

ELECTROCHEMISTRY. PART I : IONIC EQUILIBRIUM

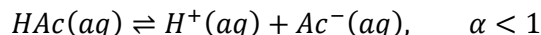
Introduction:

Electrolytes are chemical substances which in fused state or in aqueous solution can conduct electricity. This is due to the fact that they are partially or completely dissociated into ions and ions are responsible for conducting electricity through the solutions. These substances are also decomposed by passing electricity through its aqueous solution. This is why ions are called current carriers.

Water is unique solvent and we use always it as solvent if otherwise is not mentioned.

The electrolytes, which are completely dissociated in aqueous solutions, are called **strong electrolytes**. The degree of dissociation i.e. fraction of molecules dissociated (α) is one for strong electrolytes.

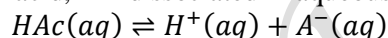
Those electrolytes (generally organic acids and bases) which are partially dissociated ($\alpha < 1$) in aqueous solution are called **weak electrolytes**; the dissociated ions remain in equilibrium with the undissociated neutral molecules. Such as acetic acid dissociated as hydrogen ion and acetate ion in aqueous solution and the dissociated ions are in equilibrium with the undissociated molecules:



This is called **ionic equilibrium**. This ionic equilibrium has the criteria similar to the chemical equilibrium. Laws of chemical equilibrium are equally applicable to the ionic equilibrium also. The law of mass action could be applied to the ionic equilibrium and similar equilibrium constant is also obtained. Dependence of these equilibrium constants with temperature also follow the van't Hoff equation.

Oswald's dilution law:

Let us take a weak acid, HA dissociated in aqueous solution as



Let c (M) conc. of HA is taken initially and α is the degree of dissociation at this conc. When equilibrium is attained, the conc. of the species at that state are: $[HA] = c(1 - \alpha)$, $[H^+] = \alpha c$ and $[A^-] = \alpha c$.

When the mass action law is applied to this ionic equilibrium, the expressions of equilibrium constant, called **dissociation constant** of the acid (K_a) is:

$$K_a = \frac{a_{H^+} \times a_{A^-}}{a_{HA}}, \quad \text{where } a \text{'s are the equilibrium activities of the species in solution.}$$

Converting into conc. terms, we have, $K_a = \frac{[H^+] \times [A^-]}{[HA]} \times \frac{f_{H^+} \times f_{A^-}}{f_{HA}}$ where f 's are the molar scale activity

coefficients and $[]$ are molar conc. terms. $f_{HA} = 1$ since HA are neutral molecules and behave ideal in solution.

Therefore, $K_a = \frac{[H^+] \times [A^-]}{[HA]} \times f_{\pm}^2$, where f_{\pm} is the mean ionic activity coefficient and $f_{\pm}^2 = f_{H^+} \times f_{A^-}$.

Since the acid is very weak and is dissociated to a small extent, the interionic Coulombic attraction of the ions is negligible and the whole solution is assumed to behave ideal and $f_{\pm} = 1$.

Therefore, the expression of dissociation constant of the weak acid in ideal solution is

$$K_a = \frac{[H^+] \times [A^-]}{[HA]} = \frac{\alpha c \times \alpha c}{c(1 - \alpha)} \quad \text{or,} \quad K_a = \frac{\alpha^2 c}{(1 - \alpha)}$$

Determination of degree of dissociation (α):

This expression is useful to calculate K_a of the weak electrolyte since the degree of dissociation (α) can be experimentally determined mainly by conductance measurements, $\alpha = \lambda_c / \lambda_0$, where λ_c and λ_0 are the equivalent conductance of the solution at the conc. c (M) and at infinite dilution respectively. However, α can also be determined from the colligative properties of the solution using van't Hoff 'i' factor, $i = 1 + (n - 1)\alpha$, where n is the number of ions produced from the dissociation of one molecule of the electrolyte and

$$i = \frac{\text{observed colligative property}}{\text{calculated colligative property}} \quad \text{and thus} \quad \alpha = \frac{i - 1}{n - 1}$$

The dilution law:

K_a is constant of the weak acid at a given temperature. Thus at a given temperature, if conc. (c) of the solution is decreased, $\alpha^2/(1-\alpha)$ is to be increased to keep K_a constant. This means that if the solution of a weak electrolyte is diluted at a given temperature, the degree of dissociation (α) is enhanced.

This is called Oswald's dilution law.

Approximate expression of the law:

Again, the equation can be written as: $\alpha^2 c = K_a (1-\alpha)$. This implies that when the solution is infinitely diluted, $c \rightarrow 0$, the degree of dissociation, $\alpha \rightarrow 1$. This suggests that weak electrolyte is completely dissociated when the solution is infinitely diluted.

In moderately concentrated solution the degree of dissociation, $\alpha \ll 1$ as the electrolyte is feebly dissociated.

Thus the above equation reduces to $K_a = \alpha^2 c$ or, $\alpha = \sqrt{K_a/c}$, α is increased with lowering of c .

Conc. of hydrogen ion, $[H^+]$ in solution:

From the expression, we have $[H^+] = \alpha \times c = \sqrt{\frac{K_a}{c}} \times c = \sqrt{K_a \times c}$. This shows that though α is increased but $[H^+]$ is decreased with the dilution of the solution. This suggests that decrease of conc. c is more dominating than the increase of α with dilution of the solution.

Temperature-dependence of α :

Since K_a is equilibrium constant hence it varies with temperature according to the van't Hoff isochore. The dissociation process is endothermic always so with rise of temperature, K_{diss} value is increased and thereby α is also increased accordingly. The van't Hoff equation at two temperatures is given as:

$$\ln \frac{K_2}{K_1} = \frac{\Delta H}{R} \left(\frac{T_2 - T_1}{T_2 T_1} \right), \text{ where } K_2 \text{ and } K_1 \text{ are the dissociation constants at temperatures, } T_2 \text{ and } T_1$$

respectively and ΔH is the enthalpy of dissociation of the weak electrolyte in solution.

Problem: A decinormal solution of acetic acid is ionized to the extent of 1.3%. Find the ionization constant of acetic acid. How does the extent of ionization change as the temperature is increased?

[Burdwan Univ. 1996]

Solution: 1st part: $K_a = \alpha^2 c / (1-\alpha)$, K_a is dissociation constant of acetic acid. Given, $\alpha = 0.013$ and $c = 0.1$ (N) = 0.1 (M), since for uni-univalent electrolyte, normality and molarity are same.

$$\text{Putting the values, we get } K_a = \frac{(0.013)^2 \times 0.1}{1-0.013} = 1.78 \times 10^{-5}.$$

2nd part: See the text above. With increase of temperature, α is increased from value of 1.3%.

Problem: A weak acid, HA has K_a of 1.00×10^{-5} . If 0.100 mole of this acid is dissolved in one liter of water, the percentage of acid dissociated at equilibrium is closed to

(A) 0.100% (B) 1.00% (C) 99.0% (D) 99.9% (E) 100% [GRE Sample Question]

Answer: $\alpha = \sqrt{\frac{K_a}{c}} = \sqrt{\frac{1.00 \times 10^{-5}}{0.100}} = 1.0 \times 10^{-2} = 1.0\%$. So the option (B) is correct.

pK_w of aqueous solution:

Water is poor conductor of electricity and it is feebly dissociated into H^+ and OH^- as $H_2O \rightleftharpoons H^+ + OH^-$. Since most ionic equilibria are studied in aqueous solutions, so H^+ ion plays an important role in controlling

the factor of the equilibria. The equilibrium constant, called dissociation constant of water, $K_d = \frac{a_{H^+} \times a_{OH^-}}{a_{H_2O}}$.

Assuming the system as ideal due to negligible interionic interaction, we can write $K_d = \frac{[H^+][OH^-]}{[H_2O]}$.

$[H_2O]$ remains practically constant and so, $[H^+][OH^-] = K_d \times [H_2O] = K_w$, called ionic product of water.

$[H_2O] = 1000 \text{ gm lit}^{-1} / 18 \text{ gm mol}^{-1} = 55.5 \text{ (M)}$ and $K_w = 1.0 \times 10^{-14}$ at 25 °C. K_d has thus the value of

$K_d = \frac{1.0 \times 10^{-14}}{1000/18} = 1.8 \times 10^{-16}$. It is constant at a given temperature. Thus, the ionic product of water,

$$K_w = [H^+][OH^-].$$

In pure water, $[H^+] = [OH^-]$ and so, $[H^+] = [OH^-] = \sqrt{K_w} = \sqrt{1.0 \times 10^{-14}} = 10^{-7} \text{ (M)}$

Therefore, at 25 °C, in pure water, $\text{pH} = -\log [H^+] = -\log 10^{-7} = 7$.

In general, the symbol $\text{pb} = -\log b$, where b is some physical quantity.

Thus, $\text{pOH} = -\log [OH^-]$, $\text{p}K_a = -\log K_a$, $\text{p}K_b = -\log K_b$, etc.

The above expression of K_w is written as $(-\log [H^+]) + (-\log [OH^-]) = (-\log K_w)$

$$\text{or, pH} + \text{pOH} = \text{p}K_w.$$

At 25 °C, $K_w = 1.0 \times 10^{-14}$ and so, $\text{p}K_w = 14$, and hence $\text{pH} + \text{pOH} = 14$.

According to Arrhenius concept of acids and bases, an acid is a substance which increases H^+ ion conc. and a base that increases OH^- ion conc. in water.

Thus in a neutral aqueous solution, $[H^+] = [OH^-] = 10^{-7} \text{ (M)}$ and so, $\text{pH} = \text{pOH} = 7$.

In acid solution, $[H^+] > 10^{-7} \text{ (M)}$ and $[OH^-] < 10^{-7} \text{ (M)}$, so $\text{pH} < 7$ and $\text{pOH} > 7$.

In alkali solution, $[H^+] < 10^{-7} \text{ (M)}$ and $[OH^-] > 10^{-7} \text{ (M)}$, so $\text{pH} > 7$ and $\text{pOH} < 7$.

