

MME 2010

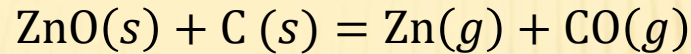
METALLURGICAL THERMODYNAMICS II

Reaction Extent and Equilibrium in Reacting Systems

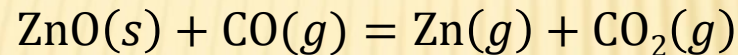
Industrial processes should be maintained at a high rate and high efficiency for feasibility

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



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



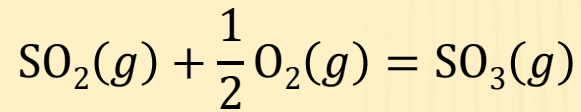
Thermodynamics does not indicate which reaction has the higher rate, the mass diffusion and transport rates are subjects of Kinetics

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 variable that determines the progress and 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



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 criterion for chemical reactions

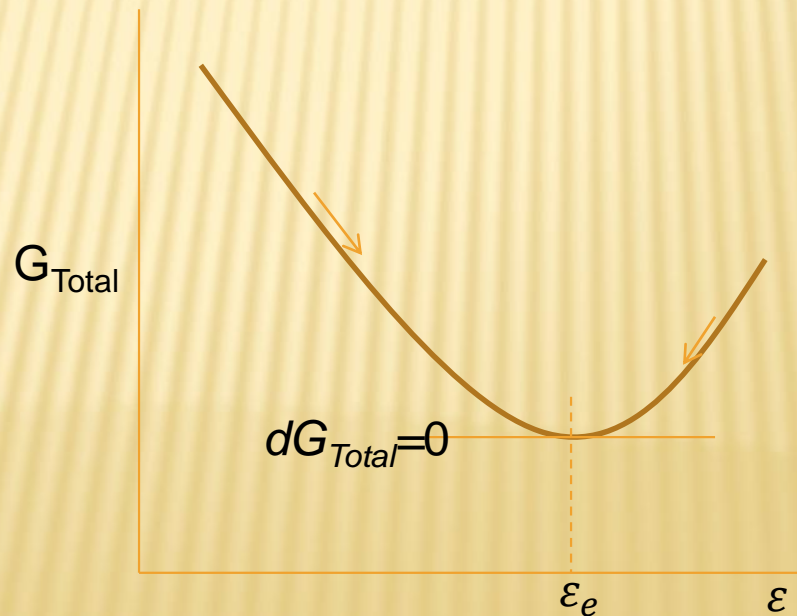
Recall that the total Gibbs free energy of a closed system at constant temperature and pressure must decrease during an irreversible process

The condition for equilibrium is reached when

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

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



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

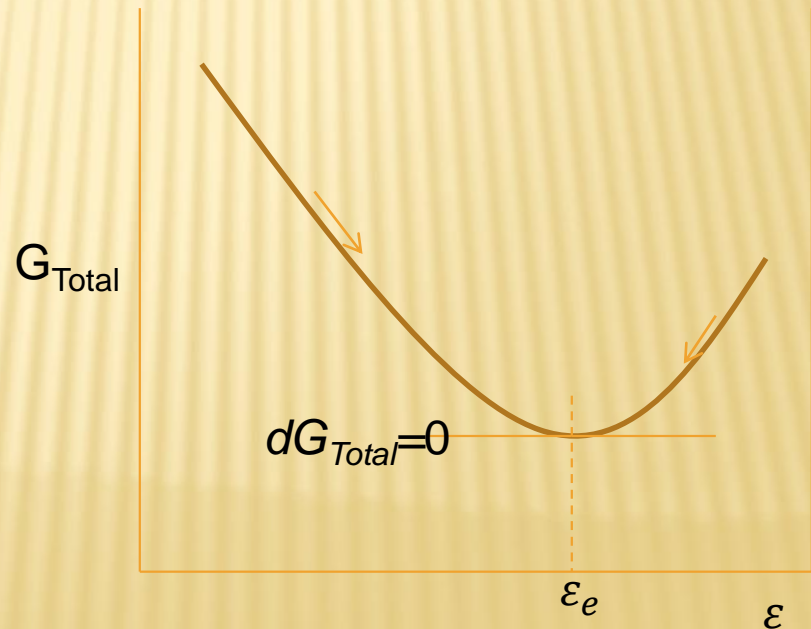
$$d(nG) = (nV)dP - (nS)dT + \sum \mu_i dn_i$$

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

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



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

$$\sum \nu_i (G^o_i + RT \ln a_i) = 0$$

$$\sum \nu_i G^o_i + RT \sum \ln(a_i)^{\nu_i} = 0$$

$$\sum \ln(a_i)^{\nu_i} = \ln \prod (a_i)^{\nu_i} = \frac{-\sum \nu_i G^o_i}{RT}$$

or

$$\prod (a_i)^{\nu_i} = \exp \frac{-\sum \nu_i G^o_i}{RT} = K$$

in simpler form

$$-RT \ln K = \sum \nu_i G^o_i = \Delta G^o$$

The equilibrium constant K is the connection between Gibbs free energy of a reaction and the reaction extent (by the activity term)

