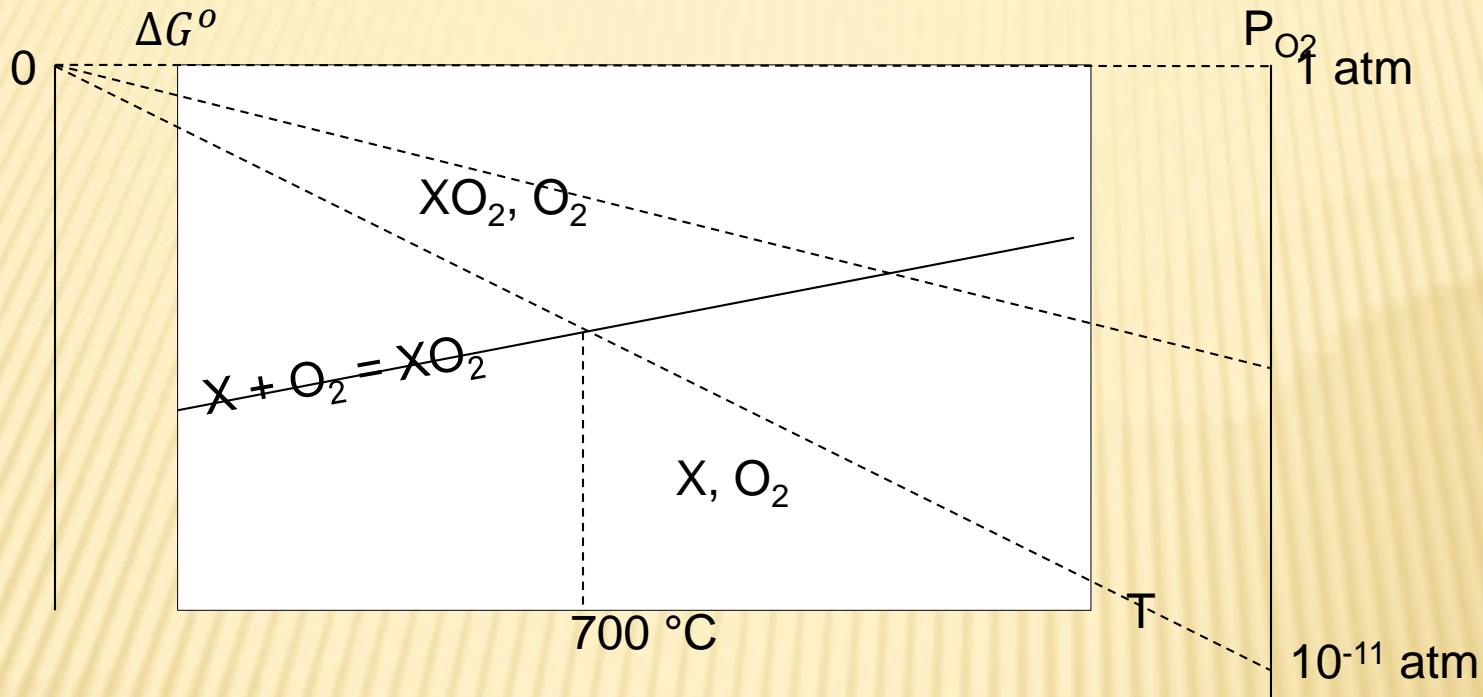


MME 3514 MATERIALS THERMODYNAMICS

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

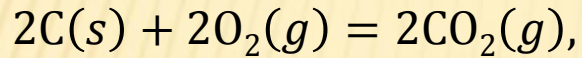
For constant P_{O_2} values, ΔG° vs T is represented by straight lines with $R \ln P_{O_2}$ slope and $\Delta G^\circ = 0$ intercept

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

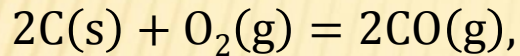
Carbon is extensively used in materials processing

The two oxides of carbon, CO and CO₂ are both gaseous species and it is important to know how they are distributed in an environment containing these gases

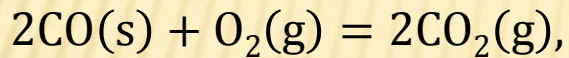
Ellingham for the oxides yield another line that represent the equilibrium between CO and CO₂:



$$\Delta G^\circ = -394321 - 0.84T \text{ J}$$

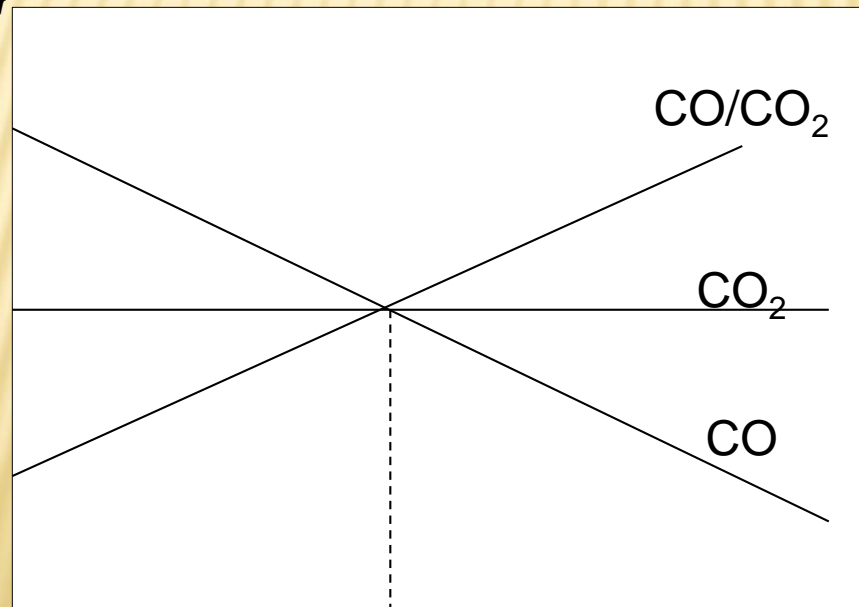


$$\Delta G^\circ = -223532 - 175.4T \text{ J}$$



$$\Delta G^\circ = -565110 - 173.72T \text{ J}$$

ΔG°

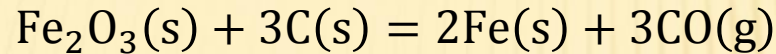


978.4 K, 1 atm

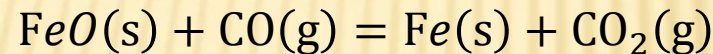
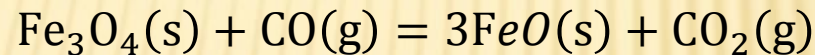
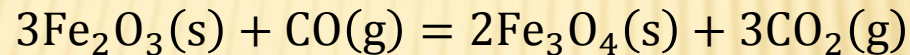
T

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

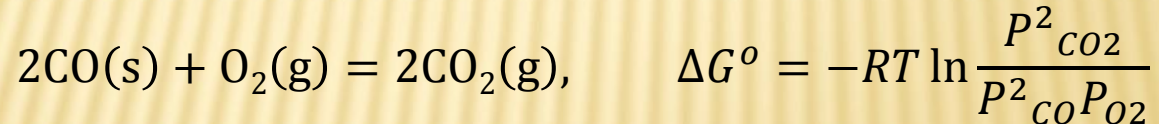
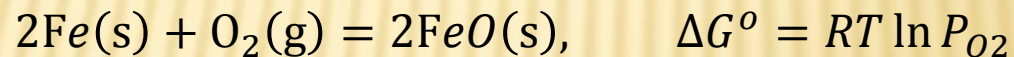
For example hematite is in contact with carbon in oxygen blast furnace and reacts as:



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



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



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

The net reaction is $2\text{Fe}(\text{s}) + 2\text{CO}_2(\text{g}) = 2\text{FeO}(\text{s}) + 2\text{CO}(\text{s})$, $\Delta G^\circ = \Delta G^\circ_{\text{Fe-CO}} = -RT \ln \frac{P_{\text{CO}_2}}{P_{\text{CO}}}$

$$\Delta G^\circ_{\text{Fe}} = \Delta G^\circ_{\text{CO}} - 2RT \ln \frac{P_{\text{CO}_2}}{P_{\text{CO}}}$$

CO/CO₂ grid lines can be related to the oxygen partial pressure in a system using the CO-CO₂-O₂ equilibrium

