

Solutions Manual
to accompany

INTRODUCTION TO
THE THERMODYNAMICS OF MATERIALS

Fifth Edition

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INTRODUCTION

This solutions manual provides worked-out answers to all problems appearing in *Introduction to the Thermodynamics of Materials, 5th Edition*, with the exception of the problems in Chapter 5 and two problems from Chapter 9 (9.6 and 9.7), which are included in the answer section in the back of the book.

As well as featuring complete answers to new problems, this solutions manual contains revised answers to problems appearing in the previous edition. All solutions are accurate and comprehensive, making this supplement a useful instructional tool for professors and students.

- 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 $1.5 R$.

$$\text{State 1. } P_1 V_1 = nRT_1 \quad \therefore n = \frac{15 \times 15}{0.08206 \times 300} = 9.14 \text{ mol sr.}$$

$$\text{isothermal expansion to state 2. } P_1 V_1 = P_2 V_2 \quad \therefore V_2 = \frac{15 \times 15}{10} = 22.5 \text{ l}$$

$$T_2 = 300 \text{ K}$$

adiabatic expansion from state 1 to state 3.

$$P_1 V_1^{\delta} = 15 \times 15^{\frac{5}{3}} = P_3 V_3^{\frac{5}{3}} = 10 V_3^{\frac{5}{3}} \quad \therefore V_3 = 19.13 \text{ l}$$

$$T_3 = \frac{P_3 V_3}{nR} = \frac{10 \times 19.13}{9.14 \times 0.08206} = 255 \text{ K.}$$

a) isothermal expansion

$$1) V_2 = 22.5 \text{ l}$$

$$2) W = q = nRT_2 \ln \frac{V_2}{V_1} = 9.14 \times 8.3144 \times 300 \times \ln \frac{22.5}{15} = 9244 \text{ J}$$

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

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

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

b) adiabatic expansion

$$1) V_3 = 19.13 \text{ l}$$

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

$$= 5130 \text{ J}$$

$$3) q = 0$$

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

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

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

- A doubling of its volume at constant pressure,
- then a doubling of its pressure at constant volume,
- 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.

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

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

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

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

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

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

$$2 \rightarrow 3; \quad W = 0 \quad \Delta V = q = \frac{3}{2} \times 8.3144 (1092 - 546) = 6809 \text{ J}$$

$$\begin{aligned} \text{3} \rightarrow 1; \quad W &= \int_3^1 P dV = \int_3^1 (6.643 \times 10^{-4}V^2 + 0.6667) dV \\ &= \frac{6.643 \times 10^{-4}}{3} [V_1^3 - V_3^3] + 0.6667 [V_1 - V_3] \\ &= \frac{6.643 \times 10^{-4}}{3} [22.4^3 - 44.8^3] + 0.6667 [22.4 - 44.8] \\ &= -32.35 \text{ l.atm} = -3278 \text{ J} \end{aligned}$$

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

$$q = \Delta V + w = -10214 - 3278 = -13492 \text{ J}$$

$$W_{\text{TOTAL}} = 2270 - 3278 = -1008 \text{ J}$$

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

- 2.3 The initial state of a quantity of monatomic ideal gas is $P = 1 \text{ atm}$, $V = 1 \text{ liter}$ and $T = 373 \text{ K}$. 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.

$$n = \frac{P_1 V_1}{RT} = \frac{1 \times 1}{0.08206 \times 373} = 0.0327 \text{ moles}$$

$$\text{isothermal expansion: } P_2 = \frac{P_1 V_1}{V_2} = \frac{1}{2} = 0.5 \text{ atm}$$

constant pressure compression to state 3 at which

$$P_1 V_1^{5/3} = P_3 V_3^{5/3} \therefore 1 = 0.5 V_3^{5/3} \quad V_3 = 1.52 \text{ l.}$$

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

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

$$\begin{aligned} 3 \rightarrow 1; \quad W &= -\Delta U = -nC_V(T_1 - T_3) \\ &= -0.0327 \times \frac{3}{2} \times 8.3144 (373 - 282) \\ &= -37.1 \text{ J} \end{aligned}$$

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

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.

$$\begin{aligned}\Delta U &= q - w = 34166 - 1216 \text{ J} \\ &= 32950 \text{ J} \\ &= nC_V(T_2 - T_1) \\ &= 2 \times \frac{3}{2} \times 8.3144 (T_2 - 300) \\ \therefore T_2 &= 1620 \text{ K.}\end{aligned}$$

- 2.5 One mole of N₂ 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 N₂. Assume that nitrogen behaves as an ideal gas, and that the above change of state is conducted reversibly.

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

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

$$\therefore V_2 = 30.61 \text{ l}$$

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

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

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

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

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

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

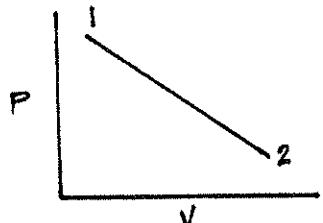
2.6 10 moles of ideal gas, in the initial state $P_1 = 10 \text{ atm}$, $T_1 = 300 \text{ K}$ are taken round the following cycle.

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

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

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

a) $1 \rightarrow 2 \quad P_2 = 1 \quad T_2 = 300 \quad V_2 = 10V_1 = 246.2 \text{ l}$



$w = \text{area below the line}$

$$\begin{aligned} &= \left[\frac{1}{2} [(10-1)(246.2 - 24.6) \right] \\ &\quad + 1(246.2 - 24.6) \left] \times 101.32 \text{ J} \right. \\ &= +123.4 \text{ kJ} \end{aligned}$$

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

$$\begin{aligned} w &= P(V_3 - V_2) = 1(24.6 - 246.2) \times 101.32 \\ &= -22.5 \text{ kJ} \end{aligned}$$

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

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

done by the gas

2.7 One mole of an ideal gas at 25°C and 1 atm undergoes the following reversible 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 pressure 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.

$$T_1 = 298 \quad P_1 = 1 \quad V_1 = 0.08206 \times 298 = 24.45 \text{ L}$$

First cycle:

$$1 \rightarrow 2 \quad T_2 = 298 \quad P_2 = 0.5, \quad V_2 = 2V_1 = 48.90 \text{ L}$$

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

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

$$W = P(V_3 - V_2) = 0.5(61.22 - 48.90) \times 101.32 = 624 \text{ J}$$

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

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

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

Second cycle:

$$1 \rightarrow 2 \quad P_2 = 1, \quad T_2 = 373, \quad V_2 = 0.08206 \times 373 = 30.61 \text{ L}$$

$$W = P(V_2 - V_1) = 1(30.61 - 24.45) \times 101.32 = 624 \text{ J}$$

2.7. continued.

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

$$3 \rightarrow 4. \quad V_f = 24.5 \quad P_f = P$$

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

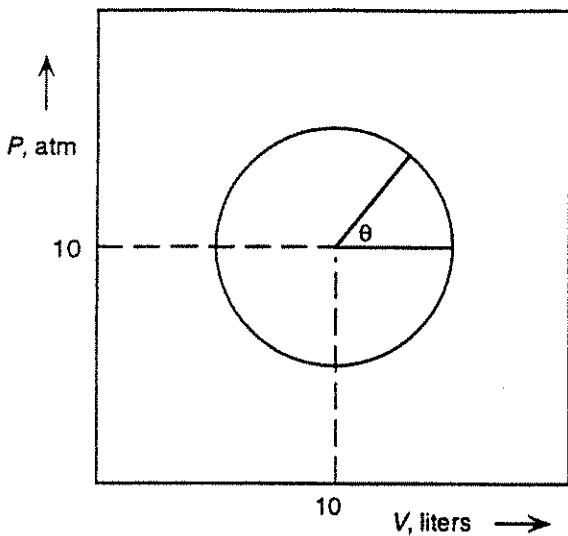
$$4 \rightarrow 1 \quad \Delta V = 0 \quad \therefore W = 0$$

$$\therefore W_{1\text{st cycle}} = -W_{2\text{nd cycle}}$$

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

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

- 2.8 Two moles of an ideal gas, in an initial state $P = 10$ atm, $V = 5$ liters, are taken reversibly in a clockwise direction around a circular path given by $(V-10)^2 + (P-10)^2 = 25$. Calculate the amount of work done by the gas as a result of the process, and calculate the maximum and minimum temperatures attained by the gas during the cycle.



$$\begin{aligned}
 \text{Work done} &= \text{area enclosed by} \\
 &\text{the circle} = \pi \times (\text{diameter})^2 \text{ l.atm} \\
 &= \pi \times 5^2 \times \frac{8.3144}{0.08206} \text{ J} \\
 &= 7958 \text{ J}
 \end{aligned}$$

The pressure of the gas can be expressed as $P = 5\sin\theta + 10$ and the volume as $V = 5\cos\theta + 10$.

$$\text{Thus } PV = nRT = (5\sin\theta + 10)(5\cos\theta + 10) \text{ l.atm}$$

The maximum and minimum temperatures occur at

$$\frac{dT}{d\theta} = \frac{1}{nR} \frac{d(PV)}{d\theta} = 0$$

$$PV = 25\sin\theta\cos\theta + 50\sin\theta + 50\cos\theta$$

$$= \frac{25}{2}\sin 2\theta + 50\sin\theta + 50\cos\theta$$

$$\begin{aligned}
 \therefore \frac{d(PV)}{d\theta} &= 25\cos 2\theta + 5\cos\theta - 50\sin\theta \\
 &= 25(\cos^2\theta - \sin^2\theta) + 50\cos\theta - 50\sin\theta \\
 &= 25\cos\theta(\cos\theta + 2) - 25\sin\theta(\sin\theta + 2)
 \end{aligned}$$

which is zero when $\cos\theta = \sin\theta$, i.e. at

$$\theta = \frac{\pi}{4} \text{ or } \frac{3\pi}{4}$$

L.8 continued.

The extreme temperatures are thus

$$\begin{aligned}T &= \frac{1}{nR} (5 \sin \frac{\pi}{4} + 10)(5 \cos \frac{\pi}{4} + 10) \\&= \frac{1}{2 \times 0.08206} (5 \sin \frac{\pi}{4} + 10)(5 \cos \frac{\pi}{4} + 10) \\&= 1116 \text{ K}\end{aligned}$$

and $T = \frac{1}{nR} (5 \sin \frac{3\pi}{4} + 10)(5 \cos \frac{3\pi}{4} + 10)$

$$= 255 \text{ K}$$

These temperatures occur at the points of intersection of the line $P = V$ with the circle.

- 3.1 The initial state of one mole of a monatomic ideal gas is $P = 10 \text{ atm}$ and $T = 300 \text{ K}$. 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.

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

$$\text{a)} \quad P_2 = 5 \quad T_2 = 300 \quad V_2 = \frac{P_1 V_1}{P_2} = 4.924 \text{ L}$$

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

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

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

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

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

- Starting at 300 K and 10 atm, the gas expands freely into a vacuum to triple its volume.
- The gas is next heated reversibly to 400 K at constant volume.
- The gas is reversibly expanded at constant temperature until its volume is again tripled.
- 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 .

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

$$\text{a) } 1 \rightarrow 2 \quad T_2 = 300, V_2 = 3V_1 = 7.386 \text{ L}, P_2 = \frac{P_1}{3} = 3.33 \text{ atm}$$

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

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

$$\Delta V = 0 \therefore w = 0 \quad \therefore q = \Delta U = C_V(T_3 - T_2) = 1.5 \times 8.3144 \times 100 \\ = 1247 \text{ J.}$$

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

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

$$\text{c) } 3 \rightarrow 4 \quad T_4 = 400, V_4 = 3V_3 = 22.158 \text{ L}, P_4 = \frac{P_3}{3} = 1.48 \text{ atm}$$

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

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

$$\text{d) } 4 \rightarrow 5 \quad T_5 = 300 \text{ K} \quad P_5 = 1.48 \text{ atm} \quad V_5 = \frac{0.08206 \times 300}{1.48} \\ = 16.623 \text{ L}$$

3.2 continued.

$$\Delta U = C_p(T_5 - T_4) = 1.5 \times 8.3144 (300 - 400) = -1247 \text{ J}$$

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

$$W = q - \Delta U = -2078 + 1247 = -831 \text{ J}$$

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

	ΔU	ΔH	W	q	ΔS
$1 \rightarrow 2$	0	0	0	0	9.134
$2 \rightarrow 3$	1247	2078	0	1247	3.588
$3 \rightarrow 4$	0	0	3654	3654	9.134
$4 \rightarrow 5$	-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.

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

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

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

$$\therefore T_2 - T_1 = 300$$

$$\therefore T_2 = 600K \text{ and } T_1 = 300K$$

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

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

- 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

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

$$\begin{aligned}\Delta H &= \int_{T_1}^{T_2} c_p dT \\ &= 50.79 [1273 - 298] + \frac{1.97 \times 10^{-3}}{2} [1273^2 - 298^2] + 4.92 \times 10^6 \left[\frac{1}{1273} - \frac{1}{298} \right] \\ &\quad - \frac{8.20 \times 10^8}{2} \left[\frac{1}{1273^2} - \frac{1}{298^2} \right] \\ &= 49520 + 1509 - 12645 + 4364 \\ &= 42750 \text{ J.}\end{aligned}$$

$$\begin{aligned}\Delta S &= \int_{T_1}^{T_2} \frac{c_p dT}{T} \\ &= 50.79 \ln \frac{1273}{298} + 1.97 \times 10^{-3} (1273 - 298) + \frac{4.92 \times 10^6}{2} \left[\frac{1}{1273^2} - \frac{1}{298^2} \right] \\ &\quad - \frac{8.20 \times 10^8}{3} \left[\frac{1}{1273^3} - \frac{1}{298^3} \right] \\ &= 73.7 + 1.9 - 26.2 + 10.2 \\ &= 59.7 \text{ J/K}\end{aligned}$$

- 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

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

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

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

$$\therefore 22.64(T_f - 273) + 3.14 \times 10^{-3}(T_f^2 - 273^2) + 22.64(T_f - 373) + 3.14 \times 10^{-3}(T_f^2 - 373^2) = 0$$

$$T_f = 323.32 \text{ K } (50.72^{\circ}\text{C})$$

C_p increases with increasing T . $\therefore \Delta T$ caused by withdrawing heat q from hot Cu is less than ΔT caused by adding heat q to cold Cu.

$$323.32$$

$$\Delta S_{\text{cold}} = \int_{273}^{323.32} \frac{C_p dT}{T} = 22.64 \ln \frac{323.32}{273} + 6.28 \times 10^{-3} \int_{273}^{323.32} \frac{dT}{T} \\ = 4.15 \text{ J/K.}$$

$$\Delta S_{\text{hot}} = \int_{373}^{323.32} \frac{C_p dT}{T} = 22.64 \ln \frac{323.32}{373} + 6.28 \times 10^{-3} \int_{373}^{323.32} \frac{dT}{T} \\ = -3.55 \text{ J/K}$$

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

$$\text{Heat transferred} = 22.64(323.32 - 273) + 3.14 \times 10^{-3}(323.32^2 - 273^2) \\ = 1233 \text{ J}$$

- 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

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

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

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

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

$$W = q_2 - q_1 = [-C_2(T_f - T_2)] - [C_1(T_f - T_1)]$$

- 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 $\therefore \Delta S_B = R \ln 2$

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

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 $\therefore \Delta S_B = R \ln 2$

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

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 $\frac{2}{3}$

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

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

- 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 .

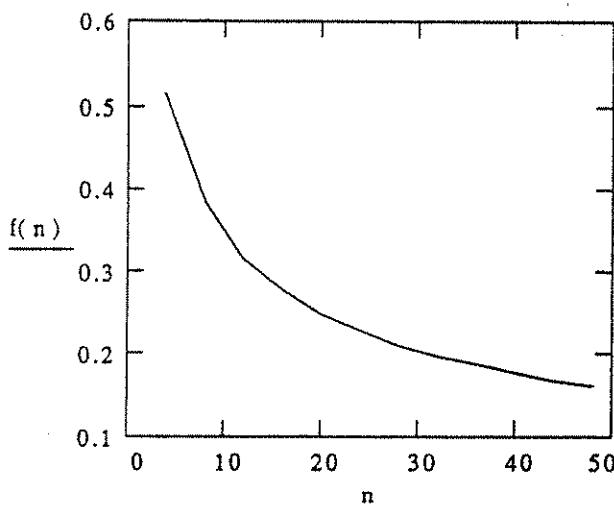
$$\text{Total number of distinguishable complexions} = \frac{(2n)!}{n!n!}$$

With n being a multiple of 4, the number of complexions

$$\text{in the most probable distribution} = \frac{n!}{(\frac{n}{2})!(\frac{n}{2})!} \times \frac{n!}{(\frac{n}{2})!(\frac{n}{2})!}$$

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

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.

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

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

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

$$= k [(n_{Au} + n_{Ag}) \ln (n_{Au} + n_{Ag}) - n_{Au} \ln n_{Au} - n_{Ag} \ln n_{Ag}]$$

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

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

- 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.

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

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

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

$$- n_{\text{Ni}} \ln n_{\text{Ni}} - n_{\text{Cu}} \ln n_{\text{Cu}} \left. \right]$$

$$= 1.2805 \times 10^{-23} \left[(1.026 \times 10^{24} + n_{\text{Cu}}) \ln(1.026 \times 10^{24} + n_{\text{Cu}}) \right.$$

$$- 1.026 \times 10^{24} \ln(1.026 \times 10^{24}) - n_{\text{Cu}} \ln n_{\text{Cu}} \left. \right]$$

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

$$\text{mass of Cu} = \frac{6.161 \times 10^{23}}{6.023 \times 10^{23}} \times 63.55 = 65.09$$

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

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

For $Zr(\alpha) + O_2 = ZrO_2(\alpha)$ in the range $298-1136 \text{ K}$

$$\Delta G_p = 17.69 - 8.28 \times 10^3 T - 12.39 \times 10^5 T^{-2} \text{ J/K}$$

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

For $Zr(\beta) + O_2 = ZrO_2(\alpha)$ in the range $1136-1478 \text{ K}$

$$\Delta G_p = 16.44 - 1.29 \times 10^3 T - 12.39 \times 10^5 T^{-2} \text{ J/K}$$

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

For $Zr(\beta) + O_2 = ZrO_2(\beta)$ in the range $1478-1600 \text{ K}$

$$\Delta G_p = 21.3 - 8.82 \times 10^3 T + 1.67 \times 10^5 T^{-2} \text{ J/K}$$

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

$$= -1100800$$

$$+ 17.69(1136-298) - 4.14 \times 10^3 (1136^2 - 298^2) + 12.39 \times 10^5 \left(\frac{1}{1136} - \frac{1}{298} \right)$$

$$- 3900$$

$$+ 16.44(1478-1136) - 0.645 \times 10^3 (1478^2 - 1136^2) + 12.39 \times 10^5 \left(\frac{1}{1478} - \frac{1}{1136} \right)$$

$$+ 5900$$

$$+ 21.3(1600-1478) - 4.41 \times 10^3 (1600^2 - 1478^2) - 1.67 \times 10^5 \left(\frac{1}{1600} - \frac{1}{1478} \right)$$

$$= -1086000 \text{ J}$$

6.1 continued

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

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

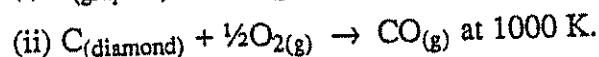
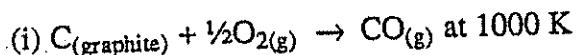
$$+ 17.69 \ln \left(\frac{1136}{298} \right) - 8.28 \times 10^{-3} (1136 - 298) + 6.185 \times 10^5 \left(\frac{1}{1136^2} - \frac{1}{298^2} \right)$$
$$- \frac{3900}{1136}$$

$$+ 16.44 \ln \frac{1478}{1136} - 1.29 \times 10^{-3} (1478 - 1136) + 6.185 \times 10^5 \left(\frac{1}{1478^2} - \frac{1}{1136^2} \right)$$
$$+ \frac{5900}{1478}$$

$$+ 21.7 \ln \frac{1600}{1478} - 8.82 \times 10^{-3} (1600 - 1478) - 0.835 \times 10^5 \left(\frac{1}{1600^2} - \frac{1}{1478^2} \right)$$

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

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



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

$$= 11830 \text{ J}$$

$$H_{diamond, 1000} = 1500 + 9.12(1000 - 298) + \frac{13.22 \times 10^3}{2} (1000^2 - 298^2) \\ + 6.19 \times 10^5 \left(\frac{1}{1000} - \frac{1}{298} \right) \\ = 12867 \text{ J.}$$

For diamond \rightarrow graphite

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

$$\therefore \text{For } C_{(graphite)} + \frac{1}{2}O_2 = CO \quad \Delta H,$$

$$C_{(diamond)} = C_{(graphite)} \quad \Delta H = -1037$$

$$\therefore C_{(diamond)} + \frac{1}{2}O_2 = CO \quad \Delta H, -1037$$

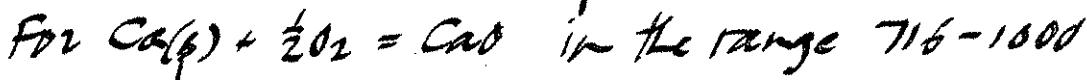
The oxidation of diamond is 1037 J more exothermic than the oxidation of graphite on a molar basis

6.3 Calculate the change in enthalpy and the change in entropy at 1000K for the reaction
 $\text{CaO}_{(s)} + \text{TiO}_{2(s)} = \text{CaTiO}_{3(s)}$



In the range 298-716 K

$$\Delta Cp = 9.42 + 9.68 \times 10^{-3} T - 6.115 \times 10^5 T^{-2}$$



$$\Delta Cp = 35.15 - 38.83 \times 10^{-3} T - 6.115 \times 10^5 T^{-2}$$

$$\Delta H_{1000} = -634900$$

$$+ 9.42(716 - 298) + 4.84 \times 10^{-3} (716^2 - 298^2) + 6.115 \times 10^5 \left(\frac{1}{716} - \frac{1}{298}\right)$$

$$- 900$$

$$+ 35.15(1000 - 716) - 19.415 \times 10^{-3} (1000^2 - 716^2) + 6.115 \times 10^5 \left(\frac{1}{1000} - \frac{1}{716}\right)$$

$$= -636700 \text{ J}$$



In the range 298-1000 K

$$\Delta Cp = 23.14 - 13.47 \times 10^{-3} T - 16.53 \times 10^5 T^{-2}$$

$$\therefore \Delta H_{1000} = -944000$$

$$+ 23.14(1000 - 298) - 6.735 \times 10^{-3} (1000^2 - 298^2) + 16.53 \times 10^5 \left(\frac{1}{1000} - \frac{1}{298}\right)$$

$$= -937800 \text{ J}$$

6.3 continued



In the range 298-716 K

$$\Delta Q = 35.09 - 3.78 \times 10^3 T - 25.485 \times 10^5 T^{-2} \text{ J/K}$$



In the range 716-1000 K, for $\text{Ca}(\gamma) + \text{Ti} + \frac{3}{2}\text{O}_2 = \text{CaTiO}_3$

$$\Delta Q = 60.82 - 52.29 \times 10^3 T - 25.485 \times 10^5 T^{-2} \text{ J/K}$$

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

$$+ 35.09(716 - 298) - 1.69 \times 10^3 (716^2 - 298^2) + 25.485 \times 10^5 \left(\frac{1}{716} - \frac{1}{298}\right)$$

$$- 900$$

$$+ 60.82(1000 - 716) - 26.145 \times 10^3 (1000^2 - 716^2) + 25.485 \times 10^5 \left(\frac{1}{1000} - \frac{1}{298}\right)$$

$$= -1649000 \text{ J}$$



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



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

$$+ 9.42 \ln \left(\frac{716}{298}\right) + 9.68 \times 10^3 (716 - 298) + 3.0525 \times 10^5 \left(\frac{1}{716^2} - \frac{1}{298^2}\right)$$

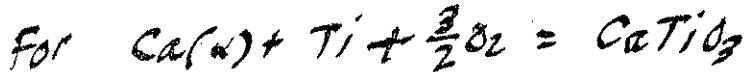
6.3 Continued (2)

$$\begin{aligned}
 & - \frac{900}{716} \\
 & + 35.15 \ln\left(\frac{1000}{716}\right) - 38.83 \times 10^{-3} (1000 - 716) + 3.0525 \times 10^5 \left(\frac{1}{1000^2} - \frac{1}{716^2} \right) \\
 & = - 97.42 \text{ J/K}
 \end{aligned}$$

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

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

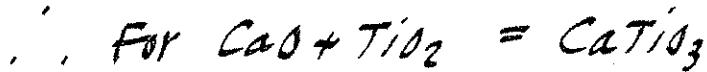
$$\begin{aligned}
 & + 23.14 \ln\left(\frac{1000}{298}\right) - 13.47 \times 10^{-3} (1000 - 298) + 8.265 \times 10^5 \left(\frac{1}{1000^2} - \frac{1}{298^2} \right) \\
 & = - 175.1 \text{ J/K}
 \end{aligned}$$



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

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

$$\begin{aligned}
 & + 35.09 \ln\left(\frac{716}{298}\right) - 3.78 \times 10^{-3} (716 - 298) + 12.743 \times 10^5 \left(\frac{1}{716^2} - \frac{1}{298^2} \right) \\
 & - \frac{900}{716} \\
 & + 60.82 \ln\left(\frac{1000}{716}\right) - 52.29 \times 10^{-3} (1000 - 716) + 12.743 \times 10^5 \left(\frac{1}{1000^2} - \frac{1}{716^2} \right) \\
 & = - 256.9 \text{ J/K}
 \end{aligned}$$



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

- 6.4 Copper exists in the state $T = 298\text{K}$, $P = 1 \text{ atm}$. 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 $0.493 \times 10^{-3} \text{ K}^{-1}$. These values can be taken as being independent of pressure in the range 1 – 1000 atm.

