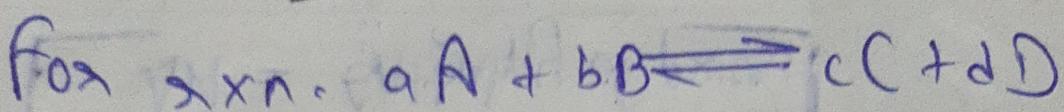


Chemical Equilibrium



In terms of conc.

$$K_c = \frac{K_f}{K_b} = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

In terms of partial pressure

$$K_p = \frac{(P_c)^c (P_d)^d}{(P_A)^a (P_B)^b}$$

In terms of mole fraction

$$K_x = \frac{(x_c)^c (x_d)^d}{(x_A)^a (x_B)^b}$$

Now,

$$K_p = K_c (RT)^{\Delta n_g}$$

$$\Delta n_g = n_p(g) - n_R(g)$$

no. of moles of products no. of moles of reactants

Cases :-

1.) If $\Delta n_g > 0$

$$K_p > K_c$$

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Q.) If $\Delta n_g < 0$

$$K_p < K_c$$

Q.) If $\Delta n_g = 0$,

$$K_p = K_c$$

* 4.)

If $T = 12.18 \text{ K}$

$$R = 0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1}$$

$$K_p = K_c$$

Relation b/w K_p & K_c $P_T = \frac{\text{Total Pressure}}{\text{Total}}$

$$K_p = K_c (P_T)^{\Delta n_g}$$

$$\Delta n_g = n_p(g) - n_R(g)$$

Also,

$$K_c = K_c \left(\frac{P_T}{RT} \right)^{\Delta n_g}$$

Characteristics

1.) If we reverse the eqn., equi. const. becomes reciprocal

$$K'_c = \frac{1}{K_c}$$

2.) If eqn. is not stoichiometric
coeff. are :-

a) doubled :-

$$K_c' = (K_c)^2$$

b) tripled :-

$$K_c' = (K_c)^3$$

c) half :-

$$K_c' = \frac{1}{2} K_c$$

3) If rxn. is split into n parts & adding we get our required eqn.

then, $K_c = K_1 \times K_2 \times K_3 \dots K_n$

Units :-

1) Units of $K_c = (\text{mol L}^{-1})^{\Delta n_g}$

2) Units of $K_p = (\text{atm})^{\Delta n_g}$

~~Effect of temp. on equ. const.~~

Vant Hoff equation is :- enthalpy change in J/mol.

$$\log_{10} \frac{K_2}{K_1} = \frac{\Delta H}{2.303R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

equ. const. at temp. T_1

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Case 2

- i) When $\Delta H = 0 \rightarrow K_1 = K_2$,
No effect of temp. on eq. const
- ii) When $\Delta H = +ve$ [Endothermic]
 $K \propto T$
- iii) When $\Delta H = -ve$ [Exothermic]
 $K \propto \frac{1}{T}$

Reaction Quotient $[Q_c] = \frac{[C]^c [D]^d}{[A]^a [B]^b}$

It can be written at any time
not just at equilibrium like
equilibrium const.

- i) $Q_c < K_c \Rightarrow$ Rxn. is proceeding in forward dirn.
- ii) $Q_c = K_c \Rightarrow$ Rxn. is at equilibrium
- iii) $Q_c > K_c \Rightarrow$ Rxn. is proceeding in backward dirn.

Degree of Dissociation

$$\alpha = \frac{M_T - M_0}{M_0 (n-1)}$$

* theoretical mol. mass at $t=0$
obs. mol. mass at $t=t$
no. of gaseous molecules formed by dissociation of 1 gas molecule

& In terms of Vapour Density,

$$M_T = \alpha \times D_T$$

$$\alpha = \frac{D_T - D_0}{D_0 (n-1)}$$

theoretical V.D. (V.D. of reactant)
observed vapour density (V.D. of equil. mixture)

Degree of Association

$$\alpha = \frac{n(M_T - M_0)}{(1-n) M_0}$$

No. of particles combine with each other to form 1 molecule

$$\alpha = \frac{D_T - D_0}{D_0 (1-n)} = \frac{n(D_T - D_0)}{(1-n) D_0}$$

M_T :- K_p & K_c changes only for some rxn
when temp. PS changes

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Relation b/w ΔG & ΔG°

\downarrow Gibbs free energy

Standard Gibbs free energy

$$\Delta G = \Delta G^\circ + RT \ln Q \rightarrow \text{Reaction Quotient}$$

$$\Delta G = \Delta G^\circ + RT \log_{10} (2.303)$$

At equi.,

$$\Delta G = 0$$

$$\therefore \Delta G^\circ = -2.303 RT \log_{10} K$$

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

Tonic Equilibrium

→ Ostwald's Dilution Law → (For weak electrolytes)

$$x = C\alpha$$

Conc. of dissociate Initial concu

$$K_a = \frac{C\alpha^2}{1-\alpha}$$

Diss. const. of acid
or Ionisation const. of acid

If $\alpha \ll 1$

$$K_a = C\alpha^2$$

→ If α is not given in questn.

