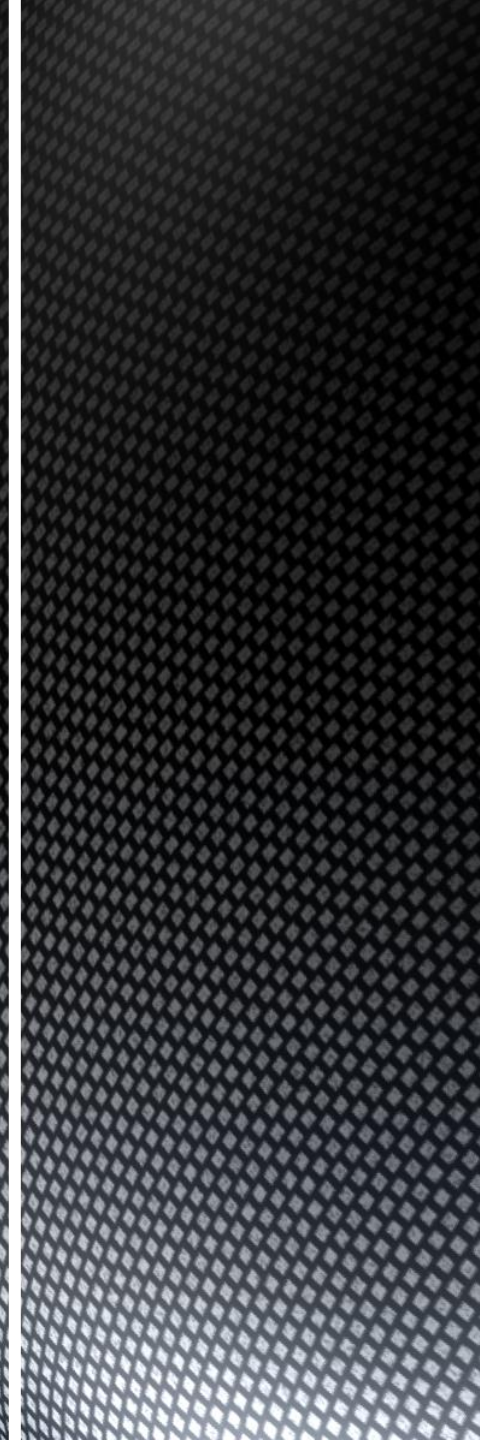
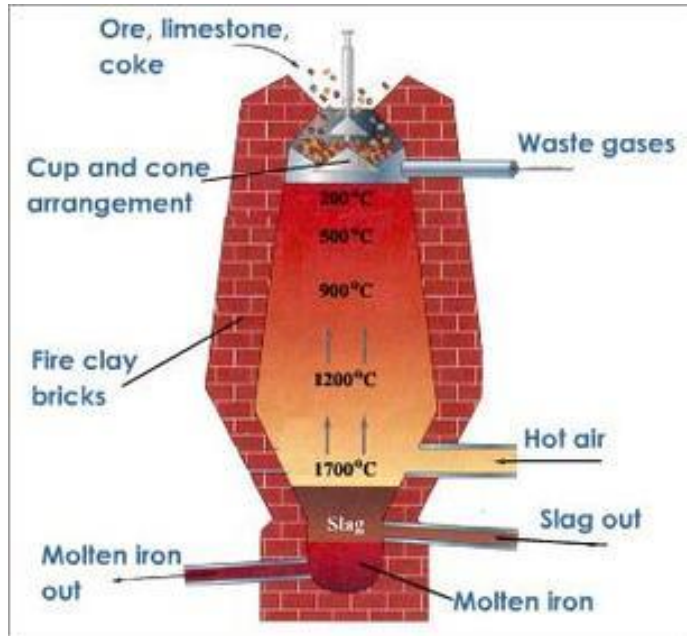


# Materials and Energy Balance

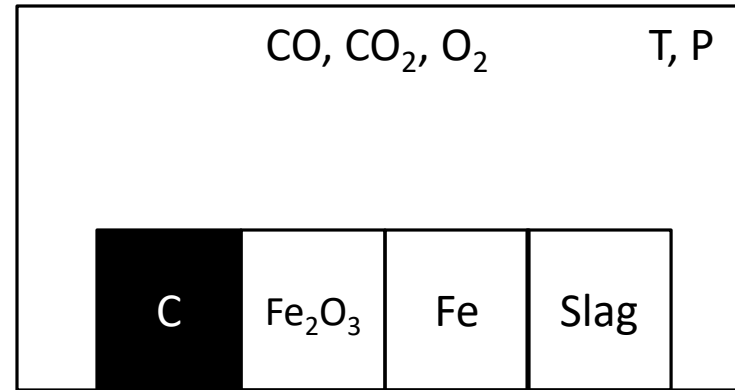
Chemical Equilibria in Reacting Systems



Consider a smelting process where a metal oxide is reduced by carbon in a furnace



Technical drawing of a smelting furnace



Analytical drawing of a smelting furnace

Recall from thermodynamics that a phase is a homogeneous region that is a physically separable part in a mixture of matter

There are mainly 5 phases in the smelting furnace at equilibrium:

Solid carbon

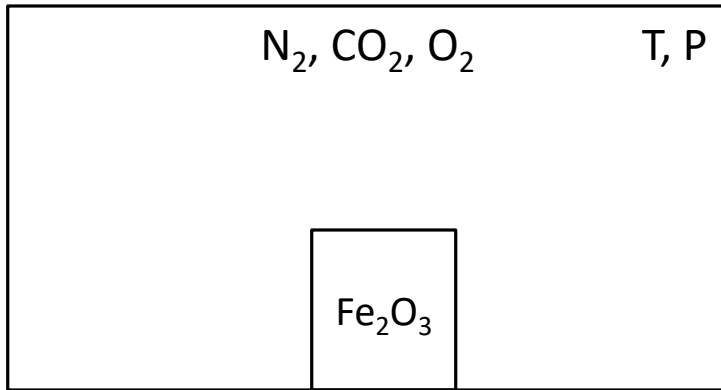
Solid iron oxide

Liquid iron

Liquid slag

Gas mixture containing CO, CO<sub>2</sub>, O<sub>2</sub>

The number of variables that can be controlled in a system (i.e. the degrees of freedom) may change if the system is reacting



Non-reacting system

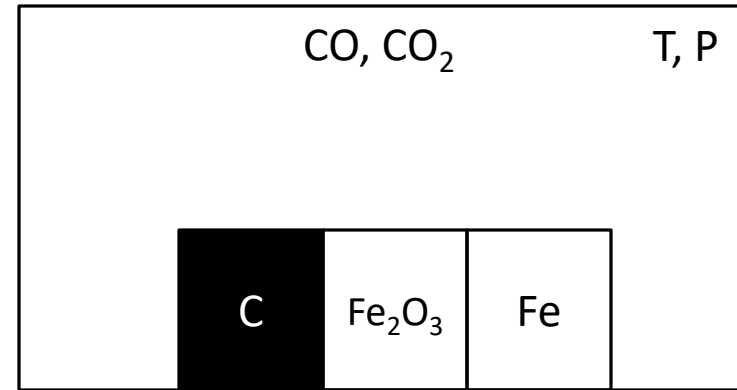
$$F = 2 - \pi + N$$

Phases: Solid iron oxide, gaseous air

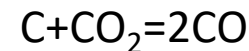
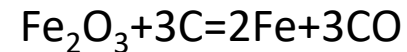
Degrees of freedom=  $2+4-2=4$

Variables that are free to control:

Temperature, pressure  
concentration of 2 species



Reacting system



$$F = 2 - \pi + N - R$$

Solid carbon, solid iron oxide, liquid iron, gas mixture

$2+5-4-2=1$

Temperature

The number of variables which must be arbitrarily specified in order to fix the intensive state of a system at equilibrium is the difference between the total number of variables and the number of independent equations that can be written connecting these variables

Phase rule variables for a non-reacting system containing  $N$  chemical species and  $\pi$  phases in equilibrium:

Temperature  $T$

Pressure  $P$

$N-1$  mole fractions  $X$  for each phase (only  $N-1$  because  $\sum X_i = 1$ )

