MME 2009 Metallurgical Thermodynamics
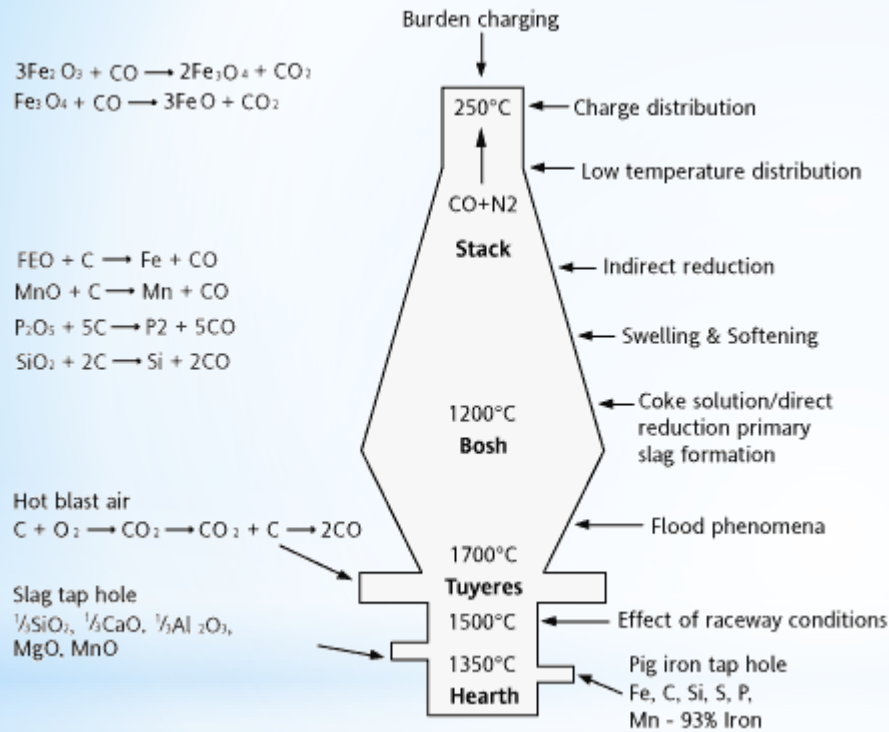
Chemical reaction equilibria

Chemical reaction equilibria in metallurgical processes and the conditions that maintain equilibrium are important to obtain maximum efficiency from production processes

For example, steel production takes place in a blast furnace that is aimed to collect liquid iron, slag and flue gases formed as a result of reaction with C and CO


$3Fe_2O_3 + CO \longrightarrow 2Fe_3O_4 + CO_2$
$Fe_3O_4 + CO \longrightarrow 3FeO + CO_2$

$FEO + C \longrightarrow Fe + CO$
$MnO + C \longrightarrow Mn + CO$
$P_2O_5 + 5C \longrightarrow P2 + 5CO$
$SiO_2 + 2C \longrightarrow Si + 2CO$

Hot blast air
$C + O_2 \longrightarrow CO_2 \longrightarrow CO_2 + C \longrightarrow 2CO$

Slag tap hole
½SiO₂, ½CaO, ½Al₂O₃,
MgO. MnO

Burden charging

250°C — Charge distribution
— Low temperature distribution
CO+N2
Stack — Indirect reduction
— Swelling & Softening
1200°C — Coke solution/direct reduction primary slag formation
Bosh
— Flood phenomena
1700°C
Tuyeres
1500°C — Effect of raceway conditions
1350°C — Pig iron tap hole
Hearth — Fe, C, Si, S, P, Mn - 93% Iron

The liquid phases iron and slag in the blast furnace consist of solutions of Fe, C, Si, Mn, P and SiO_2, Al_2O_3, CaO, FeO respectively

Flue gases typically contain CO, CO_2 and N_2 as main components

Iron oxide is reduced by CO to metallic iron while impurities in liquid iron are subjected to reaction with gaseous oxygen in converting stage

