Exercises on Ch.18 *Methods of modelling*

18.3 *Reference states*

Exercise 18.3.1

Find an argument why it would be less convenient to give the Gibbs energies for various forms of pure Fe relative to the bcc form instead of the fcc form.

Hint

These values can be read as the differences between the curves in Fig. 18.1.

Solution

All the curves would show the very strong curvature at about 1300 K, which is due to the properties of bcc-Fe.

Exercise 18.3.2

All the curves in Fig. 18.1 and two of the three curves in Fig. 18.2 are parallel to the *T* axis at the left-hand side of the diagram. What determines the slope of the third curve in Fig. 18.2?

Hint

$\Delta S = - \mathrm{d}\Delta G/\mathrm{d}T$.

Solution

For the third curve we get, for the slope at $T = 0$, $\mathrm{d}\Delta G/\mathrm{d}T = \mathrm{d}[G - H(298) + TS(298)]/\mathrm{d}T = \mathrm{d}G/\mathrm{d}T + S(298) = S(298) - S(0)$.

18.4 *Representation of Gibbs energy of formation*

Exercise 18.4.1

Give the lattice stability of hcp-Fe relative to fcc-Fe as a linear function of T for 800–1800 K.

Hint

The information can be obtained from Fig. 18.1 by fitting a straight line.

Solution

$$\Delta^o G_{Fe}^{hcp/fcc} = {}^o G_{Fe}^{hcp} - H^{REF} - {}^o G_{Fe}^{fcc} + H^{REF} = {}^o G_{Fe}^{hcp} - {}^o G_{Fe}^{fcc} = -2400 + 5T$$

18.5 *Use of power series in T*

Exercise 18.5.1

The modelling of heat capacity at low temperatures is based on C_v but we have discussed the use of C_P. In order to get a feeling for the difference between C_P and C_v it may be instructive to estimate roughly the difference between C_P and C_v at 1500 K for an element with a thermal expansion of $\alpha = 3 \cdot 10^{-5}$ K^{-1}.

Hint

Suppose this temperature is so high that $C_v = 3R$. The Grüneisen constant γ may be estimated as 2.

Solution

$C_P - C_V = C_V T \gamma \alpha = 3R \cdot 1500 \cdot 2 \cdot 3 \cdot 10^{-5} = 0.27R$

18.6 *Representation of pressure dependence*

Exercise 18.6.1

Examine where the power series representation of the Gibbs energy of a pure substance, given as the first equation in this section, should be truncated in order for the sum of the P terms to be PV_m.

Hint

Evaluate PV_m from the expression given for V_m.

Solution

$PV_m = eP + fTP + 2gP^2$. However, the G_m expression contains $eP + fTP + gP^2$. It is thus necessary to omit gP^2 and higher terms.

18.7 *Application of physical models*

Exercise 18.7.1

Let us examine a very simple physical model. Measurements on alloys indicate that metallic melts undergo a glass transition if undercooled to a temperature, T_{glass}, which may be about one-third of the melting point, $T_{m.p.}$. On cooling down to that temperature the melt has lost most of its excess entropy relative to the crystalline state. Below the glass temperature C_P of the amorphous phase is close to C_P of the crystalline phase. Just above the glass temperature it is much larger. At higher temperatures it decreases gradually from this large value and we shall assume that it approaches C_P of the (superheated) crystalline phase at high temperatures, a behaviour which can be modelled by the following expression above T_{glass} : $G_m^L = G_m^{cryst} + a + bT + c\exp(-T/T_{glass})$.

Use this crude model to evaluate the difference in enthalpy between the glassy and crystalline phases at absolute zero. By first evaluating the model parameters from the information given above.

Hint

If there is practically no difference in C_P below T_{glass} then we can approximate $H_m^L - H_m^{cryst}$ as constant up to T_{glass} and there is practically no entropy difference. $H_m^L - H_m^{cryst}$ at absolute zero can thus be estimated as $G_m^L - G_m^{cryst}$ at the glass temperature. The information on S at the glass temperature, $T_{glass} = T_{m.p.}/3$, gives one equation. The information on phase equilibrium at $T_{m.p.}$ gives a second equation and Richard's rule that the entropy of melting of ordinary metals is equal to about R gives a third one.

