Exercises on Ch.19 *Modelling of disorder*

19.1 *Introduction*

Exercise 19.1.1

Boltzmann's relation relates the configurational entropy, ΔS, to the number of ways, W, the system can be arranged under the conditions given, $\Delta S = k\ln W$, where k is Boltzmann's constant. Use this relation to prove that the configurational entropy of a system, consisting of two parts, is equal to the sum of the configuration entropy for each part.

Hint

If each part can be arranged in W_1 and W_2 ways, respectively, then the whole system can be arranged in $W = W_1 \cdot W_2$ ways.

Solution

$\Delta S = k\ln W = k\ln(W_1\ W_2) = k\ln W_1 + k\ln W_2 = \Delta S_1 + \Delta S_2$.

19.2 *Thermal vacancies in a crystal*

Exercise 19.2.1

Suppose a solid metal in equilibrium has 10^{-3} vacancies per atom at the melting point. How much lower would the melting point be if there were no vacancies?

Hint

Apply Richard's rule, $\Delta S \cong R$ on melting. Close to the melting point it yields $\Delta G \cong (T_{\mathrm{m.p.}} - T)R$.

Solution

With vacancies we have $G^{\mathrm{liquid}} - G^{\mathrm{solid}} = \Delta G = (T_{\mathrm{m.p.}} - T)R$ and without we get <inline>.

Exercise 19.2.2

The temperature dependence of the entropy due to thermal vacancies in a metal is sometimes given by the expression $\Delta S / R = -(T_{m.p.} - T) \cdot (y_V^o)^{T_{m.p.}/T} \cdot \ln y_V^o$ where y_o is the value of y_V^{eq} at $T = T_{\mathrm{m.p.}}$. Check if this expression is correct.

Hint

We are asked to compare an expression in y_V^o with our known expression in y_V^{eq}. For equilibrium at all T we know $-g = kT \ln y_V^{eq}$ and thus $y_V^{eq} = (y_V^o)^{T_{m.p.}/T}$ if g is independent of T, because $y_V = y_V^o$ at $T = T_{\mathrm{m.p.}}$.

Solution

The new expression gives $\Delta S / R = y_V^{eq} \ln y_V$ which is the approximate value of $\Delta S / R = -\ln(1 - y_V^{eq}) - [y_V^{eq} / (1 - y_V^{eq})] \cdot \ln y_V^{eq}$ for small y_V^{eq}.

19.4 *Heat capacity due to thermal vibrations*

Exercise 19.4.1

Derive the expression for S as a function of T at constant P by integrating $C_P = C_V(1 + 2\alpha T)$ assuming that α is a constant. Examine if there are any other approximations.

Hint

V changes during this integration since P is kept constant.

Solution

Debye gave $C_V(x)$ where $x = \Theta / T$ and Θ was treated as independent of T. Now we must assume that Θ is also independent of P, which cannot be quite true. Then we get, under constant P: $S = \int (C_P/T)\mathrm{d}T = \int (C_V/T)\mathrm{d}T + 2\alpha \int C_V \mathrm{d}T = S(x) + 2\alpha U(x)$.

Exercise 19.4.2

Einstein's treatment of lattice vibrations gave the following contribution to the Helmholtz energy $\Delta F = 3RT\ln[1 - \exp(-\Theta/T)]$. Debye's treatment is much more complicated but, in principle, the result can also be expressed as $\Delta F = T\cdot\Phi(\Theta/T)$. In a simple approach we may assume that Θ is independent of T but it certainly depends upon V. Show that the following expression for the Grüneisen parameter can then be derived, $\gamma = -d\ln\Theta/d\ln V$.

Hint

Neglect all other contributions to F. Then we have F as a function of its natural variables T and V and should be able to calculate any thermodynamic quantity. Calculate α/κ_T from $-F_{VT}$. Denote $d\Phi/d(\Theta/T)$ with Φ', etc.

Solution

$F = T\Phi(\Theta/T)$; $F_T = \Phi + T\cdot\Phi'\cdot(-\Theta/T^2) = \Phi - (\Theta/T)\cdot\Phi'$;
$C_V = -TF_{TT} = -T\cdot[\Phi'\cdot(-\Theta/T^2) + (\Theta/T^2)\cdot\Phi' - (\Theta/T)\cdot\Phi''\cdot(-\Theta/T^2)] = -(\Theta^2/T^2)\cdot\Phi''$; $\alpha/\kappa_T = (\partial V/\partial T)_P/(-\partial V/\partial P)_T = (\partial P/\partial T)_V = (-\partial F_V/\partial T) = -F_{VT} = -F_{TV} = -[\Phi'\cdot(1/T)\cdot(1/T)\cdot d\Theta/dV - d\Theta/dV\cdot(1/T)\cdot\Phi' - (\Theta/T)\cdot\Phi''\cdot d\Theta/dV\cdot(1/T)] = (\Theta/T^2)\cdot d\Theta/dV\cdot\Phi''$; $\gamma = V\alpha/C_V\kappa_T = V\cdot(\Theta/T^2)\cdot d\Theta/dV\cdot\Phi''/(-\Phi''\Theta^2/T^2) = V\cdot(d\Theta/dV)/(-\Theta) = -d\ln\Theta/d\ln V$.