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

$$\begin{aligned}\Delta H &= v(1-\alpha T)(P_2 - P_1) \\ &= 7.09 \times 10^{-3} (1 - 0.493 \times 10^{-3} \times 298)(1000 - 1) \times 101.3 \\ &= 612 \text{ J}\end{aligned}$$

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

$$\begin{aligned}\Delta H &= \int_{T_1}^T C_p dT \\ \therefore \Delta H &= 22.64(T - 298) - \frac{6.28 \times 10^{-3}}{2} (T^2 - 298^2)\end{aligned}$$

$$\therefore T = 327 \text{ K}$$

6.6 An adiabatic vessel contains 1000 g of liquid aluminum at 700°C. Calculate the mass of Cr₂O₃ at room temperature, which, when added to the liquid aluminum (with which it reacts to form Cr and Al₂O₃) raises the temperature of the resulting mixture of Al₂O₃, Cr₂O₃ and Cr to 1600K.

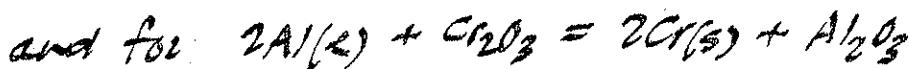


$$\Delta H_{298} = -1675700 + 1134700 = -541000 \text{ J}$$

and in the range 298 - 934 K (T_m, A)

$$\Delta C_p = -5.25 + 3.46 \times 10^3 T - 20.24 \times 10^5 T^{-2} \text{ J/K}$$

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



in the range 973 - 934

$$\Delta C_p = -27.43 + 28.22 \times 10^3 T - 20.24 \times 10^5 T^{-2} \text{ J/K}$$



$$\Delta H_{973} = -541000$$

$$- 5.25(934 - 298) + \frac{3.46 \times 10^3}{2}(934^2 - 298^2)$$

$$+ 20.24 \times 10^5 \left(\frac{1}{934} - \frac{1}{298} \right)$$

$$- 2 \times 10700$$

$$- 27.43(973 - 934) + \frac{28.22 \times 10^3}{2}(973^2 - 934^2)$$

$$+ 20.24 \times 10^5 \left(\frac{1}{973} - \frac{1}{298} \right)$$

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

6.6 continued:

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

$$= 119.37(973 - 298) + \frac{9.3 \times 10^3}{2} (973^2 - 298^2) + 15.65 \times 10^5 \left(\frac{1}{973} - \frac{1}{298}\right)$$

$$= 80920 \text{ J}$$

∴ 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

$$= 119.37(1600 - 973) + \frac{10.98 \times 10^3}{2} (1600^2 - 973^2)$$

$$+ 15.65 \times 10^5 \left(\frac{1}{1600} - \frac{1}{973}\right)$$

$$= 81720 \text{ J}$$

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

$$= 106.6(1600 - 973) + \frac{17.78 \times 10^3}{2} (1600^2 - 973^2)$$

$$+ 28.53 \times 10^5 \left(\frac{1}{1600} - \frac{1}{973}\right)$$

$$= 80030 \text{ J}$$

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

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

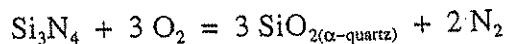
\therefore The reactants are 2 moles of Al + 5.35 moles of Cr_2O_3

or 5.35 \times 152 g Cr_2O_3 per 2 \times 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



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

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

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

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

$$\therefore \Delta H_{800} = -1987900 + 26.99(800 - 298)$$

$$- \frac{99.74 \times 10^3}{2} (800^2 - 298^2) + 13.05 \times 10^5 \left(\frac{1}{800} - \frac{1}{298} \right)$$

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

$$\Delta S_{800} = -220.8 + 26.99 \ln \left(\frac{800}{298} \right)$$

$$- 99.74 \times 10^3 (800 - 298) + \frac{13.05 \times 10^5}{2} \left(\frac{1}{800^2} - \frac{1}{298^2} \right)$$

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

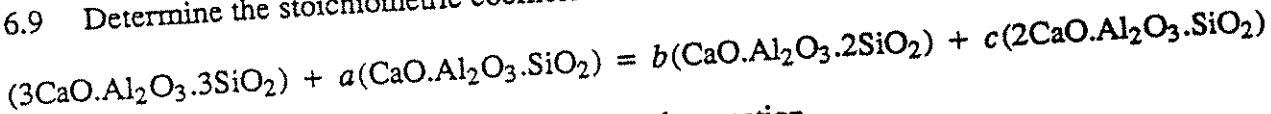
$$\therefore \Delta G_{800} = -2005000 + 800 \times 250.5 = -1,805,000 \text{ J}$$

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



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

Mass balance on

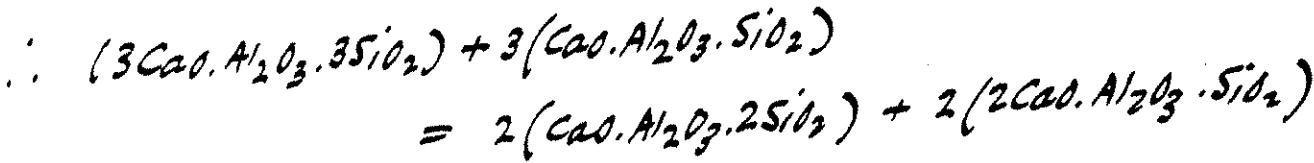
CaO	$3+a = b+2c$
Al_2O_3	$1+a = b+c$
SiO_2	$3+a = 2b+c$

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

$$\left. \begin{array}{l} \downarrow \\ c-3 = -1 \\ \therefore c = 2 \end{array} \right\}$$

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

$$\therefore b=2 \quad \text{and} \quad a = b+2c-3 = 3$$



$$\begin{aligned}\Delta H_{298} &= -2 \times 6646300 - 2 \times 3989400 + 3 \times 3293200 + 6646300 \\ &= 99700 \text{ J}\end{aligned}$$

$$\begin{aligned}\Delta S_{298} &= 2 \times 202.5 + 2 \times 198.3 - 241.4 - 3 \times 144.8 \\ &= 125.8 \text{ J/K}\end{aligned}$$

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

6.10 How much heat is required to increase the temperature of 1 kg of cordierite, $2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$, from 298 K to its incongruent melting temperature of 1738 K?

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

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

∴ Heat required per mole

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

$$= 979799 \text{ J}$$

∴ Heat required for 1 kg

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

7.1 Using the vapor pressure-temperature relationships for $\text{CaF}_2(\alpha)$, $\text{CaF}_2(\beta)$ and liquid CaF_2 , calculate:

1. The temperatures and pressures of the triple points for the equilibria $\text{CaF}_2(\alpha)$ - $\text{CaF}_2(\beta)$ - $\text{CaF}_2(v)$ and $\text{CaF}_2(\beta)$ - $\text{CaF}_2(l)$ - $\text{CaF}_2(v)$,
2. the normal boiling temperature of CaF_2 ,
3. the molar latent heat of the transformation $\text{CaF}_2(\alpha) \rightarrow \text{CaF}_2(\beta)$,
4. the molar latent heat of melting of $\text{CaF}_2(\beta)$.

$$\ln P_{\text{CaF}_2(\alpha)} = \frac{-54350}{T} - 4.525 \ln T + 56.57$$

$$\ln P_{\text{CaF}_2(\beta)} = \frac{-53780}{T} - 4.525 \ln T + 56.08$$

$$\ln P_{\text{CaF}_2(l)} = \frac{-50200}{T} - 4.525 \ln T + 53.96$$

1) At the α - β -vapor triple point

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

$$\therefore T = 1163\text{K} \text{ and } P_{\text{CaF}_2} = 2.52 \times 10^{-10} \text{ atm}$$

At the β -liquid-vapor triple point.

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

$$\therefore T = 1689\text{K} \text{ and } P_{\text{CaF}_2} = 8.35 \times 10^{-5} \text{ atm}$$

2) At T_b , $P_{\text{CaF}_2} = 1 \text{ atm}$

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

which gives $T_b = 2776\text{K}$

7.1 continued

3) For α -vapor equilibrium

$$\ln p_{\text{CAF}_2} = -\frac{54350}{T} - 4.525 \ln T + 56.57$$

$$\frac{d \ln p_{\text{CAF}_2}}{dT} = \frac{54350}{T^2} - \frac{4.525}{T} = \frac{\Delta H(\alpha \rightarrow v)}{RT^2}$$

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

For β -vapor equilibrium

$$\ln p_{\text{CAF}_2} = -\frac{53780}{T} - 4.525 \ln T + 56.08$$

$$\frac{d \ln p_{\text{CAF}_2}}{dT} = \frac{53780}{T^2} - \frac{4.525}{T} = \frac{\Delta H(\beta \rightarrow v)}{RT^2}$$

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

$$\begin{aligned}\Delta H(\alpha \rightarrow \beta) &= \Delta H(\alpha \rightarrow v) - \Delta H(\beta \rightarrow v) \\ &= 8.3144(54350 - 53780) \\ &= 4739 \text{ J.}\end{aligned}$$

4) For ℓ - v equilibrium

$$\ln p_{\text{CAF}_2} = -\frac{50200}{T} - 4.525 \ln T + 53.96$$

$$\frac{d \ln p_{\text{CAF}_2}}{dT} = \frac{50200}{T^2} - \frac{4.525}{T} = \frac{\Delta H(\ell \rightarrow v)}{RT^2}$$

$$\therefore \Delta H(\ell \rightarrow v) = R(50200 - 4.525T)$$

$$\begin{aligned}\Delta H(\beta \rightarrow \ell) &= \Delta H(\beta \rightarrow v) - \Delta H(\ell \rightarrow v) \\ &= 8.3144(53780 - 50200) \\ &= 29765 \text{ J}\end{aligned}$$

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

The saturated vapor pressure of liquid Hg is

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

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

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 $V = \frac{nRT}{P} = \frac{0.082057 \times 350}{1} = 28.72 \text{ L}$ and cooling causes the pressure of the vapor to decrease according to $P = \frac{nR \cdot T}{V} = \frac{0.082057}{28.72} T = 2.857 \times 10^{-3} T$

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

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

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

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

$$\text{is } n = \frac{PV}{RT} = \frac{0.1396 \times 28.72}{0.082057 \times 280} = 0.175$$

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

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

and

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

Which of the two equations is for solid zinc?

$$\text{I} \quad \frac{d \ln p}{dT} = \frac{15780}{T^2} - \frac{0.755}{T} = \frac{\Delta H_I}{RT^2}$$
$$\therefore \Delta H_I = R(15780 - 0.755T)$$

$$\text{II} \quad \frac{d \ln p}{dT} = \frac{15250}{T^2} - \frac{1.255}{T} = \frac{\Delta H_{II}}{RT^2}$$
$$\therefore \Delta H_{II} = R(15250 - 1.255T)$$

$$\text{Now } \Delta H_{S \rightarrow L} > \Delta H_{L \rightarrow g}$$

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

\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 $3.72 \times 10^{-3} \text{ atm/K}$. 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 $P = 1 \text{ atm}$ and $T = 3330 \text{ K}$ is

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

$$\text{Then } \frac{dP}{dT} = \frac{\Delta H_{(l \rightarrow g)}}{T\Delta V_{(l \rightarrow g)}} = \frac{\Delta H_b}{TV_V}$$

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

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

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

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

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 exerted by liquid CO_2 at 25°C and explain why solid CO_2 is referred to as "dry ice".

The triple point pressure is

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

and $\frac{d \ln p}{dT} = \frac{3116}{T^2} = \frac{\Delta H(s \rightarrow l)}{RT^2}$

$$\therefore \Delta H(s \rightarrow l) = 8.3144 \times 3116 = 25907 \text{ J}$$

$$\Delta H(s \rightarrow g) = 8330 \text{ J}$$

$$\therefore \Delta H(l \rightarrow g) = 25907 - 8330 = 17577 \text{ J}$$

For liquid CO_2

$$\ln p_{\text{CO}_2(l)} = -\frac{\Delta H(l \rightarrow g)}{RT} + \text{constant.}$$

At the triple point

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

$$\text{constant} = 11.39$$

\therefore At 298 K

$$\ln p_{\text{CO}_2(l)} = -\frac{17577}{8.3144 \times 298} + 11.39$$

$$p_{\text{CO}_2(l)} = 73.3 \text{ atm}$$

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.

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

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

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

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

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

$$\therefore P_2 - P_1 = \frac{4810}{0.55} \times \frac{82.052}{8.3144} \ln \frac{620}{600}$$

$$= 2821 \text{ atm}$$

\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 $V_\beta - V_\alpha = 0.043$ cm³/mole and $V_\alpha - V_\gamma = 0.165$ cm³/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 $\Delta V = 0.22$ cm³/mole. Sketch the phase diagram for nitrogen at low temperatures.

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

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

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

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

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

$$S_\beta - S_\alpha = 4.59 \text{ J/K}$$

$$S_\alpha - S_\gamma = 1.25 \text{ J/K}$$

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

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

β is stable at high T , γ at low T

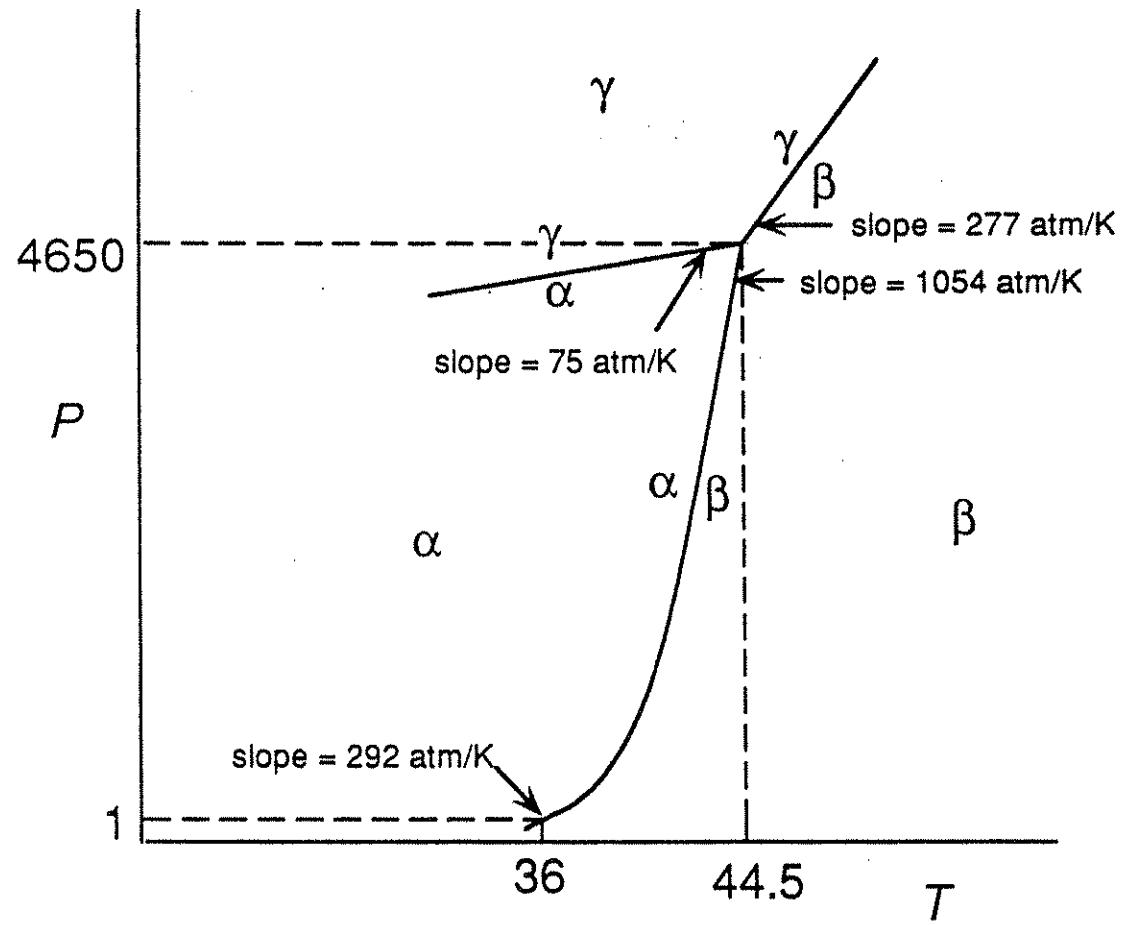
$$\alpha \rightarrow \beta \quad \frac{dP}{dT} = \frac{4.59}{0.043} \times \frac{82.057}{8.3144} = 1053 \text{ atm/K}$$

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

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

At 1 atm and 36K

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



Problem 7.8

- 7.9 Measurements of the saturated vapor pressure of liquid NdCl₅ give 0.3045 atm at 478K and 0.9310 atm at 520K. Calculate the normal boiling temperature of NdCl₅.

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 $B = 12.65$

∴ At $p = 1 \text{ atm}$

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

$$\text{or } T_b = 523 \text{ K}$$

- 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.

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

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

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

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

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

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

$$dU = TdS - PdV$$

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

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

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

- 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
 $P = 1 \text{ atm}$

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

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

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

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

Increasing the pressure from 1 atm to $P \text{ atm}$
increases the free energy by

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

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

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

- 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 $a = 1.36 \text{ l}^2 \cdot \text{atm} \cdot \text{mole}^{-2}$ and $b = 0.0318 \text{ l/mole}$.

$$\text{The volume of the tank is } \pi r^2 h = 3.142 \times 0.1^2 \times 2 \\ = 0.06284 \text{ m}^3 \\ = 62.84 \text{ l}$$

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

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

$$(200 + \frac{1.36n^2}{62.84^2})(62.84 - 0.0318n) = n \cdot 0.08206 \times 300$$

which gives $n = 565 \text{ moles}$.

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 $A = -265 \text{ cm}^3/\text{g.mole}$ and $B = 30250 \text{ cm}^6/\text{g.mole}^2$. 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

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

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

At $P_1 = 50 \text{ atm}$, this gives $V_1 = 394.6 \text{ cm}^3$

and at $P_2 = 100 \text{ atm}$, $V_2 = 176.9 \text{ cm}^3$

$$\begin{aligned}\therefore W &= \int_1^2 P dV = RT \int_1^2 \left[\frac{1}{V} - \frac{265}{V^2} + \frac{30250}{V^3} \right] dV \\ &= RT \left[\ln \frac{V_2}{V_1} + 265 \left[\frac{1}{V_2} - \frac{1}{V_1} \right] - \frac{30250}{2} \left[\frac{1}{V_2^2} - \frac{1}{V_1^2} \right] \right] \\ &= 8.3144 \times 460 \left\{ \ln \frac{176.9}{394.6} + 265 \left(\frac{1}{176.9} - \frac{1}{394.6} \right) - \frac{30250}{2} \left(\frac{1}{176.9^2} - \frac{1}{394.6^2} \right) \right\} \\ &= -1384 \text{ J}\end{aligned}$$

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

- the critical van der Waals constants for the gas
- the critical volume of van der Waals SO_2 ,
- 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.