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

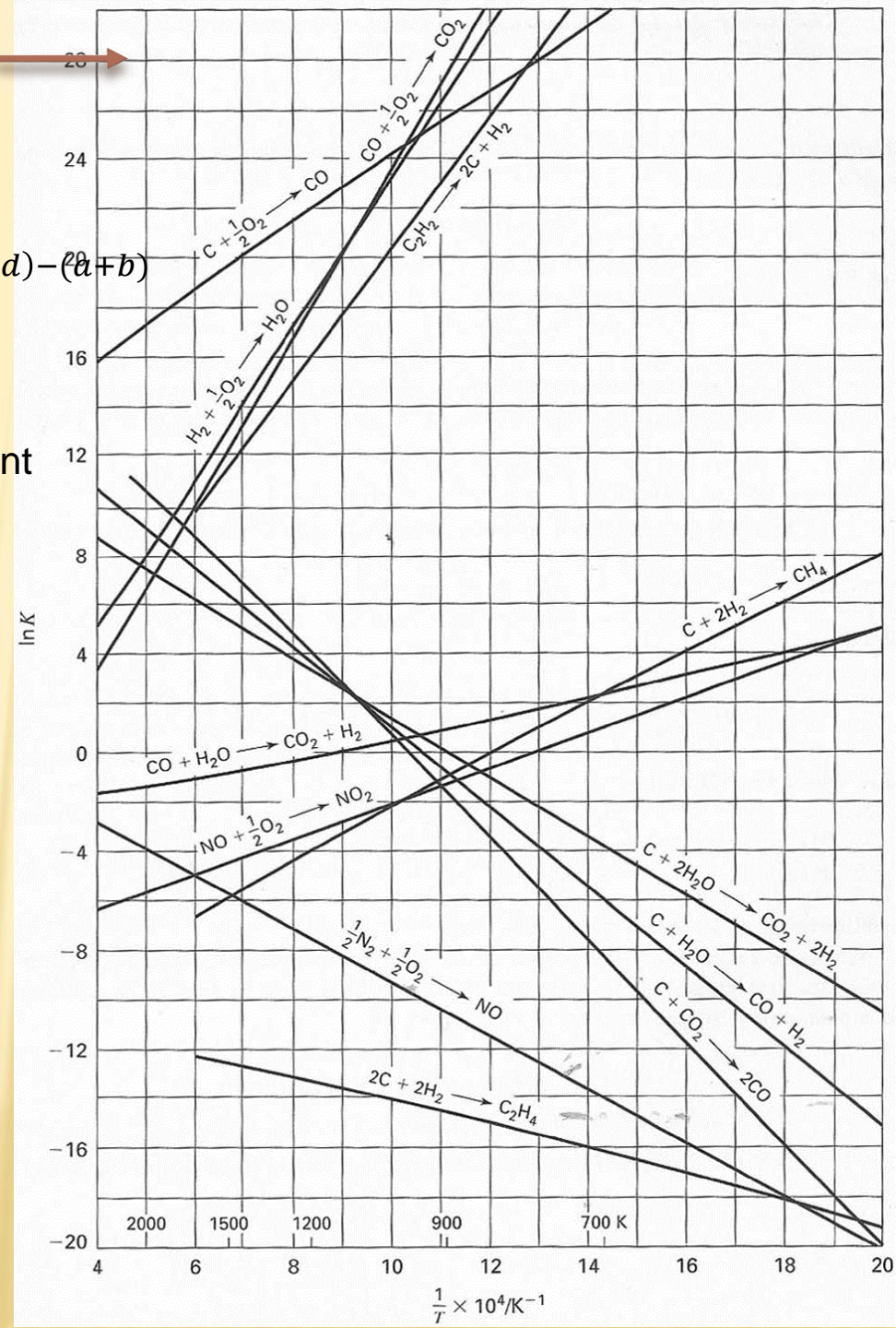
Equilibrium constant is a function of T only

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

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



Definition of reaction extent

Consider the reaction $\text{CH}_4(g) + \text{H}_2\text{O}(g) = \text{CO}(g) + 3\text{H}_2(g)$

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

$$\nu_{\text{CH}_4} = -1$$

$$\nu_{\text{H}_2\text{O}} = -1$$

$$\nu_{\text{CO}} = 1$$

$$\nu_{\text{H}_2} = 3$$

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

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

The variable ε , called the reaction extent or reaction coordinate characterizes the degree to which a reaction has advanced

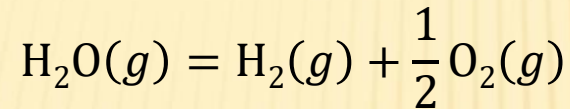
Summing over all species gives

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

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:



$$\begin{aligned} v_{\text{H}_2\text{O}} &= -1 \\ v_{\text{H}_2} &= 1 \\ v_{\text{O}_2} &= 0.5 \\ v_{\text{total}} &= 0.5 \end{aligned}$$

$$\begin{aligned} n_{\text{H}_2\text{O}} &= n_0 - \varepsilon \\ n_{\text{H}_2} &= \varepsilon \\ n_{\text{O}_2} &= 0.5\varepsilon \\ n_{\text{total}} &= n_0 + 0.5\varepsilon \end{aligned}$$

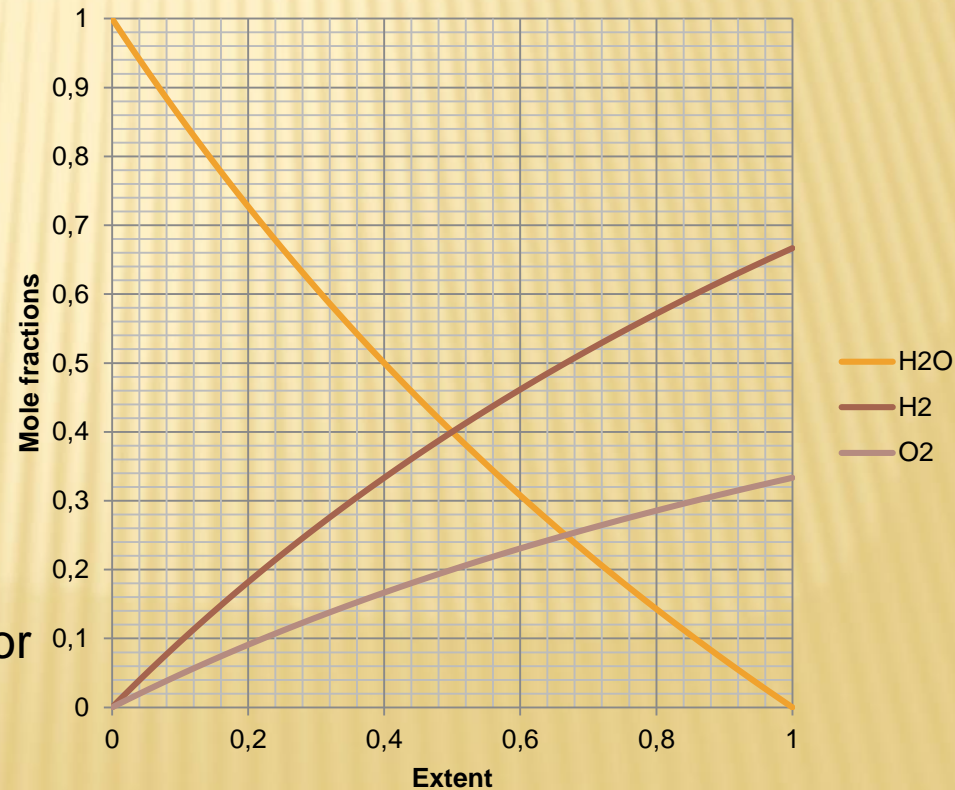
$$y_{\text{H}_2\text{O}} = \frac{n_0 - \varepsilon}{n_0 + 0.5\varepsilon}$$

$$y_{\text{H}_2} = \frac{\varepsilon}{n_0 + 0.5\varepsilon}$$

$$y_{\text{O}_2} = \frac{0.5\varepsilon}{n_0 + 0.5\varepsilon}$$

The fractional decomposition of water vapor

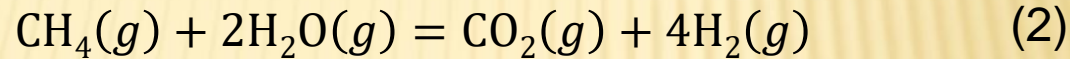
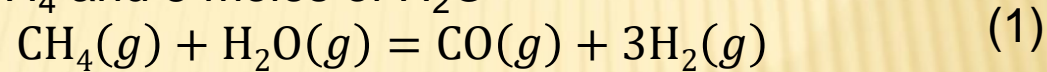
$$\frac{n_0 - n_{\text{H}_2\text{O}}}{n_0} = \frac{n_0 - (n_0 - \varepsilon)}{n_0} = \frac{\varepsilon}{n_0}$$