then find $\frac{K_a}{C} = ?$

a) If $\frac{K_a}{C} > 25 \times 10^{-4} \Rightarrow K_a = \frac{C\alpha^2}{1-\alpha}$

b) If $\frac{K_a}{C} \leq 25 \times 10^{-4} \Rightarrow K_a = C\alpha^2$

→ If α is given then

a) If $\alpha \geq 0.05 \Rightarrow K_a = \frac{C\alpha^2}{1-\alpha}$
 $\% \alpha > 5\%$

b) If $\alpha \leq 0.05 \Rightarrow K_a = C\alpha^2$
 $\% \alpha \leq 5\%$

Degree of Dissociation = No. of moles dissociate

$\frac{DC}{DC + C} = \alpha$ Total no. of moles taken initially

Ionic Product of Water

$$K_w = [H_3O^+] [\bar{O}H^-]$$

At $25^\circ C$ (or $298 K$)

$$K_w = 10^{-14}$$

Le Chatelier's principle is not applicable to common ion effect

ESTIMATE 1.) Effect of temp. on K_w

→ K_w increase with increase in temperature

$$K_w \propto T$$

→ for pure water $[H_3O^+] = [\bar{O}H] = 10^{-7}$

$$\downarrow [H^+]$$

2.) Effect of Addition of Bases :-

$$[H_3O^+] = \frac{10^{-14}}{[\bar{O}H]}$$

K_w will remain same

3.) Effect of Addition of Acid :-

$$[\bar{O}H] = \frac{10^{-14}}{[H_3O^+]}$$

K_w will remain

$\text{pH} \approx$

For dil. Solutions, [i.e. $[H^+] < 1M$]

$$\text{pH} = -\log_{10} [H^+]$$

* On increasing temp. pH scale shortens

- At 298 K pH scale \rightarrow 0 to 14
- At 283 K pH scale \rightarrow 0 to 15
- At 233 K pH scale \rightarrow 0 to 13
- At 210 K pH scale \rightarrow 0 to 13.6

M-I⁺ If $[H^+]$ _{acid} $< 10^{-6} M$ then

$[H^+]$ _{water} $= 10^{-7} M$, cannot be neglected

For calculation of pH of strong acid / bases

$$pOH = -\log [\bar{O}H]$$

$$pK_w = -\log K_w$$

$$pH = 14 - pOH$$

$$pK_w = 14$$

Salt Hydrolysis

1) Salt of strong acid & strong base

Soln. of strong acid & strong base is neutral in nature.

2) Salt of weak acid & strong base

$$K_h = \frac{Ch^2}{1-h} \quad \text{If } h \ll \ll 1$$

$$1-h \approx 1$$

Step 1 →
ESTIMATE

$$\text{So, } K_h = C h^2$$

degree of hydrolysis

$$h = \sqrt{\frac{K_h}{C}}$$

Anion hydrolysis
Sln. is basic in nature

Step 2 →

$$\frac{K_h}{K_w} \times K_a = 1$$

$$K_h = \frac{K_w}{K_a}$$

Step 3 →

$$pH = 7 + \frac{1}{2} [pK_a + \log_{10} C]$$

3) Salt of Strong acid & Weak Base

$$K_h = \frac{K_w}{K_b}$$

$$h = \sqrt{\frac{K_h}{C}}$$

Cation hydrolysis
Sln. is acidic

$$pH = 7 - \frac{1}{2} [pK_b + \log_{10} C]$$

4) Salt of Weak acid & Weak Base

$$h = \sqrt{K_h}$$

$$\frac{K_h}{K_w} \times K_a \times K_b = 1$$

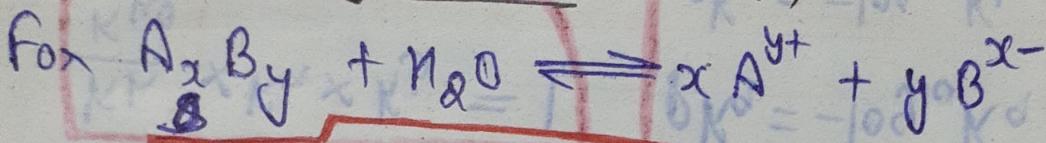
$$pK_a = -\log_{10} K_a$$

$$pK_b = -\log_{10} K_b$$

$$pH = 7 + \frac{1}{2} (pK_a - pK_b)$$

- If $K_a > K_b \Rightarrow$ soln. acidic in nature
- If $K_a < K_b \Rightarrow$ soln. basic in nature

