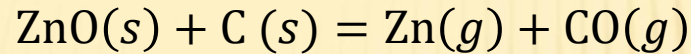# MME 2010 METALLURGICAL THERMODYNAMICS II

Reaction Extent in Homogeneous Systems

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

$$ZnO(s) + CO(g) = Zn(g) + CO_2(g)$$
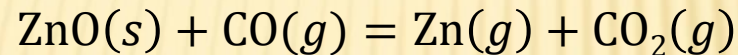
Thermodynamics does not indicate which reaction has the higher rate, the mass diffusion and transport rates are subjects of Kinetics

However one can estimate the maximum conversion of reactants to products at equilibrium temperature and pressure by computing the free energy of the reactions

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

Consider the oxidation of sulfur dioxide to sulfur trioxide

$$SO_2(g) + \frac{1}{2}O_2(g) = SO_3(g)$$
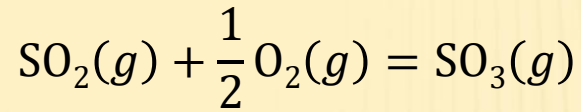
The rate of the reaction is very low at ambient temperatures and a vanadium pentoxide catalyst promotes the reaction appreciably above 300 C

The equilibrium conversion of sulfur dioxide to trioxide below 500 C is greater than 90% The reaction extent decreases rapidly at higher temperatures, to as low as 50% around 700 C

One would operate the reactor at a high temperature on the basis of rate alone but half of the reactants would be wasted

The optimum operating temperature would be between 300-500 C

The effect of temperature, pressure and composition on both reaction equilibrium and rate should be considered
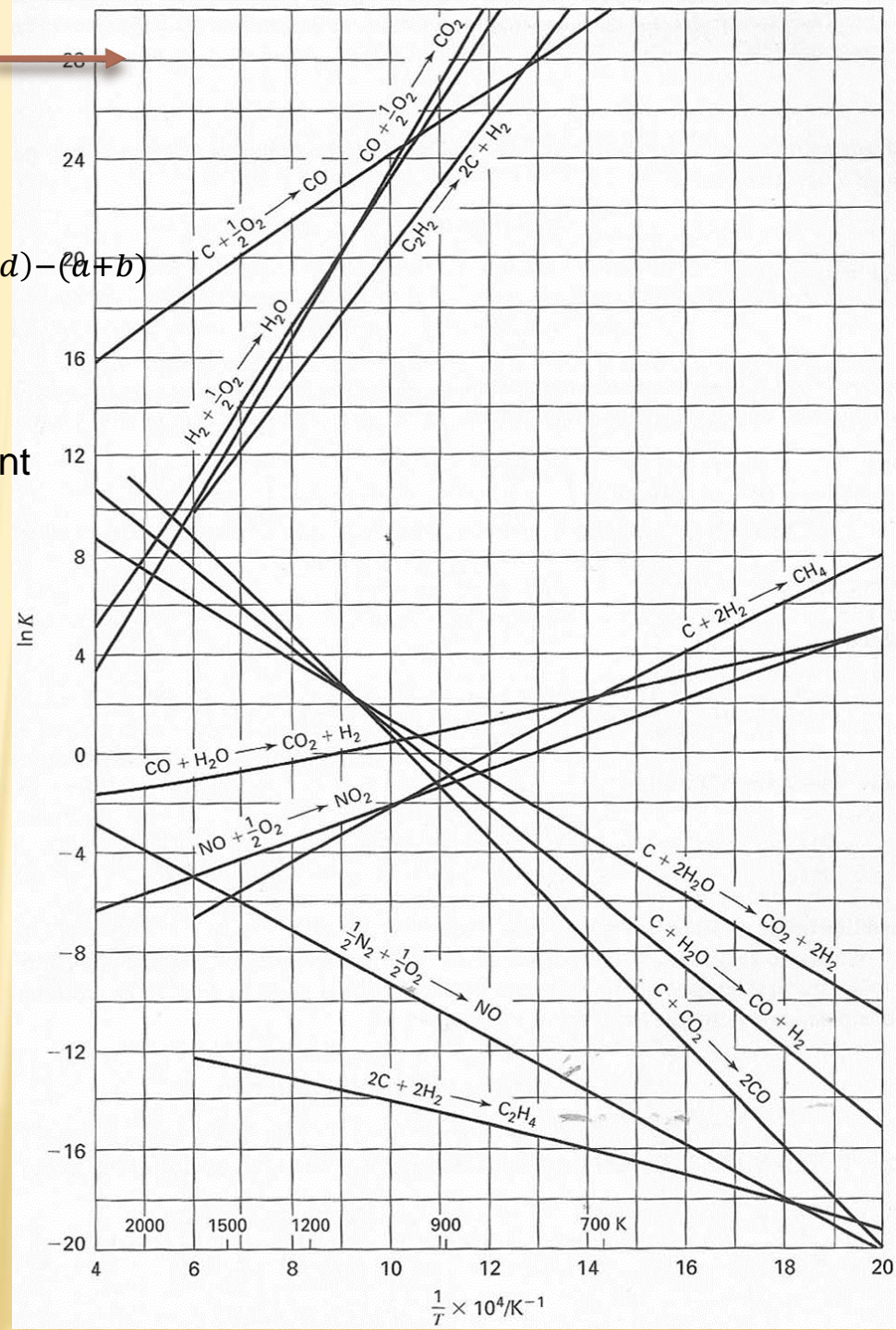
Equilibrium constant is a function of T only

Effect of P on equilibrium composition

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

A new parameter for the yield of a reaction: extent

$$n = n_0 + \nu \varepsilon$$

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 or extent is 80%

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
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 any change in the 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