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

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

$$a = 27b^2 P_{cr} = 27 \times 0.0567^2 \times 77.8 = 6.77 \frac{\text{l.atm}}{\text{mole}^2}$$

$$V_{cr} = 3b = 0.170 \text{ l/mole}$$

$$P(\text{van der Waals}) = \frac{RT}{V-b} - \frac{a}{V^2} = \frac{0.08206 \times 500}{0.5 - 0.0567} - \frac{6.77}{0.5^2} \\ = 65.5 \text{ atm.}$$

$$P(\text{ideal gas}) = \frac{RT}{V} = \frac{0.08206 \times 500}{0.5} = 82.1 \text{ atm}$$

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 $a = 0.2461 \text{ l}^2 \cdot \text{atm mole}^{-2}$ and $b = 0.02668 \text{ l/mole}$, 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.

$$n = 100 \text{ moles}, T = 298K, V_1 = 30 \text{ L}, V_2 = 10 \text{ L}$$

$$PV = nRT(1 + 6.4 \times 10^{-4}P)$$

$$W = \int PdV \quad V = nRT \left[\frac{1}{P} + 6.4 \times 10^{-4} \right]$$

$$dV = nRT d\left(\frac{1}{P}\right) = -RTn \frac{dP}{P^2}$$

$$\therefore W = nRT \ln \frac{P_1}{P_2}$$

$$PV - 6.4 \times 10^{-4} RTPn = nRT \quad \therefore P = \frac{nRT}{V - n6.4 \times 10^{-4}RT}$$

$$\therefore P_1 = \frac{100 \times 0.08206 \times 298}{30 - 100 \times 6.4 \times 10^{-4} \times 0.08206 \times 298} = 86 \text{ atm}$$

$$P_2 = \frac{100 \times 0.08206 \times 298}{10 - 100 \times 6.4 \times 10^{-4} \times 0.08206 \times 298} = 290 \text{ atm}$$

$$\therefore W = 100 \times 8.3144 \times 298 \ln \frac{86}{290} = -301 \text{ kJ}$$

van der Waals gas:

$$P = \frac{nRT}{V - bn} - \frac{a}{V^2} \quad a = 0.2461 \frac{\text{l}^2 \cdot \text{atm}}{\text{mole}}$$

$$b = 0.02668 \text{ l/mole}$$

8.6 continued

$$\begin{aligned} W &= \int PdV = \int \left(\frac{nRT}{V-nb} - \frac{n^2a}{V^2} \right) dV \\ &= nRT \ln \left[\frac{V_2-nb}{V_1-nb} \right] - n^2a \left[-\frac{1}{V_2} + \frac{1}{V_1} \right] \\ &= 100 \times 8.3144 \times 298 \ln \left[\frac{10 - 100 \times 0.02668}{30 - 100 \times 0.02668} \right] \\ &\quad - 100^2 \times 0.2461 \times \frac{8.3144}{0.08206} \left[-\frac{1}{10} + \frac{1}{30} \right] \\ &= -309 \text{ kJ} \end{aligned}$$

$$\begin{aligned} \text{ideal gas } W &= nRT \ln \frac{V_2}{V_1} = 100 \times 8.3144 \times 298 \ln \frac{10}{30} \\ &= -272 \text{ kJ.} \end{aligned}$$

8.7 Using the virial equation of state for hydrogen at 298K given in Problem 8.6, calculate

- the fugacity of hydrogen at 500 atm and 298K.
- the pressure at which the fugacity is twice the pressure,
- 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?

$$a) \frac{P_f}{RT} = z = 1 + 6.4 \times 10^{-4} P \quad \therefore z-1 = 6.4 \times 10^{-4} P$$

$$\ln \frac{f}{P} = \int_0^P \frac{z-1}{P} dP = 6.4 \times 10^{-4} [500 - 0] = 0.3194$$

$$\therefore \frac{f}{P} = 1.376 \text{ and } f = 1.376 \times 500 = 688 \text{ atm}$$

$$b) \frac{f}{P} = 2 \quad \therefore \ln \frac{f}{P} = 0.693 = 6.4 \times 10^{-4} [P - 0]$$

$$\therefore \frac{f}{P} = 2 \text{ at } P = 1083 \text{ atm.}$$

$$c) \Delta G = \int V dP \quad \text{where } V = RT \left[\frac{1}{P} + 6.4 \times 10^{-4} \right]$$

$$\therefore \Delta G = RT \ln \frac{P_2}{P_1} + RT 6.4 \times 10^{-4} (P_2 - P_1)$$

$$= 8.3144 \times 298 \ln \frac{500}{1} + 8.3144 \times 298 \times 6.4 \times 10^{-4} [500 - 1]$$

$$= 15400 + 790$$

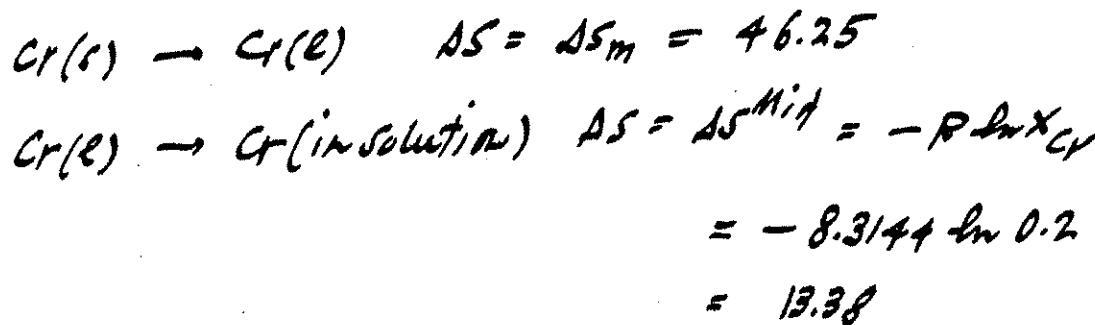
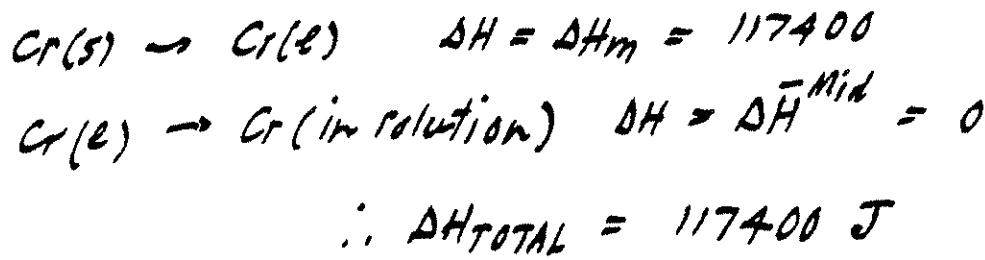
$$= 16190 \text{ J}$$

and the contribution due to non-ideal behavior is 790 J

- 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 $X_{\text{Cr}_2\text{O}_3} = 0.2$ 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 $\Delta S_{m,\text{Al}_2\text{O}_3} = \Delta S_{m,\text{Cr}_2\text{O}_3}$.

$$\Delta H_m, \text{Al}_2\text{O}_3 = 107500 \text{ J} \therefore \Delta S_m, \text{Al}_2\text{O}_3 = \frac{107500}{2324} = 46.25 \text{ J/K} \\ = \Delta S_m, \text{Cr}_2\text{O}_3$$

$$\therefore \Delta H_m, \text{Cr}_2\text{O}_3 = T_m \Delta S_m = 2538 \times 46.25 \\ = 117400 \text{ J}$$



$$\therefore \Delta S_{\text{TOTAL}} = 46.25 + 13.38 = 59.63 \text{ J/K}$$

- 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

$$\exp \left(-\frac{33440}{1863} - 3.12 \ln 1863 + 37.68 \right) = 0.0493 \text{ atm.}$$

$$\text{The number of moles of Mn removed} = \frac{1.50}{54.94} = 0.0273$$

$$\begin{aligned} \text{The partial pressure of Mn in the gas mixture} &= \frac{n_{Mn}}{n_{Mn} + n_{Ar}} \\ &= \frac{0.0273}{1.0273} = 0.0266 = p_{Mn} \end{aligned}$$

$$\therefore \alpha_{Mn} = \frac{p_{Mn}}{p_{Mn}^{\circ}} = \frac{0.0266}{0.0493} = 0.539$$

$$\text{and } \delta_{Mn} = \frac{\alpha_{Mn}}{X_{Mn}} = \frac{0.539}{0.5} = 1.08$$

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 $\bar{G}_{\text{Fe}}^{\text{xs}}$ and $\bar{G}_{\text{Mn}}^{\text{xs}}$ at $X_{\text{Mn}} = 0.6$.
- c. Calculate ΔG^M at $X_{\text{Mn}} = 0.4$.
- d. Calculate the partial pressures of Mn and Fe exerted by the alloy of $X_{\text{Mn}} = 0.2$.

X_{Mn}	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
$G^{\text{xs}}, \text{joules}$	395	703	925	1054	1100	1054	925	703	395

- 2) Calculation of $-T_h = \frac{G''}{x_{\text{Fe}} x_{\text{Mn}}}$ for each composition gives an average value of $4396 \pm 6 \text{ J}$. Therefore, with respect to G^{xs} , the system is regular.
- b) $\bar{G}_{\text{Fe}}^{\text{xs}} = -2x_{\text{Mn}}^2 = 4396 \times 0.6^2 = 1583 \text{ J}$
 $\bar{G}_{\text{Mn}}^{\text{xs}} = -2x_{\text{Fe}}^2 = 4396 \times 0.4^2 = 703 \text{ J}$
- c) $\Delta G^M = 8.3144 \times 1863 (0.4 \ln 0.4 + 0.6 \ln 0.6) + 4396 \times 0.4 \times 0.6$
 $= -9370 \text{ J}$.

d) At $X_{\text{Mn}} = 0.2$ $f_{\text{Mn}} = \exp\left(\frac{4396 \times 0.8^2}{8.3144 \times 1863}\right) = 1.2$

9.3 continued.

$$\therefore \alpha_{Mn} = 1.2 \times 0.2 = 0.24$$

$$P_{Mn}^{\circ} = \exp\left(\frac{-33440}{1863} - 3.02 \ln 1863 + 37.68\right) = 0.0493 \text{ atm}$$

$$\begin{aligned}\therefore P_{Mn} &= \alpha_{Mn} P_{Mn}^{\circ} = 0.24 \times 0.0493 \\ &= 0.0018 \text{ atm.}\end{aligned}$$

$$\delta_{Fe} = \exp\left(\frac{4396 \times 0.2^2}{8.3144 \times 1863}\right) = 1.011$$

$$\therefore \alpha_{Fe} = 1.011 \times 0.8 = 0.809$$

$$P_{Fe}^{\circ} = \exp\left(\frac{-45390}{1863} - 1.27 \ln 1863 + 23.93\right) = 4.55 \times 10^{-5} \text{ atm}$$

$$\begin{aligned}P_{Fe} &= \alpha_{Fe} \cdot P_{Fe}^{\circ} = 0.809 \times 4.55 \times 10^{-5} \\ &= 3.68 \times 10^{-5} \text{ atm.}\end{aligned}$$

- 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 $\Delta H^M = -20590X_{Cu}X_{Ag}$.

Heat 1 mole of Cu from 298 K to 1356 K and melt it.

$$\Delta H = \int_{298}^{1356} C_p, Cu, dT + \Delta H_{m,Cu}$$

$$= 22.64 (1356 - 298) + \frac{6.28 \times 10^{-3}}{2} (1356^2 - 298^2)$$

$$+ 12970 \text{ J}$$

$$= 42420 \text{ J.}$$

Heat 1 mole of Ag from 298 to 1356

$$\Delta H = \int_{298}^{1234} C_p, Ag(s) dT + \Delta H_{m,Ag} + \int_{1234}^{1356} C_p, Ag(l) dT$$

$$= 21.3 (1234 - 298) + \frac{8.54 \times 10^{-3}}{2} (1234^2 - 298^2)$$

$$- 1.51 \times 10^5 \left(\frac{1}{1234} - \frac{1}{298} \right) + 11090 + 30.5 (1356 - 1234)$$

$$= 41260 \text{ J}$$

in 2 moles of equimolar liquid solution.

$$\Delta H = 2(-20590 \times 0.5^*) = -10300$$

$$\text{Total heat requirement} = 42420 + 41260 - 10300 \\ = 73380 \text{ J.}$$

9.5 Melts in the system Pb-Sn exhibit regular solution behavior. At 473°C $a_{\text{Pb}} = 0.055$ in a liquid solution of $X_{\text{Pb}} = 0.1$. Calculate the value of Ω for the system and calculate the activity of Sn in the liquid solution of $X_{\text{Sn}} = 0.5$ at 500°C .

$$\delta_{\text{Pb}} = \frac{a_{\text{Pb}}}{y_{\text{Pb}}} = \frac{0.055}{0.1} = 0.55$$

$$\therefore \Omega = \frac{8.3144 \times 746 \times \ln 0.55}{0.9^2} = -4578 \text{ J}$$

At 500°C (773 K) and $X_{\text{Sn}} = 0.5$

$$\ln \delta_{\text{Sn}} = \frac{-4578 \times 0.5^2}{8.3144 \times 773} = -0.178$$

$$\therefore a_{\text{Sn}} = 0.5 \times \exp(-0.178) = 0.418$$

- 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

$$\ln \gamma_{\text{Sn}} = -840/T + 1.58$$

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

$$\Delta \bar{H}_{\text{Sn}}^M = \frac{R \frac{\partial \ln \gamma_{\text{Sn}}}{\partial (\frac{1}{T})}}{2} = -8.3144 \times 840 = -6984 \text{ J}$$

$$\begin{aligned}\Delta H^M (\text{per mole}) &= x_{\text{Sn}} \Delta \bar{H}_{\text{Sn}}^M + x_{\text{Cd}} \Delta \bar{H}_{\text{Cd}}^M \\ &= 0.01 \times (-6984) \quad \Delta \bar{H}_{\text{Cd}}^M = 0 \\ &\approx -69.84 \text{ J} \\ &= C_p \Delta T \\ &= 29.5 \Delta T\end{aligned}$$

$$\therefore \text{Increase in } T = \frac{69.84}{29.5} = 2.37 \text{ kelvins}$$

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

$$\ln \gamma_A = \alpha_1 X_B + \frac{1}{2} \alpha_2 X_B^2 + \frac{1}{3} \alpha_3 X_B^3 + \dots$$

and

$$\ln \gamma_B = \beta_1 X_A + \frac{1}{2} \beta_2 X_A^2 + \frac{1}{3} \beta_3 X_A^3 + \dots$$

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 $\alpha_2 = \beta_2$.

$$\ln \gamma_A = \alpha_1 X_B + \frac{1}{2} \alpha_2 X_B^2 + \frac{1}{3} \alpha_3 X_B^3 + \dots$$

$$\therefore X_A d \ln \gamma_A = \alpha_1 X_A d X_B + \alpha_2 X_A X_B d X_B + \alpha_3 X_A X_B^2 d X_B + \dots$$

$$\ln \gamma_B = \beta_1 X_A + \frac{1}{2} \beta_2 X_A^2 + \frac{1}{3} \beta_3 X_A^3 + \dots$$

$$\therefore -X_B d \ln \gamma_B = \beta_1 X_B d X_A + \beta_2 X_B X_A d X_A + \beta_3 X_B X_A^2 d X_A + \dots$$

From the Gibbs-Duhem equation

$$X_A d \ln \gamma_A = X_B d \ln \gamma_B$$

$$\therefore \alpha_1 X_A d X_B + \alpha_2 X_A X_B d X_B = \beta_1 X_B d X_A + \beta_2 X_B X_A d X_A$$

if the power series are truncated at the quadratic terms.

Equality of the coefficients in terms containing 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

$$\ln \gamma_{\text{Zn}} + 0.875 X_{\text{Cd}}^2 - 0.30 X_{\text{Cd}}^3$$

Derive the corresponding expression for the dependence of $\ln \gamma_{\text{Cd}}$ on composition and calculate the activity of cadmium in the alloy of $X_{\text{Cd}} = 0.5$ at 435°C.

$$\ln \delta_{\text{Zn}} = 0.875 X_{\text{Cd}}^2 - 0.3 X_{\text{Cd}}^3$$

$$d \ln \delta_{\text{Zn}} = 1.750 X_{\text{Cd}} dX_{\text{Cd}} - 0.9 X_{\text{Cd}}^2 dX_{\text{Cd}}$$

$$-\frac{x_{\text{Zn}}}{x_{\text{Cd}}} d \ln \delta_{\text{Zn}} = -1.750 X_{\text{Zn}} dX_{\text{Cd}} + 0.9 X_{\text{Zn}} X_{\text{Cd}} dX_{\text{Cd}}$$

$$= d \ln \delta_{\text{Cd}}$$

$$= 1.75 X_{\text{Zn}} dX_{\text{Zn}} - 0.9 X_{\text{Zn}} (1-X_{\text{Zn}}) dX_{\text{Zn}}$$

$$= 0.85 X_{\text{Zn}} dX_{\text{Zn}} + 0.9 X_{\text{Zn}}^2 dX_{\text{Zn}}$$

$$\therefore \ln \delta_{\text{Cd}} = 0.425 X_{\text{Zn}}^2 + 0.3 X_{\text{Zn}}^3$$

$$\therefore \text{At } X_{\text{Cd}} = 0.5, \delta_{\text{Cd}} = 1.155 \text{ and } a_{\text{Cd}} = 0.577$$

9.11 The molar excess Gibbs free energy of formation of solid solutions in the system Au-Ni

can be represented by

$$G^{xs} = X_{Ni}X_{Au} (24140X_{Au} + 38280X_{Ni} - 14230X_{Au}X_{Ni}) \left[1 - \frac{T}{2660} \right] \text{ J}$$

Calculate the activities of Au and Ni in the alloy of $X_{Au} = 0.5$ at 1100 K.

Let $X_{Au} = x$

$$G^{xs} = x(1-x) [24140x + 38280(1-x) - 14230x(1-x)] \left[1 - \frac{1100}{2660} \right]$$

$$= [38280x - 66650x^2 + 42600x^3 - 14230x^4] \times 0.586 \quad - (i)$$

$$\frac{\partial G^{xs}}{\partial x} = [38280 - 133300x + 127800x^2 - 56920x^3] \cdot 0.586$$

$$(1-x) \frac{\partial G^{xs}}{\partial x} = [38280 - 171580x + 261100x^2 - 184720x^3 \\ + 56920x^4] \cdot 0.586$$

$$\bar{G}_{Au}^{xs} = G^{xs} + (1-x) \frac{\partial G^{xs}}{\partial x}$$

$$= [38280 - 133300x + 194450x^2 - 142120x^3 \\ + 42690x^4] \cdot 0.586$$

$$\therefore \bar{G}_{Au}^{xs} (\text{at } X_{Au} = 0.5) = 3105 \text{ J} = 8.3144 \times 1100 \ln \delta_{Au}$$

$$\therefore \delta_{Au} = 1.39 \text{ and } a_{Au} = 0.5 \times 1.39 = 0.695$$

$$\text{From (i), } G^{xs} (\text{at } X_{Au} = 0.5) = 4051 = 8.3144 \times 1100 [0.5 \ln \delta_{Ni} + 0.5 \ln 1.39]$$

$$\therefore \delta_{Ni} = 1.7 \text{ and } a_{Ni} = 1.7 \times 0.5 = 0.85$$

- 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 $X_{\text{CaF}_2} = 0.45$ and $T = 1243 \text{ K}$.

$$x \equiv X_{\text{CaF}_2}$$

For the CaF_2 liquidus line

$$\Delta G_m^\circ = 31200 - 18.45T = -8.3144T \ln x$$

for the MgF_2 liquidus line

$$\Delta G_m^\circ = 58160 - 37.86T = -8.3144T \ln(1-x)$$

Simultaneous solution gives the point of intersection of the liquidus lines at

$$T = 1317 \text{ K}$$

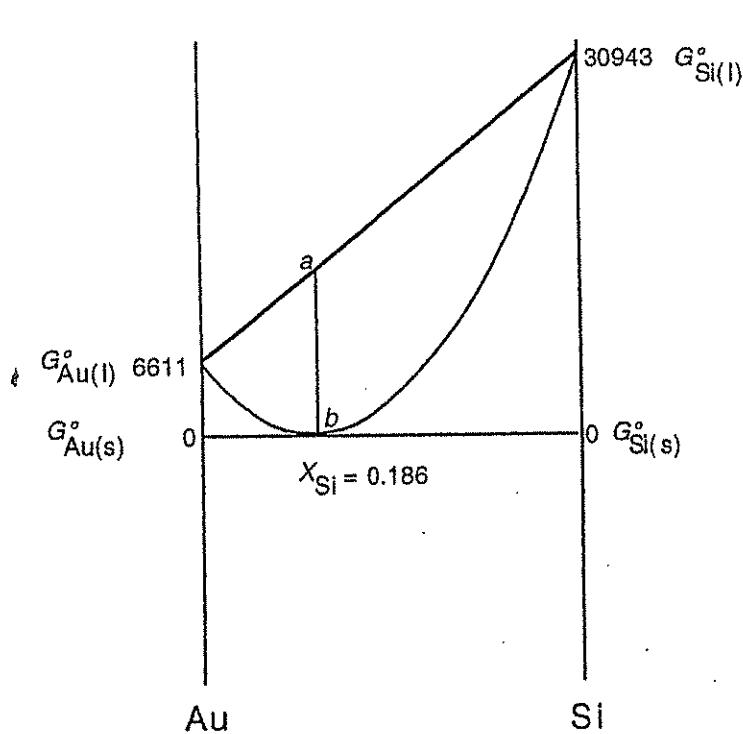
$$X_{\text{CaF}_2} = 0.53$$

The actual eutectic is $T = 1243 \text{ K}$
 $X_{\text{CaF}_2} = 0.45$

- 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.

$$\text{At } 636 \text{ K} \quad \Delta G_m^\circ, \text{Au} = 12600 \left[\frac{1338 - 636}{1338} \right] = 6611 \text{ J}$$

$$\text{and } \Delta G_m^\circ, \text{Si} = 50200 \left[\frac{1658 - 636}{1658} \right] = 30943 \text{ J}$$



$$a) \Delta G'' = ab$$

$$= -(0.186 \times 30943 + 0.814 \times 6611) \text{ J}$$

$$= -11140 \text{ J}$$

$$b) \Delta G''' = 0$$

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 $\Delta S_{m,\text{Cr}_2\text{O}_3}^\circ = \Delta S_{m,\text{Al}_2\text{O}_3}^\circ$, and that the solid and liquid solutions in the system $\text{Al}_2\text{O}_3\text{-Cr}_2\text{O}_3$ behave ideally, calculate

1. The temperature at which equilibrium melting begins when an alloy of $X_{\text{Al}_2\text{O}_3} = 0.5$ 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.

$$\frac{\Delta G_m^\circ, \text{Al}_2\text{O}_3}{RT} = \frac{12929}{T} - 5.563$$

$$\frac{\Delta G_m^\circ, \text{Cr}_2\text{O}_3}{RT} = \frac{14119}{T} - 5.563$$

1) The solidus temperature, T , at $X_{\text{Al}_2\text{O}_3} = 0.5$ 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 $T = 2418 \text{ K}$

2) The corresponding liquidus composition is

$$X_{\text{Al}_2\text{O}_3}(\text{liquidus}) = 0.5 \left[\exp\left(-\frac{12929}{2418} + 5.563\right) \right]$$

$$= 0.621$$

Problem 10.3 continued.

3) The liquidus temperature at $X_{Al_2O_3} = 0.5$ is given by

$$0.5 = \frac{1 - \exp\left(-\frac{14119}{T} + 5.563\right)}{\exp\left(-\frac{12929}{T} + 5.563\right) - \exp\left(-\frac{14119}{T} + 5.563\right)} \times \exp\left(-\frac{12929}{T} + 5.563\right)$$

which gives $T = 2444\text{ K}$

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 $\text{Na}_2\text{O} \cdot \text{B}_2\text{O}_3$ and $\text{K}_2\text{O} \cdot \text{B}_2\text{O}_3$ form complete ranges of solid and liquid solutions and the solidus and liquidus show a common minimum at the equimolar composition and $T = 1123 \text{ K}$. Calculate the molar Gibbs free energy of formation of the equimolar solid solution from solid $\text{Na}_2\text{O} \cdot \text{B}_2\text{O}_3$ and solid $\text{K}_2\text{O} \cdot \text{B}_2\text{O}_3$ at 1123 K, assuming that the liquid solutions are ideal.

