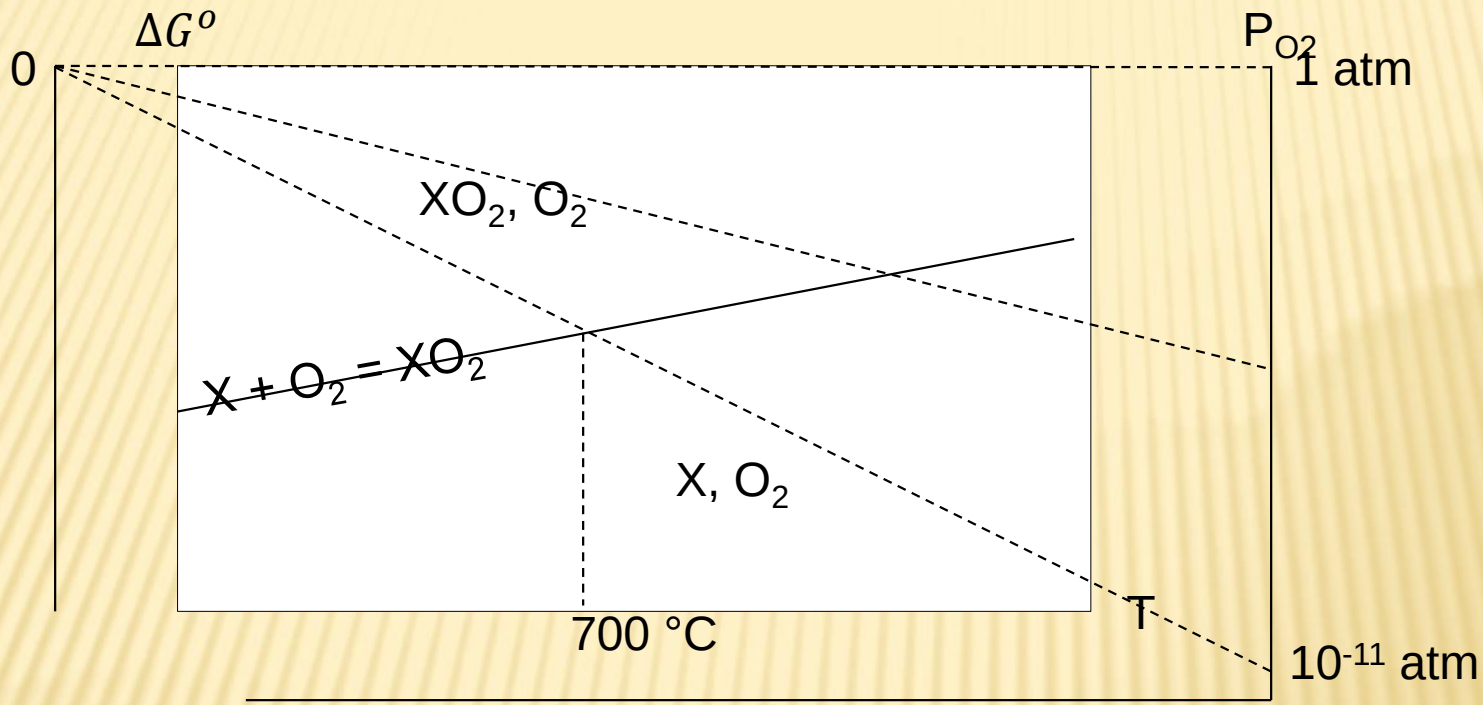
MME 2010
METALLURGICAL THERMODYNAMICS II

Chemical Reaction Equilibria Continued

Partial oxygen pressure grid lines



Ellingham diagram offers a simple and useful way to estimate equilibrium oxygen pressures as a function of temperature

For constant P_{O2} values, ΔG^o vs T is represented by straight lines with R lnP_{O2}slope and $\Delta G^o = 0$ intercept

The intersections of the constant oxygen partial pressure lines and the X-XO_2 equilibrium line give the equilibrium temperatures for this reaction at various oxygen partial pressures

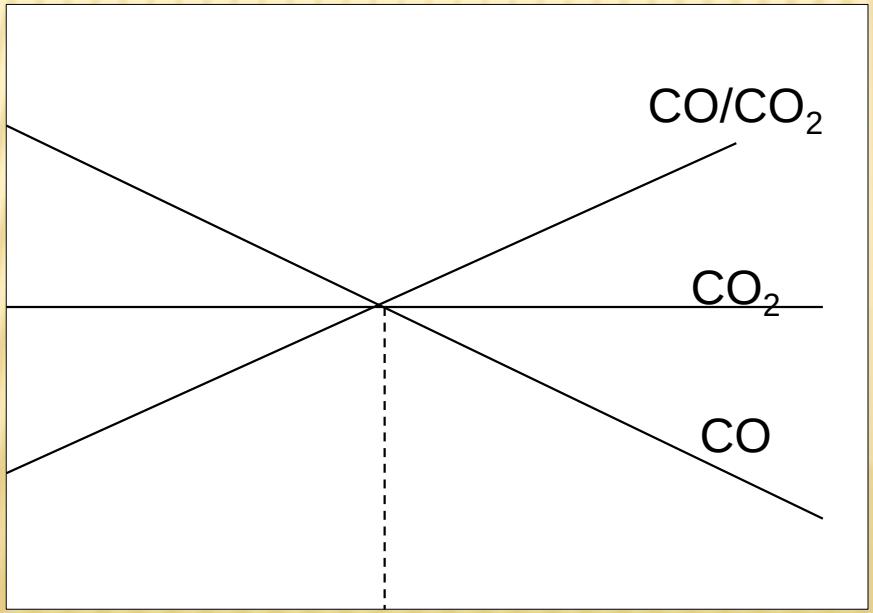
Carbon is extensively used in materials processing

The two oxides of carbon, CO and CO_2 are both gaseous species and it is important to know how they are distributed in an environment containing these gases

Ellingham for the oxides yield another line that represent the equilibrium between CO and CO_2:

$$2C(s) + 2O_2(g) = 2CO_2(g), \qquad \Delta G^o = -394321 - 0.84T\ J$$
$$2C(s) + O_2(g) = 2CO(g), \qquad \Delta G^o = -223532 - 175.4T\ J$$

$$2CO(s) + O_2(g) = 2CO_2(g), \qquad \Delta G^o = -565110 - 173.72T\ J$$



Reduction of metal oxides in industrial practice involves both carbon and CO as the reducing agent since carbon in solid state does not promote high reduction rates due to small contact area with the metal oxide

For example hematite in contact with carbon in oxygen blast furnace reacts as:

$$\mathrm{Fe_2O_3(s) + 3C(s) = 2Fe(s) + 3CO(g)}$$

This reaction proceeds slowly and the main reduction reaction occurs by CO:

$$\mathrm{3Fe_2O_3(s) + CO(g) = 2Fe_3O_4(s) + 3CO_2(g)}$$
$$\mathrm{Fe_3O_4(s) + CO(g) = 3}FeO\mathrm{(s) + CO_2(g)}$$
$$\mathrm{}FeO\mathrm{(s) + CO(g) = }Fe\mathrm{(s) + CO_2(g)}$$

Consider the oxidation of iron, as represented in the Ellingham diagram

$$\mathrm{2}Fe\mathrm{(s) + O_2(g) = 2}FeO\mathrm{(s)},\qquad \Delta G^o = RT\ln P_{O2}$$

$$\mathrm{2CO(s) + O_2(g) = 2CO_2(g)},\qquad \Delta G^o = -RT\ln\frac{P^2{}_{CO2}}{P^2{}_{CO}P_{O2}}$$

