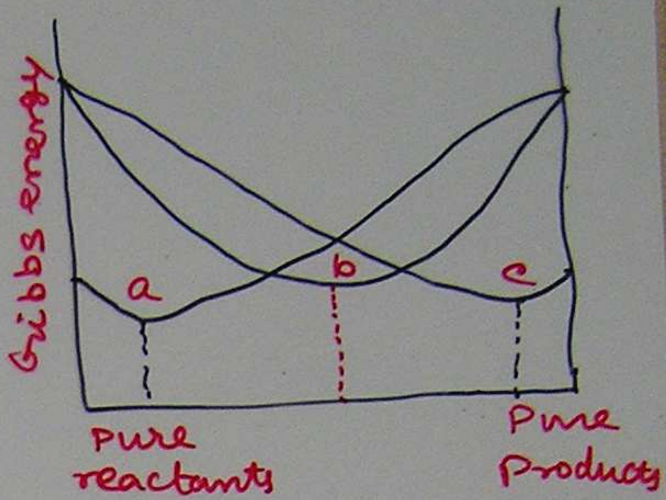
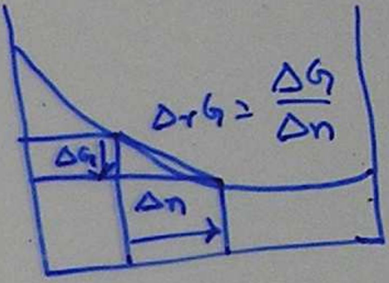
Principles of chemical Equilibrium

when
ΔG decreases reaction
Proceeds. [Spontanity]



Reaction a
Reaction b
Reaction c

Reaction Gibbs energy:



$$aA + bB \longrightarrow cC + dD$$

A & B changes by $-\Delta n$
C & D changes by $+\Delta n$

μ_A, μ_B, μ_C and μ_D - chemical potential of A, B, C, D

ΔG = Product − reactant [in terms of Gibbs energy]

$$= [c\Delta n\,\mu_C + d\Delta n\,\mu_D] - [a\Delta n\,\mu_A + b\Delta n\,\mu_B]$$

$$\Delta_r G = \frac{\Delta G}{\Delta n} = [c\mu_C + d\mu_D] - [a\mu_A + b\mu_B]$$

criteria for chemical equilibrium at constant temp and pre. is $\boxed{\Delta_r G = 0}$

<u>$\Delta_r G$ and composition [relationship]</u>

$$\Delta_r G = \Delta_r G^{\theta} + RT \ln \frac{a_C^c\, a_D^d}{a_A^a\, a_B^b}$$

$$\Delta_r G = \Delta_r G^{\theta} + RT \ln Q \quad \left[\text{where } Q = \frac{a_C^c\, a_D^d}{a_A^a\, a_B^b}\right]$$

activity a_J

Solutes in ideal solution $a_J = [J]/c^\theta$

$[J]$. molar concentration

c^θ. standard concentration. $[1 \text{ mol dm}^{-3}]$

for perfect gases $a_J = P_J/p^\theta$

P_J - Partial pre. of J

p^θ - standard pre [1 bar]

For pure solids and liquids $a_J = 1$

<u>Reactions</u> <u>at</u> <u>equilibrium</u>:

Equilibrium constant $K = \left[\frac{a_C^c \, a_D^d}{a_A^a \, a_B^b}\right]_{\text{equi}}$

At equilibrium $\Delta_r G = 0$

$$\therefore \Delta_r G = \Delta_r G^\theta + RT \ln K$$

$$0 = \Delta_r G^\theta + RT \ln K$$

$$\Delta_r G^\theta = -RT \ln K$$ — (Problem)

when $\Delta_r G^\theta < 0 \Rightarrow K > 1$
(Product dominates)

when $\Delta_r G^\theta > 0 \Rightarrow K < 1$
(reactant dominates)

ie reaction is thermodynamically not feasible.

Thermodynamic criteria of spontaneity

Exothermic $\Delta_r H^\ominus < 0$

(a) $\Delta_r S^\ominus > 0 \Rightarrow \Delta_r G^\ominus < 0 ; K > 1$ (all temp)

b) $\Delta_r S^\ominus < 0 \Rightarrow \Delta_r G^\ominus < 0 ; K > 1$

$\Rightarrow T < \Delta_r H^\ominus / \Delta_r S^\ominus$

Endothermic $\Delta_r H^\ominus > 0$

(a) $\Delta_r S^\ominus > 0 \Rightarrow \Delta_r G^\ominus < 0 ; K > 1$

$\Rightarrow T > \Delta_r H^\ominus / \Delta_r S^\ominus$

(b) $\Delta_r S^\ominus < 0 \Rightarrow \Delta_r G^\ominus < 0 ;$

$K > 1$ at no temp.

$$\Delta_r G^\ominus = \Delta_r H^\ominus - T \Delta_r S^\ominus$$

$$T = \frac{\Delta_r H^\ominus}{\Delta_r S^\ominus}$$ [for a reaction to take place]

The standard Reaction Gibbs Energy

$$\Delta_r G^\ominus = \sum \nu G_m^\ominus (\text{products}) - \sum \nu G_m^\ominus (\text{reactants}).$$

$\Delta_r G^\ominus$ cannot be calculated from $G_m^\ominus$

Step 1.