G_{Total}

$dG_{Total}=0$

ε_e ε
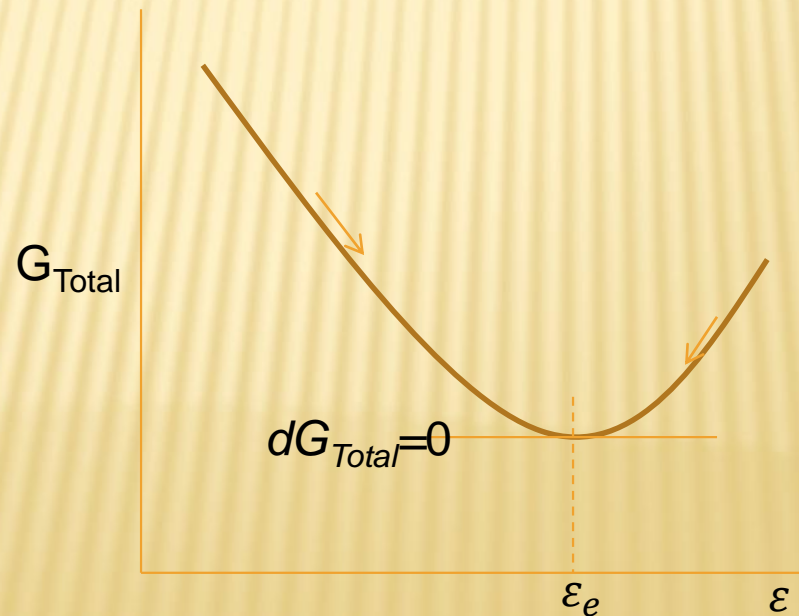
Definition of reaction extent

Consider the reaction $\qquad CH_4(g) + H_2O(g) = CO(g) + 3H_2(g)$

The stoichiometric numbers are negative for the reactants, positive for the products and zero for inert species

ν_{CH4}=-1
ν_{H2O}=-1
ν_{CO}=1
ν_{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 ε, called the reaction extent or reaction coordinate characterizes the degree to which a reaction has advanced
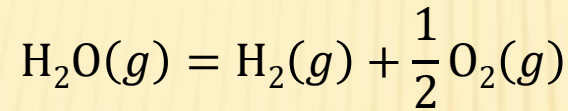
Summing over all species gives

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

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

Thus the mole fractions y_i of the species present are related to ε by

$$y_i = \frac{n_i}{n} = \frac{n_{i0} + v_i\varepsilon}{n_0 + v\varepsilon}$$

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

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

$v_{H2O} = -1$ $\qquad n_{H2O} = n_0 - \varepsilon$

$v_{H2} = 1$ $\qquad\quad n_{H2} = \varepsilon$

$v_{O2} = 0.5$ $\qquad n_{O2} = 0.5\varepsilon$
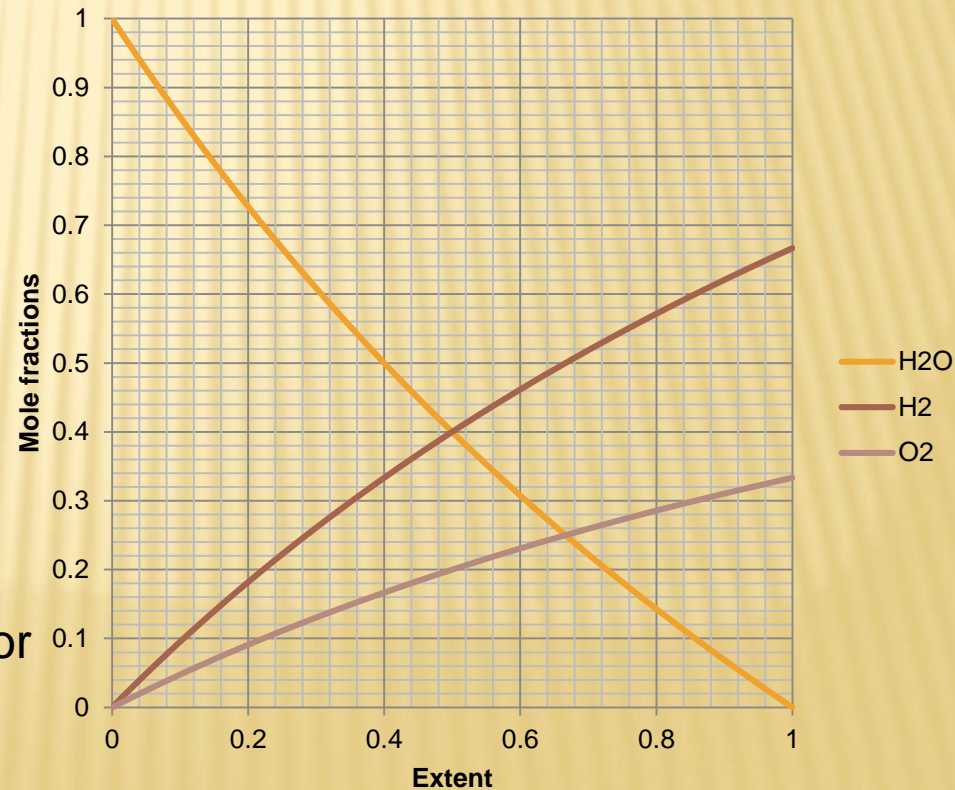
$v_{total} = 0.5$ $\qquad n_{total} = n_0 + 0.5\varepsilon$

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

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

$$y_{H2} = \frac{0.5\varepsilon}{n_0 + 0.5\varepsilon}$$
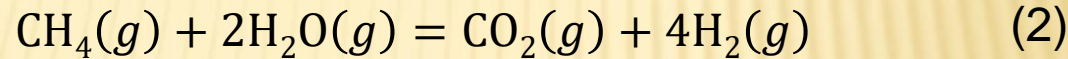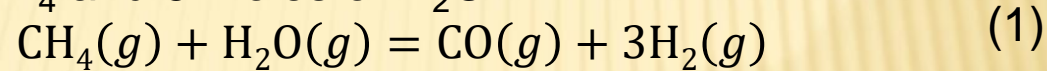
The fractional decomposition of water vapor

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

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

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

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		
$\nu_{CH4} = -1$	$\nu_{CH4} = -1$	$n_{CH4} = 2 - \varepsilon_1 - \varepsilon_2$	$y_{CH4} = \frac{2 - \varepsilon_1 - \varepsilon_2}{5 + 2\varepsilon_1 + 2\varepsilon_2}$
$\nu_{H2O} = -1$	$\nu_{H2O} = -2$	$n_{H2O} = 3 - \varepsilon_1 - 2\varepsilon_2$	$y_{H2O} = \frac{3 - \varepsilon_1 - 2\varepsilon_2}{5 + 2\varepsilon_1 + 2\varepsilon_2}$
$\nu_{CO} = 1$	$\nu_{CO} = 0$	$n_{CO} = \varepsilon_1$	$y_{CO} = \frac{\varepsilon_1}{5 + 2\varepsilon_1 + 2\varepsilon_2}$
$\nu_{CO2} = 0$	$\nu_{CO2} = 1$	$n_{CO2} = \varepsilon_2$	$y_{CO2} = \frac{\varepsilon_2}{5 + 2\varepsilon_1 + 2\varepsilon_2}$
$\nu_{H2} = 3$	$\nu_{H2} = 4$	$n_{H2} = 3\varepsilon_1 + 4\varepsilon_2$	$y_{H2} = \frac{3\varepsilon_1 + 4\varepsilon_2}{5 + 2\varepsilon_1 + 2\varepsilon_2}$
$\nu_{total} = 2$	$\nu_{total} = 2$	$n_{total} = 5 + 2\varepsilon_1 + 2\varepsilon_2$	