Total number =  $2 + (N - 1)(\pi)$

Phase equilibrium equations that may be written connecting the phase rule variables:  
Chemical potential of each species in each phase should be equal

$$\mu_i^\alpha = \mu_i^\beta = \dots = \mu_i^\pi \quad (i = 1, 2, \dots, N)$$

Total number =  $(\pi - 1)(N)$

Thus

$$F = 2 + (N - 1)(\pi) - (\pi - 1)(N) = 2 - \pi + N$$

Gibbs' Phase Rule gives the degrees of freedom of the system

Presence of more phases decreases the number of independent intensive variables that must be fixed to establish the state of a system

Phase rule variables for a reacting system containing R reactions, N chemical species and  $\pi$  phases in equilibrium:

Temperature T

Pressure P

N-1 mole fractions X for each phase (only N-1 because  $\sum X_i = 1$ )

Total number of phase rule variables =  $2 + (N - 1)(\pi)$

Phase equilibrium equations that may be written connecting the phase rule variables:

Chemical potential of each species in each phase should be equal

$$\mu_i^\alpha = \mu_i^\beta = \dots = \mu_i^\pi \quad (i = 1, 2, \dots, N)$$

Gibbs free energy should be minimum at constant T and P for each reaction

$$d(nG) = (nV)dP - (nS)dT + \sum \mu_i dn_i$$

$$\sum v_i \mu_i = \left[ \frac{\partial(nG)}{\partial \varepsilon} \right]_{T,P} = 0 \quad (i = 1, 2, \dots, N)$$

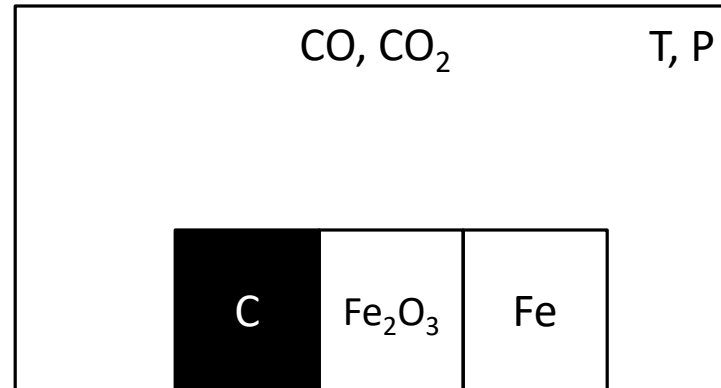
Total number of equations relating the variables =  $(\pi - 1)(N) + R$

Thus

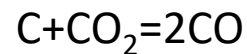
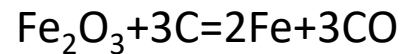
$$F = 2 + (N - 1)(\pi) - (\pi - 1)(N) - R = 2 - \pi + N - R$$

R represents the number of independent chemical reactions at equilibrium

For a reacting system at equilibrium, the number of components and phases are larger than non-reacting system at equilibrium



Reacting system



Phases: Solid carbon, solid iron oxide, liquid iron, gas mixture (4)

Components: carbon, iron, hematite, carbon monoxide, carbon dioxide (5)

Reactions:  $\text{Fe}_2\text{O}_3 + 3\text{C} = 2\text{Fe} + 3\text{CO}$ ,  $\text{C} + \text{CO}_2 = 2\text{CO}$  (2)

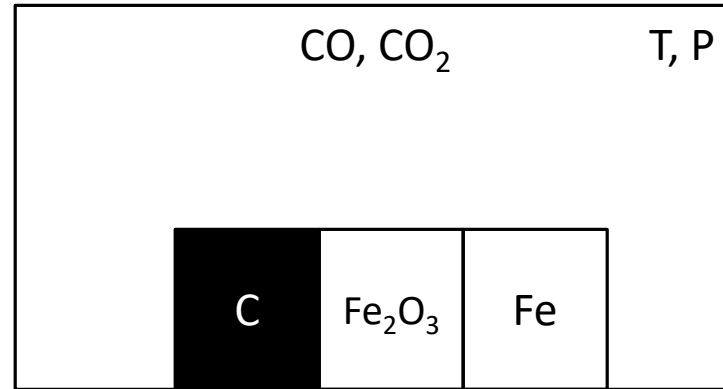
Degrees of freedom =  $2 + 5 - 4 - 2 = 1$

Variables that are free to control:

Temperature

Determining the number of independent chemical reactions in the system

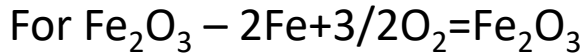
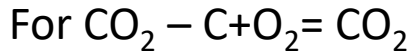
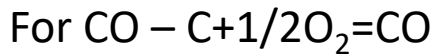
Consider the reduction of iron oxide by coke in a smelting furnace



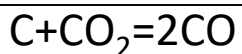
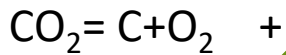
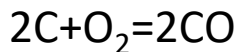
5 chemical species: C, CO, CO<sub>2</sub>, Fe, Fe<sub>2</sub>O<sub>3</sub>

4 phases: Solid carbon, solid iron oxide, liquid iron, gas mixture

Chemical equations for the formation of each compound present in the system from its constituent elements:



Combine the equations to eliminate the elements that are not considered a part of the system



1

Repeat for iron oxide to eliminate O<sub>2</sub>:  $2Fe + 3/2O_2 = Fe_2O_3 + 3C + 3/2O_2 = 3CO = Fe_2O_3 + 3C = 2Fe + 3CO$

2

If another element is not present in the system, repeat the process to eliminate the element from the new set of equations

The set of equations is usually reduced by one equation for each element eliminated

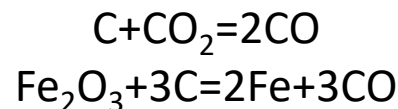
Simultaneous elimination of two or more elements may occur

More than one set is possible depending on how the reduction procedure is carried out  
All sets are equivalent and contain  $R$  equations regardless of the procedure

The reduction procedure also ensures that

$$R \geq \text{number of compounds present in the system} - \text{number of constituent elements not part of the system}$$

For the reduction of iron oxide by coke, the following set of 2 equations is a complete set of independent reactions



Compounds in the system:  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{Fe}_2\text{O}_3$

Elements not part of the system:  $\text{O}_2$

$$2 \geq 3 - 1$$



Phase equilibrium equations

$$\mu_i^\alpha = \mu_i^\beta = \dots = \mu_i^\pi$$

Chemical reaction equilibrium equations

$$\sum v_i \mu_i = 0$$

Related to phase rule variables  
to determine independent variables

Special constraints may be placed on the system that allow additional equations to be written under certain conditions

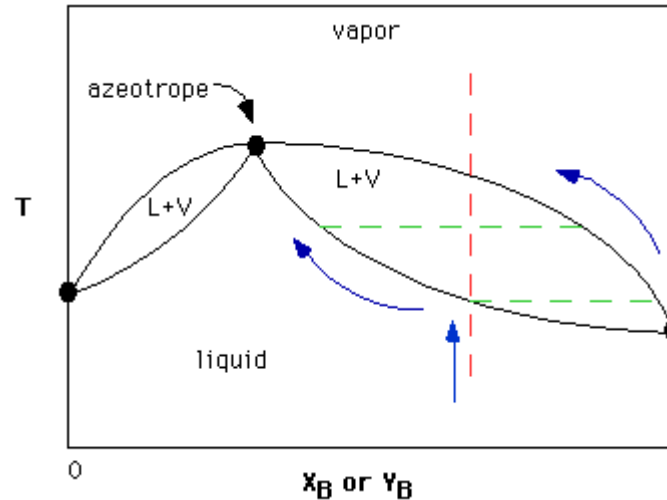
For example the concentrations of gaseous phases may add up to atmospheric pressure, bringing the interrelating equation

$$P_{CO} + P_{CO_2} = 1$$

Let  $\delta$  be the number of equations resulting from special constraints  
The general form of the phase rule for reacting systems is

$$F = 2 - \pi + N - R - \delta$$

Example – Determine the degrees of freedom for a system of two miscible non-reacting species which exists as an azeotrope in vapor/liquid equilibrium



