THERMODYNAMICS OF MATERIALS CHE701

ANSWER TO PROBLEMS

CHAPTER 1

1.

$$\Delta H = \int_{300}^{1000} 110 + 16.21 \times 10^{-3}T - 25.79 \times 10^{5}T^{-2}.dT = 78358\ \mathrm{J.mol^{-1}}$$

$$\equiv \mathbf{78.36\ kJ.mol^{-1}}$$

2. First, we must obtain the following data:

- Specific heats of components ($\mathrm{J.mol^{-1}K^{-1}}$)

  For CaO: $C_p = 49.95 + 4.88 \times 10^{-3}T - 8.25 \times 10^{5}T^{-2}$ (NIST WebBook)

  For CO_2: $C_p = 24.99 + 5.518 \times 10^{-2}T - 1.366 \times 10^{5}T^{-2}$ (NIST WebBook)

  For $CaCO_3$: $C_p = 83.43$ (MatWeb)

- Heats of formation of components ($\mathrm{kJ.mol^{-1}}$) from Table (1.2)

  For CaO: $\Delta H_f^0 = -636$

  For CO_2: $\Delta H_f^0 = -394$

  For $CaCO_3$: $\Delta H_f^0 = -1206$

  Heat of reaction at standard conditions: $\Delta H_R^0 = (-636 - 394) - (-1206) = 176$

  $\Delta H_1 = \int_{1000}^{298} 83.43.dT = -58567.86\ \mathrm{J.mol^{-1}} \equiv -58.57\ \mathrm{kJ.mol^{-1}}$

  $\Delta H_R^0 = 176\ \mathrm{kJ.mol^{-1}}$

$$\Delta H_3 = \int_{298}^{1000} (49.95 + 24.99) + (4.88 + 55.18) \times 10^{-3}T - (8.25 + 1.366) \times 10^{5}T^{-2}.dT = 77705\ \mathrm{J.mol^{-1}} \equiv 77.705\ \mathrm{kJ.mol^{-1}}$$

Hence: $\Delta H_{1000} = \Delta H_1 + \Delta H_r^0 + \Delta H_3 = \mathbf{195.135\ kJ.mol^{-1}}$

3. $dS = \frac{\delta Q}{T}$

   Since the process is isothermal, then, from the first law: $\delta Q = p.dV$

   $dS = \frac{p.dV}{T}$

For an ideal gas: $p = \frac{RT}{V}$

$dS = \frac{R.dV}{V} \rightarrow \Delta S = \int_{V_1}^{V_2} \frac{R.dV}{V} = R \ln \frac{V_2}{V_1} = R \ln \frac{p_1}{p_2}$ (Since $p.V$ = constant)

4. NaCl (*l*) → NaCl (*l*): 973 K to 1074 K:

$\Delta S_1 = \int_{973}^{1074} \frac{C_p(l).dT}{T} = 61.5 \ln \frac{1074}{973} = 6.074$ J.mol^{-1}K^{-1}

NaCl (*l*) → NaCl (*s*): at 1074 K: $\Delta S_2 = \frac{-27950}{1074} = -26.02$ J.mol^{-1}K^{-1}

NaCl (*s*) → NaCl (*s*): 1074 K to 973 K:

$\Delta S_3 = \int_{1074}^{973} \frac{C_p(s).dT}{T} = \int_{1074}^{973} \frac{50.dT}{T} = 50 \ln \frac{973}{1074} = -4.94$ J.mol^{-1}K^{-1}

Thus, the change in entropy = $6.074 - 26.02 - 4.94 = \mathbf{-24.886}$ **J.mol^{-1}K^{-1}**

To obtain the entropy change of surroundings, one first must calculate the amount of heat transferred to the surroundings which is the amount of heat produced by the cycle.

NaCl (*l*) → NaCl (*l*): 973 K to 1074 K: $\Delta H_1 = \int_{973}^{1074} C_{pl}.dT = 61.5 \times (1074 - 973)$ = 6211.5 J.mol^{-1}

NaCl (*l*) → NaCl (*s*): at 1074 K: $\Delta H_2 = -27950$ J.mol^{-1}

NaCl (*s*) → NaCl (*s*): 1074 K to 973 K:

$$\Delta H_3 = \int_{1074}^{973} 50.dT = -5050 \text{ J.mol}^{-1}$$

Thus, the heat transferred to surroundings = $6211.5 - 27950 - 5050 = -26788.5 \text{ J.mol}^{-1}$.

Hence, the heat gained by the surroundings = $26788.5 \text{ J.mol}^{-1}$

The change in entropy of surroundings = $\Delta S_{surr} = \frac{26788.5}{973} = 27.53 \text{ J.mol}^{-1}\text{K}^{-1}$

(We note that the total change in entropy = $-25.1 + 27.53 = 2.43 \text{ J.mol}^{-1}\text{K}^{-1} > 0$)

5. The pressure is increased from $p_1 = 101325$ to $p_2 = 1013250000$ Pa

$dS = \frac{\delta Q}{T}$

Since the process is isothermal, then, from the first law: $\delta Q = p.dV$

$\Delta S = \frac{p.dV}{T} = -\int_{p_1}^{p_2} \frac{V\beta p.dp}{T} = \frac{-0.005 \times 0.762 \times 10^{-11} \times 0.5 \times [1013250000^2 - 101325^2]}{300}$

$= \mathbf{-65.19\ J.K^{-1}}$.

