Gaskell 6th - Solutions

engineering thermodynamics (دانشگاه صنعتی امیرکبیر)

SOLUTIONS MANUAL FOR INTRODUCTION TO THE THERMODYNAMICS OF MATERIALS 6TH EDITION GASKELL

SOLUTIONS

2.1 An ideal gas at 300 K has a volume of 15 liters at a pressure of 15 atm. Calculate (1) the final volume of the system, (2) the work done by the system, (3) the heat entering or leaving the system, (4) the change in the internal energy and (5) the change in the enthalpy when the gas undergoes

- *a*, a reversible isothermal expansion to a pressure of 10 atm,
- *b*, a reversible adiabatic expansion to a pressure of 10 atm,

The constant volume molar heat capacity of the gas, c_v, has the value 1.5 R.

State 1. $P_1V_1 = nRT_1$ ∴ $n = \frac{15\times 15}{0.08206\times 300} = 9.14$ moles.

isothermal expansion to state 2. $P_1V_1 = P_2V_2$ ∴ $V_2 = \frac{15\times 15}{10} = 22.5\,\ell$

$T_2 = 300\text{ K}$

adiabatic expansion from state 1 to state 3.

$$P_1V_1^{\gamma} = 15\times 15^{5/3} = P_3V_3^{5/3} = 10V_3^{5/3} \quad \therefore V_3 = 19.13\,\ell$$

$$T_3 = \frac{P_3V_3}{nR} = \frac{10\times 19.13}{9.14\times 0.08206} = 255\text{ K}$$

a) isothermal expansion

1) $V_2 = 22.5\,\ell$

2) $w = q = nRT\ln\frac{V_2}{V_1} = 9.14\times 8.3144\times 300\times \ln\frac{22.5}{15} = 9244\text{ J}$

3) $q = w = 9244\text{ J}$

4) $\Delta T = 0$ ∴ $\Delta U = 0$

5) $\Delta T = 0$ ∴ $\Delta H = 0$

b) adiabatic expansion

1) $V_3 = 19.13\,\ell$

2) $w = -\Delta U = -nc_v(T_3 - T_1) = -9.14\times 1.5\times 8.3144\times(255-300)$

$= 5130\text{ J}$

3) $q = 0$

4) $\Delta U = -w = -5130\text{ J}$

5) $\Delta H = nc_p(T_3 - T_1) = 9.14\times\frac{5}{2}\times 8.3144\times(255-300) = -8549\text{ J.}$

2.2 One mole of a monatomic ideal gas, in the initial state $T = 273$ K, $P = 1$ atm, is subjected to the following three processes, each of which is conducted reversibly:

a, A doubling of its volume at constant pressure,

b, then a doubling of its pressure at constant volume,

c, then a return to the initial state along the path $P = 6.643 \times 10^{-4} V^2 + 0.6667$.

Calculate the heat and work effects which occur during each of the three processes.

$$V_1 = \frac{RT_1}{P_1} = \frac{0.08206 \times 273}{1} = 22.4\ \ell.$$

a) $1 \rightarrow 2$; $V_2 = 2 \times 22.4 = 44.8\ \ell$; $T_2 = \frac{1 \times 448}{0.08206} = 546$ K

b) $2 \rightarrow 3$; $V_3 = 44.8\ \ell$ $P_3 = 2$ atm. $T_3 = \frac{2 \times 44.8}{0.08206} = 1092$ K

$1 \rightarrow 2$; $w = P(V_2 - V_1) = 1(44.8 - 22.4) = 22.4\ \ell.\text{atm} = 2270$ J

$\Delta U = nc_V(T_2 - T_1) = \frac{3}{2} \times 8.3144 \times (546 - 273) = 3405$ J

$= q - w$ $\therefore$ $w = 3405 + 2270 = 5675$ J

$2 \rightarrow 3$; $w = 0$ $\Delta U = q = \frac{3}{2} \times 8.3144 (1092 - 546) = 6809$ J

$3 \rightarrow 1$; $w = \int_3^1 PdV = \int_3^1 (6.643 \times 10^{-4} V^2 + 0.6667) dV$

$= \frac{6.643 \times 10^{-4}}{3} [V_1^3 - V_3^3] + 0.6667 [V_1 - V_3]$

$= \frac{6.643 \times 10^{-4}}{3} [22.4^3 - 44.8^3] + 0.6667 [22.4 - 44.8]$

$= -32.35\ \ell.\text{atm} = -3278$ J

$\Delta U = \frac{3}{2} R (T_1 - T_3) = \frac{3}{2} \times 8.3144 \times (273 - 1092) = -10214$ J

$q = \Delta U + w = -10214 - 3278 = -13492$ J

$w_{TOTAL} = 2270 - 3278 = -1008$ J

$q_{TOTAL} = 5675 + 6809 - 13492 = -1008$ J

2.3 The initial state of a quantity of monatomic ideal gas is $P = 1$ atm, $V = 1$ liter and $T = 373$ K. The gas is isothermally expanded to a volume of 2 liters and is then cooled at constant pressure to the volume V. This volume is such that a reversible adiabatic compression to a pressure of 1 atm returns the system to its initial state. All of the changes of state are conducted reversibly. Calculate the value of V and the total work done on or by the gas.

$$n = \frac{P_1V_1}{RT} = \frac{1\times 1}{0.08206\times 373} = 0.0327 \text{ moles}$$

isothermal expansion: $P_2 = \frac{P_1V_1}{V_2} = \frac{1}{2} = 0.5$ atm

constant pressure compression to state 3 at which

$$P_1V_1^{5/3} = P_3V_3^{5/3} \quad \therefore \quad 1 = 0.5V_3^{5/3} \quad V_3 = 1.52\ \ell.$$

$1 \to 2$; $W = nRT\ln\frac{V_2}{V_1} = 0.0327\times 8.3144\times 373\times \ln 2 = 70.3$ J

$2 \to 3$; $W = P(V_3 - V_1) = 0.5[1.52-2] = -0.24\ \ell.\text{atm} = -24.5$ J

$3 \to 1$; $W = -\Delta U = -nc_V(T_1 - T_3)$

$= -0.0327\times\frac{3}{2}\times 8.3144\,(373-282)$

$= -37.1$ J

$\therefore$ $W_{TOTAL} = 70.3 - 24.5 - 37.1 = 8.7$ J

work done by the gas

2.4 Two moles of a monatomic ideal gas are at contained at a pressure of 1 atm and a temperature of 300 K. 34166 J of heat are transferred to the gas, as a result of which the gas expands and does 1216 J of work against its surroundings. The process is reversible. Calculate the final temperature of the gas.

$$\Delta U = q - w = 34166 - 1216 \text{ J}$$

$$= 32950 \text{ J}$$

$$= nc_v(T_2 - T_1)$$

$$= 2 \times \frac{3}{2} \times 8.3144\,(T_2 - 300)$$

$$\therefore T_2 = 1620 \text{ K.}$$

2.5 One mole of N_2 gas is contained at 273 K and a pressure of 1 atm. The addition of 3000 J of heat to the gas at constant pressure causes 832 J of work to be done during the expansion. Calculate (i) the final state of the gas, (ii) the values of ΔU and ΔH for the change of state and (iii) the values of c_v and c_p for N_2. Assume that nitrogen behaves as an ideal gas, and that the above change of state is conducted reversibly.

i) $$V_1 = \frac{RT_1}{P_1} = \frac{0.08206 \times 273}{1} = 22.4\,\ell.$$

$$W = 832 = P(V_2 - V_1) \times \frac{8.3144}{0.08206} = (V_2 - 22.4) \times 101.32$$

$$\therefore V_2 = 30.61\,\ell$$

$$T_2 = \frac{PV_2}{R} = \frac{1 \times 30.61}{0.08206} = 373\text{ K}$$

ii) $$\Delta U = q - w = 3000 - 832 = 2168\text{ J}$$

$$= C_V(T_2 - T_1) = 100\,C_V$$

$$\therefore C_V = 21.7\text{ J/mole.K.}$$

$$q_p = \Delta H = 3000 = C_p(T_2 - T_1) = 100\,C_p.$$

$$\therefore C_p = 30\text{ J/mole.K.}$$

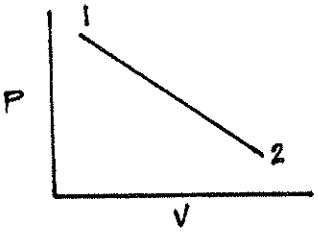
2.6 10 moles of ideal gas, in the initial state $P_1 = 10$ atm, $T_1 = 300$ K are taken round the following cycle.

- *a* a reversible change of state along a straight line path on the P–V diagram to the state $P = 1$ atm, $T = 300$ K,
- *b* a reversible isobaric compression to $V = 24.6$ liters, and
- *c* a reversible constant volume process to $P = 10$ atm.

How much work is done on or by the system during the cycle? Is this work done on the system or by the system?

$n = 10 \quad P_1 = 10 \quad T_1 = 300 \quad V_1 = \frac{10 \times 0.08206 \times 300}{10} = 24.62\ \ell.$

a) $1 \rightarrow 2 \quad P_2 = 1 \quad T_2 = 300 \quad V_2 = 10V_1 = 246.2\ \ell$



W = area below the line

$= \left[\frac{1}{2}\left[(10-1)(246.2-24.6)\right] + 1(246.2-24.6)\right] \times 101.32\ \text{J}$

$= +123.4\ \text{kJ}$

b) $2 \rightarrow 3 \quad P_3 = 1 \quad V_3 = 24.62$

$W = P(V_3 - V_2) = 1(24.6 - 246.2) \times 101.32$

$= -22.5\ \text{kJ}$

c) $\Delta V = 0 \quad \therefore \quad W = 0$

$W_{TOTAL} = 123.4 - 22.5 = 100.9\ \text{kJ}$

done by the gas

2.7 One mole of an ideal gas at 25°C and 1 atm undergoes the following reversibly conducted cycle:

- *a* An isothermal expansion to 0.5 atm, followed by,
- *b* an isobaric expansion to 100°C, followed by
- *c* an isothermal compression to 1 atm, followed by
- *d* an isobaric compression to 25°C.

The system then undergoes the following reversible cyclic process.

- *a* An isobaric expansion to 100°C, followed by
- *b* a decrease in pressure at constant volume to the pressure *P* atm, followed by
- *c* an isobaric compression at *P* atm to 24.5 liters, followed by
- *d* an increase in opressure at constant volume to 1 atm.

Calculate the value of *P* which makes the work done on the gas during the first cycle equal to the work done by the gas during the second cycle.

$T_1 = 298 \quad P_1 = 1 \quad V_1 = 0.08206 \times 298 = 24.45\,\ell$

First cycle:

$1 \rightarrow 2 \quad T_2 = 298 \quad P_2 = 0.5, \; V_2 = 2V_1 = 48.90\,\ell$

$W = RT\ln\frac{V_2}{V_1} = 8.3144 \times 298 \times \ln 2 = 1717\,J$

$2 \rightarrow 3 \quad T_3 = 373 \quad P_3 = 0.5 \quad V_3 = \frac{0.08206 \times 373}{0.5} = 61.22\,\ell$

$W = P(V_3 - V_2) = 0.5(61.27 - 48.91) \times 101.32 = 624\,J$

$3 \rightarrow 4 \quad T_4 = 373 \quad P_4 = 1 \quad V_4 = \frac{0.08206 \times 373}{1} = 30.61\,\ell$

$W = RT\ln\frac{V_4}{V_3} = 8.3144 \times 373 \ln 0.5 = -2150$

$4 \rightarrow 1 \quad W = P(V_1 - V_4) = 1(24.45 - 30.61) \times 101.32 = -624\,J$

Second cycle:

$1 \rightarrow 2 \quad P_2 = 1, \; T_2 = 373, \; V_2 = 0.08206 \times 373 = 30.61\,\ell$

$W = P(V_2 - V_1) = 1(30.61 - 24.45)101.32 = 624\,J$

2.7. continued.

$2 \rightarrow 3 \quad \Delta V = 0 \quad w = 0$

$3 \rightarrow 4. \quad V_4 = 24.5 \quad P_4 = P$

$\therefore w = P(24.5 - 30.61) \times 101.32 = -619P$ J

$4 \rightarrow 1 \quad \Delta V = 0 \quad \therefore w = 0$

$\therefore w_{1st\,cycle} = -w_{2nd\,cycle}$

$1717 + 624 - 2150 - 624 = -624 + 619P.$

$\therefore P = 0.3$ atm.

Problem 2.8* One mole of a monatomic ideal gas at standard temperature and pressure (STP) undergoes the following three processes:

1. at constant Pressure the Temperature is doubled.
2. at constant Temperature the Pressure is doubled
3. the gas is returned to STP via constant volume process

Calculate ΔU, ΔH, q and w for each of the steps.

Solution

First calculate the values of T, V and P at the states A, B and C.

<u>Step 1</u>

	T	V	P
A	T_A	V_A	P_A
B	$2T_A$	$2V_A$	P_A
C	$2T_A$	V_A	$2P_A$

Step 1 A →B

$$\Delta U_1 = C_V \Delta T = C_V(2T_A - T_A) = C_V T_A$$
$$w_1 = P_A \Delta V = P_A(2V_A - V_A) = P_A V_A = RT_A$$
$$q_1 = \Delta U + w = C_V T_A + RT_A = (C_V + R)T_A$$

Step 2 B→C

$$\Delta U_2 = C_V \Delta T = C_V(2T_A - 2T_A) = 0$$
$$w_2 = \int_{V_B}^{V_C} \frac{RT_B}{V} dV = 2RT_A \int_{V_B}^{V_C} \frac{dV}{V} = 2RT_A \ln\frac{V_C}{V_B} = -2RT_A \ln(2)$$
$$q_2 = w = -2RT_A \ln(2)$$

Step 3 C→A

$$\Delta U_3 = C_V \Delta T = C_V(T_A - 2T_A) = -C_V T_A$$
$$w_3 = \int_{V_C}^{V_A} \frac{RT}{V} dV = 0 \quad \text{since } V_C = V_A$$
$$q_3 = \Delta U_3 = -C_V T_A$$

Thus we see that for the entire process:

$$\Delta U = C_V T_A + 0 - C_V T_A = 0 \quad \text{as it should for a state function}$$
$$\sum w_i = RT_A - 2RT_A \ln(2) + 0$$
$$\sum q_i = (C_V + R)T_A - 2RT_A \ln(2) - C_V T_A = RT_A - 2RT_A \ln(2)$$

Problem 2.9*

Paramagnetic salts often obey the Curie relation: $\frac{M}{\mathcal{H}} = \frac{\text{constant}}{T} = \frac{C}{T}$

Obtain an expression for the work needed to change the magnetization from $M = 0$ to $\mathrm{M} = M$ of such a material. Assume that the field and the magnetization are parallel.

Solution

$$w = \int_0^{M_f} \mu_0 V \mathcal{H} \cdot dM = \int_0^{M_f} \mu_0 V \frac{TM}{C} \cdot dM = \mu_0 V \frac{TM_f^2}{2C} = \mu_0 V \frac{\mathcal{H}_f M_f}{2}$$

From the equality $w = \mu_0 V \frac{\mathcal{H}_f M_f}{2}$ we see that to get to the same M at higher temperature, more work is needed. Temperature works against the ordering of the moments.

From the equality $w = \mu_0 V \frac{\mathcal{H}_f M_f}{2}$ we also see that the work needed is the area under the linear $\mathcal{H}$ vs. M plot.

Problem 2.10 * One mole of a monatomic ideal gas is taken on the path A→ B → C →D →A as shown in Figure 2.7 .

(1) A→ B is a reversible isothermal expansion of the gas;

(2) B → C is a reversible adiabatic expansion of the gas;

(3) C →D is a reversible isothermal compression of the gas

(4) D → A is a reversible adiabatic compression of the gas.

a. Derive expressions for ΔU, q and w during each step in terms of V_a, V_b, V_c, V_d, t_1, t_2 c_V and R. Determine the sign of each.

b. Determine the values of $\Sigma(w_i)$, Σ (q_i) and Σ (ΔU_i) in terms of V_a, V_b, V_c, V_d, t_1, t_2 and R. Determine the sign of each.

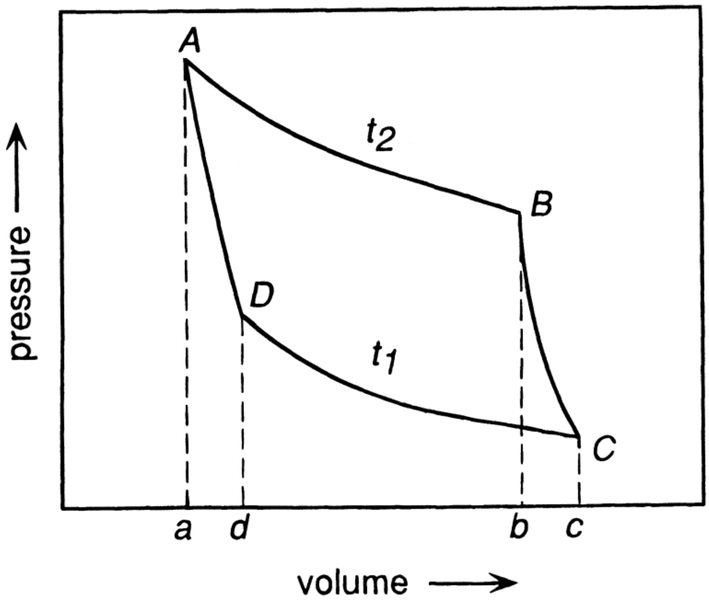


Figure 2.7

Solution

(1) $A \rightarrow B \qquad \Delta U_1 = 0;\ w_1 = q_1 = Rt_2 \ln(\frac{V_b}{V_a}) \quad > 0$

(2) $B \rightarrow C \qquad q_2 = \ 0; \quad \Delta U_2 = c_V(\mathrm{t}_2\text{-}\mathrm{t}_1) \ < 0; \quad -w_2 = \Delta U_2 \text{ so } \mathrm{w}_2 > 0$

(3) $\mathrm{C} \rightarrow \mathrm{D} \qquad \Delta U_3 = 0;\ w_3 = q_3 = Rt_1 \ln(\frac{V_d}{V_c}) \ < 0$

(4) $D \rightarrow A \qquad q_4 = \ 0\ ;\ \Delta U_4 = c_V(\mathrm{t}_2\text{-}\mathrm{t}_1) > 0 \quad -w_4 = \Delta U_4 \text{ so } \mathrm{w}_4 < 0$

SUM

$$\sum w_i = Rt_2 \ln(\frac{V_b}{V_a}) \ + Rt_1 \ln(\frac{V_d}{V_c}) > 0$$

$$\sum q_i = Rt_2 \ln(\frac{V_b}{V_a}) \ + Rt_1 \ln(\frac{V_d}{V_c}) > 0$$

$$\Delta U = 0$$

Problem 2.11 *

The change in enthalpy when one mole of solid water (ice) is melted at 273 K is 6008 J.

a. Calculate the change in enthalpy when ice is melted at 298 K. Is this process possible at 1 atm?

b. Calculate the change in enthalpy when supercooled water solidifies at 260 K.

c. Sketch the H vs. T plot for both solid and liquid water.

For this problem take the heat capacity of liquid water to be 75.44 J/k and that of solid water to be 38 J/K over the range in temperatures of the problem. The enthalpy of liquid water at 298 K may be set equal to zero.

Solution:

a.

$$H^S_{H_20}(T) = \int_{298}^{273} c_P^L dT - \Delta H_m + \int_{273}^{T} c_P^S dT$$

$$= 75.44(273-298) - 6008 + 38(T-273) \text{ J}$$

$$= -7894 + 38(T-273) \text{ J}$$

$$H^L_{H_20}(T) = \int_{298}^{T} c_P^L dT = 75.44(T-298) \text{ J}$$

Thus

$$\Delta H_M = H^L(298) - H^S(298)$$

$$= 0-(-7894)+38\cdot(298-273)$$

$$= 6944 \text{ J.}$$

Yes, ice can be superheated

b.

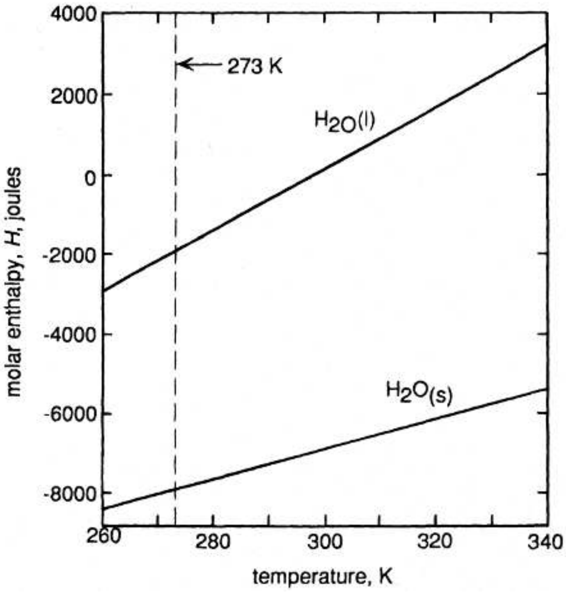
$$\Delta H_{fusion} = H^S(260) - H^L(260)$$

$$H^L(260) = 75.44(260-298) = -2866.72$$

$$H^S(260) = -7894 + 38((260-273) = -8388$$

$$\Delta H_{fusion} = (-8388) - (-2866.72) = -5521.28 \text{ J}$$

c.

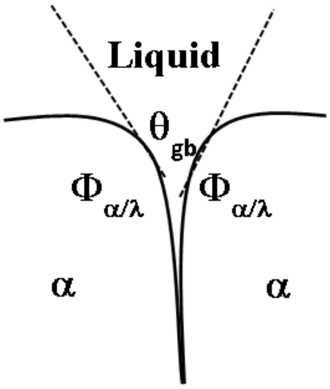

4000
2000
0
-2000
-4000
-6000
-8000
molar enthalpy, H, joules
260
280
300
320
340
temperature, K
273 K
$H_2O(l)$
$H_2O(s)$

Problem 2.12* Three phases, β ,α and δ meet as shown in Fig. 2.8a, forming three interphase interfaces, namely the β / α, the δ / α and the .δ / β It can be shown that the following holds

$$\frac{\gamma_{\alpha/\beta}}{\sin\theta_3} = \frac{\gamma_{\alpha/\delta}}{\sin\theta_2} = \frac{\gamma_{\beta/\delta}}{\sin\theta_1}$$

Using the above equation determine the equation that relates the grain boundary grooving angle θ_{gb} to the interface energy $\gamma_{\alpha/L}$ and the grain boundary energy $\gamma_{\alpha/\alpha}$.

See Fig. 2.8b.



$$\frac{\gamma_{gb}}{\sin\theta_{groove}} = \frac{\gamma_{\alpha/L}}{\sin\varphi_{\alpha/L}}$$

$$\theta_{groove} + 2\varphi_{\alpha/L} = 2\pi$$

$$\sin\varphi_{\alpha/L} = \sin(\pi - \frac{\theta_{groove}}{2}) = \sin(\frac{\theta_{groove}}{2})$$

$$\frac{\gamma_{gb}}{\sin\theta_{groove}} = \frac{\gamma_{\alpha/L}}{\sin(\frac{\theta_{groove}}{2})}$$

using: $\sin(2X) = 2\sin(X)\cos(X)$

$$\gamma_{gb} = \frac{\sin\theta_{groove}\gamma_{\alpha/L}}{\sin(\frac{\theta_{groove}}{2})} = 2\gamma_{\alpha/L}\cos(\frac{\theta_{groove}}{2})$$

using: $\sin(2X) = 2\sin(X)\cos(X)$

Solutions Manual
to accompany

Introduction to the Thermodynamics of Materials

Sixth Edition

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INTRODUCTION

This solutions manual provides worked-out answers to all problems appearing in *Introduction to the Thermodynamics of Materials*, *6th Edition*, with the exception of some of the problems in Chapter 5 and Problem 9.7), which are included in the answer section in the back of the book.

Complete solutions to all the new problems to the 6th edition are included and denoted by *.

All solutions arc comprehensive, making this supplement a useful instructional tool for professors and students.

Problem 1.1* The plot of V = V (P, T) for a gas is shown in Fig. 1.1. Determine. the expressions of the two second derivatives of the volume of this plot. (note: the princip<u>le</u> curvatures of the surface are proportional to these second derivatives). What are the signs of the curvatures? Explain.

Solution: start with the defining equations of β_T and α.

$$\left(\frac{\partial V}{\partial P}\right)_T = -V\beta_T \qquad \text{assuming } \beta_T \text{ is constant}$$

$$\left(\frac{\partial^2 V}{\partial P^2}\right)_T = \beta_T^2 V > 0$$

$$\left(\frac{\partial V}{\partial T}\right)_P = V\alpha \qquad \text{assuming } \alpha \text{ is constant}$$

$$\left(\frac{\partial^2 V}{\partial T^2}\right)_P = \alpha^2 V > 0$$

Since all terms in the expressions are positive (V, α^2 and β^2), both principle curvatures are positive. The surface is convex.

Problem 1.2* The expression for the total derivative of V with respect to the dependent variables P and T is :

$$dV = \left(\frac{\partial V}{\partial P}\right)_T dP + \left(\frac{\partial V}{\partial T}\right)_P dT$$

Substitute the values of α and β_T obtained Qualitative Problem 2 into this equation and obtain the equation of state for an ideal gas.

Solution

$$\begin{aligned}
dV &= -\beta_T V dP + \alpha V\, dT \\
dV &= -\frac{V}{P} dP + \frac{1}{T} V\, dT \\
\frac{dV}{V} &= -\frac{dP}{P} + \frac{dT}{T} \\
\ln V + c_1 &= -\ln P + c_2 + \ln T + c_3 \\
PV &= (\text{constant}) \cdot \text{T}
\end{aligned}$$

The constant is nR for n moles of the ideal gas.

Problem 1.3* The pressure temperature phase diagram (Fig. 1.4) has no two phase areas (only two phase curves), but the temperature composition diagram of Fig. 1.5 does have two phase areas. Explain.

Solution

This must be due to the number of components in each system: The system displayed in Fig. 1.4 is unary and that in Fig. 1.5 is a binary. We will see more on this later in the text.

Problem 1.4* Calculate the value of the ratio $\frac{\alpha}{\beta_T}$ for an ideal gas in terms of its volume.

Solution

$$\frac{\alpha}{\beta_T} = \frac{\frac{1}{T}}{\frac{1}{P}} = \frac{P}{T} = \frac{R}{V}$$

2.1 An ideal gas at 300 K has a volume of 15 liters at a pressure of 15 atm. Calculate (1) the final volume of the system, (2) the work done by the system, (3) the heat entering or leaving the system, (4) the change in the internal energy and (5) the change in the enthalpy when the gas undergoes

a, a reversible isothermal expansion to a pressure of 10 atm,

b, a reversible adiabatic expansion to a pressure of 10 atm,

The constant volume molar heat capacity of the gas, c_v, has the value 1.5 *R*.

State 1. $P_1V_1 = nRT_1$ $\therefore$ $n = \dfrac{15\times15}{0.08206\times300} = 9.14$ moles.

isothermal expansion to state 2. $P_1V_1 = P_2V_2$ $\therefore$ $V_2 = \dfrac{15\times15}{10} = 22.5\ \ell$

$T_2 = 300\ K$

adiabatic expansion from state 1 to state 3.

$$P_1V_1^{\gamma} = 15\times15^{5/3} = P_3V_3^{5/3} = 10V_3^{5/3} \quad \therefore V_3 = 19.13\ \ell$$

$$T_3 = \frac{P_3V_3}{nR} = \frac{10\times19.13}{9.14\times0.08206} = 255\ K.$$

a) isothermal expansion

1) $V_2 = 22.5\ \ell$

2) $w = q = nRT\ln\dfrac{V_2}{V_1} = 9.14\times8.3144\times300\times\ln\dfrac{22.5}{15} = 9244\ J$

3) $q = w = 9244\ J$

4) $\Delta T = 0$ $\therefore$ $\Delta U = 0$

5) $\Delta T = 0$ $\therefore$ $\Delta H = 0$

b) adiabatic expansion

1) $V_3 = 19.13\ell$

2) $w = -\Delta U = -nc_v(T_3 - T_1) = -9.14\times1.5\times8.3144\times(255-300)$

$= 5130J$

3) $q = 0$

4) $\Delta U = -w = -5130\ J$

5) $\Delta H = nc_p(T_3 - T_1) = 9.14\times\frac{5}{2}\times8.3144\times(255-300) = -8549\ J.$

2.2 One mole of a monatomic ideal gas, in the initial state $T = 273$ K, $P = 1$ atm, is subjected to the following three processes, each of which is conducted reversibly:

a, A doubling of its volume at constant pressure,

b, then a doubling of its pressure at constant volume,

c, then a return to the initial state along the path $P = 6.643 \times 10^{-4}V^2 + 0.6667$.

Calculate the heat and work effects which occur during each of the three processes.

$$V_1 = \frac{RT_1}{P_1} = \frac{0.08206 \times 273}{1} = 22.4\ \ell.$$

a) $1 \rightarrow 2$; $V_2 = 2 \times 22.4 = 44.8\ \ell$; $T_2 = \dfrac{1 \times 44.8}{0.08206} = 546\ K$

b) $2 \rightarrow 3$; $V_3 = 44.8\ \ell$ $P_3 = 2$ atm. $T_3 = \dfrac{2 \times 44.8}{0.08206} = 1092\ K$

$1 \rightarrow 2$; $w = P(V_2 - V_1) = 1(44.8 - 22.4) = 22.4\ \ell.atm = 2270\ J$

$$\Delta U = nC_V(T_2 - T_1) = \tfrac{3}{2} \times 8.3144 \times (546 - 273) = 3405\ J$$

$$= q - w \quad \therefore\ w = 3405 + 2270 = 5675\ J$$

$2 \rightarrow 3$; $w = 0$ $\Delta U = q = \tfrac{3}{2} \times 8.3144\,(1092 - 546) = 6809\ J$

$3 \rightarrow 1$; $w = \int_3^1 P\,dV = \int_3^1 (6.643 \times 10^{-4}V^2 + 0.6667)\,dV$

$$= \frac{6.643 \times 10^{-4}}{3}[V_1^3 - V_3^3] + 0.6667[V_1 - V_3]$$

$$= \frac{6.643 \times 10^{-4}}{3}[22.4^3 - 44.8^3] + 0.6667[22.4 - 44.8]$$

$$= -32.35\ \ell.atm = -3278\ J$$

$$\Delta U = \tfrac{3}{2}R(T_1 - T_3) = \tfrac{3}{2} \times 8.3144 \times (273 - 1092) = -10214\ J$$

$$q = \Delta U + w = -10214 - 3278 = -13492\ J$$

$$w_{TOTAL} = 2270 - 3278 = -1008\ J$$

$$q_{TOTAL} = 5675 + 6809 - 13492 = -1008\ J$$

2.3 The initial state of a quantity of monatomic ideal gas is $P = 1$ atm, $V = 1$ liter and $T = 373$ K. The gas is isothermally expanded to a volume of 2 liters and is then cooled at constant pressure to the volume V. This volume is such that a reversible adiabatic compression to a pressure of 1 atm returns the system to its initial state. All of the changes of state are conducted reversibly. Calculate the value of V and the total work done on or by the gas.

$$n = \frac{P_1V_1}{RT} = \frac{1\times 1}{0.08206\times 373} = 0.0327 \text{ moles}$$

isothermal expansion: $P_2 = \frac{P_1V_1}{V_2} = \frac{1}{2} = 0.5$ atm

constant pressure compression to state 3 at which

$$P_1V_1^{5/3} = P_3V_3^{5/3} \quad \therefore \quad 1 = 0.5V_3^{5/3} \qquad V_3 = 1.52\ \ell.$$

$1 \rightarrow 2$; $W = nRT \ln\frac{V_2}{V_1} = 0.0327\times 8.3144\times 373\times \ln 2 = 70.3$ J

$2 \rightarrow 3$; $W = P(V_3 - V_1) = 0.5[1.52 - 2] = -0.24\ \ell.\text{atm} = -24.5$ J

$3 \rightarrow 1$; $W = -\Delta U = -nc_V(T_1 - T_3)$

$$= -0.0327\times\frac{3}{2}\times 8.3144\,(373 - 282)$$

$$= -37.1 \text{ J}$$

$\therefore W_{TOTAL} = 70.3 - 24.5 - 37.1 = 8.7$ J

work done by the gas

2.4 Two moles of a monatomic ideal gas are at contained at a pressure of 1 atm and a temperature of 300 K. 34166 J of heat are transferred to the gas, as a result of which the gas expands and does 1216 J of work against its surroundings. The process is reversible. Calculate the final temperature of the gas.

$$\Delta U = q - w = 34166 - 1216 \text{ J}$$

$$= 32950 \text{ J}$$

$$= n c_v (T_2 - T_1)$$

$$= 2 \times \frac{3}{2} \times 8.3144 (T_2 - 300)$$

$$\therefore T_2 = 1620 \text{ K.}$$

2.5 One mole of N_2 gas is contained at 273 K and a pressure of 1 atm. The addition of 3000 J of heat to the gas at constant pressure causes 832 J of work to be done during the expansion. Calculate (i) the final state of the gas, (ii) the values of ΔU and ΔH for the change of state and (iii) the values of c_v and c_p for N_2. Assume that nitrogen behaves as an ideal gas, and that the above change of state is conducted reversibly.

i) $V_1 = \frac{RT_1}{P_1} = \frac{0.08206 \times 273}{1} = 22.4 \ell.$

$W = 832 = P(V_2 - V_1) \times \frac{83144}{0.08206} = (V_2 - 22.4) \times 101.32$

$\therefore V_2 = 30.61 \ell$

$T_2 = \frac{PV_2}{R} = \frac{1 \times 30.61}{0.08206} = 373 K$

ii) $\Delta U = q - w = 3000 - 832 = 2168 J$

$= C_v(T_2 - T_1) = 100 C_v$

$\therefore c_v = 21.7 J/mole.K.$

$q_p = \Delta H = 3000 = c_p(T_2 - T_1) = 100 c_p.$

$\therefore c_p = 30 J/mole.K.$

2.6 10 moles of ideal gas, in the initial state $P_1 = 10$ atm, $T_1 = 300$ K are taken round the following cycle.

a a reversible change of state along a straight line path on the P–V diagram to the state $P = 1$ atm, $T = 300$ K,

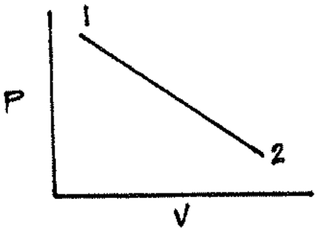
b a reversible isobaric compression to $V = 24.6$ liters, and

c a reversible constant volume process to $P = 10$ atm.

How much work is done on or by the system during the cycle? Is this work done on the system or by the system?

$n = 10 \quad P_1 = 10 \quad T_1 = 300 \quad V_1 = \frac{10 \times 0.08206 \times 300}{10} = 24.62\ \ell.$

a) $1 \rightarrow 2 \quad P_2 = 1 \quad T_2 = 300 \quad V_2 = 10V_1 = 246.2\ \ell$



W = area below the line

$= \left[\frac{1}{2}\left[(10-1)(246.2-24.6)\right] + 1(246.2-24.6)\right] \times 101.32\ \text{J}$

$= +123.4\ \text{kJ}$

b) $2 \rightarrow 3 \quad P_3 = 1 \quad V_3 = 24.62$

$W = P(V_3 - V_2) = 1(24.6 - 246.2) \times 101.32$

$= -22.5\ \text{kJ}$

c) $\Delta V = 0 \ \therefore\ W = 0$

$W_{TOTAL} = 123.4 - 22.5 = 100.9\ \text{kJ}$
done by the gas

2.7 One mole of an ideal gas at 25°C and 1 atm undergoes the following reversibly conducted cycle:

- *a* An isothermal expansion to 0.5 atm, followed by,
- *b* an isobaric expansion to 100°C, followed by
- *c* an isothermal compression to 1 atm, followed by
- *d* an isobaric compression to 25°C.

The system then undergoes the following reversible cyclic process.

- *a* An isobaric expansion to 100°C, followed by
- *b* a decrease in pressure at constant volume to the pressure *P* atm, followed by
- *c* an isobaric compression at *P* atm to 24.5 liters, followed by
- *d* an increase in opressure at constant volume to 1 atm.

Calculate the value of *P* which makes the work done on the gas during the first cycle equal to the work done by the gas during the second cycle.

$T_1 = 298$ $P_1 = 1$ $V_1 = 0.08206 \times 298 = 24.45\,l$

First cycle:

1 → 2 $T_2 = 298$ $P_2 = 0.5$, $V_2 = 2V_1 = 48.90\,l$

$W = RT\ln\frac{V_2}{V_1} = 8.3144 \times 298 \times \ln 2 = 1717\,J$

2 → 3 $T_3 = 373$ $P_3 = 0.5$ $V_3 = \frac{0.08206\times 373}{0.5} = 61.22\,l$

$W = P(V_3 - V_2) = 0.5(61.27 - 48.90)\times 101.32 = 624\,J$

3 → 4 $T_4 = 373$ $P_4 = 1$ $V_4 = \frac{0.08206\times 373}{1} = 30.61\,l$

$W = RT\ln\frac{V_4}{V_3} = 8.3144 \times 373 \ln 0.5 = -2150$

4 → 1 $W = P(V_1 - V_4) = 1(24.45 - 30.61)\times 101.32 = -624\,J$

Second cycle:

1 → 2 $P_2 = 1$, $T_2 = 373$, $V_2 = 0.08206 \times 373 = 30.61\,l$

$W = P(V_2 - V_1) = 1(30.61 - 24.45)101.32 = 624\,J$

2.7. continued.

$2 \rightarrow 3 \quad \Delta V = 0 \quad w = 0$

$3 \rightarrow 4. \quad V_4 = 24.5 \quad P_4 = P$

$\therefore \; w = P(24.5 - 30.61) \times 101.32 = -619P \text{ J}$

$4 \rightarrow 1 \quad \Delta V = 0 \; \therefore \; w = 0$

$\therefore \; w_{1st\,cycle} = -w_{2nd\,cycle}$

$1717 + 624 - 2150 - 624 = -624 + 619P.$

$\therefore \; P = 0.3 \text{ atm.}$

Problem 2.8* One mole of a monatomic ideal gas at standard temperature and pressure (STP) undergoes the following three processes:

1. at constant Pressure the Temperature is doubled.
2. at constant Temperature the Pressure is doubled
3. the gas is returned to STP via constant volume process

Calculate ΔU, ΔH, q and w for each of the steps.

Solution

First calculate the values of T, V and P at the states A, B and C.

<u>Step 1</u>

	T	V	P
A	T_A	V_A	P_A
B	$2T_A$	$2V_A$	P_A
C	$2T_A$	V_A	$2P_A$

Step 1 A →B

$$\Delta U_1 = C_V \Delta T = C_V(2T_A - T_A) = C_V T_A$$
$$w_1 = P_A \Delta V = P_A(2V_A - V_A) = P_A V_A = RT_A$$
$$q_1 = \Delta U + w = C_V T_A + RT_A = (C_V + R)T_A$$

Step 2 B→C

$$\Delta U_2 = C_V \Delta T = C_V (2T_A - 2T_A) = 0$$

$$w_2 = \int_{V_B}^{V_C} \frac{RT_B}{V} dV = 2RT_A \int_{V_B}^{V_C} \frac{dV}{V} = 2RT_A \ln \frac{V_C}{V_B} = -2RT_A \ln(2)$$

$$q_2 = w = -2RT_A \ln(2)$$

Step 3 C→A

$$\Delta U_3 = C_V \Delta T = C_V (T_A - 2T_A) = -C_V T_A$$

$$w_3 = \int_{V_C}^{V_A} \frac{RT}{V} dV = 0 \quad \text{since } V_C = V_A$$

$$q_3 = \Delta U_3 = -C_V T_A$$

Thus we see that for the entire process:

$$\Delta U = C_V T_A + 0 - C_V T_A = 0 \quad \text{as it should for a state function}$$

$$\sum w_i = RT_A - 2RT_A \ln(2) + 0$$

$$\sum q_i = (C_V + R)T_A - 2RT_A \ln(2) - C_V T_A = RT_A - 2RT_A \ln(2)$$

Problem 2.9*

Paramagnetic salts often obey the Curie relation: $\frac{M}{\mathcal{H}} = \frac{\text{constant}}{T} = \frac{C}{T}$

Obtain an expression for the work needed to change the magnetization from $M = 0$ to $\mathrm{M} = M$ of such a material. Assume that the field and the magnetization are parallel.

