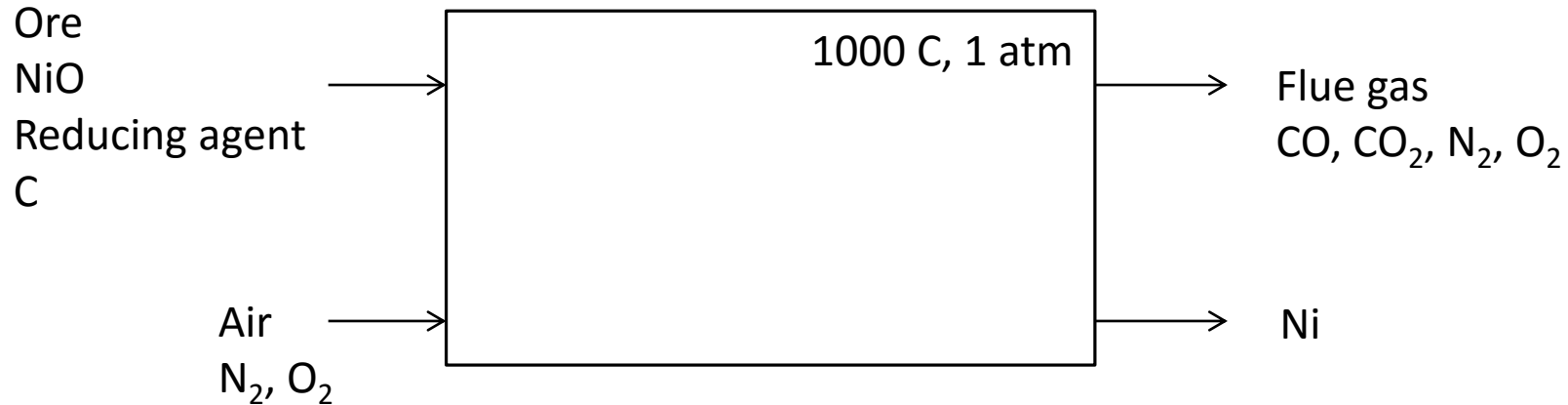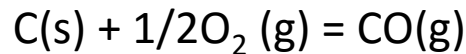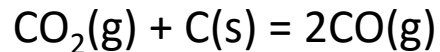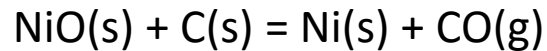# Materials and Energy Balance

Thermodynamic and Stoichiometric Principles in Materials Balance

Typical metallurgical engineering problems based on materials and energy balance

NiO is reduced in an open atmosphere furnace by excess carbon at 1000 C

Ore
NiO
Reducing agent
C

1000 C, 1 atm

Flue gas
CO, $CO_2$, $N_2$, $O_2$

Air

Ni

$N_2$, $O_2$

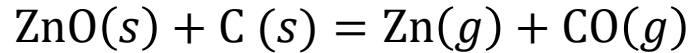| Reactions: | $\Delta G^o$ | |
|---|---|---|
| NiO(s) + C(s) = Ni(s) + CO(g) | 28970-41.07T calories | K@1000 C = 10059 |
| $CO_2$(g) + C(s) = 2CO(g) | 39810 – 40.87T calories | K@1000 C = 125.22 |
| C(s) + 1/2$O_2$ (g) = CO(g) | -27340-20.50T calories | K@1000 C = 14955000 |

How many kg-moles of Ni, CO and $CO_2$ are produced for each kg-mole of NiO and C?

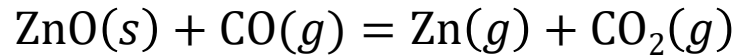Calculate the reaction extents at equilibrium

Industrial processes should be maintained at a high rate and high efficiency for feasibility

Consider the reduction of ZnO in a conventional retort to produce Zn metal

The reaction proceeds slowly due to the low contact area between solid reactants

$$ZnO(s) + C\,(s) = Zn(g) + CO(g)$$

The rate of the reaction is enhanced when CO gas is used as the reducing agent instead of solid carbon

$$ZnO(s) + CO(g) = Zn(g) + CO_2(g)$$

Thermodynamics predicts the maximum conversion of reactants to products at equilibrium temperature and pressure by computing the free energy of the reactions

Kinetics help conclude which reaction has the higher rate
The mass diffusion and transport rates are subject of Kinetics

The reaction extent is that progress variable that determines the efficiency of the reaction

Both the rate and efficiency of any reaction depend on the temperature, pressure and composition of the reactants and both are taken into account in the laboratory analysis for a commercial industrial process

Although the choice of operating conditions is determined by equilibrium considerations, many industrial reactions are not carried to equilibrium

A balance between the rate and progress of the process is established in most cases

The advantage of thermodynamic approach for process analysis is that the estimated equilibrium conversion of a reaction provides a goal by which to measure improvements in the process

R&D investigations for a new process are based on the maximum reaction extent

Consider a novel production method for a metal:

The yield of the process should be at least 50% for feasible operation


Thermodynamic analysis indicates that a yield of only 20% is possible at equilibrium
No motivation for an experimental study


An experimental program to determine the reaction rate for various temperatures, pressures
and catalysts becomes attractive if the equilibrium yield is 80%


Temperature, pressure, the stoichiometry of the chemical reactions, the initial and final
concentration of the species are the data needed in order to analyze a chemical process

Consider the following reaction

$$CH_4(g) + H_2O(g) = CO(g) + 3H_2(g)$$
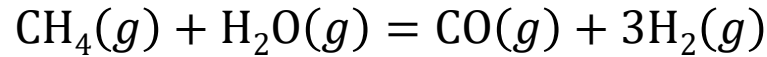
The stoichiometric numbers are negative for the reactants, positive for the products and zero for inert species

$\nu_{CH4}=-1$
$\nu_{H2O}=-1$
$\nu_{CO}=1$
$\nu_{H2}=3$

The changes in the numbers of molecules of the species present are in direct proportion to the stoichiometric numbers:

$$\frac{dn_1}{\nu_1} = \frac{dn_2}{\nu_2} = \frac{dn_3}{\nu_3} = \frac{dn_4}{\nu_4}$$

or

$$\frac{-0.5}{-1} = \frac{-0.5}{-1} = \frac{0.5}{1} = \frac{1.5}{3}$$

The terms are equal and related to an amount of reaction as represented by a change in the number of moles chemical species

The definition of reaction extent arises by collectively identifying the equal terms with a single quantity:

$$\frac{dn_1}{\nu_1} = \frac{dn_2}{\nu_2} = \frac{dn_3}{\nu_3} = \frac{dn_4}{\nu_4} = d\varepsilon$$

The general relation between a differential change $dn_i$ in the number of moles of a reacting species and the reaction extent $d\varepsilon$ is therefore:

$$dn_i = \nu_i d\varepsilon$$

Integrating from an initial unreacted state where $\varepsilon = 0$ and $n_i = n_{i0}$ to a state reached after an arbitrary amount of reaction gives

$$\int_{n_{i0}}^{n_i} dn_i = \nu_i \int_0^\varepsilon d\varepsilon \qquad \text{or} \qquad n_i = n_{i0} + \nu_i \varepsilon$$