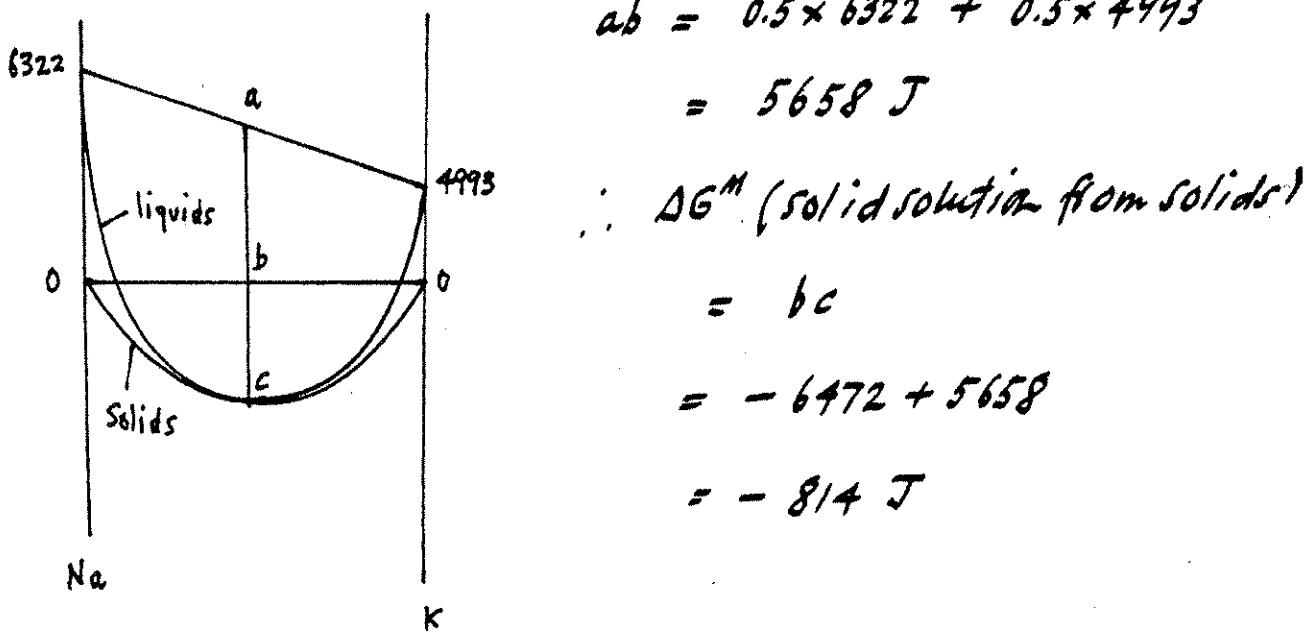
At $T = 1123 \text{ K}$

$$\Delta G_m^{\circ}, \text{Na}_2\text{O} \cdot \text{B}_2\text{O}_3 = 67000 \left(\frac{1240 - 1123}{1240} \right) = 6322 \text{ J}$$

$$\Delta G_m^{\circ}, \text{K}_2\text{O} \cdot \text{B}_2\text{O}_3 = 62800 \left(\frac{1220 - 1123}{1220} \right) = 4993 \text{ J}$$

$$\begin{aligned} \Delta G'' (\text{from liquids}) &= 8.3144 \times 1123 [0.5 \ln 0.5 + 0.5 \ln 0.5] \\ &= -6472 \text{ J.} = ac \end{aligned}$$

$$\begin{aligned} ab &= 0.5 \times 6322 + 0.5 \times 4993 \\ &= 5658 \text{ J} \end{aligned}$$



$$\begin{aligned} \therefore \Delta G'' (\text{solid solution from solids}) &= bc \\ &= -6472 + 5658 \\ &= -814 \text{ J} \end{aligned}$$

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 $X_{\text{SiO}_2} = 0.24$ and $X_{\text{SiO}_2} = 0.76$ and that the liquid solutions are regular in their behavior, what is the value of Ω_1 and at what temperature does the liquid immiscibility gap disappear?

At the composition of the double tangent to the $\Delta G''$ curve

$$\frac{d\Delta G''}{dx} = RT \ln\left[\frac{x}{1-x}\right] + \Omega_1(1-2x) = 0$$

\therefore At 2067 K .

$$8.3144 \times 2067 \ln\left[\frac{0.24}{0.76}\right] + \Omega_1(1-2 \times 0.24) = 0$$

which gives $\Omega_1 = 38096\text{ J}$.

$$\text{Then } T_g = \frac{\Omega_1}{2R} = \frac{38096}{2 \times 8.3144} = 2291\text{ K}$$

10.6 The binary system Ge-Si contains complete solid and liquid solutions. The melting temperatures are $T_{m, \text{Si}} = 1685 \text{ K}$ and $T_{m, \text{Ge}} = 1210 \text{ K}$, and $\Delta H_{m, \text{Si}}^{\circ} = 50200 \text{ J}$. At 1200°C the liquidus and solidus compositions are, respectively, $X_{\text{Si}} = 0.32$ and $X_{\text{Si}} = 0.665$. Calculate the value of $\Delta H_{m, \text{Ge}}^{\circ}$ 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 $\Delta H_{m, \text{Ge}}^{\circ}$ at $T_{m, \text{Ge}}$ is 36900 J.

$$\text{At } 1473 \text{ K}, \quad \Delta G_{m, \text{Si}}^{\circ} = 50200 \left(\frac{1685 - 1473}{1685} \right) = 6316 \text{ J}$$

$$\frac{\Delta G_{m, \text{Si}}^{\circ}}{RT} = \frac{6316}{8.3144 \times 1473} = 0.5157$$

$$\therefore X_{\text{Ge}}(\text{solidus}) = 0.335 = \frac{1 - \exp(-0.5157)}{\exp\left(\frac{-\Delta G_{m, \text{Ge}}^{\circ}}{8.3144 \times 1473}\right) - \exp(-0.5157)}$$

$$\text{gives } \Delta G_{m, \text{Ge}}^{\circ} = -7197 \text{ J}$$

$$\text{and } \Delta H_{m, \text{Ge}}^{\circ} = \frac{-7197}{\left(\frac{(1210 - 1473)}{1210} \right)} = 33111 \text{ J}$$

$$X_{\text{Ge}}(\text{liquidus}) = 0.68 = \frac{(1 - \exp(-0.5157)) \exp\left(\frac{-\Delta G_{m, \text{Ge}}^{\circ}}{8.3144 \times 1473}\right)}{\exp\left(\frac{-\Delta G_{m, \text{Ge}}^{\circ}}{8.3144 \times 1473}\right) - \exp(-0.5157)}$$

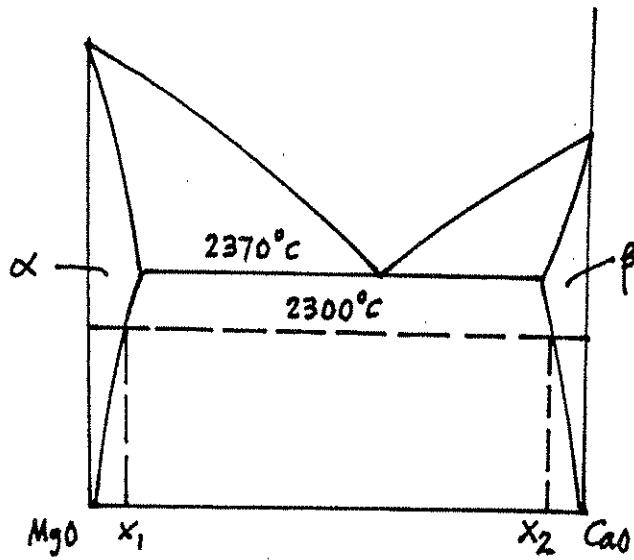
$$\text{which gives } \Delta G_{m, \text{Ge}}^{\circ} = -4679 \text{ J}$$

Problem 10.6 continued

$$\therefore \Delta H_{m, 6C}^{\circ} = \frac{-4679}{\left(\frac{1210 - 1473}{1210} \right)} = 21527 \text{ J.}$$

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_{CaO}^0 in MgO = 12.88 and γ_{MgO}^0 in CaO = 6.23 at 2300°C, calculate the solubility of CaO in MgO and the solubility of MgO in CaO at 2300°C.



$$\alpha_{\text{CaO}} \text{ (in } \beta \text{ at } x_2) = \alpha_{\text{CaO}} \text{ (in } \alpha \text{ at } x_1) \\ 1 - x_1 = 6.23(1 - x_2) \quad (i)$$

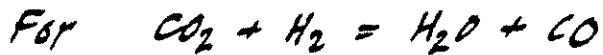
$$\alpha_{\text{MgO}} \text{ (in } \alpha \text{ at } x_1) = \alpha_{\text{MgO}} \text{ (in } \beta \text{ at } x_2) \\ 12.88 x_1 = x_2 \quad (ii)$$

Solution of (i) and (ii) gives

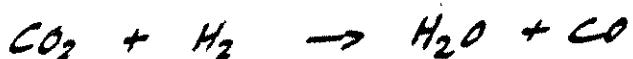
$$x_1 = x_{\text{CaO}} = 0.066$$

$$x_2 = x_{\text{CaO}} = 0.85$$

11.1 A gas mixture of 50% CO, 25% CO₂ and 25% H₂ (by volume) is fed to a furnace at 900°C. Determine the composition of the equilibrium CO-CO₂-H₂-H₂O gas if the total pressure of the gas in the furnace is 1 atm.



$$\Delta G^\circ_{1173} = -1416 \text{ J} \quad \therefore K_p = \exp\left(\frac{-1416}{8.3144 \times 1173}\right) \\ = 1.156$$



initial molar	0.25	0.25	0	0.5
upon reaction	0.25-x	0.25-x	x	0.5+x

$n_T = 1$

With $P_T = 1 \text{ atm.}$

$$K_p = \frac{P_{\text{H}_2\text{O}} \cdot P_{\text{CO}}}{P_{\text{CO}_2} \cdot P_{\text{H}_2}}$$

$$1.156 = \frac{x(0.5+x)}{(0.25-x)^2}$$

$$\therefore x = 0.0676$$

$$\therefore x_{\text{CO}_2} = x_{\text{H}_2} = 0.25 - 0.0676 = 0.182$$

$$x_{\text{CO}} = 0.5 + 0.0676 = 0.568$$

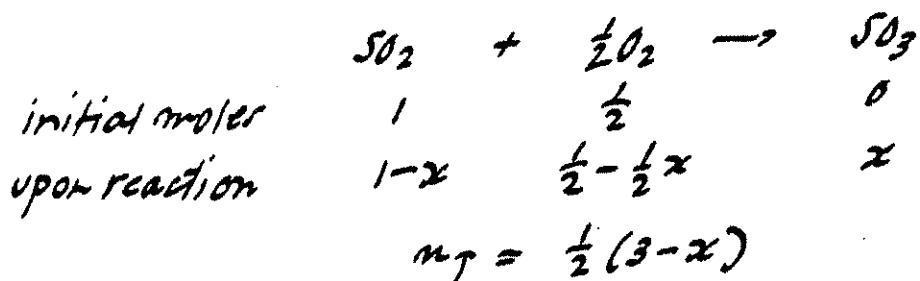
$$x_{\text{H}_2\text{O}} = 0.0676$$

- 11.2 How much heat is evolved when 1 mole of SO_2 and $\frac{1}{2}$ mole of O_2 , each at 1 atm pressure, react to form the equilibrium $\text{SO}_3\text{-SO}_2\text{-O}_2$ mixture at 1000 K and 1 atm pressure?

$$\text{For } \text{SO}_2 + \frac{1}{2}\text{O}_2 = \text{SO}_3 \quad \Delta G^\circ_{1000} = -5230 \text{ J}$$

$$K_p, 1000 = \exp\left(\frac{-5230}{8.3144 \times 1000}\right)$$

$$= 1.876$$



$$\therefore P_{\text{SO}_2} = \frac{2(1-x)}{3-x} \cdot P, \quad P_{\text{O}_2} = \frac{1-x}{3-x} P, \quad P_{\text{SO}_3} = \frac{2x}{3-x}$$

$$K_p = \frac{P_{\text{SO}_3}}{P_{\text{SO}_2} P_{\text{O}_2}}^{1/2} = 1.876 = \frac{x(3-x)^{1/2}}{(1-x)^{1/2}(1-x)}$$

$$\therefore x = 0.463$$

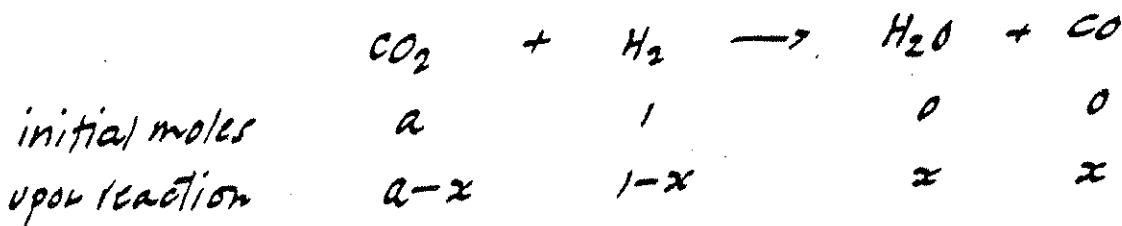
For formation of 1 mole of $\text{SO}_3 \quad \Delta H = \Delta H^\circ = -94600 \text{ J}$

For formation of 0.463 moles of SO_3

$$\begin{aligned} \Delta H &= 0.463 \times -94600 \text{ J} \\ &= -43800 \text{ J} \end{aligned}$$

$\therefore 43800 \text{ J}$ are evolved.

11.3 A $\text{CO}_2\text{-CO-H}_2\text{O-H}_2$ 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?



$$\therefore K = 9659 = \frac{p_{\text{H}_2\text{O}}}{p_{\text{H}_2} p_{\text{O}_2}^{\frac{1}{2}}} = \frac{x}{(1-x) 10^{-3.5}}$$

which gives $x = 0.753$



$$\therefore K = 2193 = \frac{p_{\text{CO}_2}}{p_{\text{CO}} \cdot p_{\text{O}_2}^{\frac{1}{2}}} = \frac{a-x}{x \cdot 10^{-3.5}} = \frac{a-0.753}{0.753 \times 10^{-3.5}}$$

which gives $a = 1.276$

$$\therefore \frac{\text{CO}_2}{\text{H}_2} = a = 1.276$$

- 11.4 Lithium bromide vapor dissociates according to $\text{LiBr}_{(g)} \rightarrow \text{Li}_{(g)} + \frac{1}{2}\text{Br}_{2(g)}$. 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	\rightarrow	$\text{Li} + \frac{1}{2}\text{Br}_2$	
initial moles	1		0	0
upon reaction	$1-x$		x	$\frac{1}{2}x \quad n_T = 1 + \frac{1}{2}x$

$$\text{At } P_T = 1 \text{ atm.} \quad p_{\text{Li}} = \frac{x}{1 + \frac{1}{2}x} = 10^{-5} \quad \therefore x = 10^{-5}$$

$$\therefore p_{\text{LiBr}} = \frac{1-x}{1 + \frac{1}{2}x} \sim 1$$

$$p_{\text{Br}_2} = 0.5 \times 10^{-5}$$

$$\therefore K = \frac{p_{\text{Br}_2}^{\frac{1}{2}} \cdot p_{\text{Li}}}{p_{\text{LiBr}}} = (0.5 \times 10^{-5})^{\frac{1}{2}} 10^{-5} = 2.236 \times 10^{-8}$$

$$\Delta G^\circ = 333900 - 42.09 T = -8.3144 T \ln 2.236 \times 10^{-8}$$

$$\text{which gives } T = 1771 \text{ K}$$

11.5 When SO_3 is decomposed at the constant pressure P and $T = 1000 \text{ K}$, 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 $p_{\text{O}_2} = 0.05 \text{ atm}$?

$$\text{For } \text{SO}_3 = \text{SO}_2 + \frac{1}{2}\text{O}_2 \quad \Delta G^\circ_{1000} = 5236 \\ \therefore K_p = 0.533$$

$$\text{From stoichiometry } p_{\text{SO}_2} = 2p_{\text{O}_2}$$

$$\text{and } p_{\text{SO}_3} = P_T - 3p_{\text{O}_2}$$

$$\therefore K = 0.533 = \frac{p_{\text{O}_2}^{1/2} \cdot p_{\text{SO}_2}}{p_{\text{SO}_3}} = \frac{(0.05)^{1/2} \cdot 2 \times 0.05}{(P_T - 0.15)}$$

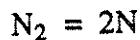
$$\text{Gives } P_T = 0.192 \text{ atm}$$

$$\text{With } P_T = 1 \text{ atm}, K = \frac{(0.05)^{1/2} \cdot 0.10}{1 - 0.15} = 0.0263$$

$$\therefore \Delta G^\circ = 94600 - 89.37 T = -8.3144 T \ln 0.0263$$

$$\text{which gives } T = 792 \text{ K}$$

11.6 For the dissociation of nitrogen according to



$$\Delta G^\circ = 945000 - 114.9T \text{ J}$$

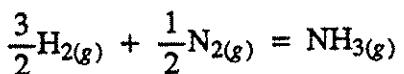
Calculate

- 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.

$$\begin{aligned} \text{For } N_2 = 2N \quad \Delta G_{3000}^\circ &= 600300 \text{ J} \\ \therefore K_p &= 3.53 \times 10^{-11} \\ &= \frac{p_N^2}{(1-p_N)} \\ \therefore p_N &= 5.94 \times 10^{-6} \text{ atm} \end{aligned}$$

$$\begin{aligned} \text{ii) } P_T &= p_{N_2} + p_N \\ &= 0.9P_T + 0.1P_T \quad \therefore K_p = 3.53 \times 10^{-11} \\ &= \frac{(0.1P_T)^2}{0.9P_T} = \frac{0.01}{0.9} P_T \\ \therefore P_T &= 3.18 \times 10^{-9} \text{ atm.} \end{aligned}$$

11.7 Ammonia gas is heated to 300°C. At what total pressure is the mole fraction of N₂ in the equilibrium gas mixture equal to 0.2. Calculate the standard enthalpy change and the standard entropy change for the reaction



at 300°C.

$$\text{For } 2\text{NH}_3 = \text{N}_2 + 3\text{H}_2 \quad \Delta G_{573}^\circ = -25021 \quad \therefore K_{p573} = 190.1$$

$$\text{As } p\text{H}_2 = 3p\text{N}_2, \quad x_{\text{H}_2} = 3x_{\text{N}_2}$$

$$\therefore x_{\text{N}_2} = 0.2, \quad x_{\text{H}_2} = 0.6 \quad x_{\text{NH}_3} = 1 - 0.2 - 0.6 = 0.2$$

$$\therefore K = 190.1 = \frac{p\text{N}_2 p\text{H}_2^3}{p^2 \text{NH}_3} = \frac{x_{\text{N}_2} \cdot x_{\text{H}_2}^3 \cdot P^2}{x_{\text{NH}_3}^2} = \frac{0.2 \times 0.6^3 P}{0.2^2}$$

$$\text{Which gives } P = 13.3 \text{ atm}$$

$$\Delta G^\circ = -87030 + 25.8T \ln T + 31.7T$$

$$\text{for } \text{N}_2 + 3\text{H}_2 = 2\text{NH}_3$$

$$\therefore \frac{\partial \Delta G^\circ}{\partial T} = -\Delta S^\circ = 25.8 \ln T + 25.8 + 31.7$$

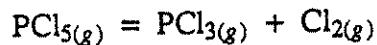
$$\therefore \Delta S_{573}^\circ = -221.4 \text{ J/K}$$

$$\text{and } \Delta H_{573}^\circ = \Delta G_{573}^\circ + 573 \Delta S_{573}^\circ = -25021 + 221.4 \times 573 \\ = -101814 \text{ J}$$

$$\therefore \text{For } \frac{1}{2}\text{N}_2 + \frac{3}{2}\text{N}_2 = \text{NH}_3$$

$$\Delta H_{573}^\circ = -50900 \text{ J} \quad \text{and} \quad \Delta S_{573}^\circ = -110.7 \text{ J/K}$$

11.8 By establishing the equilibrium



at 500 K in a mixture of PCl_3 and PCl_5 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?

$$\text{For } \text{PCl}_3 + \text{Cl}_2 \rightleftharpoons \text{PCl}_5 \quad \Delta_f H^\circ = -2672 \quad K_p, 500 = 1.901$$

	PCl_3	Cl_2	PCl_5	
initial moles	a	0	1	
upon reaction	$a+x$	x	$1-x$	$n_T = a+1+x$

$$\therefore \text{At } P_T = 1 \text{ atm.} \quad p_{\text{Cl}_2} = \frac{x}{a+1+x} = 0.1 \quad (i)$$

$$K = 1.901 = \frac{p_{\text{PCl}_5}}{p_{\text{PCl}_3} p_{\text{Cl}_2}} = \frac{(1-x)(a+1+x)}{x(a+x)} \quad (ii)$$

$$(i) \text{ and } (ii) \text{ give } a = 2.692 \quad x = 0.410$$

$$\therefore \frac{\text{PCl}_3}{\text{PCl}_5} = a = 2.692$$

11.9 Air and hydrogen are mixed in the ratio 1:4 and are heated to 1200 K. Calculate the partial pressures of H₂ and O₂ in the equilibrium gas at 1 atm pressure and at 10 atm pressure. Air contains 21 volume percent O₂.

$$n_{H_2} = 20$$

$$n_{air} = 80 \rightarrow n_{O_2} = 16.8 \\ n_{N_2} = 63.2$$



$$K = 7.178 \times 10^7 = \frac{P_{H_2O}}{P_{H_2} \cdot P_{O_2}^{1/2}}$$

$$\frac{n_H}{n_O} = \frac{20}{16.8} = 1.1905 = \frac{2n_{H_2} + 2n_{H_2O}}{2n_{O_2} + n_{H_2O}}$$

$$\frac{n_O}{n_N} = \frac{16.8}{63.2} = 0.2658 = \frac{2n_{O_2} + n_{H_2O}}{126.4}$$

$$\therefore 2n_{O_2} + n_{H_2O} = 0.2658 \times 126.4 = 33.6$$

$$\text{and } 2n_{H_2} + 2n_{H_2O} = 33.6 \times 1.1905 = 40$$

$$\therefore n_{H_2O} = 20 - n_{H_2} = 33.6 - 2n_{O_2}$$

$$n_{O_2} = 6.8 + \frac{1}{2}n_{H_2}$$

$$n_T = 20 - n_{H_2} + n_{H_2} + 6.08 + \frac{1}{2}n_{H_2} + 63.2$$

$$= 90 + \frac{1}{2}n_{H_2}$$

$$\therefore K = 7.178 \times 10^7 = \frac{n_{H_2O} \cdot n_T^{1/2}}{n_{H_2} \cdot n_{O_2}^{1/2} \cdot P^{1/2}}$$

11.9 continued.