The composition of the system is a function of two independent variables ε_1 and ε_2

Equilibrium criterion for chemical reactions

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

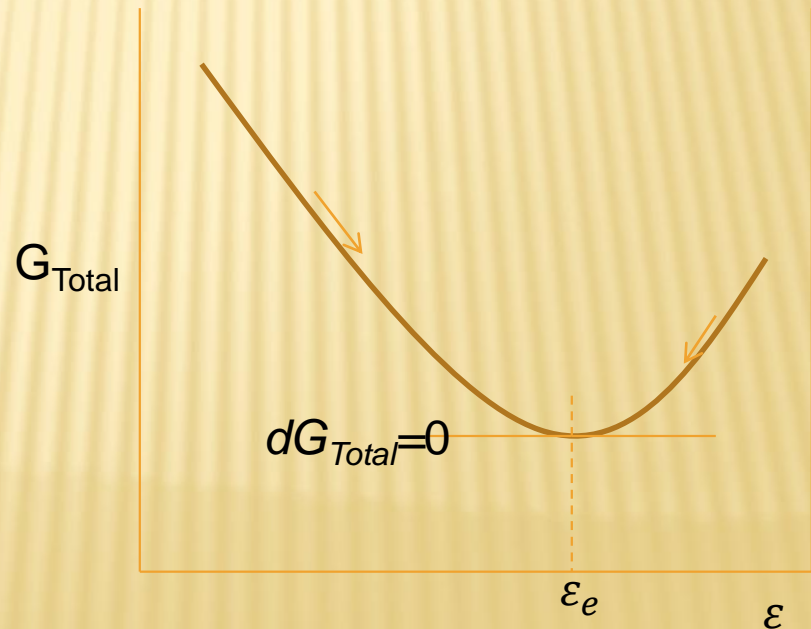In a single reaction system the total differential of G is

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

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}

$dG_{Total}=0$

ε_e

ε

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 (in activity term)

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

$$\Delta G^o = \sum v_i G^o{}_i$$

ΔG^o is the difference between the Gibbs free energies of the products and reactants when each is in its standard state as a pure substance at <u>the system temperature</u> and at a fixed pressure

The value of ΔG^o is fixed for a given reaction once the temperature is established and is independent of the equilibrium pressure and composition

The general standard property change for a reaction is expressed as follows which holds also for ΔH^o and ΔS^o

$$\Delta M^o = \sum v_i M^o{}_i$$

The relations between the standard heat of reaction and the standard Gibbs free energy change of reaction was developed as

$$H^0{}_i = -RT^2 \frac{d\left(\dfrac{G^0{}_i}{RT}\right)}{dT}$$

$$\sum v_i H^o{}_i = -RT^2 \frac{d\left(\dfrac{\sum v_i G^o{}_i}{RT}\right)}{dT}$$

$$\Delta H^0 = -RT^2 \frac{d\left(\dfrac{\Delta G^0}{RT}\right)}{dT}$$

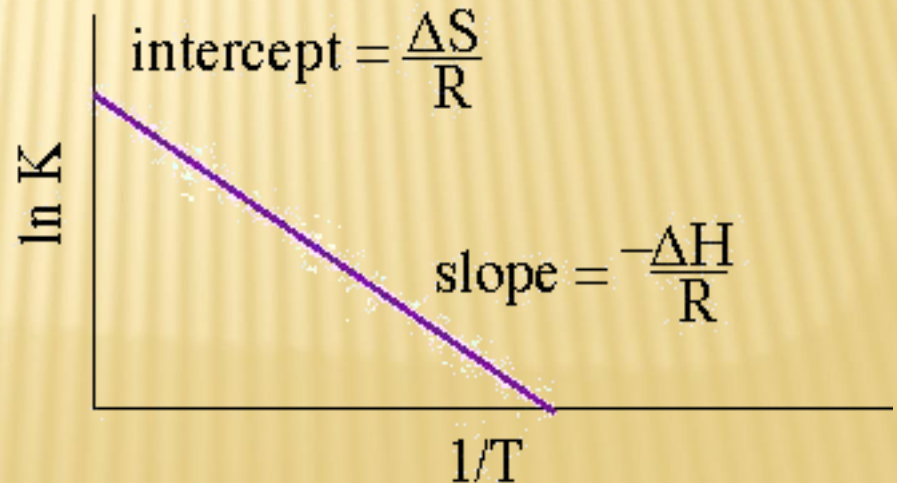The dependence of ΔG^0 on temperature was obtained as

$$\frac{d\left(\frac{\Delta G^0}{RT}\right)}{dT} = -\frac{\Delta H^0}{RT^2}$$

Since $\frac{\Delta G^0}{RT} = -\ln K$, the effect of temperature on the equilibrium constant is obtained as

$$\boxed{\frac{d\ln K}{dT} = \frac{\Delta H^0}{RT^2}}$$ van't Hoff eqn

Standard enthalpy change of a reaction *may be considered independent of temperature for a reasonable approximation* with the result that a plot of $\ln K$ vs. $\frac{1}{T}$ is a straight line

$$\boxed{\ln\frac{K}{K_1} = -\frac{\Delta H^0}{R}\left(\frac{1}{T} - \frac{1}{T_1}\right)}$$

$$\ln\frac{K}{K_1} = -\frac{\Delta H^0}{R}\left(\frac{1}{T} - \frac{1}{T_1}\right)$$

The heat of reactions can be obtained by performing the reactions in a calorimeter or from the standard enthalpies of formation and the heat capacities of the species