Solubility Product (K_{sp})



$$K_{sp} = x^x y^y S^{x+y}$$

S is molec
dissociated

(S = molar
solubility)

$$K_{sp} = [A^{y+}]^x [B^{x-}]^y$$

Applicable for
saturated soln.

K_{ip} = ionic product

$$= [A^{y+}]^x [B^{x-}]^y$$

Applicable
for any
solution

If :-

- $K_{ip} < K_{sp} \Rightarrow$ solution is not saturated [ppt. not formed]
- $K_{ip} = K_{sp} \Rightarrow$ solution is saturated [ppt. not formed]
- $K_{ip} > K_{sp} \Rightarrow$ solution is supersaturated [ppt. will be formed]

* Higher the difference b/w K_{ip} & K_{sp} , faster is the precipitation

ESTIMATE

Common ion effect in

Just for e.g.
may be any other ion

Salt S

$$[\text{Cl}^-]_{\text{strong}} = [\text{Cl}^-]_{\text{total}}$$

pH of mixture of ^{Two} strong Acid/Base

- 1) Find summation of gm equivalents
- 2) Find N of H^+ = $\frac{\text{gm equi.}}{\text{Total vol. (L)}}$
- 3) Find M = $\frac{N}{\text{nf}} = [\text{H}^+]$
- 4) $\text{pH} = -\log_{10} [\text{H}^+]$

pH of mixture of 2 strong acid & 1 str. base

Step 1 \rightarrow

$$\text{gm equi. left} = \text{gm equi. of acid} - \text{gm equi. of base}$$

Step 2 \rightarrow

$$N_{\text{H}^+} \text{ or } N_{\text{OH}^-} = \frac{\text{gm equi. left [of } [\text{H}^+] \text{ or } [\text{OH}^-] \text{]}}{\text{Total vol. (L)}}$$

Step 3 \rightarrow $M = N = [\text{H}^+]$

$$\text{So, } \text{pH} = -\log_{10} [\text{H}^+]$$

pH of Strong acid & Weak acid

$$pH = -\log_{10} [H^+]_{\text{Strong}}$$

Buffer Solution

→ soln. which resist the change in its pH

* Acidic Buffer

Mixture of weak acid & salt of weak acid with strong base

pH of ~~weak~~ acidic buffer,

$$pH = pK_a + \log_{10} \frac{[\text{Salt}]}{[\text{Acid}]}$$

Range of a buffer →

$$pH = pK_a \pm 1$$

* Basic Buffer \Leftrightarrow mixt. of weak base & salt of weak base with strong acid.

$$pOH = pK_b + \log_{10} \frac{[\text{Salt}]}{[\text{Base}]}$$

$$\text{then } [pH = 14 - pOH]$$

ESTIMATE

Buffer Capacity

Buffer Capacity (ϕ) =

$$\phi = \frac{\text{No. of moles of acid or base added to 1L of soln}}{\text{Change in pH}}$$

Tonicity of Equilibrium



If we incre. the conc. of product, rxn. shifted toward

backward.

- If we incre. the conc. of reactants, rxn. shifted towards forward.
- If we decr. the conc. of products, rxn. shifted towards forward.
- If we decr. the conc. of reactants, equilibrium shifted towards backward.

Effect of Temperature

(i) For Endothermic Rxn. ($\Delta H = +ve$)

- If we incrs. the temp., equi. will shift towards forward rxn.
- ESTIMATE

- If we decrs. the temp., equi. will shift towards backward rxn.

(ii) For exothermic Rxn. ($\Delta H = -ve$)

- If we incrs. the temp., then equi. will be shifted towards backwards.
- If we decrs. the temp., then equi. will be shifted towards forward

Effect of Pressure

- If we incrs. the pressure, equilibrium will shift towards lesser number of gaseous molecules

Effect of addition of Inert Gas

- (i) At Const. Volume \rightarrow No effect on equilibrium

- (ii) At Const. Pressure \rightarrow Equilibrium will shift towards greater no. of gaseous molecules