Consider a general reaction in equilibrium:

$$aA + bB \rightarrow cC + dD$$
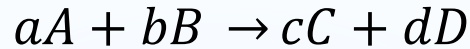
The general criterion for equilibrium under constant T and P is $\Delta G = 0$

$$\Delta G = \sum G_{products} - \sum G_{reactants}$$

$$= cG_C + dG_D - aG_A - bG_B$$

The complete differential of G in terms of T and P is

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

$$dG = VdP - SdT$$

Consider the reaction in a mixture of ideal gases at constant temperature
The change in Gibbs free energy of each ideal gas component as a function of its pressure is given as

$$\frac{\partial G_i}{\partial P_i} = V_i$$

$$dG_i = \frac{RTdP_i}{P_i}$$

$$\int dG_i = \int \frac{RT \, dP_i}{P_i}$$

$$G_i = G_i{}^o + RT \ln \frac{P_i}{P_i{}^o}$$

The change in free energy of the system at constant temperature is the sum of the free energy change of its components

$$nG = \sum n_i G_i$$

$$d(nG) = \sum n_i \, dG_i + \sum G_i \, dn_i$$

$$\Delta(nG) = \sum \frac{RT n_i}{P_i} dP_i + \sum G_i \, dn_i$$

Since mole number and pressure of ideal gases are proportional, n_i / P_i is constant and since the total pressure of the system is constant, $\sum dP_i = 0$

$$\Delta G = \sum G_i \, dn_i$$

In the case of system equilibrium

$$\Delta G = \sum G_i \, dn_i = 0$$

$$\Delta G = \sum G_i{}^o \, dn_i + RT \sum \ln(P_i dn_i)$$

The stoichiometric coefficients a, b, c, d of each component in the ideal gas mixture can be used to represent dn_i:

$$cG_C{}^o + dG_D{}^o - aG_A{}^o - bG_B{}^o + RT \ln P_C{}^c + RT \ln P_D{}^d + RT \ln P_A{}^{-a} + RT \ln P_B{}^{-b} = 0$$

$$\Delta G^o + RT \ln \frac{P_C{}^c P_D{}^d}{P_A{}^a P_B{}^b} = 0$$

where $\Delta G^o = cG_C{}^o + dG_D{}^o - aG_A{}^o - bG_B{}^o$

Absolute Gibbs free energy is computed for gass phases as:

$$G_i = G_i{}^o + RT \ln P_i$$

The equation for gas phases can be written as

$$\Delta G = \Delta G^o + RT \ln \frac{P_C{}^c P_D{}^d}{P_A{}^a P_B{}^b} = \Delta G^o + RT \ln Q_R$$

Q_R is called the reaction quotient

Q_R = K when $\Delta G = 0$

$$\Delta G = 0 = \Delta G^o + RT \ln K$$

ΔG^o is readily given in literature for most compounds at STP

The relationship between ΔG^o and K at 298 K

$\Delta G°$ (kJ)	K	Significance
200	9×10^{-36}	Essentially no forward reaction;
100	3×10^{-18}	reverse reaction goes to completion
50	2×10^{-9}	
10	2×10^{-2}	
1	7×10^{-1}	
0	1	Forward and reverse reactions proceed
-1	1.5	to same extent
-10	5×10^{1}	
-50	6×10^{8}	
-100	3×10^{17}	Forward reaction goes to completion;
-200	1×10^{35}	essentially no reverse reaction

FORWARD REACTION

REVERSE REACTION

Example - Estimate ΔG^o for the decomposition of NO_2 at 25°C
At 25°C and 1.00 atmosphere pressure, K = 4.3×10^{-13}

$$\Delta G = RT \ln Q_R - RT \ln K = RT \ln \frac{Q_R}{K}$$

ΔG can be calculated for any temperature, since $\Delta G^o = \Delta H^o - T\Delta S^o$

$$\Delta G = \Delta H^o{}_{298} + \int_{298}^{T} \Delta C_P dT - T\left(\Delta S^o{}_{298} + \int_{298}^{T} \frac{\Delta C_P dT}{T}\right)$$

where $C_P = a + bT + \frac{c}{T^2}$

and $\Delta C_P = \Delta a + \Delta bT + \frac{c}{T^2}$ where $\Delta a, b, c = \sum \Delta a, b, c_{products} - \sum \Delta a, b, c_{reactants}$