The variable $\varepsilon$, called the reaction extent or reaction coordinate characterizes the degree to which a reaction has advanced
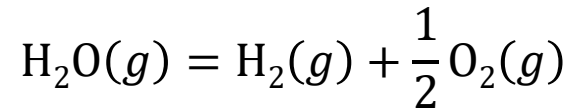
Summing over all species gives

$$n = \sum n_i = \sum n_{i0} + \varepsilon \sum \nu_i \quad \text{or} \quad \boxed{n = n_0 + \nu\varepsilon} \quad \text{where}$$

$$n = \sum n_i, \; n_0 = \sum n_{i0}, \; \nu = \sum \nu_i$$

Thus the mole fractions $y_i$ of the species present are related to $\varepsilon$ by

$$y_i = \frac{n_i}{n} = \frac{n_{i0} + \nu_i \varepsilon}{n_0 + \nu \varepsilon}$$

Example – Consider a vessel which initially contains only $n_0$ moles of water vapor that decomposes according to the reaction:

$$\mathrm{H_2O}(g) = \mathrm{H_2}(g) + \frac{1}{2}\mathrm{O_2}(g)$$

$\nu_{H2O} = -1$      $n_{H2O} = n_0 - \varepsilon$

$\nu_{H2} = 1$      $n_{H2} = \varepsilon$

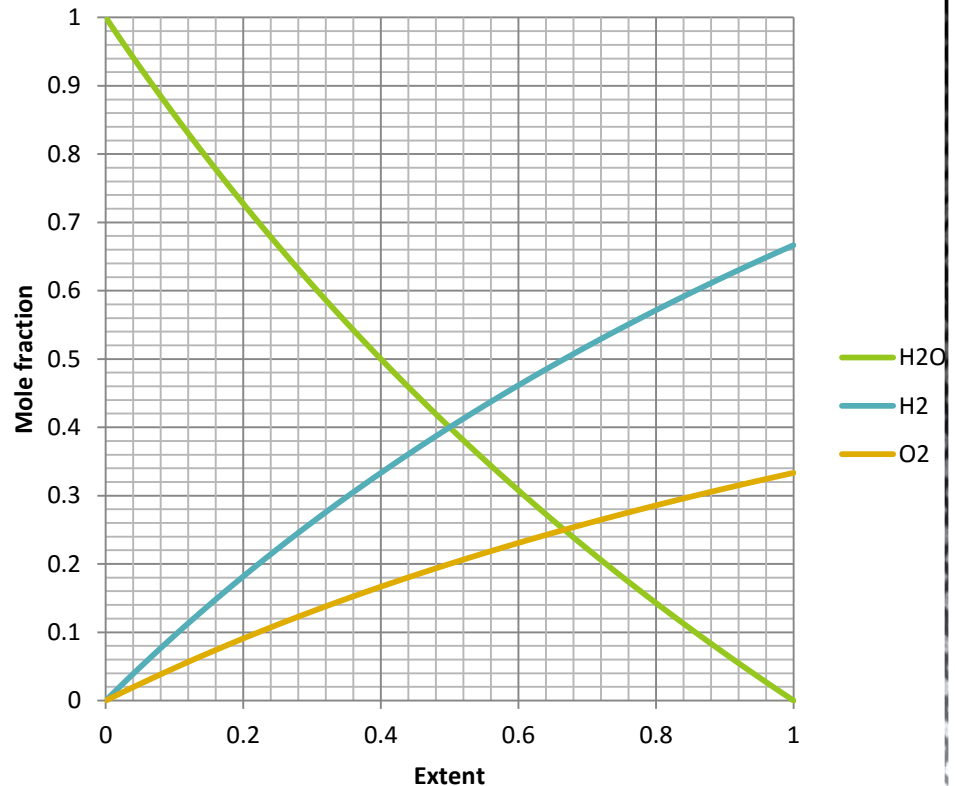$\nu_{O2} = 0.5$      $n_{O2} = 0.5\varepsilon$

$\nu_{total} = 0.5$      $n_{total} = n_0 + 0.5\varepsilon$

$$y_{H2O} = \frac{n_0 - \varepsilon}{n_0 + 0.5\varepsilon}$$

$$y_{H2} = \frac{\varepsilon}{n_0 + 0.5\varepsilon}$$

$$y_{H2} = \frac{0.5\varepsilon}{n_0 + 0.5\varepsilon}$$

The fractional decomposition of water vapor

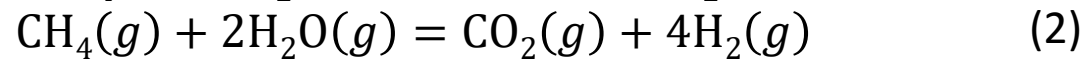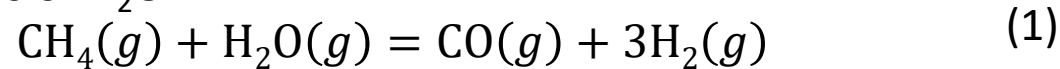$$\frac{n_0 - n_{H2O}}{n_0} = \frac{n_0 - (n_0 - \varepsilon)}{n_0} = \frac{\varepsilon}{n_0}$$

The mole fractions $y_i$ of the species present in all reactions related to extents $\varepsilon_j$ of j reactions are obtained as

$$y_i = \frac{n_i}{n} = \frac{n_{i0} + \sum_j v_{i,j}\varepsilon_j}{n_0 + \sum_j v_j \varepsilon_j}$$

Example – Consider a system with two reactions occurring simultaneously in the presence of 2 moles of $CH_4$ and 3 moles of $H_2O$

$$CH_4(g) + H_2O(g) = CO(g) + 3H_2(g) \qquad (1)$$
$$CH_4(g) + 2H_2O(g) = CO_2(g) + 4H_2(g) \qquad (2)$$

| Reaction 1 | Reaction 2 | | |
|---|---|---|---|
| $v_{CH4} = -1$ | $v_{CH4} = -1$ | $n_{CH4} = 2 - \varepsilon_1 - \varepsilon_2$ | $y_{CH4} = \dfrac{2 - \varepsilon_1 - \varepsilon_2}{5 + 2\varepsilon_1 + 2\varepsilon_2}$ |
| $v_{H2O} = -1$ | $v_{H2O} = -2$ | $n_{H2O} = 3 - \varepsilon_1 - 2\varepsilon_2$ | $y_{H2O} = \dfrac{3 - \varepsilon_1 - 2\varepsilon_2}{5 + 2\varepsilon_1 + 2\varepsilon_2}$ |
| $v_{CO} = 1$ | $v_{CO} = 0$ | $n_{CO} = \varepsilon_1$ | $y_{CO} = \dfrac{\varepsilon_1}{5 + 2\varepsilon_1 + 2\varepsilon_2}$ |
| $v_{CO2} = 0$ | $v_{CO2} = 1$ | $n_{CO2} = \varepsilon_2$ | $y_{CO2} = \dfrac{\varepsilon_2}{5 + 2\varepsilon_1 + 2\varepsilon_2}$ |
| $v_{H2} = 3$ | $v_{H2} = 4$ | $n_{H2} = 3\varepsilon_1 + 4\varepsilon_2$ | $y_{H2} = \dfrac{3\varepsilon_1 + 4\varepsilon_2}{5 + 2\varepsilon_1 + 2\varepsilon_2}$ |
| $v_{total} = 2$ | $v_{total} = 2$ | $n_{total} = 5 + 2\varepsilon_1 + 2\varepsilon_2$ | |

The composition of the system is a function of two independent variables $\varepsilon_1$ and $\varepsilon_2$

# Equilibrium criterion for chemical reactions

Recall that the total Gibbs free energy of a closed system at constant temperature and pressure must decrease during an irreversible process and the condition for equilibrium is reached when

$$\Delta G_{T,P} = 0 = \Delta G^o + RT \ln K$$

Considering this criterion for a single chemical reaction, it is seen that irreversible reaction at constant T and P should decrease the total Gibbs free energy