6. To get the value of ΔH, we use the relation: $\left(\frac{\partial\left(\frac{\Delta G}{T}\right)}{\partial\left(\frac{1}{T}\right)}\right)_P = \Delta H = \left(\frac{\partial\left(\frac{\Delta G}{T}\right)}{\partial T}\right)_P . -T^2$

$$\frac{\Delta G}{T} = = -16.8T^{-1} + 0.00368 - 0.0721T^{-1}\ln T$$

$$\left(\frac{\partial\left(\frac{\Delta G}{T}\right)}{\partial T}\right)_P = 16.8T^{-2} - 0.0721(-T^{-2}.\ln T + T^{-1}T^{-1})$$

$$= 16.8T^{-2} - 0.0721T^{-2}(1 - \ln T) \rightarrow \Delta H = -T^2T^2[16.8 - 0.0721(1 - \ln T)]$$

At 400K: $\Delta H = [-16.8 + 0.0721(1 - \ln 400)] = \mathbf{-17.16}$ **kJ.mol^{-1}**

To get the value of ΔS, we first obtain the value of ΔG at 400:

$$\Delta G = -16.8 + 0.00368 \times 400 - 0.0721\ln 400 = -15.76$$

$$\Delta G = \Delta H - T.\Delta S \rightarrow$$

$$-15.76 = -17.16 - 400\Delta S \rightarrow \boldsymbol{\Delta S = -0.0035\ \mathrm{kJ.mol^{-1}K^{-1}} \equiv -3.5\ \mathrm{J.mol^{-1}K^{-1}}}$$

7. Since the molecules are **similar**, we apply the expression: $W = \frac{n+i-1!}{n!i-1!}$

$$W = \frac{100+50-1!}{100!50-1!} = \frac{149!}{100!49!}$$

Hence: $\ln W = \ln 149! - \ln 100! - \ln 49!$

Applying Stirling approximation:

$$\ln W = (149\ln 149 - 149) - (100\ln 100 - 100) - (49\ln 49 - 49) = 94.37$$

Hence $W = e^{94.37} = \mathbf{9.66 \times 10^{40}}$

8. $dG = V.dp - S.dT$ Since T is constant, hence: $dG = V.dp = \frac{RT}{p}\,dp$

Therefore: $\Delta G = \int_1^{100}\frac{8.314\times 298}{p}\,dp = 8.314 \times 298 \times \ln\frac{100}{1} = \mathbf{11409.6}$ **J.mol^{-1}**

CHAPTER 2

1. $\Delta T = 1090 - 1083 = 7$ K

   $\Delta H_t = 13590$ J.mol^{-1}

   $T_t = 1083 + 273 = 1356$ K

   Atomic volume of solid = $V_1 = \frac{63.55}{8.95}$ = 7.1 cm^3.mol^{-1} ≡ 7.1×10^{-6} m^3.mol^{-1}

   Atomic volume of liquid = $V_2 = \frac{63.55}{7.93}$ = 8.014 cm^3.mol^{-1} ≡ 8.014×10^{-6} m^3.mol^{-1}

   $\Delta V = 0.914 \times 10^{-6}$ m^3.mol^{-1}

   Substituting in the equation $\frac{\Delta p}{\Delta T} = \frac{\Delta H_t}{\Delta V.T_t}$

   $\frac{\Delta p}{7} = \frac{13590}{0.914\times10^{-6}\times1356}$

   Hence: $\Delta p = 76755872$ Pa ≡ $\mathbf{756.7}$ **atm**

2.

log p	-7	-6	-5	-4	-3	-2	-1	0	1	2
T K	1020	1075	1172	1243	1374	1498	1669	1805	2023	2255
ln p	0.00098	0.00093	0.00085	0.0008	0.00073	0.00067	0.0006	0.00055	0.00049	0.00044
$1/T$	-16.121	-13.818	-11.515	-9.212	-6.909	-4.606	-2.303	0	2.303	4.606

The plot between ln p and $1/T$ yields a straight line of equation $\ln p = -\frac{37693}{T} + 20.84$

This slope (37693) corresponds to a latent heat of vaporization = 313.4 kJ.mol^{-1}

The normal boiling point is the boiling point at 1 atm ≡ 1013.2 millibar.

Substitution in the equation of the straight line, we get: $\boldsymbol{T_{normal\ b}} = \mathbf{2708}$ **K** (Actually 2743 K).

3. The reaction under study is: C $(a = 0.0038)$ = C $(a = 0.00572)$

   The free energy of carbon at its standard state = 0, hence:

   $$\Delta G = \Delta G^0 + RT \ln\frac{0.00572}{0.0038} = 0 + 8.314 \times 1600 \ln\frac{0.00572}{0.0038} \rightarrow \Delta G = \mathbf{5440.3\ J.mol^{-1}}$$

   The positive sign of free energy change indicates that this increase cannot take place spontaneously.

4. The reaction is: Cu $(a = 1)$ = Cu (a)

The activity of Cu in solution = $\frac{p}{p^0}$.

The vapor pressure in solution = 0.03 mmHg ≡ $\frac{0.03\times1.013\times10^5}{760}$ = 4 Pa

Hence, $a = \frac{4}{975}$ = 0.0041

$\Delta G = \Delta G^0 + RT\ln\frac{0.0041}{1} = 0 + 8.314 \times 873\ln\frac{0.0041}{1} \rightarrow \Delta G = \mathbf{-39896\ J}$

The negative sign of free energy change indicates that dissolution can take place spontaneously.