∴ with $P = 1 \text{ atm}$.

$$7.178 \times 10^7 = \frac{(20 - n_{H_2})(90 + \frac{1}{2}n_{H_2})^{1/2}}{n_{H_2}(6.8 + \frac{1}{2}n_{H_2})^{1/2}}$$

which gives $n_{H_2} = 9.43 \times 10^{-7} \text{ moles}$

∴ $n_{O_2} = 6.8$ and $n_T = 90 \text{ moles}$

$$\therefore P_{H_2} = \frac{n_{H_2} \cdot P_T}{n_T} = \frac{9.43 \times 10^{-7}}{90} = 1.05 \times 10^{-8} \text{ atm}$$

$$\text{and } P_{O_2} = \frac{6.8}{90} \cdot P_T = 0.0756 \text{ atm}$$

with $P_T = 10 \text{ atm}$

$$7.178 \times 10^7 = \frac{(20 - n_{H_2})(90 + \frac{1}{2}n_{H_2})^{1/2}}{n_{H_2}(6.8 + \frac{1}{2}n_{H_2})^{1/2} \sqrt{10}}$$

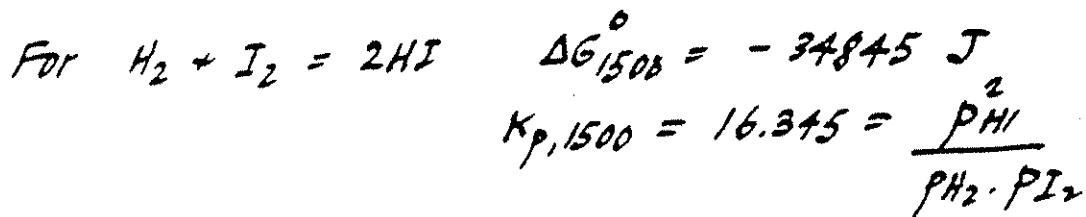
which gives $n_{H_2} = 2.98 \times 10^{-7} \text{ moles}$

and $n_{O_2} = 6.8 \text{ moles}$

$$\therefore P_{H_2} = \frac{2.98 \times 10^{-7}}{90} \times 10 = 3.31 \times 10^{-8} \text{ atm}$$

$$P_{O_2} = \frac{6.8}{90} \times 10 = 0.756 \text{ atm}$$

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?



before	1	1	1	
at equilibrium	$1-x$	$1-x$	$1+2x$	$\therefore n_T = 3$

$$\therefore K = \frac{(1+2x)^2}{(1-x)^2} = 16.345 \quad \text{which gives } x = 0.504$$

$$\therefore x_{H_2} = x_{I_2} = \frac{1-0.504}{3} = 0.165$$

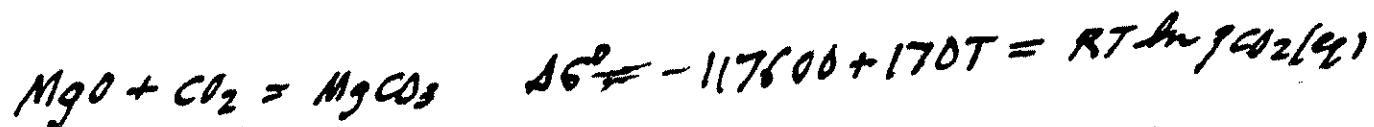
$$x_{HI} = \frac{1+2 \times 0.504}{3} = 0.669$$

$$\text{For } p_{HI} = 5p_{H_2}, \quad K = \frac{(5p_{H_2})^2}{p_{H_2}^2} = 25$$

$$\therefore \Delta G^\circ = -8370 - 17.65 T = -8.3144 T \ln 25$$

gives $T = 918 \text{ K.}$

- 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?



\therefore At $p_{CO_2}(q) = 10^{-2}$ atm.

$$-117600 + 170T = 8.3144 T \ln 10^{-2} = -38.29T$$

which gives $T = 565K$.

- 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.



Adding gives

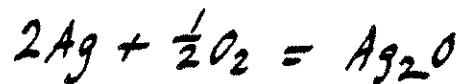


$$\therefore T_{m,Ni} = \frac{34980}{20.2} = 1731 \text{ K}$$

$$\Delta H_{m,Ni}^\circ = \frac{34980}{2} = 17490 \text{ J}$$

$$\Delta S_{m,Ni}^\circ = \frac{20.2}{2} = 10.1 \text{ J/K.}$$

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.



$$\Delta G^\circ = -30540 + 66.11 T \text{ J.}$$

For $p_{\text{O}_2}(\text{eq}) = 1 \text{ atm.}$

$$-30540 + 66.11 T = RT \ln p_{\text{O}_2(\text{eq})}^{\frac{1}{2}} = 0$$

$$\therefore T = 462 \text{ K}$$

For $p_{\text{O}_2(\text{eq})} = 0.21 \text{ atm.}$

$$-30540 + 66.11 T = \frac{1}{2} \times 8.3144 T \ln 0.21$$

$$\text{gives } T = 421 \text{ K}$$

- 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?



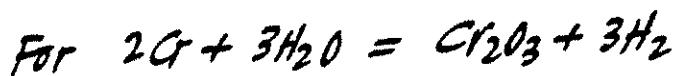
Adding gives



$$= 1500 \times 8.3144 \times 3 \ln \frac{p_{H_2O}}{p_{H_2}}$$

$$\therefore \frac{p_{H_2O}}{p_{H_2}} = 1.32 \times 10^{-3}$$

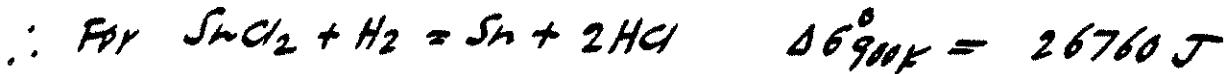
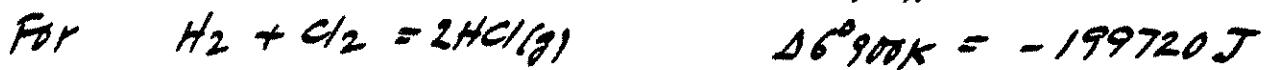
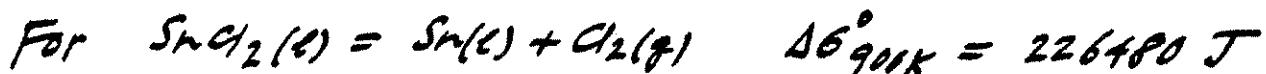
$$\therefore \text{with } p_{H_2} = 1, \quad p_{H_2O(\max)} = 1.32 \times 10^{-3} \text{ atm}$$



$$\Delta H^\circ = -371200 \text{ J}$$

and the reaction is exothermic.

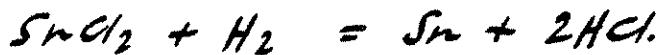
12.5 A mixture of argon gas and hydrogen gas at 1 atm total pressure is passed through a reaction vessel containing a mixture of liquid Sn and liquid SnCl_2 at 900 K. The composition of the gas leaving the vessel is 50% H_2 , 7% HCl and 43% Ar. Has equilibrium been attained between the gas phase and the liquid phases in the vessel?



$$\therefore K = \exp\left(\frac{-26760}{8.3144 \times 900}\right) = 0.028 = \frac{P^2\text{HCl}}{P\text{H}_2}$$

In the exit gas $\frac{P^2\text{HCl}}{P\text{H}_2} = \frac{0.07^2}{0.5} = 0.0098$, which, being less than K , indicates that equilibrium has not been attained.

The gas entering contains $0.5 + 0.035 = 0.535$ mols of H_2 and 0.43 mols of Ar



before	0.535		
after	$0.535-x$	$2x$	$m_f = 0.535+x+0.43$
			$= 0.965+x \text{ mols}$

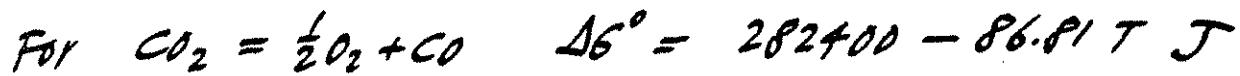
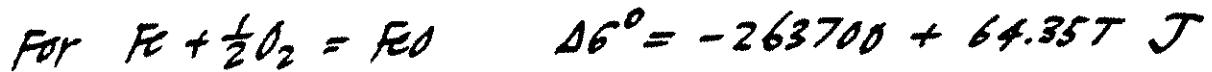
$$\therefore K = 0.028 = \frac{(2x)^2}{(0.965+x)(0.535-x)} \quad \therefore x = 0.0584$$

$$\therefore \text{HCl} \rightarrow \frac{2 \times 0.0584}{0.965 + 0.0584} \rightarrow 11.4 \%$$

$$\text{H}_2 \rightarrow \frac{0.535 - 0.0584}{0.965 + 0.0584} \rightarrow 46.6 \%$$

$$\text{Ar} \rightarrow \frac{0.43}{0.965 + 0.0584} \rightarrow 42 \%$$

12.6 Fe and FeO are in equilibrium with a gas mixture of composition 71.8% CO - 28.2% CO₂ 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?



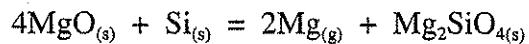
As written, the reaction is endothermic. Thus a decrease in temperature causes the equilibrium to shift at.



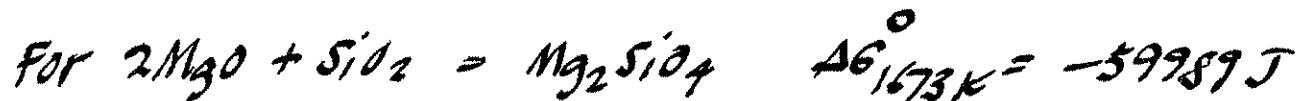
which decreases $p_{\text{CO}}(\text{eq})$ and increases $p_{\text{CO}_2}(\text{eq})$.

Thus decreasing the temp at const. p_{CO} and constant p_{CO_2} cause the FeO phase to disappear.

- 12.7 Calculate the vapor pressure of Mg exerted at 1400°C by the system in which the reaction



is established



$$\Delta G^\circ_{1673K} = 183474 \text{ J}$$

$$= -2 \times 8.3144 \times 1673 \cdot \ln p_{\text{Mg}}(\text{eq})$$

$$\therefore p_{\text{Mg}}(\text{eq}) = 2.42 \times 10^{-2} \text{ atm.}$$

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.



$$\therefore \ln p_{\text{CO}_2}(q) = -\frac{161300}{RT} + \frac{137.2}{R} = -\frac{19400}{T} + 16.50 \quad (\text{i})$$

$1 \text{ g. CaCO}_3 = \frac{1}{100} = 0.01 \text{ moles} \quad \therefore \text{The vessel contains } 0.01 \text{ moles of CO}_2. \text{ If all of the } 0.01 \text{ moles of CO}_2 \text{ occurs in the gas phase then}$

$$p_{\text{CO}_2} = \frac{nRT}{V} = \frac{0.01 \times 0.082057T}{1} = 8.2057 \times 10^{-4} \quad (\text{ii})$$

$$\text{From (i)} \quad p_{\text{CO}_2}(q) = \exp \left[-\frac{19400}{T} + 16.50 \right] \quad (\text{iii})$$

Lines (ii) and (iii) intersect at $p_{\text{CO}_2} = 0.96$, $T = 1173 \text{ K}$ which is the highest temperature at which CaCO_3 exists.

At $T = 1000 \text{ K}$ eq (iii) gives $p_{\text{CO}_2}(q) = 0.055 \text{ atm}$ and at $T = 1500 \text{ K}$ eq. (ii) gives $p_{\text{CO}_2} = 1.23 \text{ atm}$.

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.

$$CoO + SO_3 = CoSO_4 \quad \Delta\text{G}^\circ_{1223K} = -25698 \text{ J} \\ = 8.3144 \times 1223 \ln p_{SO_3(\text{eq})}$$

$$\therefore p_{SO_3(\text{eq})} = 7.99 \times 10^{-2} \text{ atm}$$

$$SO_3 = SO_2 + \frac{1}{2} O_2 \quad \Delta\text{G}^\circ_{1223K} = -14699 \text{ J} \\ = -1223 \times 8.3144 \ln \frac{p_{SO_2} \cdot p_{O_2}^{\frac{1}{2}}}{p_{SO_3}}$$

$$\therefore \frac{p_{SO_2} \cdot p_{O_2}^{\frac{1}{2}}}{p_{SO_3}} = 4.244 \quad \text{and } p_{O_2} = \frac{1}{2} p_{SO_2}$$

$$\therefore 4.244 = \frac{p_{SO_2} [0.5 p_{SO_2}]^{\frac{1}{2}}}{7.99 \times 10^{-2}}$$

$$\therefore p_{SO_2} = 0.612$$

$$p_{O_2} = 0.306$$

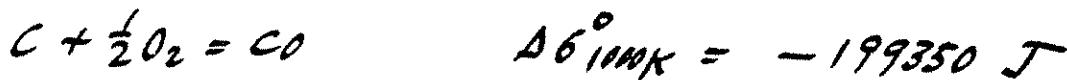
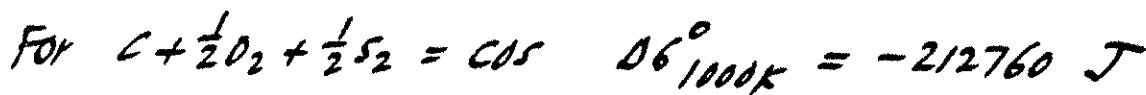
$$p_{SO_3} = 0.0799$$

$$\therefore P_T = 1.0 \text{ atm}$$

12.10 A gas mixture initially containing 90% CO, 0.4% COS and 9.6% inert constituents (v, volume) is passed over sponge iron at 1000 K to remove sulfur by the following reaction.



(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 S₂ in the effluent gas.

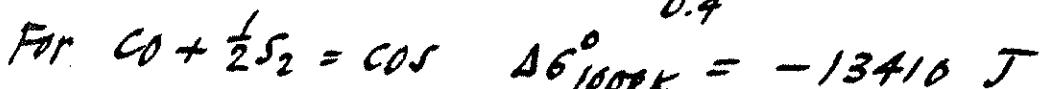


$$\text{and } K = \exp \left[\frac{-84240}{8.3144 \times 1000} \right] = 25130 = \frac{p_{\text{CO}}}{p_{\text{COS}}}$$

before	COS	+ Fe	= CO	+ FeS
	0.4		90	
after	0.4-x		90+x	

$$\therefore 25130 = \frac{p_{\text{CO}}}{p_{\text{COS}}} = \frac{90+x}{0.4-x} \quad \text{which gives } x = 0.3964$$

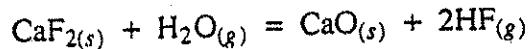
$$\therefore \% \text{ S removed} = \frac{0.3964}{0.4} \times 100 = 99.1$$



$$\therefore K_{1000} = 5.017 = \frac{p_{\text{COS}}}{p_{\text{CO}} \cdot p_{S_2}^{\frac{1}{2}}} = \frac{0.0036}{90.3964 p_{S_2}^{\frac{1}{2}}}$$

$$\therefore p_{S_2} = 6.3 \times 10^{-11} \text{ atm}$$

12.11 An Ar-H₂O gas mixture of $p_{H_2O} = 0.9 \text{ atm}$ ($P_{\text{total}} = 1 \text{ atm}$) is passed over solid CaF₂, as a result of which CaO forms according to



The reaction proceeds to equilibrium and solid CaO and solid CaF₂ 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.



$$\text{MW} \quad 78.08 \quad 56.08$$

\therefore A weight loss of 22 g produces 2HF and consumes 1 H₂O

\therefore A weight loss of 1 g produces 0.0709 HF and consumes 0.0455 H₂O
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 H₂O

In 60 l of gas in which $p_{H_2O} = 0.9 \text{ atm}$.

$$n_{H_2O} = \frac{0.9 \times 60}{0.082057 \times 298} = 2.208 \text{ moles}$$

\therefore consumption of 1.22×10^{-5} moles of H₂O is insignificant.

$$\therefore p_{HF} = \frac{2.44 \times 10^{-5} \times 0.082057 \times 298}{60} = 9.94 \times 10^{-6} \text{ atm}$$

$$\therefore K_{900} = \frac{p_{HF}^2}{p_{H_2O}} = \frac{(9.94 \times 10^{-6})^2}{0.9} = 1.09 \times 10^{-10}$$

$$\text{and } \Delta G^\circ_{900} = -8.3144 \times 900 \ln 1.09 \times 10^{-10} = 171596 \text{ J.}$$

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12.11 continued.

At 1100 K 0.0082 grams per hr

 = 7.545×10^{-4} mole/hr

$$\therefore P_{HF} = \frac{7.545 \times 10^{-4} \times 0.082057 \times 298}{60} = 3.075 \times 10^{-4} \text{ atm}$$

$$\therefore k_{1100} = \frac{(3.075 \times 10^{-4})^2}{0.9} = 1.051 \times 10^{-7} \quad \therefore \Delta G^\circ = 146962 \text{ J}$$

$$\begin{aligned}\Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\ &= A + BT\end{aligned}$$

$$\therefore 171596 = A + 900B$$

$$146962 = A + 1100B$$

$$\text{which gives } B = -123 \text{ J/K}$$

$$A = 282449 \text{ J.}$$

$$\therefore \Delta G^\circ = 282000 - 123T$$

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.

$$\text{For } 3\text{Fe} + 2\text{O}_2 = \text{Fe}_3\text{O}_4 \quad \Delta G_{800}^\circ = -856280 \text{ J} \\ = -8.3144 \times 800 \ln \frac{P_{\text{O}_2}}{P_{\text{O}_2}^0}$$

$$\therefore P_{\text{O}_2} \text{ in the exit gas} = 1.11 \times 10^{-28} \text{ atm.}$$

$$\text{For } \text{H}_2 + \frac{1}{2}\text{O}_2 = \text{H}_2\text{O} \quad \Delta G_{800}^\circ = -202560 \text{ J} \\ = -8.3144 \times 800 \ln \frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2} P_{\text{O}_2}}$$

$$\therefore \frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2} P_{\text{O}_2}} = 1.681 \times 10^{13} \quad \text{and} \quad \frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2}} = 0.1771 \quad - (i)$$

$$\text{For } 2\text{CO} + \text{O}_2 = 2\text{CO}_2 \quad \Delta G_{800}^\circ = -425904 \text{ J} \\ = -8.3144 \times 800 \ln \frac{P_{\text{CO}_2}}{P_{\text{CO}} P_{\text{O}_2}}$$

$$\therefore \frac{P_{\text{CO}_2}}{P_{\text{CO}} P_{\text{O}_2}} = 8.02 \times 10^{13} \quad \text{and} \quad \frac{P_{\text{CO}_2}}{P_{\text{CO}}} = 0.845 \quad - (ii)$$

$$P_{\text{H}_2} + P_{\text{H}_2\text{O}} + P_{\text{CO}} + P_{\text{CO}_2} = 1 \quad - (iii)$$

All of the C and the H in the gas come from the CH_4

$$\therefore \frac{n_C}{n_H} = \frac{1}{4} = \frac{P_{\text{CO}} + P_{\text{CO}_2}}{2P_{\text{H}_2} + 2P_{\text{H}_2\text{O}}}$$

$$\therefore P_{\text{H}_2\text{O}} + P_{\text{H}_2} = 2P_{\text{CO}} + 2P_{\text{CO}_2} \quad - (iv)$$

12.12 continued.