The equilibrium state of a closed system at constant T and P is the state for which the total Gibbs free energy is a minimum with respect to all possible changes

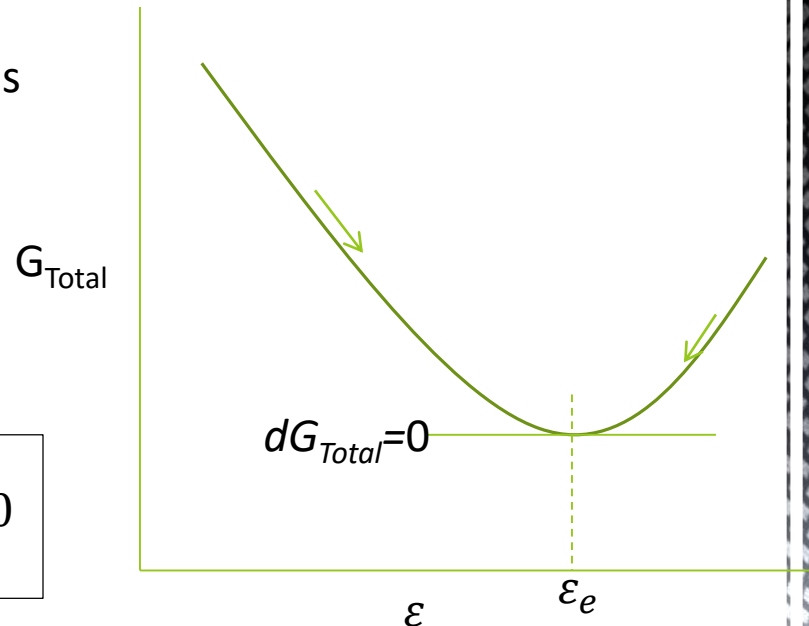In a single reaction system the total differential of G is

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

$dn_i$ may be replaced by $\nu_i d\varepsilon$

$$d(nG) = (nV)dP - (nS)dT + \sum \nu_i \mu_i \, d\varepsilon$$

Criterion for equilibrium 
$$\boxed{\sum \nu_i \mu_i = \left[\frac{\partial(nG)}{\partial \varepsilon}\right]_{T,P} = 0}$$

G_Total

$dG_{Total}=0$

$\varepsilon$

$\varepsilon_e$

The chemical potential of a species in a solution is the partial Gibbs free energy of that component

$$\mu_i = G^o{}_i + RT \ln a_i$$

Applying the equality to the equilibrium criterion yields

$$\sum v_i(G^o{}_i + RT \ln a_i) = 0$$

$$\sum v_i G^o{}_i + RT \sum \ln(a_i)^{v_i} = 0$$

$$\sum \ln(a_i)^{v_i} = \ln \prod (a_i)^{v_i} = \frac{-\sum v_i G^o{}_i}{RT}$$

or

$$\boxed{\prod (a_i)^{v_i} = \exp \frac{-\sum v_i G^o{}_i}{RT} = K}$$

in simpler form

$$\boxed{-RT \ln K = \sum v_i G^o{}_i = \Delta G^o}$$

The equilibrium constant K is the connection between Gibbs free energy of a reaction and the reaction extent

K is a function of only T and represented by the activities of the individual species

Example – The following reaction is carried out under different sets of conditions
Assuming the mixture behaves as an ideal gas, calculate the fraction of steam reacted in each case
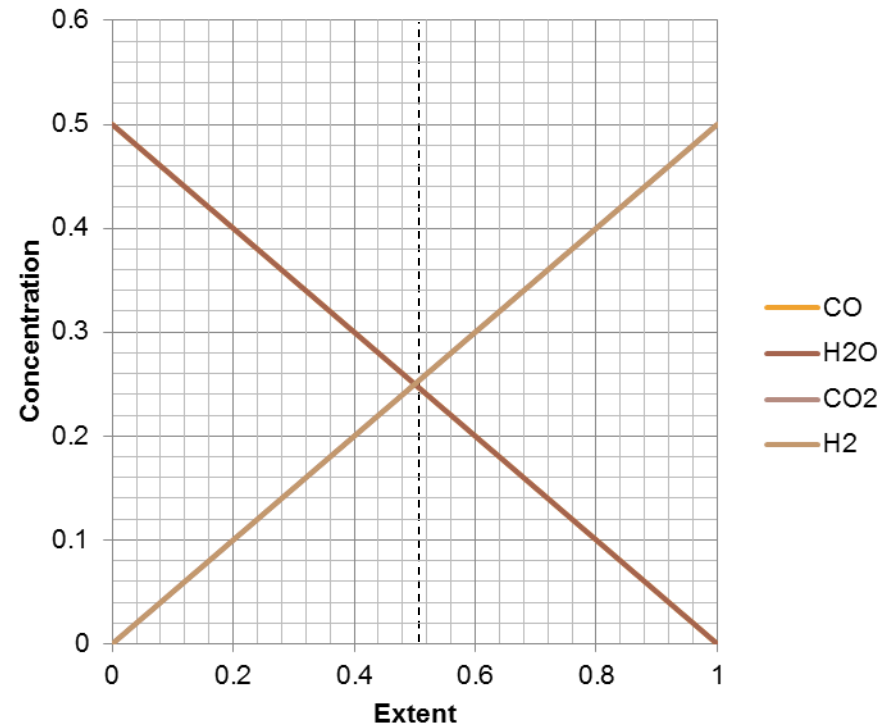
$$CO(g) + H_2O(g) = CO_2(g) + H_2(g)$$
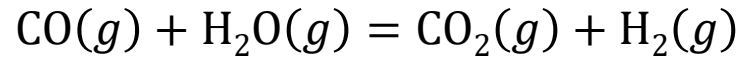
a) There are initially 1 mole of $H_2O$ vapor and 1 mole of CO at 1100 K and 1 bar
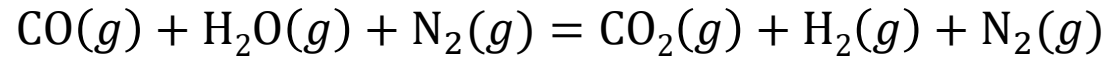
From the lnK vs 1/T figure K=1 obtained at 1100 K