In aqueous solution, $\text{pH} + \text{pOH} = \text{p}K_w$ is always valid. Thus if pH is increased in a solution, pOH is correspondingly decreased.

pH Scale: S P L Sorensen, a Danish Chemist (1868 – 1935) introduced a scale called pH scale to express the H^+ ion concentration specially when its value is very low of the order of 10^{-1} M to 10^{-14} M . It is defined as

$$\text{pH} = -\log a_{H^+} \text{ or, } a_{H^+} = 10^{-\text{pH}}, \text{ where } a_{H^+} = \text{activity of } H^+ \text{ ion in solution} = [H^+] \times f_{H^+}.$$

However, the solution is very dilute so assumed ideal and $f_{H^+} = 1$. Replacing activity by molar conc. we have

the definition, $\text{pH} = -\log [H^+] \text{ or, } [H^+] = 10^{-\text{pH}}$.

Thus, for $[H^+] = 10^{-3} \text{ M}$, the $\text{pH} = 3$ and for $[H^+] = 10^{-4}$, the $\text{pH} = 4$. The PH is increased by one unit for ten-times dilution of H^+ ion conc. of the solution. Conc. is expressed in mole/liter. One benefit of using pH scale is that trouble of using (– ve) power of ten is avoided for low conc. of H^+ ion.

The effective range of the pH scale may be set to as follows; for a solution of 1 mole of H^+ ions per liter, the $\text{pH} = -\log 1 = 0$. For a solution containing one mole of OH^- ion per liter, $[H^+]$ is calculated from the ionic product of water. At 25 °C, $K_w = [H^+] \times [OH^-] = 10^{-14}$ so $[H^+] = 10^{-14} \text{ M}$ and its $\text{pH} = 14$.

The value of K_w thus puts a practical limit to the pH scale – between 0 to 14 with a neutral solution at the mid-point at $\text{pH} = 7$ at 25 °C.

Calculation of pH of some solutions:

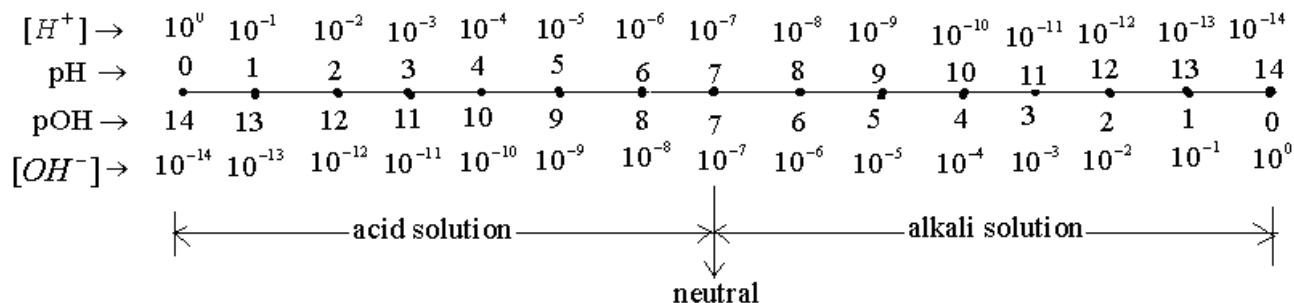
(i) For 0.002(M) HCl solution: Since HCl is strong electrolyte and completely dissociated, so

$$[H^+] = [HCl] = 0.002 \text{ (M)} = 2 \times 10^{-3} \text{ (M)}. \text{ pH} = -\log [H^+] = -\log (2 \times 10^{-3}) = 3 - \log 2 = 2.7$$

(ii) For 0.002 (M) H_2SO_4 solution, $[H^+] = 2[H_2SO_4] = 2 \times 0.002 \text{ (M)}$ so $\text{pH} = -\log [H^+] = -\log (4 \times 10^{-3}) = 2.4$.

- (iii) For 0.002 acetic acid solution, $[H^+] = \sqrt{K_a \times [HAc]} = \sqrt{2 \times 10^{-5} \times 0.002} = 2 \times 10^{-4} (M)$,
 since, K_a of acetic acid = 2×10^{-5} at $25^\circ C$. Thus $pH = -\log [H^+] = -\log(2 \times 10^{-4}) = 3.7$.

The pH scale in aqueous solution at $25^\circ C$, is given below:



Effect of Temperature on pH:

Dissociation of water is an endothermic process and hence K_w is increased with rise in temperature. Since K_w is also equilibrium constant so it obeys van't Hoff isochore quantitatively for its temperature-dependency.

$$\ln \frac{K_w(T_2)}{K_w(T_1)} = \frac{\Delta H}{R} \left(\frac{T_2 - T_1}{T_2 T_1} \right), \text{ where } \Delta H \text{ is enthalpy of dissociation and it is always (+ve).}$$

Thus, if $pH = 7$ for pure water at $25^\circ C$, then $pH < 7$ at temperature higher than $25^\circ C$. If say, $K_w = 10^{-12}$ at $50^\circ C$ then $pK_w = 12$ and for pure water at $50^\circ C$, $pH = 6$ and it becomes the neutral point. The pH scale is changed and at $50^\circ C$, it is 0 to 12 with neutral point at $pH = 6$. It does not mean that at higher temperature than $25^\circ C$, pure water becomes acidic. Since $[H^+] = [OH^-]$ so it remains neutral.

Accurate calculation of pH when $[H^+]$ is comparable to $10^{-7} (M)$:

Problem: Calculate the pH of a $10^{-8} (M)$ HCl solution.

Solution: Since $[H^+]$ from the acid is comparable to that from the dissociation of water, the latter is to be taken into account for calculation of pH. It is wrong to state the $pH = 8$, since this assumes the contribution of H^+ ion from acid only, whereas contribution of H^+ ion from H_2O is greater than this.

$$pH = -\log([H^+]_{acid} + [H^+]_{water}) = -\log(10^{-8} + 10^{-7}) = -\log(1.1 \times 10^{-7}) = 6.96.$$

More accurate calculation could be done if common ion effect of H^+ ion is considered.

H^+ ion is generated by both H_2O and HCl. Water is weak acid and its dissociation is affected by the H^+ ion from the acid. Let the dissociation of water in presence of HCl is $H_2O \rightleftharpoons H^+ + OH^-$ with $[OH^-] = x$.

The total conc. of H^+ ion in the acid solution = $(x + 10^{-8})$. Since in aqueous solution, $[H^+][OH^-] = K_w$,

hence, $(x + 10^{-8}) \times x = 10^{-14}$ at $25^\circ C$. Or, $x^2 + 10^{-8}x - 10^{-14} = 0$ or, $x = [OH^-] = 9.5 \times 10^{-8} (M)$.

$$[H^+] = 9.5 \times 10^{-8} + 10^{-8} = 10.5 \times 10^{-8} (M). \text{ Hence, } pH = -\log(10.5 \times 10^{-8}) = 6.9778.$$

Problem: Justify or criticize the following statement: For an infinitely dilute acid solution, $pH = \infty$.

[Burdwan Univ. 1992]

Answer: For very dilute acid solution, $[H^+]$ from dissociation of water has to be included in the calculation of pH.

Thus $pH = -\log\{[H^+]_{acid} + [H^+]_{water}\}$. For infinite dilute acid solution, $[H^+]_{acid} \rightarrow 0$ and

$[H^+]_{water} \approx 10^{-7} (M)$. So, $pH \approx -\log\{0 + 10^{-7}\} \approx 7$.

Buffer solution:

Buffer solutions are useful when pH is required to be kept reserved during a chemical reaction.

Definition:

These solutions possess the capacity to reserve acidity or alkalinity in spite of the addition of small amount of strong acid or base. These solutions are called buffer solutions or simply buffers. They can resist the appreciable change of pH and keep pH nearly constant though small amount of strong acid or base is added.

Compositions of buffer solution: Buffer solutions consist of large amount of either weak acid and its salt or weak base and its salt. Thus, these are of two types:

(a) Acid buffer: It is a mixture of weak acid and its salt such as, acetic acid and sodium acetate.

(b) Alkali buffer: It a mixture of weak base and its salt such as ammonium hydroxide and ammonium chloride.

Illustration: If one drop (0.05 cc) of conc. HCl (12 N) added to 1 liter pure water, its pH changes from 7 to 3.

But if the same amount of acid is added to 1 liter of buffer solution containing 0.1(M) HAc and 0.1(M) NaAc of pH 4.73, the pH of the solution remains practically same at 4.73.

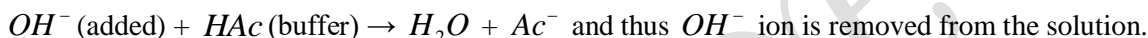
Mechanism of buffer action:

The buffer solution maintains steady pH by adjusting equilibrium between weak acid or weak base and its conjugated ion provided by the salt. Let us take the example of an acid buffer consisting of HAc and NaAc.

(a) If small amount of strong acid is added to the above buffer, the following reaction occurs.



(b) If small amount of strong alkali added,



This is called **buffer action**. However, a salt of weak acid and weak base in solution can alone act as buffer.

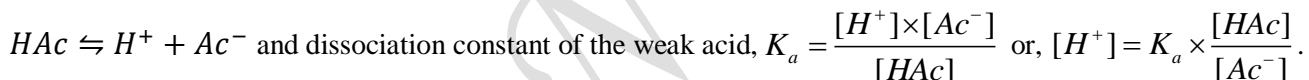
The buffer action of NH_4Ac can be given as illustration. In aqueous solution, NH_4Ac remains as NH_4^+ and OH^- ions.



Thus, adjusting equilibrium, added H^+ or OH^- is removed from the solution. Similarly, KHF_2 can also act as buffer, as it is the combination of weak acid HF and its salt KF.

pH of Buffer solution:

Let us take an acid buffer of HAc and NaAc. The weak acid HAc dissociates and attains equilibrium as



The pH of the buffer solution is then $pH = -\log[H^+] = -\log \frac{K_a \times [HAC]}{[Ac^-]}$ or, $pH = -\log K_a - \log \frac{[HAC]}{[Ac^-]}$.

