General & Organic Chemistry

Lecture 8

L8: Sections 13.4 ~ 13.7
Heterogeneous Equillibria

6/Nov/2024

★ Heterogeneos Equilibria

- they involve more than one Phase/state of Substances unlike homogenous reactions

- earlier we studied Homogeneos Equilibria in which the substances are all in the same state [Liquid, gas, solid ..]

Ex: $2KClO_{3(s)} \rightleftharpoons 2KCl_{(s)} + 3O_{2(g)}$

Ex: $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$

$$\underbrace{\begin{matrix} K_P = (P_{O_2})^3 & , K_P > K \\ K = [O_2]^3 & \Delta n_g = 3 > 0 \end{matrix}}_{\text{why?}}$$

- because the Position of heterogenous equilibrium does NOT depend on the amounts of Pure solids or Liquids and that because their concentrations are constant

- So we don't count them when calculating K_p or K_c

Note: if we are talking about aqueous state (aq) we use concentration bc it can change

* The extent of a reaction :

- A value of K much larger than 1 means that :
  at equilibrium the Reaction system consists of mostly Products
  or [The equilibrium lies/shifts to the right]

- while a very small value of K means that :
  the system at equilibrium Consists of mostly reactants
  or [The equilibrium Position lies / shifts far to the left]

So the reaction does NOT occur to any significant extent
(if very small K there is almost no reaction]
be you still have a Ton of reactants

So $K > 1 \rightsquigarrow$ equilibrium lies to the right (Products)
$K < 1 \rightsquigarrow$ equilibrium lies to the left (Reactants)

★ Numerical Problems on equilibrium ★

- Numerical Problems Come in two different ways

(I). The initial Concentrations & the equilibrium Concentration of ONE of the reactants or products are known and you are asked to calculate K

Ex: Consider this reaction

$$Fe^{3+}_{(aq)} + SCN^{-}_{(aq)} \rightleftharpoons FeSCN^{2+}_{(aq)}$$ - Homogeneous

6.00 M $Fe^{3+}_{(aq)}$ & 10.0 M $SCN^{-}_{(aq)}$ are mixed at a certain temp° and at equilibrium, the concentration of $FeSCN^{2+}_{(aq)}$ is 4.00M

Find K

$$K = \frac{[FeSCN^{2+}]}{[Fe^{3+}][SCN^{-}]}$$

using the reaction:

	Fe^{3+} +	SCN^{-} $\rightleftharpoons$	$FeSCN^{2+}$
initial [ ]	6.00M	10.0M	$\cancel{*}$0
final (equilib) [ ]	6.00-X	10.0-X	+4.00M (→X)
	2.00M	6.00M	

X = 4.00M so

So $K = \frac{[4.00]}{[2.00][6.00]} = \frac{1}{3} = 0.3\overline{33}$

we had to get [ ] of the Reactants at equilibrium and from the equation
1 Mol Fe^{3+} = 1 Mol $FeSCN^{2+}$
& 1 Mo SCN^{-} = 1 mol $FeSCN^{2+}$
and if there was 4 mols of the Product that was created
then the initial [ ]s of the reactants will decrease by the same amount the Product was created which is 4.00M
bc it 1:1 ratio

Ex2:

$$A_{(g)} + 2B_{(g)} \rightleftharpoons C_{(g)}$$

at equilibrium $[C] = 3.00M$

	A	B	C
initially:	8	10	0
at equilibrium:	8-3	10-6	0+3
$\hookrightarrow$ =	5	4	3

$$K = \frac{[C]}{[A][B]^2} = \frac{3}{5.16} = 0.0375$$

- Calculate Kp at 25°c = 298.15°K

$$K_p = K(RT)^{\Delta ng}$$

$\Delta ng = 1 - 3 = -2$

$$K_p = 0.0375(0.08206 \times 298.15)^{-2}$$

$$K_p = 6.265 \times 10^{-5}$$

(II) The initial concentrations of the reactants and the value of the equilibrium constant are known, asks to calculate the equilibrium concentrations:

Ex: initial [ ]s are: 10.0M $Fe^{3+}_{(aq)}$ & 8.00M $SCN^-_{(aq)}$ what is the equilibrium [ ] of $FeSCN^{2+}_{(aq)}$

$K = 0.3\overline{33}$

$$Fe^{3+}_{(aq)} + SCN^-_{(aq)} \leftrightharpoons FeSCN^{2+}_{(aq)}$$

	Fe^{3+}	SCN^-	$FeSCN^{2+}$
init: [ ]	10.0	8.00	0
equil: [ ]	10.0-X	8.00-X	+X

so

$$K = \frac{[FeSCN^{2+}]}{[Fe^{3+}][SCN^-]}$$

$$\frac{0.33}{1} = \frac{X}{(10.0-X)(8.00-X)}$$

$\Rightarrow$ ★

★ $0.33(80 - 10X - 8X + X^2) = X$

$0.33(X^2 - 18X + 80) = X$

$0.33X^2 - 6X + 26.6 = X$

$3(\frac{X^2}{3} - 7X + 26.6) = 0$

$X^2 - 21X + 80 = 0$

$$\frac{21 \mp \sqrt{121}}{2}$$

$$= \frac{21 \pm 11}{2} = \begin{cases} \boxed{5} \\ 16 \text{ x bc} \end{cases}$$

$10 - 16 = -6M$ $\hookrightarrow$ there is no such thing

$\boxed{X = 5}$

Ex: Consider the reaction, the initial [ ]s of reactants is <u>6.0M</u>

$$Fe^{3+}_{(aq)} + SCN^-_{(aq)} \rightleftharpoons FeSCN^{2+}_{(aq)} \qquad K' = \frac{1}{3}$$

init[ ]:	6	6	0
equil[ ]:	6-X	6-X	X

$$K' = \frac{[FeSCN^{2+}]}{[Fe^{3+}][SCN^-]}$$

$$\frac{1}{3} = \frac{X}{(6-X)(6-X)}$$

$$\frac{1}{3} = \frac{X}{(6-X)^2}$$

$$(6-X)^2 = 3X$$

$$36 - 12X + X^2 = 3X$$

$$X^2 - 15X + 36 = 0$$

$$\frac{15 \pm \sqrt{81}}{2}$$

$$= \frac{15 \pm 9}{2}$$

12 ∝ does not work (6-12 = -6M ∝)

$\boxed{3}$

$\boxed{So \quad X = 3}$ = $[FeSCN^{2+}]$

★ Applications of the Equilibrium Constant

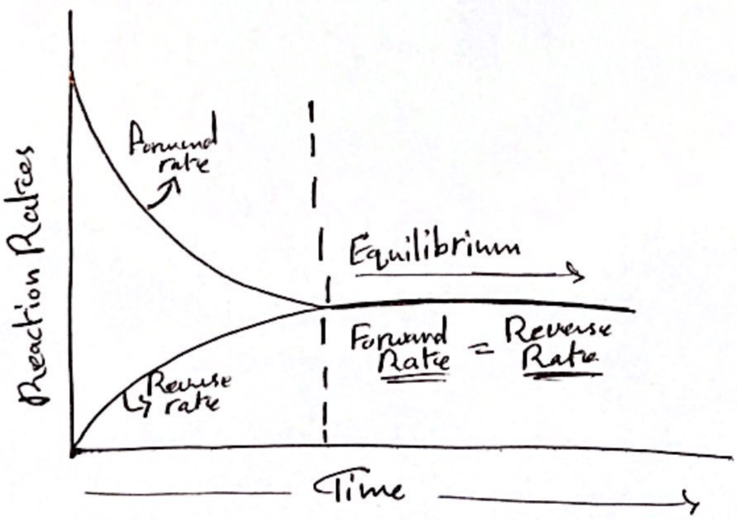
- Reaction Quotient : Q
  * used when all of the initial concentrations are non-zero and we apply the law of mass action using initial concentrations instead of equilibrium concentrations