The system consists of two non-reacting species A and B in two phases liquid and vapor

The fact that the solution is an azeotrope introduces a special constraint to the system so that

$$x_A = y_A$$

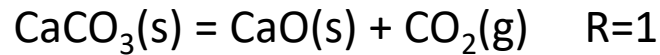
$$F = 2 - \pi + N - R - \delta$$

$$F = 2 - 2 + 2 - 0 - 1 = 1$$

Just one phase rule variable among T, P or  $x_A=y_A$  may be arbitrarily specified

Example – Determine the degrees of freedom for a system prepared by partially decomposing  $\text{CaCO}_3$  to  $\text{CaO}$

There is a single chemical reaction in the system:



Chemical species in the system:  $\text{CaCO}_3$ ,  $\text{CaO}$ ,  $\text{CO}_2$

Phases in the system: Solid Ca carbonate, solid Ca oxide, gaseous  $\text{CO}_2$

Number of compounds in the system: 3

Number of elements not part of the system: 3

$$F = 2 - \pi + N - R - \delta$$

$$F = 2 - 3 + 3 - 1 - 0 = 1$$

There is a single degree of freedom

Calcium carbonate exerts a fixed decomposition pressure at a fixed temperature

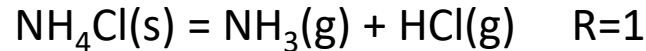
If the furnace had an isolated atmosphere and it was aimed to consist of  $\text{CO}_2$  at 1 atm,  $\delta=1$

$$F = 2 - 3 + 3 - 1 - 1 = 0$$

1 atm  $\text{CO}_2$  pressure could only be attained at a fixed temperature

Example – Determine the degrees of freedom for a system prepared by partially decomposing  $\text{NH}_4\text{Cl}$  into gaseous species

There is a single chemical reaction in the system:



Chemical species in the system:  $\text{NH}_4\text{Cl}$ ,  $\text{NH}_3$ ,  $\text{HCl}$

Phases in the system: Solid ammonium chloride, gaseous mixture containing  $\text{NH}_3$  and  $\text{HCl}$

Number of compounds in the system: 3

Number of elements not part of the system: 3

$$F = 2 - \pi + N - R - \delta$$

$$F = 2 - 2 + 3 - 1 - 0 = 2$$

However there is a special constraint: the requirement that the system be formed by gaseous decomposition means that the gas phase is equimolar in  $\text{NH}_3$  and  $\text{HCl}$

$$y_{\text{HCl}} = y_{\text{NH}_3} = 0.5$$

$$F = 2 - 2 + 3 - 1 - 1 = 1$$

$\text{NH}_4\text{Cl}$  has a fixed decomposition pressure at a fixed temperature

Example – Determine the degrees of freedom for a system consisting of the gases CO, CO<sub>2</sub>, H<sub>2</sub>, H<sub>2</sub>O, CH<sub>4</sub> in chemical equilibrium

Chemical species in the system: CO, CO<sub>2</sub>, H<sub>2</sub>, H<sub>2</sub>O, CH<sub>4</sub>

Phases in the system: Gaseous mixture containing CO, CO<sub>2</sub>, H<sub>2</sub>, H<sub>2</sub>O, CH<sub>4</sub>

Number of compounds in the system: 4

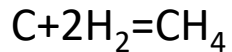
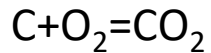
Number of elements not part of the system: 2

$$R \geq 4 - 2$$

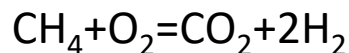
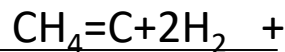
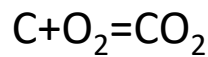
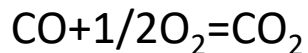
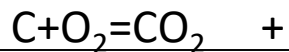
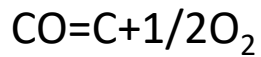
There should be at least 2 independent reaction in the system

$$F = 2 - 1 + 5 - R - 0 = 6 - R$$

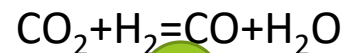
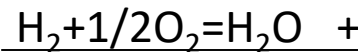
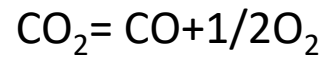
Formation reactions



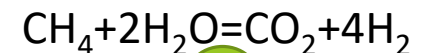
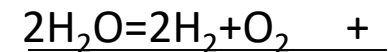
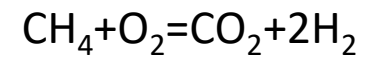
Eliminate C



Eliminate O<sub>2</sub>



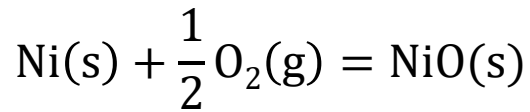
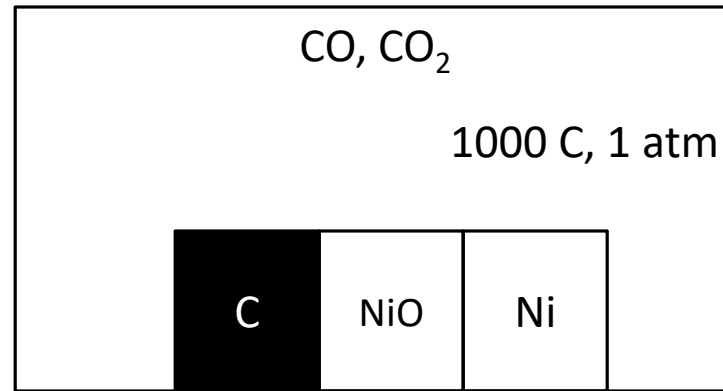
1



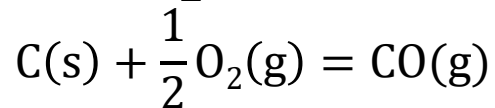
2

Example – NiO concentrate is reduced to Ni by excess carbon in a reduction furnace that is open to atmosphere at 1000 C

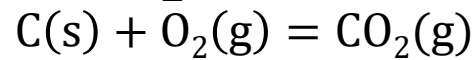
Show that NiO reduction is possible and it is completely used in the furnace



$$\Delta G^\circ = -56310 + 20.57T \text{ calories}$$

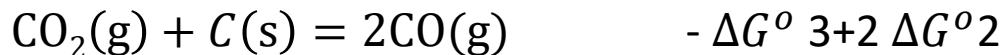
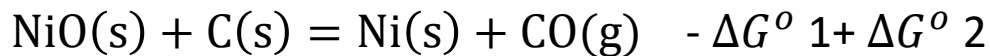