The entropy change of reactions can be calculated from the absolute standard entropy values and the heat capacities of the species
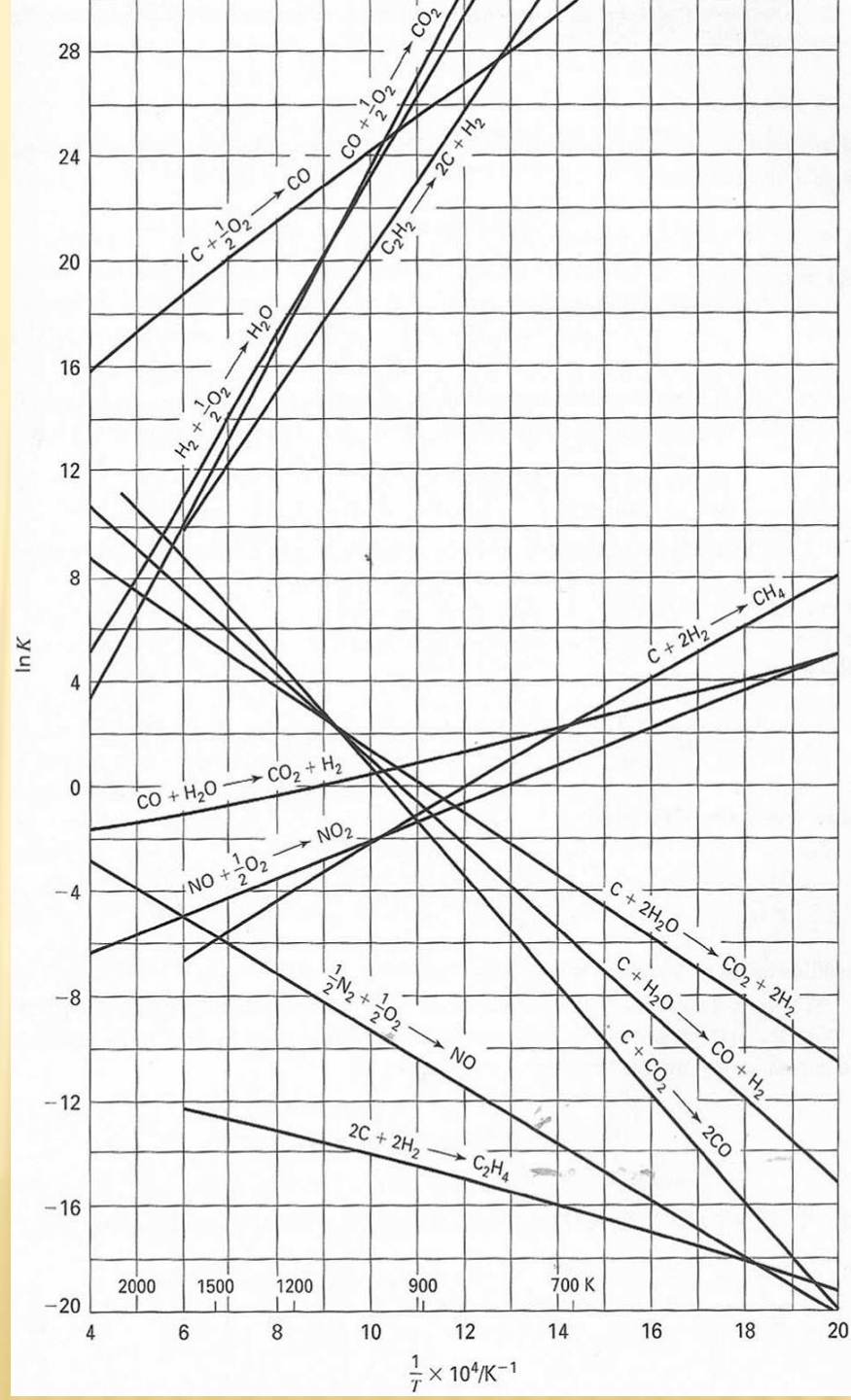
Dependence of the equilibrium constant on temperature of the reaction (considering properties at reference T=0)

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

$$\Delta H^\circ = \Delta H_0^\circ + R \int_{T_0}^{T} \frac{\Delta C_P^\circ}{R} dT \qquad \Delta S^\circ = \Delta S_0^\circ + R \int_{T_0}^{T} \frac{\Delta C_P^\circ}{R} \frac{dT}{T}$$

$$\Delta G^\circ = \Delta H_0^\circ + R \int_{T_0}^{T} \frac{\Delta C_P^\circ}{R} dT - T \Delta S_0^\circ - RT \int_{T_0}^{T} \frac{\Delta C_P^\circ}{R} \frac{dT}{T}$$

$$\Delta S_0^\circ = \frac{\Delta H_0^\circ - \Delta G_0^\circ}{T_0}$$

$$\frac{\Delta G^\circ}{RT} = \frac{\Delta G_0^\circ - \Delta H_0^\circ}{RT_0} + \frac{\Delta H_0^\circ}{RT} + \frac{1}{T} \int_{T_0}^{T} \frac{\Delta C_P^\circ}{R} dT - \int_{T_0}^{T} \frac{\Delta C_P^\circ}{R} \frac{dT}{T}$$

$$K = K_0 K_1 K_2$$

$$K_0 \equiv \exp\left(\frac{-\Delta G_0^\circ}{RT_0}\right)$$

$$K_1 \equiv \exp\left[\frac{\Delta H_0^\circ}{RT_0}\left(1 - \frac{T_0}{T}\right)\right]$$

$$K_2 \equiv \exp\left(-\frac{1}{T} \int_{T_0}^{T} \frac{\Delta C_P^\circ}{R} dT + \int_{T_0}^{T} \frac{\Delta C_P^\circ}{R} \frac{dT}{T}\right)$$

Example – Calculate the equilibrium constant for the vapor-phase hydration of ethylene at 145 C and at 320 C

$$C_2H_4(g) + H_2O(g) \rightarrow C_2H_5OH(g)$$
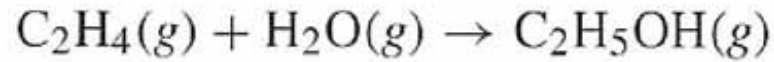
Heat capacity data
Ethylene hydroxide – 3.518+0.02T-0.000006T2
Ethylene – 1.424+0.0144T-0.0000044T2
Water – 3.47+0.00145T+12100/T2

Standard Enthalpy of formation
Ethylene hydroxide – -235100 J/mol
Ethylene – 52510 J/mol
Water – -241818 J/mol

Standard Gibbs free energy
Ethylene hydroxide – -168490 J/mol
Ethylene – 68460 J/mol
Water – -228572 J/mol

$$\frac{\Delta G^\circ_{418}}{RT} = \frac{-8,378 + 45,792}{(8.314)(298.15)} + \frac{-45,792}{(8.314)(418.15)} + \frac{-23.121}{418.15} + 0.0692 = 1.9356$$

$$\frac{\Delta G^\circ_{593}}{RT} = \frac{-8,378 + 45,792}{(8.314)(298.15)} + \frac{-45,792}{(8.314)(593.15)} + \frac{22.632}{593.15} - 0.0173 = 5.8286$$