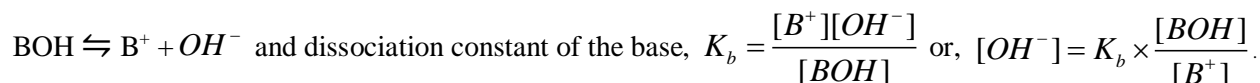
$$\text{or, } pH = pK_a + \log \frac{[Ac^-]}{[HAC]}.$$

Material balance shows that $[Ac^-] = [salt] + [H^+]$, since Ac^- accumulates from complete dissociation of the salt and from partially dissociation of HAc that is equal to $[H^+]$. Similarly, $[HAC] = [acid] - [H^+]$, where $[acid]$ = initial conc. of HAc and $[H^+]$ which is dissociated from HAc.

$$\text{Therefore, } pH = pK_a + \log \frac{[salt] + [H^+]}{[acid] - [H^+]}.$$

Since acid is weak electrolyte and dissociated in small extent specially in presence of common ion, Ac^- , we can write for acid buffer solution, $pH = pK_a + \log \frac{[salt]}{[acid]}$ since, $[salt] \gg [H^+]$ and $[acid] \gg [H^+]$.

Similarly, alkali buffer solution contains weak base BOH and its salt B^+ . The weak base dissociates as



or, $pOH = pK_b + \log \frac{[B^+]}{[BOH]}$. But, $[B^+] = [salt] + [OH^-]$ and $[BOH] = [base] - [OH^-]$.

The weak base is very feebly dissociated especially in presence of common B^+ ion and so $[base] \gg [OH^-]$ and $[salt] \gg [OH^-]$.

Therefore, the equation for alkali buffer solution, $pOH = pK_b + \log \frac{[salt]}{[base]}$.

Since, $pH = pK_w - pOH$ so for alkali buffer, $pH = (pK_w - pK_b) - \log \frac{[salt]}{[base]}$.

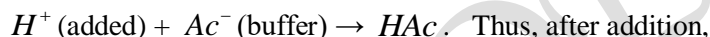
These are called Henderson equations and are widely used to calculate the pH of the buffer solutions.

Problem(1): What will be the pH of a buffer solution containing 0.06 mol acetic acid and 0.04 mole of Na-acetate per liter? Calculate the change in pH resulting from the addition of (a) 0.015 mol of a strong acid and (b) 0.03 mol of a strong base per liter of the buffer solution? (Given, pK_a of acetic acid = 4.76).

[Calcutta Univ. 1989]

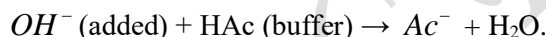
Solution: The Henderson equation for acid buffer is, $pH = pK_a + \log \frac{[salt]}{[acid]} = 4.76 + \log \frac{0.04}{0.06} = 4.54$.

(a) When 0.015 mol of strong acid is added to the above buffer, the following change takes place:



$$pH = 4.76 + \log \left(\frac{0.04 - 0.015}{0.06 + 0.015} \right) = 4.28, \text{ so change in pH of the buffer} = 4.54 - 4.28 = 0.26.$$

(b) When 0.03 mol of a strong base is added to the buffer of pH = 4.54, following change occur:



$$\text{After addition, } pH = 4.76 + \log \left(\frac{0.04 + 0.03}{0.06 - 0.03} \right) = 4.65, \text{ the change in pH of the buffer} = 4.65 - 4.54 = 0.09.$$

Problem(2) An artificial soft drink contains 11.0 g / L of tartaric acid $C_4H_6O_6$ and 20 g / L of its potassium salt $C_4H_5O_2K$. What is the pH of the drink? (Given K_a of tartaric acid = 1.0×10^{-3})

(A) 4.24 (B) 5.21 (C) 3.82 (D) 3.16 [TIFR adm. to M Sc, 2014]

Answer: (D)

Problem (3) 0.050 mol of acetic acid and 0.20 mol of sodium acetate are mixed and total volume is adjusted to 500 ml in water. The pK_a for acetic acid (CH_3COOH) is 4.75. If now 0.010 mol of NaOH is added to the above mixture, what will the final pH of the solution be?

(A) > pH 7 (B) pH will stay at 4.75 because it is buffer solution (C) > pH 4.75 (D) not sufficient information has been given. [TIFR adm. to M Sc, 2014]

Answer: [C].

Problem (4): The pH of blood stream is maintained by a proper balance of H_2CO_3 and $NaHCO_3$ concentration.

What volume of 5 M $NaHCO_3$ solutions should be mixed with a 10 ml sample of blood which is 2M in H_2CO_3 in order to maintain a pH of 7.4? K_a for H_2CO_3 in blood is 7.8×10^{-7} . [2]

[IIT'93/B.Tech/Entrance test]

Solution: Henderson equation, $pH = pK_a + \log \frac{[salt]}{[acid]}$ or, $\log \frac{[salt]}{[acid]} = pH - pK_a = 7.4 - (-\log 7.8 \times 10^{-7}) = 1.3$

$$\text{or, } \frac{[salt]}{[acid]} = 20. \text{ Now, 10ml of 2M } H_2CO_3 \text{ contains } \frac{2 \times 10}{1000} \text{ mol} = 0.02 \text{ mol.}$$

Hence salt i.e. $NaHCO_3$ requires $20 \times 0.02 = 0.4$ moles and this contains in $\frac{1000}{5} \times 0.4 \text{ ml} = 80 \text{ ml}$

i.e. 80ml of 5(M) $NaHCO_3$ should be mixed with 10ml sample of blood to maintain pH = 7.4.

Buffer capacity (β):

The efficiency of a buffer action to resist the change in pH on the addition of small amount of strong acid or base is quantitatively expressed by a term, called buffer capacity (β). It is defined as:

$$\beta = \frac{db}{d(\text{pH})} \quad \text{or, } \beta = -\frac{da}{d(\text{pH})},$$

where db or da is the moles of base or acid added to one liter of solution to change the pH of buffer by unity. Thus buffer capacity is defined as the number of moles of acid or base that changes the pH of the buffer solution by one unit. Higher the value of buffer capacity better is the buffer.

The buffer capacity (β) can be estimated from the plot of pH vs. moles of alkali added (b) to the weak acid in the neutralization curve, the slope of the curve is $\left[\frac{d(\text{pH})}{db} \right]$. The buffer capacity, β is reciprocal of the slope.

Greater the slope less is the value of β . Thus at the equivalence point of the solution, the slope is maximum and so buffer capacity is minimum.

When the weak acid is half-neutralized, the slope is minimum and so buffer capacity is maximum. It can be shown also by mathematics. Thus, when $[\text{salt}] = [\text{acid}]$ or $\frac{[\text{salt}]}{[\text{acid}]} = 1$ in the buffer, it shows maximum value of β and the

buffer becomes maximum efficient in resisting the pH change. As the ratio, $[\text{salt}] / [\text{base}]$ changes from unity in either direction, the buffer capacity decreases. It is generally observed that buffer acts good in the pH range $(\text{p}K_a - 1)$ to $(\text{p}K_a + 1)$. Hence different acids are used in the preparation of buffer mixture to cover a wide range of pH (1 to 14). Similarly, the buffer capacity is maximum, when $[\text{salt}] / [\text{base}] = 1$ for alkali buffer.

Mathematical interlude to show β is maximum when $[\text{salt}] = [\text{acid}]$ in acid buffer:

Let a be the initial conc. in molarity of weak acid HA and b be the amount of a strong monoacid base, MOH. The base is added to the acid during the titration of the weak acid. Let $a > b$ and so the mixture becomes buffer solution of weak acid and its salt, MA (which is fully dissociated in solution). As the base is added, composition of the buffer is being changed with the progress of titration. Thus, $[\text{salt}] = b$ and $[\text{acid}] = (a - b)$ in the mixture. The Henderson equation for this buffer is,

$$\text{pH} = \text{p}K_a + \log\left(\frac{b}{a-b}\right)$$

or, $\text{pH} = \text{p}K_a + \frac{1}{2.303} \ln\left(\frac{b}{a-b}\right)$, where K_a is the dissociation constant of the weak acid.

In the equation, b varies while a is constant.

Since b varies so pH of the buffer is also changed.

Differentiating with respect to b , we get

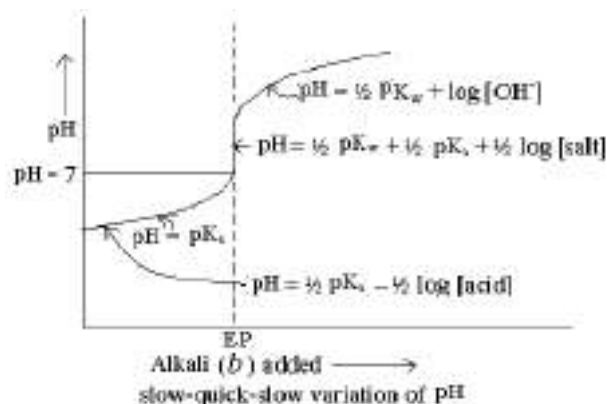
$$\frac{d(\text{pH})}{db} = 0 + \frac{1}{2.303} \left(\frac{1}{b} + \frac{1}{a-b} \right) = \frac{1}{2.303} \left(\frac{a}{b(a-b)} \right).$$

$$\text{Therefore, } \beta = \frac{db}{d(\text{pH})} = \frac{2.303b(a-b)}{a}.$$

Now to show β maximum at a certain value of b , the above equation is differentiated with respect to b and we get

$$\frac{d\beta}{db} = \frac{2.303}{a} (a - 2b). \text{ For the extreme value of } \beta \text{ at a given value of } b, \text{ we have } \frac{d\beta}{db} = 0 \text{ and so}$$

$$\frac{2.303}{a} (a - 2b) = 0 \text{ or, } a - 2b = 0 \text{ or, } b = \frac{a}{2}.$$



This implies that β attains extreme value when the weak acid is half-neutralised i.e., when $[\text{salt}] = [\text{acid}]$

Again, $\frac{d^2\beta}{db^2} = -\frac{2.303 \times 2}{a} = (-ve)$ and so β attains maximum at the half-neutralization point, $b = \frac{a}{2}$.