$\nu_{CO} = -1$          $n_{CO} = 1 - \varepsilon_e$

$\nu_{H2O} = -1$       $n_{H2O} = 1 - \varepsilon_e$

$\nu_{CO2} = 1$         $n_{CO2} = \varepsilon_e$

$\nu_{H2} = 1$          $n_{H2} = \varepsilon_e$

$\nu_{total} = 0$        $n_{total} = 2$

$$y_{CO} = \frac{1 - \varepsilon_e}{2}$$

$$y_{H2O} = \frac{1 - \varepsilon_e}{2}$$

$$y_{CO2} = \frac{\varepsilon_e}{2}$$

$$y_{H2} = \frac{\varepsilon_e}{2}$$



$$K = \frac{y_{CO2}y_{H2}}{y_{CO}y_{H2O}} = \frac{\varepsilon_e^2}{(1 - \varepsilon_e)^2} = 1 \longrightarrow \varepsilon_e = \frac{1}{2} \longrightarrow \frac{n_0 - n_{H2O}}{n_0} = \frac{n_0 - (n_0 - \varepsilon_e)}{n_0} = \frac{\varepsilon_e}{n_0} = \frac{1}{2}$$
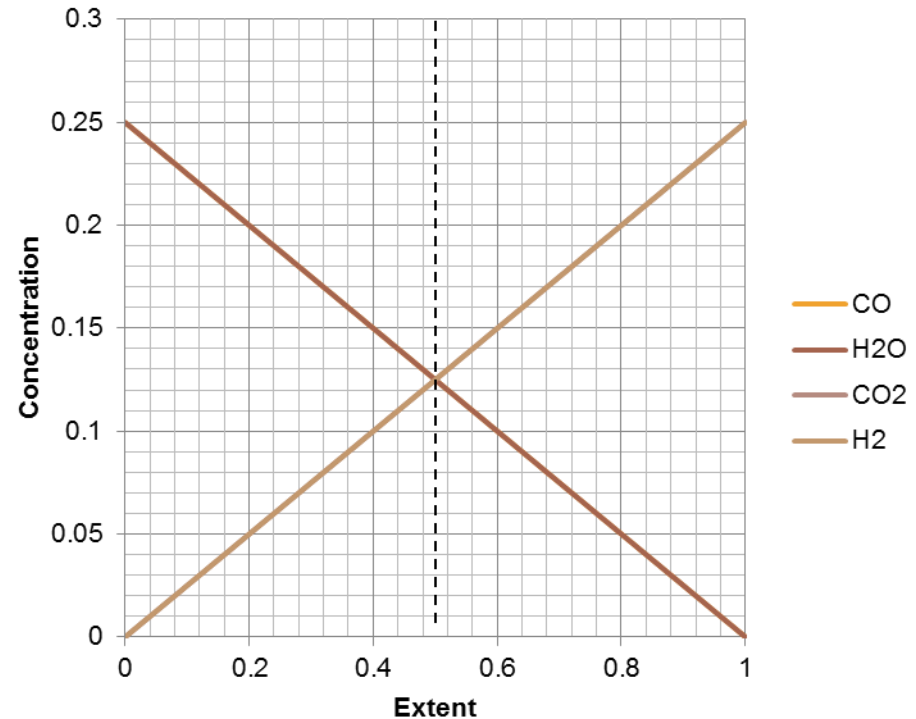
Example – The following reaction is carried out under different sets of conditions
Assuming the mixture behaves as an ideal gas, calculate the fraction of steam reacted in each case

$$CO(g) + H_2O(g) + N_2(g) = CO_2(g) + H_2(g) + N_2(g)$$

b) Same as (a) except 2 mole $N_2$ added to the reactants

$N_2$ dilutes the mixture so that the initial number of moles are increased to 4

$\nu_{CO} = -1$ $\qquad n_{CO} = 1 - \varepsilon_e$

$\nu_{H2O} = -1$ $\qquad n_{H2O} = 1 - \varepsilon_e$

$\nu_{CO2} = 1$ $\qquad n_{CO2} = \varepsilon_e$

$\nu_{H2} = 1$ $\qquad n_{H2} = \varepsilon_e$

$\nu_{N2} = 0$ $\qquad n_{N2} = 2$

$\nu_{total} = 0$ $\qquad n_{total} = 4$

$$y_{CO} = \frac{1 - \varepsilon_e}{4}$$

$$y_{H2O} = \frac{1 - \varepsilon_e}{4}$$

$$y_{CO2} = \frac{\varepsilon_e}{4}$$

$$y_{H2} = \frac{\varepsilon_e}{4}$$



Equilibrium constant and reaction extent is unaffected

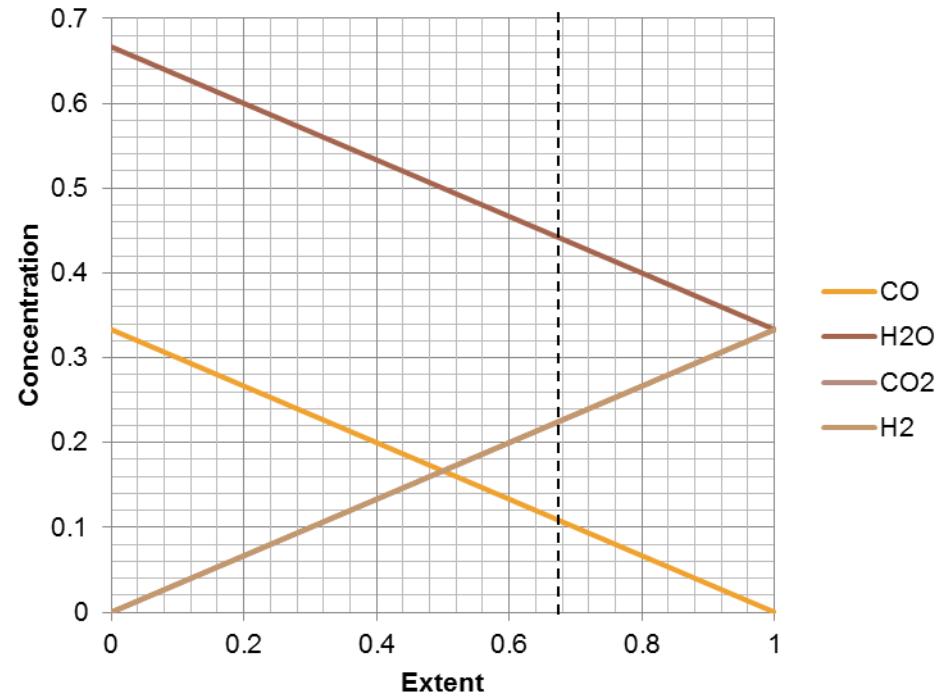$$K = \frac{y_{CO2}y_{H2}}{y_{CO}y_{H2O}} = \frac{\varepsilon_e^2}{(1 - \varepsilon_e)^2} = 1 \longrightarrow \varepsilon_e = \frac{1}{2} \longrightarrow \frac{n_0 - n_{H2O}}{n_0} = \frac{n_0 - (n_0 - \varepsilon_e)}{n_0} = \frac{\varepsilon_e}{n_0} = \frac{1}{2}$$

Example – The following reaction is carried out under different sets of conditions
Assuming the mixture behaves as an ideal gas, calculate the fraction of steam reacted in each case

$$CO(g) + H_2O(g) = CO_2(g) + H_2(g)$$
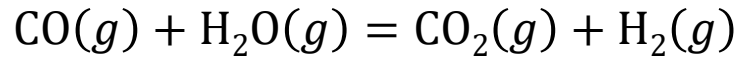
c) There are initially 2 moles of $H_2O$ vapor and 1 mole of CO at 1100 K and 1 bar

$\nu_{CO} = -1$ $\qquad n_{CO} = 1 - \varepsilon_e$

$\nu_{H2O} = -1$ $\qquad n_{H2O} = 2 - \varepsilon_e$

$\nu_{CO2} = 1$ $\qquad n_{CO2} = \varepsilon_e$

$\nu_{H2} = 1$ $\qquad n_{H2} = \varepsilon_e$

$\nu_{total} = 0$ $\qquad n_{total} = 3$

$y_{CO} = \dfrac{1 - \varepsilon_e}{3}$

$y_{H2O} = \dfrac{2 - \varepsilon_e}{3}$

$y_{CO2} = \dfrac{\varepsilon_e}{3}$

$y_{H2} = \dfrac{\varepsilon_e}{3}$
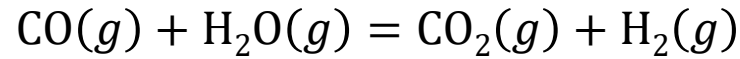


Extra $H_2O$ increases the reaction extent but the conversion of steam decreases

$$K = \frac{y_{CO2}y_{H2}}{y_{CO}y_{H2O}} = \frac{\varepsilon_e{}^2}{(1 - \varepsilon_e)(2 - \varepsilon_e)} = 1$$

$$\varepsilon_e = \frac{2}{3} \longrightarrow \frac{n_0 - n_{H2O}}{n_0} = \frac{n_0 - (n_0 - \varepsilon_e)}{n_0} = \frac{\varepsilon_e}{n_0} = \frac{1}{3}$$