Relation between equilibrium constant and composition

For a reaction occurring in the liquid phase, the equilibrium constant is expressed as

$$K = \prod (a_i)^{\nu_i}$$

Activity is a function of activity coefficient and concentration of the components

$$a_i = \frac{P_i}{P_i^o} = \gamma_i x_i \frac{f_i}{f_i^o}$$

So for liquid phase reactions

$$K = \prod (\gamma_i x_i)^{\nu_i}$$

For a reaction occurring in the gas phase, the equilibrium constant is expressed as

$$K = \prod (a_i)^{\nu_i}$$

Activity reflects the nonidealities of the equilibrium mixture and is a function of temperature, pressure and composition
Equilibrium constant K is a function of temperature only

The composition at equilibrium must change with pressure for $\prod (a_i)^{\nu_i}$ to remain constant at a fixed temperature

So K is expressed as $K = \prod (\gamma_i y_i P)^{\nu_i}$ since $a_i = \gamma_i y_i P$

where γ_i is the activity coefficient, y_i is concentration and P is pressure

or

$$\boxed{\prod (\gamma_i y_i)^{\nu_i} = P^{-\nu} K}$$

Equation relates reaction extent ε_e to pressure since concentration y_i is a function of ε_e

Equilibrium compositions and reaction extent is calculated by specifying temperature, pressure and equilibrium constant

Some basic conclusions that hold for all reactions are derived from the equations by considering the mixture as an ideal gas so that $\gamma_i = 1$

$$\prod(y_i)^{\nu_i} = P^{-\nu}K$$

$$\frac{d\ln K}{dT} = \frac{\Delta H^0}{RT^2}$$

• The effect of temperature on the equilibrium constant is determined by the sign of ΔH^0

When the reaction is endothermic, an increase in T results in an increase in K which results in an increase in $\prod(y_i)^{\nu_i}$ at constant P
For positive ΔH^0,   T↑ K↑ ε↑
For negative ΔH^0,   T↑ K↓ ε↓

• The effect of pressure on the reaction extent is determined by the sign of total stoichiometric number ν

When ν is negative, an increase in pressure at constant temperature causes an increase in $\prod(y_i)^{\nu_i}$ which means a shift of the reaction to the right
For positive ν, P↑ ε↓
For negative ν, P↑ ε↑

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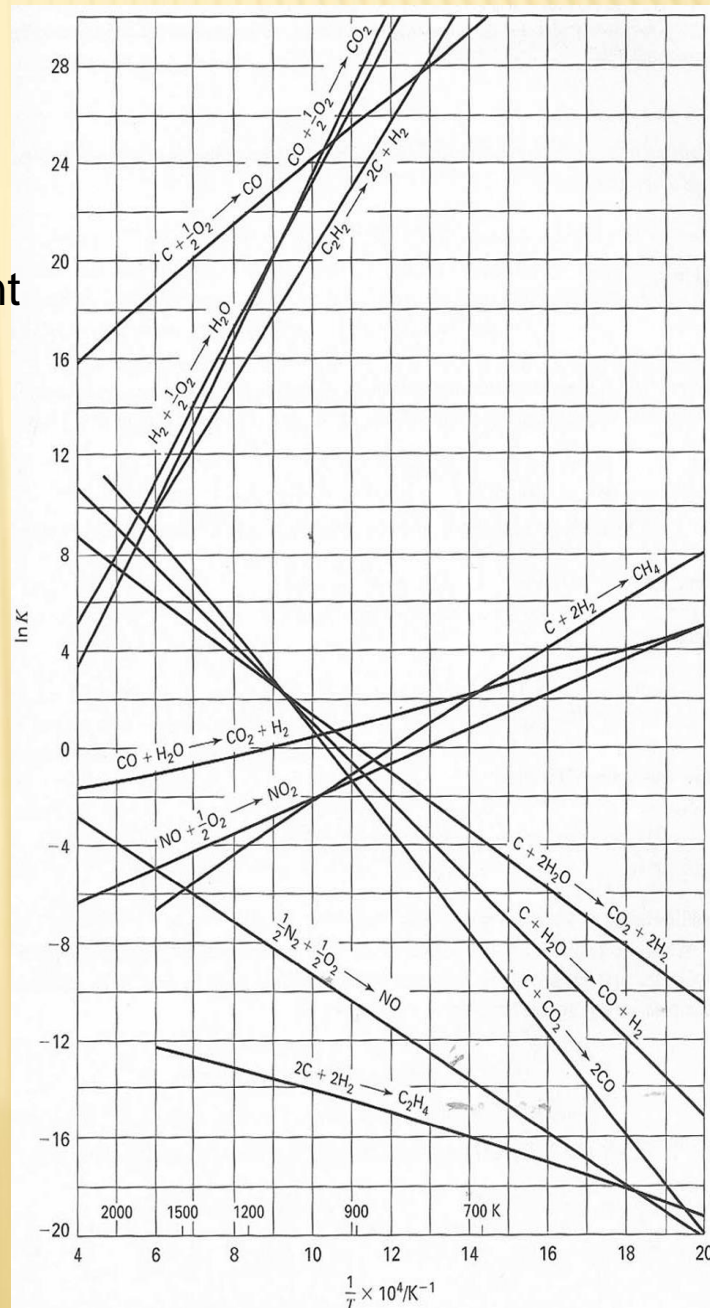
Example – The following reaction is carried out under different sets of conditions
Assuming the mixture behaves as an ideal gas, calculate the fraction of steam reacted in each case

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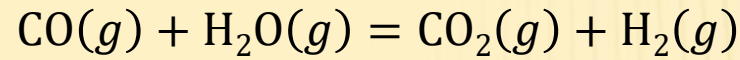
a) There are initially 1 mole of H_2O vapor and 1 mole of CO at 1100 K and 1 bar