β_{\max} is obtained by putting $b = \frac{a}{2}$ in the expression of $\beta = \frac{2.303b(a-b)}{a}$ and we get, $\beta_{\max} = \frac{2.303a}{4}$.

This shows β_{\max} is independent of nature of the weak acid used in the buffer as β_{\max} does not contain K_a .

Thus, for acetic acid – acetate buffer, β is maximum at $\text{pH} = \text{p}K_a = 4.73$ at 25°C .

Similarly, for alkali buffer, let in b mole of weak base, a mole of strong monobasic acid is added in one liter solution such that $b > a$. Then it becomes an alkali buffer solution in which a is varying but b remains fixed.

The Henderson equation for alkali buffer, $\text{pH} = (\text{p}K_w - \text{p}K_b) - \log \frac{[\text{salt}]}{[\text{base}]} = (\text{p}K_w - \text{p}K_b) - \frac{1}{2.303} \ln \frac{a}{b-a}$.

Or, $\frac{d(\text{pH})}{da} = 0 - \frac{1}{2.303} \left[\frac{1}{a} + \frac{1}{b-a} \right] = -\frac{1}{2.303} \left[\frac{b}{a(b-a)} \right]$ or, $\beta = -\frac{da}{d(\text{pH})} = \frac{2.303a(b-a)}{b}$.

Now, for extreme value of β , we have $\frac{d\beta}{da} = \frac{2.303}{b}(b-2a) = 0$ or, $a = \frac{b}{2}$. This also shows that when the weak

base is half-neutralised, buffer capacity attains maximum value. Thus, when alkali buffer contains equal amount of weak base and its salt, it has maximum capacity to resist the change of pH.

The maximum value of β is $\beta_{\max} = \frac{2.303b}{4}$. Again, β_{\max} does not depend on the nature of the base used in the buffer.

Effect of dilution and presence of inert ion on the pH of buffer:

If conc. terms are replaced by more accurate activity terms in the Henderson equation for acid buffer,

we have $\text{pH} = \text{p}K_a + \log \frac{a_{A^-}}{a_{HA}} = \text{p}K_a + \log \frac{[A^-]}{[HA]} + \log f_{A^-}$, since HA is a neutral molecule so, $f_{HA} = 1$ and f_{A^-} is

the activity coefficient of the salt, A^- . So more accurate Henderson equation is,

$$\text{pH} = \text{p}K_a + \log \frac{[\text{salt}]}{[\text{acid}]} + \log f_{A^-}.$$

When the buffer solution is diluted, ionic interaction decreases, the solution approaches to the ideality and f_{A^-} also approaches to the ideal value of one. Thus with dilution, pH of buffer solution increases slightly.

Again, when inert ions are added to the buffer, it becomes more non-ideal due to increased ion-interaction.

Value of f_{A^-} decreases and pH of the buffer solution decreases slightly.

Importance of buffer solution:

In analytical chemistry, many reactions are to be conducted within a narrow pH range. Buffer solutions are extensively used in these cases to maintain the desired pH range. Selective precipitation, solvent extraction or titration of a particular ion in a mixture is thereby made possible.

Buffer solutions are also widely useful in biological systems. Enzyme catalysed reactions are highly sensitive to pH change and effective pH range is maintained by buffer solutions. For example, pH of human blood is controlled within the range of 7.3 to 7.5 by buffering action of carbonic acid (H_2CO_3) and NaHCO_3 .

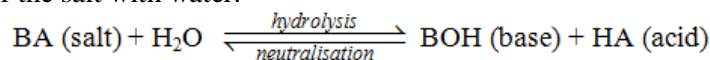
Hydrolysis and hydrolysis constant of salts:

Introduction:

It is interesting to find that an aqueous solution of a neutral salt does not show always neutral. For example, aqueous solution of sodium chloride, ammonium chloride and sodium acetate reacts neutral, acidic and alkaline respectively. These observations could be explained by a process, called **hydrolysis** or solvolysis in general.

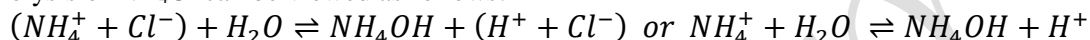
Definition of hydrolysis:

Formerly, hydrolysis was defined as the reverse process of neutralization of acid and base. It is the reaction of the salt with water.



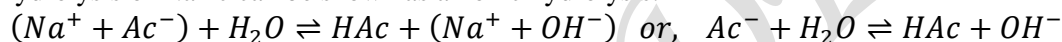
The nature of the salt solution is determined by the relative strengths of acid and base generated by hydrolysis. If acid is stronger than base then the salt solution shows acidic while if base be stronger than acid, then the salt solution shows alkaline and if both are of same strength, then it shows neutral.

Now it is considered that salt is strong electrolyte, it is completely dissociated in aqueous solution. Thus the hydrolysis of NH_4Cl can be viewed as follows:



The net reaction is the hydrolysis of cation only and this **cationic hydrolysis** produces free H^+ ion in the solution resulting acidic in nature. NH_4OH is a weak electrolyte and feebly dissociated especially in presence of NH_4^+ common ion. pH of this solution is thus less than 7.0 at 25 °C.

Similarly, the hydrolysis of NaAc can be shown as anionic hydrolysis:



Thus **anionic hydrolysis** increases the conc. of OH^- and so creating the solution alkaline. The pH of the solution has greater than 7.0 at 25 °C.

However, when NaCl reacts with water, it produces NaOH and HCl. Both are strong electrolytes and dissociated fully, resulting the net reaction $(\text{Na}^+ + \text{Cl}^-) + \text{H}_2\text{O} \rightleftharpoons (\text{Na}^+ + \text{OH}^-) + (\text{H}^+ + \text{Cl}^-)$ or, $\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$.

Since the solution contains equal conc. of H^+ and OH^- so the solution reacts neutral.

Type of salts:

Salts could be classified into four types on the basis of their origin of formation.

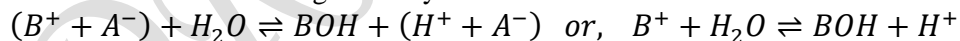
(A) Salt of strong acid and strong base (viz. NaCl):

These salts do not undergo hydrolysis and the aqueous solution thus shows neutral (pH = 7.0 at 25 °C).

Explanation is given as above.

(B) Salt of strong acid and weak base (viz. NH_4Cl):

If this type of salt is represented by BA, it undergoes cationic hydrolysis producing excess [H^+] in solution. Since salt and the acid are strong electrolytes so it reacts with water as:



If c is the initial salt conc. and x is the degree of hydrolysis at this molar conc., then equilibrium molar conc. of the species are $[\text{B}^+] = c(1-x)$, $[\text{BOH}] = xc$ and $[\text{H}^+] = xc$.

The equilibrium constant, here called **hydrolysis constant** of the salt (K_h) is defined as

$$K_h = \frac{[\text{BOH}][\text{H}^+]}{[\text{B}^+]} = \frac{xc \times xc}{c(1-x)} = \frac{x^2c}{1-x} \approx x^2c.$$

[Since the degree of hydrolysis is very small i.e. $x \ll 1$]. Accurate expression of K_h is in terms of activities. But assuming ideal behaviour, activities are replaced by conc. terms.

In the expression, $K_h = \frac{x^2c}{1-x}$, the hydrolysis constant (K_h) is constant for the salt at a given temperature.

Thus, the expression shows that as c decreases, x increases and $x \rightarrow 1$ as $c \rightarrow 0$.

There are other two equilibria existing in the solution.

(a) Weak base is dissociated as $BOH \rightleftharpoons B^+ + OH^-$, the dissociation constant of base $K_b = \frac{[B^+][OH^-]}{[BOH]}$

(b) Water is dissociated as $H_2O \rightleftharpoons H^+ + OH^-$, the ionic product of water, $K_w = [H^+][OH^-]$.

The relation between these three equilibrium constants is given as $K_h = \frac{K_w}{K_b}$ and $K_h = x^2c$.

Hence, $x^2c = \frac{K_w}{K_b}$ or, $(xc)^2 = \left(\frac{K_w}{K_b}\right) \times c$, but $xc = [H^+]$ hence, $[H^+] = \sqrt{\frac{K_w \times c}{K_b}}$.

This is the expression of $[H^+]$ in the salt solution. The pH of the solution can be obtained as

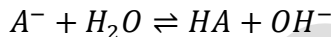
$$(-\log[H^+]) = \frac{1}{2}(-\log K_w) - \frac{1}{2}(-\log K_b) - \frac{1}{2}\log c \text{ or, } pH = \frac{1}{2}pK_w - \frac{1}{2}pK_b - \frac{1}{2}\log c.$$

But at 25 °C, $K_w = 1.0 \times 10^{-14}$ so, $pK_w = 14$. Thus, the expression of pH of this type of salt solution is

$$pH = 7 - \frac{1}{2}pK_b - \frac{1}{2}\log c. \text{ The salt solution is acidic and } pH < 7.0.$$

(C) Salt of weak acid and strong base (viz. CH_3COONa):

Anionic hydrolysis occurs producing excess conc. of OH^- in the salt solution.



The hydrolysis constant of the salt BA is $K_h = \frac{[HA][OH^-]}{[A^-]} = \frac{x^2c}{1-x}$ and $K_h = \frac{K_w}{K_a}$.