At equilibrium temperature both reactions are in equilibrium with the same partial oxygen pressure

The net reaction is $\mathrm{2Fe(s) + 2CO_2(g) = 2FeO(s) + 2CO(s)}, \Delta G^o = \Delta G^o{}_{Fe-CO} = RT\ln\frac{P^2{}_{CO2}}{P^2{}_{CO}}$

$$\Delta G^o{}_{Fe} = \Delta G^o{}_{CO} - 2RT\ln\frac{P_{CO}}{P_{CO2}}$$

CO/CO_2 grid lines can be related to the oxygen partial pressure in a system using the $CO\text{-}CO_2\text{-}O_2$ equilibrium

$$\Delta G^o = -\mathrm{RT}\ln\frac{P^2{}_{CO2}}{P^2{}_{CO}P_{O2}}$$

$$\Delta G^o = \mathrm{RT}\ln P_{O2} - 2\mathrm{RT}\ln\frac{P_{CO2}}{P_{CO}}$$

Partial pressure of oxygen is converted to the ratio of CO and CO_2 pressures as

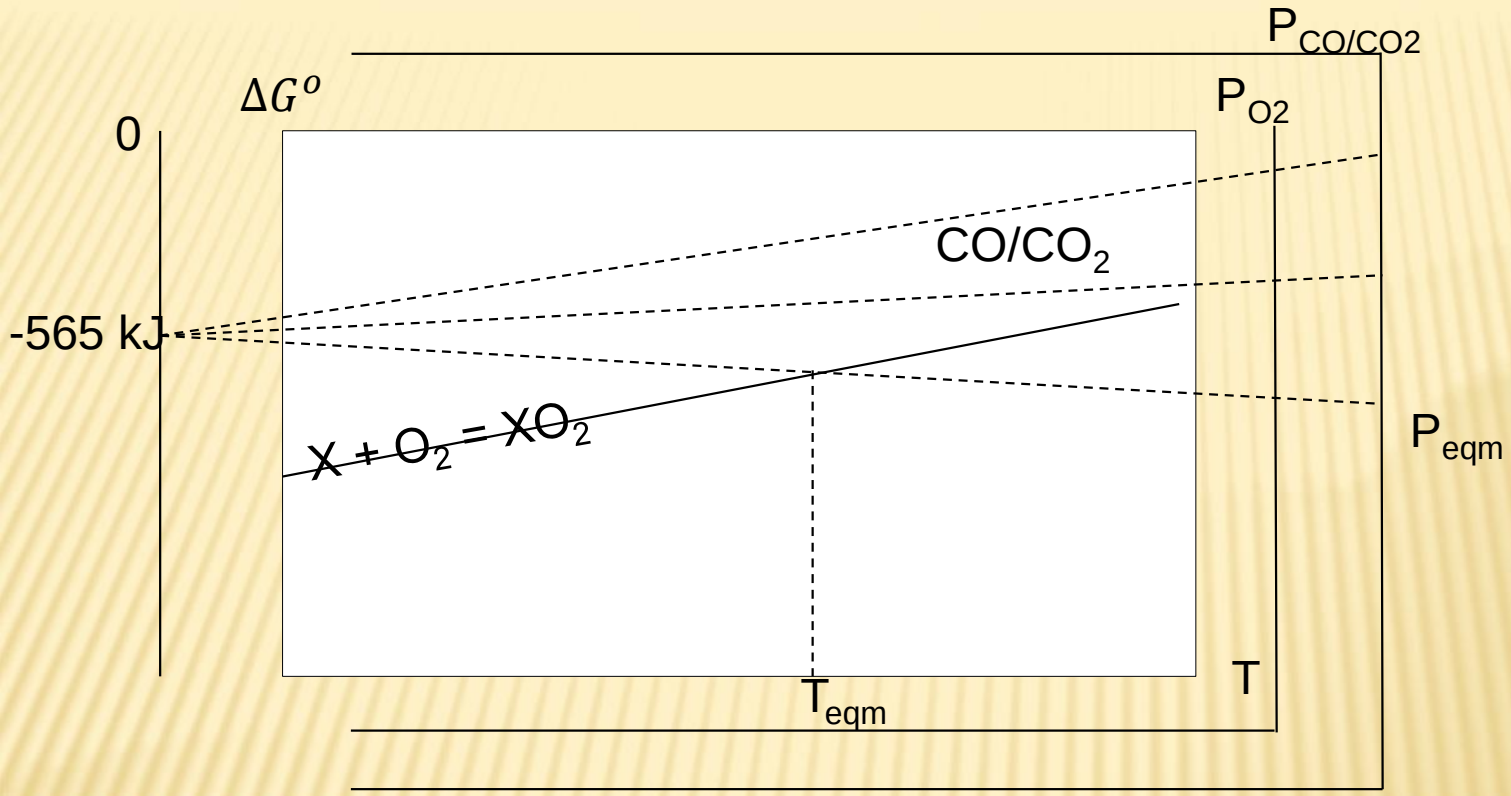
$$\mathrm{RT}\ln P_{O2} = \Delta G^o - 2\mathrm{RT}\ln\frac{P_{CO}}{P_{CO2}}$$

$$\Delta G^o = -565110 + 173.72\mathrm{T\ J}$$

$$\mathrm{RT}\ln P_{O2} = -565110 + (173.72 - 2\mathrm{R}\ln\frac{P_{CO}}{P_{CO2}})T$$

Constant CO/CO_2 ratios fall on straight lines on Ellingham diagram since RT $\ln P_{O2}$ is the ordinate:

Intercept at -565110 Joules and
slopes of 173.72-2R $\ln(P_{CO}/P_{CO2})$



P_{CO}/ P_{CO2} is constant along a straight line that passes through -565 kJ at 0 K and can be read from the ratio scale

At the intersection of the CO/CO_2 lines with a metal oxidation line, all metal X, XO_2, O_2, CO and CO_2 coexist at equilibrium

Metal oxide is reduced by CO at higher $P_{CO/CO2}$ than the equilibrium ratio
At lower ratios CO_2 is reduced while metal oxide forms

Example – What is the equilibrium $P_{CO/CO2}$ for reduction of MnO by CO at 1000 C?

$$2Mn(\mathrm{s}) + \mathrm{O_2(g)} = 2MnO(\mathrm{s}), \qquad \Delta G^o{}_{1273} = -140\ kcal$$
$$2\mathrm{CO(g)} + \mathrm{O_2(g)} = 2\mathrm{CO_2(g)}, \qquad \Delta G^o{}_{1273} = -82\ kcal$$