Example – The following reaction is carried out under different sets of conditions
Assuming the mixture behaves as an ideal gas, calculate the fraction of steam reacted in each case

$$CO(g) + H_2O(g) = CO_2(g) + H_2(g)$$

d) There are initially 1 mole of $H_2O$ vapor and 2 moles of CO at 1100 K and 1 bar

$\nu_{CO} = -1$    $n_{CO} = 2 - \varepsilon_e$

$\nu_{H2O} = -1$    $n_{H2O} = 1 - \varepsilon_e$

$\nu_{CO2} = 1$    $n_{CO2} = \varepsilon_e$

$\nu_{H2} = 1$    $n_{H2} = \varepsilon_e$

$\nu_{total} = 0$    $n_{total} = 3$

$y_{CO} = \dfrac{2 - \varepsilon_e}{3}$

$y_{H2O} = \dfrac{1 - \varepsilon_e}{3}$

$y_{CO2} = \dfrac{\varepsilon_e}{3}$

$y_{H2} = \dfrac{\varepsilon_e}{3}$



Extra CO increases both the reaction extent and the conversion of steam

$$K = \frac{y_{CO2}y_{H2}}{y_{CO}y_{H2O}} = \frac{\varepsilon_e^2}{(2 - \varepsilon_e)(1 - \varepsilon_e)} = 1 \longrightarrow \varepsilon_e = \frac{2}{3} \longrightarrow \frac{n_0 - n_{H2O}}{n_0} = \frac{n_0 - (n_0 - \varepsilon_e)}{n_0} = \frac{\varepsilon_e}{n_0} = \frac{2}{3}$$
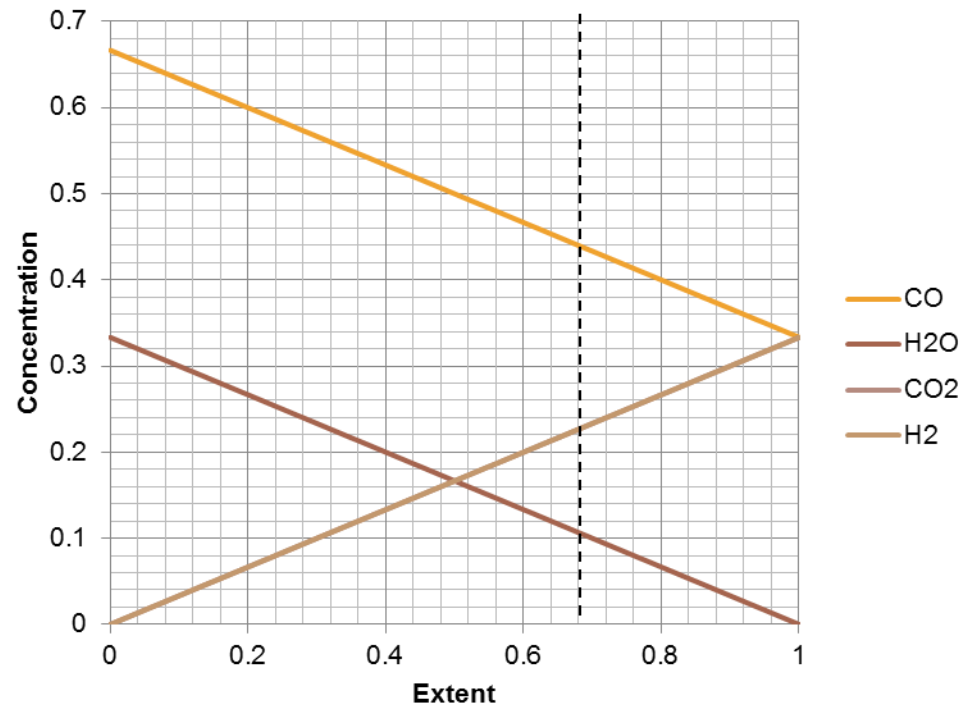
Example – The following reaction is carried out under different sets of conditions
Assuming the mixture behaves as an ideal gas, calculate the fraction of steam reacted in each case

$$CO(g) + H_2O(g) = CO_2(g) + H_2(g)$$
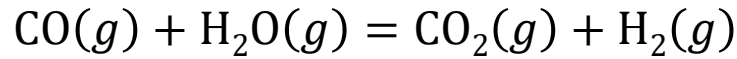
e) There are initially 1 mole of $H_2O$ vapor,1 mole of CO and 1 mole of CO2 at 1100 K and 1 bar

$\nu_{CO} = -1$          $n_{CO} = 1 - \varepsilon_e$

$\nu_{H2O} = -1$         $n_{H2O} = 1 - \varepsilon_e$

$\nu_{CO2} = 1$          $n_{CO2} = 1 + \varepsilon_e$

$\nu_{H2} = 1$           $n_{H2} = \varepsilon_e$

$\nu_{total} = 0$        $n_{total} = 3$

$$y_{CO} = \frac{1 - \varepsilon_e}{3}$$

$$y_{H2O} = \frac{1 - \varepsilon_e}{3}$$

$$y_{CO2} = \frac{1 + \varepsilon_e}{3}$$

$$y_{H2} = \frac{\varepsilon_e}{3}$$



Extra $CO_2$ decreases both reaction extent and conversion of steam

$$K = \frac{y_{CO2}y_{H2}}{y_{CO}y_{H2O}} = \frac{(1 + \varepsilon_e)\varepsilon_e}{(1 - \varepsilon_e)^2} = 1 \longrightarrow \varepsilon_e = \frac{1}{3} \longrightarrow \frac{n_0 - n_{H2O}}{n_0} = \frac{n_0 - (n_0 - \varepsilon_e)}{n_0} = \frac{\varepsilon_e}{n_0} = \frac{1}{3}$$

Example – The following reaction is carried out under different sets of conditions
Assuming the mixture behaves as an ideal gas, calculate the fraction of steam reacted in each case
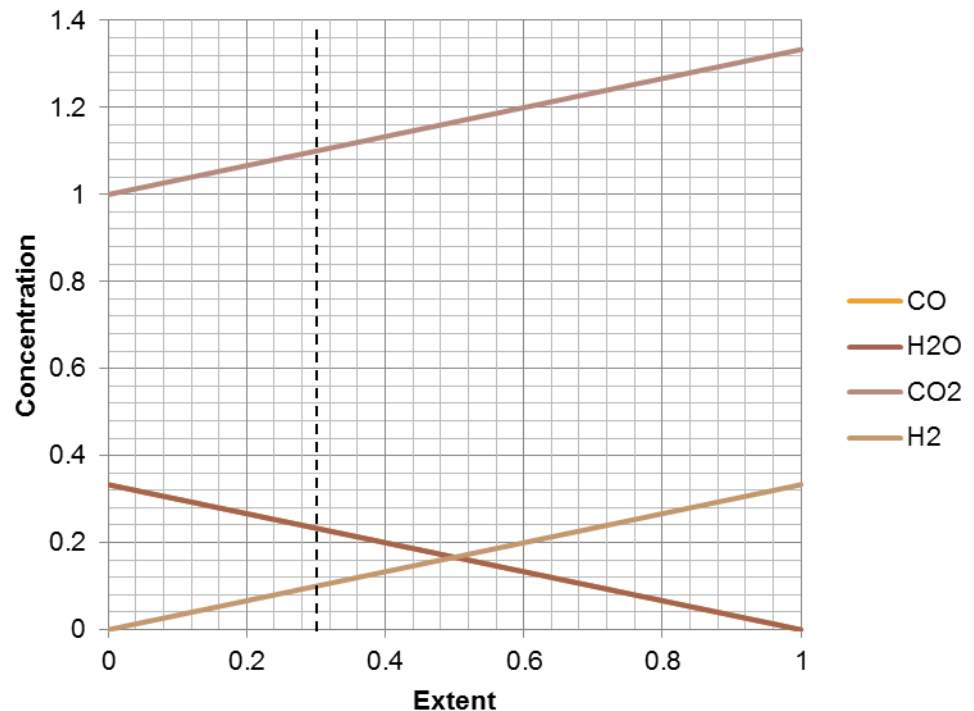
$$CO(g) + H_2O(g) = CO_2(g) + H_2(g)$$
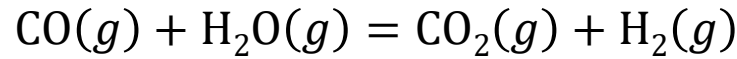
f) There are initially 1 mole of $H_2O$ vapor and 1 mole of CO at 1650 K and 1 bar