Using the similar process as above,

we have $[OH^-] = \sqrt{\frac{K_w \times c}{K_a}}$, or, $pOH = \frac{1}{2}pK_w - \frac{1}{2}pK_a - \frac{1}{2}\log c$,

but $pH + pOH = pK_w$ so $pH = \frac{1}{2}pK_w + \frac{1}{2}pK_a + \frac{1}{2}\log c$. At 25 °C, $pH = 7 + \frac{1}{2}pK_a + \frac{1}{2}\log c$.

The salt solution is alkaline and $pH > 7.0$. This is the expression of pH in this type of salt solution.

(D) Salt of weak acid and weak base (viz. CH_3COONH_4):

Both the cation and anion of the salt undergo hydrolysis in the aqueous solution.

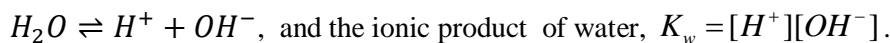
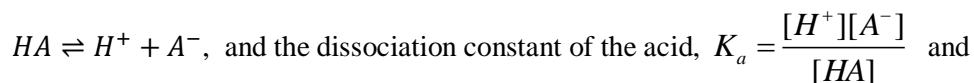
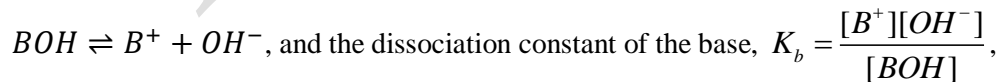


The nature of solution depends on the relative strength of BOH and HA.

The hydrolysis constant of the salt BA is $K_h = \frac{[HA][BOH]}{[B^+][A^-]} = \frac{xc \times xc}{(1-x)c \times (1-x)c}$ or, $K_h = \left(\frac{x}{1-x}\right)^2$.

The relation shows that degree of hydrolysis (x) is independent of salt solution (c).

Besides the above equilibrium, the solution contains three other equilibria as given below.



The relation among these four equilibrium constants is given as $K_h = \frac{K_w}{K_a \times K_b}$.

But pH of the solution is obtained from the H^+ dissociated from the acid HA.

$$[H^+] = K_a \times \frac{[HA]}{[A^-]} = K_a \times \frac{xc}{(1-x)c} = K_a \times \left(\frac{x}{1-x}\right) = K_a \sqrt{K_h} \quad \text{or, } [H^+] = K_a \sqrt{\frac{K_w}{K_a \times K_b}} = \sqrt{\frac{K_w \times K_a}{K_b}}$$

Thus, $pH = \frac{1}{2} pK_w + \frac{1}{2} (pK_a - pK_b)$ and at 25 °C, $pH = 7 + \frac{1}{2} (pK_a - pK_b)$.

Three cases may arise depending on the value of pK_a and pK_b

(1) When $pK_a = pK_b$ or, $K_a = K_b$, $pH = 7$ and the solution is neutral.

(2) when $pK_a < pK_b$ or, $K_a > K_b$, $pH < 7$ and the solution is acidic.

(3) When $pK_a > pK_b$ or, $K_a < K_b$, $pH > 7$ and the solution is alkaline.

It is interesting to note that pH of the solution does not depend on the conc. of the solution.

Problem: 20 ml of 0.1 N acetic acid is titrated against 0.1 N NaOH. Calculate the pH of the solution (i) at the start (ii) at the half neutralization point and (iii) at the equivalence point. (pK_a of acetic acid = 4.8).

[Calcutta Univ. 1990]

Solution: (i) $pH = \frac{1}{2} pK_a - \frac{1}{2} \log[acid] = \frac{1}{2} \times 4.8 - \frac{1}{2} \log(0.1) = 2.4 + 0.5 = 2.9$. (ii) $pH = pK_a = 4.8$.

(iii) $pH = 7 + \frac{1}{2} pK_a + \frac{1}{2} \log[salt] = 7 + \frac{1}{2} \times 4.8 - \frac{1}{2} \log\left(\frac{0.1}{2}\right) = 7 + 2.4 + \frac{1}{2} \times (-1.26) = 8.77$.

Solution is double diluted at the equivalence point and hence conc. of the salt in the solution becomes half.

Problem: Which of the following is correct when a solution is obtained by mixing 50.0 mL of 0.100 M HA and 50.0 mL of 0.100 M NaOH? [Graduate Record Exam. Sample Question]

I. Neutral if HA is a strong acid. II. Basic if HA is a weak acid. III. Neutral if HA is a weak acid.

(A) I only (B) II only (C) III only (D) I and II (E) I and III. [Answer (D)]

Indicators: acid-base and its function.

Titration is an operation forming the basis of volumetric analysis. Measured amount of a solution of one reagent from a burette (called titrant) is added to a definite amount of another reagent (titre) until the action between them is complete i.e. till the second reagent is completely used up.

Indicators are substances that identify the end point of the titration by their colour-change when they are added in small amount in the titre.

We shall here restrict our discussion for the acid- base titration only and the indicator is often called acid-base indicator. These are phenolphthalein, methyl red, methyl orange, thymolphthalein, etc.

When an acid is titrated by a base, a small amount of a suitable indicator is added to the acid. As the base is added from the burette, PH of the acid solution increases. At the PH of the equivalence point, the added suitable indicator changes its colour and thus indicates the end-point of the titration. This is why it is called indicator.

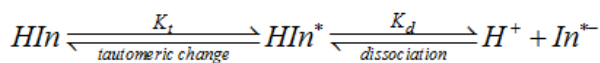
The PH at which the indicator changes its colour depends on the nature of the indicator. However, the PH of colour-change of the indicator depends slightly on temperature and also on the ionic strength of the acid solution. At the equivalence point, by using the relation $V_1 S_1 = V_2 S_2$, it is possible to calculate S_2 if S_1 is known or vice-versa.

Function of acid-base indicators:

Acid base indicators are either weak organic acids or bases. They dissociate partially in the titre (usually acid solution) and remains in two forms - ionized and unionized. These two forms have two different contrasting colours. The relative amount of the two forms depends on the pH of the titre solution. At the equivalence point of the titration, there occurs a sharp pH-jump and so the relative amount of the two forms of the indicator (which is added to the titre solution) changes abruptly. This change of pH results a colour change of the titre solution at the equivalence point and helps to detect the end-point.

Let us illustrate the functions of the indicator by taking the example of phenolphthalein.

This indicator is a weak organic acid and this undergoes the following changes as given below.



(keto form) (enol form)

Applying mass action law, we get the expression of the two equilibrium constants.

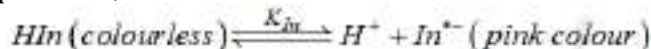
$$K_t = \frac{a_{HIn^*}}{a_{HIn}} \text{ and } K_d = \frac{a_{H^+} \times a_{In^{*-}}}{a_{HIn^*}}, \text{ thus } K_t \times K_d = K_{in} = \frac{a_{H^+} \times a_{In^{*-}}}{a_{HIn}}$$

other equilibrium constant, its value depends on temperature and not on individual activities.

When the activities are changed into conc. assuming ideal behaviour, the indicator constant,

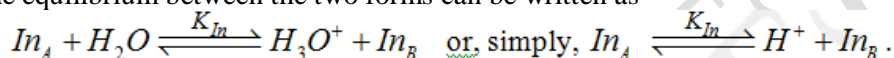
$$K_{in} = \frac{[H^+][In^{*-}]}{[HIn]} \text{ or, } [H^+] = K_{in} \times \frac{[HIn]}{[In^{*-}]} \text{ or, } pH = pK_{in} + \log \frac{[In^{*-}]}{[HIn]}$$

The situation appears like the equilibrium,



Similarly, methyl orange is weak organic base whose benzenoid form is yellow and quinonoid form is red.

In general, we can take an indicator (In) that has the acidic form In_A and the basic form In_B , and they are of different in colour. The equilibrium between the two forms can be written as



In acid medium when $[H^+]$ is high, the equilibrium remains in the left side and the indicator shows the colour of In_A (acid colour). In alkali medium when $[H^+]$ is low, the equilibrium remains in the right side and the indicator shows the colour of In_B (base colour).

$$\text{and the indicator constant is } K_{in} = \frac{[H^+][In_B]}{[In_A]} \text{ or, } [H^+] = K_{in} \times \frac{[In_A]}{[In_B]} \text{ or, } pH = pK_{in} + \log \frac{[In_B]}{[In_A]}$$

Human eye and colour change of the indicator:

The conc. ratio of In_B and In_A depends on pH of the solution and the nature of the indicator (pK_{in}). Colour of the indicator, as seen by the human eye is dependent on this ratio. The eye can recognize the colour of In_A when its conc. is

ten times at least greater than the conc. of In_B , i.e. $\frac{[In_A]}{[In_B]} \geq 10$. Thus, the pH of the solution when the indicator shows

acid colour (colour of In_A) is given by $pH = pK_{in} + \log \frac{1}{10}$ or, $pH = pK_{in} - 1$,

and for recognition of base colour of the indicator (colour of In_B), the ratio $\frac{[In_B]}{[In_A]} \geq 10$ and $pH = pK_{in} + 1$.

In brief, we can say that the indicator shows the acid colour at and below the pH of $(pK_{in} - 1)$ and base colour at and above the pH of $(pK_{in} + 1)$. In between the pH of $pK_{in} - 1$ to $pK_{in} + 1$, mixed colour of the indicator is seen.

So, pK_{in} of phenolphthalein is 9.6. Thus, in solution, phenolphthalein will remain colourless (acid colour) up to $pH = 8.6$ and it will show pink colour (base colour) above $pH = 10.6$.

Similarly, pK_{in} of methyl red is 5.1 hence in solution, it shows red (acid colour) up to 4.1 and yellow (base colour) above $pH = 6.1$.

It is evident that base colour dominates at higher pH and acid colour dominates at lower pH of the solution.

Acid base titration and choice of indicator:

When an acid is titrated with a base, the pH of the acid solution (titre) is changing. With the addition of base, the pH is increased slowly and at the equivalence point, there is quick rise of pH. After the equivalence point, again pH increases slowly. This slow-quick-slow variation of pH is the typical feature of logarithmic dependence. Exact calculation can show this trend of variation in the titration of 10 ml of 0.1 N acid with 0.1 N alkali in a burette.