Solution

$$w = \int_0^{M_f} \mu_0 V \mathcal{H} \cdot dM = \int_0^{M_f} \mu_0 V \frac{TM}{C} \cdot dM = \mu_0 V \frac{TM_f^2}{2C} = \mu_0 V \frac{\mathcal{H}_f M_f}{2}$$

From the equality $w = \mu_0 V \frac{\mathcal{H}_f M_f}{2}$ we see that to get to the same M at higher temperature, more work is needed. Temperature works against the ordering of the moments.

From the equality $w = \mu_0 V \frac{\mathcal{H}_f M_f}{2}$ we also see that the work needed is the area under the linear $\mathcal{H}$ vs. M plot.

Problem 2.10 * One mole of a monatomic ideal gas is taken on the path A→ B → C →D →A as shown in Figure 2.7 .

(1) A→ B is a reversible isothermal expansion of the gas;

(2) B → C is a reversible adiabatic expansion of the gas;

(3) C →D is a reversible isothermal compression of the gas

(4) D → A is a reversible adiabatic compression of the gas.

a. Derive expressions for ΔU, q and w during each step in terms of V_a, V_b, V_c, V_d, t_1, t_2 c_V and R. Determine the sign of each.

b. Determine the values of $\Sigma(w_i)$, $\Sigma\ (q_i)$ and $\Sigma\ (\Delta U_i)$ in terms of V_a, V_b, V_c, V_d, t_1, t_2 and R. Determine the sign of each.

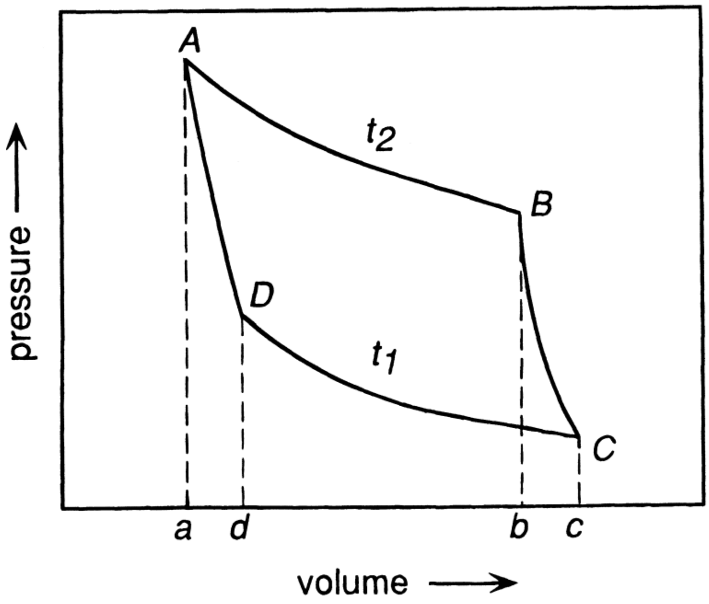


Figure 2.7

Solution

$(1) A \rightarrow B \quad \Delta U_1 = 0;\ w_1 = q_1 = Rt_2 \ln(\frac{V_b}{V_a}) \ > 0$

$(2) B \rightarrow C \quad q_2 = \ 0; \ \ \Delta U_2 = c_V(\mathrm{t}_2\text{-}\mathrm{t}_1) \ < 0; \ \ -w_2 = \Delta U_2 \text{ so } \mathrm{w}_2 > 0$

$(3) \mathrm{C} \rightarrow \mathrm{D} \quad \Delta U_3 = 0;\ w_3 = q_3 = Rt_1 \ln(\frac{V_d}{V_c}) \ < 0$

$(4) D \rightarrow A \quad q_4 = \ 0\ ;\ \Delta U_4 = c_V(\mathrm{t}_2\text{-}\mathrm{t}_1) > 0 \ \ \text{-}w_4 = \Delta U_4 \text{ so } \mathrm{w}_4 < 0$

$$SUM \qquad \sum w_i = Rt_2 \ln(\frac{V_b}{V_a}) \ + Rt_1 \ln(\frac{V_d}{V_c}) > 0$$

$$\sum q_i = Rt_2 \ln(\frac{V_b}{V_a}) \ + Rt_1 \ln(\frac{V_d}{V_c}) > 0$$

$$\Delta U = 0$$

Problem 2.11 *

The change in enthalpy when one mole of solid water (ice) is melted at 273 K is 6008 J.

a. Calculate the change in enthalpy when ice is melted at 298 K. Is this process possible at 1 atm?

b. Calculate the change in enthalpy when supercooled water solidifies at 260 K.

c. Sketch the H vs. T plot for both solid and liquid water.

For this problem take the heat capacity of liquid water to be 75.44 J/k and that of solid water to be 38 J/K over the range in temperatures of the problem. The enthalpy of liquid water at 298 K may be set equal to zero.

Solution:

a.

$$H^S_{H_20}(T) = \int_{298}^{273} c^L_P dT - \Delta H_m + \int_{273}^{T} c^S_P dT$$

$$= 75.44(273-298) - 6008 + 38(T-273) \text{ J}$$

$$= -7894 + 38(T-273) \text{ J}$$

$$H^L_{H_20}(T) = \int_{298}^{T} c^L_P dT = 75.44(T-298) \text{ J}$$

Thus

$$\Delta H_M = H^L(298) - H^S(298)$$

$$= 0 - (-7894) + 38\cdot(298-273)$$

$$= 6944 \text{ J.}$$

Yes, ice can be superheated

b.

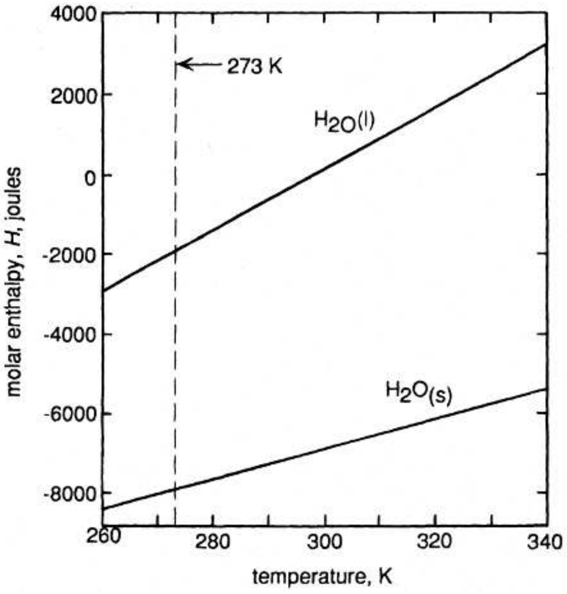
$$\Delta H_{fusion} = H^S(260) - H^L(260)$$

$$H^L(260) = 75.44(260-298) = -2866.72$$

$$H^S(260) = -7894 + 38((260-273) = -8388$$

$$\Delta H_{fusion} = (-8388) - (-2866.72) = -5521.28 \text{ J}$$

c.

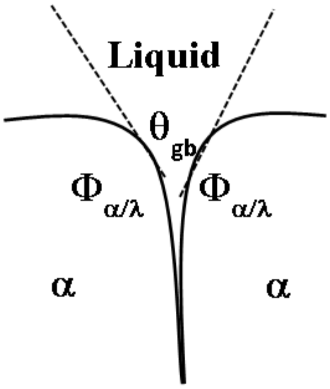

4000
2000
0
-2000
-4000
-6000
-8000
molar enthalpy, H, joules
260
280
300
320
340
temperature, K
273 K
$H_2O(l)$
$H_2O(s)$

Problem 2.12* Three phases, β ,α and δ meet as shown in Fig. 2.8a, forming three interphase interfaces, namely the β / α, the δ / α and the .δ / β It can be shown that the following holds

$$\frac{\gamma_{\alpha/\beta}}{\sin\theta_3} = \frac{\gamma_{\alpha/\delta}}{\sin\theta_2} = \frac{\gamma_{\beta/\delta}}{\sin\theta_1}$$

Using the above equation determine the equation that relates the grain boundary grooving angle θ_{gb} to the interface energy $\gamma_{\alpha/L}$ and the grain boundary energy $\gamma_{\alpha/\alpha}$.

See Fig. 2.8b.



$$\frac{\gamma_{gb}}{\sin\theta_{groove}} = \frac{\gamma_{\alpha/L}}{\sin\varphi_{\alpha/L}}$$

$$\theta_{groove} + 2\varphi_{\alpha/L} = 2\pi$$

$$\sin\varphi_{\alpha/L} = \sin(\pi - \frac{\theta_{groove}}{2}) = \sin(\frac{\theta_{groove}}{2})$$

$$\frac{\gamma_{gb}}{\sin\theta_{groove}} = \frac{\gamma_{\alpha/L}}{\sin(\frac{\theta_{groove}}{2})}$$

using: $\sin(2X) = 2\sin(X)\cos(X)$

$$\gamma_{gb} = \frac{\sin\theta_{groove}\gamma_{\alpha/L}}{\sin(\frac{\theta_{groove}}{2})} = 2\gamma_{\alpha/L}\cos(\frac{\theta_{groove}}{2})$$

using: $\sin(2X) = 2\sin(X)\cos(X)$

3.1 The initial state of one mole of a monatomic ideal gas is $P = 10$ atm and $T = 300$ K. Calculate the change in the entropy of the gas for (*a*) an isothermal decrease in the pressure to 5 atm; (*b*) a reversible adiabatic expansion to a pressure of 5 atm; (*c*) a constant-volume decrease in the pressure to 5 atm.

$$P_1 = 10 \text{ atm} \quad T_1 = 300K \quad V_1 = \frac{0.08206 \times 300}{10} = 2.462 \ l$$

$$a) \quad P_2 = 5 \quad T_2 = 300 \quad V_2 = \frac{P_1V_1}{P_2} = 4.924 \ l$$

$$\Delta S = R \ln \frac{V_2}{V_1} = 8.3144 \times \ln 2 = 5.76 \ J/K$$

$$b) \quad q = 0, \text{reversible} \ \therefore \Delta S = 0$$

$$c) \quad P_2 = 5, V_2 = 2.462, \quad T_2 = \frac{P_2V_2}{R} = \frac{5 \times 2.462}{0.08206} = 150 \ K$$

$$\Delta S = c_V \ln \frac{T_2}{T_1} = 1.5 \times 8.3144 \times \ln \frac{1}{2} = -8.65 \ J/K$$

3.2 One mole of a monatomic ideal gas is subjected to the following sequence of steps:

a. Starting at 300 K and 10 atm, the gas expands freely into a vacuum to triple its volume.

b. The gas is next heated reversibly to 400 K at constant volume.

c. The gas is reversibly expanded at constant temperature until its volume is again tripled.

d. The gas is finally reversibly cooled to 300 K at constant pressure.

Calculate the values of q and w and the changes in U, H and S.

$T_1 = 300\,K$, $P_1 = 10$ atm. $V_1 = \frac{0.08206\times300}{10} = 2.462\ l$

a) $1 \rightarrow 2$ $T_2 = 300$, $V_2 = 3V_1 = 7.386\ l$, $P_3 = \frac{P_1}{3} = 3.33$ atm.

$q = w = \Delta U = \Delta H = 0$, $\Delta S = R\ln\frac{V_2}{V_1} = 8.3144\ln 3 = 9.134\ J/K$

b) $2 \rightarrow 3$ $T_3 = 400$, $V_3 = 7.386\ l$, $P_3 = \frac{T_3 P_2}{T_2} = \frac{4}{3}\times 3.33 = 4.44$ atm

$\Delta V = 0 \therefore w = 0 \therefore q = \Delta U = c_V(T_3 - T_2) = 1.5\times 8.3144\times 100$

$= 1247\ J.$

$\Delta H = c_p(T_3 - T_2) = \frac{5}{3}\times 1247 = 2078\ J.$

$\Delta S = c_p \ln\frac{T_3}{T_2} = 1.5\times 8.3144 \ln\frac{400}{300} = 3.588\ J/K$

c) $3 \rightarrow 4$ $T_4 = 400$, $V_4 = 3V_3 = 22.158\ l$, $P_4 = \frac{P_3}{3} = 1.481$ atm

$\Delta U = \Delta H = 0$ $q = w = RT_4 \ln\frac{V_4}{V_3} = 8.3144\times 400 \ln 3 = 3654\ J$

$\Delta S = \frac{q}{T} = \frac{3654}{400} = 9.134\ J/K$

d) $4 \rightarrow 5$ $T_5 = 300\,K$ $P_5 = 1.48$ at $V_5 = \frac{0.08206\times 300}{1.481}$

$= 16.623\ l$

3.2 continued.

$$\Delta U = c_v(T_5 - T_4) = 1.5 \times 8.3144\,(300 - 400) = -1247\ J$$

$$\Delta H = q_p = 2.5 \times 8.3144\,(300 - 400) = -2078\ J$$

$$w = q - \Delta U = -2078 + 1247 = -831\ J$$

$$\Delta S = c_p \ln \frac{T_5}{T_4} = 2.5 \times 8.3144 \ln \frac{300}{400} = -5.980\ J/K$$

	ΔU	ΔH	w	q	ΔS
1 → 2	0	0	0	0	9.134
2 → 3	1247	2078	0	1247	3.588
3 → 4	0	0	3654	3654	9.134
4 → 5	−1247	−2078	−831	−2078	−5.980
	0	0	2823	2823	15.88

3.3 One mole of a monatomic ideal gas undergoes a reversible expansion at constant pressure during which the entropy of the gas increases by 14.41 J/K and the gas absorbs 6236 joules of heat. Calculate the initial and final temperatures of the gas. One mole of a second monatomic ideal gas undergoes a reversible isothermal expansion during which it doubles its volume, performs 1729 joules of work and increases its entropy by 5.763 J/K. Calculate the temperature at which the expansion was conducted.

a) $\Delta S = 14.41 = c_p \ln \frac{T_2}{T_1} = 2.5 \times 8.3144 \ln \frac{T_2}{T_1}$

$\therefore \frac{T_2}{T_1} = 2$

$q = 6236 = c_p (T_2 - T_1) = 2.5 \times 8.3144 (T_2 - T_1)$

$\therefore T_2 - T_1 = 300$

$\therefore T_2 = 600\,K$ and $T_1 = 300\,K$

b) $w = q = 1729.$ $\Delta S = \frac{q}{T} = 5.763$

$\therefore T = \frac{1729}{5.763} = 300\,K$

3.4 Calculate the change in the enthalpy and the change in entropy when one mole of SiC is heated from 25°C to 1000°C. The constant pressure molar heat capacity of SiC varies with temperature as

$$c_p = 50.79 + 1.97 \times 10^{-3}T - 4.92 \times 10^{6}T^{-2} + 8.20 \times 10^{8}T^{-3} \text{ J/mole.K}$$

$$\Delta H = \int_{T_1}^{T_2} c_p dT$$

$$= 50.79[1273-298] + \frac{1.97\times10^{-3}}{2}[1273^2-298^2] + 4.92\times10^{6}\left[\frac{1}{1273}-\frac{1}{298}\right]$$

$$- \frac{8.20\times10^{8}}{2}\left[\frac{1}{1273^2}-\frac{1}{298^2}\right]$$

$$= 49520 + 1509 - 12645 + 4364$$

$$= 42750 \text{ J.}$$

$$\Delta S = \int_{T_1}^{T_2} \frac{c_p dT}{T}$$

$$= 50.79 \ln\frac{1273}{298} + 1.97\times10^{-3}(1273-298) + \frac{49.2\times10^{5}}{2}\left[\frac{1}{1273^2}-\frac{1}{298^2}\right]$$

$$- \frac{8.20\times10^{8}}{3}\left[\frac{1}{1273^3}-\frac{1}{298^3}\right]$$

$$= 73.7 + 1.9 - 26.2 + 10.2$$

$$= 59.7 \text{ J/K}$$

3.5 One mole of copper at a uniform temperature of 0°C is placed in thermal contact with a second mole of copper which, initially, is at a uniform temperature of 100°C. Calculate the temperature of the two-mole system, which is contained in an adiabatic enclosure, when thermal equilibrium is attained. Why is the common uniform temperature not exactly 50°C? How much heat is transferred and how much entropy is produced by the transfer? The constant pressure molar heat capacity of solid copper varies with temperature as

$$c_p = 22.64 + 6.28 \times 10^{-3} T \quad \text{J/mole.K}$$

$$q = \Delta H = \Delta H_{hot} + \Delta H_{cold} = 0$$

$$\therefore \int_{273}^{T_f} C_p dT + \int_{373}^{T_f} C_p dT = 0$$

$$\therefore 22.64(T_f - 273) + 3.14\times10^{-3}(T_f^2 - 273^2)$$

$$+ 22.64(T_f - 373) + 3.14\times10^{-3}(T_f^2 - 373^2) = 0$$

$$T_f = 323.32 \text{ K} \quad (50.32^\circ C)$$

Cp increases with increasing T. ∴ ΔT caused by withdrawing heat q from hot Cu is less than ΔT caused by adding heat q to cold Cu.

$$\Delta S_{cold} = \int_{273}^{323.32} \frac{C_p dT}{T} = 22.64 \ln \frac{323.32}{273} + 6.28\times10^{-3}[323.32-273$$

$$= 4.15. \text{ J/K.}$$

$$\Delta S_{hot} = \int_{373}^{323.32} \frac{C_p dT}{T} = 22.64 \ln \frac{323.32}{373} + 6.28\times10^{-3}[323.32-373$$

$$= -3.55 \text{ J/K}$$

$$\Delta S_{irr} = 0.6 \text{ J/K}$$

$$\text{Heat transferred} = 22.64(323.23 - 273) + 3.14\times10^{-3}(323.23^2 - 273^2)$$

$$= 1233 \text{ J}$$

3.6 A reversible heat engine, operating in a cycle, withdraws heat from a high-temperature reservoir (the temperature of which consequently decreases), performs work w, and rejects heat into a low-temperature reservoir (the temperature of which consequently increases). The two reservoirs are, initially, at the temperatures T_1 and T_2 and have constant heat capacities C_1 and C_2 respectively. Calculate the final temperature of the system and the maximum amount of work which can be obtained from the engine.

Process is reversible

$$\therefore \Delta S = 0 = \Delta S_{heat\,source} + \Delta S_{heat\,sink}$$

$$\therefore \int_{T_2}^{T_f} C_2 \frac{dT_2}{T_2} = -\int_{T_1}^{T_f} C_1 \frac{dT_1}{T_1}$$

$$\therefore \left(\frac{T_f}{T_2}\right)^{C_2} = \left(\frac{T_1}{T_f}\right)^{C_1}$$

$$T_f = \left(T_1^{C_1} T_2^{C_2}\right)^{\frac{1}{C_1+C_2}}$$

$$w = q_2 - q_1 = \left[-C_2(T_f - T_2)\right] - \left[C_1(T_f - T_1)\right]$$

Problem 3.7* In deriving the equation for the efficiency of a Carnot engine in Section 3.11 it was stated that $\frac{V_B}{V_A} = \frac{V_C}{V_D}$. Show that this equality is valid.

Solution

Along the adibatic curve BC

$$P_B V_B^{\gamma} = P_C V_C^{\gamma}$$

since the gas is ideal

$$P_B V_B = RT_2 \text{ and } P_C V_C = RT_1$$

Thus $T_2 V_B^{\gamma-1} = T_1 V_C^{\gamma-1}$

or $$T_2^{1-\gamma} V_B = T_1^{1-\gamma} V_C \qquad \text{(i)}$$

Also, along the DA adiabatic curve

$$P_D V_D^{\gamma} = P_A V_A^{\gamma}$$

since the gas is ideal

$$P_D V_D = RT_1 \text{ and } P_A V_A = RT_2$$

Thus $T_1 V_D^{\gamma-1} = T_2 V_A^{\gamma-1}$

or $$T_1^{1-\gamma} V_D = T_2^{1-\gamma} V_A \qquad \text{(ii)}$$

Dividing (i) by (ii) we obtain: $\frac{T_2^{1-\gamma} V_B}{T_2^{1-\gamma} V_A} = \frac{T_1^{1-\gamma} V_C}{T_1^{1-\gamma} V_D} : \quad \frac{V_B}{V_A} = \frac{V_C}{V_D}$

Problem 3.8* a. Calculate the change in entropy at 273 K for the freezing of water.

b. Calculate the change in entropy for the freezing of water at 260 K.

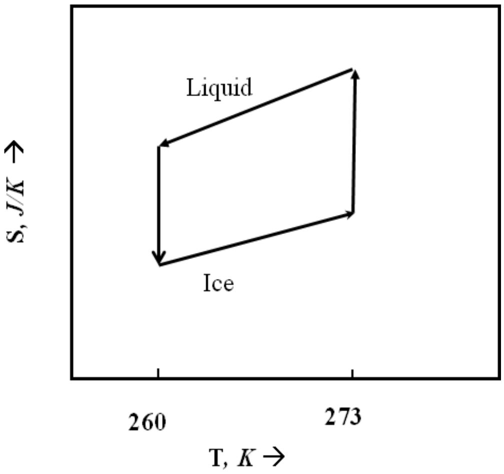
The change in enthalpy when one mole of solid water (ice) is melted at 273 K is 6008 J. Take the heat capacity of liquid water to be 75.44 J/K and that of solid water to be 38 J/k over the range in temperatures of the problem.

Solution

a. The change in entropy of one mole of water on freezing at its equilibrium freezing temperature is:

$$\frac{\Delta H_{L \to S}}{273} = \frac{-6008\ J}{273\ K} = -21.23 \frac{J}{K}$$

b. The freezing of water at 260 K is an irreversible process since 260 is below the Equilibrium freezing point of water. But since entropy is a state function we can perform a cyclic calculation as shown below:



$$\Delta S_{L\to S}(260) + \Delta S_S^{260\to 273} + \Delta S_{S\to L}(273) + \Delta S_L^{273\to 260} = 0$$

$$\Delta S_{L\to S}(260) + \int_{260}^{273} \frac{C_P^S}{T} dT + \frac{6008\ J}{273\ K} + \int_{260}^{273} \frac{C_P^L}{T} dT = 0$$

$$\Delta S_{L\to S}(260) + 38\ln\frac{273}{260} + \frac{6008\ J}{273\ K} + 75.44\ln\frac{260}{273} = 0$$

$$\Delta S_{L\to S}(260) + 1.85 + 21.23 - 3.68 = 0$$

$$\Delta S_{L\to S}(260) = -19.40\frac{J}{K}$$

Problem 3.9* Calculate the work performed by the Carnot cycle for the shown in Fig. 3.4 using the T-S diagram of Fg. 3.9.

Solution

The area enclosed by the box in Fig.3.9 is first calculated.

Area = $(t_2 - t_1)\Delta S$

Where $\Delta S = S_C - S_D = S_B - S_A$

$$\frac{q_1}{t_2} = (S_B - S_A) = \Delta S$$

$$\frac{q_2}{t_1} = -(S_D - S_C) = (S_C - S_D) = \Delta S$$

$$w = q_2 - q_1 = t_2\Delta S - t_1\Delta S$$

$$w = (t_2 - t_1)\Delta S, \text{ the area of the box in the T-S plot}$$

4.1 A rigid container is divided into two compartments of equal volume by a partition. One compartment contains 1 mole of ideal gas A at 1 atm, and the other contains 1 mole of ideal gas B at 1 atm. Calculate the increase in entropy which occurs when the partition between the two compartments is removed. If the first compartment had contained 2 moles of ideal gas A, what would have been the increase in entropy when the partition was removed? Calculate the corresponding increases in entropy in each of the above two situations if both compartments had contained ideal gas A

i) When the partition is removed:

The volume occupied by 1 mole of A doubles $\therefore \Delta S_A = R\ln 2$

The volume occupied by 1 mole of B doubles $\therefore \Delta S_B = R\ln 2$

$\therefore \Delta S_{TOTAL} = \Delta S_A + \Delta S_B = R\ln 4.$

ii) The volume occupied by 2 moles of A doubles $\therefore \Delta S_A = 2R\ln 2$

The volume occupied by 1 mole of B doubles $\therefore \Delta S_B = R\ln 2$

$\therefore \Delta S_{TOTAL} = 3R\ln 2 = R\ln 8$

iii) No change $\therefore \Delta S = 0$

iv) Double the volume of the 2 moles of A $\Delta S = 2R\ln 2$

Remove the partition $\Delta S = 0$

Decrease the volume of the 3 moles of A by the factor $\frac{2}{3}$

$\Delta S = 3R\ln\frac{2}{3}$

$\therefore \Delta S_{TOTAL} = 2R\ln 2 + 3R\ln\frac{2}{3} = R\ln\frac{32}{27}$

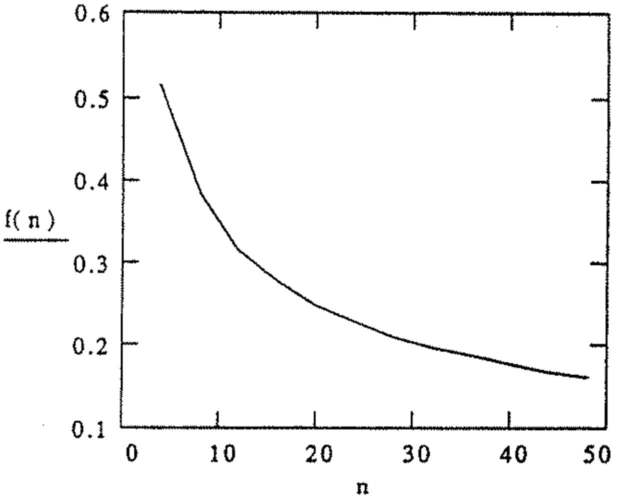
4.2 Show that, when *n* atoms of *A* and *n* atoms of *B* form a randomly-mixed solution, the fraction of the total number of distinguishable complexions which occur in the most probable distribution decreases with increasing value of *n*.

Total number of distinguishable complexions $= \dfrac{(2n)!}{n!n!}$

With n being a multiple of 4, the number of complexions in the most probable distribution $= \dfrac{n!}{(\frac{n}{2})!(\frac{n}{2})!} \times \dfrac{n!}{(\frac{n}{2})!(\frac{n}{2})!}$

$$\therefore \text{ The fraction } f(n) = \frac{\left[\dfrac{n!}{(0.5n)!(0.5n)!}\right]^2}{\dfrac{(2n)!}{n!n!}} = \frac{(n!)^4}{[(0.5n)!]^4(2n)!}$$

which decreases with increasing n



4.3 Assuming that a silver-gold alloy is a random mixture of gold and silver atoms, calculate the increase in entropy when 10 g of gold are mixed with 20 g of silver to form an ideal homogeneous alloy. The gram atomic weights of Au and Ag are, respectively, 198 and 107.9.

n_{Au} = number of atoms of Au $= \frac{10}{198} \times 6.023 \times 10^{23}$

n_{Ag} = number of atoms of Ag $= \frac{20}{107.9} \times 6.023 \times 10^{23}$

$$\Delta S_{conf} = k \ln \frac{(n_{Au} + n_{Ag})!}{n_{Au}!\, n_{Ag}!}$$

$$= k\left[(n_{Au} + n_{Ag}) \ln (n_{Au} + n_{Ag}) - n_{Au} \ln n_{Au} - n_{Ag} \ln n_{A}\right.$$

$$= 1.3805 \times 10^{-23} \left[7.574 - 1.575 - 5.925\right] \times 10^{24}$$

$$= 1.02 \text{ J/K}$$

4.4 On the assumption that copper and nickel form ideal solutions, calculate the mass of copper which, when mixed with 100 g of nickel, causes an increase in entropy of 15 J/K. The gram atomic weights of Cu and Ni are, respectively, 63.55 and 58.69.

$$\text{number of atoms of Ni} = \frac{100}{58.69} \times 6.023 \times 10^{23} = 1.026 \times 10^{24}$$

$$\text{number of atoms of Cu} = n_{Cu}$$

$$\Delta S_{conf} = 15 = k\left[(n_{Ni} + n_{Cu}) \ln (n_{Ni} + n_{Cu}) - n_{Ni} \ln n_{Ni} - n_{Cu} \ln n_{Cu}\right]$$

$$= 1.3805 \times 10^{-23}\left[(1.026 \times 10^{24} + n_{Cu}) \ln (1.026 \times 10^{24} + n_{Cu}) - 1.026 \times 10^{24} \ln (1.026 \times 10^{24}) - n_{Cu} \ln n_{Cu}\right]$$

$$\therefore n_{Cu} = 6.161 \times 10^{23}$$

$$\text{mass of Cu} = \frac{6.161 \times 10^{23}}{6.023 \times 10^{23}} \times 63.55 = 65.0\text{g}$$

Problem 4.5* We saw in Sec. 4.6 (Eq. 4.xx) that $A = -nk_B T \ln \mathcal{Z}$. We will see in the next chapter that: $\left(\frac{\partial A}{\partial T}\right)_V = -S$. Perform the differentiation of A with respect to temperature and obtain the relationship for the entropy of an isolated system in terms of its partition function $\mathcal{Z}$.

$$A = -nk_B T \ln \mathcal{Z}$$

$$\left(\frac{\partial A}{\partial T}\right)_V = -S = -nk_B \ln \mathcal{Z} - nk_B T \frac{\partial \ln \mathcal{Z}}{\partial T}$$

Thus

$$S = nk_B \ln \mathcal{Z} + nk_B T \frac{\partial \ln \mathcal{Z}}{\partial T}$$

Note that if we multiply both sides by T we obtain:

$$S = nk_B \ln \mathcal{Z} + nk_B T \frac{\partial \ln \mathcal{Z}}{\partial T}$$

$$TS = -A + nk_B T^2 \frac{\partial \ln \mathcal{Z}}{\partial T}$$

Thus: $\mathrm{U} = nk_B T^2 \frac{\partial \ln \mathcal{Z}}{\partial T}$

Problem 4.6* A weak magnetic field is applied to a system of up and down spins. The up spins have a slightly lower energy state than those with down spins. This is because the up spins are favored by the weak magnetic field. Thus

$$\varepsilon^{\uparrow} < \varepsilon^{\downarrow}$$

a. Determine the partition function for this system under the influence of the weak magnetic field.

b. Determine the ratio of: $\dfrac{n^{\uparrow}}{n^{\downarrow}}$ for very high temperatures and very low temperatures.

SOLUTION

$$a. \quad \mathcal{Z} = \sum \exp(\frac{\varepsilon_i}{k_B T}) = \exp(\frac{\varepsilon^{\uparrow}}{k_B T}) + \exp(\frac{\varepsilon^{\downarrow}}{k_B T})$$

$$\frac{n^{\uparrow}}{n} = \frac{\exp(\frac{-\varepsilon^{\uparrow}}{k_B T})}{\exp(\frac{-\varepsilon^{\uparrow}}{k_B T}) + \exp(\frac{-\varepsilon^{\downarrow}}{k_B T})} \quad \text{and} \quad \frac{n^{\downarrow}}{n} = \frac{\exp(\frac{-\varepsilon^{\downarrow}}{k_B T})}{\exp(\frac{-\varepsilon^{\uparrow}}{k_B T}) + \exp(\frac{-\varepsilon^{\downarrow}}{k_B T})}$$

Thus:

$$\frac{n^{\uparrow}}{n^{\downarrow}} = \frac{\exp(\frac{-\varepsilon^{\uparrow}}{k_B T})}{\exp(\frac{-\varepsilon^{\downarrow}}{k_B T})} \quad \text{as T gets large:} \frac{n^{\uparrow}}{n^{\downarrow}} = \frac{1 - \frac{\varepsilon^{\uparrow}}{k_B T}}{1 - \frac{\varepsilon^{\downarrow}}{k_B T}} = 1$$

equal numbers of up and down

$$\text{b.} \quad \frac{n^{\uparrow}}{n^{\downarrow}} = \frac{\exp(\frac{-\varepsilon^{\uparrow}}{k_B T})}{\exp(\frac{-\varepsilon^{\downarrow}}{k_B T})} = \exp(\frac{\varepsilon^{\downarrow} - \varepsilon^{\uparrow}}{k_B T})$$

The numerator of the exponental is poitive: Thus as T gets small the exponential get large.

As T $\to 0$ $n^{\uparrow} \to n$ and $n^{\downarrow} \to 0$

5.13* Show that the three TdS equations can be written as:

1. $TdS = C_V dT + \frac{T\alpha}{\beta_T} dV$
2. $TdS = C_P dT - TV\alpha dP$
3. $TdS = C_V \frac{\beta_T}{\alpha} dP + \frac{C_P}{\alpha V} dV$

Solution

1. $TdS = C_V dT + T\left(\frac{\partial P}{\partial T}\right)_V dV$

We need to obtain an expression for $\left(\frac{\partial P}{\partial T}\right)_V$

$$\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial V}{\partial P}\right)_T = -1$$

$$\left(\frac{\partial P}{\partial T}\right)_V = -\frac{1}{\left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial V}{\partial P}\right)_T} = \frac{-\alpha V}{-\beta_T V} = \frac{\alpha}{\beta_T}$$

$$TdS = C_V dT + T\frac{\alpha}{\beta_T} dV$$

2. $TdS = C_P dT - T\left(\frac{\partial V}{\partial T}\right)_P dP$

We need an expression for $\left(\frac{\partial V}{\partial T}\right)_P$

We know that $\left(\frac{\partial V}{\partial T}\right)_P = V\alpha$

Thus

$TdS = C_P dT - TV\alpha dP$

3. $TdS = C_V \left(\frac{\partial T}{\partial P}\right)_V dP + C_P \left(\frac{\partial T}{\partial V}\right)_P dV$

We need expressions for $\left(\frac{\partial T}{\partial P}\right)_V$ and $\left(\frac{\partial T}{\partial V}\right)_P$

$\left(\frac{\partial T}{\partial P}\right)_V = \frac{\beta_T}{\alpha}$ see first TdS equation above

$$\left(\frac{\partial T}{\partial V}\right)_P = \frac{1}{\alpha V}$$

Thus

$$TdS = C_V \frac{\beta_T}{\alpha} dP + \frac{C_P}{\alpha V} dV$$

5.14* Starting from the following equation valid for a closed system, obtain Maxwell relationships.

$$dH = TdS + VdP - \mu_0 V\boldsymbol{M}d\mathcal{H}$$

Solution

$$\left(\frac{\partial T}{\partial P}\right)_{S,\mathcal{H}} = \left(\frac{\partial V}{\partial S}\right)_{P,\mathcal{H}}$$

$$\left(\frac{\partial V}{\partial \mathcal{H}}\right)_{S,P} = -\mu_0 V\left(\frac{\partial M}{\partial P}\right)_{S,\mathcal{H}}$$

$$\left(\frac{\partial T}{\partial \mathcal{H}}\right)_{S,P} = -\mu_0 V\left(\frac{\partial M}{\partial S}\right)_{P,\mathcal{H}}$$

5.15* Starting from the following equation valid for a closed system, obtain Maxwell relationships.

$$dA = -SdT - PdV + \mu_0 V \mathcal{H} d\boldsymbol{M}$$

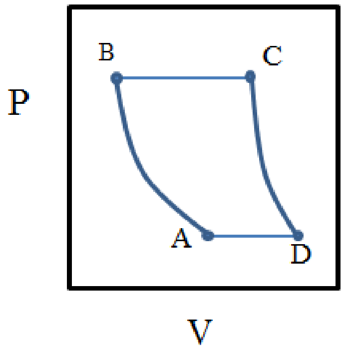
Solution

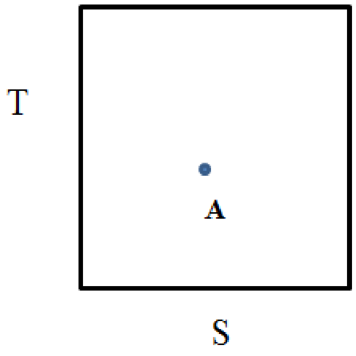
$$\left(\frac{\partial S}{\partial V}\right)_{T,M} = \left(\frac{\partial P}{\partial T}\right)_{V,M}$$

$$\left(\frac{\partial S}{\partial M}\right)_{T,V} = -\mu_0 V \left(\frac{\partial \mathcal{H}}{\partial T}\right)_{M,V}$$

$$\left(\frac{\partial P}{\partial M}\right)_{V,T} = -\mu_0 V \left(\frac{\partial \mathcal{H}}{\partial V}\right)_{M,T}$$

5.16* The cycle shown below consists of two isotherms (AB and CD) and two isobars (BC and DA). Use the TdS equations to draw the T-S diagram for this cycle.





Use the following TdS equations

1. $TdS = C_V dT + \frac{T\alpha}{\beta_T} dV$
2. $TdS = C_P dT - TV\alpha dP$
3. $TdS = C_V \frac{\beta_T}{\alpha} dP + \frac{C_P}{\alpha V} dV$

A→B from 1, at constant T, ifV decreases, S decreases

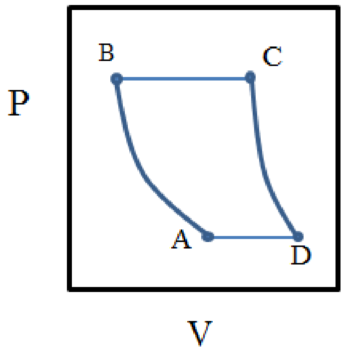
B→C from 3, at constant P, V increases then S increases.

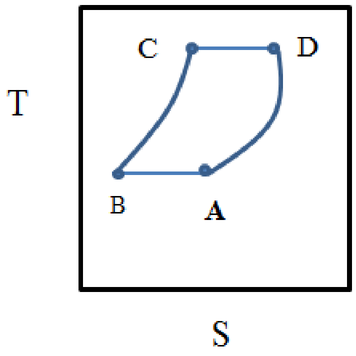
From 2, at constant P if S increases T increases

C—D from 2, at constant T if P increases then S increases

D—A from 3, at constant P, if V decreases S decreases

From 2, at contant P is S decreases, T decreases.





5.17* Show that: $\dfrac{\beta_T}{\beta_S} = \dfrac{c_P}{c_V} = \gamma$ where $\beta_T \equiv \dfrac{1}{V}\left(\dfrac{\partial V}{\partial P}\right)_T$ and $\beta_S \equiv \dfrac{1}{V}\left(\dfrac{\partial V}{\partial P}\right)_S$

Hint: use the TdS equations.