$$\Delta G^\circ = -27340 + 20.50T \text{ calories}$$

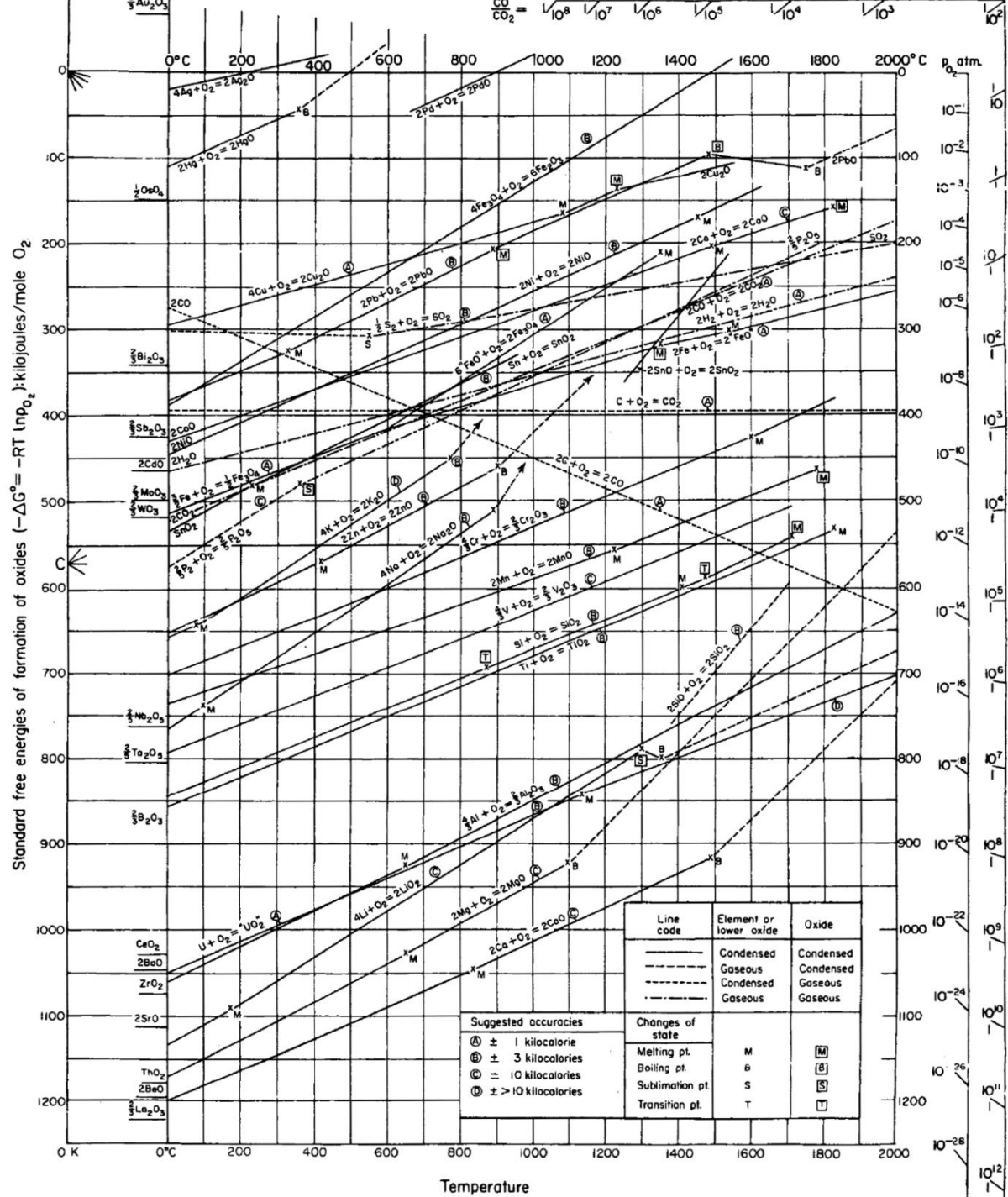


$$\Delta G^\circ = -94490 + 41.13T \text{ calories}$$

$R \geq 3 - 1 = 2$  independent reactions



$$\text{CO}/\text{CO}_2 = 1.23/98.77 \approx 10^{-2}$$



The equilibrium composition of species in a metal smelting furnace where the equilibrium state depends on two or more simultaneous chemical reactions can be found by equilibrium constants

First a set of independent reactions are determined

There is associated a reaction coordinate with each independent reaction and a separate equilibrium constant  $K$

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

$$K_j = \prod (a_i)^{\nu(i,j)}$$

Where  $j$  is the reaction index and  $i$  is the reacting chemical species

Recall that activity of a species is

$$a_i = \gamma_i * x_i$$

The concentration  $x_i$  is obtained from the extent of reactions which involve the species  $i$

$$x_i = \frac{n_i}{n} = \frac{n_{i0} + \sum_j \nu_{i,j} \epsilon_j}{n_0 + \sum_j \nu_j \epsilon_j}$$



The set of equations relating the equilibrium constant  $K$  for a reaction to the reaction extent  $\varepsilon$  are solved simultaneously to obtain the extent of each reaction and hence the concentrations

Example – Consider the combustion of 2 moles of carbon at 1000 K and 1 atm



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

$$395161 \text{ J} = -8314 \ln K$$

$$K = 4.38 * 10^{20}$$

$$K = \frac{a_{CO_2}^2}{a_{O_2}^2 * a_C^2} = \frac{P^2 x_{CO_2}^2}{P^2 x_{O_2}^2 * \gamma^2 x_C^2} \approx \frac{x_{CO_2}^2}{x_{O_2}^2 * x_C^2}$$

$$v_{CO_2} = 2$$

$$v_C = -2$$

$$v_{O_2} = -2$$

$$v_{total} = -2$$

$$2\varepsilon$$

$$x_{CO_2} = \frac{2\varepsilon}{2n_0 - 2\varepsilon}$$

$$x_C = \frac{n_0 - 2\varepsilon}{2n_0 - 2\varepsilon}$$

$$x_{O_2} = \frac{n_0 - 2\varepsilon}{2n_0 - 2\varepsilon}$$

$$n_{CO_2} = 2\varepsilon$$

$$n_C = n_0 - 2\varepsilon$$

$$n_{O_2} = n_0 - 2\varepsilon$$

$$n_{total} = 2n_0 - 2\varepsilon$$

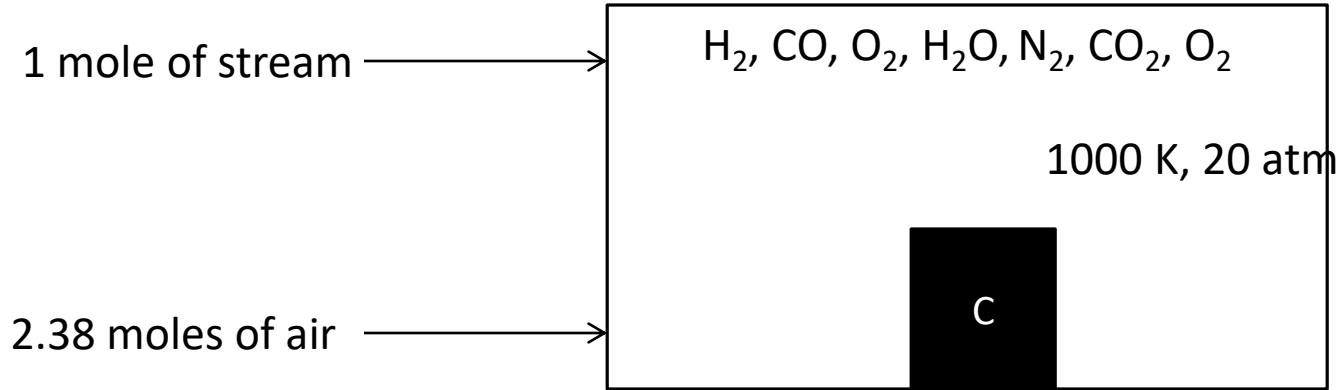
$$K = \frac{(4 - 2\varepsilon)^2 2\varepsilon^2}{(2 - 2\varepsilon)^4}, \quad \varepsilon \approx 1.00$$

$$n_{CO_2} \approx 2, x_{CO_2} \approx 2$$

$$n_C \approx 0, x_C \approx 0$$

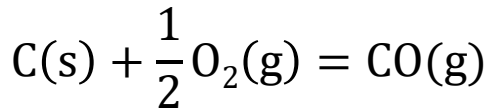
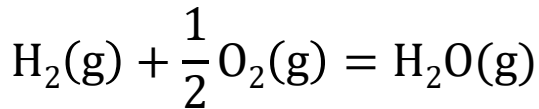
$$n_{O_2} \approx 0, x_{O_2} \approx 0$$

Example – A bed of coal of 100 moles in a coal gasifier is fed with steam and air to produce a gas stream containing  $H_2$ ,  $CO$ ,  $O_2$ ,  $H_2O$ ,  $N_2$ ,  $CO_2$ ,  $O_2$  at 1000 K and 20 atm