From the previous figure K=1 obtained at 1100 K

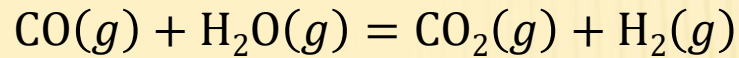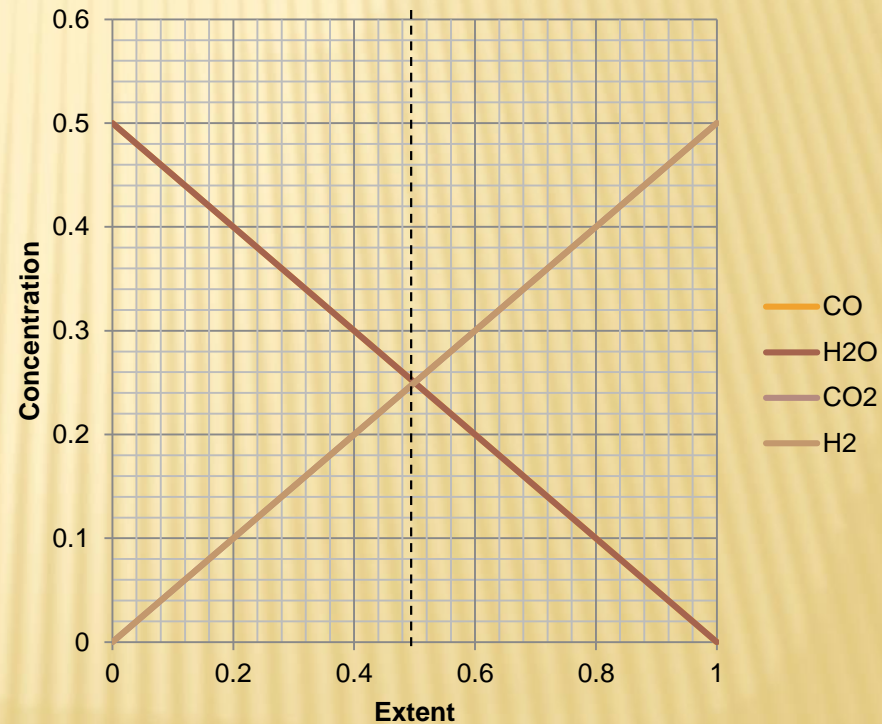$\nu_{CO} = -1$ $\qquad$ $n_{CO} = 1 - \varepsilon_e$

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

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

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

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

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

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

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

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

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

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

$$CO(g) + H_2O(g) = CO_2(g) + H_2(g)$$
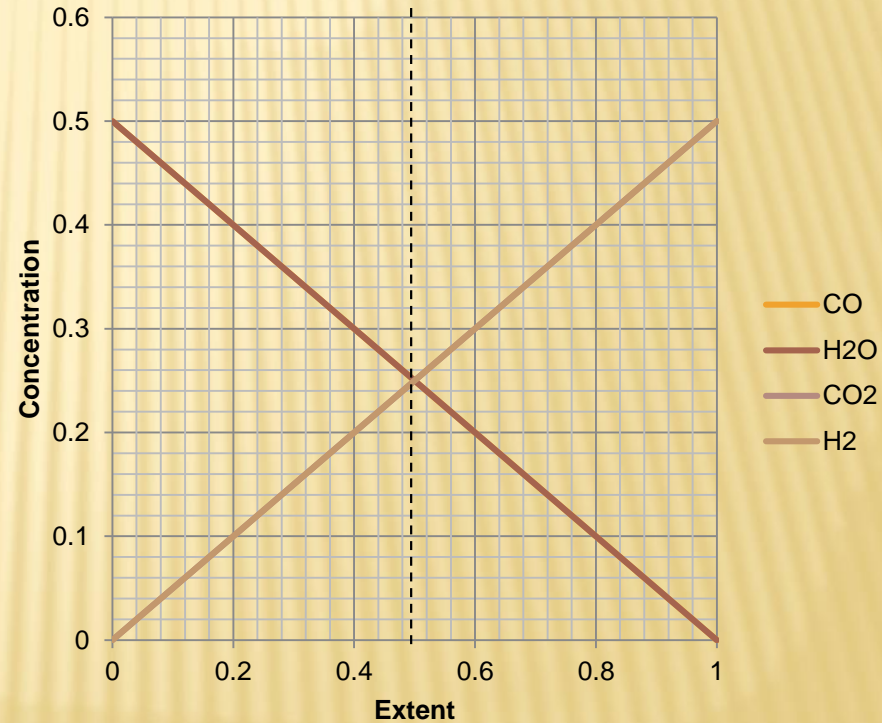
b) Same as (a) except the pressure is 10 bar

The increase in P has no effect on the extent since the total stoichiometric number is 0

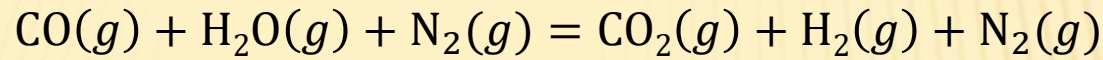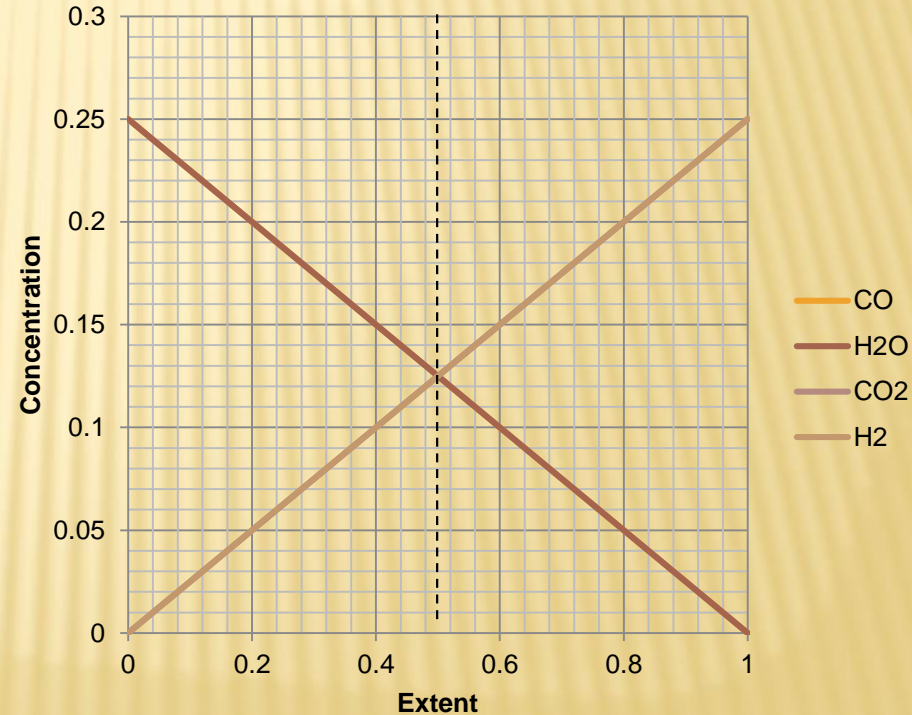ν_{CO} =-1 $n_{CO} = 1 - \varepsilon_e$