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



Reaction 1

$$\nu_{\text{CH}_4} = -1$$

$$\nu_{\text{H}_2\text{O}} = -1$$

$$\nu_{\text{CO}} = 1$$

$$\nu_{\text{CO}_2} = 0$$

$$\nu_{\text{H}_2} = 3$$

$$\nu_{\text{total}} = 2$$

Reaction 2

$$\nu_{\text{CH}_4} = -1$$

$$\nu_{\text{H}_2\text{O}} = -2$$

$$\nu_{\text{CO}} = 0$$

$$\nu_{\text{CO}_2} = 1$$

$$\nu_{\text{H}_2} = 4$$

$$\nu_{\text{total}} = 2$$

$$n_{\text{CH}_4} = 2 - \varepsilon_1 - \varepsilon_2$$

$$n_{\text{H}_2\text{O}} = 3 - \varepsilon_1 - 2\varepsilon_2$$

$$n_{\text{CO}} = \varepsilon_1$$

$$n_{\text{CO}_2} = \varepsilon_2$$

$$n_{\text{H}_2} = 3\varepsilon_1 + 4\varepsilon_2$$

$$n_{\text{total}} = 5 + 2\varepsilon_1 + 2\varepsilon_2$$

$$y_{\text{CH}_4} = \frac{2 - \varepsilon_1 - \varepsilon_2}{5 + 2\varepsilon_1 + 2\varepsilon_2}$$

$$y_{\text{H}_2\text{O}} = \frac{3 - \varepsilon_1 - 2\varepsilon_2}{5 + 2\varepsilon_1 + 2\varepsilon_2}$$

$$y_{\text{CO}} = \frac{\varepsilon_1}{5 + 2\varepsilon_1 + 2\varepsilon_2}$$

$$y_{\text{CO}_2} = \frac{\varepsilon_2}{5 + 2\varepsilon_1 + 2\varepsilon_2}$$

$$y_{\text{H}_2} = \frac{3\varepsilon_1 + 4\varepsilon_2}{5 + 2\varepsilon_1 + 2\varepsilon_2}$$

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

Effect of T on equilibrium

$$\Delta G^o = \sum v_i G^o_i$$

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 the system temperature 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

$$\begin{aligned} H^o_i &= -RT^2 \frac{d\left(\frac{G^o_i}{RT}\right)}{dT} \\ \sum v_i H^o_i &= -RT^2 \frac{d\left(\frac{\sum v_i G^o_i}{RT}\right)}{dT} \\ \Delta H^o &= -RT^2 \frac{d\left(\frac{\Delta G^o}{RT}\right)}{dT} \end{aligned}$$

The dependence of ΔG^0 on temperature was obtained as

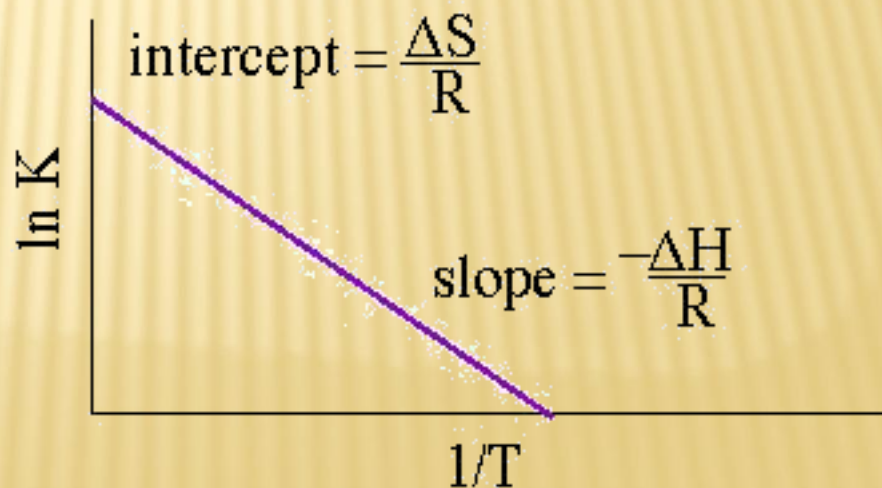
$$\frac{d\left(\frac{\Delta G^0}{RT}\right)}{dT} = -\frac{\Delta H^0}{RT^2}$$

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

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

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

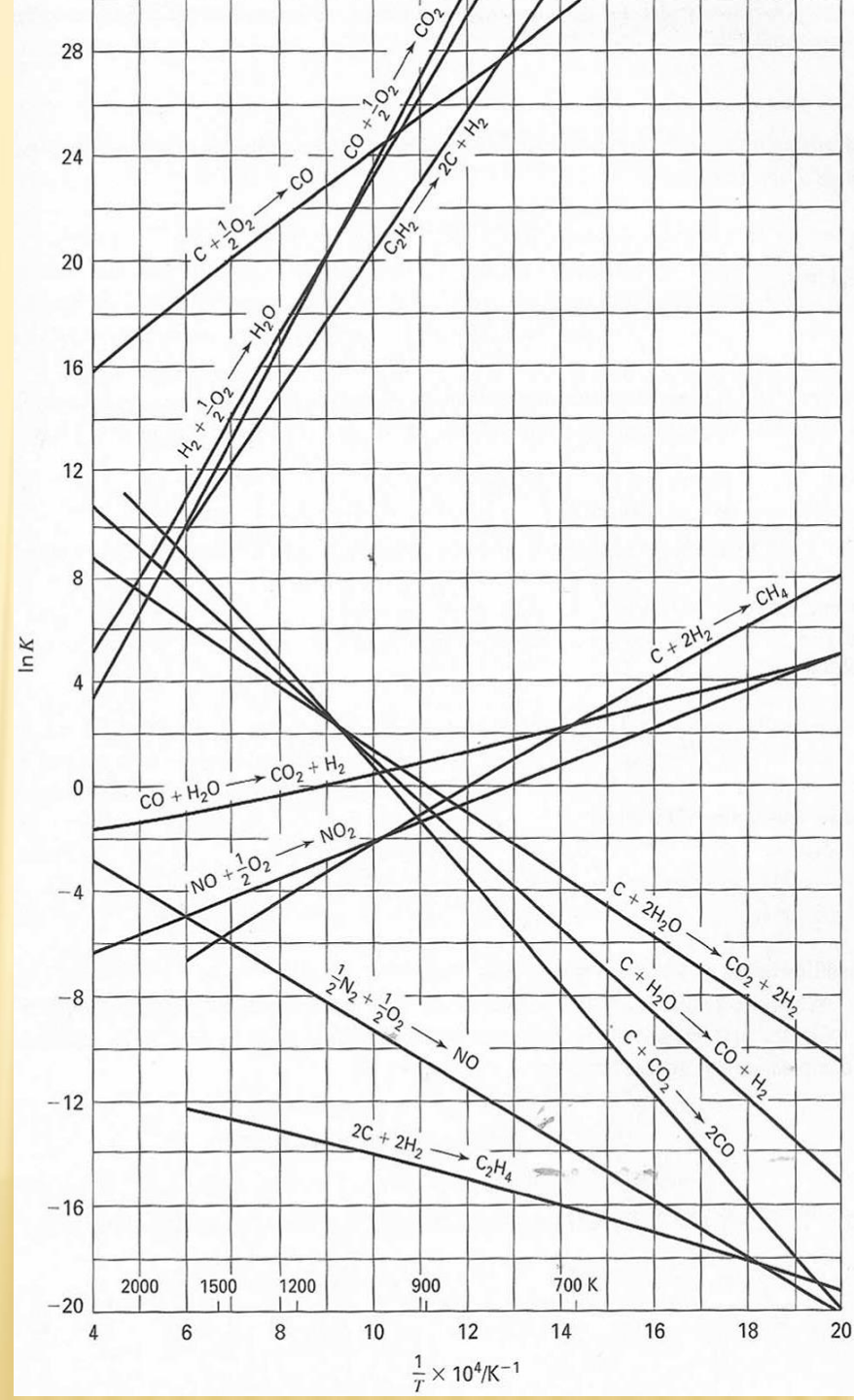
$$\boxed{\ln \frac{K}{K_1} = -\frac{\Delta H^0}{R} \left(\frac{1}{T} - \frac{1}{T_1} \right)}$$