Calculate the equilibrium composition of the gas stream

Independent equations:



$$K_1 = \frac{x_{H_2O}}{x_{O_2}^{1/2} * x_{H_2}} P^{-1/2}, \quad \Delta G^{\circ} = -164310 J$$

$$K_2 = \frac{x_{CO}}{x_{O_2}^{1/2} * x_C} P^{1/2}, \quad \Delta G^{\circ} = -243740 J$$

$$K_3 = \frac{x_{CO_2}}{x_{O_2} * x_C}, \quad \Delta G^{\circ} = -396160 J$$

$$v_{H_2O} = \varepsilon_1$$

$$v_C = -\varepsilon_2 - \varepsilon_3$$

$$v_{O_2} = -\frac{1}{2} \varepsilon_1 - \frac{1}{2} \varepsilon_2 - \varepsilon_3$$

$$v_{H_2} = -\varepsilon_1$$

$$v_{CO} = \varepsilon_2$$

$$v_{CO_2} = \varepsilon_3$$

$$n_{H_2O} = 1 + \varepsilon_1$$

$$n_C = 100 - \varepsilon_2 - \varepsilon_3$$

$$n_{O_2} = 0.5 - \frac{1}{2} \varepsilon_1 - \frac{1}{2} \varepsilon_2 - \varepsilon_3$$

$$n_{H_2} = -\varepsilon_1$$

$$n_{CO} = \varepsilon_2$$

$$n_{CO_2} = \varepsilon_3, n_{N_2} = 1.88, n_{total} = 103.38 + \left( \frac{\varepsilon_2 - \varepsilon_1}{2} \right)$$

$$x_{H_2O} = \frac{1 + \varepsilon_1}{103.38 - \left(\frac{2\varepsilon_3 + \varepsilon_2 + \varepsilon_1}{2}\right)}$$

$$x_{H_2} = \frac{-\varepsilon_1}{103.38 - \left(\frac{2\varepsilon_3 + \varepsilon_2 + \varepsilon_1}{2}\right)}$$

$$x_C = \frac{100 - \varepsilon_2 - \varepsilon_3}{103.38 - \left(\frac{2\varepsilon_3 + \varepsilon_2 + \varepsilon_1}{2}\right)}$$

$$x_{CO} = \frac{\varepsilon_2}{103.38 - \left(\frac{2\varepsilon_3 + \varepsilon_2 + \varepsilon_1}{2}\right)}$$

$$x_{N_2} = \frac{1.88}{103.38 - \left(\frac{2\varepsilon_3 + \varepsilon_2 + \varepsilon_1}{2}\right)}$$

$$x_{O_2} = \frac{0.5 - \frac{1}{2}\varepsilon_1 - \frac{1}{2}\varepsilon_2 - \varepsilon_3}{103.38 - \left(\frac{2\varepsilon_3 + \varepsilon_2 + \varepsilon_1}{2}\right)}$$

$$x_{CO_2} = \frac{\varepsilon_3}{103.38 - \left(\frac{2\varepsilon_3 + \varepsilon_2 + \varepsilon_1}{2}\right)}$$

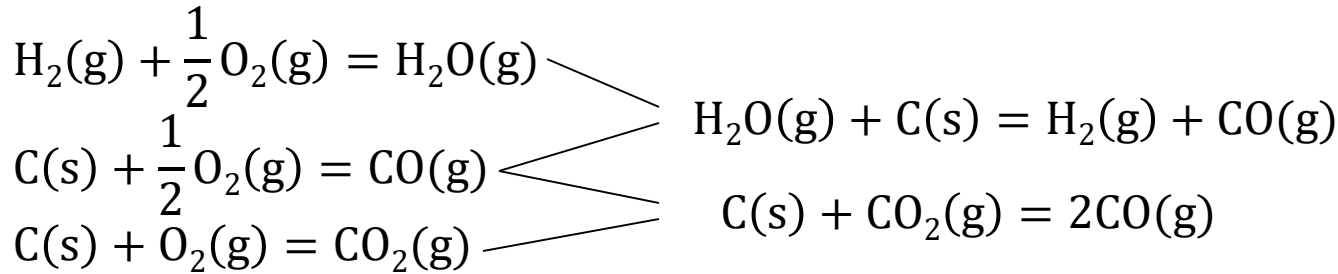
$$K_1 = \frac{(1 + \varepsilon_1) \left(103.38 - \left(\frac{2\varepsilon_3 + \varepsilon_2 + \varepsilon_1}{2}\right)\right)^{1/2} P^{-1/2}}{\left(0.5 - \frac{1}{2}\varepsilon_1 - \frac{1}{2}\varepsilon_2 - \varepsilon_3\right)^{1/2} * (-\varepsilon_1)} P^{-1/2} \approx 10^6$$

$$K_2 = \frac{\varepsilon_2 \left(103.38 - \left(\frac{2\varepsilon_3 + \varepsilon_2 + \varepsilon_1}{2}\right)\right)^{1/2}}{\left(0.5 - \frac{1}{2}\varepsilon_1 - \frac{1}{2}\varepsilon_2 - \varepsilon_3\right)^{1/2} * (100 - \varepsilon_2 - \varepsilon_3)} P^{1/2} \approx 10^8$$

$$K_3 = \frac{\varepsilon_3 * \left(103.38 - \left(\frac{2\varepsilon_3 + \varepsilon_2 + \varepsilon_1}{2}\right)\right)}{\left(0.5 - \frac{1}{2}\varepsilon_1 - \frac{1}{2}\varepsilon_2 - \varepsilon_3\right) * (100 - \varepsilon_2 - \varepsilon_3)} \approx 10^{14}$$

A reformulation of the problem is done by eliminating O<sub>2</sub> from the reactions

Independent equations:



$$K_4 = \frac{x_{\text{H}_2} * x_{\text{CO}}}{x_{\text{H}_2\text{O}} * x_{\text{C}}} P, \quad \Delta G^o = -7820 \text{ J}$$

$$K_5 = \frac{x_{\text{CO}}^2}{x_{\text{CO}} * x_{\text{C}}} P, \quad \Delta G^o = -4690 \text{ J}$$

$$v_{\text{H}_2\text{O}} = -\varepsilon_4$$

$$v_{\text{C}} = -\varepsilon_4 - \varepsilon_5$$

$$v_{\text{H}_2} = \varepsilon_4$$

$$v_{\text{CO}} = \varepsilon_4 + 2\varepsilon_5$$

$$v_{\text{CO}_2} = -\varepsilon_5$$

$$n_{\text{H}_2\text{O}} = 1 - \varepsilon_4$$

$$n_{\text{C}} = 100 - \varepsilon_4 - \varepsilon_5$$

$$n_{\text{H}_2} = \varepsilon_4$$

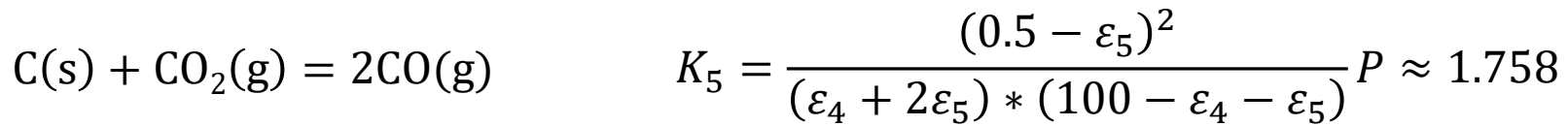
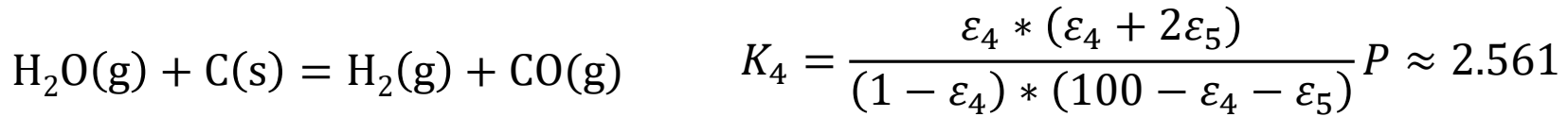
$$n_{\text{CO}} = \varepsilon_4 + 2\varepsilon_5$$

$$n_{\text{CO}_2} = 0.5 - \varepsilon_5$$

$$n_{\text{N}_2} = 1.88, n_{\text{total}} = 103.38$$

$$x_{\text{H}_2\text{O}} = \frac{1 - \varepsilon_4}{103.38} \quad x_{\text{C}} = \frac{100 - \varepsilon_4 - \varepsilon_5}{103.38} \quad x_{\text{H}_2} = \frac{\varepsilon_4}{103.38} \quad x_{\text{CO}} = \frac{\varepsilon_4 + 2\varepsilon_5}{103.38} \quad x_{\text{CO}_2} = \frac{0.5 - \varepsilon_5}{103.38}$$