Solution

Start with the First and Second TdS equations:

1. $TdS = C_V dT + \dfrac{T\alpha}{\beta_T} dV$
2. $TdS = C_P dT - TV\alpha dP$

Set S = 0 and divide 2 by 1

1. $C_V dT = -\dfrac{T\alpha}{\beta_T} dV$
2. $C_P dT = TV\alpha dP$

$$\frac{C_P}{C_V} = -\frac{TV\alpha}{\frac{T\alpha}{\beta_T}}\left(\frac{dP}{dV}\right)_S = (V\beta_T)\frac{1}{(V\beta_S)} = \frac{\beta_T}{\beta_S}$$

6.1 Calculate ΔH_{1600} and ΔS_{1600} for the reaction $Zr_{(\beta)} + O_2 = ZrO_{2(\beta)}$

For $Zr(\alpha) + O_2 = ZrO_2(\alpha)$ $\Delta H_{298} = -1100800$ J

For $Zr(\alpha) + O_2 = ZrO_2(\alpha)$ in the range 298 − 1136 K

$\Delta c_p = 17.69 - 8.28\times10^{-3}T - 12.39\times10^{5}T^{-2}$ J/K

At 1136 K $Zr(\alpha) \rightarrow Zr(\beta)$ $\Delta H_{trans} = 3900$ J

For $Zr(\beta) + O_2 = ZrO_2(\alpha)$ in the range 1136 − 1478 K

$\Delta c_p = 16.44 - 1.29\times10^{-3}T - 12.39\times10^{5}T^{-2}$ J/K

At 1478 K $ZrO_2(\alpha) \rightarrow ZrO_2(\beta)$ $\Delta H_{trans} = 5900$ J

For $Zr(\beta) + O_2 = ZrO_2(\beta)$ in the range 1478 − 1600 K

$\Delta c_p = 21.3 - 8.82\times10^{-3}T + 1.67\times10^{5}T^{-2}$ J/K

$\therefore$ ΔH_{1600} for $Zr(\beta) + O_2 = ZrO_2(\beta)$

$= -1100800$

$+ 17.69(1136-298) - 4.14\times10^{-3}(1136^2-298^2) + 12.39\times10^{5}\left(\frac{1}{1136}-\frac{1}{298}\right)$

$- 3900$

$+ 16.44(1478-1136) - 0.645\times10^{-3}(1478^2-1136^2) + 12.39\times10^{5}\left(\frac{1}{1478}-\frac{1}{1136}\right.$

$+ 5900$

$+ 21.3(1600-1478) - 4.41\times10^{-3}(1600^2-1478^2) - 1.67\times10^{5}\left(\frac{1}{1600}-\frac{1}{1478}\right.$

$= -1086000$ J

6.1 continued

$$\Delta S_{298} = 50.4 - 205.1 - 39 = -193.7 \text{ J/K}$$

$$\therefore \Delta S_{1600} = -193.7$$

$$+ 17.69 \ln\left(\frac{1136}{298}\right) - 8.28\times10^{-3}(1136-298) + 6.185\times10^{5}\left(\frac{1}{1136^2} - \frac{1}{298^2}\right)$$

$$- \frac{3980}{1136}$$

$$+ 16.44 \ln \frac{1478}{1136} - 1.29\times10^{-3}(1478-1136) + 6.185\times10^{5}\left(\frac{1}{1478^2} - \frac{1}{1136^2}\right)$$

$$+ \frac{5901}{1478}$$

$$+ 21.3 \ln \frac{1600}{1478} - 8.82\times10^{-3}(1600-1478) - 0.835\times10^{5}\left(\frac{1}{1600^2} - \frac{1}{1478^2}\right)$$

$$= -178.5 \text{ J/K}$$

6.2 Which of the following two reactions is the more exothermic?

(i) $C_{(graphite)} + \frac{1}{2}O_{2(g)} \rightarrow CO_{(g)}$ at 1000 K

(ii) $C_{(diamond)} + \frac{1}{2}O_{2(g)} \rightarrow CO_{(g)}$ at 1000 K.

$$H_{graphite,1000} = 0.11(1000-298) + \frac{38.94}{2}\times 10^{-3}(1000^2-298^2) + 1.48\times 10^{5}\left(\frac{1}{1000}-\frac{1}{298}\right) - \frac{17.38\times 10^{6}}{3}(1000^3-298^3)$$

$$= 11830 \text{ J}$$

$$H_{diamond,1000} = 1500 + 9.12(1000-298) + \frac{13.22\times 10^{-3}}{2}(1000^2-298^2 + 6.19\times 10^{5}\left(\frac{1}{1000}-\frac{1}{298}\right)$$

$$= 12867 \text{ J.}$$

∴ For diamond → graphite

$$\Delta H_{1000} = 11830 - 12867 = -1037 \text{ J}$$

∴ For $C(graphite) + \frac{1}{2}O_2 = CO.$ ΔH_1

$C(diamond) = C(graphite.$ $\Delta H = -1037$

∴ $C(diamond) + \frac{1}{2}O_2 = CO$ ΔH_1 -1037

∴ The oxidation of diamond is 1037 J more exothermic than the oxidation of graphite on a molar basis

6.3 Calculate the change in enthalpy and the change in entropy at 1000K for the reaction
$CaO_{(s)} + TiO_{2(s)} = CaTiO_{3(s)}$

For $Ca(\alpha) + \frac{1}{2}O_2 = CaO$ $\Delta H_{298} = -634900\ J$

In the range 298 – 716 K

$\Delta c_p = 9.42 + 9.68\times10^{-3}T - 6.115\times10^{5}T^{-2}$

At 716 K $Ca(\alpha) \rightarrow Ca(\beta)$ $\Delta H_{trans} = 900\ J$

For $Ca(\beta) + \frac{1}{2}O_2 = CaO$ in the range 716 – 1000

$\Delta c_p = 35.15 - 38.83\times10^{-3}T - 6.115\times10^{5}T^{-2}$

$$\Delta H_{1000} = -634900$$
$$+ 9.42(716-298) + 4.84\times10^{-3}(716^2-298^2) + 6.115\times10^{5}\left(\frac{1}{716}-\frac{1}{298}\right)$$
$$- 900$$
$$+ 35.15(1000-716) - 19.415\times10^{-3}(1000^2-716^2) + 6.115\times10^{5}\left(\frac{1}{1000}-\frac{1}{716}\right)$$
$$= -636700\ J$$

For $Ti + O_2 = TiO_2$ $\Delta H_{298} = -944000\ J$

In the range 298 – 1000 K

$\Delta c_p = 23.14 - 13.47\times10^{-3}T - 16.53\times10^{5}T^{-2}$

$$\therefore \Delta H_{1000} = -944000$$
$$+ 23.14(1000-298) - 6.735\times10^{-3}(1000^2-298^2)$$
$$+ 16.53\times10^{5}\left(\frac{1}{1000}-\frac{1}{298}\right)$$

$$= -937800\ J$$

6.3 continued

For $Ca(\alpha) + Ti + \frac{3}{2}O_2 = CaTiO_3 \quad \Delta H_{298} = -1660600\ J$

In the range 298 - 716 K

$$\Delta c_p = 35.09 - 3.78\times10^{-3}T - 25.485\times10^{5}T^{-2}\ J/K$$

At 716 K $\quad Ca(\alpha) \rightarrow Ca(\beta) \quad \Delta H_{trans} = 900\ J$

In the range 716 - 1000 K, for $Ca(\beta) + Ti + \frac{3}{2}O_2 = CaTiO_3$

$$\Delta c_p = 60.82 - 52.29\times10^{-3}T - 25.485\times10^{5}T^{-2}\ J/K$$

$$\Delta H_{1000} = -1660600$$

$$+ 35.09(716-298) - 1.69\times10^{-3}(716^2-298^2) + 25.485\times10^{5}\left(\frac{1}{716}-\frac{1}{298}\right)$$

$$-900$$

$$+ 60.82(1000-716) - 26.145\times10^{-3}(1000^2-716^2) + 25.485\times10^{5}\left(\frac{1}{1000}-\frac{1}{298}\right)$$

$$= -1649000\ J$$

For $CaO + TiO_2 = CaTiO_3$

$$\Delta H_{1000} = -1649000 + 937800 + 630700 = -80500\ J$$

For $Ca(\alpha) + \frac{1}{2}O_2 = CaO \quad \Delta S_{298} = 38.1 - 46.1 - \frac{205.1}{2} = -106.05\ J,$

$\therefore$ For $Ca(\beta) + \frac{1}{2}O_2 = CaO$

$$\Delta S_{1000} = -106.05$$

$$+ 9.42\ln\left(\frac{716}{298}\right) + 9.68\times10^{-3}(716-298) + 3.0525\times10^{5}\left(\frac{1}{716^2}-\frac{1}{298^2}\right.$$

6.3 Continued (2)

$$-\frac{900}{716}$$

$$+35.15\ln\left(\frac{1000}{716}\right)-38.83\times10^{-3}(1000-716)+3.0525\times10^{5}\left(\frac{1}{1000^2}-\frac{1}{716^2}\right)$$

$$= -97.42 \text{ J/K}$$

For $Ti + O_2 = TiO_2$ $\Delta S_{298} = 50.6 - 205.1 - 30.7 = -185.2$ J/K

$$\therefore \Delta S_{1000} = -185.2$$

$$+23.14\ln\left(\frac{1000}{298}\right)-13.47\times10^{-3}(1000-298)+8.265\times10^{5}\left(\frac{1}{1000^2}-\frac{1}{298^2}\right)$$

$$= -175.1 \text{ J/K}$$

For $Ca(\alpha) + Ti + \frac{3}{2}O_2 = CaTiO_3$

$$\Delta S_{298} = 93.7 - 41.6 - 30.7 - \frac{3}{2}\times 205.1 = -286.25 \text{ J/K}$$

$$\Delta S_{1000} = -286.25$$

$$+35.09\ln\left(\frac{716}{298}\right)-3.78\times10^{-3}(716-298)+12.743\times10^{5}\left(\frac{1}{716^2}-\frac{1}{298^2}\right)$$

$$-\frac{900}{716}$$

$$+60.82\ln\left(\frac{1000}{716}\right)-52.29\times10^{-3}(1000-716)+12.743\times10^{5}\left(\frac{1}{1000^2}-\frac{1}{716^2}\right)$$

$$= -256.9 \text{ J/K}$$

$\therefore$ For $CaO + TiO_2 = CaTiO_3$

$$\Delta S_{1000} = -256.9 + 97.4 + 175.1 = 6.6 \text{ J/K}$$

6.4 Copper exists in the state $T =$ 298K, $P = 1$ atm. Calculate the temperature to which the copper must be raised at 1 atm pressure to cause the same increase in molar enthalpy as is caused by increasing its pressure to 1000 atm at 298K. The molar volume of copper at 298K is 7.09 cm^3 and the thermal expansivity is 0.493 x 10^{-3} K^{-1}. These values can be taken as being independent of pressure in the range 1 – 1000 atm.

$P_1 = 1\,\text{atm}, \quad P_2 = 1000\,\text{atm}, \quad T = 298\,K$

$$\Delta H = v(1-\alpha T)(P_2 - P_1)$$

$$= 7.09 \times 10^{-3}(1 - 0.493 \times 10^{-3} \times 298)(1000-1) \times 101.3$$

$$= 612\,J$$

$T_1 = 298, \quad T_2 = T, \quad P = 1\,\text{atm}$

$$\Delta H = \int_{T_1}^{T} C_p\,dT$$

$$707 = 22.64(T-298) - \frac{6.28 \times 10^{-3}}{2} \cdot (T^2 - 298^2)$$

$$\therefore \quad T = 327\,K$$

6.6 An adiabatic vessel contains 1000 g of liquid aluminum at 700°C. Calculate the mass of Cr_2O_3 at room temperature, which, when added to the liquid aluminum (with which it reacts to form Cr and Al_2O_3) raises the temperature of the resulting mixture of Al_2O_3, Cr_2O_3 and Cr to 1600K

For $2Al + Cr_2O_3 = 2Cr + Al_2O_3$

$$\Delta H_{298} = -1675700 + 1134700 = -541000 \text{ J}$$

and in the range 298 – 934 K (T_m, Al)

$$\Delta c_p = -5.25 + 3.46\times10^{-3}T - 20.24\times10^{5}T^{-2} \quad \text{J/K}$$

At 934 K $Al_{(s)} \rightarrow Al_{(l)}$ $\Delta H_m = 10700$ J

and for $2Al(l) + Cr_2O_3 = 2Cr(s) + Al_2O_3$

in the range 973 – 934

$$\Delta c_p = -27.43 + 28.22\times10^{-3}T - 20.24\times10^{5}T^{-2} \quad \text{J/K}$$

∴ For $2Al(l) + Cr_2O_3 = 2Cr(s) + Al_2O_3$

$$\begin{aligned}\Delta H_{973} &= -541000 \\ &\quad -5.25(934-298) + \frac{3.46\times10^{-3}}{2}(934^2-298^2) \\ &\quad +20.24\times10^{5}\left(\frac{1}{934}-\frac{1}{298}\right) \\ &\quad -2\times10700 \\ &\quad -27.43(973-934) + \frac{28.22\times10^{-3}}{2}(973^2-934^2) \\ &\quad +20.24\times10^{5}\left(\frac{1}{973}-\frac{1}{298}\right) \\ &= -562400 \text{ J}\end{aligned}$$

6.6 continued

Heat required to increase the temperature of 1 mole of Cr_2O_3 from 298 to 973 K

$$= 119.37(973-298) + \frac{9.3\times10^{-3}}{2}(973^2-298^2) + 15.65\times10^5\left(\frac{1}{973}-\frac{1}{298}\right)$$

$$= 80920 \text{ J}$$

∴ Sensible heat available at 973 K, per mole of Cr_2O_3 reacted

$$= 562400 - 80920 = 481480 \text{ J}$$

Heat required to raise the temperature of 1 mole of Cr_2O_3 from 973 to 1600 K

$$= 119.37(1600-973) + \frac{10.38\times10^{-3}}{2}(1600^2-973^2)$$
$$+ 15.65\times10^5\left(\frac{1}{1600}-\frac{1}{973}\right)$$

$$= 81720 \text{ J}$$

Heat required to raise the temperature of 1 mole of Al_2O_3 from 973 to 1600 K

$$= 106.6(1600-973) + \frac{17.78\times10^{-3}}{2}(1600^2-973^2)$$
$$+ 28.53\times10^5\left(\frac{1}{1600}-\frac{1}{973}\right)$$

$$= 80030 \text{ J}$$

Heat required to raise the temperature of 1 mole Cr

6.6 continued (2)

from 973 to 1600K

$$= 24.43(1600-973) + \frac{9.87\times 10^{-3}}{2}(1600^2-973^2) + 3.68\times 10^5\left(\frac{1}{1600}-\frac{1}{973}\right)$$

$$= 23130 \text{ J}$$

$\therefore$ Sensible heat available to increase the temperature of the excess Cr_2O_3

$$= 481400 - 2\times 23130 - 80030 = 355190 \text{ J}$$

$\therefore$ Number of excess moles of Cr heated

$$= \frac{355190}{81720} = 4.35$$

$\therefore$ The reactants are 2 moles of Al + 5.35 moles of Cr_2O_3

or 5.35×152 g Cr_2O_3 per 2×26.98 g Al

or 813.2 g Cr_2O_3 per 53.96 g Al

or 15.1 kg Cr_2O_3 per kg Al

6.8 Calculate the value of ΔG for the reaction

$$Si_3N_4 + 3\,O_2 = 3\,SiO_{2(\alpha-\text{quartz})} + 2\,N_2$$

At 800 K. What percentage of error occurs if it is assumed that Δc_p for the reaction is zero?

$$\Delta H_{298} = -3\times 910900 + 744800 = -1987900\text{ J}$$

$$\Delta S_{298} = 2\times 191.5 + 3\times 41.5 - 3\times 205.1 - 113.0 = -220.8\text{ J/K}$$

$$\Delta c_p = 26.99 - 99.74\times 10^{-3}T - 13.05\times 10^{5}T^{-2}$$

$$\therefore \Delta H_{800} = -1987900 + 26.99(800-298) - \frac{99.74\times 10^{-3}}{2}(800^2-298^2) + 13.05\times 10^{5}\left(\frac{1}{800}-\frac{1}{298}\right)$$

$$= -2{,}005{,}000\text{ J}$$

$$\Delta S_{800} = -220.8 + 26.99\ln\left(\frac{800}{298}\right) - 99.74\times 10^{-3}(800-298) + \frac{13.05}{2}\times 10^{5}\left(\frac{1}{800^2}-\frac{1}{298^2}\right)$$

$$= -250.5\text{ J/K}$$

$$\therefore \Delta G_{800} = -2005000 + 800\times 250.5 = -1{,}805{,}000\text{ J}$$

Assume $\Delta c_p = 0$

$$\Delta G_{800} = -1987900 + 800\times 220.8 = -1{,}811{,}000\text{ J}$$

$$\text{Error}\quad \frac{1811000 - 1805000}{1805000} = 0.003 \quad (0.3\%)$$

6.9 Determine the stoichiometric coefficients for the reaction

$$(3CaO.Al_2O_3.3SiO_2) + a(CaO.Al_2O_3.SiO_2) = b(CaO.Al_2O_3.2SiO_2) + c(2CaO.Al_2O_3.SiO_2)$$

and calculate ΔH_{298}, ΔS_{298} and ΔG_{298} for the reaction.

Mass balance on

$CaO \quad 3 + a = b + 2c$

$Al_2O_3 \quad 1 + a = b + c$

$SiO_2 \quad 3 + a = 2b + c$

$\therefore \quad a = b + 2c - 3 = b + c - 1 = 2b + c - 3$

$c - 3 = -1$

$\therefore \; c = 2$

$2c - 3 = b + c - 3$

$\therefore \; b = 2 \quad$ and $\quad a = b + 2c - 3 = 3$

$$\therefore (3CaO.Al_2O_3.3SiO_2) + 3(CaO.Al_2O_3.SiO_2) = 2(CaO.Al_2O_3.2SiO_2) + 2(2CaO.Al_2O_3.SiO_2)$$

$$\Delta H_{298} = -2 \times 6646300 - 2 \times 3989400 + 3 \times 3293200 + 6646300$$

$$= 99700 \text{ J}$$

$$\Delta S_{298} = 2 \times 202.5 + 2 \times 198.3 - 241.4 - 3 \times 144.8$$

$$= 125.8 \text{ J/K}$$

$$\therefore \Delta G_{298} = 99700 - 298 \times 125.8 = 62210 \text{ J}$$

6.10 How much heat is required to increase the temperature of 1 kg of cordierite, $2MgO.2Al_2O_3.5SiO_2$, from 298 K to its incongruent melting temperature of 1738 K?

$M.W = 2\times 40.31 + 2\times 101.96 + 5\times 60.09 = 585$

$c_p = 626.34 + 91.21\times 10^{-3}T - 200.83\times 10^{5}T^{-2}$ J/K.mole

∴ Heat required per mole

$$= 626.34(1738-298) + \frac{91.21\times 10^{-3}}{2}(1738^2 - 298^2) + 200.83\times 10^5\left(\frac{1}{1738} - \frac{1}{298}\right)$$

$= 979799$ J

∴ Heat required for 1 kg

$$= \frac{979799}{585}\times 1000 = 1675000 \text{ J}$$

6.11* A function $\Omega \equiv -F + \mu N$, where F is the Helmholtz free energy , μ is the chemical potential and N is the number of particles in the system.

Obtain an expression for $d\Omega$ and thus determine the independent variables for this function.

$$d\,\Omega = -dF + \mu dN + Nd\mu$$

but $F \equiv U - TS$ so

$$dF = dU - TdS - SdT = -PdV - Nd\mu - SdT$$

$$d\,\Omega = SdT + PdV + Nd\mu$$

$$\Omega = \Omega\,(T, V, \mu)$$

6.12* (a) Given that the Helmholtz energy can be written as:

$$F = -N_{system} k_B T \ln \mathcal{Z}$$

Obtain simplified expressions for both F and S of an Einstein solid.

(b) Show that the entropy approaches 0 as the temperature approaches 0 in such a solid.

From the text we saw that $\mathcal{Z}$ for the Einstein solid can be written as:

$$\mathcal{Z} = \exp\left[-\frac{1}{2}\frac{\mathrm{h}\nu}{\mathrm{k}_B\mathrm{T}}\right]\left[\frac{1}{1-\exp\left(\frac{-h\nu}{k_BT}\right)}\right]$$

$$\mathrm{F} = -\mathrm{N}_{system} k_B T \ln \mathcal{Z}$$

$$\mathrm{F} = \frac{3}{2}\mathrm{N}_{system}\mathrm{h}\nu + 3\mathrm{N}_{system} k_B T \ln\left[1-\exp\left(\frac{-h\nu}{k_BT}\right)\right]$$

$$-\frac{\partial F}{\partial T} = \mathrm{S} = \mathrm{N}_{\mathrm{sys}}\ \mathrm{k}_B\ \ln\mathcal{Z} + \mathrm{N}_{\mathrm{sys}} kT\left(\frac{\partial \ln \mathcal{Z}}{\partial T}\right)_V$$

$$\mathrm{S} = \mathrm{N}_{system} k_B \left(\frac{h\nu}{kT}\right)\frac{\exp\left(-\frac{h\nu}{k_BT}\right)}{1\text{-}\exp\left(-\frac{h\nu}{k_BT}\right)} - \mathrm{N}_{system} k_B \ \ln\left[1\text{-}\exp\left(-\frac{h\nu}{k_BT}\right)\right]$$

Since $\mathrm{N}_{\mathrm{system}} = 3\mathrm{n}$

$$\mathrm{S} = 3\mathrm{n}k_B \left(\frac{h\nu}{k_BT}\right)\frac{\exp\left(-\frac{h\nu}{k_BT}\right)}{1\text{-}\exp\left(-\frac{h\nu}{k_BT}\right)} - 3\mathrm{n}k_B \ \ln\left[1\text{-}\exp\left(-\frac{h\nu}{k_BT}\right)\right]$$

$$\mathrm{S} = 3\mathrm{nk}\left(\frac{h\nu}{k_B T}\right)\frac{\exp\left(-\frac{h\nu}{k_B T}\right)}{1\text{-}\exp\left(-\frac{h\nu}{k_B T}\right)} - 3\mathrm{n}k_B \ln\left[1\text{-}\exp\left(-\frac{h\nu}{k_B T}\right)\right]$$

$$\frac{\exp\left(-\frac{h\nu}{k_B T}\right)}{1\text{-}\exp\left(-\frac{h\nu}{k_B T}\right)} \rightarrow 0 \text{ as T } \rightarrow 0$$

$$1\text{-}\exp\left(-\frac{h\nu}{k_B T}\right) \rightarrow 1 \text{ as T } \rightarrow 0\text{: ln 1 =0}$$

So S $\rightarrow 0$ as T $\rightarrow 0$

6.13* Obtain an expression for the internal energy of an Einstein solid as the temperature gets very large and differentiate it with respect to T and show that the Dulong and Petit value for the heat capacity is attained.

$$U' = \frac{3}{2}nh\nu + \frac{3nh\nu}{(\exp(\frac{h\nu}{k_BT}) - 1)}$$

$$\text{as T } \to \infty \ \exp(\frac{h\nu}{k_BT}) \to 1 + \frac{h\nu}{k_BT}$$

$$U' = \frac{3}{2}nh\nu + \frac{3nh\nu}{(\frac{h\nu}{k_BT})} = \frac{3}{2}nh\nu + 3nk_BT$$

$$\text{Thus } C_V = \frac{\partial U'}{\partial T} = 3nk_B = 3R \quad \text{for one mole}$$

7.1 Using the vapor pressure-temperature relationships for $CaF_{2(\alpha)}$, $CaF_{2(\beta)}$ and liquid CaF_2, calculate:

1. The temperatures and pressures of the triple points for the equilibria $CaF_{2(\alpha)}$-$CaF_{2(\beta)}$-$CaF_{2(v)}$ and $CaF_{2(\beta)}$-$CaF_{2(l)}$-$CaF_{2(v)}$,
2. the normal boiling temperature of CaF_2,
3. the molar latent heat of the transformation $CaF_{2(\alpha)} \rightarrow CaF_{2(\beta)}$,
4. the molar latent heat of melting of $CaF_{2(\beta)}$.

$$\ln p_{CaF_2}(\alpha) = \frac{-54350}{T} - 4.525 \ln T + 56.57$$

$$\ln p_{CaF_2}(\beta) = \frac{-53780}{T} - 4.525 \ln T + 56.08$$

$$\ln p_{CaF_2}(l) = \frac{-50200}{T} - 4.525 \ln T + 53.96$$

1) At the α-β-vapor triple point

$$\frac{-54350}{T} + 56.57 = \frac{-53780}{T} + 56.08$$

$\therefore$ $T = 1163K$ and $p_{CaF_2} = 2.52 \times 10^{-10}$ atm

At the β-liquid-vapor triple point.

$$-\frac{53780}{T} + 56.08 = -\frac{50200}{T} + 53.96$$

$\therefore$ $T = 1689K$ and $p_{CaF_2} = 8.35 \times 10^{-5}$ atm

2) At T_b, $p_{CaF_2} = 1$ atm

$$\therefore \ln(1) = 0 = \frac{-50200}{T} - 4.525 \ln T + 53.96$$

which gives $T_b = 2776K$

7.1 continued

3) For α-vapor equilibrium

$$\ln p_{CaF_2} = -\frac{54350}{T} - 4.525 \ln T + 56.57$$

$$\frac{d \ln p_{CaF_2}}{dT} = \frac{54350}{T^2} - \frac{4.525}{T} = \frac{\Delta H(\alpha \to v)}{RT^2}$$

$$\therefore \Delta H(\alpha \to v) = R(54350 - 4.525T)$$

For β-vapor equilibrium

$$\ln p_{CaF_2} = \frac{-53780}{T} - 4.525 \ln T + 56.08$$

$$\frac{d \ln p_{CaF_2}}{dT} = \frac{53780}{T^2} - \frac{4.525}{T} = \frac{\Delta H(\beta \to v)}{RT^2}$$

$$\therefore \Delta H(\beta \to v) = R(53780 - 4.525T)$$

$$\Delta H(\alpha \to \beta) = \Delta H(\alpha \to v) - \Delta H(\beta - v)$$

$$= 8.3144(54350 - 53780)$$

$$= 4739 \text{ J.}$$

4) For $l - v$ equilibrium

$$\ln p_{CaF_2} = -\frac{50200}{T} - 4.525 \ln T + 53.96$$

$$\frac{d \ln p_{CaF_2}}{dT} = \frac{50200}{T^2} - \frac{4.525}{T} = \frac{\Delta H(l \to v)}{RT^2}$$

$$\therefore \Delta H(l \to v) = R(50200 - 4.525T)$$

$$\therefore \Delta H(\beta \to l) = \Delta H(\beta \to v) - \Delta H(l \to v)$$

$$= 8.3144(53780 - 50200)$$

$$= 29765 \text{ J}$$

7.2 Calculate the approximate pressure required to distill mercury at 100°C.

The saturated vapor pressure of liquid Hg is

$$\ln p\,(\text{atm}) = \frac{-7611}{T} - 0.795 \ln T + 17.168$$

$\therefore$ At $T = 373$ K, $p_{Hg} = 3.55 \times 10^{-4}$ atm

and Hg will be distilled at pressures lower than this value.

7.3 One mole of $SiCl_4$ vapor is contained at 1 atm pressure and 350 K in a rigid container of fixed volume. The temperature of the container and its contents is cooled to 280 K. At what temperature does condensation of the $SiCl_4$ vapor begin and what fraction of the vapor has condensed when the temperature is 280 K?

Assuming ideal behavior of $SiCl_4$ vapor, the volume of the container is $V = \frac{nRT}{P} = 0.082057 \times 350 = 28.72\ l$

and cooling causes the pressure of the vapor to decrease according to $P = \frac{nR}{V} \cdot T = \frac{0.082057}{28.72} T = 2.857 \times 10^{-3} T$

The saturated vapor pressure of liquid $SiCl_4$ is

$$p(\text{atm}) = \exp\left(-\frac{3620}{T} + 10.96\right)$$

and thus condensation begins at T given by

$$2.857 \times 10^{-3} T = \exp\left(-\frac{3620}{T} + 10.96\right)$$

$$\text{i.e. } T = 328\ K$$

At 280 K the saturated vapor pressure is

$$\exp\left(-\frac{3620}{280} + 10.96\right) = 0.1396\ \text{atm}$$

and the number of moles of $SiCl_4$ in the vapor phase is $n = \frac{PV}{RT} = \frac{0.1396 \times 28.72}{0.082057 \times 280} = 0.175$

The number of moles in the liquid phase $= 1 - 0.175 = 0.825$

and thus 82.5% has condensed

7.4 The vapor pressures of zinc have been written as

$$\ln p\ (\mathrm{atm}) = -\frac{15780}{T} - 0.755 \ln T + 19.25 \qquad \mathrm{I}$$

and

$$\ln p\ (\mathrm{atm}) = -\frac{15250}{T} - 1.255 \ln T + 21.79 \qquad \mathrm{II}$$

Which of the two equations is for solid zinc?

$$\mathrm{I} \quad \frac{d\ln p}{dT} = \frac{15780}{T^2} - \frac{0.755}{T} = \frac{\Delta H_I}{RT^2}$$

$$\therefore \Delta H_1 = R(15780 - 0.755T)$$

$$\mathrm{II} \quad \frac{d\ln p}{dT} = \frac{15250}{T^2} - \frac{1.255}{T} = \frac{\Delta H_{II}}{RT^2}$$

$$\therefore \Delta H_{II} = R(15250 - 1.255T)$$

Now $\Delta H_{s\to v} > \Delta H_{\ell \to v}$

$$\Delta H_I > \Delta H_{II}$$

$\therefore$ I is for solid Zn and II is for liquid Zn

7.5 At the normal boiling temperature of iron, $T_b = 3330\text{K}$, the rate of change of the vapor pressure of liquid iron with temperature is 3.72×10^{-3} atm/K. Calculate the molar latent heat of boiling of iron at 3330K.

Assuming that Fe vapor behaves as an ideal gas at its normal boiling point, the molar volume of Fe vapor at $P = 1$ atm and $T = 3330$ K is

$$V = \frac{nRT}{P} = 0.082057 \times 3330 = 273.2 \ l$$

Then $$\frac{dP}{dT} = \frac{\Delta H(l \to v)}{T\Delta V(l \to v)} = \frac{\Delta H_b}{T V_v}$$

$$\therefore \Delta H_b = T V_v \cdot \frac{dP}{dT}$$

$$= 3330 \times 273.2 \times 3.72 \times 10^{-3} \ l.\text{atm}$$

$$= 3378 \ l.\text{atm}$$

$$= 3378 \times \frac{8.3144}{0.082057} = 342376 \ \text{J}$$

7.6 Below the triple point (−56.2°C) the vapor pressure of solid CO_2 is given as

$$\ln p\ (\text{atm}) = -\frac{3116}{T} + 16.01$$

The molar latent heat of melting of CO_2 is 8330 joules. Calculate the vapor pressure exterted by liquid CO_2 at 25°C and explain why solid CO_2 is referred to as "dry ice".

The triple point pressure is

$$\ln p = \frac{-3116}{216.8} + 16.01 \quad \text{or} \quad p = 5.14 \text{ atm}$$

$$\text{and} \quad \frac{d\ln p}{dT} = \frac{3116}{T^2} = \frac{\Delta H(s\to v)}{RT^2}$$

$$\therefore \quad \Delta H(s\to v) = 8.3144\times 3116 = 25907 \text{ J}$$

$$\Delta H(s\to l) = 8330 \text{ J}$$

$$\therefore \quad \Delta H(l\to v) = 25907 - 8330 = 17577 \text{ J}$$

For liquid CO_2

$$\ln p_{CO_2(l)} = -\frac{\Delta H(l\to v)}{RT} + \text{constant.}$$

At the triple point

$$\ln(5.14) = \frac{-17577}{216.8R} + \text{constant.}$$

$$\text{constant} = 11.39$$

∴ At 298K

$$\ln p_{CO_2(l)} = \frac{-17577}{8.3144\times 298} + 11.39$$

$$p_{CO_2(l)} = 73.3 \text{ atm}$$

The 1 atm isobar does not pass through the stability field for liquid CO_2

7.7 The molar volumes of solid and liquid lead at the normal melting temperature of lead are, respectively, 18.92 cm^3 and 19.47 cm^3. Calculate the pressure which must be applied to lead in order to increase its melting temperature by 20 centigrade degrees.

The molar volume of solid Pb is $\frac{207}{10.94} = 18.92 \frac{cm^3}{mole}$

The molar volume of liquid Pb is $\frac{207}{10.63} = 19.47 \frac{cm^3}{mole}$

$$\Delta V(s \to l) = 19.47 - 18.92 = 0.55 \frac{cm^3}{mole}$$

$$\Delta H(s \to l) = 4810 \text{ J}$$

$$\therefore \frac{dP}{dT} = \frac{\Delta H}{T \Delta V}$$

$$\therefore P_2 - P_1 = \frac{4810}{0.55} \times \frac{82.057}{8.3144} \ln \frac{620}{600}$$

$$= 2821 \text{ atm}$$

$\therefore$ The pressure must be increased to 2822 atm

7.8 Nitrogen has a triple point at $P = 4650$ atm and $T = 44.5$K, at which state the allotropes α, β and γ coexist in equilibrium with one another. At the triple point $V_\beta - V_\alpha = 0.043$ cm^3/mole and $V_\alpha - V_\gamma = 0.165$ cm^3/mole. Also at the triple point $S_\beta - S_\alpha = 4.59$ J/K and $S_\alpha - S_\gamma = 1.25$ J/K. The state $P = 1$ atm, $T = 36$K lies on the boundary between the fields of stability of the α and β phases, and at this state, for the transformation $\alpha \rightarrow \beta$, $\Delta S = 6.52$ J/K and $\Delta V = 0.22$ cm^3/mole. Sketch the phase diagram for nitrogen at low temperatures.

$V_\beta - V_\alpha = 0.043$ cm^3/mole

$V_\alpha - V_\gamma = 0.165$ cm^3/mole

$V_\beta - V_\gamma = 0.165 + 0.043 = 0.208$ cm^3/mole

$\therefore V_\beta > V_\alpha > V_\gamma$

$\therefore$ γ is stable at high pressures and β is stable at low pressures

$S_\beta - S_\alpha = 4.59$ J/K

$S_\alpha - S_\gamma = 1.25$ J/K

$S_\beta - S_\gamma = 4.95 + 1.25 = 5.84$ J/K

$\therefore S_\beta > S_\alpha > S_\gamma$

β is stable at high T, γ at low T

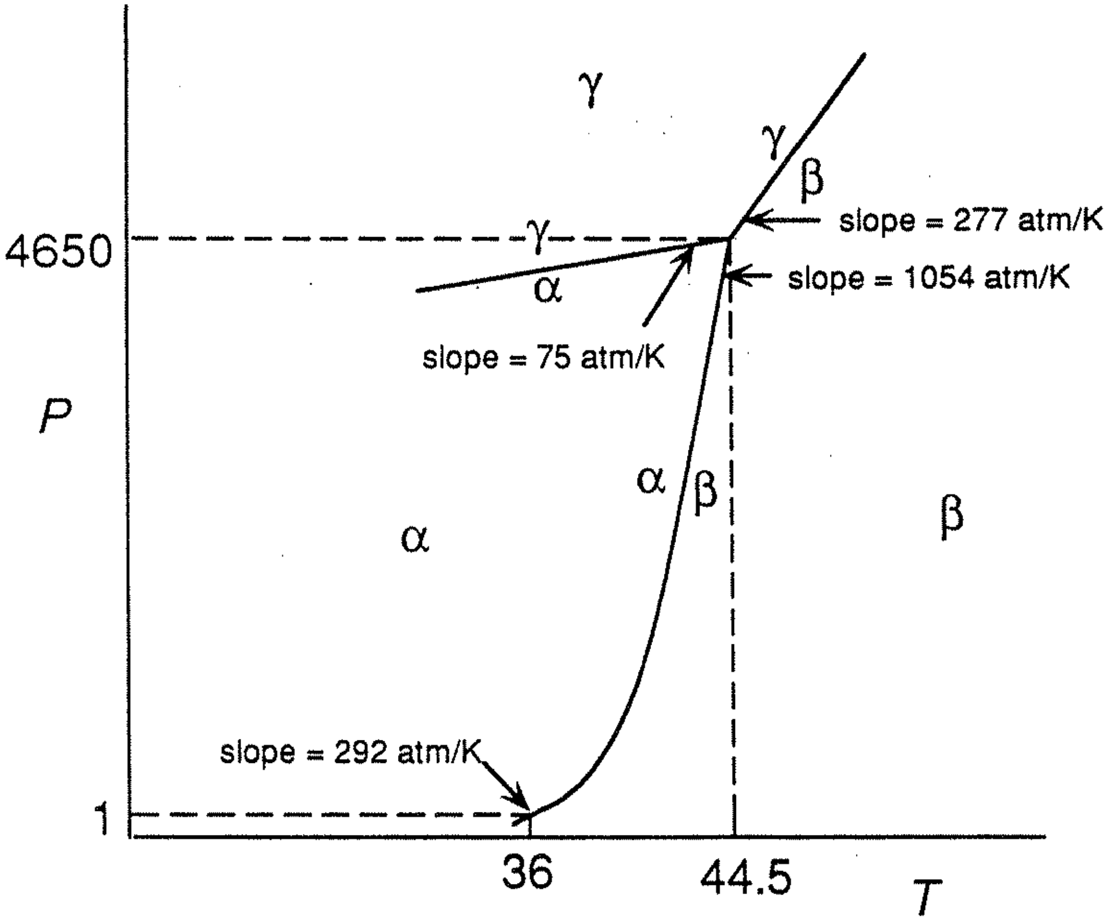
$\alpha \rightarrow \beta \quad \frac{dP}{dT} = \frac{4.59}{0.043} \times \frac{82.057}{8.3144} = 1053$ atm/K

$\gamma \rightarrow \alpha \quad \frac{dP}{dT} = \frac{1.25}{0.165} \times \frac{82.057}{8.3144} = 74.8$ atm/K

$\gamma \rightarrow \beta \quad \frac{dP}{dT} = \frac{5.84}{0.208} \times \frac{82.057}{8.3144} = 277$ atm/K

At 1 atm and 36 K

$\alpha \rightarrow \beta \quad \frac{dP}{dT} = \frac{6.52}{0.22} \times \frac{82.057}{8.3144} = 292$ atm/K


γ
γ
β
slope = 277 atm/K
4650
γ
α
slope = 1054 atm/K
slope = 75 atm/K
P
α
β
α
β
slope = 292 atm/K
1
36
44.5
T

Problem 7.8

7.9 Measurements of the saturated vapor pressure of liquid $NdCl_5$ give 0.3045 atm at 478K and 0.9310 atm at 520K. Calculate the normal boiling temperature of $NdCl_5$.

The vapor pressure equation is of the form

$$\ln p = \frac{A}{T} + B$$

$$\ln(0.3045) = \frac{A}{478} + B$$

$$\ln(0.9310) = \frac{A}{520} + B$$

This gives $A = -6614$ and $B = 12.65$

$\therefore$ At $p = 1$ atm

$$\ln(1) = 0 = -\frac{6614}{T_b} + 12.65$$

or $T_b = 523$ K

7.10* Three allotropes α, β and γ of a certain element are in equilibrium at its triple point See Figure 7.18. It is known that:

$$V_m^{\gamma} > V_m^{\alpha} \text{ and } S_m^{\gamma} < S_m^{\beta}$$

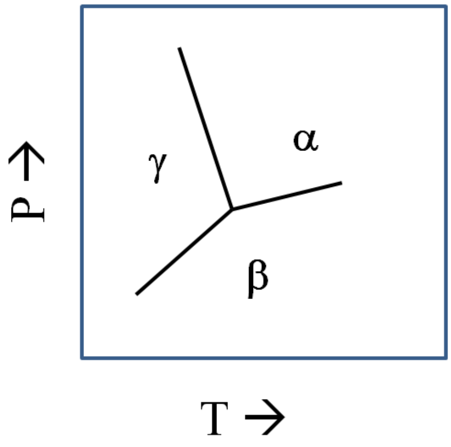
Determine which regions of the diagram are α, β and γ
Explain your reasoning.

Solution

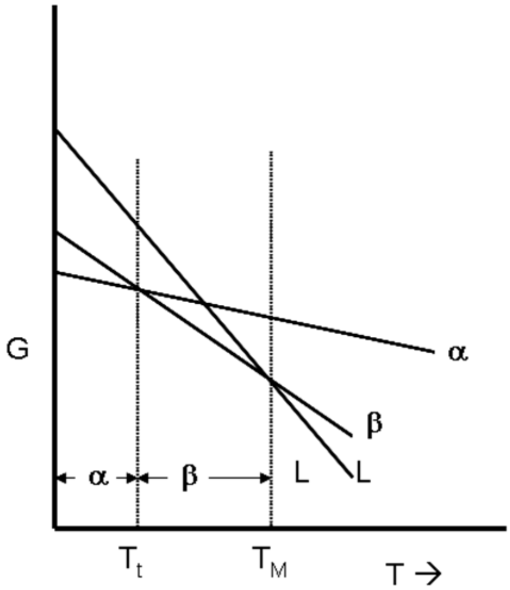
If the pressure is increased, equilibrium of the system favors the lowest molar volume phase. Therefore α is in either region I or II of Fig. 7.18, since $V_m^{\gamma} > V_m^{\alpha}$. But at the triple point, increasing the pressure moves equilibrium to the lowest molar volume phase. Thus, region II is the α phase field.

If the temperature is increased, equilibrium of the system favors the phase of the highest entropy. Therefore the β phase is in either region II or III since $S_m^{\gamma} < S_m^{\beta}$ But at the triple point increasing the temperature moves equilibrium to the highest entropy phase: therefore region III is the phase field for the β phase.

The phases are as they appear below.



7.11*. Fig. 7.11 shows a pressure vs. temperature phase diagram for a system exhibiting two solid state phases. Sketch the Gibbs free energy curves v. temperature for the two solid phases and the liquid phase. Comment on the slopes of the curves.