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

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)

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

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

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

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

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

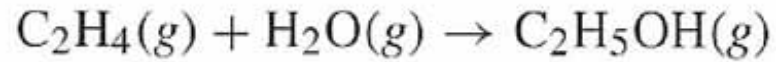
$$K = K_0 K_1 K_2$$

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

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

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

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



Heat capacity data

Ethylene hydroxide – $3.518 + 0.02T - 0.000006T^2$

Ethylene – $1.424 + 0.0144T - 0.0000044T^2$

Water – $3.47 + 0.00145T + 12100/T^2$

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

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

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

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

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

Liquid phase components are insensitive to gas pressure, 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

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

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 , $T \uparrow$ $K \uparrow$ $\varepsilon \uparrow$

For negative ΔH^0 , $T \uparrow$ $K \downarrow$ $\varepsilon \downarrow$

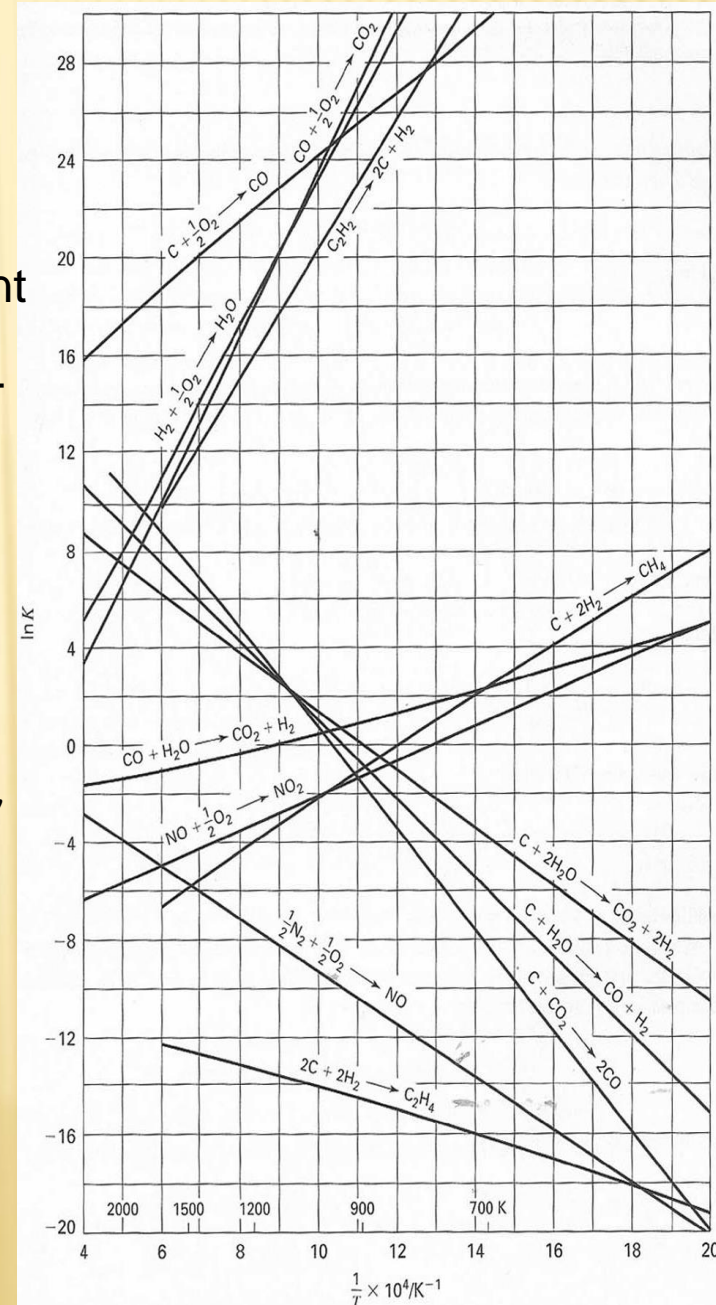
- The effect of pressure on the reaction extent is determined by the sign of total stoichiometric number ν

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

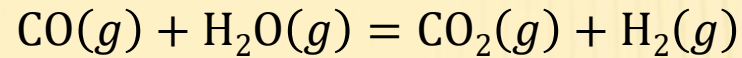
For positive ν , $P \uparrow$ $\varepsilon \downarrow$