5. The reaction is: $CaCO_3$ (s) = CaO (s) + CO_2 (g)

   Since $p_{CO_2} = 0.0005$ atm, hence the calcination temperature can be calculated from:

   $p_{\mathrm{CO_2}} = 4.137 \times 10^7 e^{-\frac{20474}{T}}$

   $0.0005 = 4.137 \times 10^7 e^{-\frac{20474}{T}} \rightarrow \boldsymbol{T} = \mathbf{814.4K}$

   The two solid phases being at their standard states, the standard free energy change can be written as:

   $\Delta G^0 = -RT\ln p_{CO_2} = -8.314 \times 814.4 \times \ln 0.0005 = 51465 = \Delta H^0 - T\Delta S^0$

   Calculation of ΔH^0 at 814.4 K:

   - Cool $CaCO_3$ from 814.4 to 298: $\Delta H_1 = 83.48 \times (298 - 814.4) = -43109$
   - Reaction at 298 K: $\Delta H_R = -394 - 635.5 - (-1205.6) = 176.1$ kJ/mol^{-1}
   - Heat CaO + CO_2 to 814.4 K: $\Delta H_1 = (47.5 + 36) \times (814.4 - 298)$= 43119.4

   ΔH^0 at 814.4 K = $-43.109 + 176.1 + 43.119 = 176.11$ kJ/mol^{-1}

   Since $\Delta G^0 = \Delta H^0 - T\Delta S^0$, therefore: $51376 = 176110 - 814.4\Delta S^0$

   Hence, $\Delta S^0 = \mathbf{153.16}$ **J.mol^{-1}.K^{-1}**

6. $\Delta G^0 = -75.7 \times 10^4 - 7.5 \times 1500 \times \log 1500 + 145 \times 1500 = -575231\ \mathrm{J.mol^{-1}}$

   $-575231 = -8.314 \times 1500\ln K_e \rightarrow \boldsymbol{K_e} = \mathbf{1.076 \times 10^{20}}$

   $$\left(\frac{\partial\left(\frac{\Delta G}{T}\right)}{\partial\left(\frac{1}{T}\right)}\right)_P = \Delta H = \left(\frac{\partial\left(\frac{\Delta G}{T}\right)}{\partial T}\right)_P . -T^2$$

   $$\frac{\Delta G}{T} = -75.7 \times 10^4 T^{-1} - 7.5 \times 0.4343\ln T + 145$$

   $$-\frac{\Delta H}{T^2} = \left(\frac{\partial\left(\frac{\Delta G}{T}\right)}{\partial T}\right)_P = 75.7 \times 10^4 T^{-2} - 7.5 \times 0.4343/T$$

   $$\Delta H = -(75.7 \times 10^4 T^{-2} - 7.5 \times 0.4343/T) \times T^2$$

   $$\Delta H = -75.7 \times 10^4 + 7.5 \times 0.4343 \times 1500 = \mathbf{-752114\ J.mol^{-1}}$$

$$1500\Delta S = -752114 - (-575231) \rightarrow \Delta S = \mathbf{-117.9\ J.mol^{-1}.K^{-1}}$$

7. $\left(\frac{\partial \ln K_e}{\partial T}\right)_p = \frac{-410000}{8.314\times T^2} = -49314.4T^{-2}$

$$\int_{1500}^{1400} -49341.4T^{-2}.dT = \ln K_{e,1400} - \ln 8.903\times 10^{15}$$

$\ln K_{e,1400} = 39.074 \rightarrow K_{e,1500} = \mathbf{9.33\times 10^{16}}$

(Note that the reaction being exothermic, the value of the equilibrium constant has increased on decreasing the temperature).

8. $\Delta H_R = -1860 + 0.013T$, at 1000K: $\Delta H_R = -1847$ kJ.mol^{-1}

$$\frac{\Delta H}{T^2} = -\left(\frac{\partial\left(\frac{\Delta G}{T}\right)}{\partial T}\right)_P \rightarrow \frac{\Delta G}{T} = -\int \frac{\Delta H}{T^2}.dT = -\int -1860T^{-2} + 0.013T^{-1}.dT$$

$\frac{\Delta G}{T} = -1860T^{-1} - 0.013\ln T + C \rightarrow \Delta G = -1860 - 0.013T.\ln T + C\,T$

At $T = 298, \Delta G = -1705 = -1860 - 0.013\times 298\times \ln 298 + 298C \rightarrow C = 0.594$

At 1000K:

$\Delta G = -1860 - 0.013\times 1000\times \ln 1000 + 0.594\times 1000 = \mathbf{-1355.8}$ **kJ.mol^{-1}**

$\Delta G = \Delta H - T\Delta S \rightarrow -1355.8 = -1847 - 1000\Delta S \rightarrow \Delta \boldsymbol{S} = \mathbf{-0.491}$ **kJ.mol^{-1}K^{-1}**

9.