$$\Delta G^o = -RT \ln \frac{P_{CO_2}^2}{P_{CO}^2 P_{O_2}}$$

$$\Delta G^o = RT \ln P_{O_2} - 2RT \ln \frac{P_{CO_2}}{P_{CO}}$$

Partial pressure of oxygen is converted to the ratio of CO and CO₂ gases as

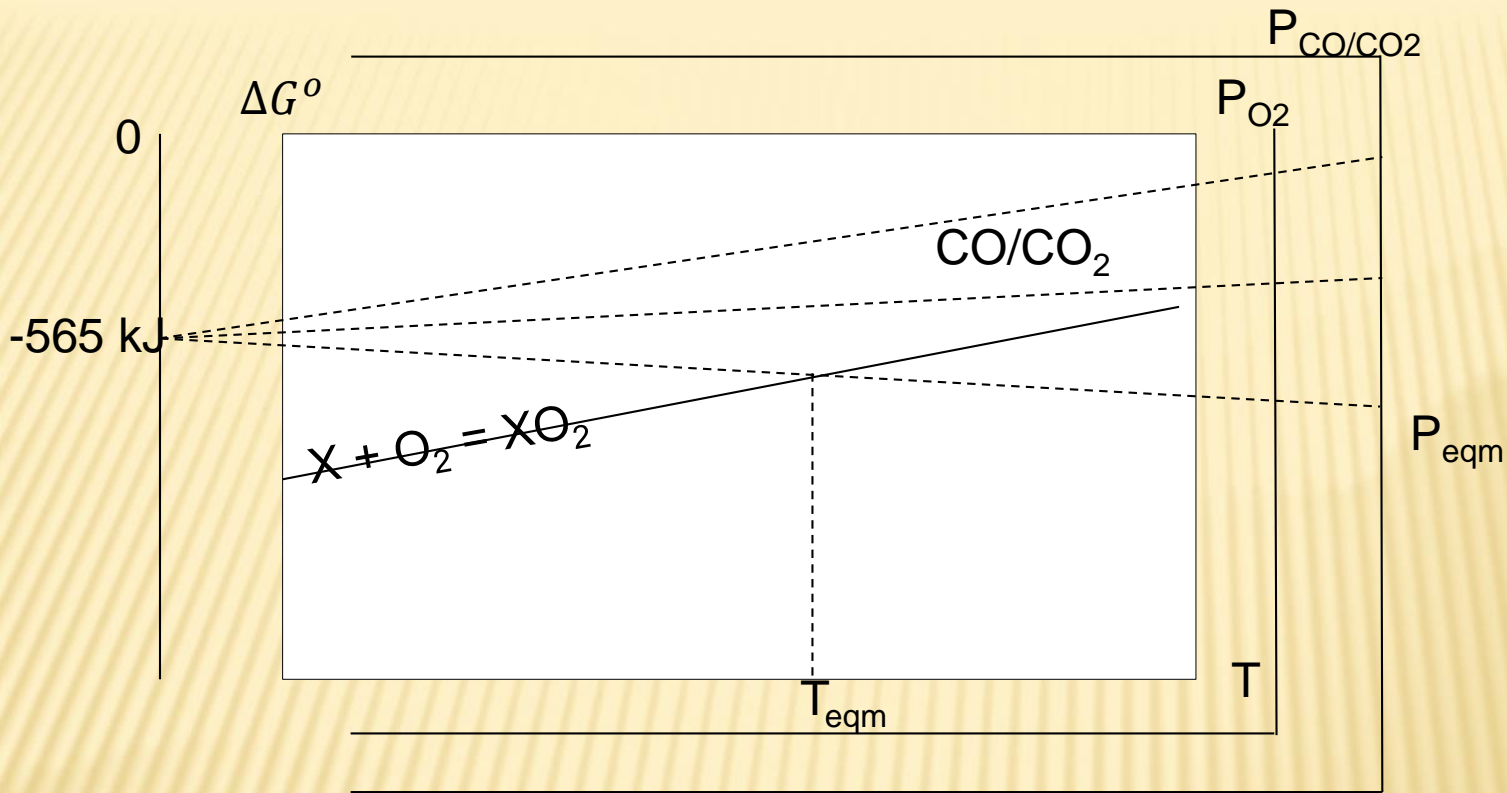
$$RT \ln P_{O_2} = \Delta G^o - 2RT \ln \frac{P_{CO}}{P_{CO_2}}$$

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

$$RT \ln P_{O_2} = -565110 + (173.72 - 2R \ln \frac{P_{CO}}{P_{CO_2}})T$$

Constant CO/CO₂ 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})

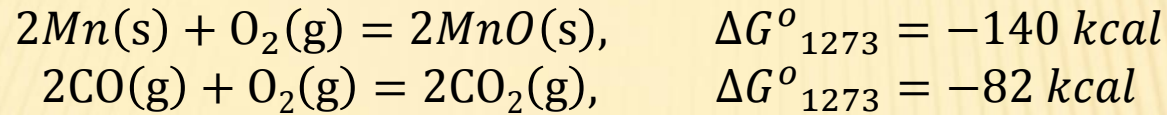


P_{CO} / P_{CO_2} is constant along a straight line that passes through -565 kJ at 0 K and can be read from the ratio scale

At the intersection of the CO/CO₂ lines with a metal oxidation line, all metal X, XO₂, O₂, CO and CO₂ coexist at equilibrium

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

Example – What is the equilibrium P_{CO/CO_2} for CO to reduce MnO at 1000 C?



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

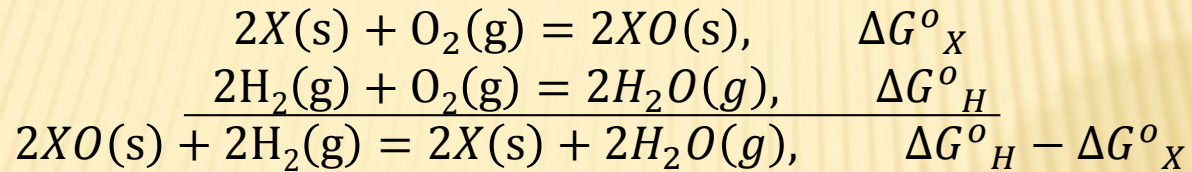
$$\begin{aligned} \Delta G^o &= RT \ln P_{O_2} \\ -140000 &= 1.987154 * 1273 * \ln P_{O_2} \\ P_{O_2} &= 10^{-24} \text{ atm} \end{aligned}$$

The free energy change for the carbon oxidation reaction is used to calculate P_{CO/CO_2}

$$\begin{aligned} \Delta G^o &= -RT \ln \frac{P^2_{CO_2}}{P^2_{CO} P_{O_2}} \\ -82000 &= -1.987154 * 1273 * \ln \frac{P^2_{CO_2}}{P^2_{CO} * 10^{-24}} \\ \frac{P_{CO}}{P_{CO_2}} &= 10^5 \end{aligned}$$

