + RT(\partial \ln a/\partial T)_p \\ &= R \ln a/\beta + \Delta H_{\mathrm{sol}}/T. \qquad (74) \end{aligned}$$

For the regular interstitial solution, $\Delta H_{\mathrm{sol}}/T = -H_{\mathrm{HH}}/2T$ (from Equation 71) and from Equation 45, $H_{\mathrm{HH}}/2T = R \ln a/\beta$ in the limit as $a \to 0$. Therefore, $\Delta S_{\mathrm{sol}}^{\mathrm{E}} = 0$ (as $a \to 0$) for the regular interstitial solution.

It can also be shown for the regular interstitial solution that $\Delta V_{\mathrm{sol}} = 0$. This follows from Equations 34 to 36 and from the definition of the solvus process. This result leads to the conclusion that there should be no effect of a uniform hydrostatic stress on the solvus composition for a regular interstitial solution [16].

3.5. Formation of stoichiometric hydrides

Standard thermodynamic quantities for hydride (stoichiometric) formation refer to the reaction:

$$\begin{aligned} &M\,(\text{pure}) + \frac{b}{2}\mathrm{H}_2\ (\mathrm{g, 1\ atm}) \\ &\quad = MH_{\mathrm{b}};\ \text{where } b \text{ is an integer.} \qquad (75) \end{aligned}$$

From the two reactions

$$\begin{aligned} &\frac{1}{(b-a)}MH_{\mathrm{a}} + \tfrac{1}{2}\mathrm{H}_2\ (\mathrm{g, 1\ atm}) \\ &= \frac{1}{(b-a)}MH_{\mathrm{b}}\ (b \text{ is an integer});\ \Delta H(\tfrac{1}{2}\mathrm{H}_2 + \mathrm{a} \to \mathrm{b}) \qquad (76) \end{aligned}$$

and

$$M(r = 0) + \frac{a}{2}\mathrm{H}_2\ (\mathrm{g, 1\ atm}) = MH_{\mathrm{a}};\ \Delta H_{\mathrm{s}}^{\mathrm{a}}, \qquad (77)$$

where a is not an integer. We can derive an expression for $\Delta H_{\mathrm{f}}(MH_{\mathrm{b}})$ as follows:

$$\Delta H_{\mathrm{f}}^{0}(MH_{\mathrm{b}}) = (b-a)\,\Delta H(\tfrac{1}{2}\mathrm{H}_2 + \mathrm{a} \to \mathrm{b}) + \Delta H_{\mathrm{s}}^{\mathrm{a}}. \qquad (78)$$

For the regular interstitial solution using Equation 65 and the relation

$$\Delta H_{\mathrm{s}}^{\mathrm{a}} = \int_0^{\mathrm{a}} \Delta H_{\mathrm{H}}\,\mathrm{d}r = a\Delta H_{\mathrm{H}}^{0} + \frac{a^2}{2}\frac{H_{\mathrm{HH}}}{\beta} \qquad (79)$$

we obtain for $\Delta H_{\mathrm{f}}^{0}(MH_{\mathrm{b}})$

$$\begin{aligned} \Delta H_{\mathrm{f}}^{0}(MH_{\mathrm{b}}) &= b\Delta H_{\mathrm{H}}^{0} + \frac{H_{\mathrm{HH}}}{2}\left[a\left(\frac{a}{\beta} - a\right) + b\right] \\ &= (b-a)\,\Delta H(\tfrac{1}{2}\mathrm{H}_2\ \mathrm{a} \to \mathrm{b}) + a\Delta H_{\mathrm{H}}^{0} + \frac{a^2}{2}\frac{H_{\mathrm{HH}}}{\beta}; \qquad (80) \end{aligned}$$

when $a \to 0$, $\Delta H_{\mathrm{f}}^{0} = b\Delta H_{\mathrm{H}}^{0} + (b/2)H_{\mathrm{HH}} = b\Delta H(\tfrac{1}{2}\mathrm{H}_2 + \mathrm{a} \to \mathrm{b})$. In order to evaluate $\Delta H_{\mathrm{f}}^{0}$, therefore, values for the thermodynamic parameters near $r \to 0$ are needed, that is values of $\Delta H_{\mathrm{H}}^{0}$ and H_{HH}. Alternatively, $\Delta H_{\mathrm{f}}^{0}$ values can be expressed in terms of the solvus using Equations 71 and 78 to eliminate $\Delta H_{\mathrm{a} \to \mathrm{b}}$,

$$\begin{aligned} \Delta H_{\mathrm{f}}^{0} &= b\Delta H_{\mathrm{H}}^{0} + \left(ab - \frac{a^2}{2}\right)\frac{H_{\mathrm{HH}}}{\beta} - (b-a)\frac{aH_{\mathrm{HH}}}{\beta RT} \\ &\quad + \frac{\beta}{\beta - a}\,\Delta H_{\mathrm{sol}}; \qquad (81) \end{aligned}$$

when $a \to 0$,

$$\Delta H_{\mathrm{f}}^{0} = b(\Delta H_{\mathrm{H}}^{0} - \Delta H_{\mathrm{sol}}). \qquad (82)$$

In the limit as $a \to 0$, H_{HH} is not required; only ΔH_{sol} and $\Delta H_{\mathrm{H}}^{0}$ are needed.