Solution

$S_m^L - S_m^{cryst} = -b + (c/T_{glass})\exp(-T/T_{glass}) = -b + (3c/T_{m.p.})\exp(-3T/T_{m.p.})$.
At $T = T_{glass} = T_{m.p.}/3$: $S_m^L - S_m^{cryst} = -b + (3c/T_{m.p.})\exp(-1) = 0$.

At $T = T_{\text{m.p.}}$: $S_m^L - S_m^{cryst} = -b + (3c/T_{\text{m.p.}})\exp(-3) = R$. Therefore, $c = -(R\, T_{\text{m.p.}}/3)/[\exp(-1) - \exp(-3)] = -1.048RT_{\text{m.p.}}$; $b = (3c/T_{\text{m.p.}})\exp(-1) = -1.157R$.

$G_m^L = G_m^{cryst}$ at $T_{\text{m.p.}}$ gives $a + bT_{\text{m.p.}} + c\exp(-3) = 0$; $a = 1.209R\, T_{\text{m.p.}}$.

At $T = T_{\text{m.p.}}/3$: $G_m^L - G_m^{cryst} = 0.438RT_{m.p.} \cong H_m^L - H_m^{cryst}$ at 0 K.

18.8 Ideal gas

Exercise 18.8.1

Suppose a numerical expression for $K(T)$ has been evaluated for a gas which obeys the ideal gas model very well. The evaluation was made with P measured in pascal. How should one change the numerical expression if one would like to give P in bar (1 bar = 100 000 pascal)?

Hint

P(in pascal) = 100 000·P(in bar)

Solution

$G_m - H^{SER} = K(T) + RT\ln[P(\text{in pascal})] = K(T) + RT\ln[100\,000.P(\text{in bar})] = K(T) + 11.51RT + RT\ln[P(\text{in bar})]$

18.10 Mixtures of gas species

Exercise 18.10.1

Show how one can calculate the heat of reaction for C(graphite) +

O_2(gas) $\rightarrow$ CO_2(gas) where O_2 and CO_2 are taken from a gas mixture which is ideal.

Hint

We want $\Delta H_m = H_{CO_2} - {}^oH_C^{gr} - H_{O_2}$ where H_{CO_2} and H_{O_2} are partial quantities for the gas.

Solution

$G_m^{gas} = y_{CO_2}{}^oG_{CO_2} + y_{O_2}{}^oG_{O_2} + RT(y_{CO_2}\ln y_{CO_2} + y_{O_2}\ln y_{O_2}) + RT\ln P$ yields
$H_m^{gas} = \partial(G_m^{gas}/T)/\partial(1/T) = y_{CO_2}{}^oH_{CO_2} + y_{O_2}{}^oH_{O_2}$
and $y_{O_2} = 0$ and 1 yields $H_{CO_2} = {}^oH_{CO_2}$ and $H_{O_2} = {}^oH_{O_2}$, respectively.
The result is $\Delta H_m = H_{CO_2} - {}^oH_C^{gr} - H_{O_2} = {}^oH_{CO_2} - {}^oH_C^{gr} - {}^oH_{O_2}$.

18.11 *Black-body radiation*

Exercise 18.11.1

Consider a container filled with N moles of an ideal gas and black-body radiation. Derive an expression for G_m as a function of its natural variables.

Hint

Suppose that the expressions for Helmholtz's energy F are additive. Then use $G = F + PV$. Finally, eliminate V by introducing P.

Solution

$F_1 = aT^4V/3$; $F_2 = NK(T) + NRT\ln(NRT/V) - NRT$; $F = F_1 + F_2 = -aT_4V/3 + NK(T) + NRT\ln(NRT/V) - NRT$; $P = -\partial F/\partial V = aT^4/3 + NRT/V$; $G = F + PV = -aT^4V/3 + NK(T) + NRT\ln(NRT/V)NRT + aT^4V/3 + NRT = NK(T) + NRT\ln(NRT/V) = NK(T) + NRT\ln(P - aT^4/3)$