ΔG^o is the free energy change that would accompany the complete conversion of all reactants, initially present in their standard states, to all products in their standard states

ΔG is the free energy change for other temperatures and pressures

$$\Delta G = RT \ln Q_R - RT \ln K = RT \ln \frac{Q_R}{K}$$

ΔG has a very large positive or negative value if Q_R and K are very different

The reaction releases or absorbs a large amount of free energy

ΔG has a very small positive or negative value if Q_R and K are close

The reaction releases or absorbs a small amount of free energy

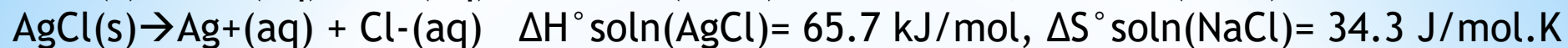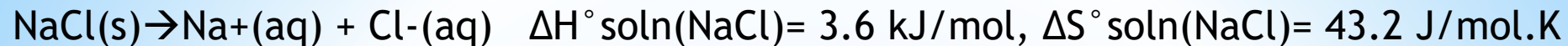Example -The equilibrium constant at different temperatures for the following reaction is given:

$SO_3(g) = SO_2(g) + ½ O_2(g)$
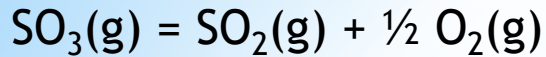
K= 0.146 @ 900K

K= 0.516 @ 1000K

K= 1.45   @ 1100K

Estimate the enthalpy change of the reaction at 1000K and the equilibrium composition at the same temperature

Example - Consider the equilibria in which two salts dissolve in water to form aqueous solutions of ions:

$NaCl(s) \rightarrow Na^+(aq) + Cl^-(aq)$ $\Delta H°soln(NaCl)= 3.6$ kJ/mol, $\Delta S°soln(NaCl)= 43.2$ J/mol.K

$AgCl(s) \rightarrow Ag^+(aq) + Cl^-(aq)$ $\Delta H°soln(AgCl)= 65.7$ kJ/mol, $\Delta S°soln(NaCl)= 34.3$ J/mol.K

a) Calculate the value of $\Delta G°$ at 298 K for each of the reactions. How will $\Delta G°$ for the solution process of NaCl and AgCl change with increasing T? What effect should this change have on the solubility of the salts?

b) Is the difference between two free energies primarily due to the enthalpy term or the entropy term of the standard free-energy change?

c) Use the values of $\Delta G°$ to calculate the K values for the two salts at 298 K

d) Sodium chloride is considered a soluble salt, whereas silver chloride is considered insoluble. Are these descriptions consistent with the answers to part c?

e) How will $\Delta G°$ for the solution process of these salts change with increasing T? What effect should this change have on the solubility of the salts?

Effect of pressure on equilibrium

Although equilibrium constant is independent of pressure, Le Chetelier's principle states that an increase in total pressure at constant temperature will shift the equilibrium in the direction which decreases the number of moles of gaseous species in the system

$$K = \frac{P_C{}^c P_D{}^d}{P_A{}^a P_B{}^b} = \frac{(X_C P)^c (X_D P)^d}{(X_A P)^a (X_B P)^b}$$

K is not affected by changes in pressure, but consists of two terms; K_X and P:

$$K = K_X P^{(c+d-a-b)}$$

Change in pressure may have effect on K_X, quotient of mole fractions depending on the values of a, b, c, and d

If
c+d>a+b, increasing pressure decreases K_X, reaction shifts towards reactants
c+d=a+b, pressure does not affect K_X
c+d<a+b, K_X is proportional to pressure, reaction shifts towards products with increasing K_X

Effect of temperature on equilibrium

At equilibrium, $\Delta G^o = -RT \ln K$

$$\Delta G^o = \Delta H^o + T\left(\frac{\partial \Delta G^o}{\partial T}\right)_P$$