Calculate $H_r^\ominus$ from $H_f^\ominus$ and $\Delta_r S^\ominus$

$$\Delta_r G^\ominus = \Delta_r H^\ominus - T \Delta_r S^\ominus$$

-* Std Gibbs energy of formation

$\Delta_r G^\ominus \Rightarrow$ Std. reaction Gibbs energy (per mole) for its formation from the elements in their reference state.

For ex. $\Delta_r G^\ominus (H_2O(l))$ is given by

$$H_2(g) + \tfrac{1}{2} O_2(g) \rightarrow H_2O(l)$$

Formation of

$C(s)$ graphite $\rightarrow$ $C(s)$ Graphite $\left[\Delta_f G^\ominus = 0\right]$

$C(s)$ graphito $\rightarrow$ $C(s)$ diamond $\left[\Delta_f G^\ominus = 2.9\ \text{kJ mol}^{-1}\right]$

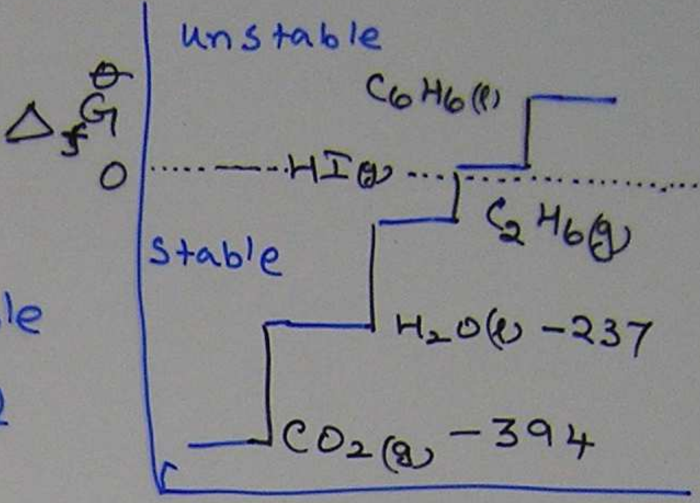
Thus

$$\Delta_r G^\ominus = \sum \nu \Delta_f G^\ominus (\text{product}) - \sum \nu \Delta_f G^\ominus (\text{reactants})$$

$\Delta_f G^\theta$ used for calculation K.

If $\Delta_f G^\theta$ = +ve

It will move from unstable state to stable elemental state spontaneously.



$\Delta_f G^\theta > 0$ means thermodynamically unstable with respect to its elements, or that is endergonic.

(i) $O_3 \rightleftharpoons \frac{3}{2} O_2$ $K = 2.7 \times 10^{-29}$

$\Delta_f G^\theta = +163$ kJ mol^{-1}.

This is a spontaneous reaction. $O_3 \Rightarrow O_2$. However the rate is so slow that under normal conditions this does not take place at measurable speed.

ii) $C_6H_6 \rightleftharpoons 6C + 3H_2$ $\Delta_f G^\theta = +124$ kJ mo

$K = 1.8 \times 10^{-22}$

It is not possible to make thermodynamical unstable compounds [where $\Delta_f G^\theta > 1$] from its elements. Because the reverse reaction "decomposition" is predominant.

∴ Endergonic substance should be made by different methods where $\Delta_f G^\ominus < 1$.

$\Delta_f G^\ominus < 0$ $[K > 1]$ are thermodynamically stable [exergonic] with respect to its elements.

$$2C + 2H_2 \longrightarrow C_2H_4 \qquad \Delta_f G^\ominus = -33 \text{ kJm}$$

$$K = 7{\cdot}1 \times 10^{5}$$

The equilibrium composition:

If $K >> 1$ (ie $K > 10^3$) corresponds t $\Delta_r G^\ominus < -17$ kJ mol^{-1}. This reaction gives products quickly.

If $K << 1$ (ie $K < 10^{-3}$) corresponds to $\Delta_r G^\ominus > +17$ kJ mol^{-1}. This reaction does not proceed at all.