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

ν_{CO2} =1 $n_{CO2} = \varepsilon_e$

ν_{H2} =1 $n_{H2} = \varepsilon_e$

ν_{total} =0 $n_{total} = 2$

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

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

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

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

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

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

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

c) 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

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

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

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

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

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

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

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

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

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

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

Legend: CO, H2O, CO2, H2 (Concentration vs Extent)

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

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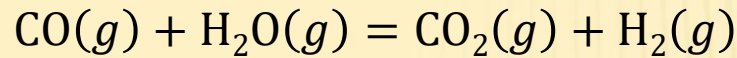
d) There are initially 2 moles of H_2O vapor and 1 mole of CO at 1100 K and 1 bar

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

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

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

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

ν_{total} =0 $\qquad$ $n_{total} = 3$

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

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

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

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

Extent

— CO
— H2O
— CO2
— H2
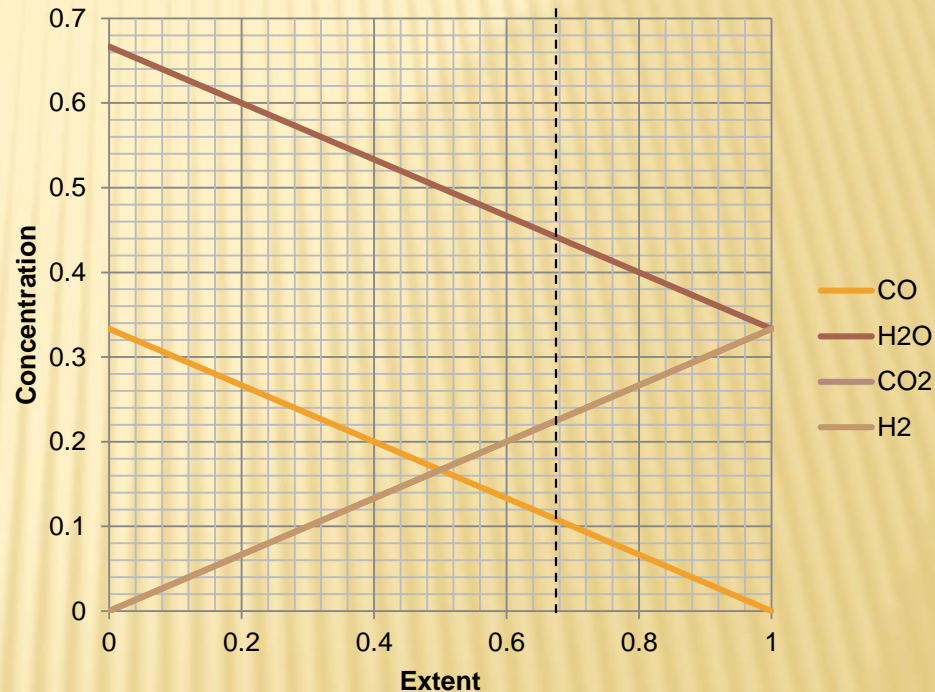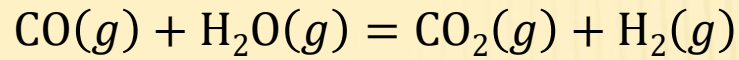
Extra H_2O increases the reaction extent but the conversion of steam decreases

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

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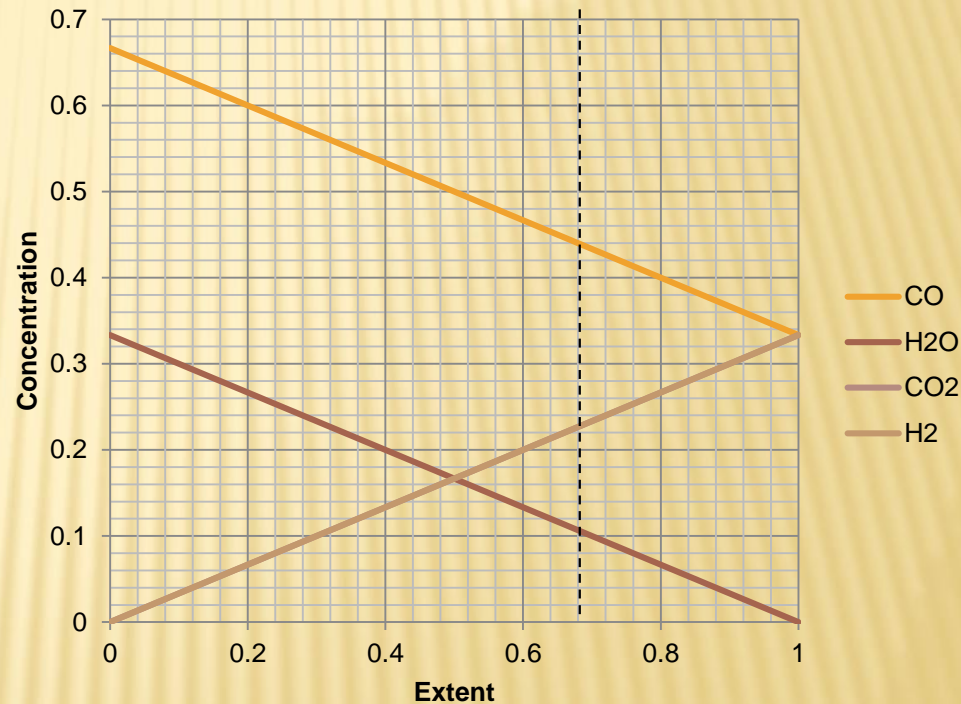
Example – The following reaction is carried out under different sets of conditions
Assuming the mixture behaves as an ideal gas, calculate the fraction of steam reacted in each case

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

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

$\nu_{CO} = -1$
$\nu_{H2O} = -1$
$\nu_{CO2} = 1$
$\nu_{H2} = 1$
$\nu_{total} = 0$

$n_{CO} = 2 - \varepsilon_e$
$n_{H2O} = 1 - \varepsilon_e$
$n_{CO2} = \varepsilon_e$
$n_{H2} = \varepsilon_e$
$n_{total} = 3$