H₂/H₂O grid lines

In industrial processes involving H₂ 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



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

$$\Delta G^o_X = RT \ln P_{O_2}$$

$$\Delta G^o_H = -RT \ln \frac{P^2_{H_2O}}{P^2_{H_2} P_{O_2}} = RT \ln P_{O_2} + 2RT \ln \frac{P_{H_2}}{P_{H_2O}} = \Delta G^o_X + 2RT \ln \frac{P_{H_2}}{P_{H_2O}}$$

The net reaction is

$$\Delta G^o_X = \Delta G^o_H - 2RT \ln \frac{P_{H_2}}{P_{H_2O}}$$

H₂/H₂O grid lines can be related to the oxygen partial pressure in a system using the H₂-H₂O-O₂ equilibrium



$$\Delta G^\circ = -RT \ln \frac{P_{\text{H}_2\text{O}}^2}{P_{\text{H}_2}^2 P_{\text{O}_2}}$$

$$\Delta G^\circ = RT \ln P_{\text{O}_2} - 2RT \ln \frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2}}$$

Partial pressure of oxygen is converted to the ratio of H₂ and H₂O gases as

$$RT \ln P_{\text{O}_2} = \Delta G^\circ - 2RT \ln \frac{P_{\text{H}_2}}{P_{\text{H}_2\text{O}}}$$

$$\Delta G^\circ = -492887 + 109.62T \text{ J}$$

$$RT \ln P_{\text{O}_2} = -492887 + (109.62 - 2R \ln \frac{P_{\text{H}_2}}{P_{\text{H}_2\text{O}}})T$$

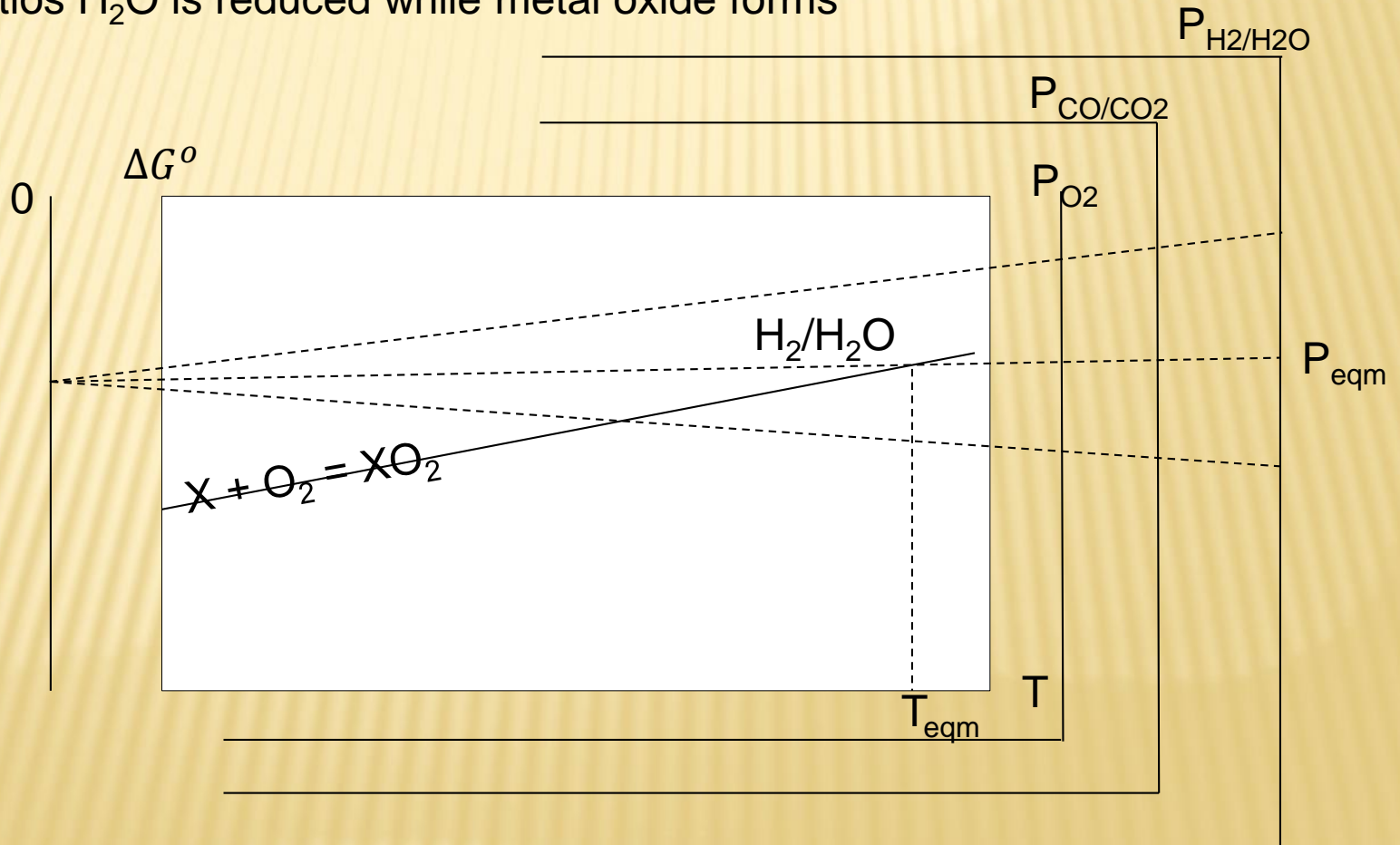
Constant H₂/H₂O ratios fall on straight lines on Ellingham diagram since RT ln P_{O₂} is the ordinate:

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

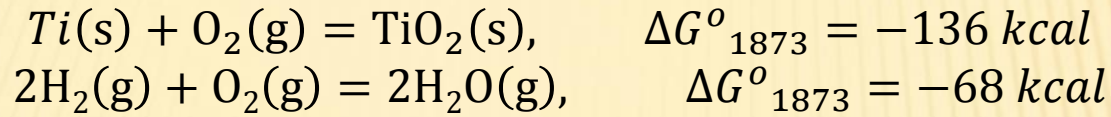
$\frac{P_{H_2}}{P_{H_2O}}$ is constant along a straight line that passes through -492387 J at 0 K and can be read from the scale on the far right of the Ellingham diagram

At the intersection of the H₂/H₂O lines with a metal oxidation line, all metal X, XO₂, O₂, H₂ and H₂O coexist at equilibrium

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



Example – What is the equilibrium P_{H_2/H_2O} for H_2 to reduce TiO_2 at 1600 C?



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

$$\begin{aligned} \Delta G^o &= RT \ln P_{O_2} \\ -136000 &= 1.987154 * 1873 * \ln P_{O_2} \\ P_{O_2} &= 10^{-16} \text{ atm} \end{aligned}$$

The free energy change for the hydrogen oxidation reaction is used to calculate P_{H_2/H_2O}

$$\begin{aligned} \Delta G^o &= -RT \ln \frac{P_{H_2}^2}{P_{H_2O}^2 P_{O_2}} \\ -68000 &= -136000 + 2 * 1.987154 * 1873 \ln \frac{P_{H_2}}{P_{H_2O}} \\ \frac{P_{H_2}}{P_{H_2O}} &= 10^4 \end{aligned}$$

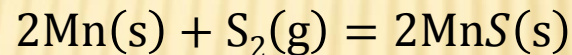
Sulfidation of metals

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



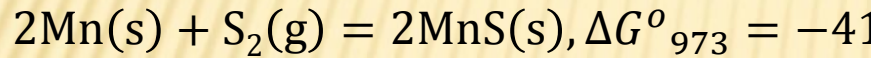
$$\Delta G^o = RT \ln P_{\text{S}_2}$$

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

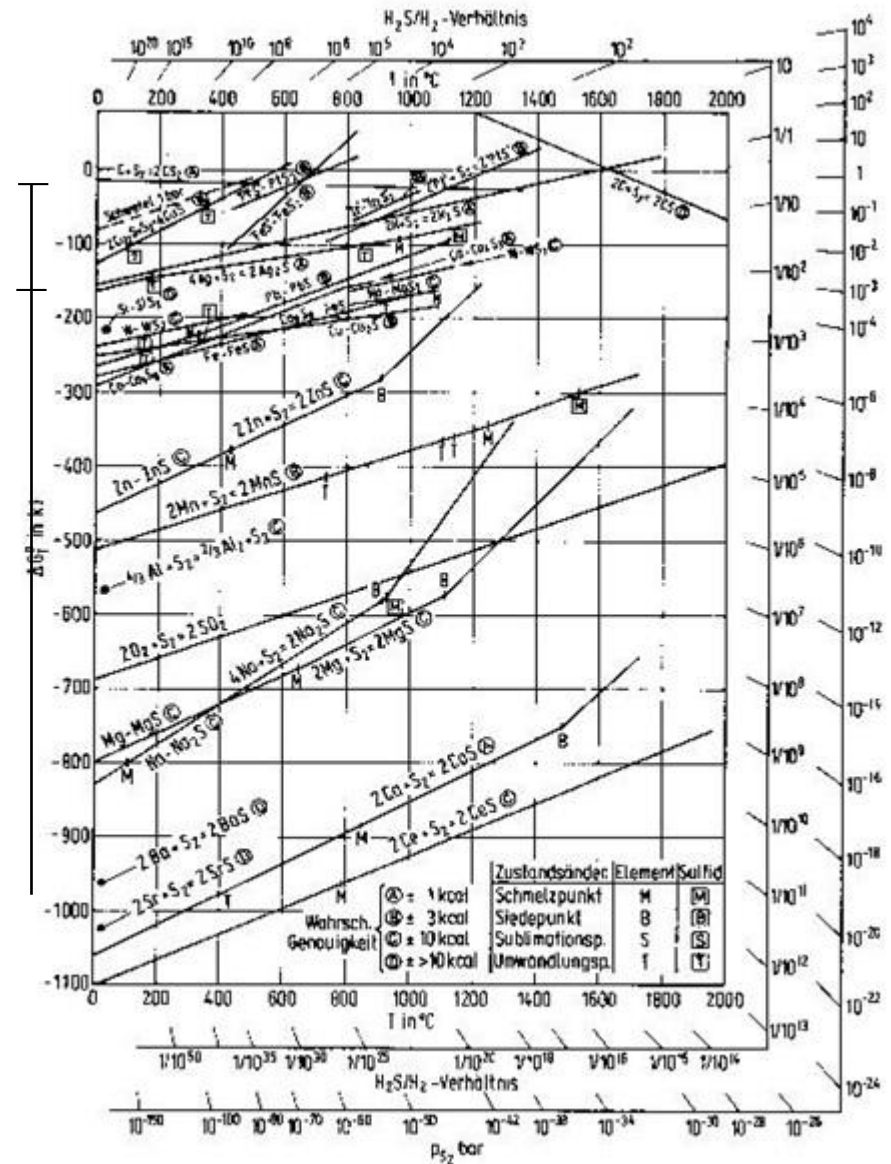
The equilibrium partial pressure of S_2 and the ratio of P_{H_2S}/H_2 can be determined graphically from the figure in the same way as described previously for oxygen, carbon and hydrogen