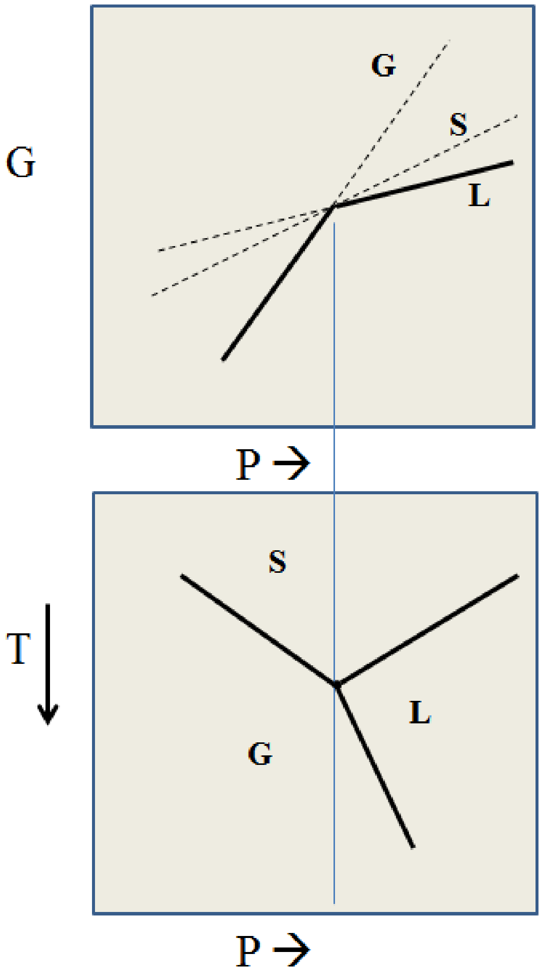


The slopes show that the β phase has a higher entropy than the α phase both of which have lower entropy than the liquid phase.

7.12* Below is the Gibbs free energy vs. Pressure plot for three phases, solid (S) liquid (L) and gas (G), near the triple point for the system. It is known that the molar volume of the solid is greater than that of the liquid.

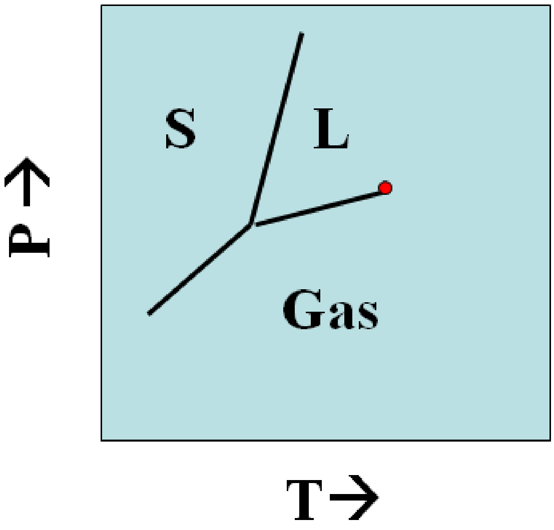
a. Label the three plots of G vs. P as S, L or G

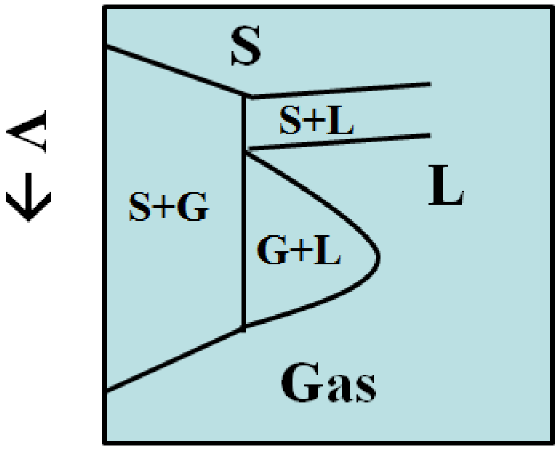
b. Below, draw the T P plot for the material. Label the S, L and G fields and any other points of interest. Note that the temperature is increasing in the downward direction.



It is important that the slope of the liquid / solid curve be as shown. His plot is the normal P-T plot rotated by 90^0 clockwise!

7.13* The Pressure Temperature phase diagram of a certain material is shown below. Construct the Volume Temperature diagram for this substance and label all phase fields.

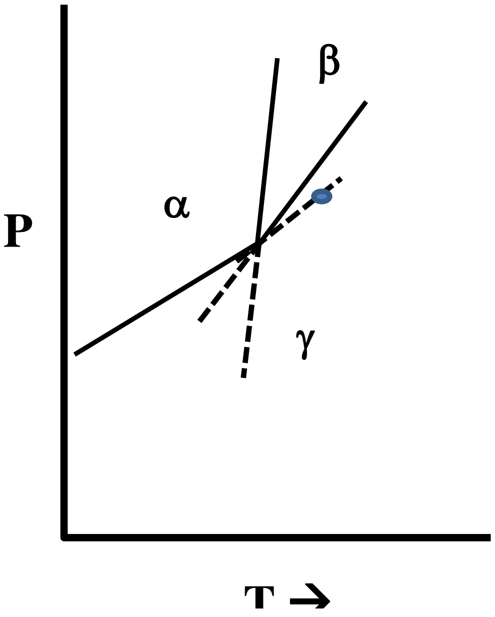




7.14* It can be seen from Fig. 7.7 that the metastable extensions of the two phase equilibria go into single phase fields. At the triple point it can be seen that the stable and metastable equilibrium curves alternate as one goes around the triple point. Show that the metastable extensions must alternate with stable two phase curves.

Solution

Assume the curves representing the stable equilibrium and those representing the metastable equilibrium do not alternate. Demonstrate that a contradiction arises. See below. The metastable extension of the α/γ curve goes into the stable γ phase field. So on the extension is the γ phase stable or metastable? This ambiguity shows that the α/γ curve can not be extended into the single γ phase field. Hence the curves must alternate.



8.1 Demonstrate the law of corresponding states by writing the van der Waals equation in terms of the reduced variables. Calculate the compressibility factor for a van der Waals gas at its critical point and compare the result with the values obtained for real gases at their critical points listed in Table 8.1. Calculate the value of $(\partial U/\partial V)_T$ for a van der Waals gas.

For one mole $\left(P+\frac{a}{V^2}\right)(V-b) = RT$

$$\left(P_R P_{cr} + \frac{a}{V_R^2 V_{cr}^2}\right)(V_R V_{cr} - b) = RT_R T_{cr}$$

$$\left(P_R \frac{a}{27b^2} + \frac{a}{V_R^2 9b^2}\right)(V_R 3b - 1) = RT_R \cdot \frac{8a}{27bR}$$

$$\frac{ab}{27b^2}\left(P_R + \frac{3}{V_R^2}\right)(3V_R - 1) = \frac{8a}{27b} T_R$$

$$\left(P_R + \frac{3}{V_R^2}\right)(3V_R - 1) = 8T_R$$

$$Z_{cr} = \frac{P_{cr}V_{cr}}{RT_{cr}} = \frac{a}{27b^2}\cdot\frac{3b}{R}\,\frac{27bR}{8a} = \frac{3}{8} = 0.375$$

$$dU = TdS - PdV$$

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P = T\left(\frac{\partial P}{\partial T}\right)_V - P$$

For a van der Waals gas $P = \frac{RT}{V-b} - \frac{a}{V^2}$

$$\therefore \left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V-b} \quad \text{and} \quad \left(\frac{\partial U}{\partial V}\right)_T = \frac{RT}{V-b} - P = \frac{a}{V^2}$$

8.2 n moles of an ideal gas A and $(1 - n)$ moles of an ideal gas B, each at 1 atm pressure, are mixed at total constant pressure. What ratio of A to B in the mixture maximizes the decrease in the Gibbs free energy of the system? If the decrease in the Gibbs free energy is ΔG^M, to what value must the pressure be increased in order to increase the Gibbs free energy of the gas mixture by $\frac{1}{2}\Delta G^M$?

Mix n moles of A and $(1-n)$ moles of B at constant $P = 1$ atm

$$\Delta G^{Mix} = RT[n \ln n + (1-n)\ln(1-n)]$$

$$\frac{d\Delta G^{Mix}}{dn} = RT[\ln n + 1 - \ln(1-n) - 1]$$

$$= RT \ln \frac{n}{1-n} = 0 \text{ when } n = 0.5$$

$\therefore$ Maximum decease occurs when $n_A = n_B = 0.5$

Increasing the pressure from 1 atm to P atm increases the free energy by

$$\Delta G = RT \ln P$$

$$\therefore -\frac{1}{2}\Delta G^{mix} = RT \ln P = \frac{1}{2} RT \ln 2$$

$$\therefore P = \sqrt{2} = 1.414 \text{ atm}$$

8.3 You are responsible for the purchase of oxygen gas which, before use, will be stored at a pressure of 200 atm at 300K in a cylindrical vessel of diameter 0.2 meters and height 2 meters. Would you prefer that the gas behaved ideally or as a van der Waals gas? The van der Waals constants for oxygen are $a = 1.36\ \text{l}^2.\text{atm.mole}^{-1}$ and $b = 0.0318$ l/mole.

The volume of the tank is $\pi r^2 h = 3.142 \times 0.1^2 \times 2$

$$= 0.06284\ \text{m}^3$$

$$= 62.84\ \ell$$

Thus, if the gas is ideal, the tank contains

$$n = \frac{PV'}{RT} = \frac{200 \times 62.84}{0.08206 \times 300} = 511 \text{ moles}$$

If the gas is a van der Waals gas

$$\left(P + \frac{an^2}{V^2}\right)(V' - nb) = nRT$$

$$\left(200 + \frac{1.36n^2}{62.84^2}\right)(62.84 - 0.0318n) = n0.08206 \times 300$$

which gives $n = 565$ moles.

It is thus less expensive to fill the tank if the gas behavior is ideal.

8.4 The virial equation of state for *n*-butane at 460K is $Z = 1 + A/V + B/V^2$ in which $A = -265$ cm^3/g.mole and $B = 30250$ cm^6/g.mole^2. Calculate the work required to reversibly compress one mole of *n*-butane from 50 atm to 100 atm at 460K.

The virial equation, with V in cm^3/mole, is

$$Z = 1 - \frac{265}{V} + \frac{30250}{V^2}$$

$$\therefore \quad P(\text{atm}) = 82.057 \times 460 \left[\frac{1}{V} - \frac{265}{V^2} + \frac{30250}{V^3}\right]$$

At $P_1 = 50$ atm, this gives $V_1 = 394.6$ cm^3

and at $P_2 = 100$ atm, $V_2 = 176.9$ cm^3

$$\therefore \; w = \int_1^2 P\,dV = RT\int_1^2 \left[\frac{1}{V} - \frac{265}{V^2} + \frac{30250}{V^3}\right]dV$$

$$= RT\left[\ln\frac{V_2}{V_1} + 265\left[\frac{1}{V_2} - \frac{1}{V_1}\right] - \frac{30250}{2}\left[\frac{1}{V_2^2} - \frac{1}{V_1^2}\right]\right]$$

$$= 8.3144 \times 460 \{ \ln\frac{176.9}{394.6} + 265\left(\frac{1}{176.9} - \frac{1}{394.6}\right) - \frac{31250}{2}\left(\frac{1}{176.9^2} - \frac{1}{394.6^2}\right)$$

$$= -1384 \text{ J}$$

8.5 For sulfur dioxide, $T_{cr} = 430.7\text{K}$ and $P_{cr} = 77.8$ atm. Calculate

a. the critical van der Waals constants for the gas

b. the critical volume of van der Waals SO_2,

c. the pressure exerted by 1 mole of SO_2 occupying a volume of 500 cm^3 at 500K. Compare this with the pressure which would be exerted by an ideal gas occupying the same molar volume at the same temperature.

$$T_{cr} = \frac{8a}{27bR} \qquad P_{cr} = \frac{a}{27b^2} \qquad \therefore \frac{T_{cr}}{P_{cr}} = \frac{8b}{R}$$

$$\therefore b = \frac{430.7 \times 0.08206}{77.8 \times 8} = 0.0567 \text{ l/mole}$$

$$a = 27b^2 P_{cr} = 27 \times 0.0567^2 \times 77.8 = 6.77 \frac{\text{l}^2.\text{atm}}{\text{mole}^2}$$

$$V_{cr} = 3b = 0.170 \text{ l/mole}$$

$$P(\text{van der Waals}) = \frac{RT}{V-b} - \frac{a}{V^2} = \frac{0.08206 \times 500}{0.5 - 0.0567} - \frac{6.77}{0.5^2}$$

$$= 65.5 \text{ atm.}$$

$$P(\text{ideal gas}) = \frac{RT}{V} = \frac{0.08206 \times 500}{0.5} = 82.1 \text{ atm}$$

8.6 One hundred moles of hydrogen gas at 298K are reversibly and isothermally compressed from 30 liters to 10 liters. The van der Waals constants for hydrogen are $a = 0.2461$ l^2.atm mole^{-2} and $b = 0.02668$ l/mole, and in the range of pressure 0 - 1500 atm, the virial equation for hydrogen is $PV = RT(1 + 6.4 \times 10^{-4} P)$. Calculate the work that must be done on the system to effect the required change in volume and compare this with the values that would be calculated assuming that (a) hydrogen behaves as a van der Waals gas and (b) hydrogen behaves as an ideal gas.

$n = 100$ moles, $T = 298K$, $V_1 = 30\,\ell$, $V_2 = 10\,\ell$.

$$PV = nRT(1 + 6.4\times10^{-4}P)$$

$$W = \int P\,dV \qquad V = nRT\left[\frac{1}{P} + 6.4\times10^{-4}\right]$$

$$dV = nRT\,d\left(\frac{1}{P}\right) = -RTn\frac{dP}{P^2}$$

$$\therefore\ W = nRT\ln\frac{P_1}{P_2}$$

$$PV - 6.4\times10^{-4}RTPn = nRT \qquad \therefore\ P = \frac{nRT}{V - n\,6.4\times10^{-4}RT}$$

$$\therefore\ P_1 = \frac{100\times0.08206\times298}{30 - 100\times6.4\times10^{-4}\times0.08206\times298} = 86\text{ atm}$$

$$P_2 = \frac{100\times0.08206\times298}{10 - 100\times6.4\times10^{-4}\times0.08206\times298} = 290\text{ atm}$$

$$\therefore\ W = 100\times8.3144\times298\ln\frac{86}{290} = -301\text{ kJ}$$

van der Waals gas:

$$P = \frac{nRT}{V - bn} - \frac{n^2a}{V^2}$$

$$a = 0.2461\ \frac{\ell^2.\text{atm}}{\text{mole}}$$

$$b = 0.02668\ \ell/\text{mole}$$

8.6 continued

$$w = \int P dV = \int \left(\frac{nRT}{V-nb} - \frac{n^2 a}{V^2} \right) dV$$

$$= nRT \ln \left[\frac{V_2 - nb}{V_1 - nb} \right] - n^2 a \left[-\frac{1}{V_2} + \frac{1}{V_1} \right]$$

$$= 100 \times 8.3144 \times 298 \ln \left[\frac{10 - 100 \times 0.02668}{30 - 100 \times 0.02668} \right]$$

$$- 100^2 \times 0.2461 \times \frac{8.3144}{0.08206} \left[-\frac{1}{10} + \frac{1}{30} \right]$$

$$= -309 \text{ kJ}$$

ideal gas $w = nRT \ln \frac{V_2}{V_1} = 100 \times 8.3144 \times 298 \ln \frac{10}{30}$

$$= -272 \text{ kJ.}$$

8.7 Using the virial equation of state for hydrogen at 298K given in Problem 8.6, calculate

a. the fugacity of hydrogen at 500 atm and 298K.

b. the pressure at which the fugacity is twice the pressure,

c. the change in the Gibbs free energy caused by a compression of one mole of hydrogen at 298K from 1 atm to 500 atm.

What is the magnitude of the contribution to (c) caused by the non-ideality of hydrogen?

a) $\frac{PV}{RT} = Z = 1 + 6.4\times10^{-4}P \quad \therefore Z - 1 = 6.4\times10^{-4}P$

$\ln\frac{f}{P} = \int_0^P \frac{Z-1}{P}\,dP = 6.4\times10^{-4}[500-0] = 0.3194$

$\therefore \frac{f}{P} = 1.376$ and $f = 1.376\times500 = 688$ atm

b) $\frac{f}{P} = 2 \quad \therefore \ln\frac{f}{P} = 0.693 = 6.4\times10^{-4}[P-0]$

$\therefore \frac{f}{P} = 2$ at $P = 1083$ atm.

c) $\Delta G = \int V\,dP$ where $V = RT\left[\frac{1}{P} + 6.4\times10^{-4}\right]$

$\therefore \Delta G = RT\ln\frac{P_2}{P_1} + RT\,6.4\times10^{-4}(P_2 - P_1)$

$= 8.3144\times298\ln\frac{500}{1} + 8.3144\times298\times6.4\times10^{-4}[500-1]$

$= 15400 + 790$

$= 16190$ J

and the contribution due to non-ideal behavior is 790 J

8.8* Show that the truncated Kammerlingh Onnes virial equation:

$$\frac{PV}{RT} = 1 + \frac{B'(T)}{V}$$

reduces to P(V - b') = RT, and find the expression for b' .

Solution 8.8

$$\frac{PV}{\left(1+\frac{B'(T)}{V}\right)} = RT$$

if $V >> B'(T)$ then using the expansion $\frac{1}{1+x} = 1 - x$ for $x << 1$

$$PV\left(1-\frac{B'(T)}{V}\right) = P\left(V - B'(T)\right)RT$$

so b' = $B'(T)$

8.9* Fig. 8.7 shows an isothermal variation, with pressure, of the volume of a van der Waals gas at a temperature below its critical temperature. Redraw this Figure and below it sketch the Helmholtz free energy vs. Volume plot. Be sure to indicate important points on the A vs. V plot.

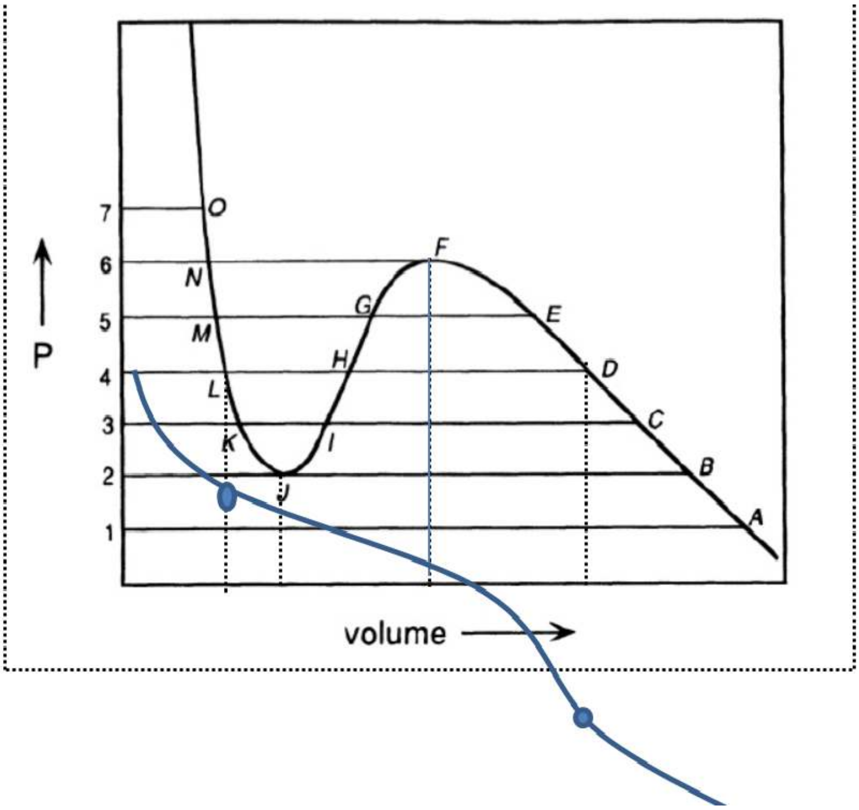
Solution to 8.9

$$dA_T = -PdV$$

$$\left(\frac{\partial A}{\partial V}\right)_T = -P \quad \text{so the slope should always be} < 0$$

$$\left(\frac{\partial^2 A}{\partial V^2}\right)_T = \left(\frac{\partial P}{\partial V}\right)_T \quad \text{and there are two extrema in P vs V.}$$

Thus there are two points where A vs. V changes its curvature.
Also the common tangent delineates the molar volumes of the equilibrium phases.



8.10* Obtain a simplified expression for the total derivative of the pressure for an van der Waals' gas.

$$dP = \left(\frac{\partial P}{\partial T}\right)_V dT + \left(\frac{\partial P}{\partial V}\right)_T dV$$

$$P = \frac{RT}{(V-b)} - \frac{a}{V^2} \quad \text{for a van der Waals' gas}$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V-b} \quad \text{for a van der Waals' gas}$$

$$\left(\frac{\partial P}{\partial V}\right)_T = -\frac{RT}{(V-b)^2} + \frac{2a}{V^3} \quad \text{for a van der Waals' gas}$$

Thus, $dP = \frac{R}{V-b}dT - (\frac{RT}{(V-b)^2} + \frac{2a}{V^3})dV$

which reduces to dP $= \frac{R}{V}dT - \frac{RT}{V^2}dV$ if a = 0 and b = 0

8.11* Obtain a simplified expression for the total derivative of the pressure for a gas that obeys the truncated Kammerlingh Onnes virial equation:

$$\frac{PV}{RT} = 1 + \frac{B'(T)}{V}$$

Solution 8.11

$$P = \left(1 + \frac{B'(T)}{V}\right)\frac{RT}{V}$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V} + \frac{B'(T)R}{V^2} + \frac{RT}{V^2}\left(\frac{\partial B}{\partial T}\right)$$

$$\left(\frac{\partial P}{\partial V}\right)_T = -\frac{RT}{V^2} - \frac{2B'RT}{V^3}$$

$$dP = \left[\frac{R}{V} + \frac{B'(T)R}{V^2} + \frac{RT}{V^2}\left(\frac{\partial B'(T)}{\partial T}\right)\right]dT - \left[\frac{RT}{V^2} + \frac{2B'(T)RT}{V^3}\right]dV$$

which reduces to dP $= \frac{R}{V}dT - \frac{RT}{V^2}dV$ if B'(T) = 0

8.12* Derive an expression for Z_{cr} of a van der Waals gas.

The equation of state for the van der Waals fluid is

$$\boldsymbol{P = \frac{RT}{v-b} - \frac{a}{v^2}}$$

Where **P** is the pressure in Pa
R is the gas constant (8.314 Joule/K)
v is the molar volume of the gas (m^3)
a and b are empirical constants that vary from gas to gas.

To calculate Z_{cr} we must obtain: P_{cr}, v_{cr} and T_{cr}

At the critical pressure and volume, the critical isotherm has a horizontal inflection:

$$\left(\frac{\partial P}{\partial v}\right)_{T_C} = \left(\frac{\partial^2 P}{\partial v^2}\right)_{T_C} = 0$$

$$\left(\frac{\partial P}{\partial v}\right)_{T_C} = -\frac{RT}{(v-b)^2} + \frac{2a}{v^3} = 0$$

$$\left(\frac{\partial^2 P}{\partial v^2}\right)_{T_C} = \frac{2RT}{(v-b)^3} - \frac{6a}{v^4} = 0$$

Solving we get:

$$\mathrm{v}_{Critical} = 3b; \quad \mathrm{RT}_{Critical} = \frac{8a}{27b}; \quad \mathrm{P}_{critical} = \frac{a}{27b^2}$$

$$Z_{cr} = \frac{P_{cr}v_{cr}}{RT_{cr}} = \frac{\frac{a}{27b^2}\cdot 3b}{\frac{8a}{27b}} = \frac{3}{8}$$

8.13*. The ideal entropy of mixing of a binary solution is given as:

$$\Delta S_{mix} = -R(X_A \ln X_A + X_B \ln X_B)$$

a. Sketch the entropy of mixing vs. X_B.

b. Calculate (using the expression for the ideal entropy of mixing) the ideal entropy of mixing at B = 0.25

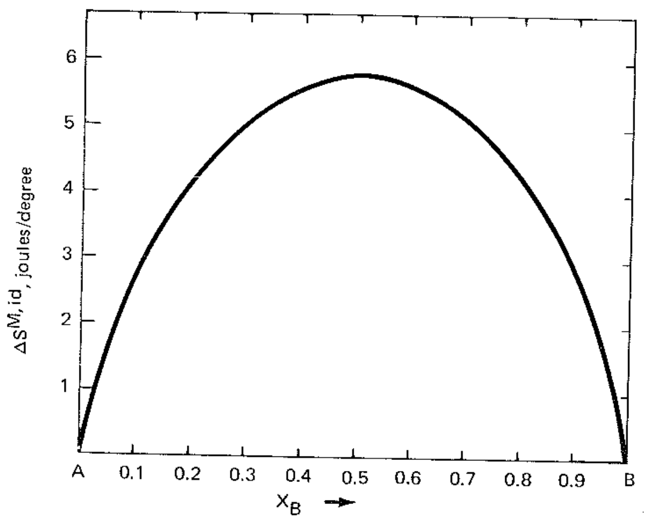
c. Calculate the slope of this curve at $X_B = 0.25$

d. Calculate the partial molar entropy of component B for the composition $X_B = 0.25$

e. Calculate the partial molar entropy of component A for the composition $X_B = 0.25$

f. Show that your answers in d and e are consistent with your answer in c.

Solution



b. $$\Delta S_{mix} = -R(X_A \ln X_A + X_B \ln X_B)$$ $$\Delta S_{mix} = -R\ln 2$$ 4.56 J/Mol

c. $$\Delta S_{mix} = -R(X_A \ln X_A + X_B \ln X_B)$$ $$\frac{d\Delta S_{mix}}{dX_B} = -R[\ln X_B - \ln X_A) = -R(-\ln 3) = R\ln 3$$ **9.13** J/Mol

d. $\bar{S}_B = -R(\ln X_B) = R\ln 4$ **11.52** J/Mol

e. $\bar{S}_A = -R(\ln X_A) = R\ln(\frac{3}{4})$ **2.39** J/Mol

f. $$\frac{d\Delta S_{mix}}{dX_B} = R\ln 3$$ **11.52-2.39 = 9.13** J/Mol

$$\Delta S_{mix} = \bar{S}_B - \bar{S}_A = R(\ln 4 + \ln 3 - \ln 4) = R\ln 3$$

9.1 One mole of solid Cr_2O_3 at 2500 K is dissolved in a large volume of a liquid Raoultian solution of Al_2O_3 and Cr_2O_3 in which $X_{Cr_2O_3} = 0.2$ and which is also at 2500 K. Calculate the changes in enthalpy and entropy caused by the addition. The normal melting temperature of Cr_2O_3 is 2538 K, and it can be assumed that the $\Delta S_{m,Al_2O_3} = \Delta S_{m,Cr_2O_3}$.

$$\Delta H_{m,Al_2O_3} = 107500\ J \quad \therefore \quad \Delta S_{m,Al_2O_3} = \frac{107500}{2324} = 46.25\ J/K$$

$$= \Delta S_{m,Cr_2O_3}$$

$$\therefore \quad \Delta H_{m,Cr_2O_3} = T_m \cdot \Delta S_m = 2538 \times 46.25$$

$$= 117400\ J$$

$$Cr(s) \rightarrow Cr(l) \qquad \Delta H = \Delta H_m = 117400$$

$$Cr(l) \rightarrow Cr(\text{in solution}) \qquad \Delta H = \Delta \bar{H}^{Mix} = 0$$

$$\therefore \quad \Delta H_{TOTAL} = 117400\ J$$

$$Cr(s) \rightarrow Cr(l) \qquad \Delta S = \Delta S_m = 46.25$$

$$Cr(l) \rightarrow Cr(\text{in solution}) \qquad \Delta S = \Delta S^{Mix} = -R \ln X_{Cr}$$

$$= -8.3144 \ln 0.2$$

$$= 13.38$$

$$\therefore \quad \Delta S_{TOTAL} = 46.25 + 13.38 = 59.63\ J/K$$

9.2 When one mole of argon gas is bubbled through a large volume of an Fe-Mn melt of $X_{Mn} = 0.5$ at 1863 K evaporation of Mn into the Ar causes the mass of the melt to decrease by 1.50 g. The gas leaves the melt at a pressure of 1 atm. Calculate the activity coefficient of Mn in the liquid alloy.

The saturated vapor pressure of liquid Mn at 1863 K is

$$\exp\left(-\frac{33440}{1863} - 3.12 \ln 1863 + 37.68\right) = 0.0493 \text{ atm.}$$

The number of moles of Mn removed $= \frac{1.50}{54.94} = 0.0273$

The partial pressure of Mn in the gas mixture $= \frac{n_{Mn}}{n_{Mn} + n_{Ar}}$

$$= \frac{0.0273}{1.0273} = 0.0266 = p_{Mn}$$

$$\therefore \quad a_{Mn} = \frac{p_{Mn}}{p^{\circ}_{Mn}} = \frac{0.0266}{0.0493} = 0.539$$

$$\text{and} \quad \gamma_{Mn} = \frac{a_{Mn}}{X_{Mn}} = \frac{0.539}{0.5} = 1.08$$

9.3 The variation, with composition, of G^{xs} for liquid Fe-Mn alloys at 1863 K is listed below.

a. Does the system exhibit regular solution behavior?

b. Calculate $\bar{G}^{xs}_{Fe}$ and $\bar{G}^{xs}_{Mn}$ at $X_{Mn} = 0.6$.

c. Calculate ΔG^M at $X_{Mn} = 0.4$.

d. Calculate the partial pressures of Mn and Fe exerted by the alloy of $X_{Mn} = 0.2$.

X_{Mn}	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
G^{xs}, joules	395	703	925	1054	1100	1054	925	703	395

a) Calculation of $\Omega = \frac{G^{xs}}{X_{Fe}X_{Mn}}$ for each composition gives an average value of 4396±6 J. Therefore, with respect to G^{xs}, the system is regular.

b) $\bar{G}^{xs}_{Fe} = \Omega X_{Mn}^2 = 4396\times 0.6^2 = 1583$ J

$\bar{G}^{xs}_{Mn} = \Omega X_{Fe}^2 = 4396\times 0.4^2 = 703$ J

c) $\Delta G^M = 8.3144\times 1863\,(0.4\ln 0.4 + 0.6\ln 0.6) + 4396\times 0.4\times 0.6$

$= -9370$ J.

d) At $X_{Mn} = 0.2$ $\gamma_{Mn} = \exp\left(\frac{4396\times 0.8^2}{8.3144\times 1863}\right) = 1.2$

9.3 continued.

$$\therefore\ a_{Mn} = 1.2 \times 0.2 = 0.24$$

$$p^{o}_{Mn} = \exp\left(\frac{-33440}{1863} - 3.02 \ln 1863 + 37.68\right) = 0.0493 \text{ atm}$$

$$\therefore\ p_{Mn} = a_{Mn}\, p^{o}_{Mn} = 0.24 \times 0.0493$$

$$= 0.0018 \text{ atm.}$$

$$\gamma_{Fe} = \exp\left(\frac{4396 \times 0.2^{2}}{8.3144 \times 1863}\right) = 1.011$$

$$\therefore\ a_{Fe} = 1.011 \times 0.8 = 0.809$$

$$p^{o}_{Fe} = \exp\left(\frac{-45390}{1863} - 1.27 \ln 1863 + 23.93\right) = 4.55 \times 10^{-5} \text{ a}$$

$$p_{Fe} = a_{Fe} \cdot p^{o}_{Fe} = 0.809 \times 4.55 \times 10^{-5}$$

$$= 3.68 \times 10^{-5} \text{ atm.}$$

9.4 Calculate the heat required to form a liquid solution at 1356 K starting with 1 mole of Cu and 1 mole of Ag at 298 K. At 1356 K the molar heat of mixing of liquid Cu and liquid Ag is given by $\Delta H^M \; -20590 X_{\text{Cu}} X_{\text{Ag}}$.

Heat 1 mole of Cu from 298K to 1356 K and melt it.

$$\Delta H = \int_{298}^{1356} c_{p,\text{Cu},} dT + \Delta H_{m,\text{Cu}}$$

$$= 22.64 (1356 - 298) + \frac{6.28\times10^{-3}}{2} (1356^2 - 298^2)$$

$$+ 12970 \quad J$$

$$= 42420 \quad J.$$

Heat 1 mole of Ag from 298 to 1356

$$\Delta H = \int_{298}^{1234} c_{p,\text{Ag}(s)} dT + \Delta H_{m,\text{Ag}} + \int_{1234}^{1356} c_{p,\text{Ag}(\ell)} dT$$

$$= 21.3 (1234 - 298) + \frac{8.54\times10^{-3}}{2} (1234^2 - 298^2)$$

$$- 1.51\times10^{5} \left(\frac{1}{1234} - \frac{1}{298}\right) + 11090 + 30.5 (1356 - 1234)$$

$$= 41260 \quad J$$

In 2 moles of equimolar liquid solution.

$$\Delta H = 2(-20590 \times 0.5^2) = -10300$$

Total heat requirement $= 42420 + 41260 - 10300$

$$73380 \quad J.$$

9.5 Melts in the system Pb-Sn exhibit regular solution behavior. At 473°C $a_{Pb} = 0.055$ in a liquid solution of $X_{Pb} = 0.1$. Calculate the value of Ω for the system and calculate the activity of Sn in the liquid solution of $X_{Sn} = 0.5$ at 500°C.

$$\gamma_{Pb} = \frac{a_{Pb}}{X_{Pb}} = \frac{0.055}{0.1} = 0.55$$

$$\therefore \quad \Omega = \frac{8.3144 \times 746 \times \ln 0.55}{0.9^2} = -4578 \text{ J}$$

At 500°C (773 K) and $X_{Sn} = 0.5$

$$\ln \gamma_{Sn} = \frac{-4578 \times 0.5^2}{8.3144 \times 773} = -0.178$$

$$\therefore \quad a_{Sn} = 0.5 \times \exp(-0.178) = 0.418$$

9.6* a. Calculate the values of $\Delta\overline{G}_B$ and a_B for an alloy of $X_B = 0.5$ at 1000 K assuming the solution is ideal.

For ideal and regular solutions $\Delta G^M(X_B = 0.5) = \Delta\overline{G}_A^M = \Delta\overline{G}_A^M$

$$\Delta G^{M,id}(X_B = 0.5) = -RT\Delta S^M(X_B = 0.5)$$
$$= -8314 * (\frac{1}{2}\ln\frac{1}{2} + \frac{1}{2}\ln\frac{1}{2}) = -5763J$$

$$\Delta\overline{G}_B = RTa_B = -5763J$$
$$a_B(X_B = 0.5) = \exp(-\frac{5763}{8314}) = 0.5$$

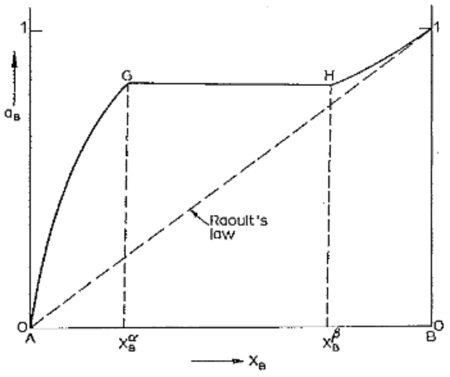
b. Calculate the values of $\Delta\overline{G}_B$ and a_B for an alloy of $X_B = 0.5$ at 1000 K that is a regular solution with a $\Delta H_{mixing} = 16{,}628 * X_A * X_B$.

$$\Delta G^{M,reg}(0.5) = 16{,}626 + 8314 * (\frac{1}{2}\ln\frac{1}{2} + \frac{1}{2}\ln\frac{1}{2})$$
$$=16{,}626 * \frac{1}{4} + 8314 * (\frac{1}{2}\ln\frac{1}{2} + \frac{1}{2}\ln\frac{1}{2})$$
$$= -1609\ J$$

$$\Delta\overline{G}_B = RTa_B = -1609\ J$$
$$a_B = \exp(-\frac{1609}{8314}) = .844$$

9.7* A regular solution exhibits a miscibility gap. Sketch the activity of X_B vs. X_A at a temperature within the miscibility gap.
Denote regions where Henry's law is obeyed and where Raoults' law is obeyed if applicable.

Solution



← X_A

9.8 Tin obeys Henry's law in dilute liquid solutions of Sn and Cd and the Henrian activity coefficient of Sn, γ°_{Sn}, varies with temperature as

$$\ln \gamma^\circ_{Sn} = -840/T + 1.58$$

Calculate the change in temperature when 1 mole of liquid Sn and 99 moles of liquid Cd are mixed in an adiabatic enclosure. The molar constant pressure heat capacity of the alloy formed is 29.5 J/K

$$\Delta \bar{H}^M_{Sn} = \frac{R\,\partial \ln \gamma_{Sn}}{\partial\left(\frac{1}{T}\right)} = -8.3144 \times 840 = -6984 \text{ J}$$

ΔH^M (per mole) $= X_{Sn}\Delta\bar{H}^M_{Sn} + X_{Cd}\Delta\bar{H}^M_{Cd}$

$= 0.01 \times (-6984)$ $\qquad \Delta\bar{H}^{Mid}_{Cd} = 0$

$= -69.84$ J

$= C_p \Delta T$

$= 29.5\,\Delta T$

$\therefore$ Increase in $T = \dfrac{69.84}{29.5} = 2.37$ kelvins

9.9 Use the Gibbs-Duhem equation to show that, if the activity coefficients of the components of a binary solution can be expressed as

$$\ln \gamma_A = \alpha_1 X_B + \frac{1}{2}\alpha_2 X_B^2 + \frac{1}{3}\alpha_3 X_B^3 + \ldots$$

and

$$\ln \gamma_B = \beta_1 X_A + \frac{1}{2}\beta_2 X_A^2 + \frac{1}{3}\beta_3 X_A^3 + \ldots$$

over the entire range of composition, then $\alpha_1 = \beta_1 = 0$, and that, if the variation can be represented by the quadratic terms alone, then $\alpha_2 = \beta_2$.

$$\ln \gamma_A = \alpha_1 X_B + \tfrac{1}{2}\alpha_2 X_B^2 + \tfrac{1}{3}\alpha_3 X_B^3 + \cdots$$

$$\therefore X_A d\ln\gamma_A = \alpha_1 X_A dX_B + \alpha_2 X_A X_B dX_B + \alpha_3 X_A X_B^2 dX_B + \cdots$$

$$\ln \gamma_B = \beta_1 X_A + \tfrac{1}{2}\beta_2 X_A^2 + \tfrac{1}{3}\beta_3 X_A^3 + \cdots$$

$$\therefore -X_B d\ln\gamma_B = \beta_1 X_B dX_B + \beta_2 X_B X_A dX_B + \beta_3 X_B X_A^2 dX_B + \cdots$$

From the Gibbs-Duhem equation

$$X_A d\ln\gamma_A = X_B d\ln\gamma_B$$

$$\therefore \alpha_1 X_A dX_B + \alpha_2 X_A X_B dX_B = \beta_1 X_B dX_B + \beta_2 X_A X_B dX_B$$

if the power series are truncated at the quadratic terms.

Equality of the coefficients in terms containg X_A (or X_B) requires that $\alpha_1 = \beta_1 = 0$ and equality of the coefficients in the quadratic terms requires that $\alpha_2 = \beta_2$

9.10 The activity coefficient of Zn in liquid Zn-Cd alloys at 435°C can be represented as

$$\ln \gamma_{Zn} + 0.875\, X_{Cd}^2 - 0.30\, X_{Cd}^3$$

Derive the corresponding expression for the dependence of ln γ_{Cd} on composition and calculate the activity of cadmium in the alloy of $X_{Cd} = 0.5$ at 435°C.

$$\ln \gamma_{Zn} = 0.875\, X_{Cd}^2 - 0.3\, X_{Cd}^3.$$

$$d\ln \gamma_{Zn} = 1.750\, X_{Cd}\, dX_{Cd} - 0.9\, X_{Cd}^2\, dX_{Cd}.$$

$$-\frac{X_{Zn}}{X_{Cd}}\, d\ln \gamma_{Zn} = -1.750\, X_{Zn}\, dX_{Cd} + 0.9\, X_{Zn} X_{Cd}\, dX_{Cd}$$

$$= d\ln \gamma_{Cd}$$

$$= 1.75\, X_{Zn}\, dX_{Zn} - 0.9\, X_{Zn}(1 - X_{Zn})\, dX_{Zn}$$

$$= 0.85\, X_{Zn}\, dX_{Zn} + 0.9\, X_{Zn}^2\, dX_{Zn}$$

$$\therefore \ln \gamma_{Cd} = 0.425\, X_{Zn}^2 + 0.3\, X_{Zn}^3$$

$\therefore$ At $X_{Cd} = 0.5$, $\gamma_{Cd} = 1.155$ and $a_{Cd} = 0.577$

9.11 The molar excess Gibbs free energy of formation of solid solutions in the system Au-Ni can be represented by

$$G^{xs} = X_{Ni}X_{Au}(24140\,X_{Au} + 38280\,X_{Ni} - 14230\,X_{Au}X_{Ni})\left[1 - \frac{T}{2660}\right] \quad \text{J}$$

Calculate the activities of Au and Ni in the alloy of $X_{Au} = 0.5$ at 1100 K.