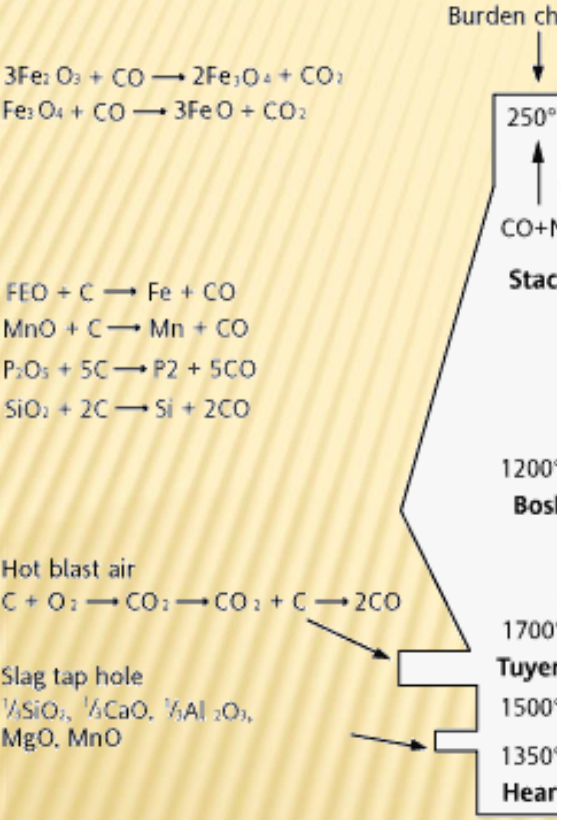
The oxygen partial pressure for the Mn oxidation reaction at equilibrium is calculated as

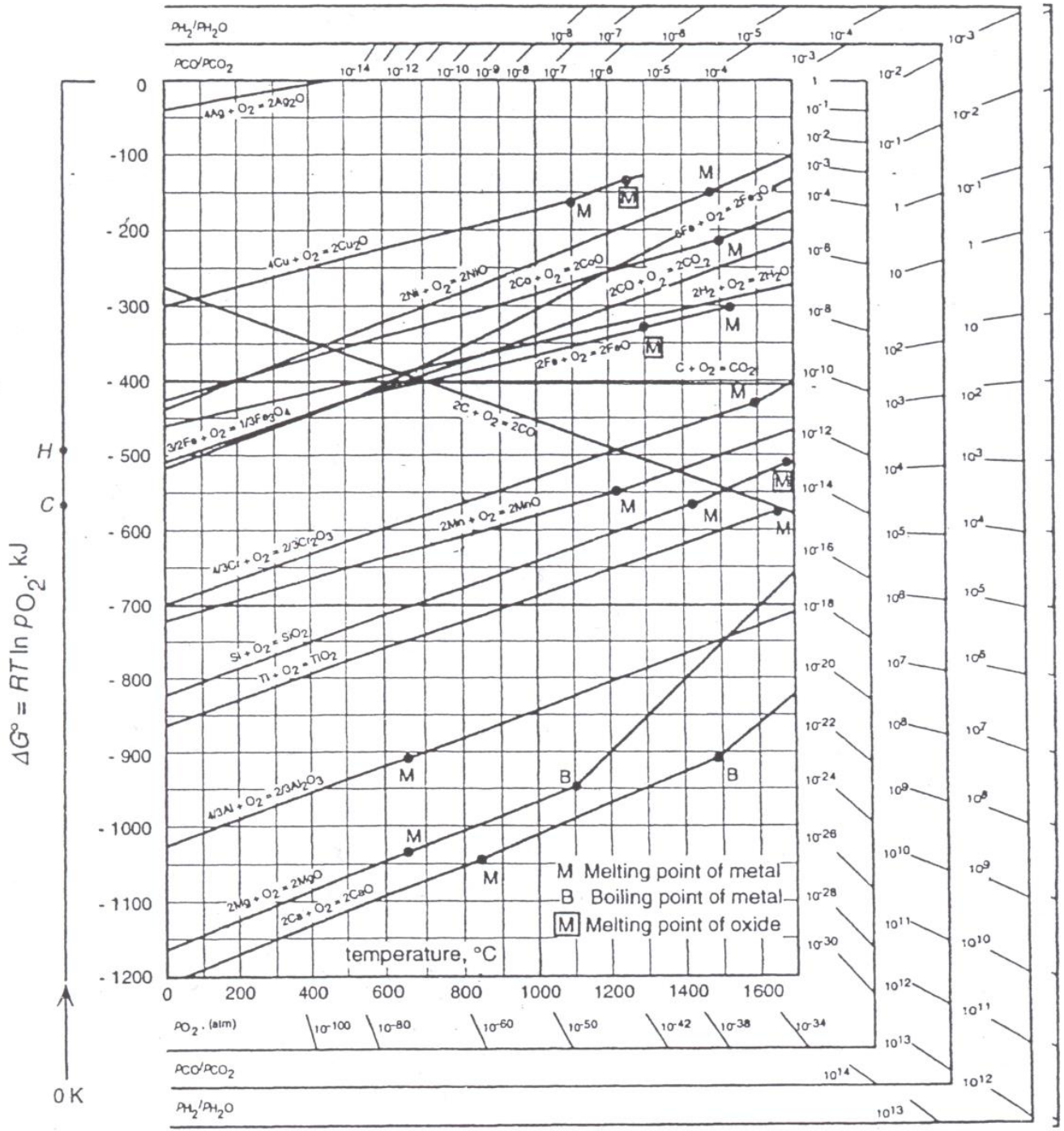
$$\Delta G^o = RT \ln P_{O2}$$
$$-140000 = 1.987154 * 1273 * \ln P_{O2}$$
$$P_{O2} = 10^{-24}\ atm$$

The free energy change for the carbon oxidation reaction is used to calculate $P_{CO/CO2}$

$$\Delta G^o = -RT \ln \frac{P^2{}_{CO2}}{P^2{}_{CO} P_{O2}}$$
$$-82000 = -1.987154 * 1273 * \ln \frac{P^2{}_{CO2}}{P^2{}_{CO} * 10^{-24}}$$
$$\frac{P_{CO}}{P_{CO2}} = 10^5$$

Evaluate the CO pressures for the iron blast furnace reactions





H_2/H_2O grid lines

In industrial processes involving H_2 as the reducing agent, the equilibrium between hydrogen and water should be taken into account as well as the equilibrium between metal and metal oxide

$$\begin{array}{l} 2X(\mathrm{s}) + \mathrm{O}_2(\mathrm{g}) = 2XO(\mathrm{s}), \qquad \Delta G^o{}_X \\ \underline{2\mathrm{H}_2(\mathrm{g}) + \mathrm{O}_2(\mathrm{g}) = 2H_2O(g), \qquad \Delta G^o{}_H} \\ 2XO(\mathrm{s}) + 2\mathrm{H}_2(\mathrm{g}) = 2X(\mathrm{s}) + 2H_2O(g), \qquad \Delta G^o{}_H - \Delta G^o{}_X \end{array}$$

At equilibrium temperature both reactions are in equilibrium with the same partial oxygen pressure

$$\Delta G^o{}_X = RT \ln P_{O2}$$

$$\Delta G^o{}_H = -RT \ln \frac{P^2{}_{H2O}}{P^2{}_{H2} P_{O2}} = RT \ln P_{O2} + 2RT \ln \frac{P_{H2}}{P_{H2O}} = \Delta G^o{}_X + 2RT \ln \frac{P_{H2}}{P_{H2O}}$$