19.7 Random mixture of atoms

Exercise 19.7.1

Stirling's approximation to three terms is: $\ln N! \cong N\ln N - N + \ln(2\pi N)^{1/2}$. Derive S for a mixture of A and B using one, two and three terms.

Hint

Only the first term was used in the text.

Solution

$\ln N! - \ln N_A! - \ln N_B! = N\ln N - N_A\ln N_A - N_B\ln N_B - N + N_A + N_B + 0.5\ln[2\pi N(2\pi N_A\cdot 2\pi N_B)] = -N(x_A\ln x_A + x_B\ln x_B) - (1/2)\ln(2\pi N_A N_B/N) \cong -N(x_A\ln x_A + x_B\ln x_B)$ for large N. The first term gives the ideal expression, the second term gives no contribution. The third term is negligible for large N.

Exercise 19.7.2

From the treatment of thermal vacancies we obtained $\Delta S_m/R = -\ln(1 - y_v) - [y_v/(1 - y_v)]\cdot\ln y_v$. Compare with the expression obtained for a binary alloy A–B if we identify B with vacancies.

Hint

Examine for what size of a system each expression is defined.

Solution

$\Delta S_m/R = -x_A \ln x_A - x_B \ln x_B = -(1-x_B)\ln(1-x_B) - x_B \ln x_B$ holds for one mole of an alloy. The quantity y_v is the site fraction but x_B is also a site fraction because there is only one kind of site and in the A–B alloy they are all filled by atoms. We could thus get complete agreement between the two cases by expressing ΔS_m for the case with vacancies per mole of sites, i.e., by multiplying with $1 - y_v$, the number of atoms per site.

19.9 *Crystals with stoichiometric vacanc*ies

Exercise 19.9.1

At 1300 K the molar content of Fe in wüstite can vary between 0.467 and 0.488 and the O content from 0.533 to 0.512. What is the range of variation of the vacancy content?

Hint

Wüstite has the NaCl structure with $a^t = a^r$. Evidently the O sublattice is filled. We have Fe vacancies. It is convenient to use y fractions.

Solution

Eq. 19.7.2 yields (a) $y^t_{Fe} = 0.467 \cdot 1/1 \cdot 0.533 = 0.876; y^t_V = 0.124$

(b) $y^t_{Fe} = 0.488 \cdot 1/1 \cdot 0.512 = 0.953; y^t_V = 0.047$

19.10 *Interstitial solutions*

Exercise 19.10.1

Consider the interstitial solution of C and N in bcc-Fe. Assume random mixing of them and derive an expression for the contribution to the chemical potential of C from the mixing.

Hint

Derive μ_C from ΔG_m, using $\mu_C = \mu_C - \mu_{Va}$. Use $y_N = 1 - y_{Va} - y_C$; $\partial y_N/\partial y_{Va} = \partial y_N/\partial y_C = -1$ if y_N is chosen as a dependent variable.

Solution

$\Delta G_m = 3RT(y_{Va}\ln y_{Va} + y_C \ln y_C + y_N \ln y_N)$ per mole Fe.

$\Delta\mu_\mathrm{C} = (1/3)(\partial\Delta G_\mathrm{m}/\partial y_\mathrm{C} - \partial G_\mathrm{m}/\partial y_\mathrm{Va}) = RT(y_\mathrm{C}/y_\mathrm{C} + \ln y_\mathrm{C} - y_\mathrm{Va}/y_\mathrm{Va} - \ln y_\mathrm{Va} = RT\ln(y_\mathrm{C}/y_\mathrm{Va}) =$
$RT\ln[y_\mathrm{C}/(1 - y_\mathrm{C} - y_\mathrm{N})]$

Exercise 19.10.2

Express the contribution to the chemical potential of carbon from random mixing in the interstitial sublattice in bcc-Fe in terms of the ordinary molar content, x_C.

Hint

The problem is to express y_C in terms of x_C. Start with the definition of y_C.

Solution

$y_\mathrm{C} = x_\mathrm{C}/3x_\mathrm{Fe} = x_\mathrm{C}/3(1 - x_\mathrm{C})$; $1 - y_\mathrm{C} = (3 - 4x_\mathrm{C})/3(1 - x_\mathrm{C})$; $\Delta\mu_\mathrm{C} = RT\ln[y_\mathrm{C}/(1 - y_\mathrm{C})]$
$= RT\ln[x_\mathrm{C}/3 - 4x_\mathrm{C}]$