Solution of (i) - (iv) gives

$$pH_2 = 0.5662 \text{ atm}$$

$$pH_2O = 0.1003 \text{ atm}$$

$$pCO = 0.1806 \text{ atm}$$

$$pCO_2 = 0.1528 \text{ atm}$$

All of the C comes from $CH_4 \rightarrow 0.1806 + 0.1528 = 0.3334 \text{ moles}$

All of the O comes from $Fe_3O_4 \rightarrow 0.1003 + 0.1806 + 2 \times 0.1528$
= 0.5865 moles

$\therefore 0.3334 \text{ moles of } CH_4 \text{ per } \frac{3}{4} \times 0.5865 = 0.4398$
moles of Fe

or. 0.76 mole 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

$$\Delta G^\circ = -604000 - 5.36T \ln T + 142.0T \text{ J} \quad (\text{I})$$

$$\Delta G^\circ = -759800 - 13.4T \ln T + 317T \text{ J} \quad (\text{II})$$

and

$$\Delta G^\circ = -608100 - 0.44T \ln T + 112.8T \text{ J} \quad (\text{III})$$

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.

$$\text{I} \quad \frac{\Delta G^\circ}{T} = -\frac{604000}{T} - 5.36 \ln T + 142.0$$

$$\frac{\partial(\frac{\Delta G^\circ}{T})}{\partial T} = \frac{604000}{T^2} - \frac{5.36}{T} = -\frac{\Delta H^\circ}{T^2}$$

$$\therefore \Delta H_I^\circ = -60400 + 5.36T$$

$$\text{Similarly } \Delta H_{\text{II}}^\circ = -759800 + 13.4T$$

$$\text{and } \Delta H_{\text{III}}^\circ = -608100 + 0.44T$$

$$|\Delta H_{Mg(g)}^\circ| > |\Delta H_{Mg(l)}^\circ| > |\Delta H_{Mg(s)}^\circ|$$

∴ II is for oxidation of $Mg(g)$

III is for oxidation of $Mg(l)$

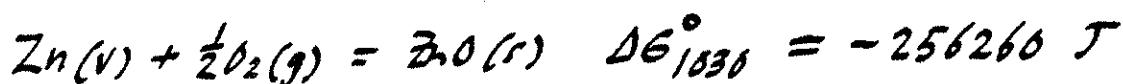
and I is for oxidation of $Mg(s)$

12.18 CONTINUED

$\Delta G_I^\circ = \Delta G_{II}^\circ$ at $T_m, Mg = 930 K$

$\Delta G_{II}^\circ = \Delta G_{III}^\circ$ at $T_b, Mg = 1372 K$

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.



$$\therefore K_{1030} = 9.9 \times 10^{12} = \frac{1}{P_{\text{Zn}} P_{\text{O}_2}}$$

$$\ln P_{\text{Zn}}^\circ (\text{atm}) = -\frac{15250}{T} - 1.255 \ln T + 21.79$$

$$\therefore \text{At } 1030 \text{ K}, P_{\text{Zn}}^\circ = 0.1787 \text{ atm}$$

$$\text{and } P_{\text{O}_2} = \left[\frac{1}{9.9 \times 10^{12} \times 0.1787} \right]^2 = 3.2 \times 10^{-25} \text{ atm}$$

$$2 \text{ moles air} \rightarrow 0.42 \text{ moles O}_2 + 1.58 \text{ moles N}_2$$

$$0.42 \text{ mole O}_2 + 0.84 \text{ mole Zn} \rightarrow 0.84 \text{ moles ZnO}$$

$$\text{and } 0.84 \text{ moles} \rightarrow 0.84 \times 65.38 = 54.92 \text{ g.}$$

$\therefore 54.92 \text{ g of Zn are oxidized to ZnO}$

$$1.58 \text{ moles of N}_2 \text{ at } 1030 \text{ K and } P_T = 0.8 \text{ atm}$$

$$\therefore P_{\text{N}_2} = 0.8 - 0.179 = 0.621 \text{ atm}$$

$$P_{\text{N}_2} V = n_{\text{N}_2} RT \quad \therefore \text{Volume of gas, } V = \frac{1.58 \times 0.082057 \times 1030}{0.621} \\ = 215 \text{ L}$$

$$P_{\text{Zn}} V = n_{\text{Zn}} RT \quad \therefore n_{\text{Zn}} = \frac{0.179 \times 215}{0.082057 \times 1030} = 0.455 \text{ moles}$$

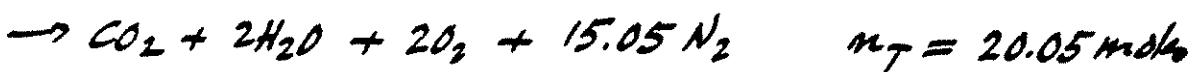
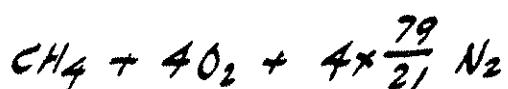
2.14 continued.

$$0.455 \text{ moles Zn} = 0.455 \times 65.38 = 29.78 \text{ g Zn}$$

∴ 29.78 g Zn are evaporated

$$\begin{aligned}\therefore \text{Liquid Zn remaining} &= 200 - 54.9 - 29.8 \\ &= 115.3 \text{ g}\end{aligned}$$

12.15 Methane gas is burned with twice the amount of stoichiometric air (i.e., the initial ratio of CH₄ to O₂ in the mixture is 0.25) and the combustion gas produced, in which the concentration of methane is negligible, is used to calcine CaCO₃ 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 CaCO₃ are decomposed per mole of CH₄ burned?



$$\text{In this gas } p_{CO_2} = \frac{1}{20.05} = 0.0499 \text{ atm}$$

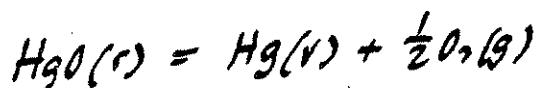
$$CaO + CO_2 = CaCO_3 \quad \Delta\text{f}_\text{1080}^\circ = -13124 \text{ J} \\ = 8.3144 \times 1080 \ln p_{CO_2}(at)$$

$\therefore p_{CO_2}(at) = 0.232$. The decomposition of x moles of CaCO₃ produces x moles of CO₂ and increases p_{CO_2} from 0.0499 to 0.232.

$$\text{i.e. } 0.232 = \frac{1+x}{20.05+x} \quad \therefore x = 4.76$$

and thus 4.76 moles of CaCO₃ are decomposed per mole of CH₄ 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 atm. Calculate the mole fractions of O_2 and Hg vapor in the gas phase.



$$\Delta G^\circ_{600} = 27880 \text{ J}$$

$$\therefore K = 3.74 \times 10^{-3} = p_{Hg} \cdot p_{O_2}^{\frac{1}{2}}$$

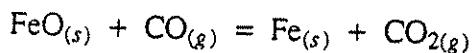
$$p_{O_2} = \frac{1}{2} p_{Hg} \quad \therefore 3.74 \times 10^{-3} = p_{Hg} [0.5 p_{Hg}]^{\frac{1}{2}}$$

$$\therefore p_{Hg} = 0.0304, \quad p_{O_2} = 0.0152, \quad p_{N_2} = 1.994$$

$$\therefore X_{Hg} = \frac{0.0304}{2} = 0.0152$$

$$X_{O_2} = \frac{0.0152}{2} = 0.0071$$

12.17 In Fig. 12.17 the line AB , which represents the equilibrium



intersects the carbon deposition line at the point A , ($T = 972\text{ K}$, $p_{\text{CO}} = 0.595\text{ atm}$, $p_{\text{CO}_2} = 0.405\text{ atm}$, $P = 1.000\text{ atm}$). 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?

$$\text{For } \text{FeO} + \text{CO} = \text{Fe} + \text{CO}_2 \quad \Delta\text{G}^\circ = -18700 + 224.7T \\ = -RT \ln \frac{p_{\text{CO}_2}}{p_{\text{CO}}}$$

\therefore At the total pressure P_T

$$\frac{2249}{T} - 2.70 = \ln \frac{p_{\text{CO}_2}}{p_{\text{CO}}} = \ln \left(\frac{P_T - p_{\text{CO}}}{p_{\text{CO}}} \right) \quad \text{(i)}$$

$$\text{For } \text{C} + \text{CO}_2 = 2\text{CO} \quad \Delta\text{G}^\circ = 170700 - 174.5T \\ = -RT \ln \frac{p_{\text{CO}}^2}{p_{\text{CO}_2}}$$

\therefore At the total pressure P_T

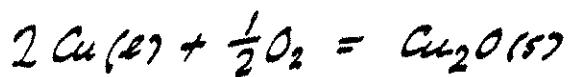
$$-\frac{20530}{T} + 20.99 = \ln \frac{p_{\text{CO}}^2}{P_T - p_{\text{CO}}} \quad \text{(ii)}$$

With $T = 1000\text{ K}$ Lines (i) and (ii) give

$$P_T = 1.651 \text{ and } p_{\text{CO}} = 1.009\text{ atm}$$

$$\therefore p_{\text{CO}_2} = 0.642\text{ atm}$$

- 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 Cu₂O), calculate the minimum activity of Cu which can be obtained in the solution.



$$\Delta G^\circ = -188300 + 88.487 T$$

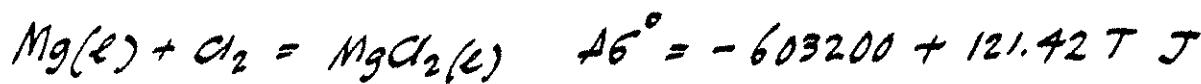
$$\Delta G_{1500K}^\circ = -55588 J = RT \ln \frac{a_{\text{Cu}}^2}{P_{\text{O}_2}}$$

$$\therefore a_{\text{Cu}}^2 (0.21)^{\frac{1}{2}} = 0.0116$$

$$a_{\text{Cu}}^2 = 0.025$$

$$a_{\text{Cu}} = 0.159$$

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 $800^\circ C$ 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 $MgCl_2$.



$$\Delta G_{1073}^\circ = -472916 \text{ J}$$



$$\Delta G_{1073}^\circ = -201933 \text{ J}$$



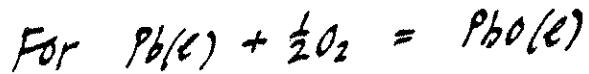
$$\Delta G_{1073}^\circ = -270983$$

$$= RT \ln \frac{a_{Mg} \cdot p_{HCl}^2}{p_{H_2}}$$

$$\frac{a_{Mg} p_{HCl}^2}{p_{H_2}} = 6.43 \times 10^{-14} = \frac{a_{Mg} \cdot (10^{-5})^2}{1}$$

$$\therefore a_{Mg} = 6.4 \times 10^{-4}$$

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.

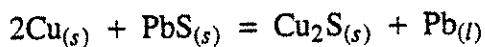


$$K_{1200\text{K}} = \frac{\alpha_{\text{PbO}}}{\alpha_{\text{Pb}} \rho_{\text{O}_2}^{1/2}} = \frac{1}{1 \times (2.16 \times 10^{-9})^{1/2}} = 21517$$

With $\alpha_{\text{Pb}} = 1$ and $\rho_{\text{O}_2(\text{eq})} = 5.41 \times 10^{-10}$ atm

$$\alpha_{\text{PbO}} = 21517 \times (5.41 \times 10^{-10})^{1/2} = 0.5$$

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

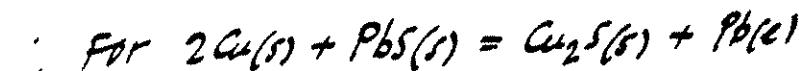
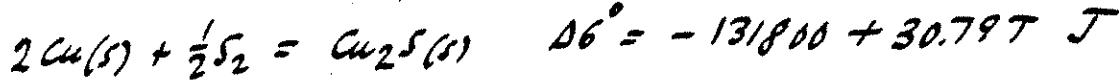


to come to equilibrium.

The solid sulfides are mutually immiscible, Pb is insoluble in solid Cu, and the Cu liquidus, below 850°C, can be represented by

$$\log X_{\text{Cu}} = -\frac{3500}{T} + 2.261$$

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?



$$\Delta G^\circ = 31400 - 57.24T$$

$$\Delta G_{1073}^\circ = -30019 \text{ J} = -RT \ln K$$

$$K = 28.93 = \frac{\alpha_{\text{Pb}}(l)}{\alpha_{\text{Cu}}^2(s)}$$

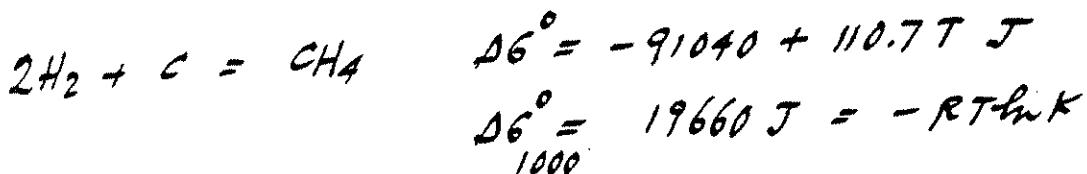
$$\text{At } 1073 \text{ K, } X_{\text{Cu}(\text{liquidus})} = 0.0998 \quad \therefore \delta_{\text{Cu}} = \frac{1}{0.0998} = 10.02$$

$$\therefore \alpha_{\text{Cu}} = 10.02 X_{\text{Cu}} \text{ and } \alpha_{\text{Pb}} = (1 - X_{\text{Cu}})$$

$$\therefore 28.93 = \frac{1 - X_{\text{Cu}}}{100.4 X_{\text{Cu}}} \quad \text{which gives } X_{\text{Cu}} = 0.018$$

At 850°C $X_{\text{Cu}} = 0.024 \quad \therefore \text{Extent of purification is increased by decreasing the temperature.}$

13.5 A $\text{CH}_4\text{-H}_2$ gas mixture at 1 atm total pressure, in which $p_{\text{H}_2} = 0.957 \text{ atm}$, 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 $P_{\text{total}} = 1 \text{ atm}$) have to be in order to saturate the Fe with graphite at 1000 K?



$$\therefore K = 9.40 \times 10^{-2} = \frac{p_{\text{CH}_4}}{a_c p_{\text{H}_2}^2} = \frac{0.043}{(0.957)^2 a_c} \quad \therefore a_c = 0.5$$

For $a_c = 1$ and $P_T = 1 \text{ atm}$

$$9.40 \times 10^{-2} = \frac{p_{\text{CH}_4}}{(1 - p_{\text{CH}_4})^2} \quad \text{which gives}$$

$$p_{\text{H}_2} = 0.92 \text{ atm}$$

$$p_{\text{CH}_4} = 0.08 \text{ atm}$$

13.6 Calculate the activity of FeO in an FeO-Al₂O₃-SiO₂ melt below which the FeO cannot be reduced to pure liquid iron by a CO-CO₂ mixture of $p_{CO}/p_{CO_2} = 10^5$ at 1600°C.

$$\Delta\text{H}_{1873}^\circ, \text{J}$$

$$\text{FeO}(l) \quad -155557$$

$$\text{CO} \quad -275868$$

$$\text{CO}_2 \quad -395673$$



$$\Delta\text{H}_{1873}^\circ = -35753 \text{ J} = -RT \ln K$$

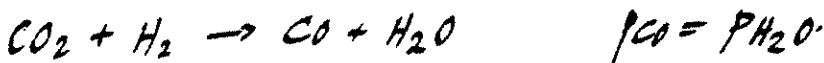
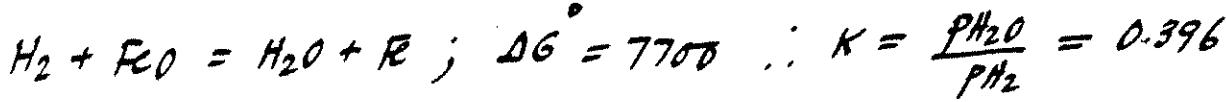
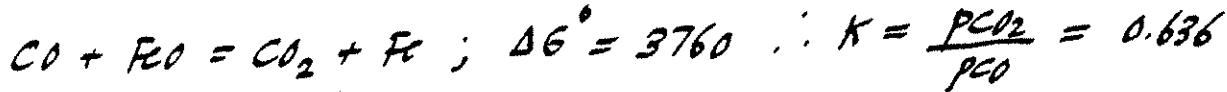
$$\therefore K = 9.93 = \frac{\alpha_{\text{FeO}} \cdot p_{\text{CO}}}{\alpha_{\text{Fe}} \cdot p_{\text{CO}_2}} = \alpha_{\text{FeO}} \times 10^5$$

$$\therefore \alpha_{\text{FeO}} = 9.9 \times 10^{-5}$$

- 13.7 A piece of iron is to be heat-treated at 1000 K in a CO-CO₂-H₂O-H₂ gas mixture at 1 atm pressure. The gas mixture is produced by mixing CO₂ and H₂ and allowing the equilibrium CO₂ + H₂ = CO + H₂O to establish. Calculate (i) the minimum H₂/CO₂ 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 H₂/CO₂ 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)

	$\Delta G^\circ_{1000K}, J$
CO	- 199350
CO ₂	- 394940
H ₂ O(g)	- 191650
FeO	- 199350



$$PCO + PCO_2 + PH_2 + PH_2O = 1 \text{ atm.}$$

$$PCO + 0.636 PCO + \frac{PH_2O}{0.396} + PH_2O = 1$$

$$\therefore PCO [1 + 0.636 + \frac{1}{0.396} + 1] = 1$$

$$\therefore PCO = 0.1938$$

$$PH_2O = 0.1938$$

$$PH_2 = 0.4894$$

$$PCO_2 = \underline{0.1233}$$

$$P_T = 1.0003$$

This gas is in equilibrium with Fe and FeO

13.7 continued

Mix CO_2 and H_2 in the ratio $\frac{\text{CO}_2}{\text{H}_2} = x$.



before	x	1	0	0	$\therefore p_{\text{CO}} = \frac{x}{1+x}$
after	$x-a$	$1-a$	a	a	$p_{\text{H}_2\text{O}} = \frac{a}{1+x}$
					$p_{\text{H}_2} = \frac{1-a}{1+x}$

$$p_{\text{CO}_2} = \frac{x-a}{1+x}$$

For equilibrium with Fe and FeO : $\frac{p_{\text{CO}_2}}{p_{\text{CO}}} = 0.636 = \frac{x-a}{a}$

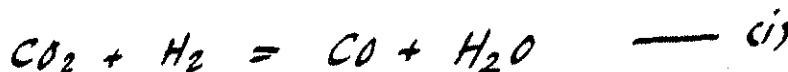
$$\frac{p_{\text{H}_2\text{O}}}{p_{\text{H}_2}} = 0.396 = \frac{a}{1-a} \quad \text{which gives } a = 0.2837$$

and $x = 0.4641 = \frac{\text{CO}_2}{\text{H}_2}$ / initial

For $\text{Fe} + \frac{1}{2}\text{O}_2 = \text{FeO}$ $\Delta G^\circ_{1000} = -199350 \text{ J} = \frac{1}{2}RT \ln p_{\text{O}_2}$

$$\therefore p_{\text{O}_2}(\text{Fe/FeO}) = 1.494 \times 10^{-21} \text{ atm.}$$

Choose a larger value of x , say $x = 1$, then.



before	1	1	0	0
after	$1-a$	$1-a$	a	a

$$\therefore p_{\text{CO}} = \frac{a}{2} = p_{\text{H}_2\text{O}} ; \quad p_{\text{CO}_2} = \frac{1-a}{2} = p_{\text{H}_2}$$

$$\Delta G^\circ_{(i),1000} = 3940 = -RT \ln \frac{p_{\text{CO}} \cdot p_{\text{H}_2\text{O}}}{p_{\text{CO}_2} p_{\text{H}_2}}$$

$$\therefore 0.6226 = \frac{a^2}{(1-a)^2} \quad \text{which gives } a = 0.441$$

$$\begin{aligned} \therefore p_{CO} &= 0.2205 & \frac{p_{CO_2}}{p_{CO}} &= 1.268 \\ p_{CO_2} &= 0.2795 \end{aligned}$$

$$\text{For } CO + \frac{1}{2}O_2 = CO_2 \quad K_{1000} = 1.64 \times 10^{-10} = \frac{p_{CO_2}/_2}{p_{CO} \cdot p_{O_2}}$$

$$= \frac{1.268}{p_{O_2}^{1/2}}$$

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 $\frac{CO_2}{H_2}$ /initial or 2.155 is the minimum allowable ratio of $\frac{H_2}{CO_2}$ /initial.

ii) $C + CO_2 = 2CO \quad \Delta G_{1000}^{\circ} = -3760 = -RT \ln \frac{p_{CO}^2}{p_{CO_2} \alpha_C}$

$$\therefore \frac{p_{CO}^2}{p_{CO_2} \alpha_C} = 1.572 = \frac{0.1938^2}{0.1233 \cdot \alpha_C} \quad \text{which gives } \alpha_C = 0.194$$

iii) For $\alpha_C = 1$ and pressure P.

$$1.572 = \frac{0.1938^2 P}{0.1233} \quad \text{which gives } P = 5.16 \text{ atm.}$$

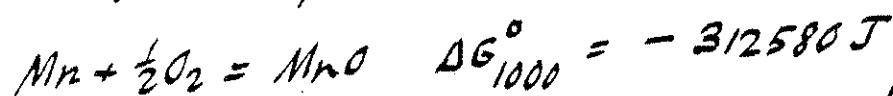
iv) The values of the ratios $\frac{p_{CO_2}}{p_{CO}}$ and $\frac{p_{H_2O}}{p_{H_2}}$ are not functions of the total pressure P.

- 13.8 An Fe-Mn solid solution containing $X_{\text{Mn}} = 0.001$ 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.

$$C = 3 (\text{Fe, Mn, O}) \quad P = 3 (\text{metal, oxide, gas})$$

$$\therefore F = C + 2 - P = 3 + 2 - 3 = 2$$

Fixing the temperature at 1000 K leaves 1 degree of freedom



$$\therefore K_{\text{Mn}} = 2.124 \times 10^{16} = \frac{x_{\text{MnO}}}{x_{\text{Mn}} \cdot P_{\text{O}_2}}$$



$$K_{\text{Fe}} = 2.587 \times 10^{10} = \frac{x_{\text{FeO}}}{x_{\text{Fe}} \cdot P_{\text{O}_2}}$$

$$\frac{K_{\text{Mn}}}{K_{\text{Fe}}} = 821215 = \frac{x_{\text{MnO}} x_{\text{Fe}}}{x_{\text{Mn}} x_{\text{FeO}}} = \frac{(1-x_{\text{FeO}}) 1.999}{0.001 x_{\text{FeO}}} \quad \text{which}$$

$$\text{gives } x_{\text{FeO}} = 1.22 \times 10^{-3}$$

$$\text{Then } K_{\text{Fe}} = 2.587 \times 10^{10} = \frac{1.22 \times 10^{-3}}{0.999 P_{\text{O}_2}}$$

$$\text{gives } P_{\text{O}_2} = 2.23 \times 10^{-27} \text{ atm.}$$

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, $B_{(s)} = B_{(v)}$

$$\Delta G^\circ = 187220 - 108.8T \text{ J}$$

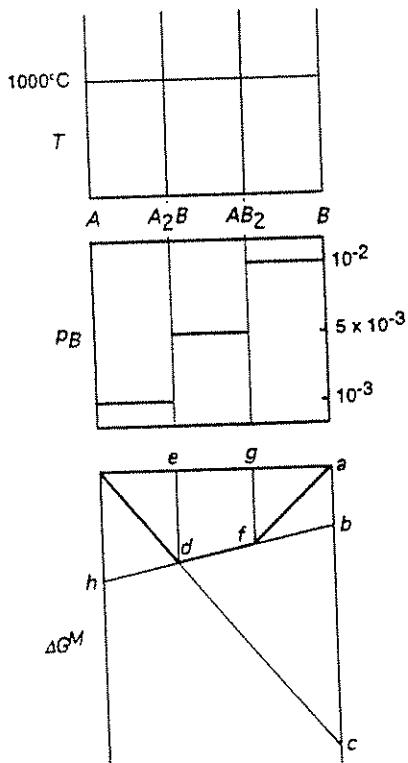
The vapor pressure exerted by an equilibrated AB_2 - A_2B mixture is given by

$$\log p(\text{atm}) = -\frac{11242}{T} + 6.53$$

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 .



$$a_B \text{ in } A_2B-AB_2 \text{ mixture} = \frac{5 \times 10^{-3}}{10^{-2}} = 0.5$$

$$\therefore ab = RT \ln a_B = -7336 \text{ J}$$

$$a_B \text{ in } A-A_2B \text{ mixture} = \frac{10^{-3}}{10^{-2}} = 0.1$$

$$\therefore ac = RT \ln a_B = -24371 \text{ J}$$

$$\therefore ed = \frac{-24371}{3} = -8123 \text{ J}$$

$$\therefore \text{For } 2A + B = A_2B$$

$$\Delta G^\circ = 3 \times ed = -24370 \text{ J}$$

$$gf = \frac{ed+ab}{2} = -7730$$

$$\text{For } A + 2B = AB_2$$

$$\Delta G^\circ = 3 \times gf = -23190 \text{ J}$$

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^0 at 1600°C. If a liquid Fe-V solution is equilibrated with pure solid VO and a gas containing $p_{O_2} = 4.72 \times 10^{-10} \text{ atm}$, 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.

$$V(s) \rightarrow V(1 \text{ wt\%}) \quad \Delta G^\circ_{1873} = RT \ln \frac{\delta_V^0}{100 \times 50.94} \quad \therefore \delta_V^0 = 0.14$$

$$V(s) + \frac{1}{2}O_2 = VO(s) \quad \Delta G^\circ_{1873} = -274785 = -RT \ln \frac{1}{a_{V(s)} [4.72 \times 10^{-10}]^{1/2}}$$

$$\therefore a_{V(s)} = 10^{-3}$$

$$V(s) \rightarrow V(l) \quad \Delta G^\circ = 22840 - \frac{22840}{2193} 1873 = 3333 \text{ J}$$

$$\therefore V(l) + \frac{1}{2}O_2 = VO(s) \quad \Delta G^\circ_{1873} = -274785 - 3333 = -278118 \text{ J}$$