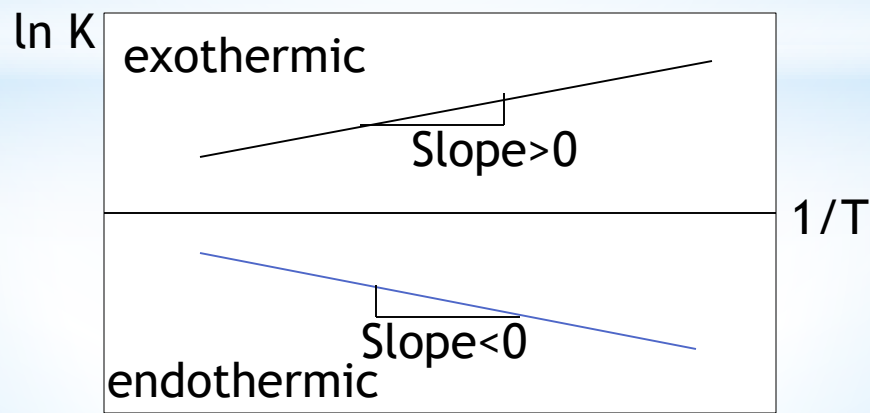$$-RT \ln K = \Delta H^o - T\left(\frac{\partial (RT \ln K)}{\partial T}\right)_P$$

$$\frac{\partial (\ln K)}{\partial T} = \frac{\Delta H^o}{RT^2}$$

$$\frac{\partial (\ln K)}{\partial (1/T)} = -\frac{\Delta H^o}{R} \qquad \text{Van't Hoff equation}$$
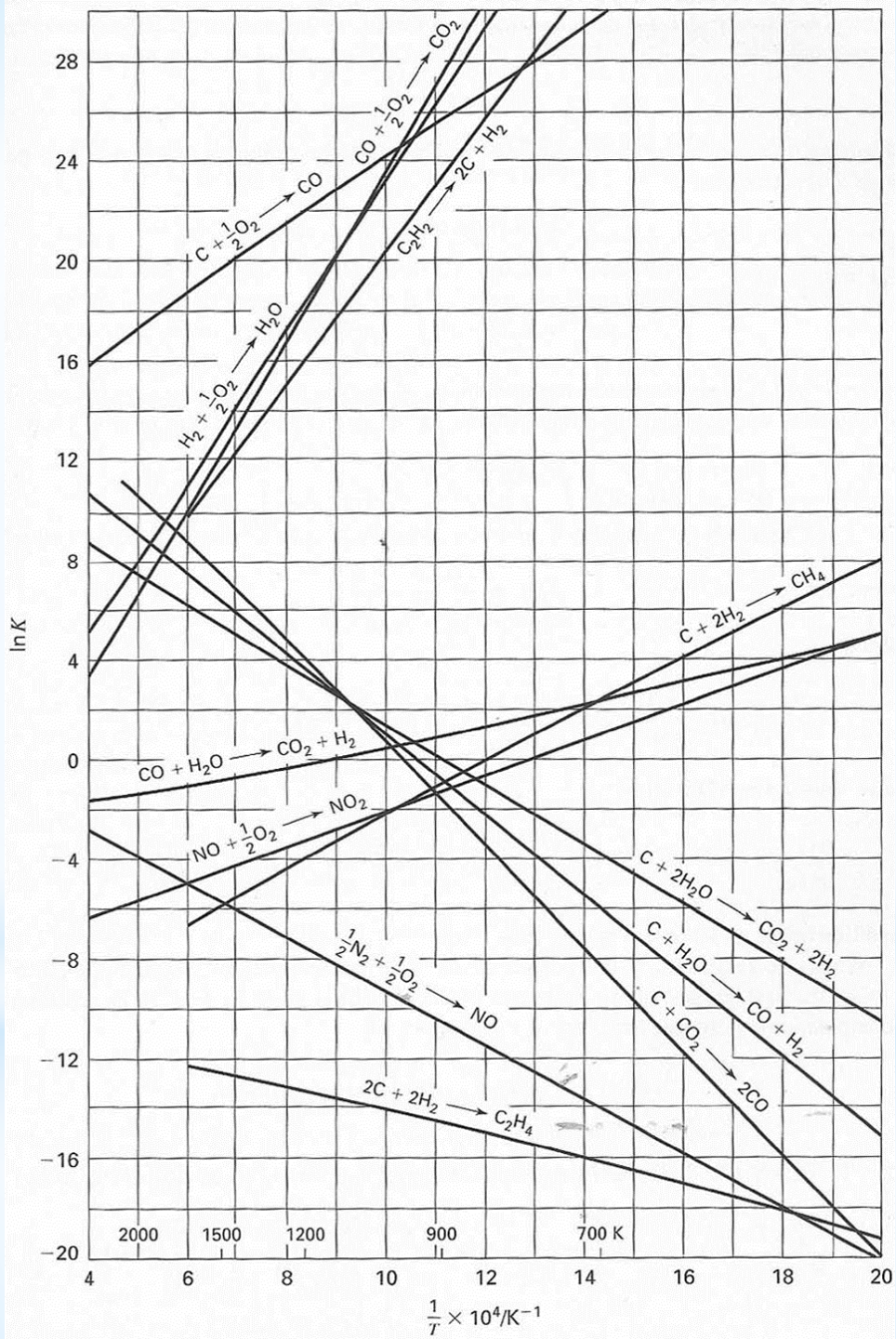
For the case of $\Delta H^o > 0$, temperature increase shifts the reaction towards products
For the case of $\Delta H^o < 0$, temperature increase shifts the reaction towards reactants