The net reaction is

$$\Delta G^o{}_H - \Delta G^o{}_X = 2RT \ln \frac{P_{H2}}{P_{H2O}}$$

$$\Delta G^o{}_X = \Delta G^o{}_H - 2RT \ln \frac{P_{H2}}{P_{H2O}}$$

H_2/H_2O grid lines can be related to the oxygen partial pressure in a system using the H_2-H_2O-O_2 equilibrium

$$2\mathrm{H_2(g)} + \mathrm{O_2(g)} = 2H_2O(g), \qquad \Delta G^o = -492887 + 109.62T\ J$$

$$\Delta G^o = -\mathrm{RT}\ln\frac{P^2{}_{H2O}}{P^2{}_{H2}P_{O2}}$$

$$\Delta G^o = \mathrm{RT}\ln P_{O2} - 2\mathrm{RT}\ln\frac{P_{H2O}}{P_{H2}}$$

Partial pressure of oxygen is converted to the ratio of H_2 and H_2O gases as

$$\mathrm{RT}\ln P_{O2} = \Delta G^o - 2\mathrm{RT}\ln\frac{P_{H2}}{P_{H2O}}$$

$$\Delta G^o = -492887 + 109.62\mathrm{T\ J}$$

$$\mathrm{RT}\ln P_{O2} = -492887 + (109.62 - 2\mathrm{R}\ln\frac{P_{H2}}{P_{H2O}})T$$

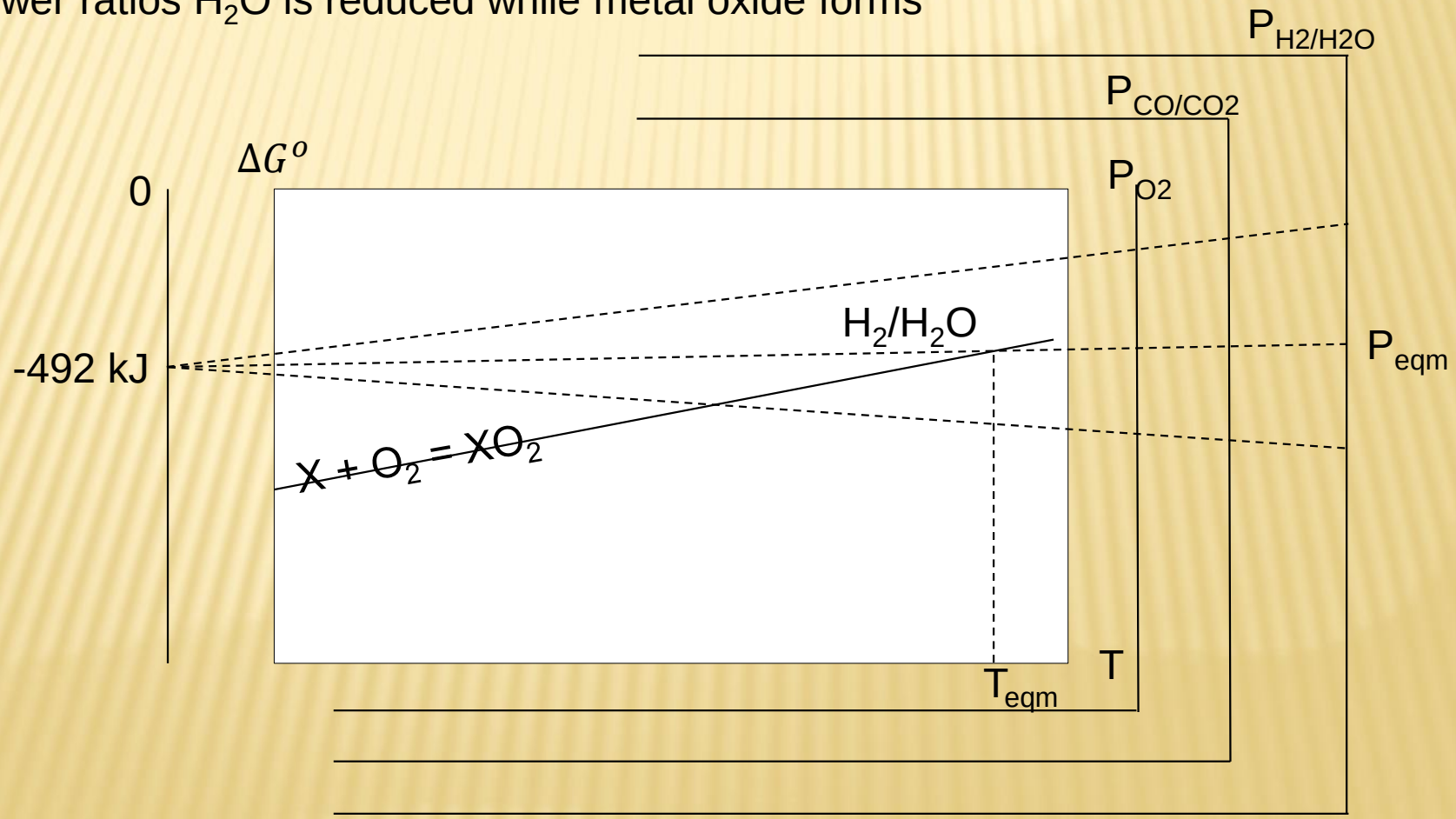
Constant H_2/H_2O ratios fall on straight lines on Ellingham diagram since RT $\ln P_{O2}$ is the ordinate:

Intercept at -492887 Joules and
slopes of 109.62-2R $\ln(P_{H2}/P_{H2O})$

$\frac{P_{H2}}{P_{H2O}}$ is constant along a straight line that passes through -492387 J at 0 K and can be read from the scale on the far right of the Ellingham diagram

At the intersection of the H_2/H_2O lines with a metal oxidation line, all metal X, XO_2, O_2, H_2 and H_2O coexist at equilibrium

The metal is reduced by H_2 at higher $P_{H2/H2O}$ than the equilibrium ratio
At lower ratios H_2O is reduced while metal oxide forms



Example – What is the equilibrium $P_{H2/H2O}$ for reduction of TiO_2 by H_2 at 1600 C?