Let $X_{Au} \equiv x$

$$G^{xs} = x(1-x)[24140x + 38280(1-x) - 14230x(1-x)]\left[1 - \frac{1100}{2660}\right]$$

$$= [38280x - 66650x^2 + 42600x^3 - 14230x^4] \times 0.586 \qquad \text{— (i)}$$

$$\frac{\partial G^{xs}}{\partial x} = [38280 - 133300x + 127800x^2 - 56920x^3].0.586$$

$$(1-x)\frac{\partial G^{xs}}{\partial x} = [38280 - 171580x + 261100x^2 - 184720x^3 + 56920x^4]\,0.586$$

$$\bar{G}^{xs}_{Au} = G^{xs} + (1-x)\frac{\partial G^{xs}}{\partial x}$$

$$= [38280 - 133300x + 194450x^2 - 142120x^3 + 42690x^4]\,0.586$$

$\therefore \bar{G}^{xs}_{Au}$ (at $X_{Au} = 0.5$) $= 3105$ J $= 8.3144 \times 1100 \ln \gamma_{Au}$

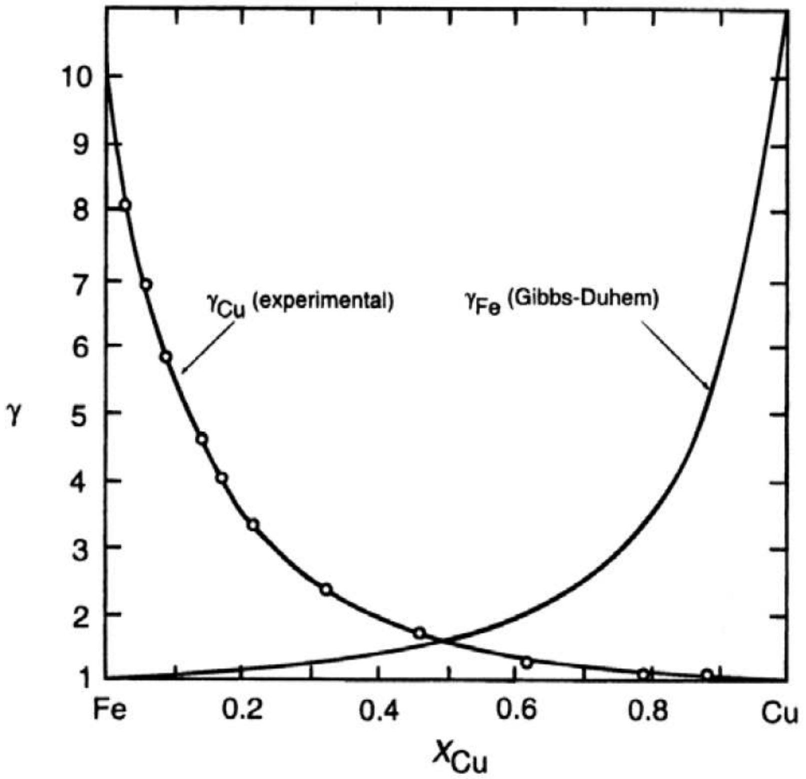
$\therefore \gamma_{Au} = 1.39$ and $a_{Au} = 0.5 \times 1.39 = 0.695$

From (i) G^{xs}(at $X_{Au} = 0.5$) $= 4051 = 8.3144 \times 1100[0.5 \ln \gamma_{Ni} + 0.5 \ln 1.39]$

$\therefore \gamma_{Ni} = 1.7$ and $a_{Ni} = 1.7 \times 0.5 = 0.85$

9.12* The activities of liquid iron-copper solutions at 1550 °C as a function of composition are shown in Fig. 9.9. Sketch the activity coefficients as a function of composition at this temperature.

Solution



9.13* Use the equation: $\Delta G^{XS} = b(T - T_C)\eta^2 + c\eta^4$ to derive the following equation

for η = η(T): $\eta_{eq} = (1 - \frac{T}{T_C})^{1/2}$ where b > 0

(Hint: Use the Third Law of Thermodynamics to set η = 1 at T = 0).

Solution

$$\Delta G^{XS} = b(T - T_C)\eta^2 + c\eta^4$$

$$\frac{\partial \Delta G^{XS}}{\partial \eta} = 0 \text{ for equilibrium}$$

$$\frac{\partial \Delta G^{XS}}{\partial \eta} = 2b(T - T_C)\eta + 4c\eta^3 = 0$$

$$\text{Thus } \eta = 0 \text{ and } \eta^2 = -\frac{b(T - T_C)}{2c} \text{ are extrema}$$

By taking the second derivative η = 0 can be shown to be a maximum when T< T_c

and the other two extrema are minima when T< T_c.

$$\eta^2 = -\frac{b(T - T_C)}{2c}$$

at T = 0, $\eta = 1$ (by the third law)

$$\text{Thus}: T_C = \frac{2c}{b} \text{ which leads to } \eta^2 = (1 - \frac{T}{T_C})$$

9.14* It has been found that in a certain solution the activity $a_A = X_A$ over a certain range of composition. Determine the relationship between $a_B = X_B$ over the same range of composition.

Solution

$a_A = X_A$

$d(\ln a_A) = d(\ln X_A)$

$X_A d(\ln a_A) + X_B d(\ln a_B) = 0$ Gibbs Duhem

$$Thus: d(\ln a_2) = -\frac{X_A}{X_B} d(\ln a_A) = -\frac{X_A}{X_B} d(\ln X_A) = \frac{dX_B}{X_B}$$

integrating: $\ln a_2 = \ln X_2 + \ln \gamma$ where γ is a constant

Thus, $a_B = \gamma X_B = \gamma_B X_B$

This is Henry's law.

9.15* All regular solutions with positive heats of mixing have the same value of the activity of its components (A or B) at the critical point of the miscibility gap.

a. Calculate this activity.

b. Plot a_B vs. X_B for a regular solution at T_C for a miscibility gap.

Solution

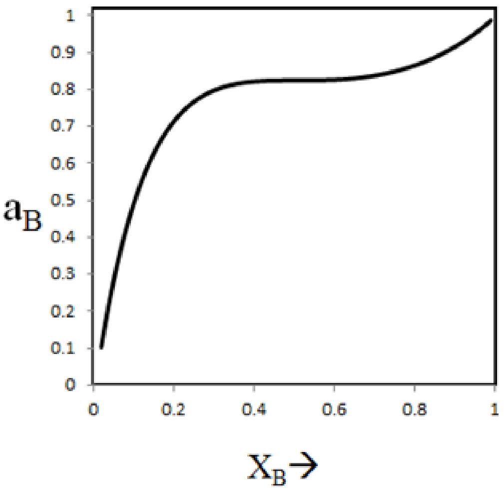
$$a_B = \gamma_B X_B$$

$$a_B = \exp\left(\frac{a_0 X_B^2}{RT}\right) X_B$$

$$T_C = \frac{a_0}{2R}$$

$$a_B = \exp\left(\frac{a_0\left(\frac{1}{2}\right)^2}{R\frac{a_0}{2R}}\right)\left(\frac{1}{2}\right) =$$

$$a_B = \exp(0.5) \bullet \left(\frac{1}{2}\right) = 0.824$$



Another way

$$\overline{G}_B = \Delta G_{mix}(0.5) = \Delta H_{mix} - T\Delta S_{mix} =$$

$$= \frac{a_0}{4} - RT(\ln 2) = RT \ln a_B$$

$$\text{But: } T = T_C = \frac{a_0}{2R}$$

$$\frac{1}{2} - \ln 2 = \ln a_B = -0.1935$$

$$a_B = 0.824$$

9.16*. At a certain temperature, T the A-B system exhibits regular solution behavior. The activity coefficient of A is given by:

$\ln(\gamma_A) = -b(1-X_A)^2$, where b is a constant at the given T

Compute the corresponding equation for the variation of γ_B with composition at the same temperature. Be sure to state justification for the steps of your solution.

Solution

$$\ln\gamma_A = -b(1-X_A)^2$$

$$Gibbs - Duhem$$

$$X_A d\overline{G}_A + X_B d\overline{G}_B = 0$$

$$d\overline{G}_A = RTd\ln a_A = RTd\ln(\gamma_A X_A)$$

$$X_A d\ln\gamma_A + X_B d\ln\gamma_B = 0$$

$$d\ln\gamma_B = -\frac{X_A}{X_B} d\ln\gamma_A = -\frac{X_A}{X_B}(-2bX_B(-dX_A)$$

$$\int_{\gamma=1}^{\gamma_B} d\ln\gamma_B = \ln\gamma_B = -bX_A^2 = -b(1-X_B)^2$$

10.1 CaF_2 and MgF_2 are mutually insoluble in the solid state and form a simple binary eutectic system. Calculate the composition and temperature of the eutectic melt assuming that the liquid solutions are Raoultian. The actual eutectic occurs at $X_{CaF_2} = 0.45$ and $T =$ 1243 K.

$x \equiv X_{CaF_2}$

For the CaF_2 liquidus line

$$\Delta G^\circ_m = 31200 - 18.45T = -8.3144\,T \ln x$$

For the MgF_2 liquidus line

$$\Delta G^\circ_m = 58160 - 37.86T = -8.3144\,T \ln(1-x)$$

Simultaneous solution gives the point of intersection of the liquidus lines at

$T = 1317$ K

$X_{CaF_2} = 0.53$

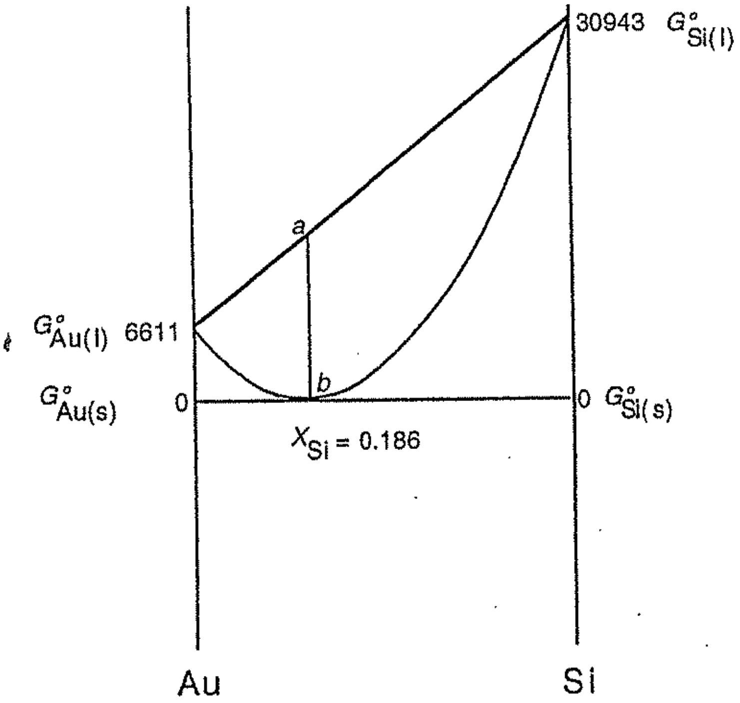
The actual eutectic is $T = 1243$ K

$X_{CaF_2} = 0.45$

10.2 Gold and silicon are mutually insoluble in the solid state and form a eutectic system with at eutectic temperature of 636 K and a eutectic composition of $X_{Si} = 0.186$. Calculate the Gibbs free energy of the eutectic melt relative to (*a*) unmixed liquid Au and liquid Si, and (*b*) unmixed solid Au and solid Si.

At 636 K $\Delta G^\circ_{m,Au} = 12600\left[\frac{1338-636}{1338}\right] = 6611$ J

and $\Delta G^\circ_{m,Si} = 50200\left[\frac{1658-636}{1658}\right] = 30943$ J



a) $\Delta G^M = ab$

$= -(0.186 \times 30943 + 0.814 \times 6611)$ J

$= -11140$ J

b) $\Delta G^M = 0$

10.3 Al_2O_3, which melts at 2324 K, and Cr_2O_3, which melts at 2538 K form complete ranges of solid and liquid solutions. Assuming that $\Delta S^{\circ}_{m,Cr_2O_3} = \Delta S^{\circ}_{m,Al_2O_3}$, and that the solid and liquid solutions in the system Al_2O_3-Cr_2O_3 behave ideally, calculate

1. The temperature at which equilibrium melting begins when an alloy of $X_{Al_2O_3} = 0.5$ is heated,
2. The composition of the melt which first forms,
3. The temperature at which equilibrium melting is complete, and
4. The composition of last-formed solid.

$$\frac{\Delta G^{\circ}_{m,Al_2O_3}}{RT} = \frac{12929}{T} - 5.563$$

$$\frac{\Delta G^{\circ}_{m,Cr_2O_3}}{RT} = \frac{14119}{T} - 5.563$$

1) The solidus temperature, T, at $X_{Al_2O_3} = 0.5$ is given by

$$0.5 = \frac{1 - \exp\left(-\frac{14119}{T} + 5.563\right)}{\exp\left(-\frac{12929}{T} + 5.563\right) - \exp\left(-\frac{14119}{T} + 5.563\right)}$$

which has the solution $T = 2418$ K

2) The corresponding liquidus composition is

$$X_{Al_2O_3}(\text{liquidus}) = 0.5\left[\exp\left(-\frac{12929}{2418} + 5.563\right)\right]$$

$$= 0.621$$

Problem 10.3 continued.

3) The liquidus temperature at $X_{Al_2O_3} = 0.5$ is given by

$$0.5 = \frac{1 - \exp\left(-\frac{14119}{T} + 5.563\right)}{\exp\left(-\frac{12929}{T} + 5.563\right) - \exp\left(-\frac{14119}{T} + 5.563\right)} \times \exp\left(\frac{-12929}{T} + 5.56\right.$$

which gives $T = 2444$ K

4) The corresponding solidus composition is

$$X_{Al_2O_3}(\text{solidus}) = \frac{1 - \exp\left(-\frac{14119}{2444} + 5.563\right)}{\exp\left(\frac{-12929}{2444} + 5.563\right) - \exp\left(\frac{-14119}{2444} + 5.563\right)}$$

$$= 0.38$$

10.4 $Na_2O.B_2O_3$ and $K_2O.B_2O_3$ form complete ranges of solid and liquid solutions and the solidus and liquidus show a common minimum at the equimolar composition and T = 1123 K. Calculate the molar Gibbs free energy of formation of the equimolar solid solution from solid $Na_2O.B_2O_3$ and solid $K_2O.B_2O_3$ at 1123 K, assuming that the liquid solutions are ideal.

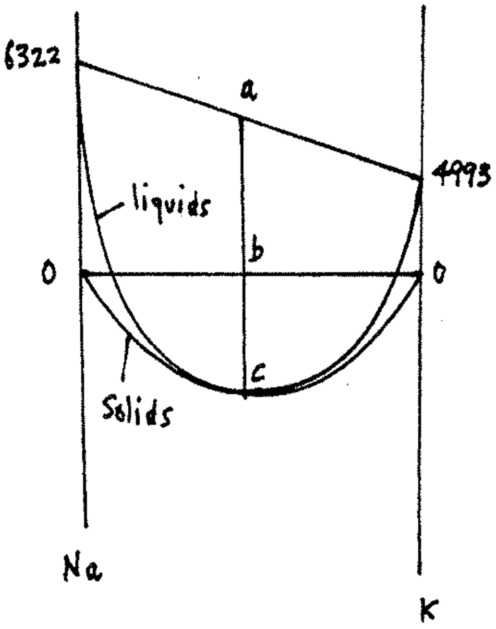
At $T = 1123\ K$

$$\Delta G^\circ_{m,\ Na_2O.B_2O_3} = 67000\left(\frac{1240-1123}{1240}\right) = 6322\ J$$

$$\Delta G^\circ_{m,\ K_2O.B_2O_3} = 62800\left(\frac{1220-1123}{1220}\right) = 4993\ J$$

$$\Delta G^M(\text{from liquids}) = 8.3144 \times 1123\,[0.5 \ln 0.5 + 0.5 \ln 0.5]$$

$$= -6472\ J. \quad = ac$$



$$ab = 0.5 \times 6322 + 0.5 \times 4993$$

$$= 5658\ J$$

$\therefore\ \Delta G^M$ (solid solution from solids)

$$= bc$$

$$= -6472 + 5658$$

$$= -814\ J$$

10.5 SiO_2, which melts at 1723°C and TiO_2, which melts at 1842°C are immiscible in the solid state and the SiO_2–TiO_2 binary system contains a monotectic equilibrium at 1794°C, at which temperature virtually pure TiO_2 is in equilibrium with two liquids containing mole fractions of SiO_2 of 0.04 and 0.76. If, for the purpose of simple calculation, it is assumed that the compositions of the two liquids are $X_{SiO_2} = 0.24$ and $X_{SiO_2} = 0.76$ and that the liquid solutions are regular in their behavior, what is the value of Ω_l and at what temperature does the liquid immiscibility gap disappear?

At the composition of the double tangent to the ΔG^M curve

$$\frac{d\Delta G^M}{dX} = RT \ln\left[\frac{X}{1-X}\right] + \Omega(1-2X) = 0$$

∴ At 2067 K.

$$8.3144 \times 2067 \ln\left[\frac{0.24}{0.76}\right] + \Omega_l(1-2\times 0.24) = 0$$

which gives $\Omega_l = 38096$ J.

Then $T_{cr} = \frac{\Omega_l}{2R} = \frac{38096}{2\times 8.3144} = 2291$ K

10.6 The binary system Ge-Si contains complete solid and liquid solutions. The melting temperatures are $T_{m,\mathrm{Si}} = 1685$ K and $T_{m,\mathrm{Ge}} = 1210$ K, and $\Delta H^{\circ}_{m,\mathrm{Si}} = 50200$ J. At 1200°C the liquidus and solidus compositions are, respectively, $X_{\mathrm{Si}} = 0.32$ and $X_{\mathrm{Si}} = 0.665$. Calculate the value of $\Delta H^{\circ}_{m,\mathrm{Ge}}$ assuming

1. that the liquid solutions are ideal

2. that the solid solutions are ideal

Which assumption gives the better estimate? The actual value of $\Delta H^{\circ}_{m,\mathrm{Ge}}$ at $T_{m,\mathrm{Ge}}$ is 36900 J.

At 1473 K, $\Delta G^{\circ}_{m,Si} = 50200\left(\frac{1685-1473}{1685}\right) = 6316$ J

$$\frac{\Delta G^{\circ}_{m,Si}}{RT} = \frac{6316}{8.3144\times 1473} = 0.5157$$

$$\therefore\ X_{Ge(solidus)} = 0.335 = \frac{1-\exp(-0.5157)}{\exp\left(\frac{-\Delta G^{\circ}_{m,Ge}}{8.3144\times 1473}\right)-\exp(-0.5157)}$$

gives $\Delta G^{\circ}_{m,Ge} = -7197$ J

and $\Delta H^{\circ}_{m,Ge} = \dfrac{-7197}{\left(\frac{1210-1473}{1210}\right)} = 33111$ J

$$X_{Ge(liquidus)} = 0.68 = \frac{(1-\exp(-0.5157))\exp\left(\frac{-\Delta G^{\circ}_{m,Ge}}{8.3144\times 1473}\right)}{\exp\left(\frac{-\Delta G^{\circ}_{m,Ge}}{8.3144\times 1473}\right)-\exp(-0.5157)}$$

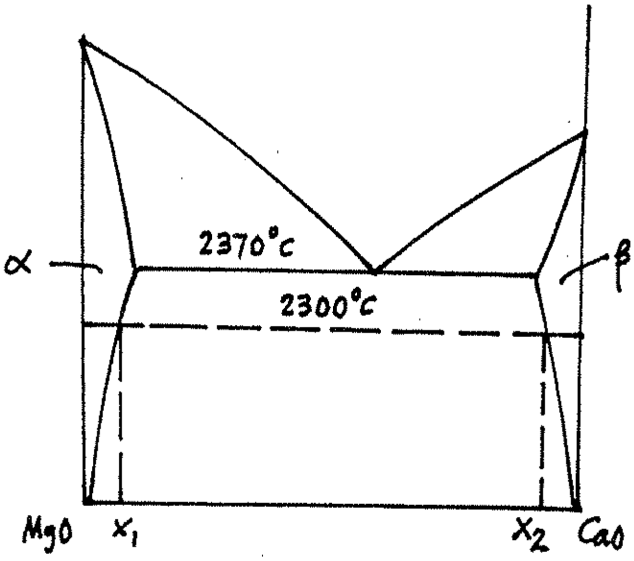
which gives $\Delta G^{\circ}_{m,Ge} = -4679$ J

Problem 10.6 continued

$$\therefore \Delta H^{\circ}_{m,Ge} = \frac{-4679}{\left(\frac{1210-1473}{1210}\right)} = 21527 \text{ J.}$$

$\therefore$ The estimate from the solidus (33100 J) is closer to the actual value of 36900 J.

10.7 CaO and MgO form a simple eutectic system with limited ranges of solid solubility. The eutectic temperature is 2370°C. Assuming that the solutes in the two solid solutions obey Henry's law with γ^{o}_{CaO} in MgO = 12.88 and γ^{o}_{MgO} in CaO = 6.23 at 2300°C, calculate the solubility of CaO in MgO and the solubility of MgO in CaO at 2300°C.



$$a_{CaO}\ (\text{in } \beta \text{ at } X_2) = a_{CaO}\ (\text{in } \alpha \text{ at } X_1)$$

$$1 - X_1 = 6.23(1 - X_2) \qquad (i)$$

$$a_{MgO}\ (\text{in } \alpha \text{ at } X_1) = a_{MgO}\ (\text{in } \beta \text{ at } X_2)$$

$$12.88\, X_1 = X_2 \qquad (ii)$$

Solution of (i) and (ii) gives

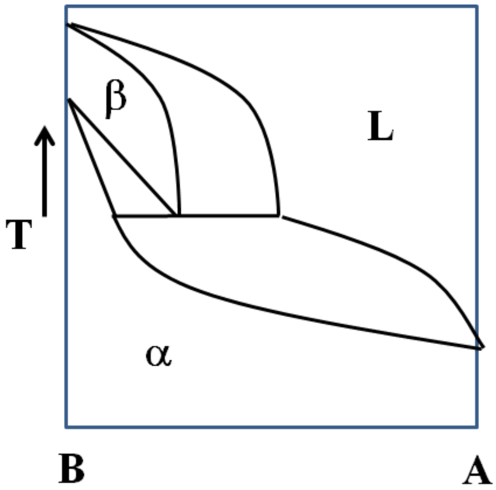
$$X_1 = X_{CaO} = 0.066$$

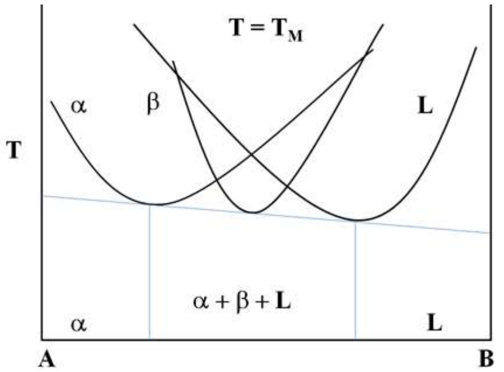
$$X_2 = X_{CaO} = 0.85$$

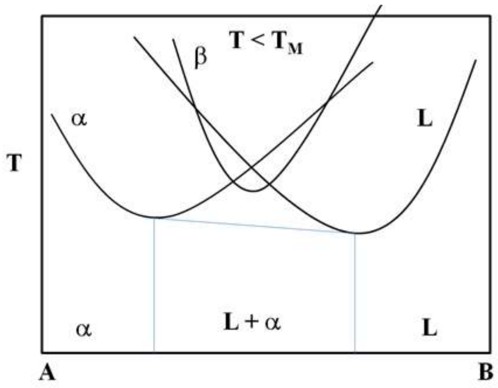
10.8* A metatectic binary phase diagram displays the following invariant transformation on cooling:

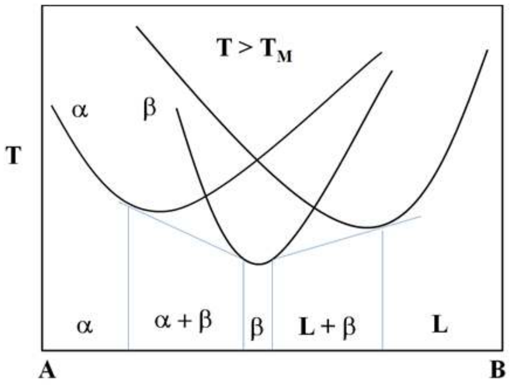
$$\rightarrow \beta \quad \alpha + L$$

Sketch such a phase diagram and then draw free energy curves of mixing just below, at and just above the invariant temperature.





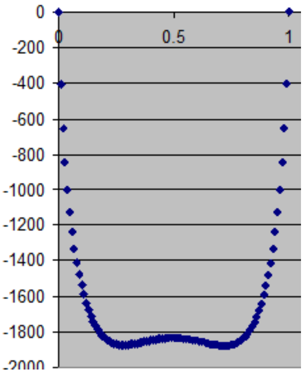




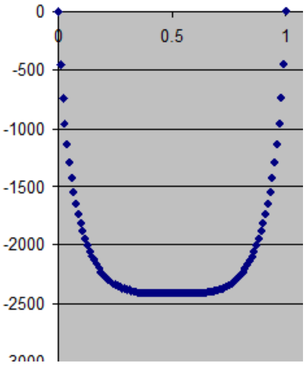
10.9* The free energy of mixing of a regular solution is given by:

$$\Delta G_{mix} = a_0 X_A X_B + RT[X_A \ln X_A + X_B \ln X_B]$$
$$\text{and } a_0 = 24,943 \text{ Joules/mole}$$

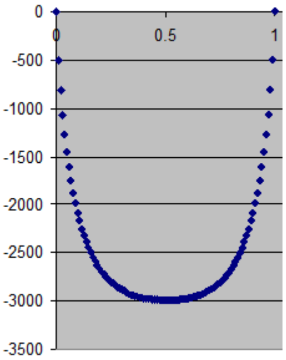
a. Plot ΔG_{mix} vs. X_B at 1400, 1500 and 1600 K.



1400 K

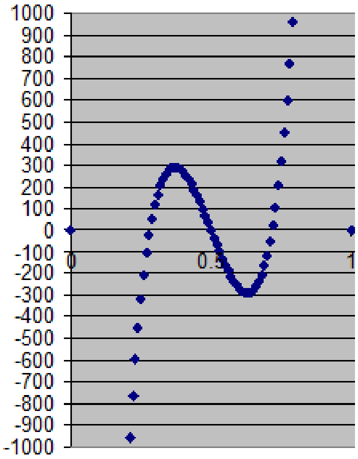


1500 K

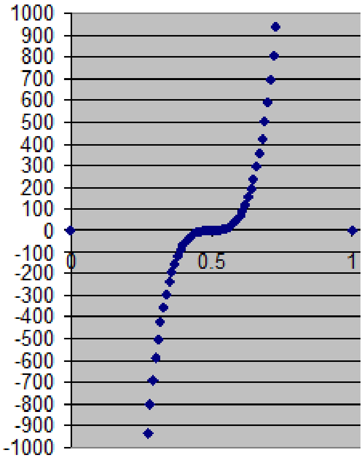


1600 K

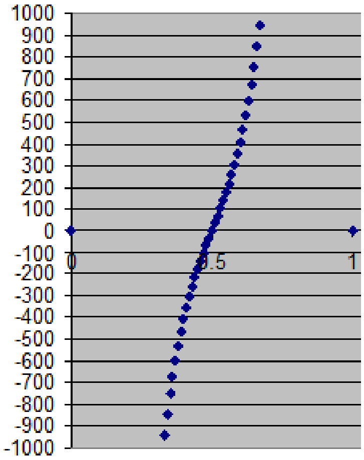
b. Plot $\frac{\partial \Delta G_{mix}}{\partial X_B}$ vs. X_B at the same temperatures as (a).



Plot of the first derivative for 1400K. The first and third zeros are the minima of free energy plot: they give the compositions of the two phases in equilibrium. The maximum in this plot and the minimum give us the spinodals



Plot of the first derivative for 1500K. Only one zero for this plot at 0.5. In fact when it passes through zero the curve has zero slope. This demonstrates that this is the critical temperature.



Plot of the first derivative for 1600K.The zero value is the minimum in free energy vs. X_B plot (0.5)

c. Determine the critical temperature for this alloy. Show work.

From the answers above we estimate T_C to 1500 K.
Or, since a regular solution we calculate it to be $T_C = a_0/2R = 1500$ K

10.10*. A certain solid solution of A and B has a ΔG_{mix}^{xs} as follows:

$$\Delta G_{mix}^{xs} = \Delta G_{mix} - \Delta G_{mix}^{id} = X_B X_A [a_1 X_A + a_2 X_B] + RT[X_A \ln X_A + X_B \ln X_B]$$

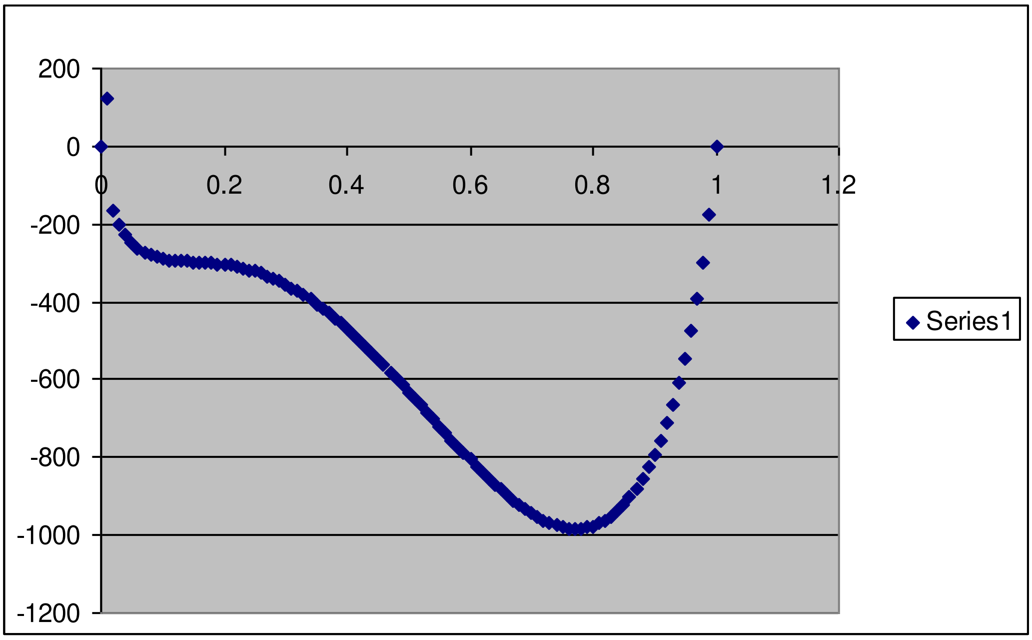
Where a_1 = 12,500 Joules/mole and a_2 = 5500 Joules/mole

a. Plot ΔG_{mix}^{xs} at T = 500 and 700 K

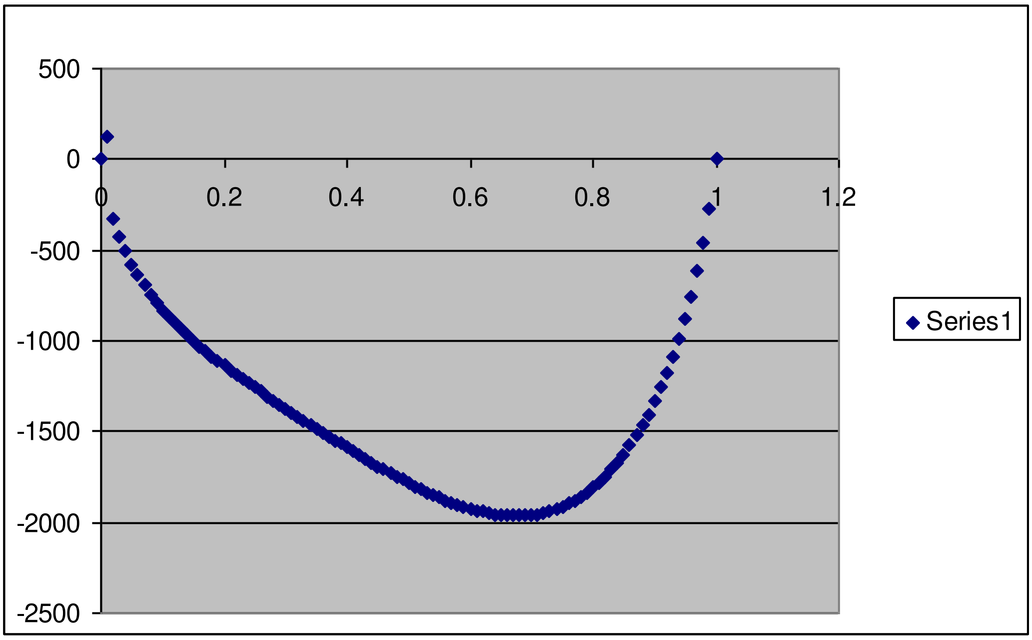
b. Sketch the T vs. X_B phase diagram of this alloy

c. Determine the critical temperature and composition of this alloy.

Solution



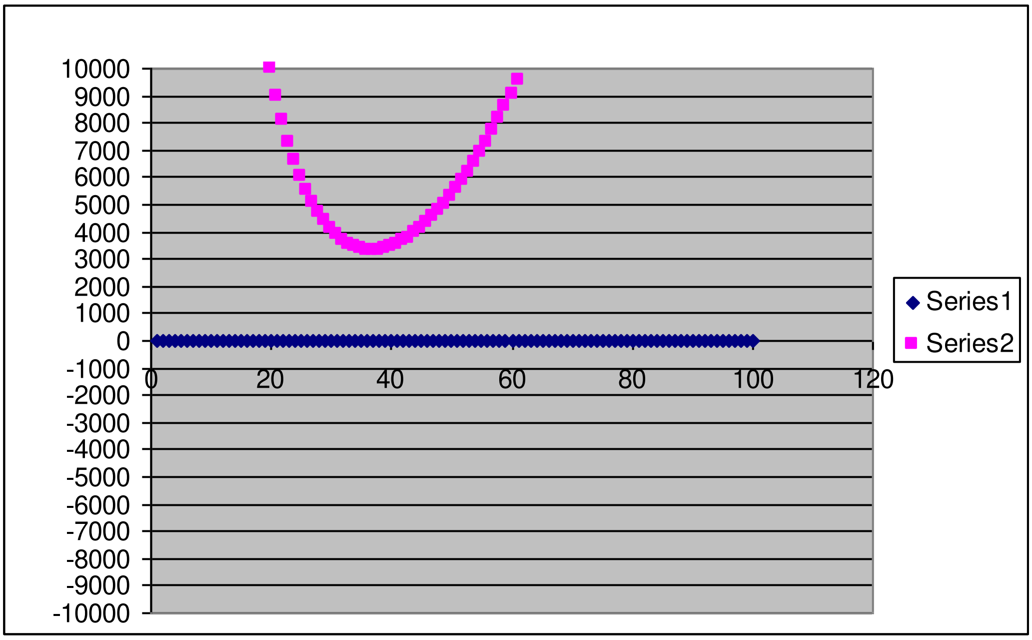
Plot of ΔG_{mix}^{xs} ve. X_B at 500 K, showing that a miscibility gap will exist in the T vs. X_B phase diagram with T_C being less than X_B = 0.5.



Plot of ΔG^{xs}_{mix} ve. X_B at 700 K, showing that 700 K is above T_C.

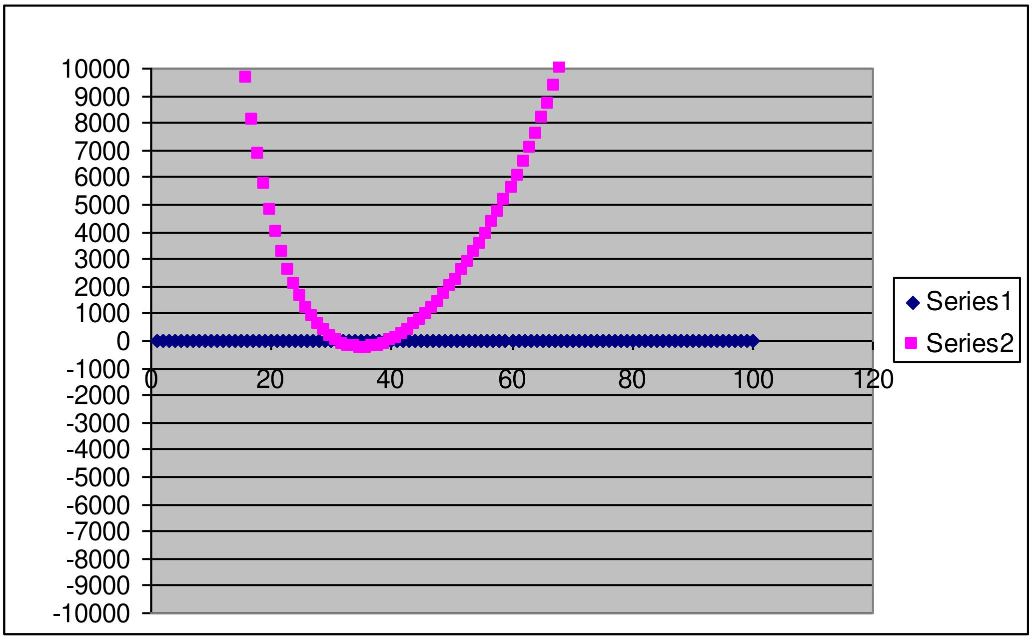
b. Plot will be asymmetric with T_C less than $X_B = 0.5$

c. A graphical way of doing this is to plot $\frac{\partial^2 \Delta G^{xs}_{mix}}{\partial X_B^2}$ vs. X_B and see what T has the curve just touching the 0 ordinate. Below is the $\frac{\partial^2 \Delta G^{xs}_{mix}}{\partial X_B^2}$ vs. X_B for 700 K



This is above T_C.

The 600 K plot shows two crossings of the $\frac{\partial^2 \Delta G^{xs}_{mix}}{\partial X_B^2} = 0$. Hence $T < T_C$.

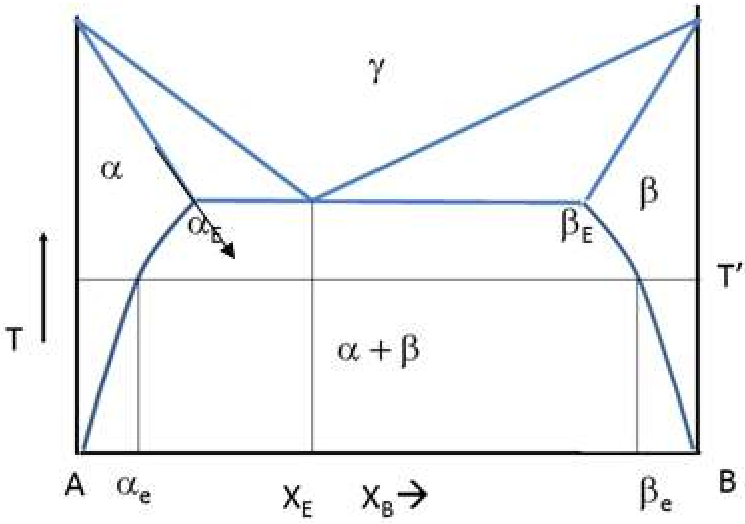


By trying various values of T, T_C can be found to be 607.5 K and the composition of the critical point is $X_B = 0.35$

10.11*. The phase diagram of an alloy that has an eutectoid transformation is shown in Fig.10.33.