Titration of strong acid by strong alkali

Alkali added	$[H^+]$	pH
0 ml	0.1 (M)	1.0
1.00 ml	$\frac{9}{11} \times 0.1 = 0.082$ (M)	$2 - \log 8.2 = 1.1$
5.0 ml	$\frac{5}{15} \times 0.1 = 0.033$ (M)	$2 - \log 3.3 = 1.5$
9.95 ml	$\frac{0.05}{19.95} \times 0.1 = 2.5 \times 10^{-4}$ (M)	$4 - \log 2.5 = 3.6$
10.0 ml	10^{-7} (M)	7.0
10.05 ml	$[OH^-] = \frac{0.05}{20.05} \times 0.1 = 2.5 \times 10^{-4}$ (M) or, $[H^+] = \frac{10^{-14}}{2.5 \times 10^{-4}} = 4.0 \times 10^{-11}$ (M)	$11 - \log 4.0 = 10.4$

This shows that pH-jump for the addition of 0.1 ml of NaOH near the equivalence point is 3.6 to 10.4.

Titration of weak acid by strong alkali

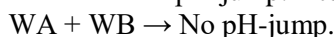
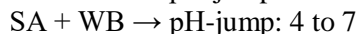
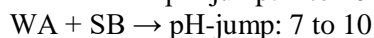
Alkali added	[acid]	[salt]	pH
0 ml	0.1 (M)	-	$\frac{1}{2} pK_a - \frac{1}{2} \log[HA] = 2.5 - \frac{1}{2} \log 0.1 = 3$
1.0 ml	$\frac{9}{11} \times 0.1$ (M)	$\frac{1}{11} \times 0.1$ (M)	$pK_a + \log \frac{[salt]}{[acid]} = 5.0 + \log \frac{1}{9} = 4.05$
2.0 ml	$\frac{8}{12} \times 0.1$ (M)	$\frac{2}{12} \times 0.1$ (M)	$pK_a + \log \frac{[salt]}{[acid]} = 5.0 + \log \frac{1}{4} = 4.4$
5.0 ml	$\frac{5}{15} \times 0.1$ (M)	$\frac{5}{15} \times 0.1$ (M)	$pK_a + \log \frac{[salt]}{[acid]} = 5.0 + \log 1 = 5.0$
6.0 ml	$\frac{4}{16} \times 0.1$ (M)	$\frac{6}{16} \times 0.1$ (M)	$pK_a + \log \frac{[salt]}{[acid]} = 5.0 + \log \frac{3}{2} = 5.2$
7.0 ml	$\frac{3}{17} \times 0.1$ (M)	$\frac{7}{17} \times 0.1$ (M)	$pK_a + \log \frac{[salt]}{[acid]} = 5.0 + \log \frac{7}{3} = 5.37$
8.0 ml	$\frac{2}{18} \times 0.1$ (M)	$\frac{8}{18} \times 0.1$ (M)	$pK_a + \log \frac{[salt]}{[acid]} = 5.0 + \log 4 = 5.6$
9.0 ml	$\frac{1}{18} \times 0.1$ (M)	$\frac{9}{18} \times 0.1$ (M)	$pK_a + \log \frac{[salt]}{[acid]} = 5.0 + \log \frac{9}{1} = 5.95$
9.95 ml	$\frac{0.05}{19.95} \times 0.1$ (M)	$\frac{9.95}{19.95} \times 0.1$ (M)	$pK_a + \log \frac{[salt]}{[acid]} = 5.0 + \log \frac{9.95}{0.05} = 7.1$
10 ml	-	0.05 (M)	$7 + \frac{1}{2} pK_a + \frac{1}{2} \log[salt] = 7 + 2.5 + \frac{1}{2} \log 0.05 = 8.85$
10.05 ml	-	$[base] = \frac{0.05}{20.05} \times 0.1 = 2.5 \times 10^{-4}$	$-\log[H^+] = \log \left(\frac{10^{-14}}{2.5 \times 10^{-4}} \right) = 10.4$

pH-jump in the titration of weak acid and strong base near the equivalence point occurs 7 to 10.

Similar calculation with strong acid by weak base shows that pH jumps from 4 to 7 near the equivalence point and there is practically no jump for titration with weak acid and weak base.

The neutralization curve with pH against amount of base added is given here.

The pH-jump at the neutralization point can be summarized as below:



Colour of an indicator changes at a certain range of pH of the solution. pH-range of colour change is

$pK_{in} - 1$ to $pK_{in} + 1$, so it depends on the nature of the indicator. The selection of indicator for the specific acid-base titration is such that pH-range of colour change of the indicator should match with the pH-jump of the titration.

Thus phenolphthalein ($pK_{in} = 9.6$) has pH-range of colour change from 8.6 to 10.6 and so this indicator is suitable for the titration of weak acid and strong base.

For the titration of strong acid and weak base, those indicators are suitable which changes their colour within pH-range 4 to 7. Methyl red ($pK_{in} = 5.1$), methyl orange ($pK_{in} = 3.7$) are suitable for the titration.

For the titration of strong acid and strong base, all indicators are suitable since pH jumps from 4 to 10 at the neutralization point and all indicators change their colour within this pH range.

However, no indicator is suitable for the titration of weak acid and weak base as there is no pH-jump occurs at the neutralization point.

If phenolphthalein indicator is used in the titration of strong acid and weak base, it changes its colour after the equivalence point and there occurs error due to over titration.

Similarly, if methyl red indicator is used in the titration of weak acid and strong base, it changes its colour before the equivalence point, and there occurs error due to under titration.

Thus, choice of suitable indicator is very important in the acid-base titration.

Problem: An indicator with a pK_{in} value of 4.5 is not suitable for detecting the equivalence point of the titration of a weak acid and strong base. **[Burdwan Univ. 1990]**

Answer: See the Text as above.

Hammett acidity function (H_0)

Introduction:

Hammett acidity function (H_0) is a measure of acidity of very concentrated solution of strong acids including superacids. It was proposed by the physical organic chemist Louis Plack Hammett is the best known acidity function.

Definition:

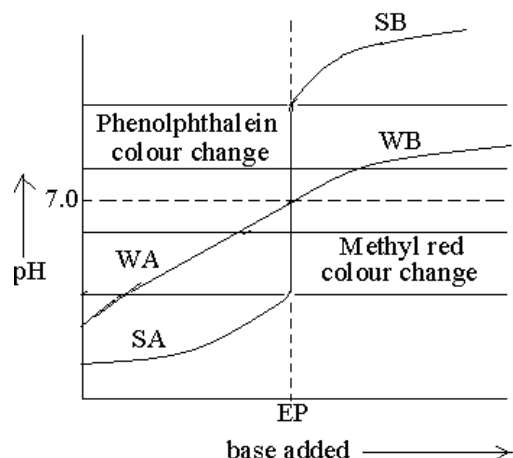
Let us take an acid, BH^+ dissociating as $BH^+ \rightleftharpoons H^+ + B$, where B is very weak base of its conjugated strong acid BH^+ . The dissociation constant of the strong acid is given as $K_{BH^+} = \frac{[H^+][B]}{[BH^+]}$ and Hammett acidity function can replace the pH in concentrated solutions. It is defined using an equation analogous to the Henderson equation as,

$$[H^+] = K_{BH^+} \times \frac{[BH^+]}{[B]} \quad \text{or,} \quad -\log[H^+] = -\log K_{BH^+} - \log \frac{[BH^+]}{[B]} \quad \text{or,} \quad H_0 = pK_{BH^+} + \log \frac{[B]}{[BH^+]}$$

Since B is very weak base of its strong conjugated acid, the value of K_{BH^+} is very high so, pK_{BH^+} has very high negative value. In this way, it is rather as if the pH scale has been extended to very negative values.

The equivalent form of Hammett acidity function **in terms of activity**, $K_{BH^+} = \frac{a_{H^+} \times a_B}{a_{BH^+}}$ or, $a_{H^+} = K_{BH^+} \times \frac{a_{BH^+}}{a_B}$

$$\text{or,} \quad a_{H^+} = K_{BH^+} \times \frac{[BH^+] \times \gamma_{BH^+}}{[B] \times \gamma_B} \quad \text{or,} \quad -\log a_{H^+} = -\log K_{BH^+} - \log \frac{[BH^+]}{[B]} - \log \frac{\gamma_{BH^+}}{\gamma_B}$$



$$\text{or, } -\log a_{H^+} = pK_{BH^+} + \log \frac{[B]}{[BH^+]} + \log \frac{\gamma_B}{\gamma_{BH^+}} \quad \text{or, } -\log a_{H^+} = H_0 + \log \frac{\gamma_B}{\gamma_{BH^+}} \quad \text{or, } H_0 = -\log \left(a_{H^+} \times \frac{\gamma_B}{\gamma_{BH^+}} \right)$$

In dilute aqueous solution (pH 0 – 14), the predominant acid species is H_3O^+ and the activity coefficients are close to unity, and thus H_0 is approximately equal to the pH. However beyond this pH range, the effective hydrogen ion activity (a_{H^+}) changes much more rapidly than hydrogen ion concentration ($[H_3O^+]$).

For example in concentrated sulphuric acid, the predominant acid species (“ H^+ ”) is not H_3O^+ but rather $H_3SO_4^+$ which is much stronger acid. For pure sulphuric acid, the value of $H_0 = -12$. But it must not be interpreted as $pH = -12$ and that may imply an impossibly high H_3O^+ conc. of 10^{12} mol/L in ideal solution. Instead it means that the acid species present ($H_3SO_4^+$) has protonating ability equivalent to H_3O^+ at a fictitious (ideal) conc. of 10^{12} mol/L, as measured by its ability to protonate weak base.

Although the Hammett acidity function is the best known acidity function, other acidity functions have been developed by authors such as Arnett, Cox, Katrizky, Yates, and Stevens.