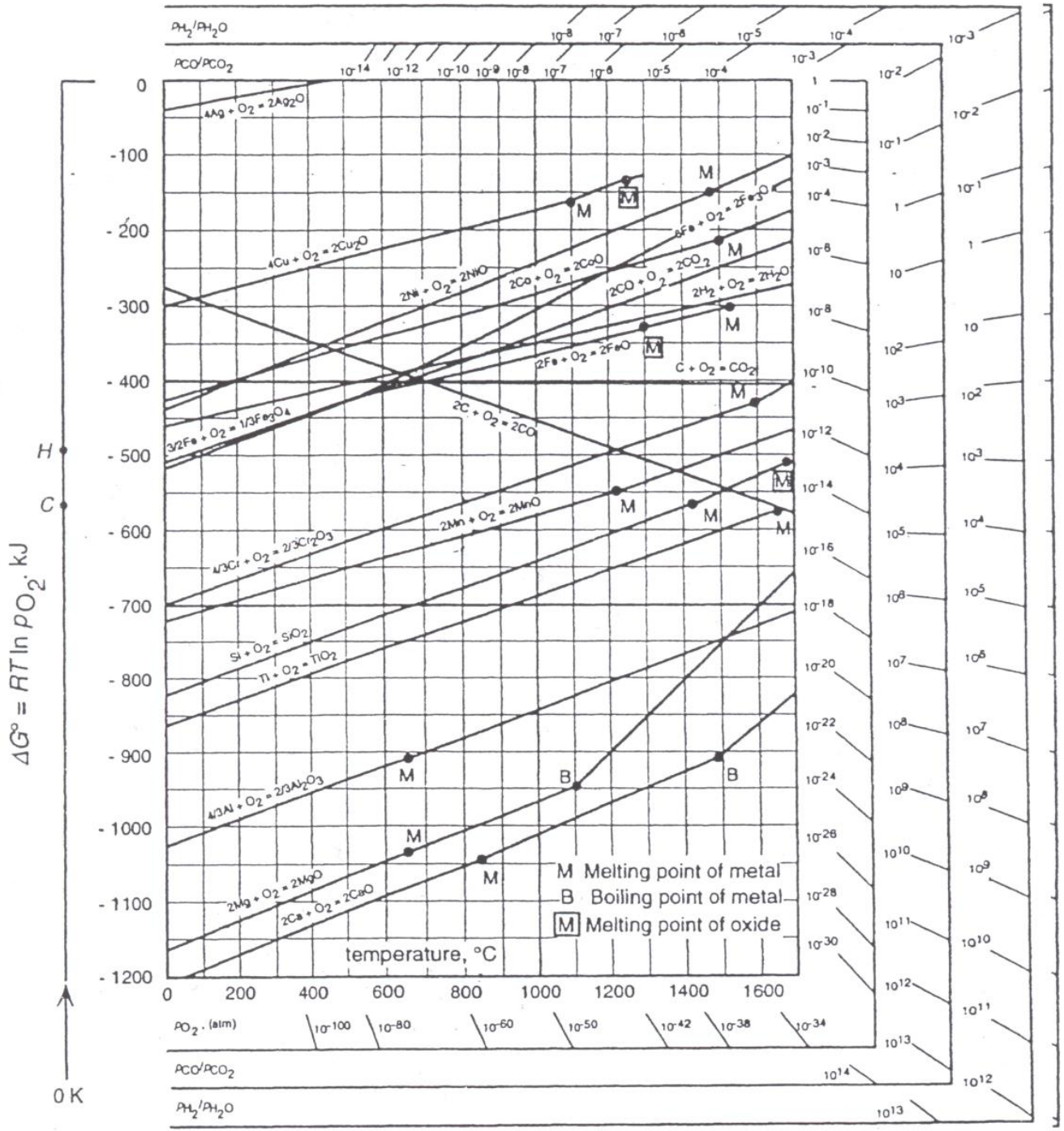
$$Ti(\mathrm{s}) + \mathrm{O_2(g)} = \mathrm{TiO_2(s)}, \qquad \Delta G^o{}_{1873} = -136\ kcal$$
$$\mathrm{2H_2(g) + O_2(g) = 2H_2O(g)}, \qquad \Delta G^o{}_{1873} = -68\ kcal$$

The oxygen partial pressure for the Ti oxidation reaction at equilibrium is calculated as

$$\Delta G^o = RT \ln P_{O2}$$
$$-136000 = 1.987154 * 1873 * \ln P_{O2}$$
$$P_{O2} = 10^{-16}\ atm$$

The free energy change for the hydrogen oxidation reaction is used to calculate $P_{H2/H2O}$

$$\Delta G^o = -RT \ln \frac{P^2{}_{H2}}{P^2{}_{H2O} P_{O2}}$$
$$-68000 = -136000 + 2 * 1.987154 * 1873 \ln \frac{P_{H2}}{P_{H2O}}$$
$$\frac{P_{H2}}{P_{H2O}} = 10^4$$


$\Delta G^\circ = RT \ln pO_2$, kJ
temperature, °C
M Melting point of metal
B Boiling point of metal
M Melting point of oxide
$4Ag + O_2 = 2Ag_2O$
$4Cu + O_2 = 2Cu_2O$
$2Ni + O_2 = 2NiO$
$2Co + O_2 = 2CoO$
$2Fe + O_2 = 2FeO$
$2CO + O_2 = 2CO_2$
$2H_2 + O_2 = 2H_2O$
$2C + O_2 = 2CO$
$C + O_2 = CO_2$
$3/2Fe + O_2 = 1/3Fe_3O_4$
$4/3Cr + O_2 = 2/3Cr_2O_3$
$2Mn + O_2 = 2MnO$
$Si + O_2 = SiO_2$
$Ti + O_2 = TiO_2$
$4/3Al + O_2 = 2/3Al_2O_3$
$2Mg + O_2 = 2MgO$
$2Ca + O_2 = 2CaO$

Sulfidation of metals

Sulphide ion has affinity for metal cations and many valuable metal ores are found in nature in sulphide forms

Economically important sulfides are Acanthite Ag_2S, Chalcocite Cu_2S, Bornite Cu_5FeS_4, Galena PbS, Sphalerite ZnS, Chalcopyrite $CuFeS_2$

Sulfidation reactions are in many ways thermodynamically similar to oxidation reactions

Sulphur in gaseous form can be considered the same with oxygen and the activity of metal sulfides can be taken as unity

$$2\mathrm{Mn(s)} + \mathrm{S_2(g)} = 2\mathrm{Mn}S\mathrm{(s)}$$

$$\Delta G^o = RT \ln P_{S2}$$

The methods for calculation of the equilibrium partial sulphur pressure at a constant temperature are the same as finding the equilibrium partial oxygen pressure

Ellingham diagram showing the standard formation free energies of sulfides

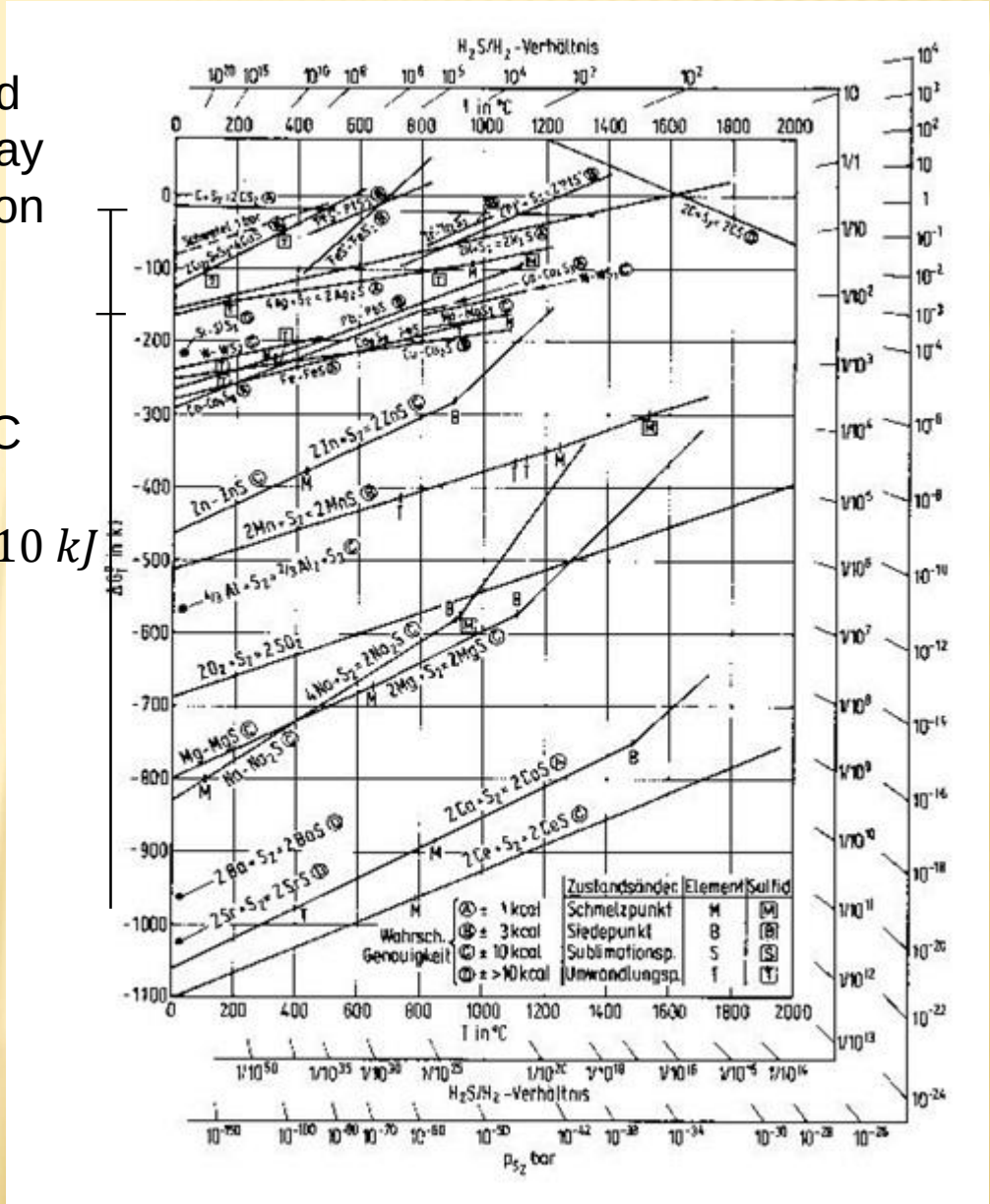
The equilibrium partial pressure of S_2 and the ratio of $P_{H2S/H2}$ can be determined graphically from the figure in the same way as described previously for oxygen, carbon and hydrogen

