Exercises on Ch.20 *Mathematical modelling of solution phases*

20.4 *Empirical approach to substitutional solutions*

Exercise 20.4.1

It has been suggested that the temperature dependence of the regular solution parameter L should be described with $A + B/T$ instead of $a + bT$ because the latter expression may make L change sign at some high temperature which is claimed to be unrealistic. Of course, the same objection can be raised against the new suggestion because it may change sign at some low temperature. Anyway, accept the new suggestion and evaluate the enthalpy and entropy parts of L.

Hint

Write $L = L_H - L_s T$.

Solution

By definition $L_s = -\partial L/\partial T = B/T^2$ and $L_H = \partial(L/T)/\partial(1/T) = A + 2B/T$.

Exercise 20.4.2

The Fe–Cr phase diagram has a two-phase region γ(fcc) + α(bcc) which cannot be described by applying the thermodynamics for dilute solutions because it has a minimum (at about 1123 K). Try to explain this behavior with the regular solution model. At the same time evaluate the 'lattice stability' of fcc-Cr as a function linear in T, i.e. ${}^oG^{\gamma}_{Cr} - {}^oG^{\alpha}_{Cr} = a + bT$. The quantity ${}^oG^{\gamma}_{Fe} - {}^oG^{\alpha}_{Fe}$ is known and is tabulated here together with information on the γ + α region. The tabulated compositions are taken in the middle of γ + α where one may assume that γ and α have the same Gibbs energy.

T(K)	x^{α}_{Cr}	${}^oG^{\gamma}_{Fe} - {}^oG^{\alpha}_{Fe} (J/mol)$
1170	0.012	10.54
1170	0.121	10.54
1600	0.057	– 30.12

Hint

From the table we get three conditions through $G^{\alpha}_m = G^{\gamma}_m$. Two parameters are already defined, a and b. Let the third one be $L^{\gamma} - L^{\alpha}$.

Solution

For each phase $G_m = x_{Fe}{}^oG_{Fe} + x_{Cr}{}^oG_{Cr} - TS^{ideal}_m + x_{Fe}x_{Cr}L$. At $x^{\alpha}_{Cr} = x^{\gamma}_{Cr} = x^{o}_{Cr}$ where $G^{\alpha}_m = G^{\gamma}_m$ we have $0 = x^o_{Fe}({}^oG^{\gamma}_{Fe} - {}^oG^{\alpha}_{Fe}) + x^o_{Cr}({}^oG^{\gamma}_{Cr} - {}^oG^{\alpha}_{Cr}) + x^o_{Fe}x^o_{Cr}(L^{\gamma} - L^{\alpha})$. The data in the table will give:

$0.988 \cdot 10.54 + 0.012(a + 1170b) + 0.988 \cdot 0.012(L^{\gamma} - L^{\alpha}) = 0;$
$0.879 \cdot 10.54 + 0.121(a + 1170b) + 0.879 \cdot 0.121(L^{\gamma} - L^{\alpha}) = 0;$
$0.943 \cdot (-30.12) + 0.057(a + 1600b) + 0.943 \cdot 0.057(L^{\gamma} - L^{\alpha}) = 0;$.

We find ${}^oG^{\gamma}_{Cr} - {}^oG^{\alpha}_{Cr} = a + bT = 3476 + 2.417T (J/mol); L^{\gamma} - L^{\alpha} (J/mol)$.

Exercise 20.4.3

For a binary solution with a constant positive L in $G_m = x_A{}^{\circ}G_A + x_B{}^{\circ}G_B + RT(x_A \ln x_A + x_B \ln x_B) + Lx_Ax_B$ there will be a symmetric miscibility gap. Show that close to the critical point the width of the gap is $\sqrt{3}$ times the width of the spinodal curve according to our model.