Typical values

On this scale, pure H_2SO_4 (18.4 M) has a H_0 value of -12 , and pyrosulphuric acid has $H_0 \sim -15$. Take note that the Hammett acidity function clearly avoids water in its equation. It is a generalization of the pH scale—in a dilute aqueous solution (where B is H_2O), pH is very nearly equal to H_0 . By using a solvent-independent quantitative measure of acidity, the implications of the leveling effect are eliminated, and it becomes possible to directly compare the acidities of different substances (e.g. using pK_a , HF is weaker than HCl or H_2SO_4 in water but stronger than HCl in glacial acetic acid; and pure HF is “stronger” than H_2SO_4 because the H_0 of pure HF is higher than that of pure H_2SO_4).

H_0 for some concentrated acids:

- Fluoroantimonic acid (1990): -31.3
- Magic acid (1974): -19.2
- Carborane superacid (1969): -18.01
- Triflic acid (1940): -14.1
- Chlorosulphuric acid (1978): -12.78
- Sulphuric acid: -12.0

For mixtures (e.g., partly diluted acids in water), the acidity function depends on the composition of the mixture and has to be determined empirically. Graphs of H_0 vs. mole fraction can be found in the literature for many acids.

Question(1): What are superacids? How the acidity of such solution is measured? Explain with examples. (3)

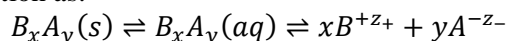
Calcutta Univ. 2010]

Question(2): What is Hammett acidity function? Show that for dilute solution it reduces to the pH of the solution. (3)

[Burdwan Univ. 2016]

Solubility and Solubility product

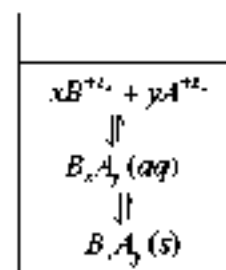
Let us take a sparingly soluble salt, B_xA_y , remaining in equilibrium in aqueous solution as:



The equilibrium of the species in different phases is represented in terms of chemical potential as

$$\mu_{B_xA_y(s)} = \mu_{B_xA_y(aq)} = x\mu_{B^{+z}} + y\mu_{A^{-z}}$$

Thus, $\mu_{B_xA_y(s)} = x\mu_+ + y\mu_-$. When expressed in terms of activities, we have



saturated solution of B_xA_y
at temperature T

$$\mu_{B_xA_y(s)}^0 + RT \ln a_{B_xA_y(s)} = x(\mu_+^0 + RT \ln a_+) + y(\mu_-^0 + RT \ln a_-),$$

but $a_{B_xA_y(s)} = 1$, so $\mu_{B_xA_y(s)}^0 = x\mu_+^0 + y\mu_-^0 + RT \ln(a_+^x \times a_-^y)$ or, $RT \ln(a_+^x \times a_-^y) = -\left[(x\mu_+^0 + y\mu_-^0) - \mu_{B_xA_y(s)}^0\right] = -\Delta\mu$

or, $a_+^x \times a_-^y = e^{-\Delta\mu/RT} = K_{sp}$ or, $K_{sp} = a_+^x \times a_-^y$, where K_{sp} is solubility product of the salt which is constant for the salt at a given temperature and a_+ and a_- are the activities of the cation and anion of the electrolyte in the saturated solution.

Replacing activities by molar conc., we get $K_{sp} = (c_+ f_+)^x \times (c_- f_-)^y = (c_+^x \times c_-^y) \times (f_+^x f_-^y)$.

Let s is the solubility of the electrolyte in mole / litre, then $c_+ = xs$, $c_- = ys$, and $f_+^x f_-^y = f_{\pm}^{x+y}$.

So,
$$K_{sp} = (x^x y^y) s^{x+y} f_{\pm}^{x+y}.$$

where f_{\pm} is the mean ionic activity coefficient of the solution. But when a pure sparingly soluble salt forms a saturated solution in water, only few ions are present in the solution and f_{\pm} is taken unity for the approximate purposes.

For uni univalent electrolyte, such as AgCl, the relation is $K_{sp} = s^2$, for bi univalent electrolyte such as CaF₂,

the relation is $K_{sp} = 4s^3$, for bi trivalent electrolyte such as Ca₃(PO₄)₂, the relation is $K_{sp} = 108s^5$, etc.

The solubility product K_{sp} is equilibrium constant and it depends on temperature according to van't Hoff reaction isochore. It can be determined if the solubility (s) of the salt is known and vice versa. The solubility product as obvious, is the ultimate value which is attained by the ionic product when equilibrium has been established between the solid state of the salt and the ions in solution.

Problem: What is the maximum pH of a solution 0.10M in Mg⁺² from Mg(OH)₂ will not precipitate?

The solubility product of Mg(OH)₂ = 1.2×10^{-11} . [IISc Entrance Test to MSc, 2002]

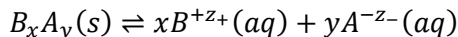
Answer: Maximum ionic product of Mg(OH)₂ = $[Mg^{2+}] \times [OH^-]^2 = \text{solubility product of Mg(OH)}_2 = 1.2 \times 10^{-11}$.

The conc. of OH⁻, $[OH^-] = (1.2 \times 10^{-11} / 0.10)^{1/2} = \sqrt{1.2} \times 10^{-5}$ but, $pH = -\log(K_w / [OH^-])$.

Putting the values, we get $pH = -\log\left(\frac{1 \times 10^{-14}}{\sqrt{1.2} \times 10^{-5}}\right) = 9.04$.

Common ion effect:

The equilibrium established in the saturated solution of a sparingly soluble salt, B_xA_y is given as



If the salt is present in a solution having one ion common such as yA^{-z-} , then the equilibrium will shift towards left and solubility (s) of the salt decreases. Let us take a very simple salt AgCl which in the saturated solution exist in equilibrium with its ions as $AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$. The solubility product of AgCl is

$$K_{sp} = [Ag^+][Cl^-].$$

K_{sp} of the salt remains constant at a given temperature. As two ions form equilibrium with the solid AgCl, any change in conc. of one ion will affect the conc. of the other ion to maintain constancy of K_{sp} .

Thus addition of common ion, say Cl^- in the form of KCl affects the conc. of Ag^+ and it changes the solubility (s) of the salt, AgCl.

Let in water, the solubility of AgCl is s_0 mol/litre and in KCl solution of conc. c mol/litre, the solubility is s mol/litre.

Therefore, in water solution, $K_{SP} = s_0^2$, but in KCl solution, $K_{SP} = s(s+c)$. Since K_{SP} is approximately constant, hence

$$s_0^2 = s(s+c) \text{ or, } s_0^2 = s(s+c) = s^2 + sc + c^2.$$

This shows that $s < s_0$, the solubility of a sparingly soluble salt is less in presence of a common ion in solution.

Further, the equation is $s^2 + sc - s_0^2 = 0$ or, $s = -\frac{1}{2}c + \sqrt{\frac{c^2}{4} - s_0^2}$.

However, s is very small, so s^2 in the equation is generally neglected and thus $s = \frac{s_0^2}{c}$.

This is the approximate value (s) of the uni univalent salt in presence of a common ion.

Problem: Calculate the maximum solubility of CaF_2 in 0.1(M) NaF solution at 25 °C.

Solubility product of $\text{CaF}_2 = 3.2 \times 10^{-11}$ at 25 °C.

[Calcutta Univ. 1999]

Answer: $\text{CaF}_2 \rightleftharpoons \text{Ca}^{2+} + 2\text{F}^-$ so, $K_{SP} = [\text{Ca}^{2+}][\text{F}^-]^2$ or, $K_{SP} = s(s+c)^2 = s(s^2 + 2sc + c^2) = s^3 + 2s^2c + sc^2$.

Neglecting s^3 and $2s^2c$ for their small values, we get $K_{SP} = sc^2$ or, $s = \frac{K_{SP}}{c^2}$.

Putting the values, we get $s = \frac{3.2 \times 10^{-11}}{(0.1)^2}$ or, $s = 3.2 \times 10^{-9}$.

Inert Ion Effect:

True or thermodynamic solubility product is defined as $K_{SP} = (x^x y^y) s^{x+y} f_{\pm}^{x+y}$.

For AgCl, $K_{SP} = s^2 f_{\pm}^2$, for CaF_2 , $K_{SP} = 4s^3 f_{\pm}^3$, for $\text{Ca}_3(\text{PO}_4)_2$, $K_{SP} = 108s^5 f_{\pm}^5$, etc.

The inert ions in solution affect f_{\pm} which actually depends on the ionic strength of the solution, though its effect is not so prominent like the common ion effect. With increase in conc. of inert ion, the solution becomes more non-ideal and f_{\pm} becomes less. Thus maintain the constancy of K_{SP} , the solubility must increase.

However, the increase of solubility is not much, for example, TiCl_3 has solubility in pure water is 0.016(M) but in presence of inert ions of 1(M) KNO_3 , the solubility rises to 0.031(M).

The common ion decreases the solubility to a large extent. For example, one litre of water dissolves 12 gm PbCl_2 at 30 °C whereas 1 litre 1 (M) KCl solution dissolves 0.5 gm PbCl_2 only.

Analytical Application: Solubility product principle states that an electrolyte will be precipitated out from the solution when the product of conc. of ions (called ionic product) exceeds the solubility product (K_{SP}) of the salt at the temperature. The precipitation will continue until the ionic product becomes equal to the solubility product of the salt. Thus for AgCl, in solution, so long $[\text{Ag}^+][\text{Cl}^-] > K_{SP}(\text{AgCl})$, the precipitation occurs and the ions Ag^+ and Cl^- ions are removed from the solution, when $[\text{Ag}^+][\text{Cl}^-] = K_{SP}(\text{AgCl})$, the precipitation stops. The solution becomes a saturated solution of AgCl.