Example – Determine the sulphur partial pressure in equilibrium with MnS at 700 C

$$2\mathrm{Mn(s)} + \mathrm{S_2(g)} = 2\mathrm{MnS(s)}, \Delta G^o{}_{973} = -410\ kJ$$

$$\Delta G^o = RT \ln P_{S2}$$
$$= -410000 = 8.314 * 973 * \ln P_{S2}$$

$$P_{S2} = 10^{-22}$$



Reduction of metal sulphurs by H_2

Just as the metal oxides are reduced by hydrogen to form metal and H_2O, metal sulphides are reduced by hydrogen to form H_2S and metal

$$\begin{gathered} 2Mn(\mathrm{s}) + \mathrm{S_2(g)} = 2MnS(\mathrm{s}), \qquad \Delta G^o{}_M \\ \underline{2\mathrm{H_2(g)} + \mathrm{S_2(g)} = 2H_2S(g), \qquad \Delta G^o{}_{HS}} \\ 2MnS(\mathrm{s}) + 2\mathrm{H_2(g)} = 2Mn(\mathrm{s}) + 2H_2S(g), \Delta G^o{}_{HS} - \Delta G^o{}_M \end{gathered}$$

At equilibrium temperature both reactions are in equilibrium with the same partial sulphur pressure

$$\Delta G^o{}_M = RT \ln P_{S2}$$

$$\Delta G^o{}_{HS} = -RT \ln \frac{P^2{}_{H2S}}{P^2{}_{H2} P_{S2}} = RT \ln P_{S2} + 2RT \ln \frac{P_{H2}}{P_{H2S}} = \Delta G^o{}_M + 2RT \ln \frac{P_{H2}}{P_{H2S}}$$

The net reaction is

$$\Delta G^o{}_{HS} - \Delta G^o{}_M = 2RT \ln \frac{P_{H2}}{P_{H2S}}$$

$$\Delta G^o{}_M = \Delta G^o{}_{HS} - 2RT \ln \frac{P_{H2}}{P_{H2S}}$$

H_2/H_2S grid lines can be related to the sulphur partial pressure in a system using the H_2-H_2S-S_2 equilibrium

$$2\mathrm{H_2(g)} + \mathrm{S_2(g)} = 2H_2S(g), \qquad \Delta G^o = -152900 + 99.37T\ J$$

$$\Delta G^o = -\mathrm{RT}\ln\frac{P^2{}_{H2S}}{P^2{}_{H2}P_{S2}}$$

$$\Delta G^o = \mathrm{RT}\ln P_{S2} - 2\mathrm{RT}\ln\frac{P_{H2S}}{P_{H2}}$$

Partial pressure of sulphur is converted to the ratio of H_2 and H_2S gases as

$$\mathrm{RT}\ln P_{S2} = \Delta G^o - 2\mathrm{RT}\ln\frac{P_{H2}}{P_{H2S}}$$

$$\mathrm{RT}\ln P_{S2} = -152900 + (99.37 - 2\mathrm{R}\ln\frac{P_{H2}}{P_{H2S}})T$$

Constant H_2/H_2S ratios fall on straight lines on Ellingham diagram since RT lnP_{S2} is the ordinate:

Intercept at -152900 Joules and
slopes of 99.37-2R ln(P_{H2}/P_{H2S})

Example – What is the equilibrium $P_{H2/H2S}$ for reduction of MnS by H_2 at 700 C?

$$2Mn(\mathrm{s}) + \mathrm{S}_2(\mathrm{g}) = 2MnS(\mathrm{s})$$

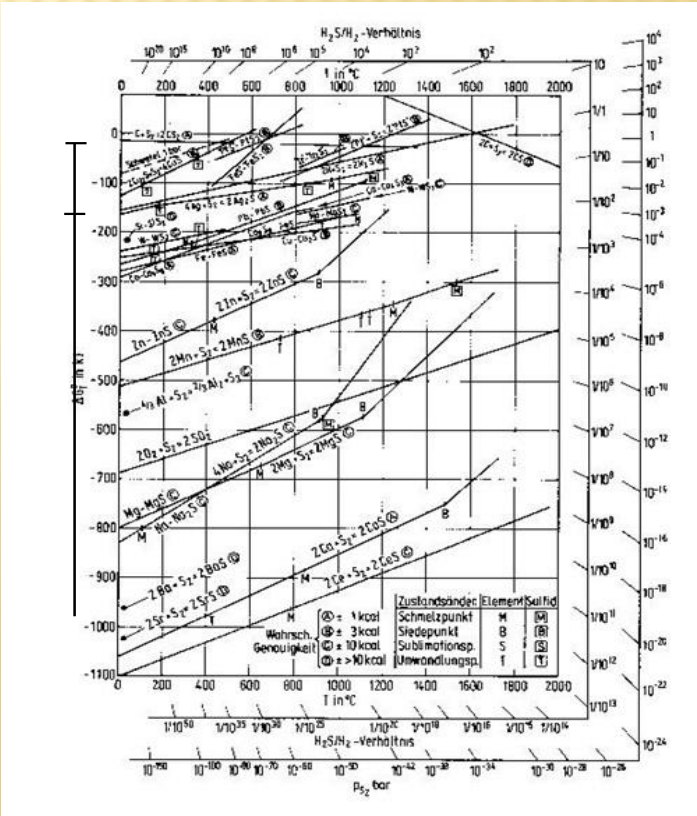
$$\Delta G^o{}_{Mn} = -410000\,J = RT \ln P_{S2}$$

$$P_{S2} = 10^{-22}\,atm$$

$$\mathrm{RT} \ln P_{S2} = -152900 + (99.37 - 2\mathrm{R} \ln \frac{P_{H2}}{P_{H2S}})973$$