Hint

We have seen that the spinodal curve for a symmetric system is described by $x_Ax_B = T/4T_{crit} = RT/2L$. Let Δx be the width of the spinodal. For symmetry reasons $x'_B = (1 - \Delta x)/2; x''_B = (1 + \Delta x)/2$ and Δx can be expressed in terms of $(T_{crit} - T)/T_{crit}$. Derive a similar equation for the binodal curve using the condition that dG_m/dx_B should have the same value for the phases in equilibrium, i.e. for $x_B^{'} = (1-\Delta x)/2$ and for $x_B^{''} = (1+\Delta x)/2$. Then introduce the approximation ln(1 + Δx) = Δx – Δx^2/2 + Δx^3/3.

Solution

Spinodal: $T/T_{\text{crit}} = 4(1 + \Delta x)(1 - \Delta x)/4 = 1 - \Delta x^2$; $\Delta x^2 = (T_{\text{crit}} - T)/T_{\text{crit}}$.
Binodal: $\mathrm{d}G_{\text{m}}/\mathrm{d}x_{\text{B}} = -{}^{\circ}G_{\text{A}} + {}^{\circ}G_{\text{B}} + RT\ln(x_{\text{B}}/x_{\text{A}}) + L(x_{\text{A}} - x_{\text{B}})$ should have the same value on both sides: $RT\ln[(1 - \Delta x)/(1 + \Delta x)] + L(1 + \Delta x - 1 + \Delta x)/2 = RT\ln[(1 + \Delta x)/(1 - \Delta x)] + L(1 - \Delta x - 1 - \Delta x)/2$. This gives $RT(-\Delta x + \Delta x^2/2 - \Delta x^3/3 - \Delta x - \Delta x^2/2 - \Delta x^3/3) + L\Delta x \cong RT(\Delta x - \Delta x^2/2 + \Delta x^3/3 + \Delta x + \Delta x^2/2 + \Delta\, x^3/3) - L\Delta x$ and $1 + \Delta x^2/3 = L/2RT = T_{\text{cons}}/T$; $\Delta x^2 = 3[(T_{\text{crit}}/T) - 1] = 3(T_{\text{crit}} - T)/T \cong 3(T_{\text{crit}} - T)/T_{\text{crit}}$.

20.5 *Real solutions*

Exercise 20.5.1

Show that for a multicomponent solution $\partial\ln f_{\text{j}}/\partial x_{\text{i}} - \Sigma x_{\text{k}}\partial\ln f_{\text{j}}/\partial x_{\text{k}} = \partial\ln f_{\text{i}}/\partial x_{\text{j}} - \Sigma x_{\text{k}}\partial\ln f_{\text{i}}/\partial x_{\text{k}}$.

Hint

From Exercise 20.3 we know that $\partial^{\text{E}}G_{\text{j}}/\partial N_{\text{i}} = \partial^{\text{E}}G_{\text{i}}/\partial N_{\text{j}}$ and thus $\partial\ln f_{\text{j}}/\partial N_{\text{i}} = \partial\ln f_{\text{i}}/\partial N_{\text{j}}$. Now consider $\ln f_{\text{i}}$ and $\ln f_{\text{j}}$ as functions of x_{i}, etc., and remember that $\partial x_{\text{i}}/\partial N_{\text{i}} = (1 - x_{\text{i}})/N$ and $\partial x_{\text{i}}/\partial N_{\text{j}} = -x_{\text{i}}/N$.

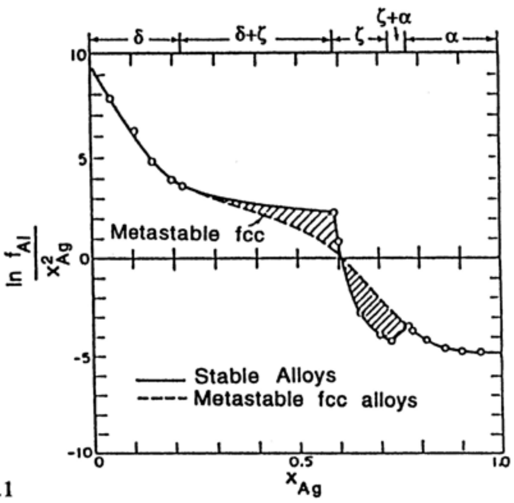
Solution

$\partial \ln f_j / \partial N_i = (\partial \ln f_j / \partial x_i)\cdot(1-x_i)/N + \sum\limits_{k\neq i}(\partial \ln f_j / \partial x_k)\cdot(1-x_k)/N = (\partial \ln f_j / \partial x_i - \Sigma x_k \partial \ln f_j / \partial x_k)/N$; $\partial \ln f_i / \partial N_j = (\partial \ln f_i / \partial x_j - \Sigma x_k \partial \ln f_i / \partial x_k)/N$. The two right-hand sides must be equal because the two left-hand sides are.