	Cu
Melting point K	1358
ΔH_m kJ.mol^{-1}	13.26
Boiling point K	2835
ΔH_v kJ.mol^{-1}	300.4

For melting:

$\ln p^0 = \frac{-13260}{8.314T} + C$ To get the value of C, we note that if $p^0 = 1$ arm, T = 1358

$0 = \frac{-13260}{8.314\times 1358} + C \rightarrow C = 1.1745$

$\ln p^0 = \frac{-13260}{8.314T} + 1.1745$ (i)

For vaporization:

$\ln p^0 = \frac{-300400}{8.314T} + C'$

To get the value of C', we note that if $p^0 = 1$ arm, T = 2835

$$0 = \frac{=300400}{8.314\times2835} + C \rightarrow C = 12.745$$

$$\ln p^0 = \frac{-300400}{8.314T} +12.745 \qquad \text{(ii)}$$

The following table shows the values obtained by substituting T into equations (i) and (ii)

T K	**$\ln p^0$ (i)**	**$\ln p^0$ (ii)**
1400	0.0352	- 13.0635
1600	0.1776	- 9.8375
1800	0.2883	- 7.328
2000	0.377	- 5.321
2200	0.4495	- 3.678
2400	0.5099	- 2.31
2600	0.5610	- 1.1519
2800	0.6048	- 0.1593
2985	0.6401	0.6405

The value of $T = 2985$ K was obtained by using Goal – Seek technique to have the differences between the values of $\ln p^0$ in both columns equal to zero.

For sublimation:

$$\ln p^0 = -\frac{313660}{8.314T} + C''$$

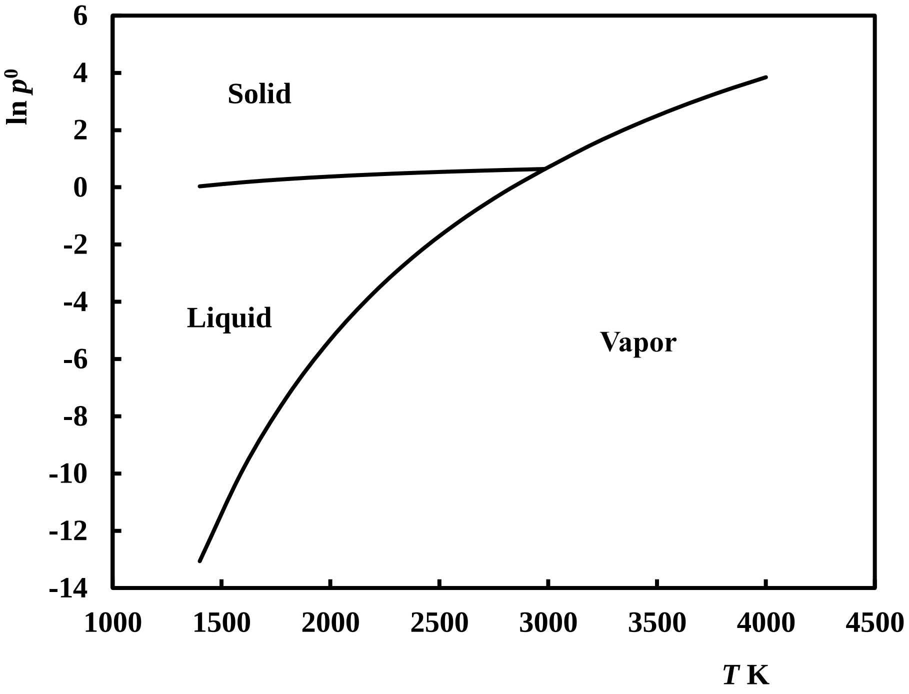
To get the value of C'', we note that if $\ln p^0 = -0.64$ arm, T = 2985

$$-0.64 = \frac{-313660}{8.314\times2985} + C \rightarrow \mathrm{C} = 13.279$$

$$\ln p^0 = \frac{313660}{8.314T} +13.279 \qquad \text{(iii)}$$

The following table shows the values of $\ln p^0$ obtained from (iii) at $T \geq 2985$ K

2985	0.6399
3200	1.4891
3400	2.1826
3600	2.7991
3800	3.3506
4000	3.8471


ln p^0
6
4
2
0
-2
-4
-6
-8
-10
-12
-14
Solid
Liquid
Vapor
1000
1500
2000
2500
3000
3500
4000
4500
T K

CHAPTER 3

1. Moles Ni = $\frac{40}{58.7}$ = 0.681 Moles Cu = $\frac{100}{63.54}$ = 1.574

$X_{Ni} = \frac{0.681}{0.681+1.574} = 0.302 \rightarrow X_{Cu} = 0.698$

$\Delta S_m = -R(X_A \ln X_A + X_B \ln X_B) = -8.314 \times (0.302 \ln 0.302 + 0.698 \ln 0.698)$

$\boldsymbol{\Delta S_m = 5.093}$ **J.mol^{-1}.K^{-1}**

Since the solution is ideal, then $\Delta \boldsymbol{H_m} = \mathbf{0}$

$\Delta G_m = \Delta H_m - T\Delta S_m = 0 - 300.\Delta S_m \rightarrow \Delta \boldsymbol{G_m} = \mathbf{-1527.9\ J.mol^{-1}}$

2.

X_{Zn}	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1
ΔG kJ.mol^{-1}	0	-0.28	-0.43	-0.5	-0.57	-0.58	-0.55	-0.5	-0.4	-0.29	0

The expression for dependence of free energy on mol fraction Zn is:

$\Delta G_m = 2.2483X_{Zn}^2 - 2.2419X_{Zn} - 0.0387$

We get the slope of tangent at $X_{Zn} = 0.4$:

$\frac{d(\Delta G_m)}{dX_{Zn}} = 4.4966X_{Zn} - 2.2419 \rightarrow 4.4966 \times 0.4 - 2.2419 = -0.4433$

Equation of tangent at $X_{Zn} = 0.4$: $\Delta G_m = -0.4433X_{Zn} + C$

At $X_{Zn} = 0, \Delta G_m$...