From the lnK vs 1/T figure K=0.316 obtained at 1650 K

$\nu_{CO} = -1$  $\qquad n_{CO} = 1 - \varepsilon_e$

$\nu_{H2O} = -1$  $\qquad n_{H2O} = 1 - \varepsilon_e$

$\nu_{CO2} = 1$  $\qquad n_{CO2} = \varepsilon_e$

$\nu_{H2} = 1$  $\qquad n_{H2} = \varepsilon_e$

$\nu_{total} = 0$  $\qquad n_{total} = 2$

$$y_{CO} = \frac{1 - \varepsilon_e}{2}$$

$$y_{H2O} = \frac{1 - \varepsilon_e}{2}$$

$$y_{CO2} = \frac{\varepsilon_e}{2}$$

$$y_{H2} = \frac{\varepsilon_e}{2}$$
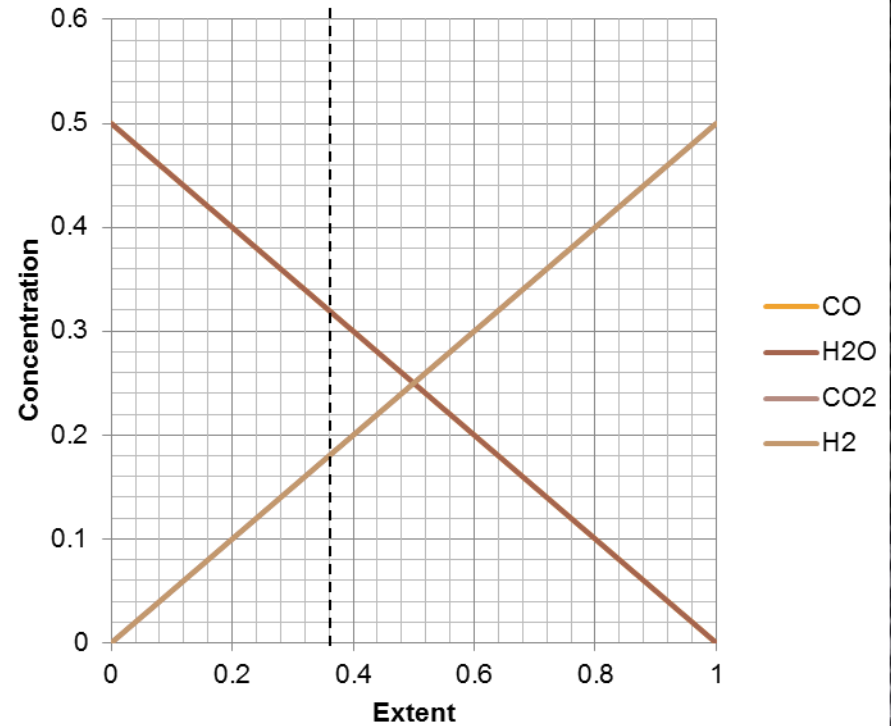


Reaction extent and steam conversion decreases with increasing T since reaction is endotherm

$$K = \frac{y_{CO2}y_{H2}}{y_{CO}y_{H2O}} = \frac{\varepsilon_e^2}{(1 - \varepsilon_e)^2} = 0.316 \rightarrow \varepsilon_e = 0.36 \rightarrow \frac{n_0 - n_{H2O}}{n_0} = \frac{n_0 - (n_0 - \varepsilon_e)}{n_0} = \frac{\varepsilon_e}{n_0} = 0.36$$

The equilibrium concentration of both products and reactants in a chemical reaction can be determined when the temperature, pressure, and equilibrium constant at that T and P is provided
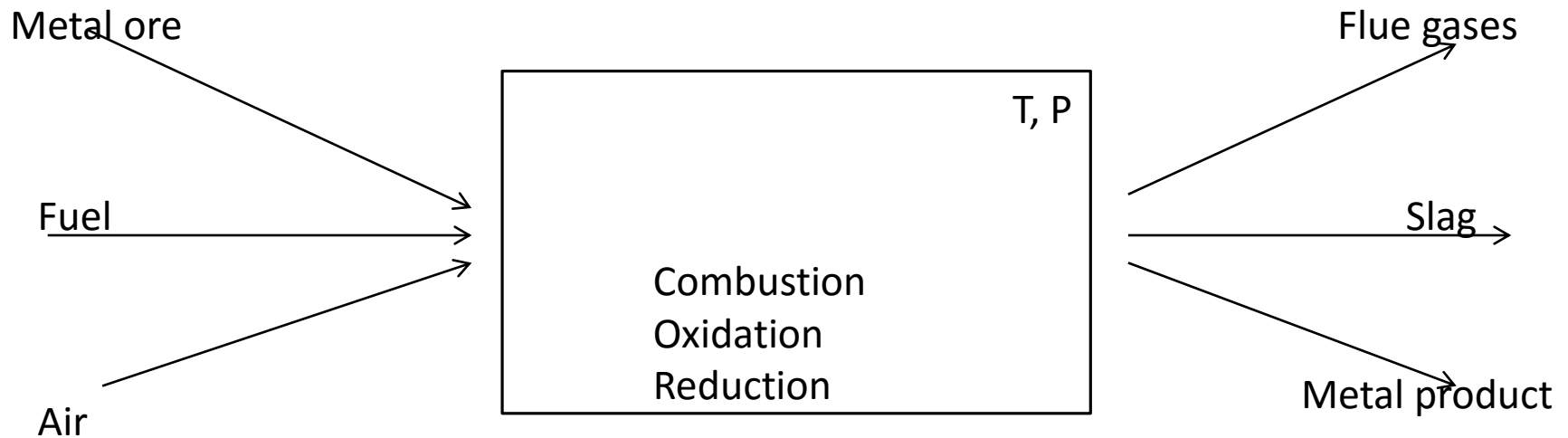
Calculation of the concentration of the species in an iron blast furnace consisting of multiple reactions is possible by careful and detailed accounting of each element in each species taking place in all reactions

Material balance is the basic procedure that enables engineers specify all the amount of species without a knowledge of the complete system

Metal ore                                                                                   Flue gases

                                    ┌─────────────────────────┐
                                    │                  T, P   │
                                    │                         │
Fuel                                │                         │            Slag
                                    │  Combustion             │
                                    │  Oxidation              │
                                    │  Reduction              │            Metal product
Air                                 └─────────────────────────┘

If the composition and the concentrations of the reactants are known, the concentration of the products can be determined thanks to the principles of mass balance