20.6 Applications of the Gibbs–Duhem relation

Exercise 20.6.1

The diagram shows experimental values of a_{Al} in A1–Ag alloys, represented through the quantity $\ln f_{Al} / x_{Ag}^2$ Accept that he solid line represents a reasonable curve across the whole system. Both Al and Ag are fcc and one can imagine a gradual change of this phase from pure Al to pure Ag provided that the ζ phase can be prevented. A corresponding curve (dashed line) has been drawn tentatively but obeying the rule that the two shaded areas must be equal. Prove that rule.



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Hint

Imagine that $^{E}G_m$ for an alloy with a low value of x_{Ag} is calculated from $\ln f_{Al}$ by integration from pure Ag, following two different routes in the middle of the system.

Solution

$^{E}G_m / RT = x_{Ag} \ln f_{Ag} + x_{Al} \ln f_{Al} = x_{Ag} \int (\ln f_{Al} / x_{Ag}^2) dx_{Al}$. The integral represents the area under the curve one follows on integration. The difference between the two shaded areas represents the difference in integrated area if we follow the two different paths. In order to yield the same result after crossing the two-phase field, the two shaded areas must be equal.

Exercise 20.6.2

Derive Raoult's law from Henry's law for a binary solution. Then examine if one can go the other way.

Hint

We assume that f_2 is constant and thus $d\ln f_2/dx_2 = 0$ from $x_2 = 0$ up to some small value.

Solution

When calculating $\ln f_1$ by integration of Eq. 20.46 we find that the integrand is zero. Thus $\ln f_1 = 0$ and $f_1 = 1$ in agreement with Raoult's law. On the other hand, if we start with Raoult's law, $f_1 = 1$, then $d\ln f_1/dx_1 = 0$ but when calculating $\ln f_2$ by integration we now find that the integrand is indeterminate, $(d\ln f_1/dx_1)/x_2 = 0/0$. It is not possible to predict the slope of the line representing Henry's law.

Exercise 20.6.3

Show that for a binary solution phase

$$2\frac{d\ln f_B}{d(x_A^2)} = 2\frac{d\ln f_A}{d(x_B^2)} = \frac{d\ln(f_B/f_A)}{dx_A} = \frac{-1}{RT}\cdot\frac{d^2\,{}^EG_m}{dx_A^2}$$

Hint

Take the derivative of ${}^{E}G_{m} = x_{A}{}^{E}G_{A} + x_{B}{}^{E}G_{B}$ remembering $x_A + x_B = 1$ and using ${}^{E}G_j = RT\ln f_j$ from Eq. 7.16.

Solution

$d^{E}G_{m}/dx_{A} = {}^{E}G_{A} - {}^{E}G_{B} = RT\ln(f_A/f_B)$ since $\Sigma x_i d^{E}G_i = 0$. Thus we get, by again using the Gibbs–Duhem relation, $(-1/RT)\cdot d^2\,{}^{E}G_m/dx_A^2 = -d\ln(f_A/f_B)/dx_A$ $= -(d\ln f_A - d\ln f_B)/dx_A = -[d\ln f_A + (x_A/x_B)d\ln f_A]/dx_A = -(1/x_B)d\ln f_A/dx_A$ $= 2d\ln f_A/d(x_B^2)$.

20.7 *Dilute solution approximations*

Exercise 20.7.1

In the ε formalism we may define ε_B^C as $\partial^{E}G_B/\partial x_C$ and ε_C^B as $\partial^{E}G_C/\partial x_B$. Examine a ternary system. Under what conditions would we have $\varepsilon_B^C = \varepsilon_C^B$?