$$x_{\text{N}_2} = \frac{1.88}{103.38}$$



Iteration of the two equations for two unknowns by excel solver add-on gives

$$\varepsilon_4 = 0.494 \longrightarrow 1.00 \text{ as } T \uparrow$$

$$\varepsilon_5 = 0.073 \longrightarrow 0.5 \text{ as } T \uparrow$$

$$x_C = \frac{100 - 0.494 - 0.073}{103.38} = 0.962$$

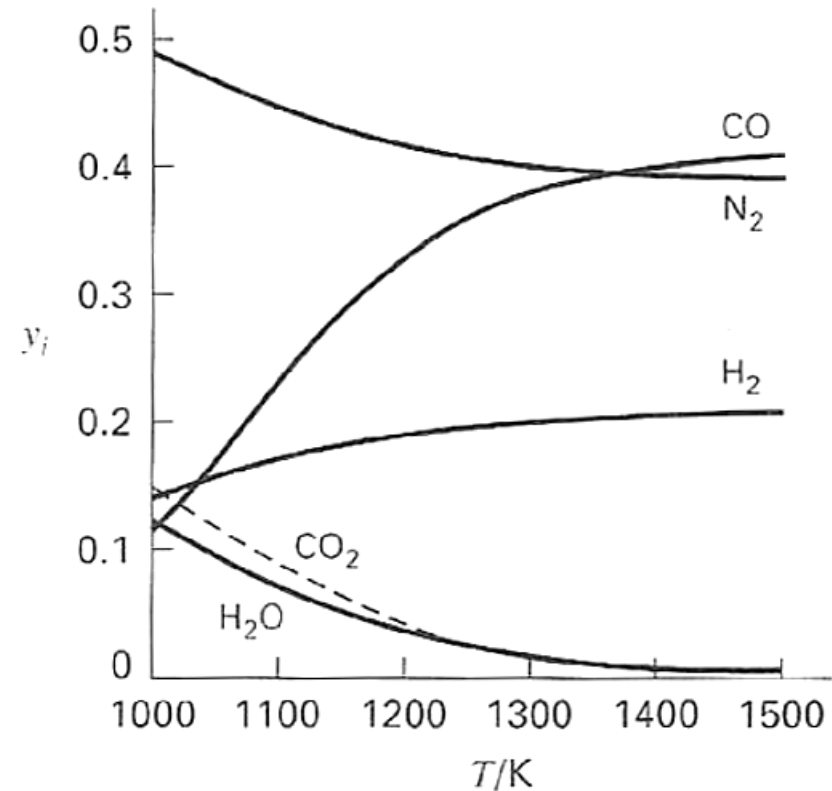
$$x_{\text{H}_2\text{O}} = \frac{1 - 0.494}{3.947} = 0.1282 \text{ excluding C}$$

$$x_{\text{H}_2} = \frac{0.494}{3.947} = 0.1252$$

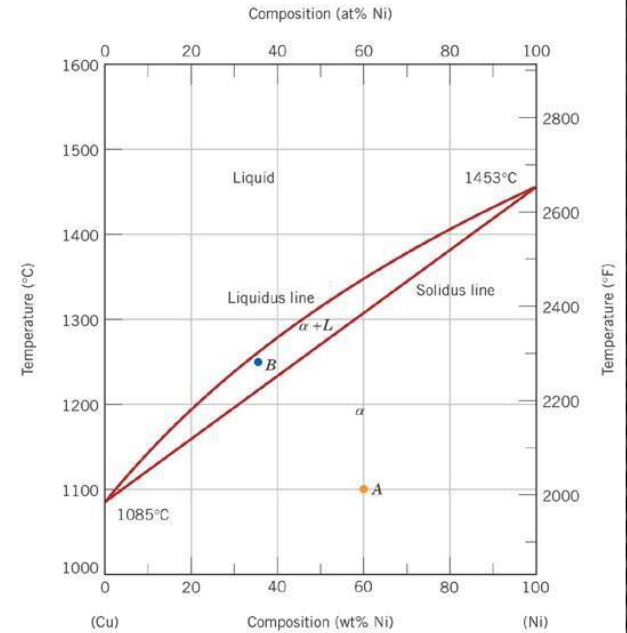
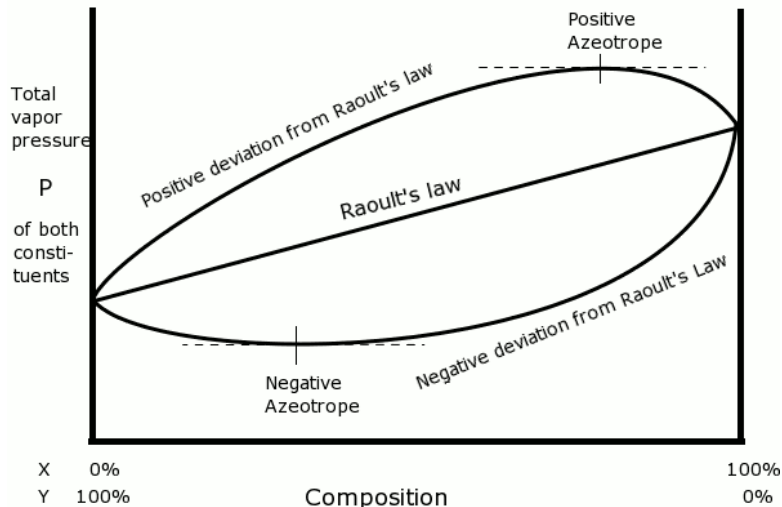
$$x_{\text{CO}} = \frac{0.494 + 0.146}{3.947} = 0.1621$$

$$x_{\text{CO}_2} = \frac{0.5 - 0.073}{3.947} = 0.1082$$

$$x_{\text{N}_2} = \frac{1.88}{3.947} = 0.4763$$



Consider a binary mixture like the Cu and Ni alloy



$$a_i = x_i \quad \lim_{x_i \rightarrow 1} \frac{da_i}{dx_i} = 1$$

$$a_i = hx_i \quad \lim_{x_i \rightarrow 0} \frac{da_i}{dx_i} = h$$

$$a_i = \gamma_i x_i \quad \text{most of the concentration range}$$

If  $\gamma_i > 1$ , solution positively deviates from Raoult's law due to repulsion between two kinds of molecules

If  $\gamma_i < 1$ , solution negatively deviates from Raoult's law due to attraction between two kinds of molecules

# Determination of the activity coefficient in binary mixtures

The activity coefficient of a dilute species in a binary mixture can be approximated by a Taylor series expansion