The account of the raw materials is held routinely in every plant by using printed forms including the type of raw material and spaces to enter the measured weights of input raw materials with their analysis

The output section is reserved to enter the measured or calculated quantities of products and their analyses

Material balances kept routinely in every plant serve as an accounting of the process and constitute valuable records of operation on the basis of which cost calculations can be made

The furnace charge has to be changed often in steelmaking practice due to changes in the specifications of the costumer

Manipulations in charge proportions can be economically and accurately made based on the concentration data

The operating variables like temperature and pressure in addition to composition can be altered in order to improve the efficiency of the process if only the exact variables of the system at the initial state is known by material balance

| ELEMENT | SYMBOL | METAL TYPE | | | |
| --- | --- | --- | --- | --- | --- |
| | | Non-alloy Free cutting steel | Silicon-electrical steel | High-speed steel | Silico-manganese steel |
| Manganese | Mn | | | | between 0.5% and 1.9% |
| Silicon | Si | | between 0.6% and 6% | | between 0.6% and 2.3% |
| Chromium | Cr | | | 3 - 6% | |
| Carbon | C | | not more than 0.08% | 0.6% or more | not more than 0.7% |
| Aluminium | Al | | can contain no more than 1% | | |
| Molybdenum | Mo | | | * | |
| Lead | Pb | 0.1% or more | | | |
| Sulphur | S | 0.08% or more | | | |
| Tungsten (Wolfram) | W | | | * | |
| Selenium | Se | more than 0.05% | | | |
| Tellurium | Te | more than 0.01% | | | |
| Bismuth | Bi | more than 0.05% | | | |
| Vanadium | V | | | * | |
| Other Elements | | | may contain no other element in a proportion that would give the steel the characteristics of another alloy steel | | may contain no other element in a proportion that would give the steel the characteristics of another alloy steel |

In a commercial industrial operation it is difficult to make direct measurements on the process variables as a whole

The composition and concentration of reactant raw materials is conveniently measured, other process variables like the concentration of flue gases have to be estimated or calculated from the given data

The principles of general chemistry including the following stoichiometric principles enable us to calculate the missing parts of material balances:

- Conservation of mass
- Mass relations in metallurgical reactions
- Volume relations in metallurgical reaction
- Molar units
- Gas laws
- Excess reactants

Mass relations in metallurgical reactions

In extractive metallurgy processes, the accounting of the weight of products obtained from a given quantity of reactants is important

The simple way to determine the weight of the products is to make use of the atomic weights of elements appearing in a reaction

1. Write a correct chemical reaction describing the particular process
$$Fe_3O_4 + 4CO = 3Fe + 4CO_2$$
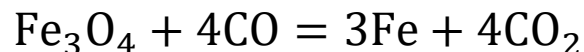
2. Obtain the molecular weights of compounds appearing in reaction from atomic weights of elements

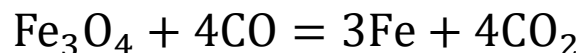| Atomic weights (g) | Molecular weights (g) |
|---|---|
| Iron: 56 | $Fe_3O_4$: 3*56+4*16 = 232 |
| Carbon: 12 | CO: 12+16 = 28 |
| Oxygen: 16 | $CO_2$: 12+2*16 = 44 |

3. Calculate the relative weights of the reactants and products involved in reaction by multiplying the respective atomic or molecular weights with the stoichiometric coefficients
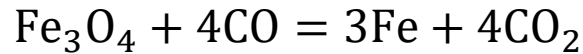
$$Fe_3O_4 + 4CO = 3Fe + 4CO_2$$

| | $Fe_3O_4$ | 4CO | 3Fe | 4$CO_2$ |
|---|---|---|---|---|
| Number of moles | (1) | (4) | (3) | (4) |
| Relative weights | 232 | 4*28=112 | 3*56=168 | 4*44=176 |

344 = 344

Example – Calculate the weights of $Fe_3O_4$ and $CO$ necessary to produce 150 kg of iron

$$Fe_3O_4 + 4CO = 3Fe + 4CO_2$$

Atomic weights (g)
Iron: 56
Carbon: 12
Oxygen: 16

Molecular weights (g)
$Fe_3O_4$: 3*56+4*16 = 232
CO: 12+16 = 28
$CO_2$: 12+2*16 = 44

Weight of $Fe_3O_4 = \left(\frac{232}{168}\right) * 150 = 207$ kg

Weight of $CO = \left(\frac{4*28}{168}\right) * 150 = 100$ kg

Weight of $CO_2 = \left(\frac{4*44}{168}\right) * 150 = 157$ kg

Conservation of mass

The relationships between the quantities and analyses of the materials entering, leaving and participating in a process are obtained by using the law of conservation of mass

For any component X which may be chosen as an element or compound depending on the specific process, the generalized mass balance equation is written as

$$\sum m_R \,(\%x)_R = \sum m_P \,(\%x)_P \pm \Delta m_x$$

where $m_R$ and $m_P$ represent the masses of substances making up the reactants and products respectively, $(\%x)_R$ and $(\%x)_P$ are the weight percentage of X present in reactants and products, $\Delta m_x$ represents an accumulation or depletion of X depending on its sign

<u>Steady state process</u>
Process yields a constant weight of outputs for a constant weight of input materials per unit time

$\Delta m_x$ for a steady state process is zero and calculations are simplified considerably
Consider the continuous process operating at steady state:   $A + B + C = D + E + F$

Explicit mass balance for x:   $m_A(\%x)_A + m_B(\%x)_B + m_C(\%x)_C = m_D(\%x)_D + m_E(\%x)_E + m_F(\%x)_F$
Explicit mass balance for y:   $m_A(\%y)_A + m_B(\%y)_B + m_C(\%y)_C = m_D(\%y)_D + m_E(\%y)_E + m_F(\%y)_F$
Explicit mass balance for z:   $m_A(\%z)_A + m_B(\%z)_B + m_C(\%z)_C = m_D(\%z)_D + m_E(\%z)_E + m_F(\%z)_F$

Example – Make explicit mass balances for Fe, C and O in the following reaction:

$$Fe_3O_4 + 4CO = 3Fe + 4CO_2$$
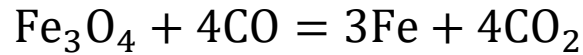
One mole excess CO is given to the furnace for each mole of magnetite

Fe balance:

$$m_{Fe_3O_4}(\%Fe)_{Fe_3O_4} + m_{CO}(\%Fe)_{CO} = m_{Fe}(\%Fe)_{Fe} + m_{CO_2}(\%Fe)_{CO_2}$$

$$232(\frac{168}{232}) \quad + 5*28(0\%) \quad = 3*56(100\%) \quad + 4*44(0\%)$$

$$168 = 168$$

C balance:

$$m_{Fe_3O_4}(\%C)_{Fe_3O_4} + m_{CO}(\%C)_{CO} = m_{Fe}(\%C)_{Fe} + m_{CO_2}(\%C)_{CO_2} \pm \Delta m_C$$

$$232(0\%) \quad + 5*28\left(\frac{12}{28}\right) \quad = 3*56(0\%) \quad + 4*44\left(\frac{12}{44}\right) \quad + 12$$

$$60 = 48 + 12$$

O balance:

$$m_{Fe_3O_4}(\%O)_{Fe_3O_4} + m_{CO}(\%O)_{CO} = m_{Fe}(\%O)_{Fe} + m_{CO_2}(\%O)_{CO_2} \pm \Delta m_C$$

$$232(\frac{64}{232}) \quad + 5*28\left(\frac{16}{28}\right) \quad = 3*56(0\%) \quad + 4*44\left(\frac{32}{44}\right) \quad + 16$$

$$144 = 128 + 16$$

Volume relations in metallurgical reactions

The volume reactions between gaseous members of a chemical reaction are obtained from their stoichiometric coefficients similar to mass relations