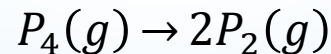$$\frac{\partial (\ln K)}{\partial \left(^1/_T\right)} = -\frac{\Delta H^o}{R}$$

Recall that $\Delta G = \Delta H - T\Delta S$

$G^o = H^o + T\left(\frac{\partial G^o}{\partial T}\right)_P$ Since $\left(\frac{\partial G^o}{\partial T}\right)_P = -S$,

Multiplying both sides by dT and dividing by T²,

$$\frac{G^o dT}{T^2} = \frac{H^o dT}{T^2} + T\left(\frac{\partial G^o}{T^2}\right)_P$$

$$\frac{H^o dT}{T^2} = \frac{G^o dT}{T^2} - \frac{T dG^o}{T^2} = -d\left(\frac{G^o}{T}\right), \qquad \frac{\Delta H^o}{T^2} = \frac{-d\left(\frac{\Delta G^o}{T}\right)}{dT}$$ Gibbs-Helmholtz Eqn

Example – Determine the heat exchange between system and surroundings for the following reaction in order to keep the temperature of the system constant at 1300 K

$$P_4(g) \rightarrow 2P_2(g)$$

$$\Delta G^o = -225000 + 18.2 T \ln T - 50.1 T$$

Oxygen pressure dependence of spontaneity of oxidation reactions

The spontaneity of any process at constant T and P is dependent on the change in the Gibbs free energy of the system:

$$\Delta G = \Delta G^o + RT \ln Q$$

ΔG can be calculated for any temperature since

$$\Delta G^o = \Delta H^o - T\Delta S^o$$

$$\Delta G = \Delta H^o{}_{298} + \int_{298}^{T} \Delta C_P dT - T\left(\Delta S^o{}_{298} + \int_{298}^{T} \frac{\Delta C_P dT}{T}\right)$$

where $C_P = a + bT + \frac{c}{T^2}$

and $\Delta C_P = \Delta a + \Delta bT + \frac{c}{T^2}$ where $\Delta a, b, c = \sum \Delta a, b, c_{products} - \sum \Delta a, b, c_{reactants}$

$$\Delta G = \Delta H^o{}_{298} + \int_{298}^{T} \left(\Delta a + \Delta bT + \Delta c/T^2\right) dT - T\left(\Delta S^o{}_{298} + \int_{298}^{T} \frac{\left(\Delta a + \Delta bT + \Delta c/T^2\right) dT}{T}\right)$$

Plotting the ΔG^o values of similar oxidation reactions as a function of T and comparing their relative reactivities would be useful for engineering complex systems like furnace charge, if it was possible to express ΔG^o of any reaction by a simple 2-term fit such as
$$\Delta G^o = A + BT$$

The following grouping lead to a condensed representation of ΔG^o which can further be simplified

$$\Delta G = \Delta H^o{}_{298} + \left(\Delta a T + \frac{\Delta b T^2}{2} - \Delta c / T \right) \Bigg]_{298}^{T} - T \left(\Delta S^o{}_{298} + \left(\Delta a \ln T + \Delta b T - \Delta c / 2T^2 \right) \right] \Bigg)_{298}^{T}$$