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



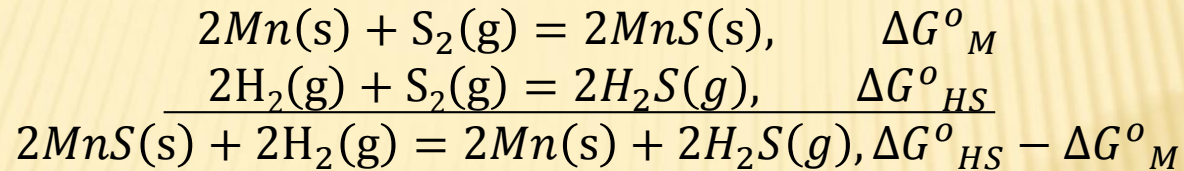
$$\Delta G^0 = RT \ln P_{S_2} = -410000 = 8.314 \cdot 973 \cdot \ln P_{S_2}$$

$$P_{S_2} = 10^{-22}$$



Reduction of metal sulphurs by H₂

Just as the metal oxides are reduced by hydrogen to form metal and H₂O, metal sulphides are reduced by hydrogen to form H₂S and metal



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

$$\Delta G^o_M = RT \ln P_{S_2}$$

$$\Delta G^o_{HS} = -RT \ln \frac{P^2_{H_2S}}{P^2_{H_2} P_{S_2}} = RT \ln P_{S_2} + 2RT \ln \frac{P_{H_2}}{P_{H_2S}} = \Delta G^o_M + 2RT \ln \frac{P_{H_2}}{P_{H_2S}}$$

The net reaction is

$$\Delta G^o_M = \Delta G^o_{HS} - 2RT \ln \frac{P_{H_2}}{P_{H_2S}}$$

H₂/H₂S grid lines can be related to the sulphur partial pressure in a system using the H₂-H₂S-S₂ equilibrium



$$\Delta G^\circ = -RT \ln \frac{P_{\text{H}_2\text{S}}^2}{P_{\text{H}_2}^2 P_{\text{S}_2}}$$

$$\Delta G^\circ = RT \ln P_{\text{S}_2} - 2RT \ln \frac{P_{\text{H}_2\text{S}}}{P_{\text{H}_2}}$$

Partial pressure of sulphur is converted to the ratio of H₂ and H₂S gases as

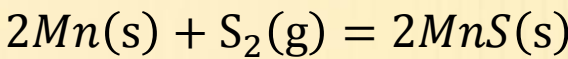
$$RT \ln P_{\text{S}_2} = \Delta G^\circ - 2RT \ln \frac{P_{\text{H}_2}}{P_{\text{H}_2\text{S}}}$$

$$RT \ln P_{\text{S}_2} = -152900 + (99.37 - 2R \ln \frac{P_{\text{H}_2}}{P_{\text{H}_2\text{S}}})T$$

Constant H₂/H₂S ratios fall on straight lines on Ellingham diagram since RT ln P_{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_{H_2/H_2S} for H_2 to reduce MnS at 700 C?