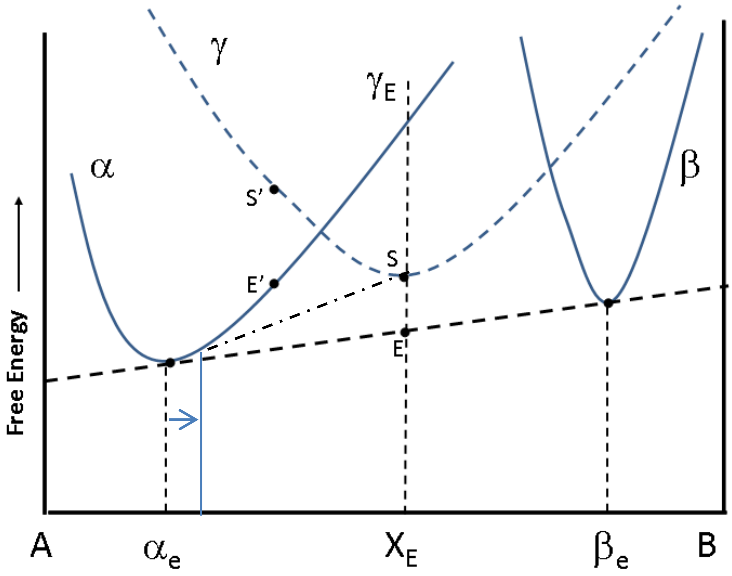
a. Sketch the Gibbs free energy curves for this alloy at T = T'.

b. Show that the α/γ solvus must enter the α/β two phase field (as shown by the arrow).



Solution

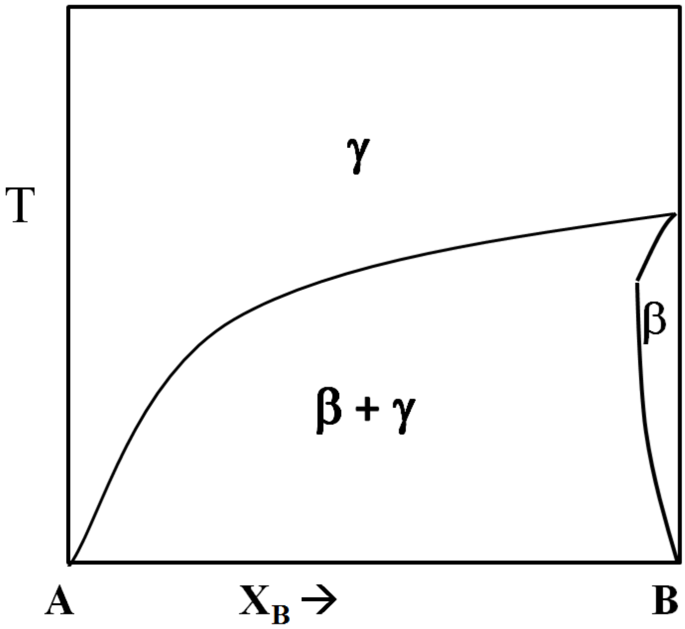
The common tangent of γ and α below T_E intersects the α free energy curve to the right of α_E.



10.12* A eutectoid phase diagram is shown in Fig. 10.33. Draw the phase diagram that would result if for some reason it were impossible to form the α phase.

SOLUTION

A possible diagram is shown below. Note that the γ / β curve is the same as the one in Fig.10.28a until the temperature where the eutectoid temperature was. is reached. It then is extrapolated to 0 K. The 0 K phases present are γ and β.



11.1 A gas mixture of 50% CO, 25% CO_2 and 25% H_2 (by volume) is fed to a furnace at 900°C. Determine the composition of the equilibrium CO-CO_2-H_2-H_2O gas if the total pressure of the gas in the furnace is 1 atm.

For $CO_2 + H_2 = H_2O + CO$

$$\Delta G^\circ_{1173} = -1416 \text{ J} \quad \therefore K_p = \exp\left(\frac{1416}{8.3144 \times 1173}\right)$$

$$= 1.156$$

	CO_2	$+$	H_2	$\rightarrow$	H_2O	$+$	CO	
initial moles	0.25		0.25		0		0.5	
upon reaction	$0.25-x$		$0.25-x$		x		$0.5+x$	$n_T = 1$

With $P_T = 1$ atm.

$$K_p = \frac{p_{H_2O} \cdot p_{CO}}{p_{CO_2} \cdot p_{H_2}}$$

$$1.156 = \frac{x(0.5+x)}{(0.25-x)^2}$$

$$\therefore x = 0.0676$$

$$\therefore X_{CO_2} = X_{H_2} = 0.25 - 0.0676 = 0.182$$

$$X_{CO} = 0.5 + 0.0676 = 0.568$$

$$X_{H_2O} = 0.0676$$

11.2 How much heat is evolved when 1 mole of SO_2 and ½ mole of O_2, each at 1 atm pressure, react to form the equilibrium SO_3-SO_2-O_2 mixture at 1000 K and 1 atm pressure?

For $SO_2 + \frac{1}{2}O_2 = SO_3$ $\quad \Delta G^\circ_{1000} = -5230\ J$

$$K_{p,1000} = \exp\left(\frac{5230}{8.3144\times 1000}\right)$$

$$= 1.876$$

	SO_2	$+\ \frac{1}{2}O_2$	$\longrightarrow\ SO_3$
initial moles	1	$\frac{1}{2}$	0
upon reaction	$1-x$	$\frac{1}{2}-\frac{1}{2}x$	x

$$n_T = \frac{1}{2}(3-x)$$

$$\therefore\ p_{SO_2} = \frac{2(1-x)}{3-x}.P\ ,\quad p_{O_2} = \frac{1-x}{3-x}P\ ,\quad p_{SO_3} = \frac{2x}{3-x}$$

$$K_p = \frac{p_{SO_3}}{p_{SO_2}p_{O_2}^{1/2}} = 1.876 = \frac{x(3-x)^{1/2}}{(1-x)^{1/2}(1-x)}$$

$$\therefore\ x = 0.463$$

For formation of 1 mole of SO_3 $\quad \Delta H = \Delta H^\circ = -94600\ J$

For formation of 0.463 moles of SO_3

$$\Delta H = 0.463 \times -94600\ J$$

$$= -43800\ J$$

$\therefore$ 43800 J are evolved.

11.3 A CO_2-CO-H_2O-H_2 gas mixture at a total pressure of 1 atm exerts a partial pressure of oxygen of 10^{-7} atm at 1600°C. In what ratio were the CO_2 and H_2 mixed to produce the gas with this oxygen pressure?

	CO_2 +	H_2 →	H_2O +	CO
initial moles	a	1	0	0
upon reaction	$a-x$	$1-x$	x	x

For $H_2 + \frac{1}{2}O_2 = H_2O$ $\qquad \Delta G^\circ_{1873} = -142892$ J

$$\therefore K = 9659 = \frac{p_{H_2O}}{p_{H_2}\, p_{O_2}^{1/2}} = \frac{x}{(1-x)\,10^{-3.5}}$$

which gives $x = 0.753$

For $CO + \frac{1}{2}O_2 = CO_2$ $\qquad \Delta G^\circ_{1873} = -119805$ J

$$\therefore K = 2193 = \frac{p_{CO_2}}{p_{CO}\cdot p_{O_2}^{1/2}} = \frac{a-x}{x \cdot 10^{-3.5}} = \frac{a-0.753}{0.753\times 10^{-3.5}}$$

which gives $a = 1.276$

$$\therefore \frac{CO_2}{H_2} = a = 1.276$$

11.4 Lithium bromide vapor dissociates according to $LiBr_{(g)} \rightarrow Li_{(g)} + \frac{1}{2}Br_{2,(g)}$. At what temperature does the partial pressure of Li reach the value of 10^{-5} atm when the gas is heated at a constant total pressure of 1 atm?

	$LiBr$	$\longrightarrow$	Li	$+$	$\frac{1}{2}Br_2$	
initial moles	1		0		0	
upon reaction	$1-x$		x		$\frac{1}{2}x$	$n_T = 1+\frac{1}{2}x$

At $P_T = 1$ atm. $\quad p_{Li} = \dfrac{x}{1+\frac{1}{2}x} = 10^{-5} \quad \therefore x = 10^{-5}$

$$\therefore p_{LiBr} = \frac{1-x}{1+\frac{1}{2}x} \sim 1$$

$$p_{Br_2} = 0.5\times10^{-5}$$

$$\therefore K = \frac{p_{Br_2}^{1/2}\cdot p_{Li}}{p_{LiBr}} = (0.5\times10^{-5})^{1/2}\,10^{-5} = 2.236\times10^{-8}$$

$$\Delta G^\circ = 333900 - 42.09\,T = -8.3144\,T\ln 2.236\times10^{-8}$$

which gives $T = 1771$ K

11.5 When SO_3 is decomposed at the constant pressure P and $T = 1000$ K, the partial pressure of O_2 in the equilibrium gas is 0.05 atm. What is the pressure P? If the pressure of this equilibrated gas is increased to 1 atm, to what value must the temperature be decreased to produce a gas mixture in which $p_{O_2} = 0.05$ atm?

For $SO_3 = SO_2 + \frac{1}{2}O_2$ $\quad \Delta G^\circ_{1000} = 5236$

$\therefore K_p = 0.533$

From stoichiometry $\quad p_{SO_2} = 2p_{O_2}$

and $\quad p_{SO_3} = P_T - 3p_{O_2}$

$$\therefore K = 0.533 = \frac{p_{O_2}^{1/2} \cdot p_{SO_2}}{p_{SO_3}} = \frac{(0.05)^{1/2}\, 2\times 0.05}{(P_T - 0.15)}$$

Gives $P_T = 0.192$ atm

$$\text{With } P_T = 1\text{ atm}, \quad K = \frac{(0.05)^{1/2} \cdot 0.10}{1 - 0.15} = 0.0263$$

$$\therefore \Delta G^\circ = 94600 - 89.37T = -8.3144T \ln 0.0263$$

which gives $T = 792$ K

11.6 For the dissociation of nitrogen according to

$$N_2 = 2N$$

$$\Delta G^\circ = 945000 - 114.9T \text{ J}$$

Calculate

i. the equilibrium partial pressure of N in nitrogen gas at 3000 K and a total pressure of 1 atm,

ii. the total pressure of the gas, at 3000 K, at which the partial pressure of N_2 is 90% of the total pressure.

For $N_2 = 2N$ $\quad \Delta G^\circ_{3000} = 600300 \text{ J}$

$$\therefore K_p = 3.53 \times 10^{-11}$$

$$= \frac{p_N^2}{(1-p_N)}$$

$$\therefore p_N = 5.94 \times 10^{-6} \text{ atm}$$

ii) $P_T = p_{N_2} + p_N$

$$= 0.9P_T + 0.1P_T$$

$$\therefore K_p = 3.53 \times 10^{-11}$$

$$= \frac{(0.1P_T)^2}{0.9P_T} = \frac{0.01}{0.9} P_T$$

$$\therefore P_T = 3.18 \times 10^{-9} \text{ atm.}$$

11.7 Ammonia gas is heated to 300°C. At what total pressure is the mole fraction of N_2 in the equilibrium gas mixture equal to 0.2. Calculate the standard enthalpy change and the standard entropy change for the reaction

$$\frac{3}{2}H_{2(g)} + \frac{1}{2}N_{2(g)} = NH_{3(g)}$$

at 300°C.

For $2NH_3 = N_2 + 3H_2$ $\quad \Delta G^\circ_{573} = -25021 \quad \therefore K_{p573} = 190.1$

As $p_{H_2} = 3p_{N_2}$, $X_{H_2} = 3X_{N_2}$

$\therefore X_{N_2} = 0.2$, $X_{H_2} = 0.6$ $\quad X_{NH_3} = 1 - 0.2 - 0.6 = 0.2$

$$\therefore K = 190.1 = \frac{p_{N_2} p_{H_2}^3}{p^2_{NH_3}} = \frac{X_{N_2} \cdot X_{H_2}^3 \cdot P^2}{X^2_{NH_3}} = \frac{0.2 \times 0.6^3 P}{0.2^2}$$

Which gives $P = 13.3$ atm

$$\Delta G^\circ = -87030 + 25.8T\ln T + 31.7T$$

for $N_2 + 3H_2 = 2NH_3$

$$\therefore \frac{\partial \Delta G^\circ}{\partial T} = -\Delta S^\circ = 25.8\ln T + 25.8 + 31.7$$

$$\therefore \Delta S^\circ_{573} = -221.4 \text{ J/K}$$

and $\Delta H^\circ_{573} = \Delta G^\circ_{573} + 573\Delta S^\circ_{573} = -25021 + 221.4 \times 573$

$= -101814$ J

$\therefore$ For $\frac{1}{2}N_2 + \frac{3}{2}N_2 = NH_3$

$\Delta H^\circ_{573} = -50900$ J and $\Delta S^\circ_{573} = -110.7$ J/K

11.8 By establishing the equilibrium

$$PCl_{5(g)} = PCl_{3(g)} + Cl_{2(g)}$$

at 500 K in a mixture of PCl_3 and PCl_3 a gas is obtained at 1 atm total pressure in which the partial pressure of Cl_2 is 0.1 atm. In what ratio were PCl_5 and PCl_3 mixed to obtain this equilibrium gas?

For $PCl_3 + Cl_2 = PCl_5$ $\quad \Delta G^\circ_{500K} = -2672$

$$K_{p,501} = 1.901$$

	$PCl_3 +$	$Cl_2 =$	PCl_5	
initial moles	a	0	1	
upon reaction	$a+x$	x	$1-x$	$n_T = a+1+x$

$$\therefore \text{ At } P_T = 1 \text{ atm.} \quad p_{Cl_2} = \frac{x}{a+1+x} = 0.1 \qquad (i)$$

$$K = 1.901 = \frac{p_{PCl_5}}{p_{PCl_3}\, p_{Cl_2}} = \frac{(1-x)(a+1+x)}{x(a+x)} \qquad (ii)$$

(i) and (ii) give $a = 2.692 \quad x = 0.410$

$$\therefore \frac{PCl_3}{PCl_5} = a = 2.692$$

11.9 Air and hydrogen are mixed in the ratio 1:4 and are heated to 1200 K. Calculate the partial pressures of H_2 and O_2 in the equilibrium gas at 1 atm pressure and at 10 atm pressure. Air contains 21 volume percent O_2.

$n_{H_2} = 20$

$n_{air} = 80 \longrightarrow n_{O_2} = 16.8$

$n_{N_2} = 63.2$

For $H_2 + \frac{1}{2}O_2 = H_2O$ $\quad \Delta G^\circ_{1200} = -180480$ J

$$K = 7.178 \times 10^7 = \frac{p_{H_2O}}{p_{H_2} \cdot p_{O_2}^{1/2}}$$

$$\frac{n_H}{n_O} = \frac{20}{16.8} = 1.1905 = \frac{2n_{H_2} + 2n_{H_2O}}{2n_{O_2} + n_{H_2O}}$$

$$\frac{n_O}{n_N} = \frac{16.8}{63.2} = 0.2658 = \frac{2n_{O_2} + n_{H_2O}}{126.4}$$

$\therefore\ 2n_{O_2} + n_{H_2O} = 0.2658 \times 126.4 = 33.6$

and $2n_{H_2} + 2n_{H_2O} = 33.6 \times 1.1905 = 40$

$\therefore\ n_{H_2O} = 20 - n_{H_2} = 33.6 - 2n_{O_2}$

$n_{O_2} = 6.8 + \frac{1}{2}n_{H_2}$

$n_T = 20 - n_{H_2} + n_{H_2} + 6.08 + \frac{1}{2}n_{H_2} + 63.2$

$= 90 + \frac{1}{2}n_{H_2}$

$$\therefore\ K = 7.178 \times 10^7 = \frac{n_{H_2O} \cdot n_T^{1/2}}{n_{H_2}\, n_{O_2}^{1/2}\, P^{1/2}}$$

11.9 continued

$\therefore$ with $P = 1$ atm.

$$7.178\times10^{7} = \frac{(20-n_{H_2})(90+\frac{1}{2}n_{H_2})^{1/2}}{n_{H_2}(6.8+\frac{1}{2}n_{H_2})^{1/2}}$$

which gives $n_{H_2} = 9.43\times10^{-7}$ moles

$\therefore n_{O_2} = 6.8$ and $n_T = 90$ moles

$$\therefore p_{H_2} = \frac{n_{H_2}}{n_T}\cdot P_T = \frac{9.43\times10^{-7}}{90} = 1.05\times10^{-8}\text{ atm}$$

$$\text{and } p_{O_2} = \frac{6.8}{90}\cdot P_T = 0.0756\text{ atm}$$

with $P_T = 10$ atm

$$7.178\times10^{7} = \frac{(20-n_{H_2})(90+\frac{1}{2}n_{H_2})^{1/2}}{n_{H_2}(6.8+\frac{1}{2}n_{H_2})^{1/2}\sqrt{10}}$$

which gives $n_{H_2} = 2.98\times10^{-7}$ moles

and $n_{O_2} = 6.8$ moles

$$\therefore p_{H_2} = \frac{2.98\times10^{-7}}{90}\times10 = 3.31\times10^{-8}\text{ atm}$$

$$p_{O_2} = \frac{6.8}{90}\times10 = 0.756\text{ atm}$$

11.10 One mole of each of hydrogen, iodine vapor and HI gas are allowed to react at 1500 K and $P = 1$ atm. Calculate the mole fractions of H_2, I_2 and HI in the equilibrium mixture. The temperature is then changed to that value at which p_{HI} in the equilibrated gas is five times p_{H_2}. What is this temperature?

For $H_2 + I_2 = 2HI$ $\quad \Delta G^{\circ}_{1500} = -34845$ J

$$K_{p,1500} = 16.345 = \frac{p^2_{HI}}{p_{H_2} \cdot p_{I_2}}$$

	H_2	$+$	I_2	$=$	$2HI$.	
before	1		1		1	
at equilibrium	$1-x$		$1-x$		$1+2x$	$\therefore n_T = 3$

$$\therefore K = \frac{(1+2x)^2}{(1-x)^2} = 16.345 \quad \text{which gives } x = 0.504$$

$$\therefore x_{H_2} = x_{I_2} = \frac{1-0.504}{3} = 0.165$$

$$x_{HI} = \frac{1+2\times 0.504}{3} = 0.669$$

For $p_{HI} = 5p_{H_2}$, $\quad K = \frac{(5p_{H_2})^2}{p^2_{H_2}} = 25$

$$\therefore \Delta G^{\circ} = -8370 - 17.65T = -8.3144\,T \ln 25$$

gives $T = 918$ K.

11.11* Consider the reduction of Magnetite by CO to form pure iron:

$$Fe_3O_4(s)+4CO(g)=3Fe(s)+4CO_2(g)$$

Calculate the partial pressure of CO and CO_2 in terms of the equilibrium constant K_P for the reaction at any temperature, T.

SOLUTION

Assume the activity of the solids to be unity and that the gases behave as ideal gases.

$$K_P=\frac{a_{Fe}^3 a_{CO_2}^4}{a_{Fe_3O_4}a_{CO}^4}=\frac{p_{CO_2}^4}{p_{CO}^4}$$

$$K_P^{\frac{1}{4}}=\frac{p_{CO_2}}{p_{CO}}$$

Also the total pressure is 1 atmosphere:

$$p_{CO_2}+p_{CO}\ =1$$

Solving the two equations simultaneously:

$$p_{CO}\ =\frac{1}{(K_P^{\frac{1}{4}}+1)}\qquad p_{CO_2}=\frac{K_P^{\frac{1}{4}}}{(K_P^{\frac{1}{4}}+1)}$$

.

11.12* It is known that at 300 K the value of K_P for a certain reaction is 10^{12}. For the reaction ΔH^0 is 100 kJ/mole.

a. Determine if this reaction is favorable at 800 K and estimate K_P (800K). Explain.

b. The actual value of K_P (800) is 35. Explain any discrepancy from your estimate.

SOLUTION

First, estimate K_P at 800 K.

$$\ln\left(\frac{K_P(800K)}{K_P(300K)}\right) = \frac{\Delta H^0}{R}\left(\frac{1}{300} - \frac{1}{800}\right)$$

$$\ln\left(\frac{K_P(800K)}{K_P(300K)}\right) = \frac{-100000}{8.3144}\left(\frac{1}{300} - \frac{1}{800}\right) = -25.06$$

$$\text{Thus } \frac{K_P(800K)}{K_P(300K)} = \exp(-25.06)$$

$$K_P(800K) = K_P(300K)\cdot\exp(-25.06) = 13.12$$

Since the value is greater than unity the reaction is possible at 800 K,

b. The above method assumed there was no temperature dependence of ΔH^0 over the span of 500 K.

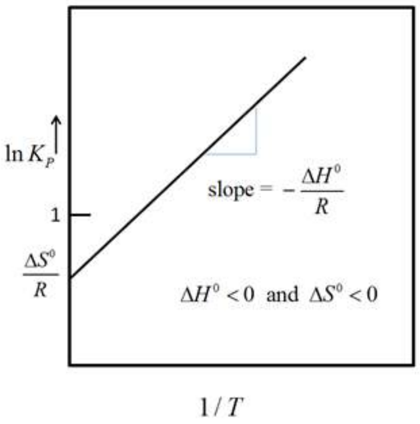
11.13* Sketch the natural log of K_P vs. $1/T$ for the cases of

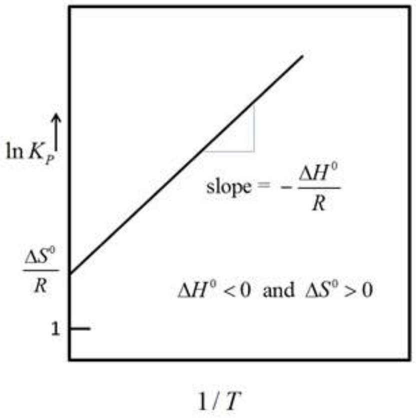
a. $\Delta H^0 < 0 \quad \Delta S^0 < 0$

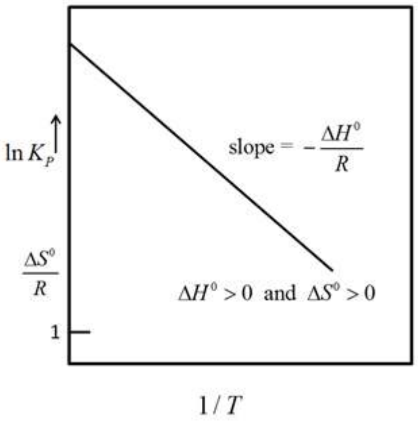
b. $\Delta H^0 < 0 \quad \Delta S^0 > 0$

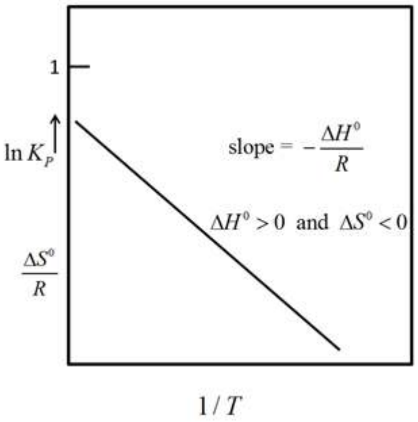
c. $\Delta H^0 > 0 \quad \Delta S^0 > 0$

d. $\Delta H^0 > 0 \quad \Delta S^0 < 0$









12.1 To what temperature must $MgCO_3$ be heated in an atmosphere containing a partial pressure of CO_2 of 10^{-2} atm to cause decomposition of the carbonate?

$MgO + CO_2 = MgCO_3 \qquad \Delta G^\circ = -117600 + 170T = RT \ln p_{CO_2(eq)}$

$\therefore$ At $p_{CO_2(eq)} = 10^{-2}$ atm.

$-117600 + 170T = 8.3144\, T \ln 10^{-2} = -38.29T$

which gives $T = 565$ K.

12.2 Using the standard Gibbs free energies of formation of NiO from solid Ni and liquid Ni, calculate the melting temperature, molar heat of melting and the molar entropy of melting of nickel.

For $2Ni_{(s)} + O_2 = 2NiO \quad \Delta G^\circ = -471200 + 172T$ J

For $2NiO = O_2 + 2Ni_{(l)} \quad \Delta G^\circ = 506180 - 192.2T$ J

Adding gives

$$2Ni(s) = 2Ni(l) \quad \Delta G^\circ = 34980 - 20.2T \ \text{J}$$

$$\therefore T_{m,Ni} = \frac{34980}{20.2} = 1731 \ \text{K}$$

$$\Delta H^\circ_{m,Ni} = \frac{34980}{2} = 17490 \ \text{J}$$

$$\Delta S^\circ_{m,Ni} = \frac{20.2}{2} = 10.1 \ \text{J/K}.$$

12.3 Calculate the temperature at which pure Ag_2O decomposes to Ag metal and O_2 gas when heated in (*a*) pure oxygen at 1 atm pressure, and (*b*) in air.

$$2Ag + \frac{1}{2}O_2 = Ag_2O$$

$$\Delta G^0 = -30540 + 66.11\,T \quad J.$$

For $p_{O_2(eq)} = 1$ atm.

$$-30540 + 66.11\,T = RT \ln p_{O_2(eq)}^{1/2} = 0$$

$$\therefore T = 462\,K$$

For $p_{O_2(eq)} = 0.21$ atm.

$$-30540 + 66.11\,T = \frac{1}{2} \times 8.3144\,T \ln 0.21$$

gives $T = 421\,K$

12.4 Determine the maximum pressure of water vapor in wet hydrogen at 1 atm pressure in which chromium can be heated without oxidation occurring at 1500 K. Is the oxidation of Cr by water vapor exothermic or endothermic?

For $2Cr + \frac{3}{2}O_2 = Cr_2O_3 \qquad \Delta G^\circ_{1500K} = -739150 \text{ J}$

For $3H_2O = 3H_2 + \frac{3}{2}O_2 \qquad \Delta G^\circ_{1500K} = 491175 \text{ J}$

Adding gives

$$2Cr + 3H_2O = Cr_2O_3 + 3H_2 \qquad \Delta G^\circ_{1500K} = -247975 \text{ J}$$

$$= 1500 \times 8.3144 \times 3 \ln \frac{p_{H_2O}}{p_{H_2}}$$

$$\therefore \frac{p_{H_2O}}{p_{H_2}} = 1.32 \times 10^{-3}$$

$\therefore$ with $p_{H_2} = 1$, $p_{H_2O}(\text{max}) = 1.32 \times 10^{-3}$ atm

For $2Cr + 3H_2O = Cr_2O_3 + 3H_2$

$$\Delta H^\circ = -371200 \text{ J}$$

and the reaction is exothermic.

12.5 A mixture of argon gas and hydrogen gas at 1 atm total pressure is passed through a reaction vessel containing a mixture of liquid Sn and liquid $SnCl_2$ at 900 K. The composition of the gas leaving the vessel is 50% H_2, 7% HCl and 43% Ar. Has equilibrium been attained between the gas phase and the liquid phases in the vessel?

For $SnCl_2(l) = Sn(l) + Cl_2(g)$ $\quad \Delta G^\circ_{900K} = 226480$ J

For $H_2 + Cl_2 = 2HCl(g)$ $\quad \Delta G^\circ_{900K} = -199720$ J

∴ For $SnCl_2 + H_2 = Sn + 2HCl$ $\quad \Delta G^\circ_{900K} = 26760$ J

$$\therefore K = \exp\left(\frac{-26760}{8.3144\times 900}\right) = 0.028 = \frac{p^2_{HCl}}{p_{H_2}}$$

In the exit gas $\frac{p^2_{HCl}}{p_{H_2}} = \frac{0.07^2}{0.5} = 0.0098$, which, being less than K, indicates that equilibrium has not been attained.

The gas entering contains $0.5 + 0.035 = 0.535$ moles of H_2 and 0.43 moles of Ar

$SnCl_2 + H_2 = Sn + 2HCl$

before $\quad 0.535$

after $\quad 0.535 - x \quad\quad 2x \quad\quad n_T = 0.535 + x + 0.43$

$= 0.965 + x$ moles

$$\therefore K = 0.028 = \frac{(2x)^2}{(0.965+x)(0.535-x)} \quad \therefore x = 0.0584$$

$$\therefore HCl \rightarrow \frac{2\times 0.0584}{0.965 + 0.0584} \rightarrow 11.4\%$$

$$H_2 \rightarrow \frac{0.535 - 0.0584}{0.965 + 0.0584} \rightarrow 46.6\%$$

$$Ar \rightarrow \frac{0.43}{0.965 + 0.0584} \rightarrow 42\%$$

12.6 Fe and FeO are in equilibrium with a gas mixture of composition 71.8% CO - 28.2% CO_2 at 1273 K. Which of the two solid phases disappears if the composition of the gas is held constant and the temperature of the system is decreased?

For $Fe + \frac{1}{2}O_2 = FeO$ $\Delta G^\circ = -263700 + 64.35T$ J

For $CO_2 = \frac{1}{2}O_2 + CO$ $\Delta G^\circ = 282400 - 86.81T$ J

$\therefore$ For $Fe + CO_2 = FeO + CO$ $\Delta G^\circ = 18700 - 22.46T$

As written, the reaction is endothermic. Then a decrease in temperature causes the equilibrium to shift as

$$FeO + CO \longrightarrow Fe + CO_2$$

which decreases $p_{CO(eq)}$ and increases $p_{CO_2(eq)}$.

Thus decreasing the temp at const. p_{CO} and constant p_{CO_2} causes the FeO phase to disappear.

12.7 Calculate the vapor pressure of Mg exerted at 1400°C by the system in which the reaction

$$4MgO_{(s)} + Si_{(s)} = 2Mg_{(g)} + Mg_2SiO_{4(s)}$$

is established

For $2MgO + SiO_2 = Mg_2SiO_4$ $\Delta G^\circ_{1673K} = -59989\ J$

$2MgO = 2Mg(v) + O_2$ $\Delta G^\circ_{1673K} = 776616\ J$

$Si + O_2 = SiO_2$ $\Delta G^\circ_{1673K} = -613153\ J$

$\therefore$ For $4MgO + Si = 2Mg(v) + Mg_2SiO_4$

$$\Delta G^\circ_{1673K} = 103474\ J$$

$$= -2 \times 8.3144 \times 1673 \ln p_{Mg(eq)}$$

$$\therefore \quad p_{Mg(eq)} = 2.42 \times 10^{-2}\ atm.$$

12.8 One gram of $CaCO_3$ is placed in an evacuated rigid vessel of volume 1 liter at room temperature, and the system is heated. Calculate (*a*) the highest temperature at which the $CaCO_3$ phase is present, (*b*) the pressure in the vessel at 1000 K, and (*c*) the pressure in the vessel at 1500 K. The molecular weight of $CaCO_3$ is 100.

For $CaO + CO_2 = CaCO_3$ $\qquad \Delta G^\circ = -161300 + 137.2T$ J

$$\therefore \ln p_{CO_2(eq)} = -\frac{161300}{RT} + \frac{137.2}{R} = -\frac{19400}{T} + 16.50 \qquad (i)$$

1 g. $CaCO_3 = \frac{1}{100} = 0.01$ moles $\therefore$ The vessel contains 0.01 moles of CO_2. If all of the 0.01 moles of CO_2 occurs in the gas phase then

$$p_{CO_2} = \frac{nRT}{V} = \frac{0.01 \times 0.082057T}{1} = 8.2057 \times 10^{-4} \qquad (ii)$$

From (i) $\qquad p_{CO_2(eq)} = \exp\left[-\frac{19400}{T} + 16.50\right] \qquad (iii)$

Lines (ii) and (iii) intersect at $p_{CO_2} = 0.96$, $T = 1173$ K which is the highest temperature at which $CaCO_3$ exists.

At $T = 1000$K eq (iii) gives $p_{CO_2(eq)} = 0.055$ atm

and at $T = 1500$K eq. (ii) gives $p_{CO_2} = 1.23$ atm.

12.9 Calculate the total pressure ($p_{SO_3} + p_{SO_2} + p_{O_2}$) exerted by equilibrated CoO and $CoSO_4$ at 1223 K.

$CoO + SO_3 = CoSO_4 \quad \Delta G^\circ_{1223K} = -25698\ J$

$= 8.3144 \times 1223 \ln p_{SO_3(eq)}$

$\therefore p_{SO_3(eq)} = 7.99 \times 10^{-2}$ atm

$SO_3 = SO_2 + \frac{1}{2}O_2 \quad \Delta G^\circ_{1223K} = -14699\ J$

$= -1223 \times 8.3144 \ln \dfrac{p_{SO_2} \cdot p_{O_2}^{1/2}}{p_{SO_3}}$

$\therefore \dfrac{p_{SO_2} \cdot p_{O_2}^{1/2}}{p_{SO_3}} = 4.244$ and $p_{O_2} = \frac{1}{2} p_{SO_2}$

$\therefore 4.244 = \dfrac{p_{SO_2}[0.5 p_{SO_2}]^{1/2}}{7.99 \times 10^{-2}}$

$\therefore p_{SO_2} = 0.612$

$p_{O_2} = 0.306$

$p_{SO_3} = 0.0799$

$\therefore P_T = 1.0$ atm

12.10 A gas mixture initially containing 90% CO, 0.4% COS and 9.6% inert constituents (by volume) is passed over sponge iron at 1000 K to remove sulfur by the following reaction.

$$COS_{(g)} + Fe_{(s)} = CO_{(g)} + FeS_{(s)}$$

(*a*) Assuming that the effluent gas is in equilibrium with Fe and FeS, calculate the percentage of sulfur removed from the gas by reaction with the sponge iron. (*b*) Calculate the partial pressure of S_2 in the effluent gas.

For $C + \frac{1}{2}O_2 + \frac{1}{2}S_2 = COS \qquad \Delta G^\circ_{1000K} = -212760\ J$

$Fe + \frac{1}{2}S_2 = FeS \qquad \Delta G^\circ_{1000K} = -97650\ J$

$C + \frac{1}{2}O_2 = CO \qquad \Delta G^\circ_{1000K} = -199350\ J$

$\therefore$ For $COS + Fe = CO + FeS \qquad \Delta G^\circ_{1000} = -84240\ J$

and $K = \exp\left[\frac{84240}{8.3144 \times 1000}\right] = 25130 = \frac{p_{CO}}{p_{COS}}$

	COS	$+ Fe =$	CO	$+ FeS$
before	0.4		90	
after	$0.4 - x$		$90 + x$	

$\therefore \quad 25130 = \frac{p_{CO}}{p_{COS}} = \frac{90+x}{0.4-x}$ which gives $x = 0.3964$

$\therefore$ % S removed $= \frac{0.3964}{0.4} \times 100 = 99.1$

For $CO + \frac{1}{2}S_2 = COS \qquad \Delta G^\circ_{1000K} = -13410\ J$

$\therefore K_{1000} = 5.017 = \frac{p_{COS}}{p_{CO} \cdot p_{S_2}^{1/2}} = \frac{0.0036}{90.3964\, p_{S_2}^{1/2}}$

$\therefore p_{S_2} = 6.3 \times 10^{-11}$ atm

12.11 An Ar-H_2O gas mixture of $p_{H_2O} = 0.9$ atm ($P_{total} = 1$ atm) is passed over solid CaF_2, as a result of which CaO forms according to

$$CaF_{2(s)} + H_2O_{(g)} = CaO_{(s)} + 2HF_{(g)}$$

The reaction proceeds to equilibrium and solid CaO and solid CaF_2 are mutually immiscible. When the gas flow rate (measured at 298 K at 1 atm pressure) over the sample is 1 liter per minute, the measured rates of weight loss of the sample are 2.69×10^{-4} and 8.30×10^{-3} grams per hour at 900 K and 1100 K, respectively. Use these data to calculate the variation of ΔG° for the above reaction with temperature. The atomic weights are O = 16, F = 19 and Ca = 40.08.

$$CaF_2 + H_2O = CaO + 2HF$$

MW 78.08 56.08

∴ A weight loss of 22g produces 2HF and consumes 1 H_2O

∴ A weight loss of 1g produces 0.0909 HF and consumes 0.0455 H_2O

At 900 K for 1 hour.

weight loss of 2.69×10^{-4} g produces 2.44×10^{-5} moles HF and consumes 1.22×10^{-5} moles H_2O

In 60 l of gas in which $p_{H_2O} = 0.9$ atm.

$$n_{H_2O} = \frac{0.9 \times 60}{0.082057 \times 298} = 2.208 \text{ moles}$$

∴ consumption of 1.22×10^{-5} moles of H_2O is insignificant.

$$\therefore p_{HF} = \frac{2.44 \times 10^{-5} \times 0.082057 \times 298}{60} = 9.94 \times 10^{-6} \text{ atm}$$

$$\therefore K_{900} = \frac{p^2_{HF}}{p_{H_2O}} = \frac{(9.94 \times 10^{-6})^2}{0.9} = 1.09 \times 10^{-10}.$$

and $\Delta G^\circ_{900} = -8.3144 \times 900 \ln 1.09 \times 10^{-10}$

$= 171596$ J.

page 93a

12.11 continued.

At 1100 K 0.0083 grams per hr

$$\equiv 7.545\times10^{-4} \text{ moles/hr}$$

$$\therefore p_{HF} = \frac{7.545\times10^{-4}\times0.082057\times298}{60} = 3.075\times10^{-4} \text{ atm}$$

$$\therefore K_{1100} = \frac{(3.075\times10^{-4})^2}{0.9} = 1.051\times10^{-7} \quad \therefore \Delta G^\circ_{1100} = 146962 \text{ J}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$= A + BT$$

$$\therefore 171596 = A + 900B$$

$$146962 = A + 1100B$$

which gives $B = -123$ J/K

$A = 282449$ J.

$$\therefore \Delta G^\circ = 282000 - 123T$$

12.12 Magnetite, (Fe_3O_4), is reduced to sponge iron, (Fe), in a continuous reactor operating at 800 K using methane gas, (CH_4), as the reducing agent. The gaseous reaction product leaving the reactor at a total pressure of 1 atm is a mixture of CO, CO_2, H_2 and H_2O with a negligible methane content. The gas is at equilibrium with the Fe-Fe_3O_4 mixture in the reactor. Calculate the consumption of methane as moles of methane used per mole of Fe produced.

For $3Fe + 2O_2 = Fe_3O_4$ $\quad \Delta G^\circ_{800} = -856280$ J

$$= 2\times 8.3144 \times 800 \ln p_{O_2(eq)}$$

$\therefore$ p_{O_2} in the exit gas $= 1.11\times10^{-28}$ atm.

For $H_2 + \frac{1}{2}O_2 = H_2O$ $\quad \Delta G^\circ_{800} = -202560$ J

$$= -8.3144\times 800 \ln \frac{p_{H_2O}}{p_{H_2}p_{O_2}^{1/2}}$$

$$\therefore \frac{p_{H_2O}}{p_{H_2}p_{O_2}^{1/2}} = 1.681\times10^{13} \text{ and } \frac{p_{H_2O}}{p_{H_2}} = 0.1771 \quad \text{— (i)}$$

For $2CO + O_2 = 2CO_2$ $\quad \Delta G^\circ_{800} = -425904$ J

$$= -8.3144\times 800 \ln \frac{p_{CO_2}}{p_{CO}p_{O_2}^{1/2}}$$

$$\therefore \frac{p_{CO_2}}{p_{CO}p_{O_2}^{1/2}} = 8.02\times10^{13} \text{ and } \frac{p_{CO_2}}{p_{CO}} = 0.845 \quad \text{— (ii)}$$

$$p_{H_2} + p_{H_2O} + p_{CO} + p_{CO_2} = 1 \quad \text{— (iii)}$$

All of the C and the H in the gas come from the CH_4

$$\therefore \frac{n_C}{n_H} = \frac{1}{4} = \frac{p_{CO}+p_{CO_2}}{2p_{H_2}+2p_{H_2O}}$$

$$\therefore p_{H_2O} + p_{H_2} = 2p_{CO} + 2p_{CO_2} \quad \text{— (iv)}$$

12.12 continued.

Solution of (i) – (iv) gives

$p_{H_2} = 0.5662$ atm

$p_{H_2O} = 0.1003$ atm

$p_{CO} = 0.1806$ atm

$p_{CO_2} = 0.1528$ atm

All of the C comes from CH_4 → $0.1806 + 0.1528 = 0.3334$ moles

All of the O comes from Fe_3O_4 → $0.1003 + 0.1806 + 2 \times 0.1528$

$= 0.5865$ moles

∴ 0.3334 moles of CH_4 per $\frac{3}{4} \times 0.5865 = 0.4398$ moles of Fe

or. 0.76 moles of CH_4 per mole of Fe produced.