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

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

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

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

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
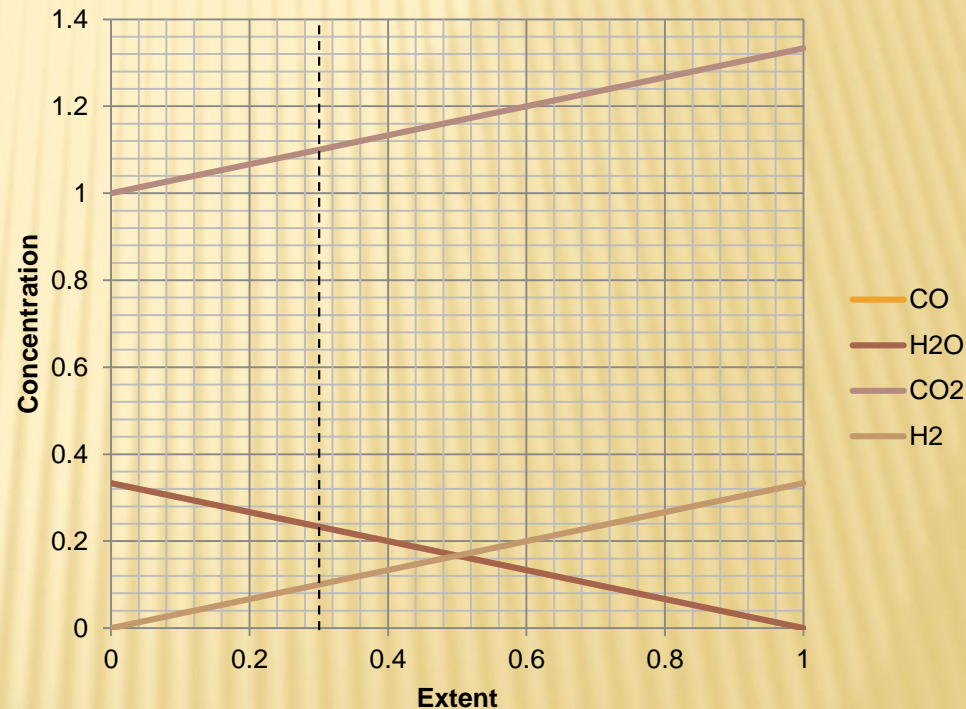Assuming the mixture behaves as an ideal gas, calculate the fraction of steam reacted in each case

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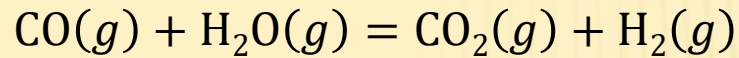
f) There are initially 1 mole of H_2O vapor,1 mole of CO and 1 mole of CO2 at 1100 K and 1 bar

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

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

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

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

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

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

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

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

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

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
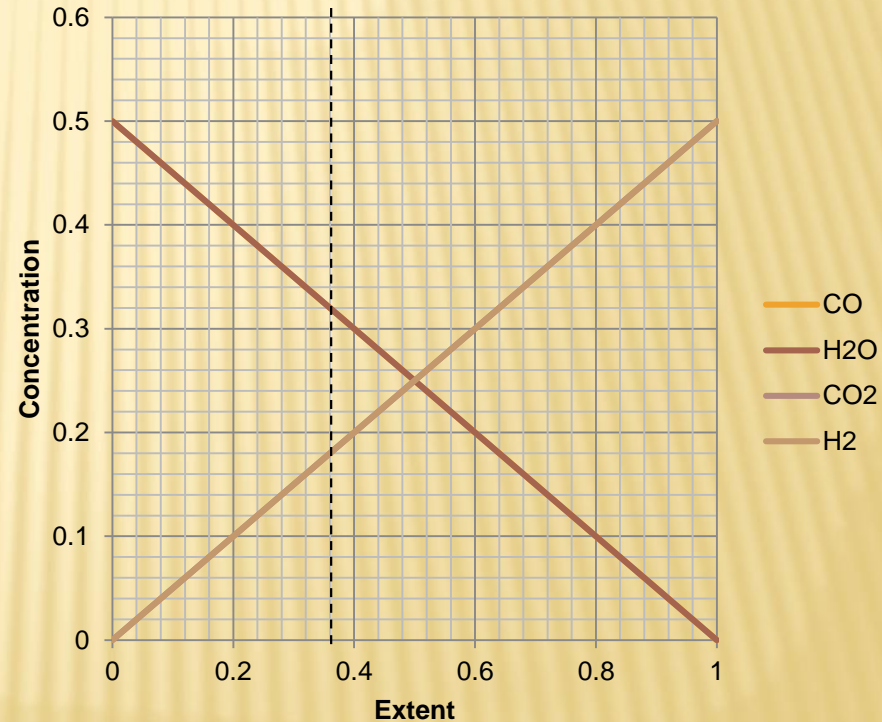
$$CO(g) + H_2O(g) = CO_2(g) + H_2(g)$$
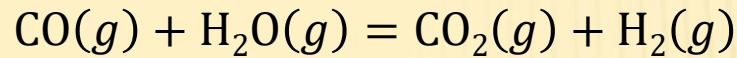
g) There are initially 1 mole of H_2O vapor and 1 mole of CO at 1650 K and 1 bar

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

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

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

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

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

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

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

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

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

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

Reaction extent and steam conversion decreases with increasing T since reaction ΔH>0

$$K = \frac{y_{CO2}y_{H2}}{y_{CO}y_{H2O}} = \frac{\varepsilon_e{}^2}{(1-\varepsilon_e)^2} = 0.316 \quad \rightarrow \varepsilon_e = 0.36 \rightarrow \frac{n_0 - n_{H2O}}{n_0} = \frac{n_0 - (n_0 - \varepsilon_e)}{n_0} = \frac{\varepsilon_e}{n_0} = 0.36$$
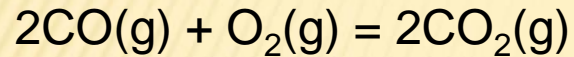
Example - A furnace is fed with 2 moles of CO fuel and stoichiometric O_2 gas for preheating to 700 C as a result of the following combustion reaction at 1 atm:
$2CO(g) + O_2(g) = 2CO_2(g)$
The free energy of the combustion reaction if 400kJ at these conditions
Express the concentrations of the species in terms of reaction extent
Obtain the reaction extent and the equilibrium mole numbers of the species