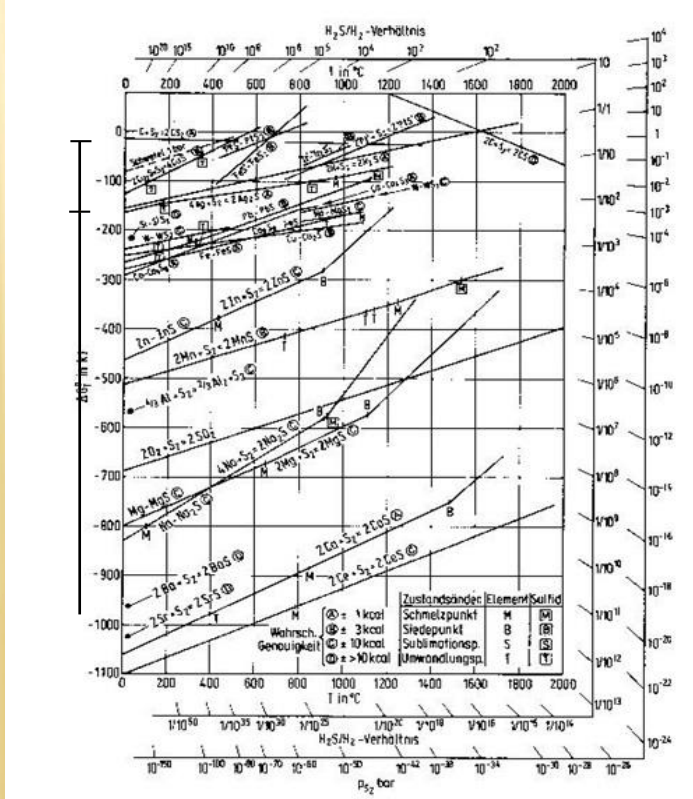
$$\Delta G^0_{Mn} = -410000 J = RT \ln P_{S_2}$$

$$P_{S_2} = 10^{-22} atm$$

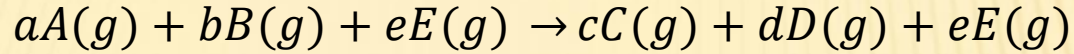
$$RT \ln P_{S_2} = -152900 + (99.37 - 2R \ln \frac{P_{H_2}}{P_{H_2S}})973$$

$$\frac{P_{H_2}}{P_{H_2S}} = 10^{-9}$$

MnS is reduced to Mn at $\frac{P_{H_2}}{P_{H_2S}} > 10^{-9}$



Determining the composition of reaction system under equilibrium



Consider the 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:

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

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

$$n_A = \text{Fraction of unreacted A} = (1 - x)a$$

$$n_B = \text{Fraction of unreacted B} = (1 - x)b$$

$$n_C = \text{Fraction of formed C} = x.c$$

$$n_D = \text{Fraction of formed D} = x.d$$

$$n_E = \text{Fraction of inert E in the system} = e$$

and

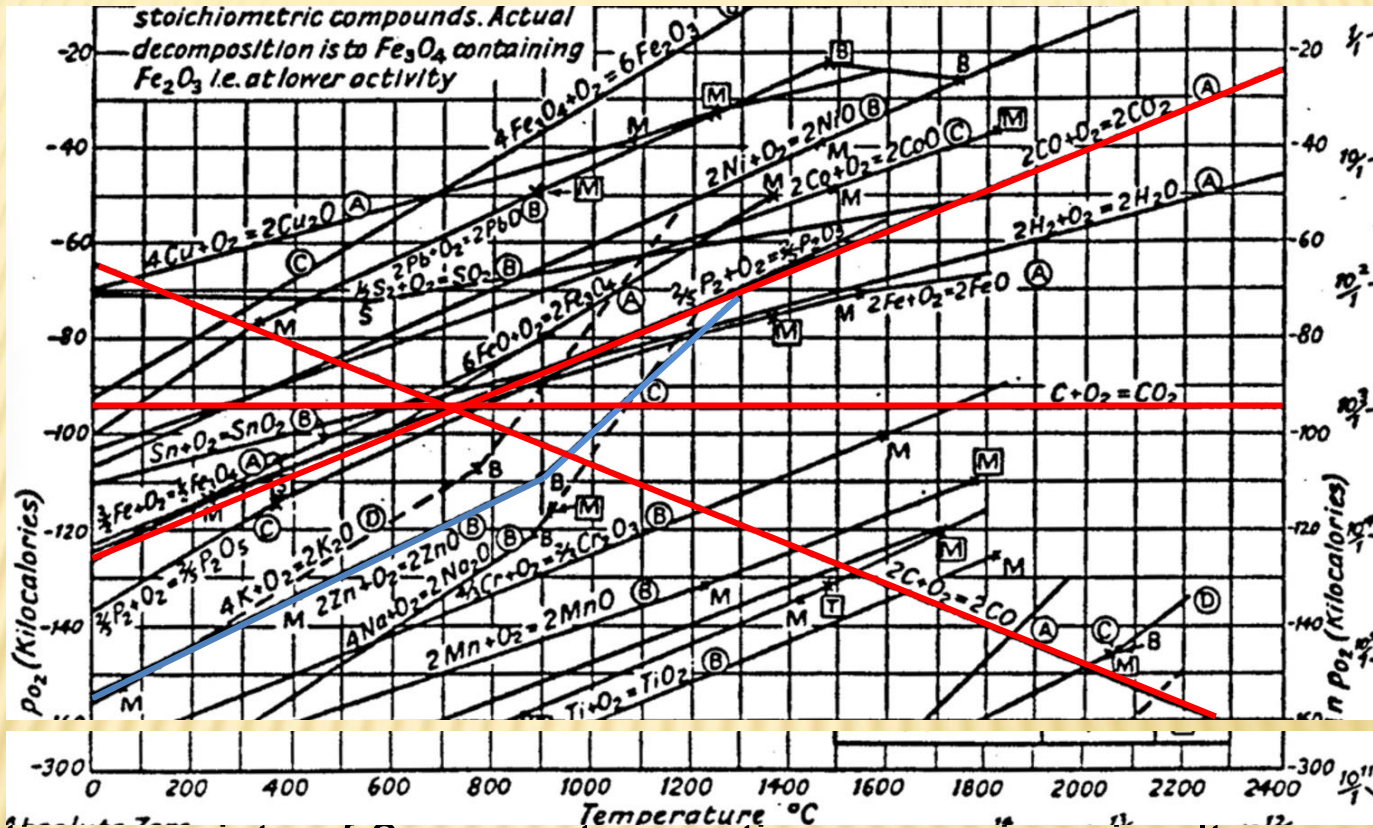
$$K = \frac{(x.c)^c (x.d)^d}{(a - ax)^a (b - bx)^b} * \left(\frac{P}{(1 - x)(a + b) + x(c + d) + e} \right)^{(c+d)-(a+b)}$$