Hint

First apply the Gibbs–Duhem relation for excess quantities to variations in x_B and take the derivative with respect to x_C. Then do it the other way and compare the results. Notice that x_A must be replaced by $1 - x_B - x_C$.

Solution

Gibbs–Duhem in this form $(1 - x_B - x_C)\partial^{E}G_A/\partial x_B + x_B\partial^{E}G_B/\partial x_B + x_C\partial^{E}G_C/\partial x_B = 0$ would give us $(1 - x_B - x_C)\partial^{2E}G_A/\partial x_B\partial x_C - \partial^{E}G_A/\partial x_B + x_B\partial^{2E}G_B/\partial x_B\partial x_C + \partial^{E}G_C/\partial x_B + x_C\partial^{2E}G_C/\partial x_B\partial x_C = 0$. Gibbs–Duhem in this form $(1 - x_B - x_C)\partial^{E}G_A/\partial x_C + x_B\partial^{E}G_B/\partial x_C + x_C\partial^{E}G_C/\partial x_C = 0$ would give us $(1 - x_B - x_C)\partial^{2E}G_A/\partial x_C\partial x_B - \partial^{E}G_A/\partial x_C + x_B\partial^{2E}G_B/\partial x_C\partial x_B + \partial^{E}G_B/\partial x_C + x_C\partial^{2E}G_C/\partial x_C\partial x_B = 0$. From the difference we obtain $\partial({}^{E}G_C - {}^{E}G_A)/\partial x_B = \partial({}^{E}G_B - {}^{E}G_A)\partial x_C$. It is thus necessary to have $\partial^{E}G_A/\partial x_B = \partial^{E}G_A/\partial x_C$. This is fulfilled in the ε formalism because these derivatives are both zero. It is not fulfilled in the quadratic formalism. We may conclude that $\varepsilon_B^C = \varepsilon_C^B$ holds for dilute solutions only.

Exercise 20.7.2

Show for a ternary system under what conditions $RT\varepsilon_B^C = g_{BC}$, which is a notation for $\partial^2 G_m/\partial x_B \partial x_C$.

Hint

From the definition of ε_B^C we have $RT\varepsilon_B^C = \partial G_B / \partial x_C$ which can be calculated from $G_B = G_m + (1 - x_B)\partial G_m/\partial x_B - x_C \partial G_m/\partial x_C$ where G_m is regarded as a function of x_B and x_C.

Solution

$RT\varepsilon_B^C = \partial G_B / \partial x_C = \partial G_m / \partial x_C + (1 - x_B)\partial^2 G_m / \partial x_B \partial x_C - \partial G_m / \partial x_C - x_C \partial^2 G_m / \partial x_C^2$ $= \partial^2 G_m / \partial x_B \partial x_C - x_B \partial^2 G_m / \partial x_B \partial x_C - x_C \partial^2 G_m / \partial x_C^2$. The second term may be neglected at small x_B but for convenience we shall keep the part which comes from the ideal entropy of mixing, RTx_B/x_A. The third term may be approximated by the part coming from the ideal entropy of mixing $RTx_C(1/x_A + 1/x_C)$. We obtain $RT\varepsilon_B^C = \partial G_m / \partial x_B \partial x_C - RT / x_A$. The last term is approximately $-RT$ and it can be neglected only when $\left|\varepsilon_B^C\right| >> 1$.

20.8 *Predictions for solutions in higher-order system*

Exercise 20.8.1

Suppose the properties of a certain solution phase are known in the binary systems A–B, B–C and C–A. When the ternary parameter I_{ABC} was evaluated from some ternary information one found that it was practically zero. In that assessment one described the binary A–B properties with an expression $x_A x_B({}^0L_B + {}^1L_B x_B)$. Suppose that the assessment is repeated using an expression $x_A x_B({}^0L_A + {}^1L_A x_A)$. What value would one then obtain for the ternary parameter?