For negative ν , $P \uparrow$ $\varepsilon \uparrow$

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

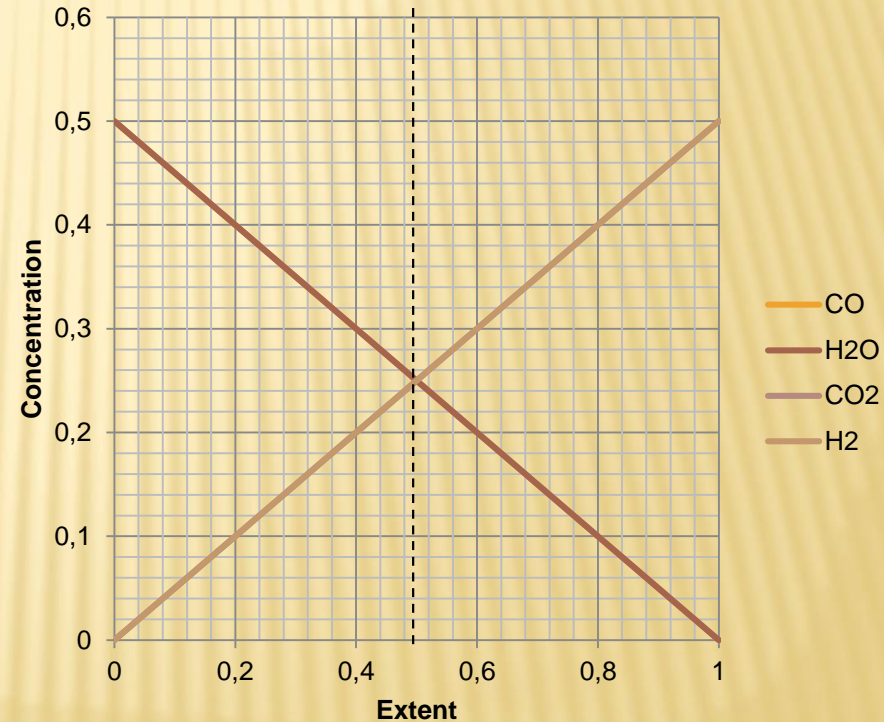


a) There are initially 1 mole of H_2O vapor and 1 mole of CO at 1100 K and 1 bar

From the previous figure $K=1$ obtained at 1100 K

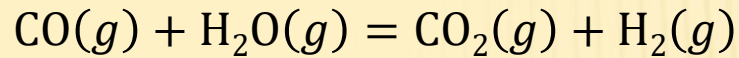
$$\begin{array}{ll} \nu_{\text{CO}} = -1 & n_{\text{CO}} = 1 - \varepsilon_e \\ \nu_{\text{H}_2\text{O}} = -1 & n_{\text{H}_2\text{O}} = 1 - \varepsilon_e \\ \nu_{\text{CO}_2} = 1 & n_{\text{CO}_2} = \varepsilon_e \\ \nu_{\text{H}_2} = 1 & n_{\text{H}_2} = \varepsilon_e \\ \nu_{\text{total}} = 0 & n_{\text{total}} = 2 \end{array}$$

$$\begin{array}{l} y_{\text{CO}} = \frac{1 - \varepsilon_e}{2} \\ y_{\text{H}_2\text{O}} = \frac{1 - \varepsilon_e}{2} \\ y_{\text{CO}_2} = \frac{\varepsilon_e}{2} \\ y_{\text{H}_2} = \frac{\varepsilon_e}{2} \end{array}$$



$$K = \frac{y_{\text{CO}_2} y_{\text{H}_2}}{y_{\text{CO}} y_{\text{H}_2\text{O}}} = \frac{\varepsilon_e^2}{(1 - \varepsilon_e)^2} = 1 \longrightarrow \varepsilon_e = \frac{1}{2} \longrightarrow \frac{n_0 - n_{\text{H}_2\text{O}}}{n_0} = \frac{n_0 - (n_0 - \varepsilon_e)}{n_0} = \frac{\varepsilon_e}{n_0} = \frac{1}{2}$$

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

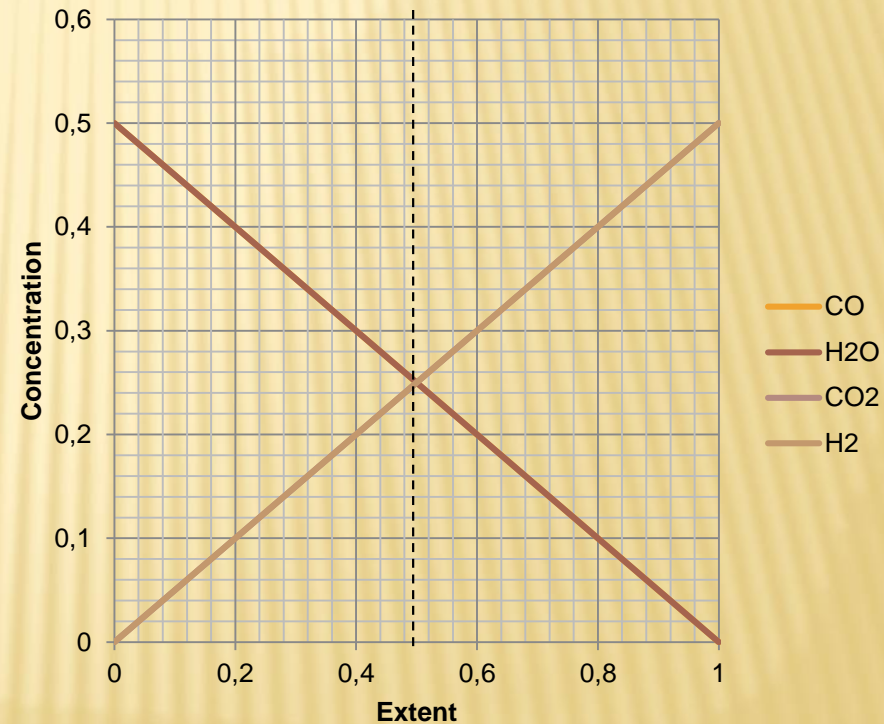


b) Same as (a) except the pressure is 10 bar

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

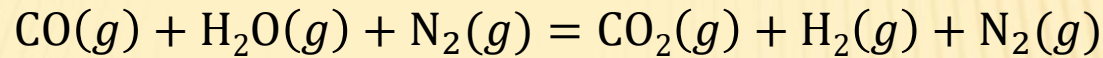
$$\begin{array}{ll} \nu_{\text{CO}} = -1 & n_{\text{CO}} = 1 - \varepsilon_e \\ \nu_{\text{H}_2\text{O}} = -1 & n_{\text{H}_2\text{O}} = 1 - \varepsilon_e \\ \nu_{\text{CO}_2} = 1 & n_{\text{CO}_2} = \varepsilon_e \\ \nu_{\text{H}_2} = 1 & n_{\text{H}_2} = \varepsilon_e \\ \nu_{\text{total}} = 0 & n_{\text{total}} = 2 \end{array}$$

$$\begin{array}{l} y_{\text{CO}} = \frac{1 - \varepsilon_e}{2} \\ y_{\text{H}_2\text{O}} = \frac{1 - \varepsilon_e}{2} \\ y_{\text{CO}_2} = \frac{\varepsilon_e}{2} \\ y_{\text{H}_2} = \frac{\varepsilon_e}{2} \end{array}$$



$$K = \frac{y_{\text{CO}_2} y_{\text{H}_2}}{y_{\text{CO}} y_{\text{H}_2\text{O}}} = \frac{\varepsilon_e^2}{(1 - \varepsilon_e)^2} = 1 \longrightarrow \varepsilon_e = \frac{1}{2} \longrightarrow \frac{n_0 - n_{\text{H}_2\text{O}}}{n_0} = \frac{n_0 - (n_0 - \varepsilon_e)}{n_0} = \frac{\varepsilon_e}{n_0} = \frac{1}{2}$$