3.6. Specific heat for a two-(condensed) phase regular interstitial solution

Equation 30 gives the integral enthalpy which can be written for a two-condensed phase coexistence region as

$$H_1 = \frac{\theta_{\mathrm{b}} - \theta}{\theta_{\mathrm{b}} - \theta_{\mathrm{a}}} H_1^{\mathrm{a}} + \frac{\theta - \theta_{\mathrm{a}}}{\theta_{\mathrm{b}} - \theta_{\mathrm{a}}} H_1^{\mathrm{b}}, \qquad (83)$$

where the coefficients in front of the enthalpy terms are the fractions of the solution in the two phases and $\theta = \theta_{\mathrm{a}} + \theta_{\mathrm{b}}$. Equation 83 can be rewritten for the regular interstitial solution using Equation 30 so that

$$H_1 = \theta H_{\mathrm{I}}^{0} + \frac{H_{\mathrm{M}}^{0}}{\beta} + \frac{H_{\mathrm{II}}}{2}\left[\theta - \theta_{\mathrm{a}}(1 - \theta_{\mathrm{a}})\right] \qquad (84)$$

and

$$H_1^c = H_1 - \theta\left(H_I^0 - \frac{\theta}{2}H_{II}\right) - \frac{H_M^0}{\beta}$$

$$= \frac{H_{II}}{2}\,[\theta(1-\theta) - \theta_a(1-\theta_a)], \quad (85)$$

where it can be seen that H_1^c is defined as the enthalpy arising from the coexistence of the two phases, that is, the enthalpy difference between a two-phase mixture at overall solute content θ and the enthalpy of a single phase of the same content. The excess heat capacity corresponding to H_1^c, is given by

$$C_1^c = \mathrm{d}H_1^c/\mathrm{d}T = \frac{H_{II}}{2}(2\theta_a - 1)\frac{\mathrm{d}\theta_a}{\mathrm{d}T}$$

$$= \frac{H_{II}}{2T_c}(2\theta_a - 1)\frac{\mathrm{d}\theta_a}{\mathrm{d}(T/T_c)}$$

$$= -2R(2\theta_a - 1)[\mathrm{d}\theta_a/\mathrm{d}(T/T_c)]. \quad (86)$$

Using Equation 46 to evaluate $\mathrm{d}\theta_a/\mathrm{d}(T/T_c)$ we obtain

$$C_1^c/R = \frac{-4(2\theta_a - 1)^2\theta_a(1-\theta_a)(T_c/T)^2}{4\theta_a(1-\theta_a)(T_c/T) - 1}$$

$$= \frac{-M^2(1-M^2)(T_c/T)^2}{(1-M^2)(T_c/T) - 1}, \quad (87)$$

where $M = 2\theta_a - 1$ and from Equation 9, $C_i^c = C_1^c/\theta$ where C_i^c is the heat capacity arising from the existence of the two phases per mole of solute. Fig. 4 shows a plot of C_1^c/R against T/T_c for $\theta = \frac{1}{2}$, (for the regular interstitial solution $\theta = 1$, but for real systems it can be less than 1).

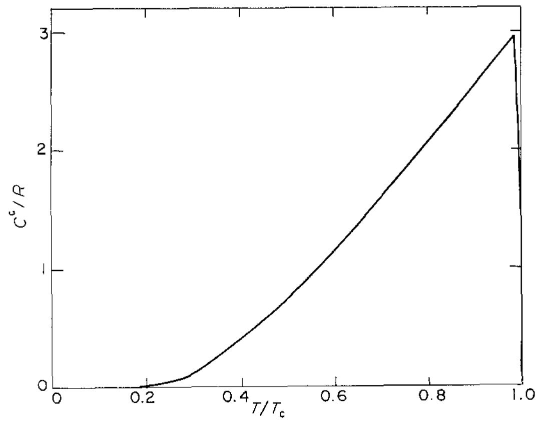

Figure 4 Excess heat capacity arising from the coexistence of two phases employing Equation 85.

When values of C for solid–H systems are considered for the two-phase coexistence region this effect should be allowed for but most workers have not done so, for example, see Nace and Aston [17]; however, recently, Heibel *et al.* [18] have derived an equation similar to Equation 87 in order to explain two-phase heat capacity data for Nb–H.

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