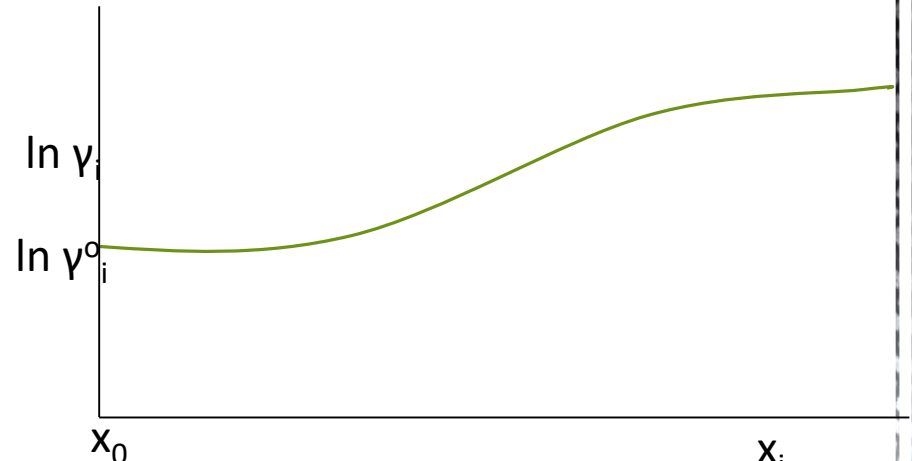
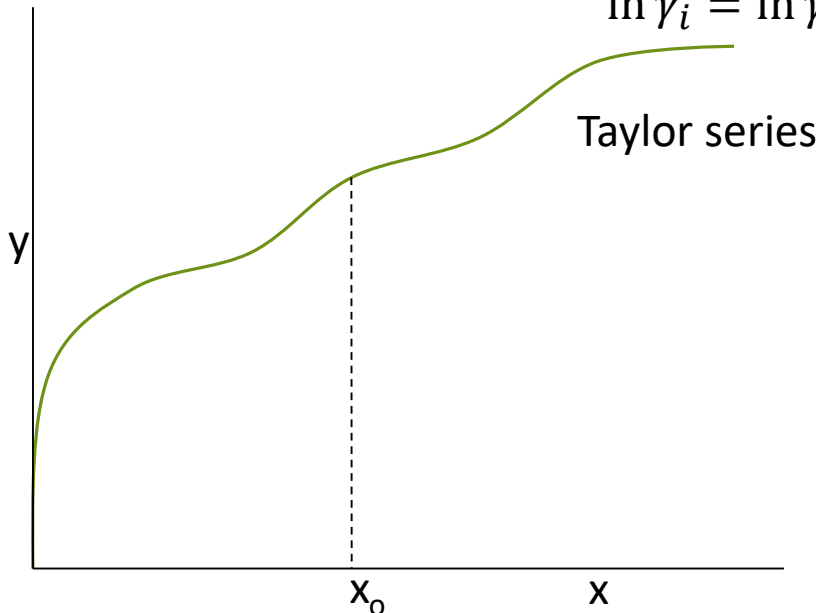
$$y = \frac{1}{0!} y_{x=x_0} + \frac{1}{1!} \left( \frac{dy}{dx} \right) (x - x_0) + \frac{1}{2!} \left( \frac{d^2 y}{dx^2} \right) (x - x_0)^2 + \dots$$

Take  $\ln \gamma_i = f(x_i)$

Expand around  $x_i = x_0 \approx 0$

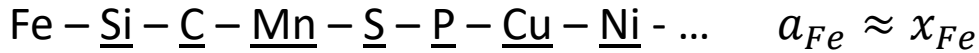
$$\ln \gamma_i = \ln \gamma_i^0 + \frac{1}{1!} \left( \frac{d \ln \gamma_i}{dx} \right)_{x_i=x_0} x_i + \frac{1}{2!} \left( \frac{d^2 \ln \gamma_i}{dx^2} \right)_{x_i=x_0} x_i^2 + \dots$$

$$\ln \gamma_i = \ln \gamma_i^0 + \epsilon_i^i x_i + \rho_i^i x_i^2 + \dots$$



# Determination of the activity coefficient in dilute multicomponent metallic solutions

Consider liquid steel containing various impurities less than 1%



$\ln \gamma_i = f(x_i, x_j, \dots)$  expanded around  $x_{Fe} \gg 1$

$$\begin{aligned} \ln \gamma_i &= \ln \gamma_i^o + \frac{1}{1!} \left( \frac{d \ln \gamma_i}{dx_i} \right)_{x_{Fe}=1} x_i + \frac{1}{1!} \left( \frac{d \ln \gamma_i}{dx_j} \right)_{x_{Fe}=1} x_j + \dots + \frac{1}{2!} \left( \frac{d^2 \ln \gamma_i}{dx_i^2} \right)_{x_{Fe}=1} x_i^2 \\ &+ \frac{1}{2!} \left( \frac{d^2 \ln \gamma_i}{dx_j^2} \right)_{x_{Fe}=1} x_j^2 + \dots \end{aligned}$$

$$\ln \gamma_i = \ln \gamma_i^o + \epsilon_i^i x_i + \epsilon_i^j x_j + \dots + \rho_i^i x_i^2 + \rho_i^j x_j^2 + \dots$$

$$\ln \gamma_i = \ln \gamma_i^o + \sum_j \epsilon_i^j x_j + \sum_j \rho_i^j x_j^2 + \dots$$

Example – Consider liquid steel of the composition Fe – 0.2% C – 0.5% Mn – 0.1% Si

Calculate the activity coefficient and activity of Si

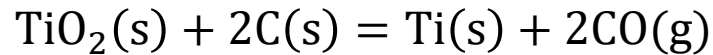
$$\ln \gamma_i = \epsilon_{Si}^{Si} x_{Si} + \epsilon_{Si}^C x_C + \epsilon_{Si}^{Mn} x_{Mn}$$

$$a_{Si} = \gamma_{Si} x_{Si}$$

$$\ln \gamma_{Si}^o = 0 \text{ since } \gamma_{Si}^o = 1$$



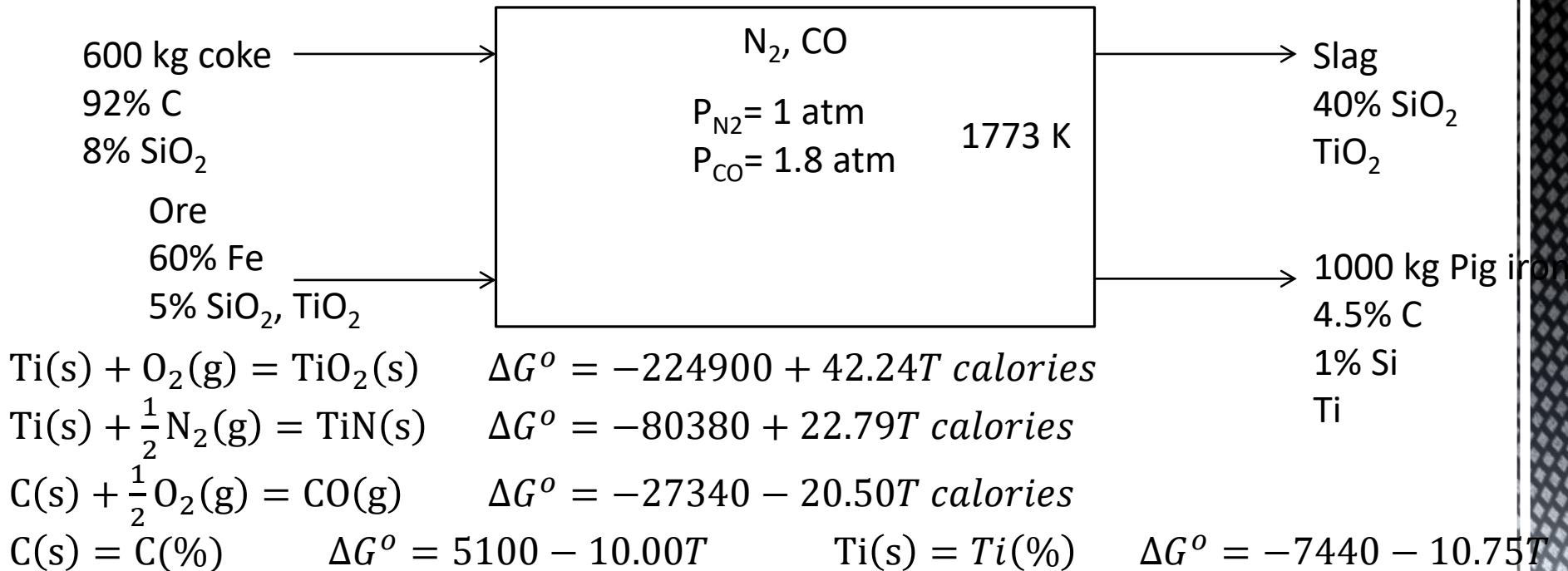
Example –  $\text{TiO}_2$  is one of the troublesome impurities in iron ores. When titaniferous ores are charged into the blast furnace, titanium is distributed between the metal and the slag in the hearth in accord with the following reaction



TiN is formed in the nitrogen rich atmosphere in the hearth of the blast furnace if the titanium content of the metal exceeds a certain limiting value

Formation of TiN is not desired as TiN melts at 2950 C and hence it remains as solid in the liquid metal and slag, which decreases their fluidity and gets collected at the bottom of the hearth, limiting hearth capacity