- this means that, K is a state of Q at equilibrium [K = Q]

and Q can be written at anytime of the reaction

Ex: $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$

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



* Reaction Quotient, Q

- if $Q = K$, The system is at equilibrium so No shift occurs

- if $Q > K$, Means the [ ]s of products is more then [ ]s of reactants
so (most of the substances we have are products)
Therefore the system shifts to the Left
because its at a point after the equilibrium
and consumes the products to form reactants to reach the equilibrium back

- if $Q < K$, The system shifts to the Right
because its at a point before the equilibrium point
and there is more reactants in the substance than products
so it consumes the ~~Products~~ Reactants & form Products
till equilibrium is reached

Q & K' Solving Equilibrium problems

*Consider the reaction: $K' = \frac{1}{3} = 0.3333$

$$Fe^{3+}_{(aq)} + SCN^-_{(aq)} \rightleftharpoons FeSCN^{2+}_{(aq)}$$

- Consider the initial [ ]s and find the equilibrium [ ]:

	Fe^{3+}	SCN^-	$FeSCN^{2+}$	Q
1	9.00 M	5.00 M	1.00 M	$\frac{1}{9\times5} = 0.0222$
2	3.00 M	2.00 M	5.00 M	$\frac{5}{2\times3} = 0.8333$
3	2.00 M	9.00 M	6.00 M	$\frac{6}{2\times9} = 0.3333$

* in 1, $Q = 0.0222 < K' = 0.3333$, shift to the right (in forward direction), bc we are before equilibrium

* in 2, $Q = 0.8333 > K' = 0.3333$, shift to the left (in reverse direction) bc we are after equil --

* in 3 $Q = K' = 0.3333$, does NOT shift, we are at equilib-

- Considering @ 2 to get the equil [ ] from:

	Fe^{3+} +	SCN^- ⇌	$FeSCN^{2+}$
init:	3	2	5
equil:	3+X	2+X	5−X

5−X ↳ this is bc the reaction is shifted to the left so we consume product to make reactant bc we are after the equil.. point

$$K' = \frac{[FeSCN^{2+}]}{[Fe^{3+}][SCN^-]}$$

⇒ *

* $\frac{1}{3} = \frac{5-X}{(3+X)(2+X)}$

$15 - 3X = 6 + 3X + 2X + X^2$

$X^2 + 8X - 9 = 0$

$\frac{-8 \pm \sqrt{100}}{2} = \frac{-8 \pm 10}{2}$ → $\boxed{1}$ ✓, → −9 ✗

$\boxed{X = 1}$

So $[Fe^{3+}] = 4$ M

$[SCN^-] = 3$ M

$[FeSCN^{2+}] = 4$ M

at equilibrium

★ Le Châtelier's Principle

- if a Change (external effect (Concentration, Temperature, Pressure) ... etc) is imposed on a system at equilibrium, the Position of the equilibrium will shift in a direction that reduces (minimize) this change

- Effect of Changes on the system:

① Concentration:

- The system will shift away upon addition of any component that is a part of the system and the opposite effect if a component is removed

Ex:

$$C_2H_5OH + 3O_2 \rightleftharpoons 2CO_2 + 3H_2O$$

- at equilibrium concentrations are constant, as an example suppose some of the CO_2 is removed, so its [ ] decreased, to account and replace the CO_2, the Ethanol & O_2 will react to make up for the CO_2 so the reaction is shifted to the right over here in this case to go to its new equilibrium

- in all this, the value of K is unchanged, bc in the end you still have numbers that get you the same value every time, the only change is in the Position of equilibrium

② Temperature :

- K will Change upon the Change of temperature

- Endothermic reaction : Requires energy so its a reactant $\Rightarrow \Delta H = (-)$
- Exothermic reaction : gives / Produces energy so its a Product $\Rightarrow \Delta H = (+)$