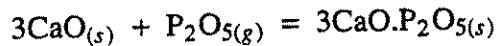
$$= -RT \ln \frac{1}{a_{V(l)} [4.72 \times 10^{-10}]^{1/2}} \quad \therefore a_{V(l)} = 8.07 \times 10^{-4}$$

$$a_{V(s)} = h_V \delta_V^0 \quad \therefore h_V = \frac{10^{-3}}{0.14} = 7.13 \times 10^{-3}$$

$$\frac{h_V(1\%)}{h_V} = \frac{50.95 \times 100}{55.85} = 91.24$$

$$\therefore h_V(1\%) = 91.24 \times 7.13 \times 10^{-3} = 0.65.$$

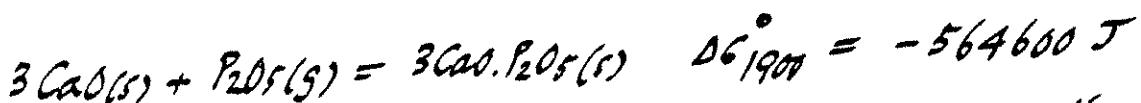
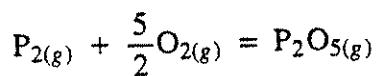
13.11 When an Fe-P liquid solution is equilibrated at 1900 K with solid CaO, solid $3\text{CaO.P}_2\text{O}_5$ and a gas phase containing $p_{\text{O}_2} = 10^{-10}$ atm, the activity of P in the iron, with respect to the 1 wt% in Fe standard state, is 20. Given that $\Delta G_{1900\text{K}}^{\circ} = -564600 \text{ J}$ for



and $\Delta G^{\circ} = -122200 - 19.22T \text{ J}$ for

$$\frac{1}{2}\text{P}_{2\text{O}_{5(g)}} = \text{P}_{(\text{1 wt\% in Fe})}$$

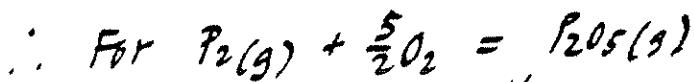
calculate $\Delta G_{1900\text{K}}^{\circ}$ for the reaction



$$\therefore K = 3.325 \times 10^{15} = \frac{1}{p_{\text{P}_2\text{O}_5}} \quad \therefore p_{\text{P}_2\text{O}_5} = 3 \times 10^{-16} \text{ atm.}$$

$$\frac{1}{2}\text{P}_{2\text{O}_{5(g)}} = \text{P}_{(\text{1 wt\%})} \quad \Delta G^{\circ} = -158680 \text{ J}$$

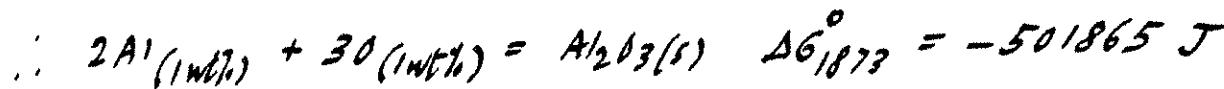
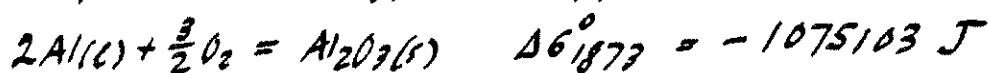
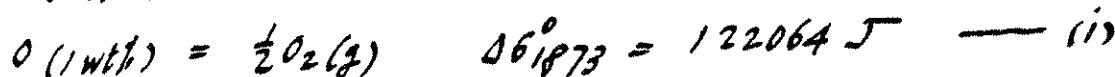
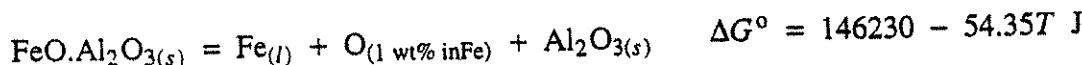
$$\therefore K = 2.303 \times 10^4 = \frac{h_p(\%)}{p_{\text{P}_2}^{1/2}} = \frac{20}{p_{\text{P}_2}^{1/2}} \quad \therefore p_{\text{P}_2} = 7.539 \times 10^{-7} \text{ atm}$$



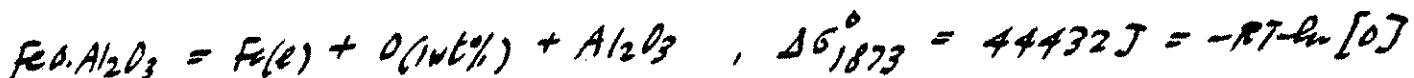
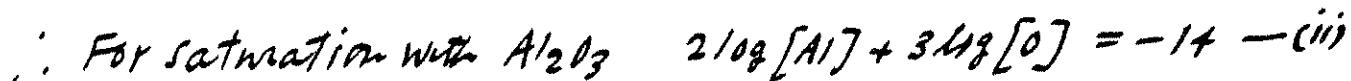
$$K = \frac{3 \times 10^{-16}}{7.539 \times 10^{-7} \times [10^{-10}]^{5/2}} = 3.99 \times 10^{15}$$

$$\therefore \Delta G^{\circ} = -RT \ln K = -567500 \text{ J.}$$

13.12 Liquid iron, contained in an Al_2O_3 crucible under a gaseous atmosphere of $p_{\text{O}_2} = 3 \times 10^{-12}$ 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 ($\text{FeO}\cdot\text{Al}_2\text{O}_3$) 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



$$= 8.3144 \times 1873 \times 2.303 \log [\text{O}]^3 [\text{Al}]^2$$



$$\therefore [\text{O}] = 5.77 \times 10^{-2} \text{ wt\%}$$

$$\text{From (i)} \quad 122064 = -RT \ln \frac{\frac{1}{2} p_{\text{O}_2}}{[\text{O}]} \quad \therefore \frac{\frac{1}{2} p_{\text{O}_2}}{[\text{O}]} = 3.944 \times 10^{-4}$$

$$\therefore p_{\text{O}_2} = 5.17 \times 10^{-10} \text{ atm}$$

$$\text{and, from (ii)} \quad [\text{Al}] = 7.215 \times 10^{-6} \text{ wt\%}$$

$$c = 3 (\text{Al}, \text{Fe}, \text{O}) : P = 4 (\text{metal, Al}_2\text{O}_3, \text{FeO}\cdot\text{Al}_2\text{O}_3, \text{gas})$$

$$\therefore F = c + 2 - P = 1 \quad \text{which is specified by selecting } T = 1600^\circ\text{C}$$

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.

$$\text{U} + \text{C} = \text{UC} \quad \Delta G^\circ = -102900 + 5.02T \text{ J}$$

$$2\text{U} + 3\text{C} = \text{U}_2\text{C}_3 \quad \Delta G^\circ = -236800 + 25.1T \text{ J}$$

$$\text{U} + 2\text{C} = \text{UC}_2 \quad \Delta G^\circ = -115900 + 10.9T \text{ J}$$

$$\therefore \text{UC} + \text{C} = \text{UC}_2 \quad \Delta G^\circ = -13000 + 5.88T$$

$$= 0 \text{ at } T = 2211 \text{ K}$$

At $T > 2211$ UC_2 metastable w.r.t. $\text{UC} + \text{C}$

$$\text{U}_2\text{C}_3 + \text{C} = 2\text{UC}_2 \quad \Delta G^\circ = 5000 - 3.3T$$

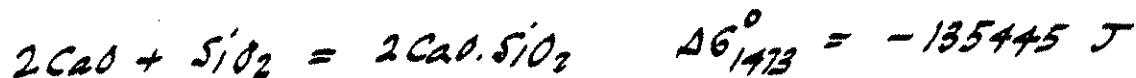
$$= 0 \text{ at } T = 1515 \text{ K}$$

\therefore At $T < 1515 \text{ K}$. UC_2 metastable w.r.t. $\text{U}_2\text{C}_3 + \text{C}$

$$\therefore T_{\max} = 2211 \text{ K}$$

$$T_{\min} = 1515 \text{ K}$$

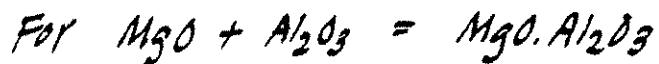
13.14 In the Pigeon process for the production of magnesium, dolomite ($\text{CaO}\cdot\text{MgO}$) is reduced by silicon to form magnesium vapor and $2\text{CaO}\cdot\text{SiO}_2$. Calculate the equilibrium pressure of magnesium vapor produced by this reaction at 1200°C . The Gibbs free energy of formation of dolomite from CaO and MgO is small enough that it can be ignored.



$$\therefore \Delta G_{(i)}^\circ = 71973 \text{ J} = -RT\ln \bar{P}_{\text{Mg}}^2$$

$$\therefore \bar{P}_{\text{Mg}} = 0.053 \text{ atm}$$

13.15 What is the minimum value that the activity of MgO can have in MgO-Al₂O₃ at 1000°C?



$$\Delta G^\circ_{1273} = -38220 = -RT \ln \frac{a_{\text{MgO}\cdot\text{Al}_2\text{O}_3}}{a_{\text{MgO}} a_{\text{Al}_2\text{O}_3}}$$

The minimum activity of MgO in MgO·Al₂O₃ occurs when it is saturated with Al₂O₃ at $a_{\text{Al}_2\text{O}_3} = 1$.

$$\therefore \text{With } a_{\text{MgO}\cdot\text{Al}_2\text{O}_3} = a_{\text{Al}_2\text{O}_3} = 1$$

$$a_{\text{MgO}} = 0.027$$

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 CO₂ that are developed.



$$\Delta\text{f}_\text{1200}^\ominus = 5720 \text{ J} = -R7 \ln p_{Zn} \cdot p_{CO}$$

$$\therefore p_{Zn} p_{CO} = 0.564$$



$$\Delta\text{f}_\text{1200}^\ominus = 50092 \text{ J} = -R7 \ln p_{Zn}^2 \cdot p_{CO_2}$$

$$\therefore p_{Zn}^2 p_{CO_2} = 6.60 \times 10^{-3}$$

In the gas phase

$$\frac{n_{Zn}}{n_0} = 1 = \frac{p_{Zn}}{p_{CO} + p_{CO_2}} \quad \therefore p_{Zn} = p_{CO} + 2p_{CO_2}$$

$$\therefore p_{CO}(p_{CO} + 2p_{CO_2}) = 0.564$$

$$p_{CO_2}(p_{CO} + 2p_{CO_2})^2 = 6.60 \times 10^{-3}$$

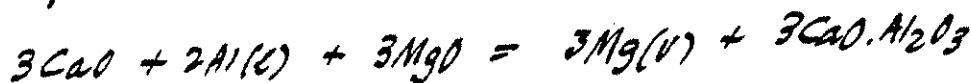
which gives $p_{CO} = 0.763 \text{ atm}$

$$p_{CO_2} = 0.0114 \text{ atm}$$

$$p_{Zn} = 0.763 \text{ atm}$$

13.17 An assemblage of solid CaO, MgO, $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ 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 $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ from CaO and Al_2O_3 and the activity of Al_2O_3 in CaO-saturated $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ at 1300 K.

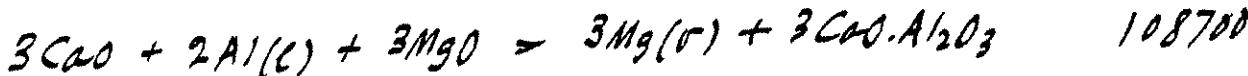
The equilibrium is



$$\text{for which } K = p_{\text{Mg}}^3 = 0.035^3 = 4.288 \times 10^{-5}$$

$$\therefore \Delta G^\circ_{1300} = -8.3144 \times 1300 \ln 4.288 \times 10^{-5} \text{ J} \\ = 108700 \text{ J}$$

$$\Delta G^\circ_{1300}, \text{J}$$



$$\therefore \text{With } a_{\text{CaO} \cdot \text{Al}_2\text{O}_3} = a_{\text{CaO}} = 1$$

$$-22140 = -RT \ln \frac{1}{a_{\text{Al}_2\text{O}_3}}$$

$$\text{and } a_{\text{Al}_2\text{O}_3} = 0.129$$

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.

$$\begin{aligned}
 (i) \quad & 2Al(s) + \frac{3}{2}O_2 = Al_2O_3 & \Delta G^\circ_{1873, J} \\
 & -1075103 & \\
 & 2[Al] = 2Al(s) & +267045 \\
 & 3[O] = \frac{3}{2}O_2 & +366193 \\
 \therefore & 2[Al] + 3[O] = Al_2O_3 & \Delta G^\circ_{1873} = -501864 J \\
 & & = RT \ln [\% Al]^2 [\% O]^3 \\
 & \therefore 2\log[\% Al] + 3\log[\% O] = -13.996 \quad — (i) \\
 & C + \frac{1}{2}O_2 = CO & \Delta G^\circ_{1873, J} \\
 & [O] = \frac{1}{2}O_2 & -275868 \\
 & [C] = C_{gr.} & +122064 \\
 & [C] + [O] = CO & +56552 \\
 & & \Delta G^\circ = -97250 \\
 & & = -RT \ln \frac{p_{CO}}{[\% C][\% O]}
 \end{aligned}$$

$$\text{with } p_{CO} = 1 \text{ atm}, \log[\% C] + \log[\% O] = -2.716 \quad — (ii)$$

$$\therefore \log[\% O] = -2.716 - \log 0.5 = -2.414 \quad \text{and } [\% O] = 0.00385$$

$$\log[\% Al] = \frac{-13.996 - 3(-2.414)}{2} = -3.377 \quad \text{and } [\% Al] = 0.00042$$

(ii)

$$\text{Eq(i) becomes } 2\log[\text{thc}] + 3\log[\text{th}_0] = -13.996$$

$$\text{Eq (ii) becomes } 2\log[\text{thc}] + \log[\text{th}_0] = -2.716$$

$$\log f_c = e_c^c[c] + e_c^o[0] + e_c^{A1}[\text{Ac}]$$

$$\log f_0 = e_o^o[0] + e_o^c[c] + e_o^{A1}[\text{Ac}]$$

$$\log f_{\text{Ac}} = e_{\text{Ac}}^{A1}[\text{Ac}] + e_{\text{Ac}}^c[c] + e_{\text{Ac}}^o[0]$$

$$\text{where } e_c^c = 22 \times 10^{-2} \quad e_o^o = -20 \times 10^{-2} \quad e_{\text{Ac}}^{A1} = 4.8 \times 10^{-2}$$

$$e_c^o = -9.7 \times 10^{-2} \quad e_o^c = -13.8 \times 10^{-2} \quad e_{\text{Ac}}^c = 11 \times 10^{-2}$$

$$e_c^{A1} = 4.8 \times 10^{-2} \quad e_o^{A1} = -94 \times 10^{-2} \quad e_{\text{Ac}}^o = -160 \times 10^{-2}$$

$$\therefore 2[\log f_{\text{Ac}} + \log[\text{Ac}]] + 3[\log f_0 + \log[0]] = -13.996$$

$$\text{or } 2\{e_{\text{Ac}}^{A1}[\text{Ac}] + e_{\text{Ac}}^c[c] + e_{\text{Ac}}^o[0] + \log[\text{Ac}]\}$$

$$+ 3\{e_o^o[0] + e_o^c[c] + e_o^{A1}[\text{Ac}] + \log[0]\} = -13.996$$

$$\log f_c + \log[c] + \log f_0 + \log[0] = -2.712$$

$$\text{or } e_c^c[c] + e_c^o[0] + e_c^{A1}[\text{Ac}] + \log[c]$$

$$+ e_o^o[0] + e_o^c[c] + e_o^{A1}[\text{Ac}] + \log[0] = -2.712$$

13.18 continued

$$\therefore 2 \{ 4.8 \times 10^{-2} [AC] + 11 \times 10^{-2} [C] - 160 \times 10^{-2} [O] + \log [AC] \} \\ + 3 \{ -20 \times 10^{-2} [O] - 13 \times 10^{-2} [C] - 94 \times 10^{-2} [AC] + \log [O] \} \\ = -13.996$$

and $22 \times 10^{-2} [C] - 9.7 \times 10^{-2} [O] + 4.8 \times 10^{-2} [AC] + \log [C] \\ - 20 \times 10^{-2} [O] - 13 \times 10^{-2} [C] - 94 \times 10^{-2} [AC] + \log [O] \\ = -2.712$

With $[C] = 0.5$.

$$\%AC = 0.000541$$

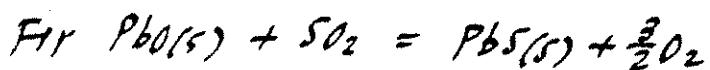
$$\%O = 0.00351$$

13.19 It is required that PbO be eliminated from an ore containing PbO, PbS and PbSO₄ by converting it to PbS or PbSO₄ by reaction with an SO₂-O₂ gas. Although the pressure of O₂ in the gas can vary within wide limits, the partial pressure of SO₂ 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.



$$\Delta G^\circ = -401200 + 261.5T = RT \ln p_{SO_2} \cdot p_{O_2}^{\frac{1}{2}}$$

$$\therefore -\frac{48253}{T} + 31.45 = \ln p_{SO_2} + \frac{1}{2} \ln p_{O_2} \quad \text{--- (i)}$$



$$\Delta G^\circ = 407200 - 80.6T = -RT \ln \frac{P_{O_2}^{3/2}}{P_{SO_2}}$$

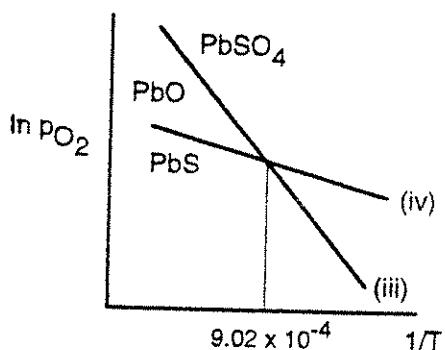
$$\therefore -\frac{48975}{T} + 9.69 = \frac{3}{2} \ln p_{O_2} - \ln p_{SO_2} \quad \text{--- (ii)}$$

With P_{SO₂} = 0.5 atm. (i) becomes

$$\ln p_{O_2} = -\frac{96506}{T} + 63.59 \quad \text{--- (iii)}$$

and (ii) becomes

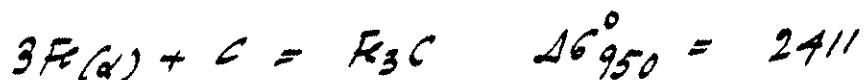
$$\ln p_{O_2} = -\frac{32650}{T} + 5.998 \quad \text{--- (iv)}$$



(iii) and (iv) intersect at $\frac{1}{T} = 9.02 \times 10^{-4}$
 $\ln p_{O_2} = -23.46$

\therefore PbO is not stable at $T > 1108K$
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 $23.92 \text{ cm}^3/\text{mole}$, calculate the pressure, at 950 K, at which Fe_3C is in equilibrium with carbon-saturated α -Fe and graphite.



$$V_{\text{Fe}} = 7.32 \text{ cm}^3/\text{mole}$$

$$V_{\text{gr}} = 5.40 \text{ cm}^3/\text{mole}$$

$$V_{\text{Fe}_3\text{C}} = 23.92 \text{ cm}^3/\text{mole}$$

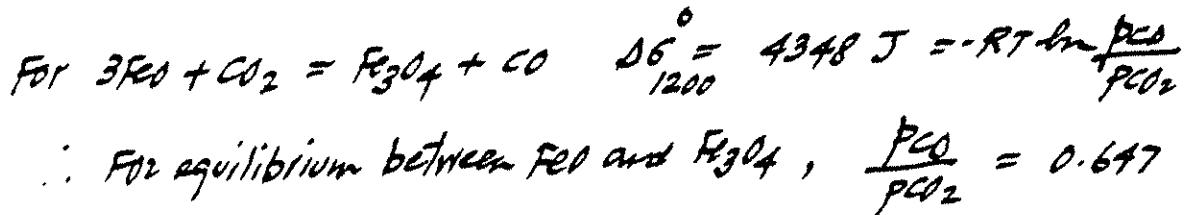
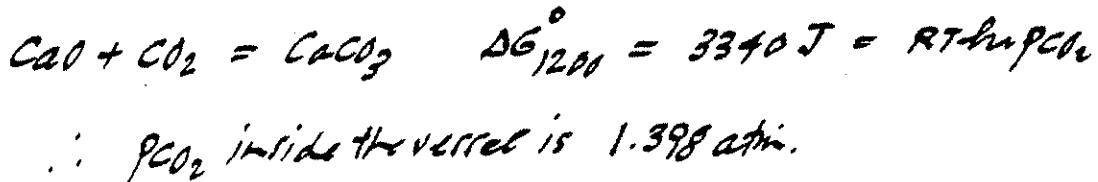
$$\therefore \Delta V = 23.92 - 5.40 - 3 \times 7.32 = -3.44 \text{ cm}^3/\text{mole}.$$

\therefore Equilibrium occurs at the pressure P at which

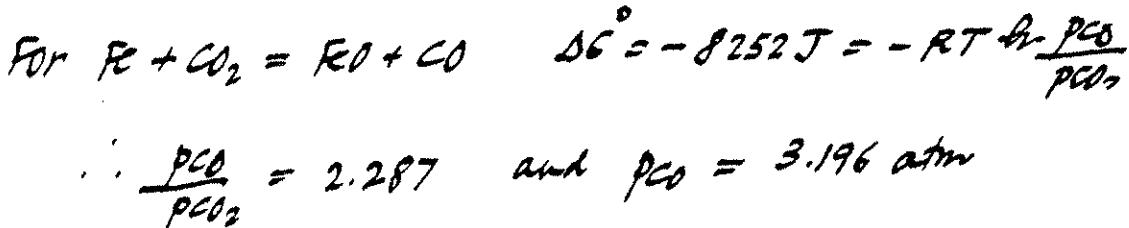
$$2411 = 3.44 (P - 1) \times \frac{8.3144}{82.057}$$

$$\text{i.e. } P = 6917 \text{ atm}$$

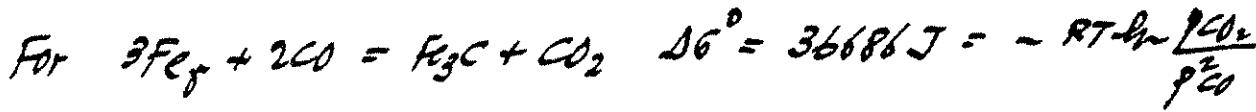
13.21 An experiment is being conducted on an equilibrated mixture of CaO and CaCO_3 contained in a closed vessel at 1200 K. The mixture is contaminated by iron in the form of hematite (Fe_2O_3). The contaminant would not be harmful to the experiment if it occurred as either wustite (FeO) or as cementite (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.