Replacement of the upper and the lower limits yields

$$\Delta G = 0 = \Delta G^o - I_o + I_1 T - \Delta a T \ln T - \frac{\Delta b}{2} T^2 - \frac{\Delta c}{2T}$$

where $I_o = \Delta H^o{}_{298} - \left(\Delta a 298 + \frac{\Delta b 298^2}{2} - \Delta c / 298 \right)$

$$I_1 = \Delta a - \Delta S^o{}_{298} + \Delta a \ln 298 + \Delta b 298 - \Delta c / 2 * 298^2$$

Tabulated thermochemical data such as $\Delta H^o{}_{298}$, $\Delta S^o{}_{298}$, ΔC_P for a specific reaction are replaced into the general equation for ΔG^o to obtain the variation of the spontaneity with temperature

Alternatively experimental variation of ΔG^o with T can be calculated from the measured oxygen partial pressure $P_{O2}(eqm)$ that is in equilibrium with a metal and metal oxide using equation:
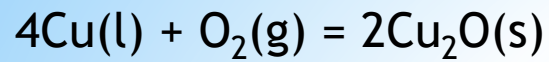
$$\Delta G^o = RT \ln P_{O2}(eqm)$$

Ellingham diagram
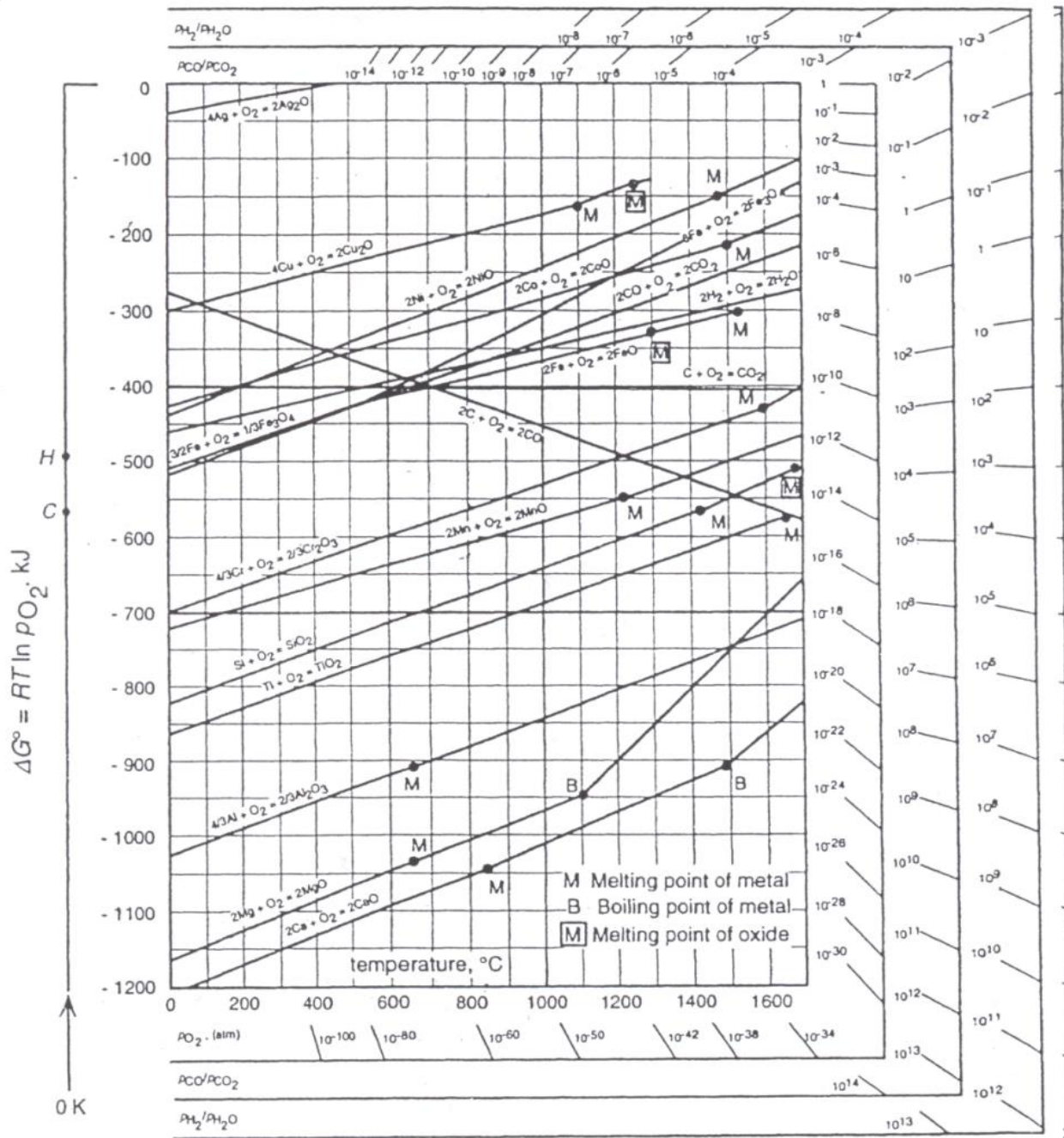
Example - Will the reaction