Ex:

★ Exothermic reaction:

$$CH_{4(g)} + 2O_{2(g)} \rightleftharpoons CO_{2(g)} + 2H_2O_{(g)} + heat$$

- you deal with heat/energy as a Part of the reaction, here its a product
So by increasing it the reaction will go/shift to the left to resist this Change
, this will cause to make Reactants and consume products

$$s \cdot \downarrow K = \frac{[CO_2^{-x}][H_2O^{-x}]^2}{\uparrow[CH_4+x][O_2+x]^2}$$ and by increasing Reactants

K decreases
and opposite of it wass cooled down

★ Endothermic reactions :

$$Ba(OH)_2 + 2NH_4Cl + heat \rightleftharpoons BaCl_2 + 2NH_3 + 2H_2O$$

- Here, when increasing the temp (after getting to the equilibrium) this with shift the reaction to the right to resist the Change
- and this will consume reactants and make Products

so:
$$\uparrow K = \frac{\uparrow[BaCl_2+x][NH_3+x]^2 [H_2O+x]^2}{[Ba(OH)_2-x][NH_4Cl_{-x}]^2}$$

this will increase K

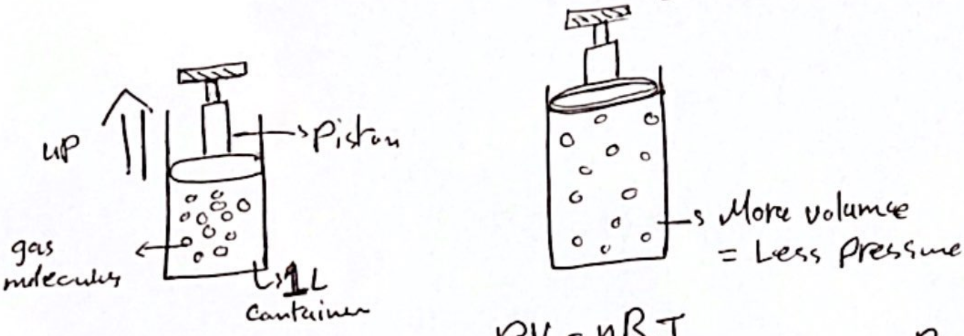
- Endothermic & K : relative relation , $\uparrow T = \uparrow K$ and viceversa
- Exothermic & K : Inverse relation , $\uparrow T = \downarrow K$

★ The reactions need to be within the activation energy range to start otherwise there would be No reaction

③ Pressure effect at Constant temperature

(Pressure due to volume change)
[Volume pressure]

- This will affect gasses / gasseous substances and its almost ineffective with solids & Liquids bc gasses have more Entropy
  ↳ عشوائية



$PV = nRT$
inverse relation

*Pressure (in a closed system) is the number of intramolecular collisions

Ex:

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

if we increased the pressure (by reducing volume) and in this example we have [4 mols in reactants and 2 in products] and to resist the increase in pressure, the reactions goes to the direction that has least amount of molecules to minimize the effect of increasing pressure

so in this case, the reaction goes to the right making products (NH_3) which has less molecules [Pressure depends on number of molecules and NOT type]
decreasing the molecules

- and the opposite when decreasing pressure happens (we want the most molecules we can get to minimize the lack) (in this case it goes to the left)

Ex2:

$$H_2O_{(g)} + CO_{(g)} \leftrightharpoons H_{2(g)} + CO_{2(g)}$$

- Here the number of molecules of reactants = Products so increasing or decreasing Pressure won't change anything

Note: Check (always) if the equation is balanced before solving

---

④ Addition of inert gas

- This does <u>NOT</u> affect equilibrium Position

inert ~~gas~~ means: Chemically unreacted under normal conditions (need vigorous conditions)

- it does <u>Not</u> <u>react</u> with the molecules so doesn't change concentration
- even though it does change the ~~volume~~ Pressure by increasing it, because it doesn't react with anything so it won't make or produces a reaction