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

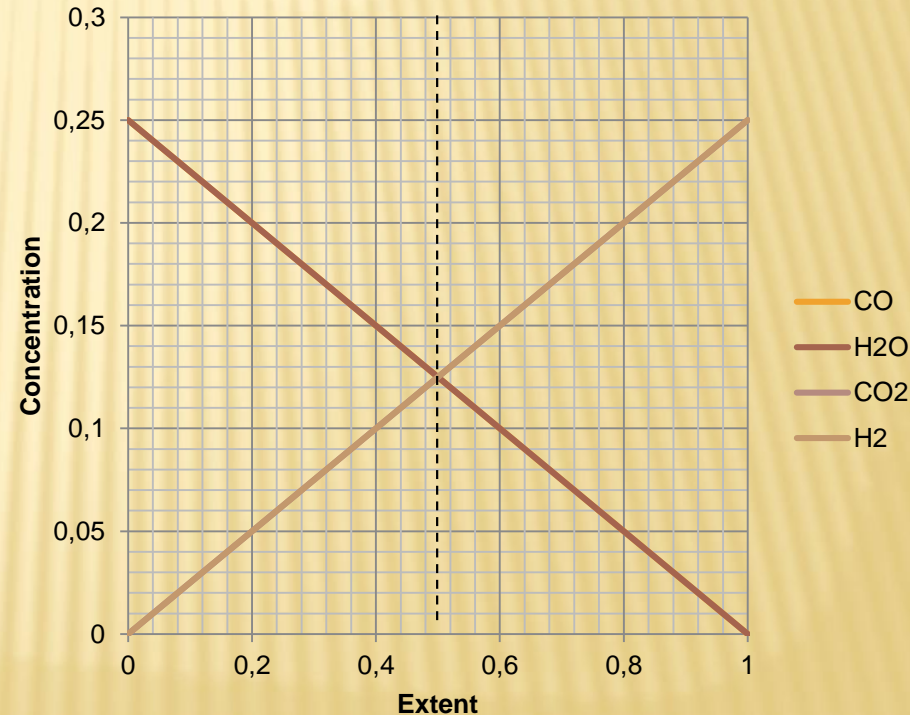


c) Same as (a) except 2 mole N_2 added to the reactants

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

$$\begin{aligned} v_{\text{CO}} &= -1 & n_{\text{CO}} &= 1 - \varepsilon_e \\ v_{\text{H}_2\text{O}} &= -1 & n_{\text{H}_2\text{O}} &= 1 - \varepsilon_e \\ v_{\text{CO}_2} &= 1 & n_{\text{CO}_2} &= \varepsilon_e \\ v_{\text{H}_2} &= 1 & n_{\text{H}_2} &= \varepsilon_e \\ v_{\text{N}_2} &= 0 & n_{\text{N}_2} &= 2 \\ v_{\text{total}} &= 0 & n_{\text{total}} &= 4 \end{aligned}$$

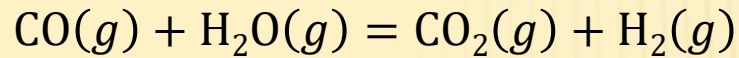
$$\begin{aligned} y_{\text{CO}} &= \frac{1 - \varepsilon_e}{4} \\ y_{\text{H}_2\text{O}} &= \frac{1 - \varepsilon_e}{4} \\ y_{\text{CO}_2} &= \frac{\varepsilon_e}{4} \\ y_{\text{H}_2} &= \frac{\varepsilon_e}{4} \end{aligned}$$



Equilibrium constant and reaction extent is unaffected

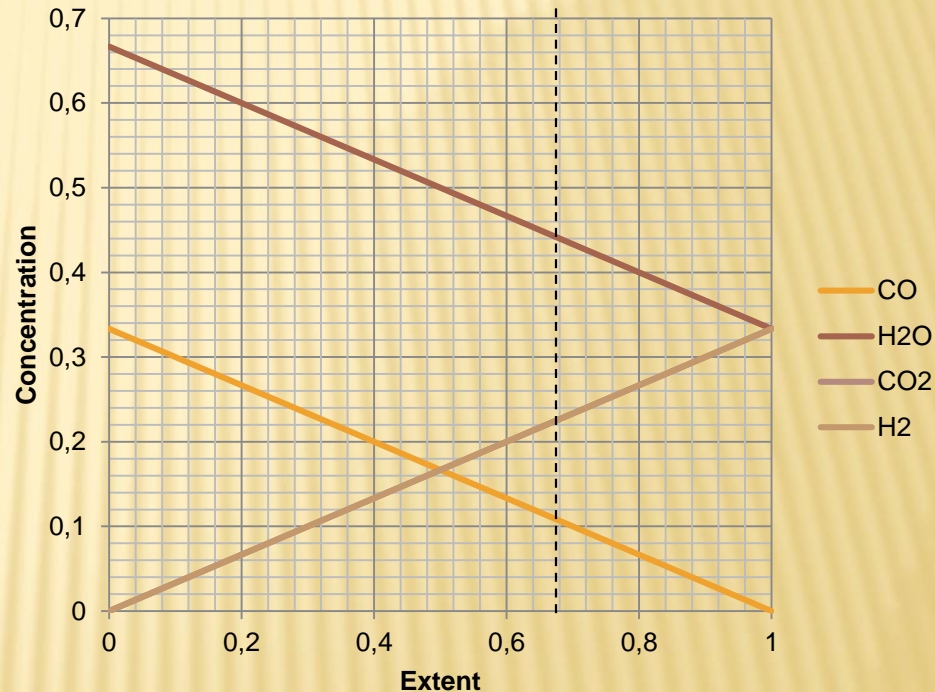
$$K = \frac{y_{\text{CO}_2} y_{\text{H}_2}}{y_{\text{CO}} y_{\text{H}_2\text{O}}} = \frac{\varepsilon_e^2}{(1 - \varepsilon_e)^2} = 1 \longrightarrow \varepsilon_e = \frac{1}{2} \longrightarrow \frac{n_0 - n_{\text{H}_2\text{O}}}{n_0} = \frac{n_0 - (n_0 - \varepsilon_e)}{n_0} = \frac{\varepsilon_e}{n_0} = \frac{1}{2}$$

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



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

$$\begin{aligned} v_{\text{CO}} &= -1 & n_{\text{CO}} &= 1 - \varepsilon_e \\ v_{\text{H}_2\text{O}} &= -1 & n_{\text{H}_2\text{O}} &= 2 - \varepsilon_e \\ v_{\text{CO}_2} &= 1 & n_{\text{CO}_2} &= \varepsilon_e \\ v_{\text{H}_2} &= 1 & n_{\text{H}_2} &= \varepsilon_e \\ v_{\text{total}} &= 0 & n_{\text{total}} &= 3 \\ y_{\text{CO}} &= \frac{1 - \varepsilon_e}{3} \\ y_{\text{H}_2\text{O}} &= \frac{2 - \varepsilon_e}{3} \\ y_{\text{CO}_2} &= \frac{\varepsilon_e}{3} \\ y_{\text{H}_2} &= \frac{\varepsilon_e}{3} \end{aligned}$$