$4Cu(l) + O_2(g) = 2Cu_2O(s)$

go spontaneously to the right or to the left at 1500K when oxygen pressure is 0.01 atm?

$Cu(s)$ $S_{298}=33.36$ J/molK, $C_p=22.65+0.00628T$ J/molK $\Delta H_m= 13000$ J/mole at 1356K

$Cu(l)$ $C_p= 31.40$ J/molK

$Cu_2O(s)$ $H_{298}=-167440$ J/mol $S_{298}=93.14$ J/molK, $C_p=83.6$ J/molK

$O_2(g)$ $S_{298}=205.11$ J/molK, $C_p=33.44$ J/molK

Determining the composition of reaction system under equilibrium

$$aA(g) + bB(g) \rightarrow cC(g) + dD(g)$$
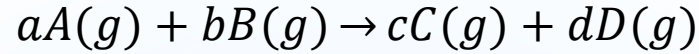
Consider the reacting A, B to produce C and D

$$K = \frac{P_C{}^c P_D{}^d}{P_A{}^a P_B{}^b}$$

The partial pressures of the components are expressed as a function of the total P:

$$P_A = \frac{n_A . P}{n_A + n_B + n_C + n_D}$$

where n_A is the mole number of A under equilibrium

Equilibrium constant can be represented as

$$K = \frac{n_C{}^c n_D{}^d}{n_A{}^a n_B{}^b} * \left(\frac{P}{n_A + n_B + n_C + n_D} \right)^{(c+d)-(a+b)}$$

Suppose the reaction reaches equilibrium after a while and x moles of A is converted to products

Then
n_A =Moles of unreacted A $= (1-x)a$
n_B = Moles of unreacted B $= (1-x)b$
n_C = Moles of formed C $= x.c$
n_D = Moles of formed D $= x.d$

and

$$K = \frac{(x.c)^c(x.d)^d}{(a-ax)^a(b-bx)^b} * \left(\frac{P}{(1-x)(a+b)+x(c+d)}\right)^{(c+d)-(a+b)}$$

If equilibrium temperature and the standard free energy change at that temperature are given, the fraction x can be conveniently determined since

$$\Delta G = \Delta G^o + RT_{eqm} \ln K = 0$$

$$\Delta G^o = -RT_{eqm} \ln\left[\frac{(x.c)^c(x.d)^d}{(a-ax)^a(b-bx)^b} * \left(\frac{P}{(1-x)(a+b)+x(c+d)}\right)^{(c+d)-(a+b)}\right]$$

Example – Determine the equilibrium composition of the system when 1 mole of P_4 reacts to form P_2 at 1300 K

$$\Delta G^o = -225000 + 18.2T\ln T - 50.1T \quad P_4(g) \rightarrow 2P_2(g)$$

$$\Delta G^o = -RT_{eqm}\ln\left[\frac{(x.c)^c(x.d)^d}{(a-ax)^a(b-bx)^b} * \left(\frac{P}{(1-x)(a+b)+x(c+d)}\right)^{(c+d)-(a+b)}\right]$$