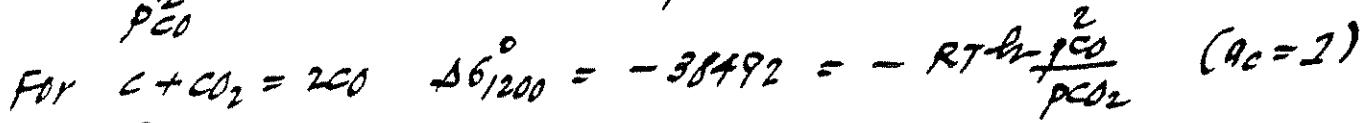
$$\text{or } p_{\text{CO}} = 0.904 \quad \therefore \text{For FeO to be stable } p_{\text{CO}} > 0.904$$



$$\therefore \text{For FeO to be stable} \quad 3.196 > p_{\text{CO}} > 0.904$$



$$\therefore \frac{p_{\text{CO}_2}}{p_{\text{CO}}^2} = 2.53 \times 10^{-2} \quad \text{and } p_{\text{CO}} = 7.43 \text{ atm}$$



$$\therefore \frac{p_{\text{CO}}^2}{p_{\text{CO}_2}} = 47.4 \quad \text{and } p_{\text{CO}} = 8.14$$

$$\therefore \text{For Fe}_3\text{C} \text{ to be stable} \quad 8.14 > p_{\text{CO}} > 7.43$$

13.22 A Cu-Au alloy of $X_{\text{Cu}} = 0.5$ 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

$$G^{\text{xs}} = -28280X_{\text{Cu}}X_{\text{Au}} \text{ J}$$

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.

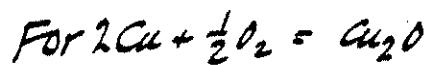
$$2\text{Cu} + \frac{1}{2}\text{O}_2 = \text{Cu}_2\text{O} \quad \Delta G^\circ_{298} = -101753 \text{ J} = RT \ln \frac{P_{\text{O}_2}^{1/2} \alpha_{\text{Cu}}^2}{P_{\text{O}_2}^0}$$

$$\therefore \alpha_{\text{Cu}}^2 P_{\text{O}_2}^{1/2} = 8.162 \times 10^{-7}$$

$$\Delta = -28280 \text{ J} \quad RT \ln \gamma_{\text{Cu}} = \Delta X_{\text{Au}}^2 \quad \therefore \ln \gamma_{\text{Cu}} = \frac{-28280 \times 0.5}{8.3144 \times 873}^2$$

$$= -0.974 \quad \therefore \gamma_{\text{Cu}} = 0.378, \alpha_{\text{Cu}} = 0.378 \times 0.5 = 0.1888 \text{ and}$$

the oxygen pressure for equilibrium between the Cu-Au alloy and Cu_2O
is $P_{\text{O}_2} = \left[\frac{8.162 \times 10^{-7}}{0.1888} \right]^2 = 5.24 \times 10^{-10} \text{ atm.}$



$$\Delta G^\circ = -162200 + 69.24T = 8.3144 T \ln \left[5.24 \times 10^{-10} \right]^{1/2}$$

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

$$\ln p_{Zn}^{\circ} = -\frac{15250}{1013} - 1.255 \ln 1013 + 21.79$$

$$\therefore p_{Zn, 1013K}^{\circ} = 0.142 \text{ atm}$$

At 900°C

$$\ln p_{Zn}^{\circ} = -\frac{15250}{1173} - 1.255 \ln 1173 + 21.79$$

$$\therefore p_{Zn, 1173K}^{\circ} = 0.923 \text{ atm.}$$

$$\therefore \alpha_{Zn} (\text{in the alloy}) = \frac{0.142}{0.923} = 0.154$$

.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 cms³ (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 cms³ (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 O₂ required to fill the chamber:

$$n_{O_2} = \frac{251.5}{82.057 \times 273} = 1.123 \times 10^{-2}$$

∴ number of moles of O₂ dissolved in liquid Ag

$$= 1.123 \times 10^{-2} - 2.232 \times 10^{-3} = 8.995 \times 10^{-3}$$

$$= 8.995 \times 10^{-3} \times 32 = 0.288 \text{ grams of oxygen}$$

$$\therefore \text{wt \% oxygen} = \frac{0.288}{0.288 + 100} \times 100 = 0.287$$

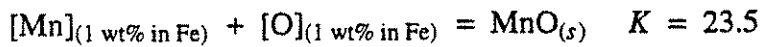
$$\text{mole fraction } \sigma, \quad \chi_O = \frac{2 \times 8.995 \times 10^{-3}}{2 \times 8.995 \times 10^{-3} + \frac{100}{107.87}} = 0.0190$$

$$\therefore \text{atom \% O} = 1.9$$

$$\text{For } \frac{1}{2} O_2(g) = [O] \quad k = \frac{[O]}{P_{O_2}} = \frac{1.9}{0.9^{1/2}} = 2.0$$

13.25 Silicon and manganese are commonly used together as deoxidizers for liquid steel. At

1600°C,



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 ($a_{\text{SiO}_2} = 1$) as the deoxidation product. Thus with 0.01 wt% Si, the oxygen content is

$$[\% \text{O}] = \left[\frac{a_{\text{SiO}_2}}{K_{\text{Si}} [\% \text{Si}]} \right]^{1/2} = \left[\frac{1}{27840 \times 0.01} \right]^{1/2} = 0.06$$

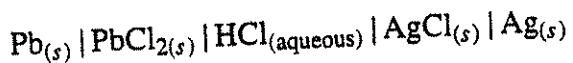
Using Si + Mn produces a liquid manganese silicate as the deoxidation product, which, if saturated with MnO gives $a_{\text{SiO}_2} = 0.02$. Thus with 0.01 wt% Si,

$$[\% \text{O}] = \left[\frac{0.02}{27840 \times 0.01} \right]^{1/2} = 0.0085.$$

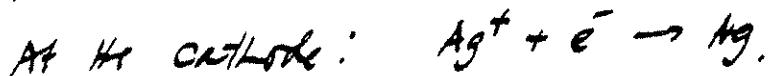
The Mn content required to saturate with MnO is calculated as

$$[\% \text{Mn}] = \frac{a_{\text{MnO}}}{K_{\text{Mn}} [\% \text{O}]} = \frac{1}{23.5 \times 0.0085} = 5.0$$

14.1 The EMF of the galvanic cell



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.



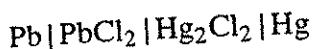
∴ Cell reaction is



$$\Delta G^\circ = -zFE^\circ = -2 \times 96487 \times 0.490 = -94560 \text{ J}$$

$$\Delta S^\circ = zF \frac{dE^\circ}{dT} = 2 \times 96487 \times (-1.84 \times 10^{-4}) = -35.5 \text{ J/K}$$

14.2 At 298 K, the EMF of the cell



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 $X_{\text{Hg}} = 0.3$ 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.

$$a) \Delta G^\circ = -2FE^\circ = -2 \times 96487 \times 0.5357 = -103401 \text{ J}$$

$$b) \Delta S^\circ = 2 \times 96487 \times 0.5353 = 27.98 \text{ J/K}$$

$$c) q = T\Delta S = 298 \times 27.98 = 8338 \text{ J/mole of Pb}$$

$$E = E^\circ - \frac{RT}{2F} \ln a_{\text{Hg}}^2$$



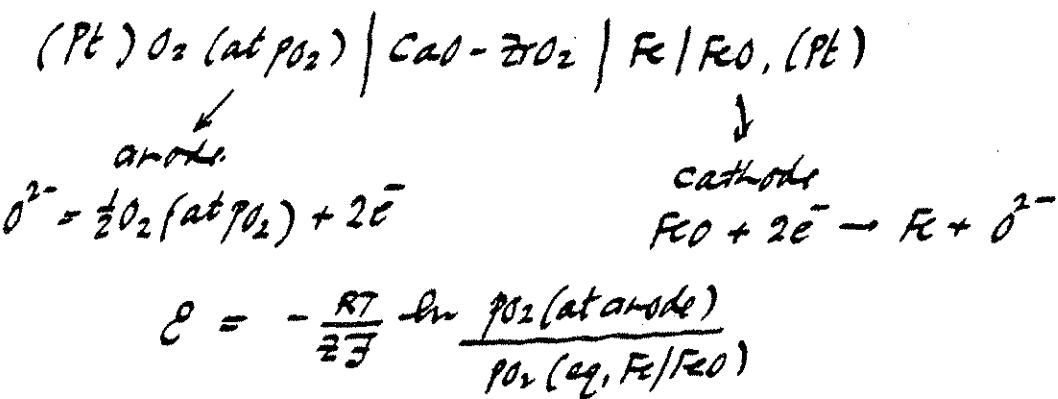
$$0.0089 = -\frac{8.3144 \times 298}{2 \times 96487} \ln a_{\text{Hg}}^2$$

$$\therefore a_{\text{Hg}} = 0.707$$

14.3 The solid-state electrochemical cell



is built to measure the partial pressure of oxygen in gases. Write an equation relating the oxygen pressure and temperature of the gas to the EMF of the cell.



$$\text{For } \text{Fe} + \frac{1}{2}\text{O}_2 = \text{FeO} \quad \Delta G^\circ = -263700 + 64.35T = \frac{1}{2}RT \ln p_{\text{O}_2(q)}^*$$

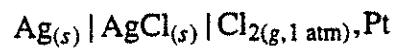
$$\therefore E = -\frac{RT}{4f} \ln p_{O_2}(\text{atm, Fe}) + \frac{RT}{4f} \ln p_{O_2}(\text{eq, Fe/FeO})$$

\downarrow
 $\frac{RT}{4f} \left[-\frac{2 \times 263700}{RT} + \frac{2 \times 64.35}{R} \right]$

$$E = 2.154 \times 10^5 \ln p_0 - 1.3665 + 3.334 \times 10^{-4} T$$

$$\text{or } \ln p_{O_2} = \frac{46620E}{T} + \frac{63440}{T} - 15.48$$

14.4 The EMF of the cell



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 $t = 100^\circ\text{C}$ to $t = 450^\circ\text{C}$. Calculate the value of Δc_p for the cell reaction.

$$\begin{aligned}\mathcal{E} &= 0.977 + 5.7 \times 10^{-4} \times 350 - 5.7 \times 10^{-4}t - 4.8 \times 10^{-7}(350)^2 \\ &\quad + 4.8 \times 10^{-7} \times 350 \times 2t - 4.8 \times 10^{-7}t^2\end{aligned}$$

$$\frac{d\mathcal{E}}{dt} = 0.000906 - 9.6 \times 10^{-7}t$$

$$\begin{aligned}\Delta S &= 2F \frac{d\mathcal{E}}{dT} = 1 \times 96487 [0.000906 - 9.6 \times 10^{-7}t] \\ &= 87.41 - 0.0926t\end{aligned}$$

$$= 87.41 - 0.0926(T - 273) \quad \text{T in Kelvins}$$

$$\frac{d\Delta S}{dT} = \frac{\Delta Q}{T} \quad \therefore \Delta c_p = -0.093 \text{ J/K.}$$

- 14.5 A galvanic cell is set up with electrodes of solid aluminum and solid aluminum-zinc alloy and an electrolyte of molten $\text{AlCl}_3\text{-NaCl}$. 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.



cell reaction $\text{Al} \rightarrow \underline{\text{Al}} \text{ in Al-Zn}$.

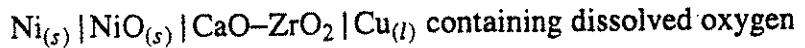
$$\begin{aligned}\Delta\bar{\mu}_{\text{Al}}^m &= -zF\bar{E} = -3 \times 96487 \times 7.43 \times 10^{-3} \\ &= -2150 \text{ J} = RT\ln a_{\text{Al}}\end{aligned}$$

$$\therefore a_{\text{Al}} = 0.673$$

$$\Delta\bar{s}_{\text{Al}}^m = zF \frac{d\bar{E}}{dT} = 3 \times 96487 \times 2.9 \times 10^{-5} = 8.39 \text{ J/K}$$

$$\begin{aligned}\Delta\bar{H}_{\text{Al}}^m &= \Delta\bar{\mu}_{\text{Al}}^m + T\Delta\bar{s}_{\text{Al}}^m \\ &= -2150 + 653 \times 8.39 \\ &= 3329 \text{ J}\end{aligned}$$

14.6 By measuring the EMF's of cells of the type

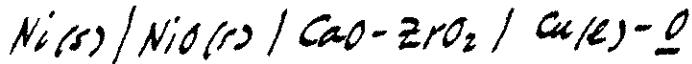


it has been established that e_0° in liquid copper at 1363 K is - 0.16 and that the standard Gibbs free energy change for

$$\frac{1}{2}\text{O}_{2(g)} = [\text{O}]_1 \text{ wt\% in Cu}$$

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



$p_{\text{O}_2}(\text{low})$

$p_{\text{O}_2}(\text{high})$

$$1) E = 0.222 = -\frac{RT}{4F} \ln \frac{p_{\text{O}_2}(\text{low})}{p_{\text{O}_2}(\text{high})} \quad \therefore \frac{p_{\text{O}_2}(\text{low})}{p_{\text{O}_2}(\text{high})} = 5.206 \times 10^{-1}$$

$$\text{For } 2\text{Ni} + \text{O}_2 = 2\text{NiO} \quad \Delta G^\circ = -471200 + 172T$$

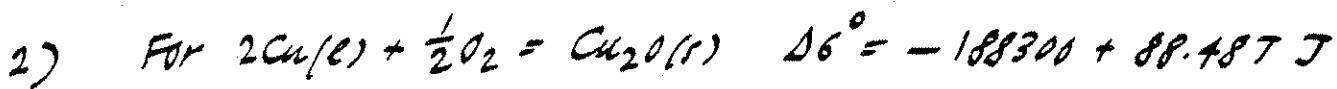
$$= -236764 = RT \ln p_{\text{O}_2(\text{low})}$$

$$\therefore p_{\text{O}_2(\text{low})} = 8.44 \times 10^{-10} \text{ atm and}$$

$$p_{\text{O}_2(\text{high})} = \text{activity of oxygen rel to } p_{\text{O}_2} = 1 \text{ atm}$$

$$= \frac{8.44 \times 10^{-10}}{5.206 \times 10^{-1}} = 1.622 \times 10^{-6}$$

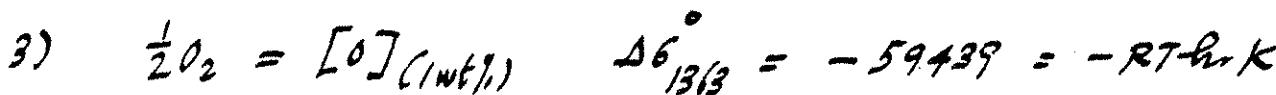
14.6 Continued.



$$\therefore \Delta\text{G}_{1363}^\circ = -67702 \text{ J} = \frac{1}{2}RT\ln p_{\text{O}_2}$$

$$\therefore p_{\text{O}_2} = 6.47 \times 10^{-6} \text{ atm}$$

$$\therefore \alpha_{\text{Cu}_2\text{O}} = \left[\frac{1.622 \times 10^{-6}}{6.47 \times 10^{-6}} \right]^{1/2} = 0.5$$



$$\therefore K = 189.6 = \frac{h_0}{P_{\text{O}_2}^{1/2}}$$

$$\therefore h_0 = 189.6 \times (1.622 \times 10^{-1})^{1/2} = 0.241$$

$$\log h_0 = e_0^\circ [\% \text{O}] + \log [\% \text{O}]$$

$$\therefore -0.617 = -0.16 [\% \text{O}] + \log [\% \text{O}]$$

$$\text{which gives } [\% \text{O}] = 0.266$$

4) $h_0 \text{ (at saturation with O)} = 189.6 \times [6.47 \times 10^{-6}]^{1/2}$
 $= 0.482.$

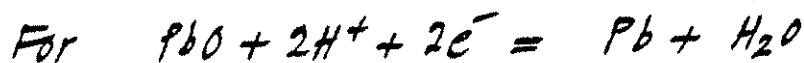
$$\therefore \log h_0 \text{ (saturation)} = -0.3167$$

 $= -0.16 [\% \text{O}] + \log [\% \text{O}]$

$$\therefore [\% \text{O}]_{\text{saturation}} = 0.602$$

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 _(m) ²⁺	- 24,310
Pb _(m) ⁴⁺	+ 302,500
HPbO _{2(m)} ⁻	- 339,000
PbO _{3(m)} ²⁻	- 277,570
PbO _{4(m)} ⁴⁻	- 28,210
H ₂ O _(l)	- 237,190



$$\Delta G^\circ = - 237190 + 189300 = - 47890 \text{ J.}$$

$$\therefore E^\circ = \frac{47890}{2F} = 0.248$$

$$\begin{aligned} \therefore E &= 0.248 - \frac{RT}{2F} \ln \left[\frac{1}{[H^+]^2} \right] = 0.248 + 0.0591 \log [H^+] \\ &= 0.248 - 0.0591 \text{ pH} \end{aligned}$$

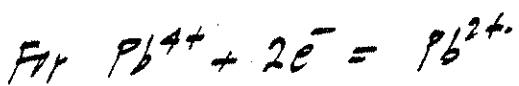
$$\text{For } Pb^{2+} + 2e^- = Pb \quad \Delta G^\circ = 24310 \quad \therefore E^\circ = \frac{-24310}{2F} = -0.126$$

$$\begin{aligned} \therefore E &= -0.126 - \frac{RT}{2F} \ln \left[\frac{1}{[Pb^{2+}]} \right] \\ &= -0.126 + 0.02957 \log [Pb^{2+}] \end{aligned}$$

$$\text{With } [Pb^{2+}] = 1 \quad E = -0.126 \text{ Volts}$$

$$\text{and } \text{pH} = \frac{0.126 + 0.248}{0.0591} = 6.33$$

14.7 CONTINUED



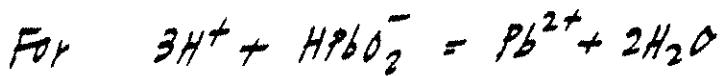
$$\Delta G^\circ = -24310 - 302500 = -326810 \quad \therefore E^\circ = \frac{326810}{2F} = 1.693$$

$$\therefore E = 1.693 - \frac{RT}{2F} \ln \frac{[Pb^{2+}]}{[Pb^{4+}]}$$

$$= 1.693 - 0.02957 \log \frac{[Pb^{2+}]}{[Pb^{4+}]}$$

$$\text{At } E = -0.126, \frac{[Pb^{2+}]}{[Pb^{4+}]} = 3.27 \times 10^{-61}$$

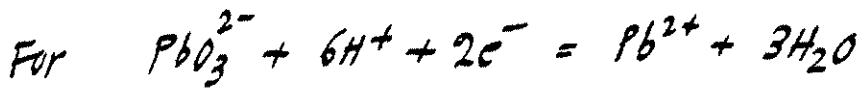
$$\text{and with } [Pb^{2+}] = 1, [Pb^{4+}] = 3.05 \times 10^{-62}$$



$$\Delta G^\circ = -159690 = -RT \ln \frac{[Pb^{2+}]}{[HPbO_2^-][H^+]^3}$$

$$\therefore 27.99 = \log \frac{[Pb^{2+}]}{[HPbO_2^-]} + 3pH.$$

$$\therefore \text{At } pH = 6.33 \text{ and } [Pb^{2+}] = 1, [HPbO_2^-] = 10^{-9}$$



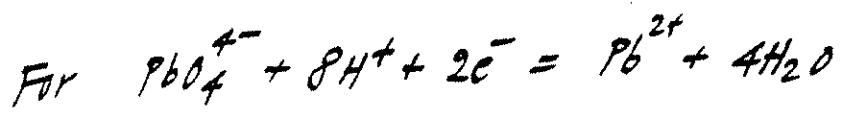
$$\Delta G^\circ = -458311 \text{ and } E^\circ = 2.375$$

$$\therefore E = 2.375 - \frac{RT}{2F} \ln \frac{[Pb^{2+}]}{[PbO_3^{2-}][H^+]^6}$$

$$= 2.375 - 0.02957 \log \frac{[Pb^{2+}]}{[PbO_3^{2-}]} - 0.1774 \text{ pH.}$$

$$\text{At } E = -0.126, \text{ pH} = 6.33 \text{ and } [Pb^{2+}] = 1,$$

$$[PbO_3^{2-}] = 2.5 \times 10^{-47}$$



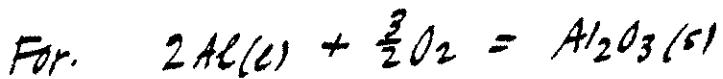
$$\Delta G^\circ = -944860 \text{ J.} \quad E^\circ = 4.896$$

$$E = 4.896 - \frac{RT}{2F} \ln \frac{[\text{Pb}^{2+}]}{[\text{PbO}_4^{4-}] [\text{H}^+]^8}$$

$$\therefore -0.126 = 4.896 - 0.0296 \log \frac{[\text{Pb}^{2+}]}{[\text{PbO}_4^{4-}]} + 0.236 \times 6.33.$$

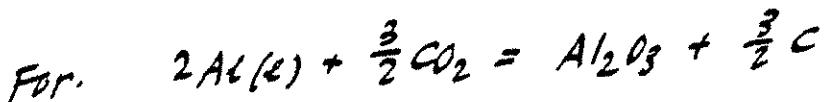
$$\text{with } [\text{Pb}^{2+}] = 1, \quad [\text{PbO}_4^{4-}] = 5.6 \times 10^{-221}$$

14.8 Aluminum can be produced by electrolysis of Al_2O_3 dissolved in molten cryolite, $3\text{NaF} \cdot \text{AlF}_3$. 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 $3\text{NaF} \cdot \text{AlF}_3$ electrolyte at 1000°C in the Hall-Heroult cell.



$$\Delta G_{1273}^\circ = -1271183 \text{ J}$$

$$\therefore E^\circ = \frac{1271183}{6F} = 2.196 \text{ volt.}$$



$$\Delta G_{1273}^\circ = -678430 \text{ J}$$

$$\therefore E^\circ = \frac{678430}{6F} = 1.17 \text{ volt.}$$

- 14.9 At 298 K the solubility of Cl_2 in H_2 , under a partial pressure of $\text{Cl}_2 = 1 \text{ atm}$, 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.

$$\text{For: } \frac{1}{2}\text{Cl}_2(g) = [\text{Cl}] \quad K = \frac{[\text{Cl}]}{P_{\text{Cl}_2}} = 0.0618$$

$$\Delta G^\circ = -8.3144 \times 298 \times \ln 0.0618 = 6897 \text{ J}$$

$$\text{For } [\text{Cl}]_{1m} \rightarrow [\text{Cl}]_{0.01m} \quad \Delta G = RT \ln 0.01 \\ = -11410$$

$$\therefore \text{For } \frac{1}{2}\text{Cl}_2(g) = [\text{Cl}]_{0.01m}$$

$$\Delta G = 6897 - 11410 = -4513 \text{ J}$$