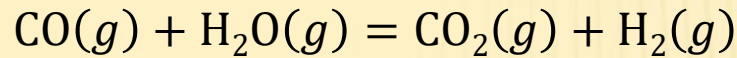


Extra H_2O increases the reaction extent but the conversion of steam decreases

$$K = \frac{y_{\text{CO}_2} y_{\text{H}_2}}{y_{\text{CO}} y_{\text{H}_2\text{O}}} = \frac{\varepsilon_e^2}{(1 - \varepsilon_e)(2 - \varepsilon_e)} = 1$$

$$\rightarrow \varepsilon_e = \frac{2}{3} \rightarrow \frac{n_0 - n_{\text{H}_2\text{O}}}{n_0} = \frac{n_0 - (n_0 - \varepsilon_e)}{n_0} = \frac{\varepsilon_e}{n_0} = \frac{1}{3}$$

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



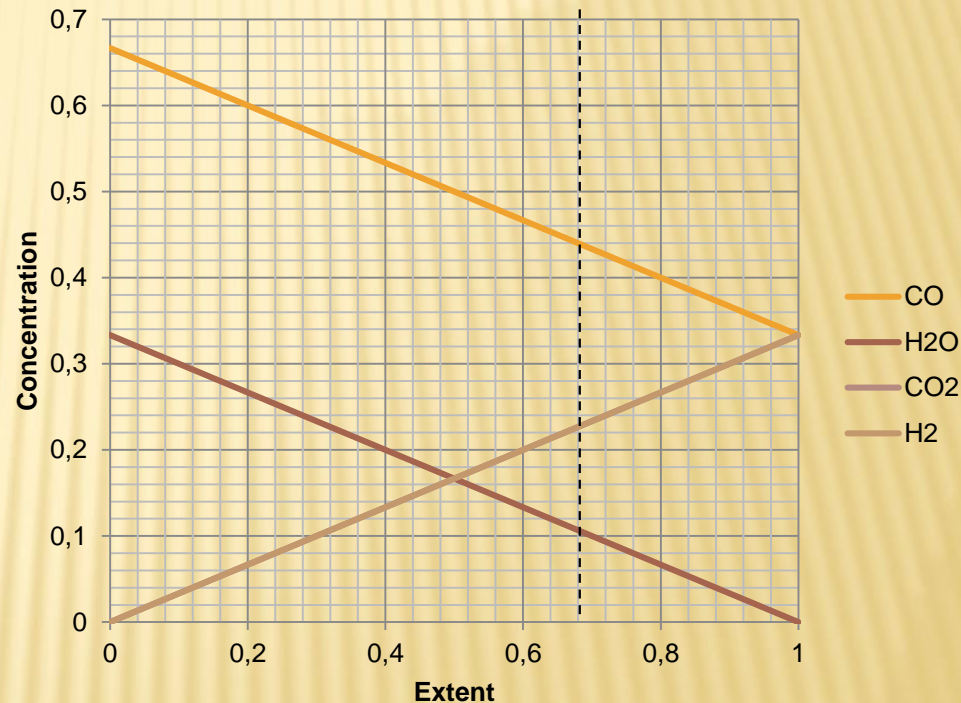
e) There are initially 1 mole of H_2O vapor and 2 moles of CO at 1100 K and 1 bar

$$\begin{aligned} v_{\text{CO}} &= -1 & n_{\text{CO}} &= 2 - \varepsilon_e \\ v_{\text{H}_2\text{O}} &= -1 & n_{\text{H}_2\text{O}} &= 1 - \varepsilon_e \\ v_{\text{CO}_2} &= 1 & n_{\text{CO}_2} &= \varepsilon_e \\ v_{\text{H}_2} &= 1 & n_{\text{H}_2} &= \varepsilon_e \\ v_{\text{total}} &= 0 & n_{\text{total}} &= 3 \end{aligned}$$

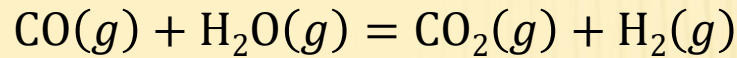
$$\begin{aligned} y_{\text{CO}} &= \frac{2 - \varepsilon_e}{3} \\ y_{\text{H}_2\text{O}} &= \frac{1 - \varepsilon_e}{3} \\ y_{\text{CO}_2} &= \frac{\varepsilon_e}{3} \\ y_{\text{H}_2} &= \frac{\varepsilon_e}{3} \end{aligned}$$

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

$$K = \frac{y_{\text{CO}_2} y_{\text{H}_2}}{y_{\text{CO}} y_{\text{H}_2\text{O}}} = \frac{\varepsilon_e^2}{(2 - \varepsilon_e)(1 - \varepsilon_e)} \longrightarrow \varepsilon_e = \frac{2}{3} \longrightarrow \frac{n_0 - n_{\text{H}_2\text{O}}}{n_0} = \frac{n_0 - (n_0 - \varepsilon_e)}{n_0} = \frac{\varepsilon_e}{n_0} = \frac{2}{3}$$



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



f) There are initially 1 mole of H_2O vapor, 1 mole of CO and 1 mole of CO_2 at 1100 K and 1 bar

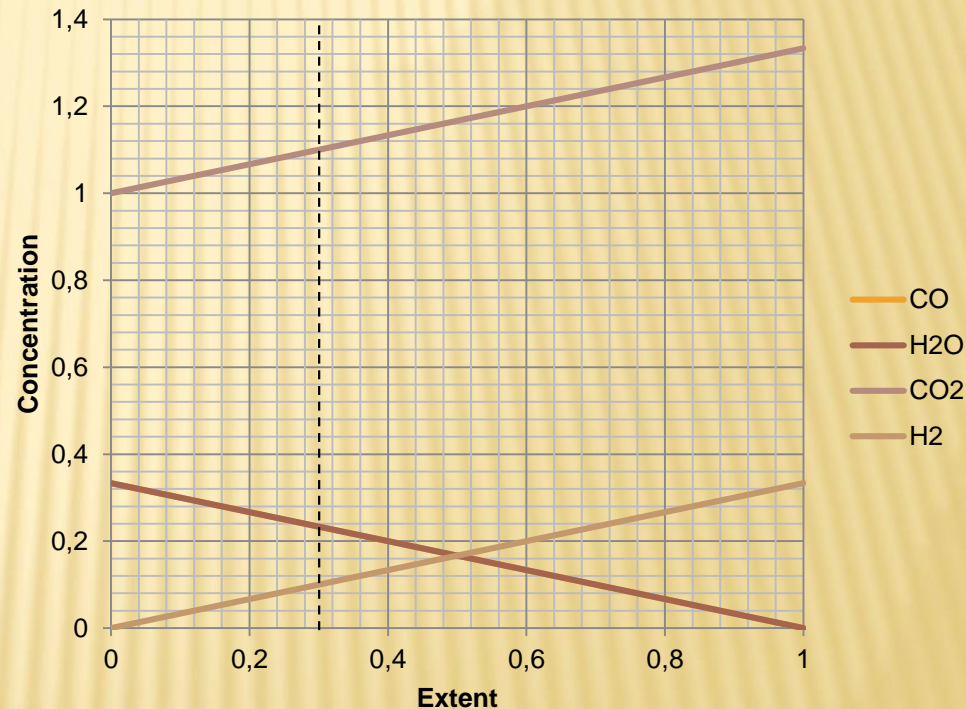
$$\begin{aligned} \nu_{\text{CO}} &= -1 \\ \nu_{\text{H}_2\text{O}} &= -1 \\ \nu_{\text{CO}_2} &= 1 \\ \nu_{\text{H}_2} &= 1 \\ \nu_{\text{total}} &= 0 \end{aligned}$$