At $X_{Zn} = 0.4, \Delta G_m = -0.57 \rightarrow C = -0.3927 \rightarrow \Delta G_m = -0.4433X_{Zn} - 0.3927$

At $X_{Zn} = 0, \Delta G_m = -0.3927 \rightarrow \boldsymbol{\bar{G}_{Ga} = -0.3927}$**kJ.mol^{-1}**

At $X_{Zn} = 1, \Delta G_m = -0.8527 \rightarrow \boldsymbol{\bar{G}_{Zn} = -0.827}$ **kJ.mol^{-1}**

3. $p^0_{\mathrm{BeO}} = 4.6 \times 10^{-3}$ and $\gamma_{\mathrm{BeO}} = 0.91$

$a_{\mathrm{BeO}} = 0.91 \times 0.02 = 0.0182$

And, since $a_B = \frac{p_B}{p_B^0}$

Therefore:

$p_{\mathrm{BeO}} = 0.0182 \times 4.6 \times 10^{-3} = 8.37 \times 10^{-5}$ atm.

Also, $a_{\mathrm{TiO_2}} = X_{\mathrm{TiO_2}} = 0.98$

$p_{\mathrm{TiO_2}} = p^0_{\mathrm{TiO_2}} X_{\mathrm{TiO_2}}$

$p_{\mathrm{TiO_2}} = 7.8 \times 10^{-5} \times 0.98 = 7.644 \times 10^{-5}$ atm

Hence:

$p = 8.37 \times 10^{-5} + 7.644 \times 10^{-5} = \mathbf{1.604 \times 10^{-4}}$ **atm**.

4. $T_{\mathrm{Al}} = 660 + 273 = 933\mathrm{K} \qquad \Delta H_f = 10800\ \mathrm{J.mol^{-1}} \qquad X_{\mathrm{Si}} = 0.023$

   $\Delta T_f \approx \frac{RT_f^2}{\Delta H_{fA}} X_B = \frac{8.314\times 933^2 \times 0.023}{-10800} = -15.4\mathrm{K}$ (The negative sign is due to freezing)

   Therefore, the solution starts melting at $660 - 15.4 = \mathbf{644.6^{o}C}$

5. $\Delta S_m = -R(X_A \ln X_A + X_B \ln X_B) =$

   $-8.314 \times (0.4 \ln 0.4 + 0.6 \ln 0.6) =$ **5.595 J.mol^{-1}K^{-1}**

   $\Delta H_m = 4510X_{\mathrm{NiO}}^2 - 4510X_{\mathrm{NiO}} = 4510 \times 0.4^2 - 4510 \times 0.4 = -1082.4$

   $\Delta G_m = \Delta H_m - T\Delta S_m = -1082.4 - 700 \times 5.595 = \mathbf{-4998.9}$ **J.mol^{-1}**

   To get the partial molal enthalpy, we need to get the equation of the tangent at the enthalpy – composition curve at $X_{\mathrm{NiO}} = 0.4$

   $\frac{d(\Delta H_m)}{dX_{Ni}} = 9020X_{Ni} - 4510 \rightarrow 9020 \times 0.4 - 4510 = -902$

. Equation of tangent at $X_{Ni} = 0.4$: $\Delta H_m = -902X_{Ni} + C$

   At $X_{Ni} = 0.4, \Delta H_m = -1082.4 \rightarrow C = -721.6 \rightarrow \Delta H_m = -902X_{Ni} - 721.6$

   At $X_{Ni} = 0, \Delta H_m = -721.6 \rightarrow \boldsymbol{\overline{H}_{MgO}} = \mathbf{-721.6}$ **J.mol^{-1}**

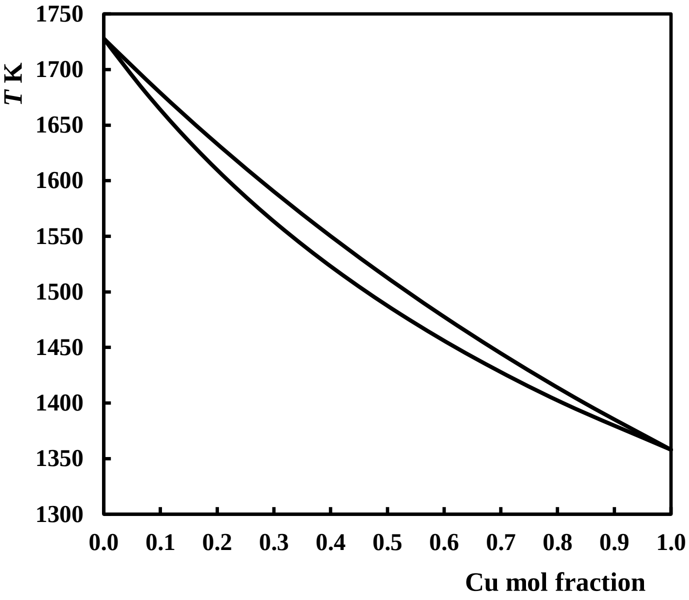
   At $X_{Ni} = 1, \Delta H_m = -902 - 721.6 \rightarrow \boldsymbol{\overline{H}_{NiO}} = \mathbf{-1623.6}$ **J.mol^{-1}**

6. The components are written as: Ni = A and Cu = B.

	Ni (A)	**Cu (B)**
Melting point K	1728	1358
ΔH_m kJ.mol^{-1}	17200	13600

T K		1358	1400	1440	1480	1520	1560	1600	1640	1680	1720	1728
$\ln X_L/X_S$			0.046	0.087	0.126	0.162	0.197	0.230	0.262	0.292	0.321	0326
X_L/X_S			1.047	1.091	1.134	1.176	1.218	1.259	1.299	1.339	1.378	1.386
$\ln(1-X_L)/(1-X_S)$			-0.281	-0.222	-0.189	-0.159	-0.130	-0.102	-0.076	-0.051	-0.027	0
$(1-X_L)/(1-X_S)$			0.755	0.801	0.828	0.853	0.878	0.903	0.927	0.950	0.973	1
X_S		1	0.810	0.656	0.523	0.408	0.308	0.220	0.142	0.073	0.011	0
X_L		1	0.848	0.715	0.593	0.480	0.375	0.277	0.184	0.098	0.016	0

The corresponding phase diagram is shown in the figure.