$$\frac{P_{H2}}{P_{H2S}} = 10^{-9}$$

MnS is reduced to Mn at $\frac{P_{H2}}{P_{H2S}} > 10^{-9}$



Determining the composition of reaction system under equilibrium

$$aA(g) + bB(g) + eE(g) \rightarrow cC(g) + dD(g) + eE(g)$$

Consider reacting A, B and inert E to produce C and D and inert E

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

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

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

where n_A is the mole number of A under equilibrium

Equilibrium constant can be represented as

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

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

Then

n_A =Fraction of unreacted A $= (1-x)a$

n_B =Fraction of unreacted B $= (1-x)b$

n_C =Fraction of formed C $= x.c$

n_D =Fraction of formed D $= x.d$

n_E =Fraction of inert E in the system= e

and

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

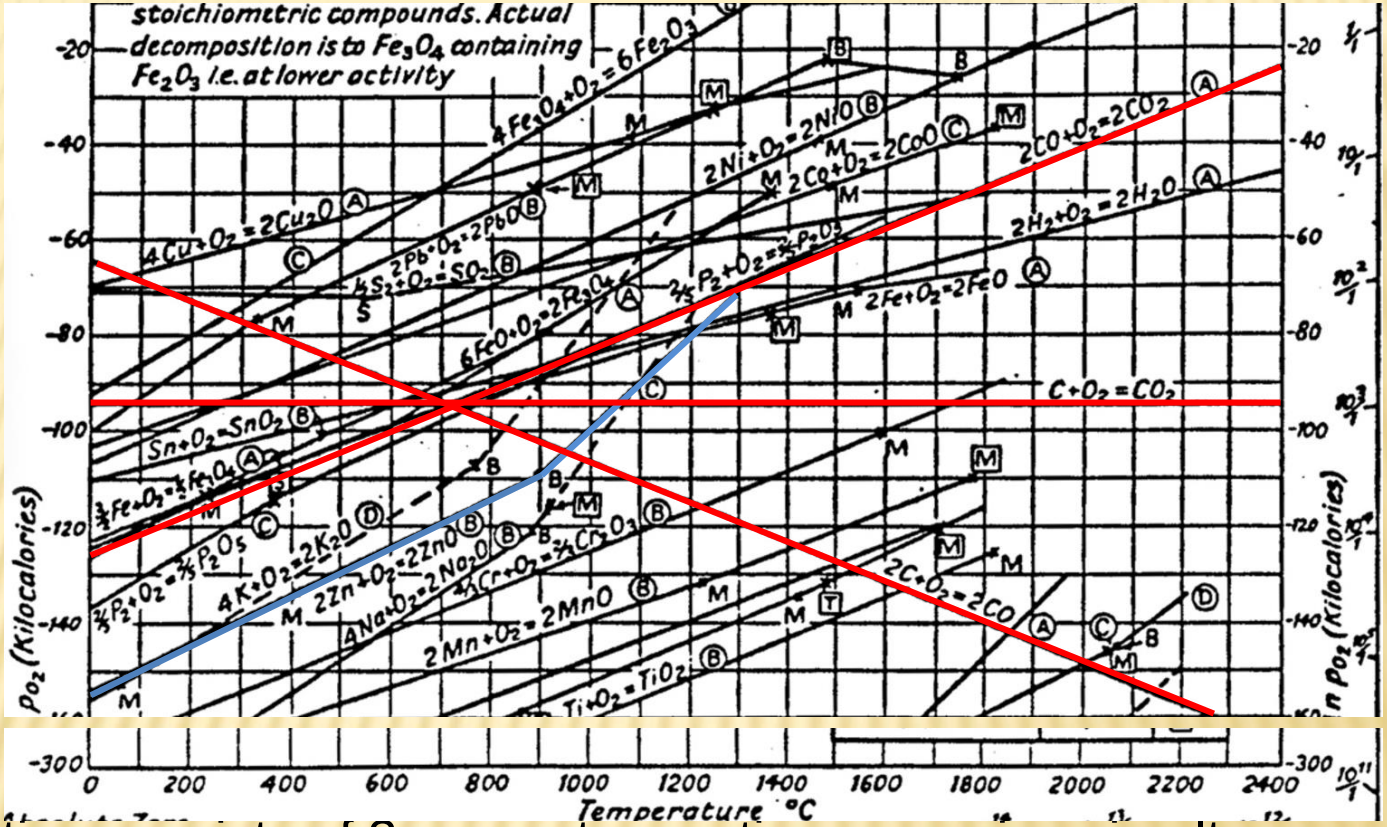
If equilibrium temperature and the standard free energy change at that temperature are given, the fraction x can be conveniently determined since

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

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

Example – 1 mole of Solid ZnO is reduced by CO gas at 1027 C and 1 atm to produce CO_2 and Zn gas:

$$\mathrm{ZnO}(s) + \mathrm{CO}(g) = \mathrm{Zn}(g) + \mathrm{CO_2}(g) \text{ @ 1027 C, 1 atm}$$



The reaction consists of 3 separate reactions occuring simultaneously

$$2\mathrm{ZnO}(s) = 2\mathrm{Zn}(g) + \mathrm{O_2}(g), \qquad \Delta G^o = 230840 + 20.7T\log T - 164.8T$$

$$2\mathrm{C}(s) + 2\mathrm{O_2}(g) = 2\mathrm{CO_2}(g), \qquad \Delta G^o = -188400 - 0.4T$$

$$2\mathrm{CO}(g) = 2\mathrm{C}(s) + \mathrm{O_2}(g), \qquad \Delta G^o = 53400 + 41.9T$$

$$2\mathrm{ZnO}(s) + 2\mathrm{CO}(g) = 2\mathrm{Zn}(g) + 2\mathrm{CO_2}(g), \qquad \Delta G^o = 95840 + 20.7T\log T - 123.3T$$

$$\mathrm{ZnO}(s) + \mathrm{CO}(g) = \mathrm{Zn}(g) + \mathrm{CO_2}(g), \qquad \Delta G^o = 47920 + 10.35T\log T - 61.65T \; cal/mole$$

The reaction constant at equilibrium temperature 1300 K is obtained as

$$\ln K = -\frac{\Delta G^o}{RT_{eqm}} = -\frac{9700\ cal}{1.987154\frac{cal}{K}.1300\ K} = -2.35$$

$$K = 0.0224$$

The initial mole number of gaseous ZnO = 0, final mole number = 0
The initial mole number of gaseous CO = 1, final mole number = 1-x
The initial mole number of gaseous Zn = 0, final mole number = x
The initial mole number of gaseous CO_2 = 0, final mole number = x

$$K = \left[\frac{x^2}{(1-x)} * \left(\frac{1}{(1-x)+2x}\right)^1\right] = 0.0224$$

$$x = 0.15$$

The reaction is completed by 15 % at equilibrium
0.15 moles CO_2
0.85 moles CO
<u>0.15 moles Zn</u>
Total = 1.15 moles

13% CO_2
74% CO
13% Zn

Example – Reduction of solid ZnO by methane gas is another industrial Zn production process:

$$\mathrm{ZnO(s)} + \mathrm{CH_4\ (g)} = \mathrm{Zn(g)} + \mathrm{CO(g)} + 2\mathrm{H_2} \text{ @ 827 C, 1 atm}$$

$\Delta G^o = 114303 - 12.93T \ln T + 0.00035T^2 - 0.00000088T^3 - 10.53T$ cal/mole