This relation is based on the Avogadro's law which states that equal volumes of different **gases** will contain the same number of molecules under the same conditions of temperature and pressure

Example – Consider again the reduction of magnetite to metallic iron by carbon monoxide at constant temperature and pressure
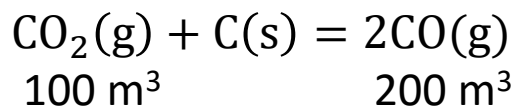
$$Fe_3O_4(s) + 4CO(g) = 3Fe(s) + 4CO_2(g)$$
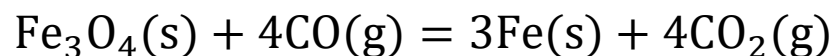
4 liters of CO will produce 4 liters of $CO_2$

There is an important difference between the mass and volume relations:
While the sum of the weights of products and reactants are equal, the sum of volumes may be different

Example -
$$CO_2(g) + C(s) = 2CO(g)$$
$$100 \text{ m}^3 \qquad\qquad 200 \text{ m}^3$$

Molar units

The coefficients preceding the formulas in reaction equations indicate the relative number of moles

Molar units used in material balance are gram-atom, kg-atom, g-mole and kg-mole

A gram-atom of an element is the mass in grams of this element in proportion to its atomic weight

$$gram - atom\ of\ an\ element = \frac{mass\ in\ grams}{atomic\ weight}$$

Example – A gram-atom of carbon is 12 grams in mass, a kg-atom of carbon is 12 kilograms

A gram-mole of a compound is the mass in grams of this compound in proportion to its molecular weight

$$gram - mole\ of\ a\ molecule = \frac{mass\ in\ grams}{molecular\ weight}$$

Example – A gram-mole of $CO_2$ is 44 grams in mass, a kg-mole of $CO_2$ is 44 kilograms

Gas laws

Extractive metallurgy processes always contain gaseous phases participating in the reactions

Gas laws provide valuable simplifications to mass balance problems in the case of missing data

Boyle's law - $P \propto \frac{1}{V}$ at constant T

Guy-Lussac's law - $V \propto T$ at constant P

Ideal gas law - $\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} = R$

Useful deductions:

- One gram-mole of any gas at standard temperature and pressure (273 K, 1 atm) occupies 22.4 liters
- One kg-mole of any gas occupies 22.4 m³ at standard conditions
- $\frac{V_T}{T} = \frac{V_{273}}{273}$

Example – Calculate the volume of air necessary to obtain blister copper in the $Cu_2S$ converting process from a charge of 5000 kg

$$Cu_2S + O_2 = 2Cu + SO_2$$
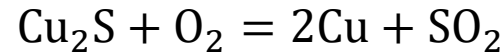
1 kg-mole $Cu_2S$ consumes 1 kg-mole of $O_2$ to yield copper

5000 kg of charge equals $\dfrac{5000}{(2*64+32)} = 31.2$ kg-moles

31.2 kg-mole $Cu_2S$ consumes 31.2 kg-mole of $O_2$

Volume of $O_2 = 31.2 * 22.4 = 700$ m³

Volume of air necessary $= 700 * \dfrac{1}{0.21} = 3300$ m³ at STP

Conducting the analysis at STP simplifies calculations and is suitable when exact gas temperatures are not known or when different gases at different temperatures are involved

The volume of gases under conditions different than STP can be calculated by the ideal gas law

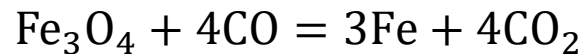$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

Excess reactants

In many metallurgical processes the quantities of reactants supplied to the system are not in the exact proportions demanded by the reaction equation

More oxygen has to be supplied above the stoichiometric requirements in combustion, roasting or converting processes to prevent unreacted reactants

The amount by which a reactant is present in excess over the theoretically required quantity is expressed as the percentage excess of this reactant
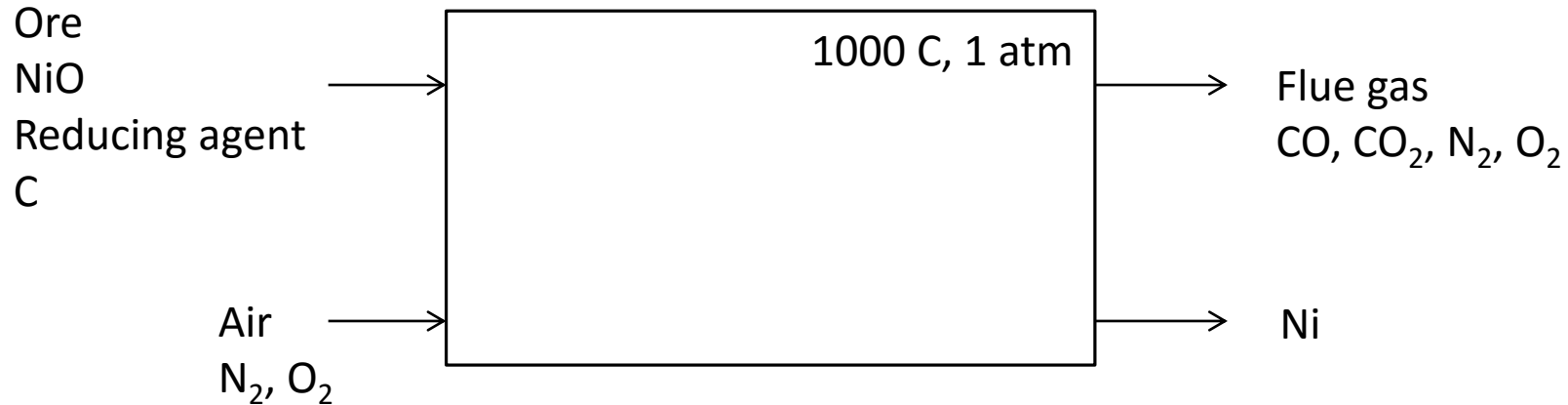
$$\% \; Excess \; air = \frac{(Volume \; of \; total \; air - Volume \; of \; theoretical \; air)}{Volume \; of \; theoretical \; air} * 100$$

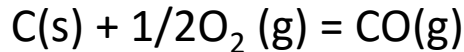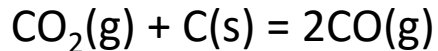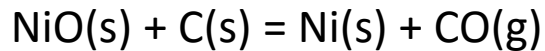Example – 25% excess CO is given to the system for each kg-mole of magnetite

$$Fe_3O_4 + 4CO = 3Fe + 4CO_2$$

Example

NiO is reduced in an open atmosphere furnace by excess carbon at 1000 C

Ore
NiO
Reducing agent
C

1000 C, 1 atm

Flue gas
CO, $CO_2$, $N_2$, $O_2$

Air
$N_2$, $O_2$

Ni

| Reactions: | $\Delta G^o$ | |
|---|---|---|
| NiO(s) + C(s) = Ni(s) + CO(g) | 28970-41.07T calories | K@1000 C = 10059 |
| $CO_2$(g) + C(s) = 2CO(g) | 39810 – 40.87T calories | K@1000 C = 125.22 |
| C(s) + 1/2$O_2$ (g) = CO(g) | -27340-20.50T calories | K@1000 C = 14955000 |

How many kg-moles of Ni, CO and $CO_2$ are produced for each kg-mole of NiO and C?

Calculate the reaction extents at equilibrium