∴ for reactions $10^3 > K > 10^{-3}$ (or) $-17 > \Delta_r G^\ominus > +17$ Those reactions tend to be in equilibrium.

Equilibrium constant $K =$ [activity 1] [activity 2]

[product/multiplication activity of equilibriu composition]

How to calculate K

(i) Know the initial molar conc: ~~or~~ Partial Pre.
[liquids] [gases]

(ii) change in their ~~to~~ quantities to reach equilibrium

(iii) The final equilibrium values

Assume the change in conc: of one species as 'x'. Based on reaction stochiometry calculate change in conc: of other species with respect to 'x'. calculate K.

Equilibrium constant in terms of con: (K).

⇒ K calculated from thermodynamic data. [gas- Phase reactions

$$K_c = \frac{[NH_3)^2}{[N_2][H_2]^3}$$

Kc is calculated from K.

Kp – K calculated from partial Pre.

Kc – K. calculated from molar conc:

$$K = K_c \left[\frac{c^\theta RT}{p^\theta} \right]^{\Delta\nu_{gas}}$$

$\Delta\nu_{gas}$ = difference in stochiometric coefficient of product and reactant

Substitute $c^\ominus$, $p^\ominus$, R.

$$K = K_c\left[\frac{T}{12.027\,K}\right]^{\Delta\nu\,gas}$$

=

Relationship between K and K_c

$$K = \frac{\left[p_C/p^\ominus\right]^c\left[p_D/p^\ominus\right]^D}{\left[p_A/p^\ominus\right]^a\left[p_B/p^\ominus\right]^b} \qquad K_c = \frac{\left([C]/c^\ominus\right)^c\left([D]/c^\ominus\right)^d}{\left([A]/c^\ominus\right)^a\left([B]/c^\ominus\right)^b}$$

· using Perfect gas equation

$$Pv = nRT \Rightarrow p_J = \frac{n_J RT}{V} = [J]RT$$

$$K = \frac{\left[[C]RT/p^\ominus\right]^c\left[[D]RT/p^\ominus\right]^d}{\left[[A]RT/p^\ominus\right]^a\left[[B]RT/p^\ominus\right]^b}$$

$$= \frac{[C]^c[D]^d}{[A]^a[B]^b} \times \left[\frac{RT}{p^\ominus}\right]^{(c+d)-(a+b)}$$

$$\boxed{K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}\left[\frac{1}{c^\ominus}\right]^{(c+d)-(a+b)}}$$

$$K = K_c\left[\frac{c^\ominus RT}{p^\ominus}\right]^{(c+d)-(a+b)}$$

Coupled Reactions.

A reaction that is not spontaneous can be driven forward by coupling it to a spontaneous reaction.

Ie. An endergonic reaction ($\Delta_r G$ +ve) can be forced to occur by coupling this to an exergonic reaction ($\Delta_r G$ −ve). The overall reaction is spontaneous if

$\Delta_r G + \Delta_r G' = -ve$.

Ex. $ATP_{(aq)} + H_2O_{(l)} \rightarrow ADP_{(aq)} + P_{i\,(aq)}^{-} + H^{+}_{(aq)}$ –(

[exergonic]

$Glucose_{(aq)} \longrightarrow G6P_{(aq)}$ [endergonic] –(2

1+2

$Glucose_{(aq)} + ATP_{(aq)} \rightarrow G6P_{(aq)} + ADP_{(aq)}$

Biological std. state $pH = 7$ $G^{\oplus}, H^{\oplus}, S^{\oplus}$

Hydrolysis of ATP

$\Delta_r G^{\oplus} = -31\ kJ\ mol^{-1}$ $\Delta_r H^{\oplus} = -20\ kJ\ mol^{-1}$

$\Delta_r S^{\oplus} = +34\ kJ\ mol^{-1}$

∴ Hydrolysis is exergonic ($\Delta_r G < 0$).

Response ~~to~~ of equilibria to the conditions

le Chatelier's Principle

when a system at equilibrium is subjected to a disturbance, the composition of the system adjusts so as to tend to minimize the effect of the disturbance.

"Change of pre, temp. affects the reaction".

(i) Presence of catalyst.

Catalyst does not change "K".