There are 1 mole of ZnO and CH_4 at the beginning of the reaction

The free energy of the reaction at the equilibrium temperature 1100 K is

$$\Delta G^o = 1470\ calories$$

$$\ln K = -\frac{\Delta G^o}{RT_{eqm}} = -\frac{1470\ cal}{1.987156\frac{cal}{K}.1100\ K} = -0.673$$

$$K = 0.51$$

$$K = \frac{P_{Zn}\ \ P_{CO}\ \ {P_{H2}}^2}{P_{CH4}}$$

$$0.51P_{CH4} = P_{Zn}.\ \ P_{CO.}\ \ {P_{H2}}^2$$

$$0.51 P_{CH4} = P_{Zn}.\ \ P_{CO.}\ \ {P_{H2}}^2$$

Since the system pressure is constant at 1 atm,

$$P_{CH4} + P_{Zn} + P_{CO} + P_{H2} = 1\ atm$$

The ratio of the partial pressures of the products at equilibrium is

$$P_{Zn}/P_{CO}\ /P_{H2} = 1/\ 1/2$$

With three equations relating 4 variables at hand, it is possible to calculate the concentration of the products if the equilibrium partial pressure of methane is given the value x

The initial mole number of gaseous ZnO = 0, final mole number = 0
The initial mole number of gaseous CH_4 = 1, final mole number = x
The initial mole number of gaseous Zn = 0, final mole number = ¼(1-x)
The initial mole number of gaseous CO = 0, final mole number = ¼(1-x)
The initial mole number of gaseous H_2 = 0, final mole number = ½ (1-x)

$$K = \frac{(1/4(1-x).\frac{1}{4}(1-x).\left(\frac{1}{2}(1-x)\right)^2 . 2^2}{x} * \left(\frac{1}{x+\frac{1}{4}(1-x)+\frac{1}{4}(1-x)+\frac{1}{2}(1-x)}\right)^3$$

$$x = 0.0275$$

The partial pressures of the gaseous components of the system are thus calculated as

$$P_{CH4} = 0.0275\ atm$$

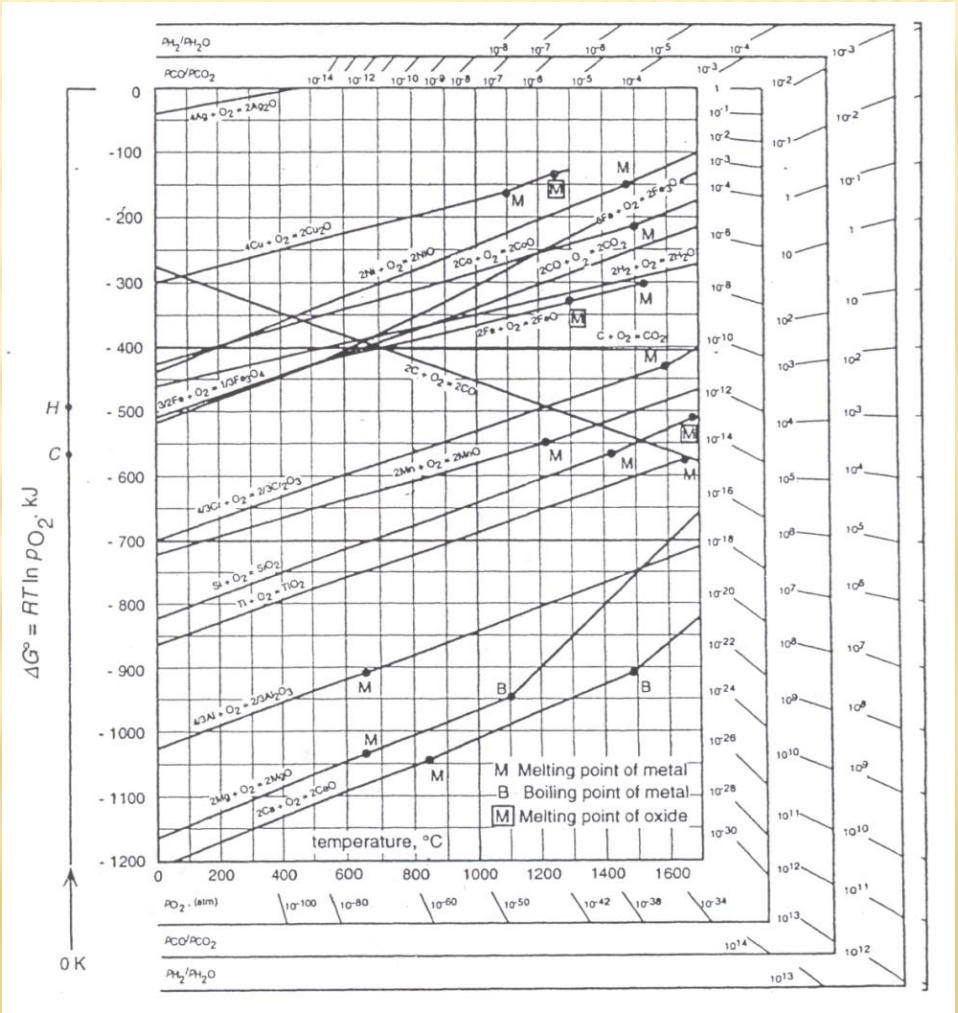
$$P_{Zn} = \frac{1}{4}(1 - 0.0275) = 0.2431\ \text{atm}$$

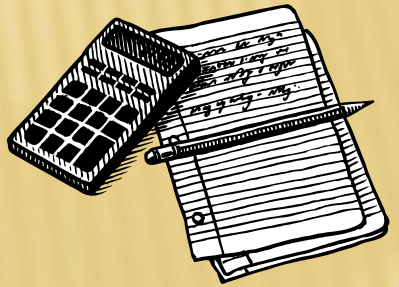
$$P_{CO} = \frac{1}{4}(1 - 0.0275) = 0.2431\ \text{atm}$$

$$P_{H2} = \frac{1}{2}(1 - 0.0275) = 0.4862\ \text{atm}$$

0.0275 moles of ZnO residue is present in the system at equilibrium

Example – A zinc production plant uses CO-CO_2 gas mixture that is obtained by combusting coal to reduce ZnO. Engineers are asked to calculate the amount of equilibrium CO gas that has to be rejected to the atmosphere for each mole of CO_2 produced. Comment on the feasibility of the process (i.e. amount of the products and reactants) in the case of reduction with a) cold gases at 27 C, b) hot gases at 1027 C
Hint: Boiling point of Zn is 908 C





Practice Questions

1. A zinc production plant uses CO-CO_2 gas mixture that is obtained by
Pure iron and oxygen react accordingly to form FeO :
$2Fe(s)+O_2(g)\rightarrow 2FeO\ (s)$
a. Determine the entropy change of the reaction
b. Determine the free energy change of the reaction as a function of temperature
c. What will be free energy and the direction of the reaction when the system is left in a furnace at 1560 C with a large amount of Mn ?

2. The variation of equilibrium constants for several reactions is given in the figure. The following reaction is of particular interest:
$C(s)+CO_2(g)\rightarrow 2CO(g)$
a. Determine the enthalpy change of the reaction at 700 K
b. Calculate the partial molar pressures of each chemical species at equilibrium attained around 700 K and 1 atm pressure

3. Estimate the enthalpy change of the following reaction at 2000K and the equilibrium composition at the same temperature
$\frac{1}{2}\ N_2 + \frac{1}{2}\ O_2 = NO$
4. Pure CO2 is admitted to an empty chamber at 1000 C. Calculate the partial pressure of oxygen generated from the thermal decomposition of CO2 within the chamber at a total pressure of 1 atm, according to the reaction:
$CO_2(g) = CO(g) + \frac{1}{2}\ O_2(g)$

5. What are the equilibrium partial pressures of CO_2, CO and O_2 at 1000 C if there was initially pure CO_2 with 1 atm partial pressure?