7. $\Delta H_m = -20150X_B(1 - X_B)$

The enthalpy of mixing reaches its minimum value as $\frac{d(\Delta H_m)}{dX_B} = 0$

$\Delta H_m = 20150X_B^2 - 20150X_B \rightarrow \frac{d(\Delta H_m)}{dX_B} = 40300X_B - 20150 = 0 \rightarrow X_B = 0.5$

$\Delta S_m = -R(X_A \ln X_A + X_B \ln X_B) =$

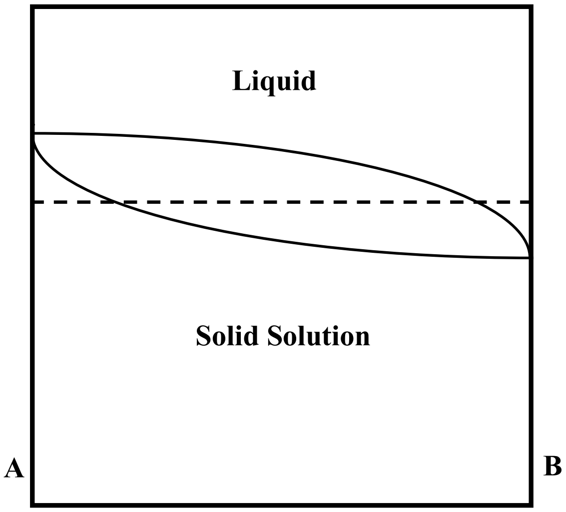
$-8.314 \times (0.5 \ln 0.5 + 0.5 \ln 0.5) =$ **5.763 J.mol^{-1}K^{-1}**

$\Delta H_m = -20150 \times (1 - 0.5) = -$ 10075 J.mol^{-1}

$\Delta G_m = \Delta H_m - T\Delta S_m$ at $T = 1200$K

$\Delta G_m = -10075 - 1200 \times 5.763 = \mathbf{-16990.6}$ **J.mol^{-1}**

8.



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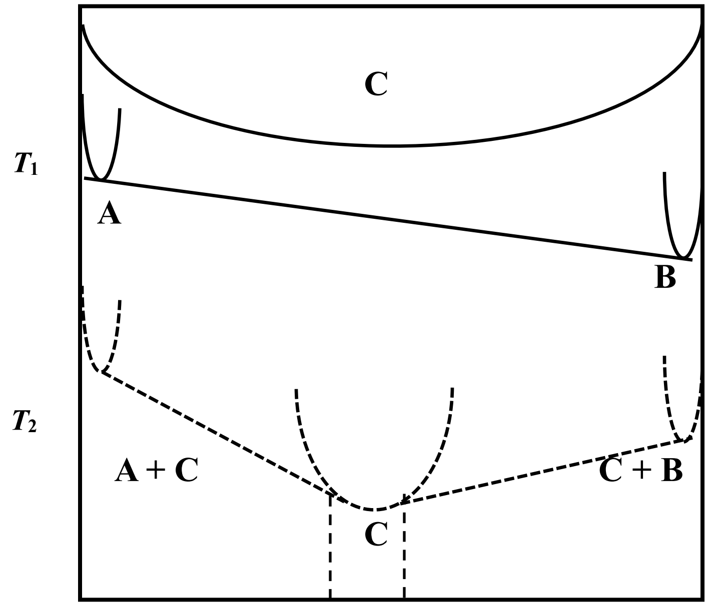


CHAPTER 4

1. Reaction: 2 Mn_3O_4 (s) = 6 MnO (s) + O_2 (g)

Hence, $\Delta H^0 = 6.\Delta H^0_{f,\mathrm{MnO}} - 2.\Delta H^0_{f,\mathrm{Mn_3O_4}} = \mathbf{465}$ **kJ.mol^{-1}**

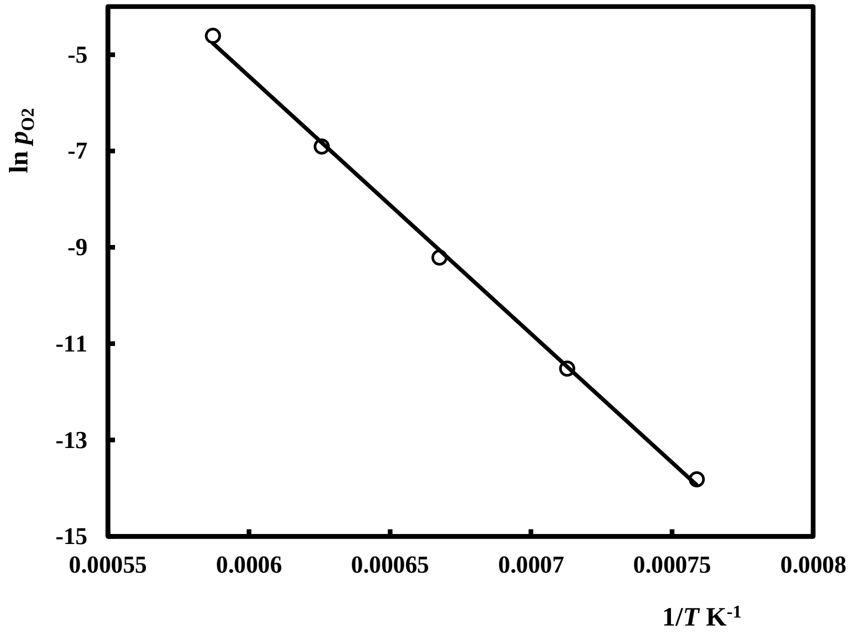
$\Delta S^0 = 6.\Delta S^0_{f,\mathrm{MnO}} - 2.\Delta S^0_{f,\mathrm{Mn_3O_4}} = \mathbf{117}$ **J.mol^{-1}K^{-1}**