(ii) Effect of temp:

Exothermic ⇒ shift towards reactants

Endothermic ⇒ shift towards Products

$\Delta_r G^\ominus$ with respect to temp. [K is similar].

$$\Delta_r G^\ominus = \Delta_r H^\ominus - T\Delta_r S^\ominus$$

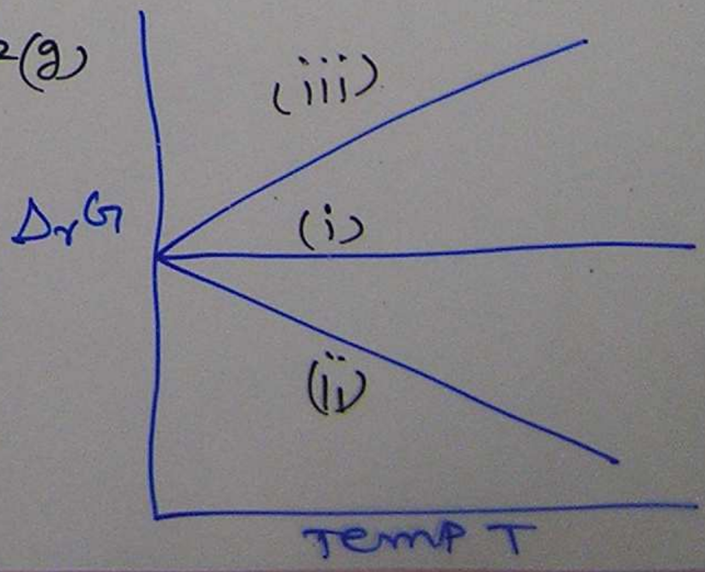
Assume "H" and "S" does not change

$\therefore \Delta_r G^\ominus$ = −(temp. change) × entropy change.

(i) $\frac{1}{2}C_{(s)} + \underline{\underline{\frac{1}{2}}}O_{2(g)} \rightarrow \underline{\underline{\frac{1}{2}}}CO_{2(g)}$

(ii) $C_{(s)} + \frac{1}{2}O_{2(g)} \rightarrow CO_{(g)}$

(iii) $CO_{(g)} + \frac{1}{2}O_{2(g)} \rightarrow CO_{2(g)}$



we know $\Delta_r G^\ominus = -RT \ln K$

$$\Rightarrow \ln K = \frac{\Delta_r G^\ominus}{RT} = \frac{-(\Delta_r H^\ominus - T\Delta_r S^\ominus)}{RT}$$

$$= \frac{-\Delta_r H^\ominus}{RT} + \frac{\Delta_r S^\ominus}{R} \quad — ①$$

when $\overset{T}{\cancel{k}} \rightarrow T'$ then $K \rightarrow K'$

$$\therefore \ln K' = \frac{-\Delta_r H^\ominus}{RT'} + \frac{\Delta_r S^\ominus}{R} \quad — ②$$

(2) −(1)

$$\ln K' - \ln K = \left[\frac{-\Delta_r H^\ominus}{RT'} + \frac{\Delta_r S^\ominus}{\underline{\underline{R}}}\right] - \left[\frac{-\Delta_r H^\ominus}{RT} + \frac{\Delta_r S^\ominus}{\underline{\underline{R}}}\right]$$

$$= \frac{\Delta_r H^\ominus}{R}\left[\frac{1}{T} - \frac{1}{T'}\right]$$

$$\ln \frac{K'}{K} = \frac{\Delta_r H^\ominus}{R}\left[\frac{1}{T} - \frac{1}{T'}\right]$$

Van't Hoff equation.

Case (i) $T' > T$

for endothermic reaction $\Delta_r H^\ominus > 0$.

$\therefore \ln K' > \ln K$ or else $K' > K$.

In other words Equilibrium constant K increases as temp. increases. ie more Product is formed for endothermic reaction.

case (ii)

for exothermic reaction $\Delta_r H^\ominus < 0$.

$K' < K$.

Effect of compression

when a system at equilibrium is compressed, the composition of a gas-phase equilibrium adjusts ~~too~~ so as to reduce the number of molecules in the gas phase.

$\Delta_r G^\ominus$ change in Gibbs energy of the substances in std. state. ie 1 bar.

whatever is the pre. ie $\Delta_r G^\ominus$ is same

$\therefore$ K is independent of pre. $[K \propto \Delta_r G^\ominus]$

$$H_{2(g)} + I_{2(s)} \rightleftharpoons 2HI_{(g)}$$

(i) Initial Pre: $= x$.

(ii) Pre: after 30 min $=$ ~~$x/2$~~ $\cdot\ 2x$

In other words partial pre is doubles.

$$K = \frac{p^2_{HI}}{p_{H_2}} \quad ; \quad K' = \frac{(2p_{HI})^2}{2P_{H_2}} = 2K.$$

But we know K is independent of pre.

So K will not change.

Hence the conc: should change to keep "K" constant. ie more product should be formed.

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}.$$

For this reaction Pre: has no effect. ie compression will not favour forward (or backward reaction.

Similarly inert gases present in the reaction (N_2, Ar etc.) does not affect equilibrium constant. In other words they do not affect the rate of the reaction.