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

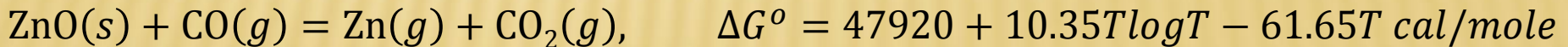
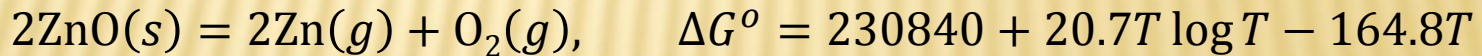
$$\Delta G = \Delta G^o + RT_{eqm} \ln K = 0$$

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

Example – Solid ZnO is reduced by CO gas at 1027 C to produce CO₂ and Zn gas. Reduction retort is filled with CO gas and atmospheric pressure is maintained by a small opening:
 $ZnO(s) + CO(g) = Zn(g) + CO_2(g) @ 1027 C, 1 atm$



The reaction consists of 3 separate reactions occurring simultaneously



The reaction constant at equilibrium temperature 1300 K is obtained as

$$\ln K = -\frac{\Delta G^{\circ}}{RT_{eqm}} = -\frac{9700 \text{ cal}}{1.987154 \frac{\text{cal}}{\text{K}} \cdot 1300 \text{ K}} = -2.35$$
$$K = 0.0224$$

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 CO₂ = 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 CO₂

0.85 moles CO

0.15 moles Zn

Total = 1.15 moles



13% CO₂

74% CO

13% Zn

Example – Reduction of solid ZnO by methane gas is another industrial Zn production process: $\text{ZnO}(s) + \text{CH}_4(g) = \text{Zn}(g) + \text{CO}(g) + 2\text{H}_2 @ 827 \text{ C}, 1 \text{ atm}$
 $\Delta G^\circ = 114303 - 12.93T \ln T + 0.00035T^2 - 0.00000088T^3 - 10.53T \text{ cal/mole}$

There are 1 mole of ZnO and CH₄ at the beginning of the reaction

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

$$\Delta G^\circ = 1470 \text{ calories}$$

$$\ln K = -\frac{\Delta G^\circ}{RT_{eqm}} = -\frac{1470 \text{ cal}}{1.987156 \frac{\text{cal}}{\text{K}} \cdot 1100 \text{ K}} = -0.673$$

$$K = 0.51$$

$$K = \frac{P_{\text{Zn}} P_{\text{CO}} P_{\text{H}_2}^2}{P_{\text{CH}_4}}$$

$$0.51 P_{\text{CH}_4} = P_{\text{Zn}} \cdot P_{\text{CO}} \cdot P_{\text{H}_2}^2$$

$$0.51P_{CH_4} = P_{Zn} \cdot P_{CO} \cdot P_{H_2}^2$$

Since the system pressure is constant at 1 atm,

$$P_{CH_4} + P_{Zn} + P_{CO} + P_{H_2} = 1 \text{ atm}$$

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

$$P_{Zn}/P_{CO} / P_{H_2} = 1/1/2$$

With three equations at hand relating 4 variables, 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 CH₄ = 1, final mole number = x

The initial mole number of gaseous Zn = 0, final mole number = $\frac{1}{4}(1-x)$

The initial mole number of gaseous CO = 0, final mole number = $\frac{1}{4}(1-x)$

The initial mole number of gaseous H₂ = 0, final mole number = $\frac{1}{2}(1-x)$

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

$$x = 0.0275$$

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

$$P_{CH_4} = 0.0275 \text{ atm}$$
$$P_{Zn} = \frac{1}{4}(1 - 0.0275) = 0.2431 \text{ atm}$$
$$P_{CO} = \frac{1}{4}(1 - 0.0275) = 0.2431 \text{ atm}$$
$$P_{H_2} = \frac{1}{2}(1 - 0.0275) = 0.4862 \text{ atm}$$

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

Homework Example – A zinc production plant uses CO-CO₂ 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 CO₂ produced. Comment on the feasibility of the process 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