p_{O_2}	ln p_{O_2}	T°C	1/T K^{-1}
10^{-6}	-13.816	1045	0.000759
10^{-5}	-11.513	1130	0.000713
10^{-4}	-9.2103	1225	0.000668
10^{-3}	-6.9078	1325	0.000626
10^{-2}	-4.6052	1430	0.000587

The $\ln p_{O_2} - 1/T$ diagram is shown below.

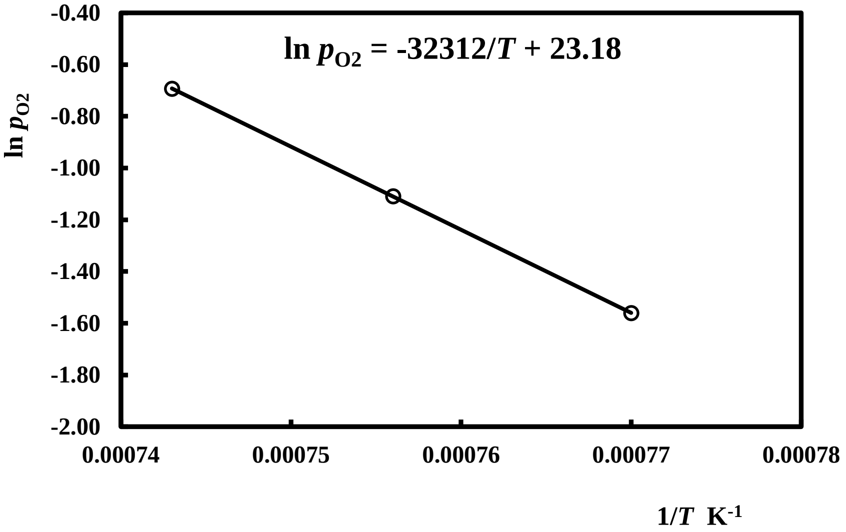
The slope = -53454 corresponding to an enthalpy of reaction = $\mathbf{444.6}$ **kJ.mol^{-1}**

The intercept = 26.64 corresponding to an entropy of reaction = $\mathbf{111.4}$ **J.mol^{-1}**



2.

p_{O_2}	ln p_{O_2}	T°C	1/T K^{-1}
0.21	-1.5606	1026	0.00077
0.33	-1.1087	1050	0.000756
0.5	-0.6931	1072	0.000743



The slope = -32312 corresponding to an enthalpy of reaction = $\mathbf{131.31}$ **kJ.mol^{-1}**

The intercept = 23.18 corresponding to an entropy of reaction = $\mathbf{96.9}$ **J.mol^{-1}**

3. The following table can be set:

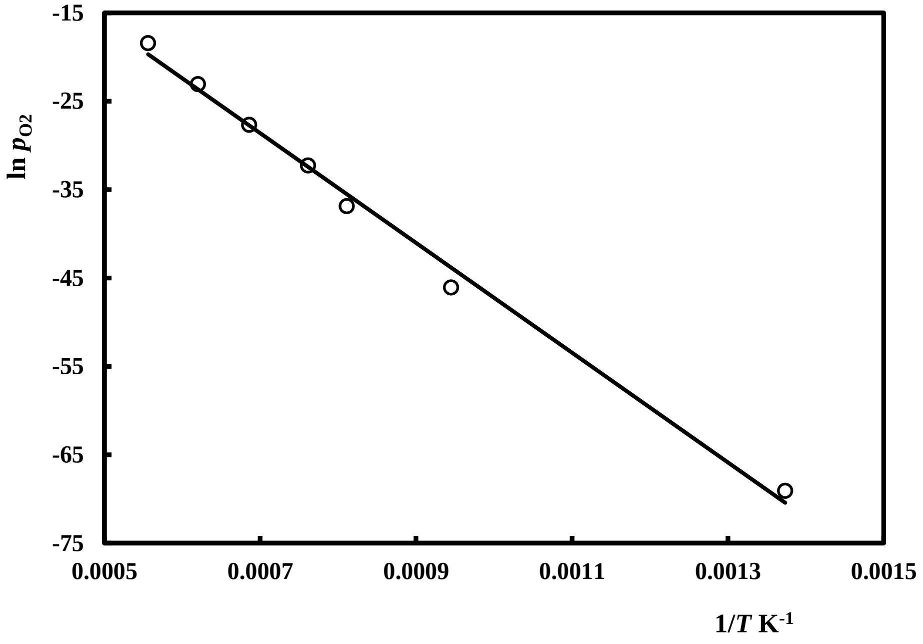
p_{O_2}	ln p_{O_2}	T°C	1/T K^{-1}
10^{-30}	-69.078	455	0.001383
10^{-20}	-46.052	785	0.000950
10^{-16}	-36.841	960	0.000811
10^{-14}	-32.236	1040	0.000762
10^{-12}	-27.631	1185	0.000686
10^{-10}	-23.026	1340	0.000620
10^{-8}	-18.421	1525	0.000556

The plot is shown in the following Figure.