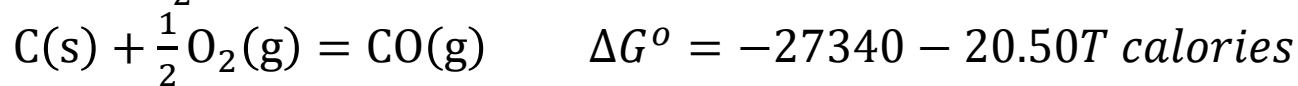
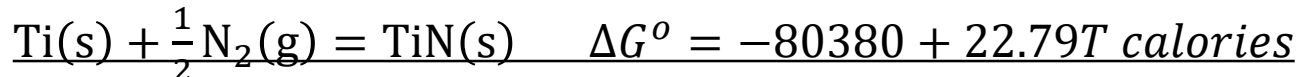
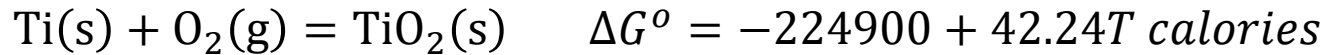
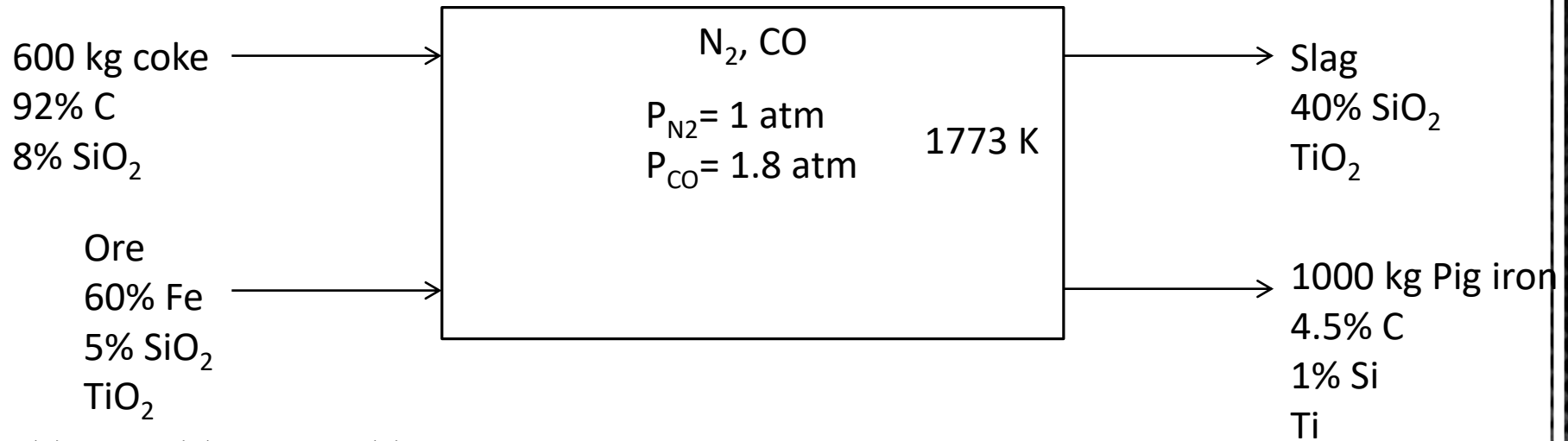
Care should be taken not to include much  $\text{TiO}_2$  in the charge



Calculate the limiting Ti content of the metal (i.e. the titanium content below which TiN will not form) in weight% in the hearth of a blast furnace at 1500 C

Interaction coefficients:  $e_{Ti}^{Ti}=0.013$ ,  $e_{Ti}^C=-0.3$ ,  $e_{Ti}^{Si}=0$ ,  $e_C^{Ti}=0$ ,  $e_C^C=0.2$ ,  $e_C^{Si}=0.08$

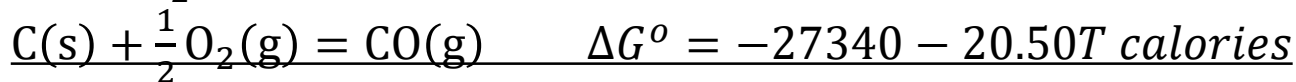
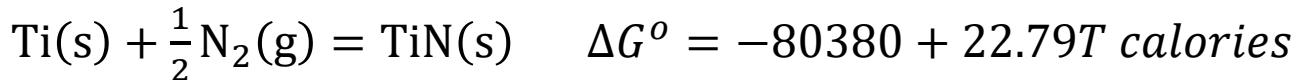
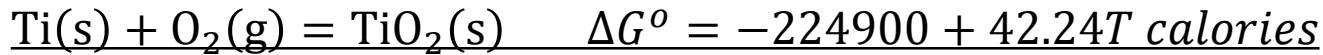
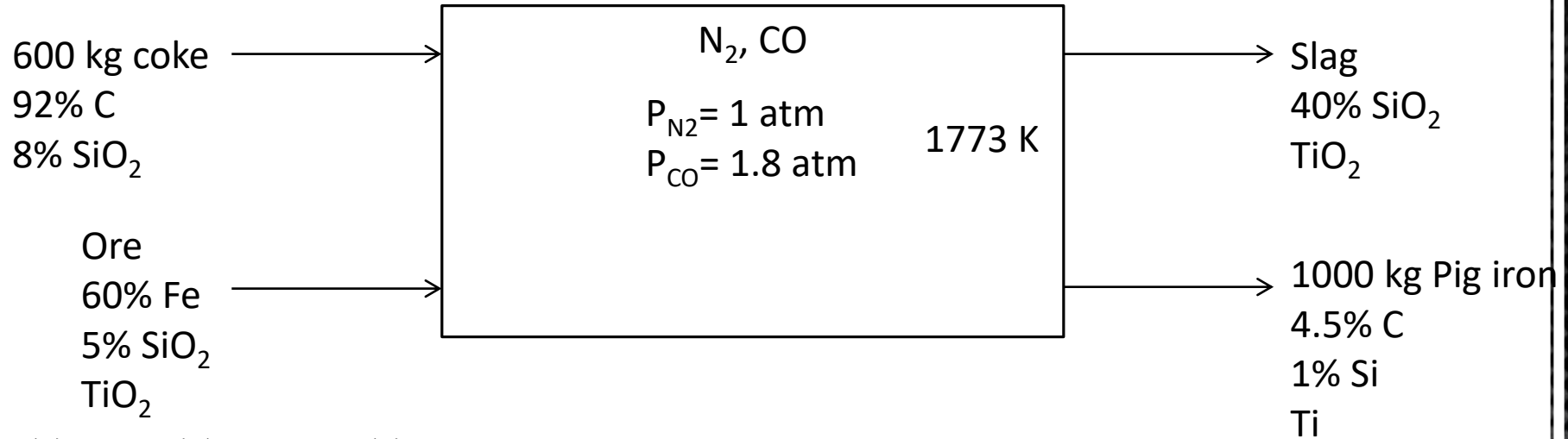
Atomic weights: Si=28, C=12, O=16, Ti=48, N=14, Fe=56



Calculate the corresponding equilibrium activity of  $\text{TiO}_2$  in the slag based on pure solid  $\text{TiO}_2$  as the standard state

Interaction coefficients:  $e_{\text{Ti}}^{\text{Ti}}=0.013$ ,  $e_{\text{Ti}}^{\text{C}}=-0.3$ ,  $e_{\text{Ti}}^{\text{Si}}=0$ ,  $e_{\text{C}}^{\text{Ti}}=0$ ,  $e_{\text{C}}^{\text{C}}=0.2$ ,  $e_{\text{C}}^{\text{Si}}=0.08$

Atomic weights: Si=28, C=12, O=16, Ti=48, N=14, Fe=56



If the weight fraction of  $\text{TiO}_2$  in the slag equals its activity in the slag, calculate the maximum permissible  $\text{TiO}_2$  content of the ore

Interaction coefficients:  $e_{\text{Ti}}^{\text{Ti}}=0.013$ ,  $e_{\text{Ti}}^{\text{C}}=-0.3$ ,  $e_{\text{Ti}}^{\text{Si}}=0$ ,  $e_{\text{C}}^{\text{Ti}}=0$ ,  $e_{\text{C}}^{\text{C}}=0.2$ ,  $e_{\text{C}}^{\text{Si}}=0.08$

Atomic weights: Si=28, C=12, O=16, Ti=48, N=14, Fe=56