$$\begin{aligned} n_{\text{CO}} &= 1 - \varepsilon_e \\ n_{\text{H}_2\text{O}} &= 1 - \varepsilon_e \\ n_{\text{CO}_2} &= 1 + \varepsilon_e \\ n_{\text{H}_2} &= \varepsilon_e \\ n_{\text{total}} &= 3 \end{aligned}$$

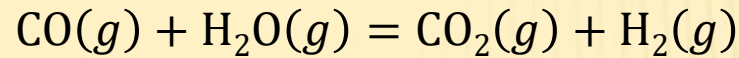
$$\begin{aligned} y_{\text{CO}} &= \frac{1 - \varepsilon_e}{3} \\ y_{\text{H}_2\text{O}} &= \frac{1 - \varepsilon_e}{3} \\ y_{\text{CO}_2} &= \frac{1 + \varepsilon_e}{3} \\ y_{\text{H}_2} &= \frac{\varepsilon_e}{3} \end{aligned}$$

Extra CO_2 decreases both reaction extent and conversion of steam

$$K = \frac{y_{\text{CO}_2} y_{\text{H}_2}}{y_{\text{CO}} y_{\text{H}_2\text{O}}} = \frac{(1 + \varepsilon_e) \varepsilon_e}{(1 - \varepsilon_e)^2} = 1 \longrightarrow \varepsilon_e = \frac{1}{3} \longrightarrow \frac{n_0 - n_{\text{H}_2\text{O}}}{n_0} = \frac{n_0 - (n_0 - \varepsilon_e)}{n_0} = \frac{\varepsilon_e}{n_0} = \frac{1}{3}$$



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

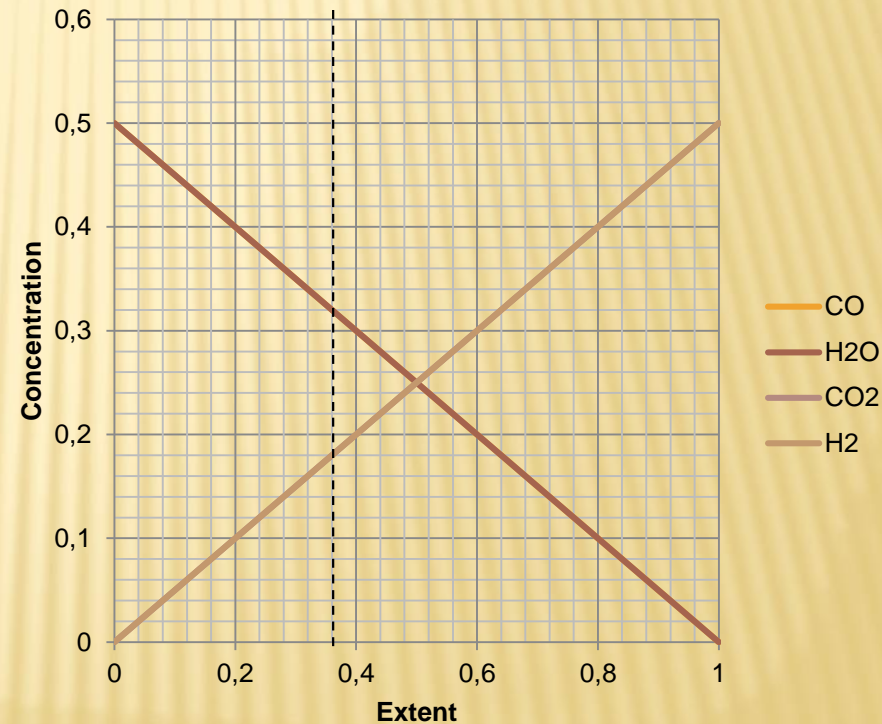


g) There are initially 1 mole of H_2O vapor and 1 mole of CO at 1650 K and 1 bar

From the $\ln K$ vs $1/T$ figure $K=0.316$ obtained at 1650 K

$$\begin{array}{ll} \nu_{\text{CO}} = -1 & n_{\text{CO}} = 1 - \varepsilon_e \\ \nu_{\text{H}_2\text{O}} = -1 & n_{\text{H}_2\text{O}} = 1 - \varepsilon_e \\ \nu_{\text{CO}_2} = 1 & n_{\text{CO}_2} = \varepsilon_e \\ \nu_{\text{H}_2} = 1 & n_{\text{H}_2} = \varepsilon_e \\ \nu_{\text{total}} = 0 & n_{\text{total}} = 2 \end{array}$$

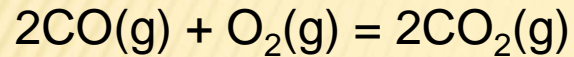
$$\begin{array}{l} y_{\text{CO}} = \frac{1 - \varepsilon_e}{2} \\ y_{\text{H}_2\text{O}} = \frac{1 - \varepsilon_e}{2} \\ y_{\text{CO}_2} = \frac{\varepsilon_e}{2} \\ y_{\text{H}_2} = \frac{\varepsilon_e}{2} \end{array}$$



Reaction extent and steam conversion decreases with increasing T since reaction $\Delta H > 0$

$$K = \frac{y_{\text{CO}_2} y_{\text{H}_2}}{y_{\text{CO}} y_{\text{H}_2\text{O}}} = \frac{\varepsilon_e^2}{(1 - \varepsilon_e)^2} = 0.316 \rightarrow \varepsilon_e = 0.36 \rightarrow \frac{n_0 - n_{\text{H}_2\text{O}}}{n_0} = \frac{n_0 - (n_0 - \varepsilon_e)}{n_0} = \frac{\varepsilon_e}{n_0} = 0.36$$

Example - A furnace is fed with 2 moles of CO fuel and stoichiometric O₂ gas for preheating to 700 C as a result of the following combustion reaction at 1 atm:



The free energy of the combustion reaction is 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