The slope = -60278 corresponding to an enthalpy of reaction = $\mathbf{516.11}$ **kJ.mol^{-1}**

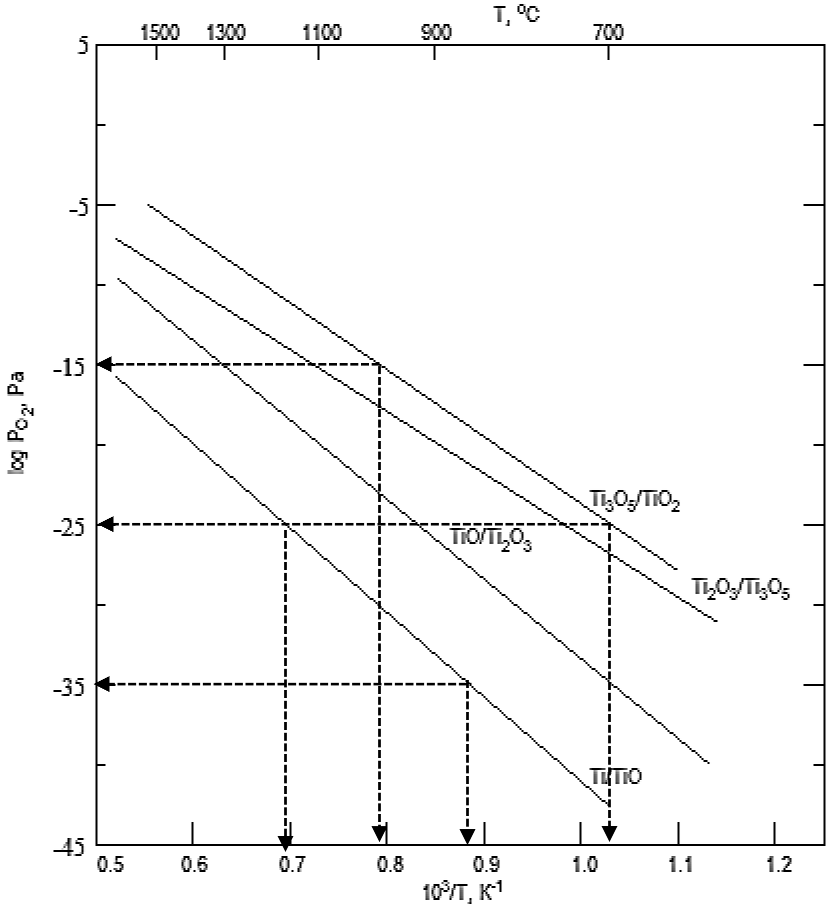
The intercept = 14.31 corresponding to an entropy of reaction = $\mathbf{119}$ **J.mol^{-1}**

The difference with the experimental value of $0-(-564.3)=564.3$ amounts to an error of about 8.54%.



-15
-25
-35
-45
-55
-65
-75
ln p_{O2}
0.0005
0.0007
0.0009
0.0011
0.0013
0.0015
1/T K^{-1}

4.



T, °C
1500
1300
1100
900
700
5
-5
-15
-25
-35
-45
log P_{O_2}, Pa
Ti_3O_5/TiO_2
TiO/Ti_2O_3
Ti_2O_3/Ti_3O_5
Ti/TiO
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
10^3/T, K^{-1}

For the reaction: $4\ TiO_2\ (s) = 2\ Ti_2O_3\ (s) + O_2\ (g)$

Two points are chosen on the line and moved to an EXCEL chart:

$\frac{1}{T} = 0.795 \times 10^{-3}, \ln p_{O_2} = -2.303 \times 15$ and

$\frac{1}{T} = 1.034 \times 10^{-3}, \ln p_{O_2} = -2.303 \times 25$

Slope = $\frac{-\Delta H}{R} = -96360 \rightarrow \boldsymbol{\Delta H_r = 801.2}$ **kJ.mol^{-1}**

Intercept = $\frac{\Delta S}{R} = 42.06 \rightarrow \boldsymbol{\Delta S_r = 349.7}$ **J.mol^{-1}K^{-1}**

For the reaction: $2\ TiO\ (s) = 2\ Ti\ (s) + O_2\ (g)$

Two points are chosen on the line and moved to an EXCEL chart:

$\frac{1}{T} = 0.696 \times 10^{-3}, \ln p_{O_2} = -2.303 \times 25$ and

$\frac{1}{T} = 0.886 \times 10^{-3}, \ln p_{O_2} = -2.303 \times 35$

Slope = $\frac{-\Delta H}{R} = -121120 \rightarrow \boldsymbol{\Delta H_r = 1008}$ **kJ.mol^{-1}**

Intercept = $\frac{\Delta S}{R} = 26.79 \rightarrow \boldsymbol{\Delta S_r = 222.7}$ **J.mol^{-1}K^{-1}**

5. The requested $\ln p_{O_2}$ vs $1/T$ diagram is shown in the Figure. Its equation takes the form:

$$\ln p_{O_2} = -\frac{76372}{T} + 4.584$$