12.13 Three equations for the oxidation of Mg according to $Mg + \frac{1}{2}O_{2(g)} = MgO_{(s)}$ are

$$\Delta G^\circ = -604000 - 5.36T \ln T + 142.0T \text{ J} \tag{I}$$

$$\Delta G^\circ = -759800 - 13.4T \ln T + 317T \text{ J} \tag{II}$$

and

$$\Delta G^\circ = -608100 - 0.44T \ln T + 112.8T \text{ J} \tag{III}$$

One of these expressions is for the oxidation of solid Mg, one is for the oxidation of liquid Mg and one is for the oxidation of gaseous Mg. Determine which equation is for which oxidation and calculate the melting and normal boiling temperature of Mg.

I $$\frac{\Delta G^\circ}{T} = -\frac{604000}{T} - 5.36 \ln T + 142.0$$

$$\frac{\partial\left(\frac{\Delta G^\circ}{T}\right)}{\partial T} = \frac{604000}{T^2} - \frac{5.36}{T} = -\frac{\Delta H^\circ}{T^2}$$

$$\therefore \Delta H_I^\circ = -60400 + 5.36T$$

Similarly $$\Delta H_{II}^\circ = -759800 + 13.4T$$

and $$\Delta H_{III}^\circ = -608100 + 0.44T$$

$$|\Delta H^\circ_{Mg(g)}| > |\Delta H^\circ_{Mg(l)}| > |\Delta H^\circ_{Mg(s)}|$$

∴ II is for oxidation of Mg(g)

III is for oxidation of Mg(l)

and I is for oxidation of Mg(s)

12.15 CONTINUED

$$\Delta G^{\circ}_{I} = \Delta G^{\circ}_{III} \quad \text{at} \quad T_{m,Mg} = 930\ K$$

$$\Delta G^{\circ}_{II} = \Delta G^{\circ}_{III} \quad \text{at} \quad T_{b,Mg} = 1372\ K$$

12.14 200 grams of liquid zinc are placed in a crucible at 1030 K. Two moles of air are bubbled through the liquid zinc and the gas comes to equilibrium with the liquid before leaving the system. If the total pressure of the gas remains constant at 0.8 atm throughout the process, how many grams of *metallic* zinc are left in the crucible? The atomic weights of Zn and O are, respectively, 65.38 and 16.

$Zn(v) + \frac{1}{2}O_2(g) = ZnO(s) \quad \Delta G^\circ_{1030} = -256260 \text{ J}$

$\therefore K_{1030} = 9.9 \times 10^{12} = \frac{1}{p_{Zn}\, p_{O_2}^{1/2}}$

$\ln p^\circ_{Zn} \text{(atm)} = -\frac{15250}{T} - 1.255 \ln T + 21.79$

$\therefore$ At 1030 K, $p^\circ_{Zn} = 0.1787$ atm

and $p_{O_2} = \left[\frac{1}{9.9 \times 10^{12} \times 0.1787}\right]^2 = 3.2 \times 10^{-25}$ atm

2 moles air $\rightarrow$ 0.42 moles O_2 + 1.58 moles N_2

0.42 moles O_2 + 0.84 moles Zn $\rightarrow$ 0.84 moles ZnO

and 0.84 moles $\rightarrow 0.84 \times 65.38 = 54.92$ g.

$\therefore$ 54.92 g of Zn are oxidized to ZnO

1.58 moles of N_2 at 1030 K and $P_T = 0.8$ atm

$\therefore p_{N_2} = 0.8 - 0.179 = 0.621$ atm

$p_{N_2} V = n_{N_2} RT \quad \therefore$ Volume of gas, $V = \frac{1.58 \times 0.082057 \times 1030}{0.621}$

$= 215$ l

$p_{Zn} V = n_{Zn} RT \quad \therefore n_{Zn} = \frac{0.179 \times 215}{0.082057 \times 1030} = 0.455$ moles

2.14 CONTINUED.

0.455 moles Zn $\equiv 0.455 \times 65.38 = 29.78$ g Zn

$\therefore$ 29.78 g Zn are evaporated

$\therefore$ Liquid Zn remaining $= 200 - 54.9 - 29.8$

$= 115.3$ g

12.15 Methane gas is burned with twice the amount of stoichiometric air (i.e., the initial ratio of CH_4 to O_2 in the mixture is 0.25) and the combustion gas produced, in which the concentration of methane is negligible, is used to calcine $CaCO_3$ in an isothermal furnace. The gas and the solids are at 1080 K and the pressure of the gas is maintained constant at 1 atm. How many moles of $CaCO_3$ are decomposed per mole of CH_4 burned?

$$CH_4 + 4O_2 + 4\times\frac{79}{21} N_2$$

$$\rightarrow CO_2 + 2H_2O + 2O_2 + 15.05\, N_2 \qquad n_T = 20.05 \text{ moles}$$

In this gas $p_{CO_2} = \dfrac{1}{20.05} = 0.0499$ atm

$$CaO + CO_2 = CaCO_3 \qquad \Delta G^\circ_{1080} = -13124 \text{ J}$$

$$= 8.3144\times 1080 \ln p_{CO_2(eq)}$$

$\therefore$ $p_{CO_2(eq)} = 0.232$. The decomposition of x moles of $CaCO_3$ produces x moles of CO_2 and increases p_{CO_2} from 0.0499 to 0.232.

i.e. $0.232 = \dfrac{1+x}{20.05+x}$ $\quad\therefore x = 4.76$

and thus 4.76 moles of $CaCO_3$ are decomposed per mole of CH_4 burned.

12.16 Mercuric oxide (HgO) is placed in a vessel which is then evacuated, filled with nitrogen and heated to 600 K, at which temperature it is observed that the total pressure in the vessel is 2 at. Calculate the mole fractions of O_2 and Hg vapor in the gas phase.

$$HgO(r) = Hg(v) + \tfrac{1}{2}O_2(g)$$

$$\Delta G^\circ_{600} = 27880 \text{ J}$$

$$\therefore K = 3.74 \times 10^{-3} = p_{Hg} \cdot p_{O_2}^{\frac{1}{2}}$$

$$p_{O_2} = \tfrac{1}{2} p_{Hg} \qquad \therefore \quad 3.74 \times 10^{-3} = p_{Hg}\left[0.5 p_{Hg}\right]^{1/2}$$

$$\therefore p_{Hg} = 0.0304, \quad p_{O_2} = 0.0152, \quad p_{N_2} = 1.994$$

$$\therefore X_{Hg} = \frac{0.0304}{2} = 0.0152$$

$$X_{O_2} = \frac{0.0152}{2} = 0.0071$$

12.17 In Fig. 12.17 the line AB, which represents the equilibrium

$$FeO_{(s)} + CO_{(g)} = Fe_{(s)} + CO_{2(g)}$$

intersects the carbon deposition line at the point A, ($T = 972$ K, $p_{CO} = 0.595$ atm, $p_{CO_2} = 0.405$ atm, $P = 1.000$ atm). At what total pressure does the point of intersection of the lines occur at 1000 K, and what are the values of the partial pressures of CO and CO_2 in this state?

For $FeO + CO = Fe + CO_2$ $\quad \Delta G^\circ = -18700 + 22.46T$

$$= -RT \ln \frac{p_{CO_2}}{p_{CO}}$$

$\therefore$ At the total pressure P_T

$$\frac{2249}{T} - 2.70 = \ln \frac{p_{CO_2}}{p_{CO}} = \ln \frac{(P_T - p_{CO})}{p_{CO}} \quad \text{— (i)}$$

For $C + CO_2 = 2CO$ $\quad \Delta G^\circ = 170700 - 174.5T$

$$= -RT \ln \frac{p^2_{CO}}{p_{CO_2}}$$

$\therefore$ At the total pressure P_T

$$-\frac{20530}{T} + 20.99 = \ln \frac{p^2_{CO}}{P_T - p_{CO}} \quad \text{— (ii)}$$

With $T = 1000K$ Lines (i) and (ii) give

$P_T = 1.651$ and $p_{CO} = 1.009$ atm

$\therefore p_{CO_2} = 0.642$ atm

13.1 Air at atmospheric pressure is blown over a Cu-rich copper-gold liquid solution at 1500 K. If only the copper is oxidized (to form pure solid Cu_2O), calculate the minimum activity of Cu which can be obtained in the solution.

$$2Cu_{(l)} + \frac{1}{2}O_2 = Cu_2O_{(s)}$$

$$\Delta G^\circ = -188300 + 88.48T \text{ J}$$

$$\Delta G^\circ_{1500K} = -55588 \text{ J} = RT \ln a_{Cu}^2 p_{O_2}^{1/2}$$

$$\therefore a_{Cu}^2 (0.21)^{1/2} = 0.0116$$

$$a_{Cu}^2 = 0.025$$

$$a_{Cu} = 0.159$$

13.2 Magnesium can be removed from Mg-Al liquid solution by selectively forming the chloride $MgCl_2$. Calculate the activity of Mg in the liquid Mg-Al system which can be achieved at 800°C by reacting the solution with an H_2-HCl gas mixture containing hydrogen at essentially 1 atm pressure and $p_{HCl} = 10^{-5}$ atm to form pure liquid $MgCl_2$.

$Mg(\ell) + Cl_2 = MgCl_2(\ell)$ $\quad \Delta G^\circ = -603200 + 121.42T$ J

$\Delta G^\circ_{1073} = -472916$ J

$H_2 + Cl_2 = 2HCl(g)$ $\quad \Delta G^\circ = -188200 - 12.80T$ J

$\Delta G^\circ_{1073} = -201933$ J

$\therefore$ $Mg + 2HCl = MgCl_2 + H_2$

$\Delta G^\circ_{1073} = -270983$

$$= RT \ln \frac{a_{Mg} \cdot p_{HCl}^2}{p_{H_2}}$$

$$\frac{a_{Mg}\, p_{HCl}^2}{p_{H_2}} = 6.43 \times 10^{-14} = \frac{a_{Mg} \cdot (10^{-5})^2}{1}$$

$\therefore$ $a_{Mg} = 6.4 \times 10^{-4}$

105

13.3 The partial pressure of oxygen in equilibrium with pure liquid lead and pure liquid lead oxide at 1200 K is 2.16×10^{-9} atm. When SiO_2 is added to the liquid PbO to form a lead silicate melt the oxygen pressure in equilibrium with pure liquid lead and the silicate melt is decreased to 5.41×10^{-10} atm. Calculate the activity of PbO in the lead silicate melt.

For $Pb(l) + \frac{1}{2}O_2 = PbO(l)$

$$K_{1200K} = \frac{a_{PbO}}{a_{Pb}\, p_{O_2}^{1/2}} = \frac{1}{1 \times (2.16 \times 10^{-9})^{1/2}} = 21517$$

with $a_{Pb} = 1$ and $p_{O_2(eq)} = 5.41 \times 10^{-10}$ atm

$$a_{PbO} = 21517 \times (5.41 \times 10^{-10})^{1/2} = 0.5$$

13.4 Copper, present as an impurity in liquid Pb, can be removed by adding PbS to the Cu-Pb alloy and allowing the exchange reaction

$$2Cu_{(s)} + PbS_{(s)} = Cu_2S_{(s)} + Pb_{(l)}$$

to come to equilibrium.

The solid sulfides are mutually immiscible, Pb is insoluble in solid Cu, and the Cu liquidus, below 850°C, can be represented by

$$\log X_{Cu} = -\frac{3500}{T} + 2.261$$

where X_{Cu} is the solubility of Cu in liquid Pb. If Cu obeys Henry's law in liquid Pb, calculate the extent to which Cu can be removed from liquid Pb by this process at 800°C. Would the extent of purification of the lead be increased by increasing or by decreasing the temperature?

$Pb(l) + \frac{1}{2}S_2 = PbS(s)$ $\quad \Delta G^\circ = -163200 + 88.03T$ J

$2Cu(s) + \frac{1}{2}S_2 = Cu_2S(s)$ $\quad \Delta G^\circ = -131800 + 30.79T$ J

$\therefore$ For $2Cu(s) + PbS(s) = Cu_2S(s) + Pb(l)$

$$\Delta G^\circ = 31400 - 57.24T$$

$$\Delta G^\circ_{1073} = -30019 \text{ J} = -RT\ln K$$

$$K = 28.93 = \frac{a_{Pb(l)}}{a^2_{Cu(s)}}$$

At 1073 K, $X_{Cu(liquidus)} = 0.0998$ $\quad \therefore \gamma_{Cu} = \frac{1}{0.0998} = 10.02$

$\therefore a_{Cu} = 10.02 X_{Cu}$ and $a_{Pb} = (1 - X_{Cu})$

$\therefore 28.93 = \frac{1 - X_{Cu}}{100.4 X_{Cu}^2}$ which gives $X_{Cu} = 0.018$

At 850°C $X_{Cu} = 0.024$ $\quad \therefore$ Extent of purification is increased by decreasing the temperature.

13.5 A CH_4-H_2 gas mixture at 1 atm total pressure, in which $p_{H_2} = 0.957$ atm, is equilibrated with an Fe-C alloy at 1000 K. Calculate the activity of C with respect to graphite in the alloy. What would the value of p_{H_2} in the gas mixture (at $P_{\text{total}} = 1$ atm) have to be in order to saturate the Fe with graphite at 1000 K?

$2H_2 + C = CH_4 \qquad \Delta G^\circ = -91040 + 110.7T \text{ J}$

$\Delta G^\circ_{1000} = 19660 \text{ J} = -RT\ln K$

$$\therefore K = 9.40\times10^{-2} = \frac{p_{CH_4}}{a_C\, p_{H_2}^2} = \frac{0.043}{(0.957)^2 a_C} \quad \therefore a_C = 0.5$$

For $a_C = 1$ and $P_T = 1$ atm

$$9.40\times10^{-2} = \frac{p_{CH_4}}{(1-p_{CH_4})^2} \quad \text{which gives}$$

$p_{H_2} = 0.92$ atm

$p_{CH_4} = 0.08$ atm.

13.6 Calculate the activity of FeO in an FeO-Al_2O_3-SiO_2 melt below which the FeO cannot be reduced to pure liquid iron by a CO-CO_2 mixture of $p_{CO}/p_{CO_2} = 10^5$ at 1600°C.

	ΔG°_{1873}, J
FeO(l)	−155557
CO	−275868
CO_2	−395673

∴ For $Fe(l) + CO_2 = FeO(l) + CO$

$$\Delta G^\circ_{1873} = -35753 \text{ J} = -RT\ln K$$

$$\therefore K = 9.93 = \frac{a_{FeO}\cdot p_{CO}}{a_{Fe}\cdot p_{CO_2}} = a_{FeO}\times 10^{5}$$

$$\therefore a_{FeO} = 9.9\times 10^{-5}$$

13.7 A piece of iron is to be heat-treated at 1000 K in a CO-CO_2-H_2O-H_2 gas mixture at 1 atm pressure. The gas mixture is produced by mixing CO_2 and H_2 and allowing the equilibrium $CO_2 + H_2 = CO + H_2O$ to establish. Calculate (i) the minimum H_2/CO_2 ratio in the inlet gas which can be admitted to the furnace without oxidizing the iron, (ii) the activity of carbon (with respect to graphite) in the equilibrated gas of this initial minimum H_2/CO_2 ratio, (iii) the total pressure to which the equilibrated gas would have to be raised to saturate the iron with graphite at 1000 K, and (iv) the effect, on the partial pressure of oxygen in the equilibrated gas, of this increase in total pressure.

(i)

	ΔG°_{1000K}, J
CO	-199350
CO_2	-394940
$H_2O(g)$	-191650
FeO	-199350

$$CO + FeO = CO_2 + Fe \; ; \; \Delta G^{\circ} = 3760 \quad \therefore K = \frac{p_{CO_2}}{p_{CO}} = 0.636$$

$$H_2 + FeO = H_2O + Fe \; ; \; \Delta G^{\circ} = 7700 \quad \therefore K = \frac{p_{H_2O}}{p_{H_2}} = 0.396$$

$$CO_2 + H_2 \rightarrow CO + H_2O \qquad p_{CO} = p_{H_2O}.$$

$$p_{CO} + p_{CO_2} + p_{H_2} + p_{H_2O} = 1 \text{ atm.}$$

$$p_{CO} + 0.636\, p_{CO} + \frac{p_{H_2O}}{0.396} + p_{H_2O} = 1$$

$$\therefore p_{CO}\left[1 + 0.636 + \frac{1}{0.396} + 1\right] = 1$$

$$\therefore \; p_{CO} = 0.1938$$
$$p_{H_2O} = 0.1938$$
$$p_{H_2} = 0.4894$$
$$p_{CO_2} = \underline{0.1233}$$
$$P_T = 1.0003$$

This gas is in equilibrium with Fe and FeO

13.7 continued

mix CO_2 and H_2 in the ratio $\frac{CO_2}{H_2} = x$.

	CO_2 +	H_2 =	CO +	H_2O
before	x	1	0	0
after	$x-a$	$1-a$	a	a

$$\therefore p_{CO} = \frac{a}{1+x}$$

$$p_{H_2O} = \frac{a}{1+x}$$

$$p_{H_2} = \frac{1-a}{1+x}$$

$$p_{CO_2} = \frac{x-a}{1+x}$$

For equilibrium with Fe and FeO: $\frac{p_{CO_2}}{p_{CO}} = 0.636 = \frac{x-a}{a}$

$\frac{p_{H_2O}}{p_{H_2}} = 0.396 = \frac{a}{1-a}$ which gives $a = 0.2837$

and $x = 0.4641 = \frac{CO_2}{H_2}\Big|_{initial}$

For $Fe + \frac{1}{2}O_2 = FeO$ $\Delta G^\circ_{1000} = -199350\ J = \frac{1}{2}RT\ln p_{O_2}$

$\therefore p_{O_2}(Fe/FeO) = 1.494 \times 10^{-21}$ atm.

Choose a larger value of x, say $x = 1$, then

$$CO_2 + H_2 = CO + H_2O \quad \text{——} (i)$$

	CO_2 +	H_2 =	CO +	H_2O
before	1	1	0	0
after	$1-a$	$1-a$	a	a

$\therefore p_{CO} = \frac{a}{2} = p_{H_2O}$; $p_{CO_2} = \frac{1-a}{2} = p_{H_2}$

$$\Delta G^\circ_{(i),1000} = 3940 = -RT\ln\frac{p_{CO}\cdot p_{H_2O}}{p_{CO_2}\,p_{H_2}}$$

$\therefore 0.6226 = \frac{a^2}{(1-a)^2}$ which gives $a = 0.441$

13.7 continued

$$\therefore \quad p_{CO} = 0.2205 \qquad \frac{p_{CO_2}}{p_{CO}} = 1.268$$

$$p_{CO_2} = 0.2795$$

For $CO + \frac{1}{2}O_2 = CO_2$ $\quad K_{1000} = 1.64 \times 10^{-10} = \dfrac{p_{CO_2}}{p_{CO} \cdot p_{O_2}^{1/2}}$

$$= \frac{1.268}{p_{O_2}^{1/2}}$$

which gives $p_{O_2} = 5.93 \times 10^{-21}$ atm, which is greater than p_{O_2}(eq. Fe/FeO) at 1000K.

$\therefore$ 0.4641 is the maximum allowable ratio of $\dfrac{CO_2}{H_2}\Big|_{\text{initial}}$

or 2.155 is the minimum allowable ratio of $\dfrac{H_2}{CO_2}\Big|_{\text{initial}}$

ii) $C + CO_2 = 2CO$ $\quad \Delta G^{\circ}_{1000} = -3760 = -RT \ln \dfrac{p^2_{CO}}{p_{CO_2} a_C}$

$$\therefore \frac{p^2_{CO}}{p_{CO_2} a_C} = 1.572 = \frac{0.1938^2}{0.1233 \cdot a_C} \quad \text{which gives } a_C = 0.194$$

iii) For $a_C = 1$ and pressure P.

$$1.572 = \frac{0.1938^2 P}{0.1233} \quad \text{which gives } P = 5.16 \text{ atm.}$$

iv) The values of the ratios $\dfrac{p_{CO_2}}{p_{CO}}$ and $\dfrac{p_{H_2O}}{p_{H_2}}$ are not functions of the total pressure P.

13.8 An Fe-Mn solid solution containing $X_{Mn} = 0.001$ is in equilibrium with an FeO-MnO solid solution and an oxygen-containing gaseous atmosphere at 1000 K. How many degrees of freedom does the equilibrium have? What is the composition of the equilibrium oxide solution, and what is the partial pressure of oxygen in the gas phase? Assume that both solid solutions are Raoultian in their behavior.

$C = 3$ (Fe, Mn, O) $P = 3$ (metal, oxide, gas)

$\therefore F = C + 2 - P = 3 + 2 - 3 = 2$

Fixing the temperature at 1000K leaves 1 degree of freedom

$$Mn + \tfrac{1}{2}O_2 = MnO \qquad \Delta G^{\circ}_{1000} = -312580\text{ J}$$

$$\therefore K_{Mn} = 2.124 \times 10^{16} = \frac{X_{MnO}}{X_{Mn} \cdot p_{O_2}^{1/2}}$$

$$Fe + \tfrac{1}{2}O_2 = FeO \qquad \Delta G^{\circ}_{1000} = -199350\text{ J}$$

$$K_{Fe} = 2.587 \times 10^{10} = \frac{X_{FeO}}{X_{Fe} \cdot p_{O_2}^{1/2}}$$

$$\frac{K_{Mn}}{K_{Fe}} = 821215 = \frac{X_{MnO}\, X_{Fe}}{X_{Mn}\, X_{FeO}} = \frac{(1 - X_{FeO})\, 0.999}{0.001 \quad X_{FeO}}$$ which

gives $X_{FeO} = 1.22 \times 10^{-3}$

Then $K_{Fe} = 2.587 \times 10^{10} = \dfrac{1.22 \times 10^{-3}}{0.999\, p_{O_2}^{1/2}}$

gives $p_{O_2} = 2.23 \times 10^{-27}$ atm.

13.9 The elements A and B, which are both solid at 1000°C, form two stoichiometric compounds A_2B and AB_2, which are also both solid at 1000°C. The system A-B does not contain any solid solutions. A has an immeasurably small vapor pressure at 1000°C, and, for the change of state, $B_{(s)} = B_{(v)}$

$$\Delta G^\circ = 187220 - 108.8T \text{ J}$$

The vapor pressure exerted by an equilibrated AB_2-A_2B mixture is given by

$$\log p(\text{atm}) = -\frac{11242}{T} + 6.53$$

and the vapor pressure exerted by an equilibrated A-A_2B mixture is given by

$$\log p(\text{atm}) = -\frac{12603}{T} + 6.9$$

From these data, calculate the standard Gibbs free energies of formation of A_2B and AB_2.

a_B in $A_2B - AB_2$ mixture $= \frac{5\times10^{-3}}{10^{-2}} = 0.5$

$\therefore ab = RT\ln a_B = -7336$ J

a_B in $A - A_2B$ mixture $= \frac{10^{-3}}{10^{-2}} = 0.1$

$\therefore ac = RT\ln a_B = -24371$ J

$\therefore ed = \frac{-24371}{3} = -8123$ J

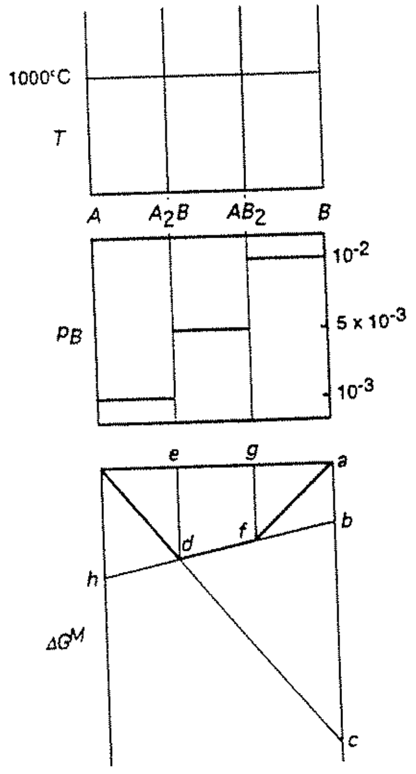
$\therefore$ For $2A + B = A_2B$

$\Delta G^\circ = 3\times ed = -24370$ J

$gf = \frac{ed+ab}{2} = -7730$

For $A + 2B = AB_2$

$\Delta G^\circ = 3\times gf = -23190$ J



13.10 For the change of standard state $V_{(s)} = V_{(1\text{ wt\% in Fe})}$

$$\Delta G^\circ = -15480 - 45.61T \text{ J}$$

Calculate the value of γ°_V at 1600°C. If a liquid Fe-V solution is equilibrated with pure solid VO and a gas containing $p_{O_2} = 4.72 \times 10^{-10}$ atm, calculate the activity of V in the liquid solution (a) with respect to solid V as the standard state, (b) with respect to liquid V as the standard state, (c) with respect to the henrian standard state and (d) with respect to the 1 wt% in iron standard state.

$V(s) \rightarrow V(1wt\%)$ $\quad \Delta G^\circ_{1873} = RT\ln\frac{\gamma^\circ_V\, 55.85}{100\times 50.94}$ $\quad \therefore \gamma^\circ_V = 0.14$

$V(s) + \frac{1}{2}O_2 = VO(s)$ $\quad \Delta G^\circ_{1873} = -274785 = -RT\ln\frac{1}{a_{V(s)}[4.72\times10^{-10}]^{1/2}}$

$\therefore a_{V(s)} = 10^{-3}$

$V(s) \rightarrow V(\ell)$ $\quad \Delta G^\circ = 22840 - \frac{22840}{2193}1873 = 3333 J$

$\therefore V(\ell) + \frac{1}{2}O_2 = VO(s)$ $\quad \Delta G^\circ_{1873} = -274785 - 3333 = -278118 J$

$= -RT\ln\frac{1}{a_{V(\ell)}[4.72\times10^{-10}]^{1/2}}$ $\quad \therefore a_{V(\ell)} = 8.07\times10^{-4}$

$a_{V(s)} = h_V.\gamma^\circ_V$ $\quad \therefore h_V = \frac{10^{-3}}{0.14} = 7.13\times10^{-3}$

$\frac{h_V(1\%)}{h_V} = \frac{50.95\times100}{55.85} = 91.24$

$\therefore h_V(1\%) = 91.24\times7.13\times10^{-3} = 0.65$

13.11 When an Fe-P liquid solution is equilibrated at 1900 K with solid CaO, solid $3CaO.P_2O_5$ and a gas phase containing $p_{O_2} = 10^{-10}$ atm, the activity of P in the iron, with respect to the 1 wt% in Fe standard state, is 20. Given that $\Delta G^\circ_{1900K} = -564600$ J for

$$3CaO_{(s)} + P_2O_{5(g)} = 3CaO.P_2O_{5(s)}$$

and $\Delta G^\circ = -122200 - 19.22T$ J for

$$\tfrac{1}{2}P_{2(g)} = P_{(1\text{ wt\% in Fe})}$$

calculate ΔG°_{1900K} for the reaction

$$P_{2(g)} + \frac{5}{2}O_{2(g)} = P_2O_{5(g)}$$

$3CaO(s) + P_2O_5(g) = 3CaO.P_2O_5(s) \qquad \Delta G^\circ_{1900} = -564600$ J

$\therefore K = 3.325\times10^{15} = \dfrac{1}{p_{P_2O_5}} \qquad \therefore p_{P_2O_5} = 3\times10^{-16}$ atm.

$\frac{1}{2}P_2(g) = P_{(1wt\%)} \qquad \Delta G^\circ = -158680$ J

$\therefore K = 2.303\times10^{4} = \dfrac{h_{P(1\%)}}{p_{P_2}^{1/2}} = \dfrac{20}{p_{P_2}^{1/2}} \qquad \therefore p_{P_2} = 7.539\times10^{-7}$ atm

$\therefore$ For $P_2(g) + \frac{5}{2}O_2 = P_2O_5(g)$

$$K = \frac{3\times10^{-16}}{7539\times10^{-7}\times[10^{-10}]^{5/2}} = 3.99\times10^{15}$$

$\therefore \Delta G^\circ = -RT\ln K = -567500$ J.

13.12 Liquid iron, contained in an Al_2O_3 crucible under a gaseous atmosphere of $p_{O_2} = 3 \times 10^{-12}$ atm at 1600°C, contains its equilibrium contents of dissolved oxygen and aluminum. To what value must the p_{O_2} be raised in order that solid hercynite. ($FeO.Al_2O_3$) appears in equilibrium with the melt and with solid Al_2O_3? What is the activity of Al (with respect to the 1 wt% in Fe standard state) in this state? How many degrees of freedom does this equilibrium have at 1600°C? Given

$$\tfrac{1}{2}O_{2(g)} = O_{(1\text{ wt\% in Fe})} \qquad \Delta G^{\circ} = -111070 - 5.87\,T \text{ J}$$

$$Al_{(l)} = Al_{(1\text{ wt\% in Fe})} \qquad \Delta G^{\circ} = -43100 - 32.26\,T \text{ J}$$

$$FeO.Al_2O_{3(s)} = Fe_{(l)} + O_{(1\text{ wt\% inFe})} + Al_2O_{3(s)} \qquad \Delta G^{\circ} = 146230 - 54.35T \text{ J}$$

$$Al(1wt\%) = Al(l) \qquad \Delta G^{\circ}_{1873} = 103523 \text{ J}$$

$$O(1wt\%) = \tfrac{1}{2}O_2(g) \qquad \Delta G^{\circ}_{1873} = 122064 \text{ J} \quad \text{—— (i)}$$

$$2Al(l) + \tfrac{3}{2}O_2 = Al_2O_3(s) \qquad \Delta G^{\circ}_{1873} = -1075103 \text{ J}$$

$$\therefore\ 2Al_{(1wt\%)} + 3O_{(1wt\%)} = Al_2O_3(s) \qquad \Delta G^{\circ}_{1873} = -501865 \text{ J}$$

$$= 8.3144 \times 1873 \times 2.303 \log [O]^3[Al]^2$$

$\therefore$ For saturation with Al_2O_3 $\quad 2\log[Al] + 3\log[O] = -14$ —(ii)

$$FeO.Al_2O_3 = Fe(l) + O(1wt\%) + Al_2O_3 \ , \quad \Delta G^{\circ}_{1873} = 44432 \text{ J} = -RT\ln[O]$$

$$\therefore [O] = 5.77 \times 10^{-2} \text{ wt\%}$$

From (i) $\quad 122064 = -RT\ln \dfrac{p_{O_2}^{1/2}}{[O]} \quad \therefore \dfrac{p_{O_2}^{1/2}}{[O]} = 3.944 \times 10^{-4}$

$$\therefore p_{O_2} = 5.17 \times 10^{-10} \text{ atm}$$

and, from (ii) $\quad [Al] = 7.215 \times 10^{-6}$ wt%

$C = 3$ (Al, Fe, O) ; $P = 4$ (metal, Al_2O_3, $FeO.Al_2O_3$, gas)

$\therefore F = C + 2 - P = 1$ which is specified by selecting $T = 1600°C$

13.13 UC_2 can be equilibrated with UC and C at high temperature and can be equilibrated with U_2C_3 and C at lower temperatures. Calculate the maximum and minimum temperatures at which UC_2 can exist.

$U + C = UC \quad \Delta G^\circ = -102900 + 5.02T$ J

$2U + 3C = U_2C_3 \quad \Delta G^\circ = -236800 + 25.1T$ J

$U + 2C = UC_2 \quad \Delta G^\circ = -115900 + 10.9T$ J

$\therefore UC + C = UC_2 \quad \Delta G^\circ = -13000 + 5.88T$

$= 0$ at $T = 2211$ K

At $T > 2211$ UC_2 metastable w.r.t $UC + C$

$U_2C_3 + C = 2UC_2 \quad \Delta G^\circ = 5000 - 3.3T$

$= 0$ at $T = 1515$ K

$\therefore$ At $T < 1515$ K. UC_2 metastable w.r.t. $U_2C_3 + C$

$\therefore T_{max} = 2211$ K

$T_{min} = 1515$ K

13.14 In the Pigeon process for the production of magnesium, dolomite (CaO.MgO) is reduced by silicon to form magnesium vapor and $2CaO.SiO_2$. Calculate the equilibrium pressure of magnesium vapor produced by this reaction at 1200°C. The Gibbs free energy of formation of dolomite from CaO and MgO is small enough that it can be ignored.

$$2MgO + 2CaO + Si \rightarrow 2Mg(v) + 2CaO.SiO_2 \qquad (i)$$

$$2CaO + SiO_2 = 2CaO.SiO_2 \qquad \Delta G^\circ_{1473} = -135445 \text{ J}$$

$$2MgO = O_2 + 2Mg(v) \qquad \Delta G^\circ_{1473} = 858216 \text{ J}$$

$$Si + O_2 = SiO_2 \qquad \Delta G^\circ_{1473} = -650798 \text{ J}$$

$$\therefore \Delta G^\circ_{(i)} = 71973 \text{ J} = -RT \ln p^2_{Mg}$$

$$\therefore p_{Mg} = 0.053 \text{ atm}$$

13.15 What is the minimum value that the activity of MgO can have in $MgO.Al_2O_3$ at 1000°C?

For $MgO + Al_2O_3 = MgO.Al_2O_3$

$$\Delta G^\circ_{1273} = -38220 = -RT\ln \frac{a_{MgO.Al_2O_3}}{a_{MgO}\cdot a_{Al_2O_3}}$$

The minimum activity of MgO in $MgO.Al_2O_3$ occurs when it is saturated with Al_2O_3 at $a_{Al_2O_3} = 1$.

$\therefore$ With $a_{MgO.Al_2O_3} = a_{Al_2O_3} = 1$

$$a_{MgO} = 0.027$$

13.16 A mixture of ZnO and graphite is placed in an evacuated vessel and heated to 1200 K. Calculate the partial pressures of Zn, CO and CO_2 that are developed.

For $ZnO + C = Zn(v) + CO$

$$\Delta G^\circ_{1200} = 5720\ J = -RT\ln p_{Zn}\cdot p_{CO}$$

$$\therefore\ p_{Zn}p_{CO} = 0.564$$

For $2ZnO + C = 2Zn(v) + CO_2$

$$\Delta G^\circ_{1200} = 50092\ J = -RT\ln p^2_{Zn}\cdot p_{CO_2}$$

$$\therefore\ p^2_{Zn}p_{CO_2} = 6.60\times 10^{-3}$$

In the gas phase

$$\frac{n_{Zn}}{n_O} = 1 = \frac{p_{Zn}}{p_{CO}+p_{CO_2}} \quad \therefore\ p_{Zn} = p_{CO} + 2p_{CO_2}$$

$$\therefore\ p_{CO}(p_{CO} + 2p_{CO_2}) = 0.564$$

$$p_{CO_2}(p_{CO} + 2p_{CO_2})^2 = 6.60\times 10^{-3}$$

which gives
$p_{CO} = 0.740$ atm
$p_{CO_2} = 0.0114$ atm
$p_{Zn} = 0.763$ atm

13.17 An assemblage of solid CaO, MgO, $3CaO.Al_2O_3$ and liquid Al exerts an equilibrium vapor pressure of Mg of 0.035 atm at 1300 K. Write the equation for the appropriate reaction equilibrium. Calculate the standard Gibbs free energy of formation of $3CaO.Al_2O_3$ from CaO and Al_2O_3 and the activity of Al_2O_3 in CaO-saturated $3CaO.Al_2O_3$ at 1300 K.

The equilibrium is

$$3CaO + 2Al(l) + 3MgO = 3Mg(v) + 3CaO.Al_2O_3$$

for which $K = p_{Mg}^3 = 0.035^3 = 4.288 \times 10^{-5}$

$$\therefore \Delta G^\circ_{1300} = -8.3144 \times 1300 \ln 4.288 \times 10^{-5} \text{ J}$$

$$= 108700 \text{ J}$$

	ΔG°_{1300}, J
$3CaO + 2Al(l) + 3MgO = 3Mg(v) + 3CaO.Al_2O_3$	108700
$Al_2O_3 = \frac{3}{2}O_2 + 2Al(l)$	1262360
$3Mg(v) + \frac{3}{2}O_2 = 3MgO$	−1393200

$\therefore$ For $3CaO + Al_2O_3 = 3CaO.Al_2O_3$ $\qquad \Delta G^\circ_{1300} = -22140$ J

$\therefore$ with $a_{CaO.Al_2O_3} = a_{CaO} = 1$

$$-22140 = -RT \ln \frac{1}{a_{Al_2O_3}}$$

and $a_{Al_2O_3} = 0.129$

13.18 An iron-carbon melt containing 0.5 wt% C is prepared in an alumina crucible under an atmosphere of $p_{CO} = 1$ atm at 1600°C. Calculate the equilibrium concentrations of O and Al in the melt (i) ignoring all solute-solute interactions and (ii) considering the solute-solute interactions. The interaction coefficients are listed in Table 13.1.

(i) $2Al(l) + \frac{3}{2}O_2 = Al_2O_3$ ΔG°_{1873}, J: -1075103

$2[Al] = 2Al(l)$ $+267045$

$3[O] = \frac{3}{2}O_2$ $+366193$

∴ $2[Al] + 3[O] = Al_2O_3$ $\Delta G^\circ_{1873} = -501864$ J

$$= RT\ln[\%Al]^2[\%O]^3$$

∴ $2\log[\%Al] + 3\log[\%O] = -13.996$ — (i)

$C + \frac{1}{2}O_2 = CO$ ΔG°_{1873}, J: -275868

$[O] = \frac{1}{2}O_2$ $+122064$

$[C] = C_{gr.}$ $+56552$

$[C] + [O] = CO$ $\Delta G^\circ = -97250$

$$= -RT\ln\frac{p_{CO}}{[\%C][\%O]}$$

with $p_{CO} = 1$ atm, $\log[\%C] + \log[\%O] = -2.716$ — (ii)

∴ $\log[\%O] = -2.716 - \log 0.5 = -2.414$

and $[\%O] = 0.00385$

$$\log[\%Al] = \frac{-13.996 - 3(-2.414)}{2} = -3.377$$

and $[\%Al] = 0.00042$

(ii)

Eq (i) becomes $2\log[h_{Al}] + 3\log[h_O] = -13.996$

Eq (ii) becomes $2\log[h_C] + \log[h_O] = -2.716$

$$\log f_C = e_C^C[C] + e_C^O[O] + e_C^{Al}[Al]$$

$$\log f_O = e_O^O[O] + e_O^C[C] + e_O^{Al}[Al]$$

$$\log f_{Al} = e_{Al}^{Al}[Al] + e_{Al}^C[C] + e_{Al}^O[O]$$

where $e_C^C = 22\times 10^{-2}$ $e_O^O = -20\times 10^{-2}$ $e_{Al}^{Al} = 4.8\times 10^{-2}$

$e_C^O = -9.7\times 10^{-2}$ $e_O^C = -13.\times 10^{-2}$ $e_{Al}^C = 11\times 10^{-2}$

$e_C^{Al} = 4.8\times 10^{-2}$ $e_O^{Al} = -94\times 10^{-2}$ $e_{Al}^O = -160\times 10^{-2}$

$$\therefore\ 2[\log f_{Al} + \log[Al]] + 3[\log f_O + \log[O]] = -13.996$$

or
$$2\{e_{Al}^{Al}[Al] + e_{Al}^C[C] + e_{Al}^O[O] + \log[Al]\}$$
$$+ 3\{e_O^O[O] + e_O^C[C] + e_O^{Al}[Al] + \log[O]\} = -13.996$$

$$\log f_C + \log[C] + \log f_O + \log[O] = -2.712$$

or
$$e_C^C[C] + e_C^O[O] + e_C^{Al}[Al] + \log[C]$$
$$+ e_O^O[O] + e_O^C[C] + e_O^{Al}[Al] + \log[O] = -2.712$$

13.18 continued

$$\therefore 2\{4.8\times10^{-2}[Al] + 11\times10^{-2}[C] - 160\times10^{-2}[O] + \log[Al]\}$$

$$+ 3\{-20\times10^{-2}[O] - 13\times10^{-2}[C] - 94\times10^{-2}[Al] + \log[O]\}$$

$$= -13.996$$

and $$22\times10^{-2}[C] - 9.7\times10^{-2}[O] + 4.8\times10^{-2}[Al] + \log[C]$$

$$-20\times10^{-2}[O] - 13\times10^{-2}[C] - 94\times10^{-2}[Al] + \log[O]$$

$$= -2.712$$

With $[C] = 0.5$. $\quad$ $\%Al = 0.000541$

$\%O = 0.00351$

13.19 It is required that PbO be eliminated from an ore containing PbO, PbS and $PbSO_4$ by converting it to PbS or $PbSO_4$ by reaction with an SO_2-O_2 gas. Although the pressure of O_2 in the gas can vary within wide limits, the partial pressure of SO_2 may not be higher than 0.5 atm. Calculate the maximum temperature at which it can be guaranteed that the PbO phase will be eliminated.