Hint

We must suppose that the two binary expressions are identical in the binary case, ${}^0L_B + {}^1L_B(1 - x_A) = {}^0L_A + {}^1L_A x_A$. Thus,${}^0L_A = {}^0L_B + {}^1L_B$ and ${}^1L_A = -\,{}^1L_B$.

Solution

Omit all terms from B–C and C–A because they are the same in both cases. The result of the second assessment is written in the form:

$x_A x_B({}^0L_A + {}^1L_A x_A) + x_A x_B x_C I_{ABC}$. By the use of $x_B = 1 - x_A - x_C$, transform the result of the first assessment to this form: $x_B x_B({}^0L_B + {}^1L_B x_B) = x_A x_B({}^0L_B + {}^1L_B - {}^1L_B x_C) = x_A x_B({}^0L_B + {}^1L_B - {}^1L_B x_A)$ a+ $x_A x_B x_C(-\,{}^1L_B)$. Comparison gives ${}^0L_A = {}^0L_B + {}^1L_B$ and ${}^1L_A = -\,{}^1L_B$ which we knew before but we also find $I_{ABC} = -\,{}^1L_B$.

20.9 *Numerical methods of predictions for higher-order systems*

Exercise 20.9.1

Prove that Muggianu's method for a ternary system correctly reproduces a term written in the form $x_i x_j (x_i - x_j)^k \cdot {}^k L_{ij}$ in the binary *ij* system.

Hint

Start by evaluating the value of ${}^E G_m^{ij}$ for the binary alloy used in the method. Then multiply by the weight recommended by Muggianu.

Solution

$$x_i^{bin} = (1 + x_i - x_j)/2; x_j^{bin} = (1 - x_i + x_j)/2; {}^E G_m^{ij} = (1 + x_i - x_j)/2 \cdot (1 - x_i + x_j)/2$$
$$\cdot [(1 + x_i - x_j - 1 + x_i - x_j)/2]^k \cdot {}^k L_{ij} = (1/4) \cdot (1 + x_i - x_j)(1 - x_i + x_j) \cdot (x_i - x_j)^k \cdot {}^k L_{ij};$$
$${}^E G_m = \sum \frac{4x_i x_j}{(1 + x_i - x_j)(1 - x_i + x_j)} \cdot (1/4) \cdot (1 + x_i - x_j)(1 - x_i + x_j)(x_i - x_j)^k \cdot {}^k L_{ij}$$
$$= \Sigma x_i x_j (x_i - x_j)^k \cdot {}^k L_{ij}$$

Exercise 20.9.2

The excess Gibbs energy for a binary system is represented with the following expression according to the subregular solution model, ${}^E G_m = x_A x_B [{}^0 L_{AB} + {}^1 L_{AB}(x_A - x_B)]$. Suppose this expression is included in the Gibbs energy for a ternary A–B–C system. Derive expressions for the corresponding contributions to the partial Gibbs energies for A and C, respectively.

Hint

Use ${}^E G_j = {}^E G_m + \partial G_m / \partial x_j - \Sigma x_i \partial G_m / \partial x_i$. Note that $x_B = 1 - x_A$ cannot be used in the ternary system.

Solution

$${}^E G_A = {}^0 L_{AB} (x_A x_B + x_B - x_A x_B - x_B x_A) + {}^1 L_{AB} (x_A^2 x_B - x_A x_B^2 + 2 x_A x_B - x_B^2 - x_A \cdot 2 x_A x_B$$
$$+ x_A x_B^2 - x_B x_A^2 + x_B \cdot 2 x_A x_B) = {}^0 L_{ij} x_B (1 - x_A) + {}^1 L_{ij} (x_A^2 x_B - x_A x_B^2 - 2 x_A^2 x_B + x_A x_B^2 - x_A^2 x_B$$
$$+ 2 x_A x_B^2) = {}^0 L_{AB} (-x_A x_B) + {}^1 L_{ij} [-2 x_A x_B (x_A - x_B)] = -x_A x_B [{}^0 L_{AB} + 2 \cdot {}^1 L_{AB} (x_A - x_B)].$$