For $PbO(s) + SO_2 + \frac{1}{2}O_2 = PbSO_4(s)$

$$\Delta G^\circ = -401200 + 261.5T = RT \ln p_{SO_2} \cdot p_{O_2}^{1/2}$$

$$\therefore -\frac{48253}{T} + 31.45 = \ln p_{SO_2} + \frac{1}{2}\ln p_{O_2} \quad \text{— (i)}$$

For $PbO(s) + SO_2 = PbS(s) + \frac{3}{2}O_2$

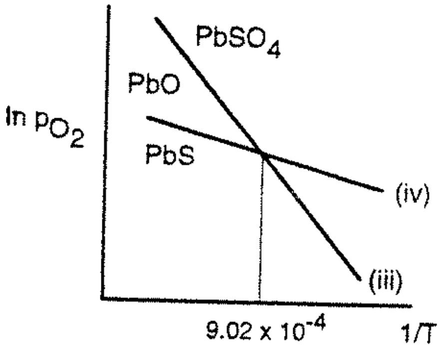
$$\Delta G^\circ = 407200 - 80.6T = -RT \ln \frac{p_{O_2}^{3/2}}{p_{SO_2}}$$

$$\therefore -\frac{48975}{T} + 9.69 = \frac{3}{2}\ln p_{O_2} - \ln p_{SO_2} \quad \text{— (ii)}$$

With $p_{SO_2} = 0.5$ atm. (i) becomes

$$\ln p_{O_2} = -\frac{96506}{T} + 63.59 \quad \text{—— (iii)}$$

and (ii) becomes $\ln p_{O_2} = -\frac{32650}{T} + 5.998$ — (iv)



(iii) and (iv) intersect at $\frac{1}{T} = 9.02 \times 10^{-4}$

$\ln p_{O_2} = -23.46$

∴ PbO is not stable at $T > 1108$ K which is thus the maximum temperature at which it is eliminated.

13.20 Cementite, Fe_3C, is metastable with respect to carbon-saturated α-iron and graphite at 950 K and 1 atm pressure. Given that the molar volumes of α-Fe, graphite and Fe_3C at 950 K are, respectively, 7.32, 5.40 and 23.92 cm^3/mole, calculate the pressure, at 950 K, at which Fe_3C is in equilibrium with carbon-saturated α-Fe and graphite.

$$3Fe(\alpha) + C = Fe_3C \qquad \Delta G^\circ_{950} = 2411$$

$V_{Fe} = 7.32\ cm^3/mole$

$V_{gr} = 5.40\ cm^3/mole$

$V_{Fe_3C} = 23.92\ cm^3/mole$

$\therefore\ \Delta V = 23.92 - 5.40 - 3\times 7.32 = -3.44\ cm^3/mole.$

$\therefore$ Equilibrium occurs at the pressure P at which

$$2411 = 3.44(P-1)\times\frac{8.3144}{82.057}$$

i.e. $P = 6917$ atm

13.21 An experiment is being conducted on an equilibrated mixture of CaO and $CaCO_3$ contained in a closed vessel at 1200 K. The mixture is contaminated by iron in the form of hematite (Fe_2O_3). The contaminant would not be harmful to the experiment if it occurred as either wustite (FeO) or as cementite (Fe_3C). The necessary changes in the chemical form of the contaminant can be effected by admitting CO gas to the vessel. Calculate the allowable limits of p_{CO} in the vessel for the occurrence of the contaminant (*a*) as wustite and (*b*) as cementite.

$CaO + CO_2 = CaCO_3 \quad \Delta G^\circ_{1200} = 3340\ J = RT \ln p_{CO_2}$

$\therefore$ p_{CO_2} inside the vessel is 1.398 atm.

For $3FeO + CO_2 = Fe_3O_4 + CO \quad \Delta G^\circ_{1200} = 4348\ J = -RT \ln \frac{p_{CO}}{p_{CO_2}}$

$\therefore$ For equilibrium between FeO and Fe_3O_4, $\frac{p_{CO}}{p_{CO_2}} = 0.647$

or $p_{CO} = 0.904$ $\therefore$ For FeO to be stable $p_{CO} > 0.904$

For $Fe + CO_2 = FeO + CO \quad \Delta G^\circ = -8252\ J = -RT \ln \frac{p_{CO}}{p_{CO_2}}$

$\therefore \frac{p_{CO}}{p_{CO_2}} = 2.287$ and $p_{CO} = 3.196$ atm

$\therefore$ For FeO to be stable $3.196 > p_{CO} > 0.904$

For $3Fe_\gamma + 2CO = Fe_3C + CO_2 \quad \Delta G^\circ = 36686\ J = -RT \ln \frac{p_{CO_2}}{p^2_{CO}}$

$\therefore \frac{p_{CO_2}}{p^2_{CO}} = 2.53 \times 10^{-2}$ and $p_{CO} = 7.43$ atm

For $C + CO_2 = 2CO \quad \Delta G^\circ_{1200} = -38492 = -RT \ln \frac{p^2_{CO}}{p_{CO_2}} \quad (a_C = 1)$

$\therefore \frac{p^2_{CO}}{p_{CO_2}} = 47.4$ and $p_{CO} = 8.14$

$\therefore$ For Fe_3C to be stable $8.14 > p_{CO} > 7.43$

13.22 A Cu-Au alloy of $X_{Cu} = 0.5$ is being annealed at 600°C in deoxidized argon. The argon is deoxidized by being passed over heated pure copper turnings prior to its admission to the annealing furnace. The solid Cu-Au system is virtually regular in its solution behavior, with a molar Gibbs excess free energy of mixing given by

$$G^{xs} = -28280 X_{Cu} X_{Au} \text{ J}$$

Assuming that equilibrium is attained in the deoxidizing furnace, calculate the maximum temperature at which the deoxidizing furnace can be operated without causing oxidation of the copper in the Cu-Au alloy being annealed.

$2Cu + \frac{1}{2}O_2 = Cu_2O \quad \Delta G^{\circ}_{873} = -101753 \text{ J} = RT\ln p_{O_2}^{1/2} a_{Cu}^{2}$

$\therefore a_{Cu}^{2} \cdot p_{O_2}^{1/2} = 8.162 \times 10^{-7}$

$\Omega = -28280 \text{ J} \quad RT\ln\gamma_{Cu} = \Omega X_{Au}^{2} \quad \therefore \ln\gamma_{Cu} = \frac{-28280 \times 0.5^{2}}{8.3144 \times 873}$

$= -0.974 \quad \therefore \gamma_{Cu} = 0.378, \; a_{Cu} = 0.378 \times 0.5 = 0.1888$ and the oxygen pressure for equilibrium between the Cu-Au alloy and Cu_2O is $p_{O_2} = \left[\frac{8.162 \times 10^{-7}}{0.1888}\right]^{2} = 5.24 \times 10^{-10}$ atm.

For $2Cu + \frac{1}{2}O_2 = Cu_2O$

$\Delta G^{\circ} = -162200 + 69.24T = 8.3144\,T \ln\left[5.24 \times 10^{-10}\right]^{1/2}$

which gives 1026 as the temperature at which 5.24×10^{-10} atm is the oxygen pressure required for equilibrium between Cu and Cu_2O. The maximum temperature at which the deoxidizing furnace can be operated is thus 1026 K

13.23 In a dew-point experiment a Cu-Zn alloy is placed in one end of an evacuated and closed tube, and is heated to 900°C. When the other end of the tube is cooled to 740°C Zn vapor begins to condense. Calculate the activity of Zn in the alloy relative to pure zinc.

At 740°C

$$\ln p^{\circ}_{Zn} = -\frac{15250}{1013} - 1.255 \ln 1013 + 21.79$$

$$\therefore p^{\circ}_{Zn,1013K} = 0.142 \text{ atm}$$

At 900°C

$$\ln p^{\circ}_{Zn} = -\frac{15250}{1173} - 1.255 \ln 1173 + 21.79$$

$$\therefore p^{\circ}_{Zn,1173K} = 0.923 \text{ atm.}$$

$$\therefore a_{Zn} (\text{in the alloy}) = \frac{0.142}{0.923} = 0.154$$

.24 A crucible containing 100.0 g of silver at 1000°C is placed in the reaction chamber of a Sieverts' apparatus. The chamber is evacuated and filled with 50 cms^3 (STP) of argon, which measures the dead volume of the chamber. An external manometer reads the pressure of argon as 0.9 atm. The chamber is re-evacuated and filled with oxygen, and it is found that 251.5 cms^3 (STP) are required to produce a gas pressure of 0.9 atm in the chamber. Calculate the solubility of O in the Ag (as atom percent) and calculate the value of the Sieverts' law constant at 1000°C.

number of moles of Ar required to fill the chamber:

$$n_{Ar} = \frac{50}{82.057 \times 273} = 2.232 \times 10^{-3}$$

number of moles of O_2 required to fill the chamber:

$$n_{O_2} = \frac{251.5}{82.057 \times 273} = 1.123 \times 10^{-2}$$

∴ number of moles of O_2 dissolved in liquid Ag

$$= 1.123 \times 10^{-2} - 2.232 \times 10^{-3} = 8.995 \times 10^{-3}$$

$$= 8.995 \times 10^{-2} \times 32 = 0.288 \text{ grams of oxygen}$$

$$\therefore \text{wt\% oxygen} = \frac{0.288}{0.288 + 100} \times 100 = 0.287$$

$$\text{mole fraction O}, \; X_O = \frac{2 \times 8.995 \times 10^{-3}}{2 \times 8.995 \times 10^{-3} + \frac{100}{107.87}} = 0.0190$$

∴ atom % O = 1.9

$$\text{For } \tfrac{1}{2}O_2(g) = [O] \qquad k = \frac{[O]}{p_{O_2}^{1/2}} = \frac{1.9}{0.9^{1/2}} = 2.0$$

13.25 Silicon and manganese are commonly used together as deoxidizers for liquid steel. At 1600°C,

$$[\mathrm{Mn}]_{(1\ \mathrm{wt\%\ in\ Fe})} + [\mathrm{O}]_{(1\ \mathrm{wt\%\ in\ Fe})} = \mathrm{MnO}_{(s)} \qquad K = 23.5$$

$$[\mathrm{Si}]_{(1\ \mathrm{wt\%\ in\ Fe})} + 2[\mathrm{O}]_{(1\ \mathrm{wt\%\ in\ Fe})} = \mathrm{SiO}_{2(s)} \qquad K = 27840$$

The values of the equilibrium constants show that SiO_2 is considerably more stable than MnO. Why, then, is a mixture of Mn and Si more effective as a deoxidizing agent than Si alone. The activities of MnO and SiO_2, with respect to solids as the standard states in MnO-SiO_2 melts at 1600°C are shown in Fig. 13.37.

Using Si alone produces solid SiO_2 ($a_{SiO_2} = 1$) as the deoxidation product. Thus with 0.01 wt% Si, the oxygen content is

$$[\%O] = \left[\frac{a_{SiO_2}}{K_{Si}[\%Si]}\right]^{1/2} = \left[\frac{1}{27840 \times 0.01}\right]^{1/2} = 0.06$$

Using Si + Mn produces a liquid manganese silicate as the deoxidation product, which, if saturated with MnO gives $a_{SiO_2} = 0.02$. Thus with 0.01 wt% Si

$$[\%O] = \left[\frac{0.02}{27840 \times 0.01}\right]^{1/2} = 0.0085.$$

The Mn content required to saturate with MnO is calculated as

$$[\%Mn] = \frac{a_{MnO}}{K_{Mn}[\%O]} = \frac{1}{23.5 \times 0.0085} = 5.0$$

14.1 The EMF of the galvanic cell

$$Pb_{(s)} \mid PbCl_{2(s)} \mid HCl_{(aqueous)} \mid AgCl_{(s)} \mid Ag_{(s)}$$

where all of the components are present as pure solids in contact with an HCl electrolyte, is 0.490 volts at 25°C and, at that temperature, the temperature coefficient of the EMF is -1.84×10^{-4} volts/degree. Write the cell reaction and calculate the Gibbs free energy change and the change in entropy for the cell reaction at 298 K.

At the anode: $Pb \rightarrow Pb^{2+} + 2e^-$

At the cathode: $Ag^+ + e^- \rightarrow Ag$.

∴ Cell reaction is

$$Pb + 2AgCl = 2Ag + PbCl_2$$

$$\Delta G^\circ = -z\mathcal{F}E^\circ = -2 \times 96487 \times 0.490 = -94560 \text{ J}$$

$$\Delta S^\circ = z\mathcal{F}\frac{dE^\circ}{dT} = 2 \times 96487 \times (-1.84 \times 10^{-4}) = -35.5 \text{ J/k}$$

14.2 At 298 K, the EMF of the cell

$$\mathrm{Pb} \,|\, \mathrm{PbCl_2} \,|\, \mathrm{Hg_2Cl_2} \,|\, \mathrm{Hg}$$

is + 0.5357 volts and the temperature coefficient of the EMF is 1.45×10^{-4} volts/degree. Calculate, (*a*) the maximum work available from the cell at 298 K per mole of Pb reacted, (*b*),the change in entropy for the cell reaction, and (*c*) the heat absorbed by the cell at 298 K per mole of Pb reacted when the cell is operating reversibly.

The Hg electrode in the cell is replaced by an Hg-X alloy in which $X_{\mathrm{Hg}} = 0.3$ and where X is inert. The EMF of the cell at 298 K is found to increase by 0.0089 volts. Calculate the activity of Hg in the alloy at 298 K.

a) $\Delta G^{0} = -z\mathcal{F}\mathcal{E}^{0} = -2 \times 96487 \times 0.5357 = -103401\,J$

b) $\Delta S^{0} = 2 \times 96487 \times 0.5353 = 27.98\ J/K$

c) $q = T\Delta S = 298 \times 27.98 = 8338\ J/\text{mole of Pb}$

$$\mathcal{E} = \mathcal{E}^{0} - \frac{RT}{z\mathcal{F}} \ln a_{Hg}^{2}$$

For the cell reaction $Pb + Hg_2Cl_2 = PbCl_2 + 2Hg$

$$0.0089 = -\frac{8.3144 \times 298}{2 \times 96487} \ln a_{Hg}^{2}$$

$$\therefore a_{Hg} = 0.707$$

14.3 The solid-state electrochemical cell

$$(\text{Pt}),\text{O}_2\ (\text{gas at } p_{\text{O}_2})\,|\,\text{CaO–ZrO}_2\,|\,\text{Fe}\,|\,\text{FeO},(\text{Pt})$$

is built to measure the partial pressure of oxygen in gases. Write and equation relating the oxygen pressure and temperature of the gas to the EMF of the cell.

$$(\text{Pt})\,O_2\,(\text{at } p_{O_2})\,|\,CaO - ZrO_2\,|\,Fe\,|\,FeO,\,(\text{Pt})$$

anode ↙ ↓ cathode

$$O^{2-} = \tfrac{1}{2}O_2(\text{at } p_{O_2}) + 2e^- \qquad FeO + 2e^- \rightarrow Fe + O^{2-}$$

$$\mathcal{E} = -\frac{RT}{2\mathcal{F}} \ln \frac{p_{O_2}(\text{at anode})}{p_{O_2}(\text{eq}, Fe/FeO)}$$

For $Fe + \tfrac{1}{2}O_2 = FeO \qquad \Delta G^\circ = -263700 + 64.35T = \tfrac{1}{2}RT \ln p_{O_2(\text{eq})}$

$$\therefore \mathcal{E} = -\frac{RT}{4\mathcal{F}} \ln p_{O_2}(\text{anode}) + \frac{RT}{4\mathcal{F}} \ln p_{O_2}(\text{eq}, Fe/FeO)$$

$$\downarrow$$

$$\frac{RT}{4\mathcal{F}}\left[-\frac{2\times263700}{RT} + \frac{2\times64.35}{R}\right]$$

$$\therefore \mathcal{E} = 2.154\times10^{-5} \ln p_{O_2} - 1.3665 + 3.334\times10^{-4}\,T$$

$$\text{or } \ln p_{O_2} = \frac{46620\mathcal{E}}{T} + \frac{63440}{T} - 15.48$$

14.4 The EMF of the cell

$$Ag_{(s)} \mid AgCl_{(s)} \mid Cl_{2(g,1\ \mathrm{atm})}, Pt$$

is found to be

$$\mathcal{E}(\text{volts}) = 0.977 + 5.7 \times 10^{-4}(350 - t) - 4.8 \times 10^{-7}(350 - t)^2$$

in the temperature range $t = 100°\mathrm{C}$ to $t = 450°\mathrm{C}$. Calculate the value of Δc_p for the cell reaction.

$$\mathcal{E} = 0.977 + 5.7\times10^{-4}\times350 - 5.7\times10^{-4}t - 4.8\times10^{-7}(350)^2 + 4.8\times10^{-7}\times350\times2t - 4.8\times10^{-7}t^2$$

$$\frac{d\mathcal{E}}{dt} = 0.000906 - 9.6\times10^{-7}t$$

$$\Delta S = z\mathcal{F}\frac{d\mathcal{E}}{dT} = 1\times96487\left[0.000906 - 9.6\times10^{-7}t\right]$$

$$= 87.41 - 0.0926t$$

$$= 87.41 - 0.0926(T - 273) \quad \text{T in Kelvins}$$

$$\frac{d\Delta S}{dT} = \frac{\Delta c_p}{T} \qquad \therefore \Delta c_p = -0.093\ \mathrm{J/K.}$$

14.5 A galvanic cell is set up with electrodes of solid aluminum and solid aluminum-zinc alloy and an electrolyte of molten $AlCl_3$-NaCl. When the mole fraction of Al in the alloy electrode is 0.38, the EMF of the cell is 7.43 millivolts at 380°C, and the temperature coefficient of the EMF is 2.9×10^{-5} volts/degree. Calculate (*a*) the activity of Al in the alloy, (*b*) the partial molar Gibbs free energy of mixing of Al in the alloy and (*c*) the partial molar enthalpy of mixing of Al in the alloy.

$$Al \,\Big|\, \begin{matrix} AlCl_3 \\ -NaCl \end{matrix} \,\Big|\, Al\text{-}Zn$$

cell reaction $Al \rightarrow \underline{Al}$ in Al-Zn.

$$\Delta\bar{G}^M_{Al} = -zFE = -3\times 96487 \times 7.43\times 10^{-3}$$

$$= -2150 \text{ J} = RT\ln a_{Al}$$

$$\therefore a_{Al} = 0.673$$

$$\Delta\bar{S}^M_{Al} = zF\frac{dE}{dT} = 3\times 96487\times 2.9\times 10^{-5} = 8.39 \text{ J/K}$$

$$\Delta\bar{H}^M_{Al} = \Delta\bar{G}^M_{Al} + T\Delta\bar{S}^M_{Al}$$

$$= -2150 + 653\times 8.39$$

$$= 3329 \text{ J}$$

14.6 By measuring the EMF's of cells of the type

$$Ni_{(s)} \,|\, NiO_{(s)} \,|\, CaO\text{–}ZrO_2 \,|\, Cu_{(l)} \text{ containing dissolved oxygen}$$

it has been established that e_O^O in liquid copper at 1363 K is - 0.16 and that the standard Gibbs free energy change for

$$\tfrac{1}{2}O_{2(g)} = [O]_{1\text{ wt\% in Cu}}$$

is $\Delta G^\circ = -74105 + 10.76T$ J. If the EMF of such a cell is 0.222 volts at 1363 K, calculate,

1. The activity of oxygen in the liquid copper cathode with respect to a standard state of oxygen gas at 1 atm pressure
2. The activity of Cu_2O in the cathode metal with respect to Cu-saturated pure solid Cu_2O
3. The weight percentage of oxygen dissolved in the copper cathode
4. The maximum solubility of oxygen in liquid copper at 1363 K

$$Ni(s) \,|\, NiO(s) \,|\, CaO\text{-}ZrO_2 \,|\, Cu(l)\text{-}\underline{O}$$

$$p_{O_2}(low) \qquad\qquad p_{O_2}(high)$$

1) $$\mathcal{E} = 0.222 = -\frac{RT}{4F}\ln\frac{p_{O_2}(low)}{p_{O_2}(high)} \quad \therefore \frac{p_{O_2}(low)}{p_{O_2}(high)} = 5.206\times10^{-4}$$

For $2Ni + O_2 = 2NiO \quad \Delta G^\circ = -471200 + 172T$

$$= -236764 = RT\ln p_{O_2}(low)$$

$\therefore p_{O_2}(low) = 8.44\times10^{-10}$ atm and

$p_{O_2}(high)$ = activity of oxygen rel to $p_{O_2} = 1$ atm

$$= \frac{8.44\times10^{-10}}{5.206\times10^{-4}} = 1.622\times10^{-6}$$

14.6 Continued.

2) For $2Cu(l) + \frac{1}{2}O_2 = Cu_2O(s)$ $\quad \Delta G^\circ = -188300 + 88.48T$ J

$$\therefore \Delta G^\circ_{1363} = -67702 \text{ J} = \frac{1}{2}RT\ln p_{O_2}$$

$$\therefore p_{O_2} = 6.47\times10^{-6} \text{ atm}$$

$$\therefore a_{Cu_2O} = \left[\frac{1.622\times10^{-6}}{6.47\times10^{-6}}\right]^{1/2} = 0.5$$

3) $\frac{1}{2}O_2 = [O]_{(1wt\%)}$ $\quad \Delta G^\circ_{1363} = -59439 = -RT\ln K$

$$\therefore K = 189.6 = \frac{h_O}{p_{O_2}^{1/2}}$$

$$\therefore h_O = 189.6\times(1.622\times10^{-6})^{1/2} = 0.241$$

$$\log h_O = e_O^O[\%O] + \log[\%O]$$

$$\therefore -0.617 = -0.16[\%O] + \log[\%O]$$

which gives $[\%O] = 0.266$

4) h_O (at saturation with O) $= 189.6\times[6.47\times10^{-6}]^{1/2}$

$= 0.482.$

$\therefore \log h_O$ (saturation) $= -0.3167$

$= -0.16[\%O] + \log[\%O]$

$$\therefore [\%O]_{saturation} = 0.602$$

14.7 Calculate the conditions under which an aqueous solution of $[Pb^{2+}] = 1$ mole/liter is in equilibrium with metallic Pb and solid PbO at 298 K. Is any other lead ion present in significant concentration in this solution?

Species	ΔG°_{298K} J
$PbO_{(s)}$	- 189,300
$Pb^{2+}_{(m)}$	- 24,310
$Pb^{4+}_{(m)}$	+ 302,500
$HPbO^{-}_{2(m)}$	- 339,000
$PbO^{2-}_{3(m)}$	- 277,570
$PbO^{4-}_{4(m)}$	- 28,210
$H_2O_{(l)}$	- 237,190

For $PbO + 2H^+ + 2e^- = Pb + H_2O$

$$\Delta G^\circ = -237190 + 189300 = -47890 \text{ J.}$$

$$\therefore \mathcal{E}^\circ = \frac{47890}{2\mathcal{F}} = 0.248$$

$$\therefore \mathcal{E} = 0.248 - \frac{RT}{2\mathcal{F}} \ln \frac{1}{[H^+]^2} = 0.248 + 0.0591 \log [H^+]$$

$$= 0.248 - 0.0591 \, pH$$

For $Pb^{2+} + 2e^- = Pb \quad \Delta G^\circ = 24310 \quad \therefore \mathcal{E}^\circ = \frac{-24310}{2\mathcal{F}} = -0.1$

$$\therefore \mathcal{E} = -0.126 - \frac{RT}{2\mathcal{F}} \ln \frac{1}{[Pb^{2+}]}$$

$$= -0.126 + 0.02957 \log [Pb^{2+}].$$

With $[Pb^{2+}] = 1 \quad \mathcal{E} = -0.126$ volts

and $pH = \frac{0.126 + 0.248}{0.0591} = 6.33$

14.7 continued

For $Pb^{4+} + 2e^- = Pb^{2+}$

$$\Delta G^\circ = -24310 - 302500 = -326810 \quad \therefore \mathcal{E}^\circ = \frac{326810}{2\mathcal{F}} = 1.693$$

$$\therefore \mathcal{E} = 1.693 - \frac{RT}{2\mathcal{F}} \ln \frac{[Pb^{2+}]}{[Pb^{4+}]}$$

$$= 1.693 - 0.02957 \log \frac{[Pb^{2+}]}{[Pb^{4+}]}$$

At $\mathcal{E} = -0.126$, $\frac{[Pb^{2+}]}{[Pb^{4+}]} = 3.27 \times 10^{61}$

and with $[Pb^{2+}] = 1$, $[Pb^{4+}] = 3.05 \times 10^{-62}$

For $3H^+ + HPbO_2^- = Pb^{2+} + 2H_2O$

$$\Delta G^\circ = -159690 = -RT \ln \frac{[Pb^{2+}]}{[HPbO_2^-][H^+]^3}$$

$$\therefore 27.99 = \log \frac{[Pb^{2+}]}{[HPbO_2^-]} + 3pH.$$

$\therefore$ At $pH = 6.33$ and $[Pb^{2+}] = 1$, $[HPbO_2^-] = 10^{-9}$

For $PbO_3^{2-} + 6H^+ + 2e^- = Pb^{2+} + 3H_2O$

$\Delta G^\circ = -458311$ and $\mathcal{E}^\circ = 2.375$

$$\therefore \mathcal{E} = 2.375 - \frac{RT}{2\mathcal{F}} \ln \frac{[Pb^{2+}]}{[PbO_3^{2-}][H^+]^6}$$

$$= 2.375 - 0.02957 \log \frac{[Pb^{2+}]}{[PbO_3^{2-}]} - 0.1774\, pH.$$

At $\mathcal{E} = -0.126$, $pH = 6.33$ and $[Pb^{2+}] = 1$,

$[PbO_3^{2-}] = 2.5 \times 10^{-47}$

For $PbO_4^{4-} + 8H^+ + 2e^- = Pb^{2+} + 4H_2O$

$$\Delta G^\circ = -944860 \text{ J.} \qquad \mathcal{E}^\circ = 4.896$$

$$\mathcal{E} = 4.896 - \frac{RT}{2\mathcal{F}} \ln \frac{[Pb^{2+}]}{[PbO_4^{4-}][H^+]^8}$$

$$\therefore -0.126 = 4.896 - 0.0296 \log \frac{[Pb^{2+}]}{[PbO_4^{4-}]} + 0.236 \times 6.33.$$

With $[Pb^{2+}] = 1$, $[PbO_4^{4-}] = 5.6 \times 10^{-221}$

14.8 Aluminum can be produced by electrolysis of Al_2O_3 dissolved in molten cryolite, $3NaF.AlF_3$. If inert electrodes are used in an electrolysis cell and the cryolite is saturated with Al_2O_3 at 1000°C, what is the decomposition voltage of the Al_2O_3? The Hall-Heroult process for electrolysis of Al_2O_3 uses graphite as the anode material, and the gas which is evolved at the anode is essentially pure CO_2 at 1 atm pressure. Calculate the decomposition voltage of Al_2O_3 in an Al_2O_3-saturated $3NaF.AlF_3$ electrolyte at 1000°C in the Hall-Heroult cell.

For. $2Al(l) + \frac{3}{2}O_2 = Al_2O_3(s)$

$$\Delta G^\circ_{1273} = -1271183 \text{ J}$$

$$\therefore \mathcal{E}^\circ = \frac{1271183}{6\mathcal{F}} = 2.196 \text{ volts.}$$

For. $2Al(l) + \frac{3}{2}CO_2 = Al_2O_3 + \frac{3}{2}C$

$$\Delta G^\circ_{1273} = -678430 \text{ J}$$

$$\therefore \mathcal{E}^\circ = \frac{678430}{6\mathcal{F}} = 1.17 \text{ volts.}$$

14.9 At 298 K the solubility of Cl_2 in H_2, under a partial pressure of $Cl_2 = 1$ atm, is 0.0618 molal. Calculate the standard Gibbs free energy of formation of an aqueous solution of chlorine and calculate the change in the Gibbs free energy to form a solution of chlorine which is 0.01 molal. Ideal solution behavior can be assumed.

For. $\frac{1}{2}Cl_2(g) = [Cl]$ $\quad K = \frac{[Cl]}{p_{Cl_2}^{1/2}} = 0.0618$

$$\Delta G^\circ = -8.3144 \times 298 \times \ln 0.0168 = 6897\ J.$$

For $[Cl]_{1m} \rightarrow [Cl]_{0.01m}$ $\quad \Delta G = RT \ln 0.01$

$$= -11410$$

$\therefore$ For $\frac{1}{2}Cl_2(g) = [Cl]_{0.01m}$

$$\Delta G = 6897 - 11410 = -4513\ J$$

15.1* 2-4 Landau Case

The excess Gibbs free energy as a function of order parameter for a solution is written as:

$$G^{XS} = G_{ord} - G_{dis} = a(T - T_C)\eta^2 + C\eta^4$$

where G_{dis} is the free energy of the disordered phase and a and C are positive constants.

a. Obtain an expression for the excess entropy of the equilibrium ordered phase as a function of temperature.

Solution

$G^{XS} = G_{ord} - G_{dis} = a(T - T_C)\eta^2 + C\eta^4$

First we obtain $\eta_{eq}^2 = -\frac{a(T - T_C)}{2C}$ by setting $\frac{\partial G^{XS}}{\partial \eta} = 0$

and solving for η_{eq}.

$G^{XS} = a(T - T_C)\eta_{eq}^2 + C\eta_{eq}^4 = -\frac{a^2(T - T_C)^2}{4C}$

$\frac{\partial G^{XS}}{\partial T} = -S^{XS} = -\frac{2a^2(T - T_C)}{4C}$

$S^{XS} = \frac{a^2(T - T_C)}{2C}$

(valid only at $T < T_C$)

S^{XS} is negative since it is the excess entropy over and above the disordered entropy!

b. Determine the value of $\Delta C_P = C_P^{ord} - C_p^{dis}$ at the transition temperature T_C.

Solution

$$C_P = T\left(\frac{\partial S}{\partial T}\right)_P$$

Thus, since $S_{ord} - S_{dis} = \dfrac{a^2(T - T_C)}{2C}$

$$\frac{\partial S_{ord}}{\partial T} - \frac{\partial S_{dis}}{\partial T} = \frac{a^2}{2C}$$

$$T_C\frac{\partial S_{ord}}{\partial T} - T_C\frac{\partial S_{dis}}{\partial T} = \frac{T_C a^2}{2C}$$

$$C_P^{ord} - C_P^{dis} = \frac{T_C a^2}{2C} > 0$$

and since $T_C = \dfrac{2C}{a}$: $\quad C_P^{ord} - C_P^{dis} = a$

The heat capacity is of the ordered phase is larger than that of the disordered phase since some thermal energy must be used to disorder the ordered phase on heating. See Figure 15.15.

15.2* 2-4-6 Landau case:

The Gibbs energy as a function of order parameter for a solution is written as:

$$G = a(T - T_C)\eta^2 + C\eta^4 + E\eta^6$$

For this case assume C < 0 and a and E are positive.

a. Find the non-zero value of the order parameter of the solution that has the same Gibbs Energy as that of the disordered solution.

SOLUTION

G^{XS} of the disorderd phase = 0. Thus G of the ordered phase also $= 0$

If equilibrium obtains: $\frac{\partial G}{\partial \eta} = 0$. Thus we have 2 equations to solve:

$$G = a(T - T_C)\eta^2 + C\eta^4 + E\eta^6 = 0$$

$$\frac{\partial G}{\partial \eta} = 0 = 2a(T - T_C)\eta + 4C\eta^3 + 6E\eta^5 = a(T - T_C)\eta^2 + C\eta^4 + E\eta^6$$

solving these two equations:

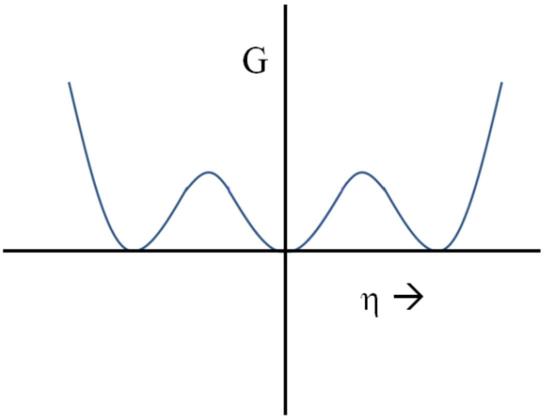
on eliminating E we obtain: $\eta = 0$ and $\eta^2 = -\frac{2a(T - T_C)}{C}$

on eliminating $a(T - T_C)$ we get $\eta = 0$ and $\eta^2 = -\frac{C}{2E}$

Thus: $-\frac{2a(T - T_C)}{C} = -\frac{C}{2E}$ (note for part d that $4AE = C^2$)

$$T = T_C + \frac{C^2}{4aE}$$

b. Sketch the Gibbs Energy vs. η curve for the temperature in question in (a). This temperature can be called T_0.



c. Determine if the transformation for this alloy is first order. Explain.

Solution

Since there are two phases at $T = T_C + \frac{C^2}{4aE}$ with the same Gibbs energy and both are minima, this is a first order transformation. This value of T can be called T_0 in line with the way we have defined T_0 in the text.

d. Calculate the heat of transformation, ΔH_0, for this disorder / order transformation in terms of a, η_0 and T_{tr}, where η_0 is the order parameter at the equilibrium transition temperatureT_{tr}.

Solution

$$\Delta H = T_0 S^{XS}$$

$$\Delta S = S_{ordered} - S_{disordered}$$

$$\left(\frac{\partial G^{XS}}{\partial T}\right)_{T_0} = -\left(S^{XS}\right)_{T_0} =$$

$$G^{XS} = a(T - T_C)\eta_0^2 + C\eta_0^4 + E\eta_0^6$$

$$\left(\frac{\partial G^{XS}}{\partial T}\right)_{T_0} = a\eta_0^2 = -\left(S^{XS}\right)_{T_0}$$

$$\Delta H = -T_0 a\eta_0^2 < 0$$

$$\Delta H = T_0 a\left(\frac{C}{2E}\right) < 0 \quad \text{since C < 0)}$$

e. What is the significance of the sign of ΔH_{tr} for this transformation?

It is an Exothermic transformation

15.3* A 2-4 Landau case:

Using the equation: $G^{XS}(\eta) = a(T - T_0)\eta^2 + C\eta^4$

show that the excess enthalpy for the Landau model with B = 0 and C > 0 is:

$$\Delta H^{XS} = \frac{a}{2}\frac{(T^2 - T_C^2)}{T_C}$$

Solution

From Eq.5.10 that $\eta_{eq}^2 = \frac{T_C - T}{T_C} = 1 - \frac{T}{T_C}$

Inserting $\eta_{eq}^2 = \frac{T_C - T}{T_C}$ and $T_C = \frac{2C}{a}$ into $G^{XS}(\eta) = a(T - T_0)\eta^2 + C\eta^4$

$$G^{XS} = -\frac{a(T_C - T)^2}{2T_C}$$

and $\quad -S^{XS} = \frac{\partial G^{XS}}{\partial T} = \frac{a(T_C - T)}{T_C}$

$$H^{XS} = G^{XS} + TS^{XS} = -\frac{a(T_C - T)^2}{2T_C} - \frac{Ta(T_C - T)}{T_C}$$

$$H^{XS} = -\frac{a(T_C^2 - 2TT_C + T^2)}{2T_C} - \frac{2aTT_C - 2aT^2}{2T_C}$$

$$H^{XS} = \frac{a(T^2 - T_C^2)}{2T_C}$$

It can be seen that

$$\frac{dH^{XS}}{dT} = C_P^{XS} = \frac{aT}{T_C}$$

at $T_C \quad C_P^{XS} = a$

15.4* A solid is held at high temperature until equilibrium is attained. Its surface displays grooves as shown in Fig. 15.19.

a. Write an expression for the relationships between the grain boundary energy of α_1 and α_2.

SOLUTION

See problem 2.12*

$$\gamma_{gb/1-2} = 2\gamma_{\alpha_1/\alpha 2}\cos(\frac{\phi_{12}}{2})$$

b. Which grain boundary has the largest energy: α_1/α_2 or α_2/α_3?

SOLUTION

The one with the smallest groove angle. Hence α_1/α_2

$$\frac{\gamma_{gb/1-2}}{\gamma_{gb/2-3}} = \frac{2\gamma_{\alpha_1/\alpha_2}\cos(\frac{\phi_{12}}{2})}{2\gamma_{\alpha_2/\alpha_2}\cos(\frac{\phi_{23}}{2})}$$

c. If ϕ_{ij} goes to π what is the value of the grain boundary energy?

SOLUTION

$$\gamma_{gb/i-j} = 2\gamma_{\alpha_i/\alpha_j}\cos(\frac{\phi_{ij}}{2}) \rightarrow 0$$

d. If ϕ_{ij} goes to 0 what is the value of the grain boundary energy?

SOLUTION

$$\gamma_{gb/i-j} = 2\gamma_{\alpha_i/\alpha_j}\cos(\frac{\phi_{ij}}{2}) \rightarrow 2\gamma_{\alpha_i/\alpha_j}$$

15.5*. Small cylindrical particles has been observed to nucleate in certain alloys system.

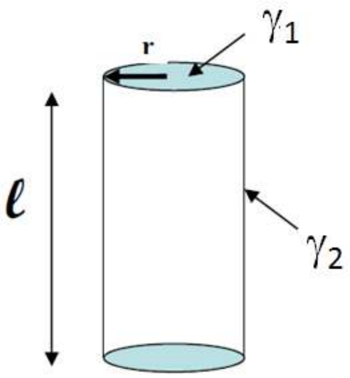
a. What values of r and ***ℓ*** will minimize the energy barrier to the formation of these particles.

b. What surface energies favor the formation of long thin cylinders? Explain

γ_1 is the surface energy of the circular face

γ_2 is the surface energy along the length of the cylinder.

Note: assume the volume of the particle is constant.



$$V=\pi r^2 l=\text{constant}$$

$$\text{S.E.=Surface Energy} = 2\pi r^2\gamma_1 + 2\pi r l\gamma_2$$

$$S.E. = 2\pi r^2\gamma_1 + \frac{V2\pi r\gamma_2}{\pi r^2} = 2\pi r^2\gamma_1 + \frac{V2\gamma_2}{\pi r}$$

$$\frac{d(S.E.)}{dr} = 0 = 4\pi r\gamma_1 - V\frac{2\gamma_2}{\pi r^2}$$

$$\frac{r^*}{l^*} = \frac{1}{\pi}\frac{\gamma_2}{\gamma_1} \quad \text{for small } \gamma_1 \quad \text{large r}$$

Long rod for small γ_2 or large γ_1
Thin disc for large γ_2 or small γ_1

15.6*

Solution

$G = 0\, for\;\; \eta = 0$ (disordered)

for the ordered phase $\text{G} = 0 = a(T - T_C)\eta^2 + E\eta^6$

$$or\;\; \eta^4 = -\frac{a(T - T_C)}{E}$$

$Also$ since in equilibrium: $\dfrac{\partial \text{G}}{\partial \eta} = 0 = 2a(T - T_C)\eta + 6E\eta^5$

$$or\;\; \eta^4 = -\frac{a(T - T_C)}{3E}$$

For both to be true: $\text{T}_0 = T_C$

b. What is the value of the order parameter at T_0?

0: that is, the phase is just beginning to order

c. Is this a first order or higher order phase transition? Explain**.**

Must be a higher order transition

d. Show mathematically that for T < T_C, the disordered phase is unstable.

$$\text{G} = a(T - T_C)\eta^2 + E\eta^6$$

$$\frac{\partial \text{G}}{\partial \eta} = 2a(T - T_C)\eta + 6E\eta^5$$

$$\frac{\partial^2 \text{G}}{\partial \eta^2} = 2a(T - T_C) + 30E\eta^4 = 2a(T - T_C)\, for\;\; \eta = 0$$

Thus $\dfrac{\partial^2 \text{G}}{\partial \eta^2} = 2a(T - T_C) < 0$ for $\text{T} < \text{T}_\text{C}$

Therefore unstable (a maximum)