In qualitative Analysis: In group analysis of basic radicals, II group radicals (such as Cu^{2+}) forms precipitate a CuS when H_2S is passed in acidic medium but IIIB radicals (such as Ni^{2+}) does not form NiS precipitate from such solution. NiS precipitate when H_2S passed in the solution in alkaline medium. This can be explained as follows:

H_2S in solution dissociates as $\text{H}_2\text{S} \rightleftharpoons 2\text{H}^+ + \text{S}^{2-}$.

In acid medium (H^+ ion is high), and due to common ion effect, $[\text{S}^{2-}]$ is low

and so $[\text{Cu}^{2+}][\text{S}^{2-}] > K_{SP}(\text{CuS})$ hence CuS becomes precipitated since $K_{SP}(\text{CuS})$ is very small. But

$[\text{Ni}^{2+}][\text{S}^{2-}] < K_{SP}(\text{NiS})$ i.e. ionic product of Ni^{2+} and S^{2-} does not exceed the solubility product of NiS hence it is not precipitated out from the solution.

In alkaline medium (H^+ ion is low), and so $[S^{2-}]$ is high and the $[Ni^{2+}][S^{2-}] > K_{sp}(NiS)$ so NiS is precipitated out from the solution. [Given, $K_{sp}(CuS) = 1 \times 10^{-44}$ and $K_{sp}(NiS) = 1.4 \times 10^{-24}$].

In Quantitative Analysis:

In the titration of NaCl solution with $AgNO_3$ solution, K_2CrO_4 can be used as indicator.

This is due to preferential precipitation of AgCl from the solution. When all Cl^- ions are precipitated out in the form of AgCl, a single drop of $AgNO_3$ solution forms precipitate Ag_2CrO_4 from the solution. This is red in colour and thus indicates the end point when white precipitate ends with red precipitate. This preferential precipitation occurs due to

$$K_{sp}(AgCl) < K_{sp}(K_2CrO_4).$$

DR. N. C. DEY

Answer to Burdwan Univ. Questions on the Ionic Equilibrium.

[Burdwan Univ. 2000]

Q 8(a). Derive an expression for the pH of an aqueous solution of sodium acetate in terms of its concentration. [8]

Ans. See P14

Q 8(b). How is the dissociation equilibrium of water distributed by addition of NH_4Cl to it? Why is acid medium unsuitable for the precipitation of ZnS from a solution containing Zn^{2+} by passing H_2S ? [4+4]

Ans. See P13.

1st Part. Water forms equilibrium in the process of its dissociation as $\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$ and it shows neutral with equal concentration of H^+ and OH^- . At 25°C , $[\text{H}^+] = [\text{OH}^-] = 10^{-7} \text{ (M)}$ and $\text{pH} = 7$

But when NH_4Cl which is strong electrolyte is added to water, NH_4^+ combines with OH^- ion forming an excess of $[\text{H}^+]$. $\text{NH}_4^+ + \text{OH}^- + \text{H}^+ \rightleftharpoons \text{NH}_4\text{OH} + \text{H}^+$ the resulting solution reacts acidic and $\text{pH} < 7$. This process of disturbances on the dissociation equilibrium is called cationic hydrolysis. It could be shown that the solution of NH_4Cl will have $\text{pH} = 7 - \frac{1}{2}PK_b - \frac{1}{2}\log c$, where c is Salt constant.

2nd Part. H_2S is weak acid and dissociates as $\text{H}_2\text{S} \rightleftharpoons 2\text{H}^+ + \text{S}^{2-}$. In acid medium ($[\text{H}^+] = \text{high}$), the dissociation equilibrium shifts in the left side and concentration of S^{2-} is low. The $[\text{S}^{2-}]$ is so low that the ionic product of Zn^{2+} and S^{2-} doesn't exceed the solubility product of ZnS and so the precipitation of ZnS doesn't occur. However, in alkaline medium ($[\text{H}^+] = \text{low}$), dissociation equilibrium lies in the right side and $[\text{S}^{2-}]$ is so high that the ionic product of Zn^{2+} and S^{2-} exceeds the solubility product of ZnS and precipitation of ZnS takes place, ie. In acid medium, $[\text{Zn}^{2+}] \times [\text{S}^{2-}] < K_{sp}$ and precipitation does not occur & in alkaline medium, $[\text{Zn}^{2+}] \times [\text{S}^{2-}] > K_{sp}$ and precipitation occurs. Thus acid medium is unsuitable for precipitation of ZnS from a solution containing Zn^{2+} by passing H_2S .

[Burdwan Univ. 2001]

Q 5(b). The dissociation constant of NH_4OH is 1.8×10^{-5} . The solubility product of $\text{Mg}(\text{OH})_2$ is 1.22×10^{-11} . How many gms of solid NH_4Cl must be added to a mixture of 50cc of (N) NH_4OH solution and 50cc of (N) MgCl_2 solution so that the precipitate of $\text{Mg}(\text{OH})_2$ just disappears? It is assumed that the volume of the solution is not changed by dissolving solid NH_4Cl and that the dissociation of the neutral salt is complete. [5]

Ans. Conc. of Mg^{2+} in the solution = $50 \times 1.0/100 \text{ (N)} = 0.50 \text{ (N)} = 0.25 \text{ (M)}$ and conc. of $\text{NH}_4\text{OH} = 0.50 \text{ (M)}$.

We have $K_{sp} = [\text{Mg}^{2+}][\text{OH}^-]^2$ or, $1.22 \times 10^{-11} = 0.25 \times [\text{OH}^-]^2$

$$\text{or, } [\text{OH}^-] = \sqrt{\frac{1.22 \times 10^{-11}}{0.25}} = 6.98 \times 10^{-6} \text{ (M)}.$$

This is the conc. of OH^- just to prevent the precipitation of $\text{Mg}(\text{OH})_2$ from the resulting solution. The OH^- is obtained from the dissociation of NH_4OH and it dissociates as $\text{NH}_4\text{OH} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$ and

$K_b = \frac{[\text{NH}_4^+] \times [\text{OH}^-]}{[\text{NH}_4\text{OH}]}$. However, dissociation of NH_4OH is highly suppressed by the presence of common

ion, $[\text{NH}_4^+] = \frac{K_b \times [\text{NH}_4\text{OH}]}{[\text{OH}^-]} = \frac{1.8 \times 10^{-5} \times 0.50}{6.98 \times 10^{-6}} = 1.289 \text{ (M)}$. Assuming very small contribution of

NH_4OH to the value of NH_4^+ , $[\text{NH}_4^+] = [\text{NH}_4\text{Cl}]$ all NH_4^+ is obtained from NH_4Cl .

thus 1.289 mole NH_4Cl is to be added per 1000cc of the solution to prevent the precipitation of $\text{Mg}(\text{OH})_2$.

Hence for 100 cc solution NH_4Cl to be added in gms = $\frac{1.289}{1000} \times 100 \times 53.5 = 6.89$.

[Burdwan Univ. 2002]

Q 1(o). Remark if the pH range for boric acid –borax buffer lies in the acidic range. [1]

Ans. pKa of boric acid is 9.24 & hence boric acid – borax buffer lies in the alkaline range 8.24-10.24.

Q 2(e). If $pH = 7 - (\log x)/2$, find K_w of pure water. [2]

Ans. $pH = -\log [H^+] = 7 - (\log x)/2$ or, $\log C_{H^+}^2 = -14 + \log x$ or, $C_{H^+}^2 = x \times 10^{-14}$.

In pure water $K_w = [H^+][OH^-] = [H^+]^2 = x \times 10^{-14}$.

Q 5(e). The solubility product of MgF_2 is 7×10^{-4} . Find its solubility in water and in 0.01(M) aqueous NaF solution approximately. [5]

Ans. For $MgF_2 \rightleftharpoons Mg^{2+} + 2F^-$ $K_{sp} = 4s_0^3$, s_0 = Solubility of MgF_2 in water. So, $4s_0^3 = 7 \times 10^{-4}$ or, $s_0 = 0.056(M)$.

In 0.01(M) NaF solution $s(s + 0.01)^2 = 7 \times 10^{-4}$ or, $s \approx 7 \times 10^{-4} / 0.01 \approx 7 \times 10^{-2}(M)$

[Note: K_{sp} of MgF_2 should be 7×10^{-9} (Wrong data supplied)]

Q 6(a)(ii). Calculate a_{\pm} of a solution of $Al_2(SO_4)_3$ of strength $8.25 \times 10^{-4} m$, given $\gamma_{\pm} = 0.9913$ and that of compound dissociated completely. [5]

Ans. For the electrolyte B_xA_y , $a = a_{\pm}^{x+y} = (x^x y^y) m^{x+y} \gamma_{\pm}^{x+y}$.

For $Al_2(SO_4)_3$, $a_{\pm}^5 = (2^2 \times 3^3) m^5 \gamma_{\pm}^5$ or, $a_{\pm} = \sqrt[5]{108 m \gamma_{\pm}}$, $a_{\pm} = \sqrt[5]{108} (8.25 \times 10^{-4}) \times (0.9913)$

or, $a_{\pm} = 2.08 \times 10^{-3} m$.

Q 6(b). Define buffer capacity, Consider the acetic acid-acetate buffer to show that it is maximum when $pH = pK_a$.

Given, $K_a = 1.8 \times 10^{-5}$ for acetic acid, find the degree of hydrolysis of a 0.01(M) Na-acetate solution [10]

Ans. For 1st and 2nd part, see P9 and P10.

3rd part: the relation, $K_b = K_w / K_a \approx x^2 c$ where x = degree of hydrolysis of salt

$$\text{so, } x = \sqrt{\frac{K_w}{K_a \times c}} = \sqrt{\frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5} \times 0.01}} = 2.35 \times 10^{-4}.$$

the degree of hydrolysis of sodium acetate in 0.01M solution is 2.35×10^{-4} .

Q 2(a). The pH of a weak monobasic acid decreases by 0.1 unit when the temperature changes from 300K. Calculate the value of ΔH for the dissociation of the acid. [2]

[Neglect the change in concentration due to the change in temperature.]

Ans. For monobasic acid, $[H^+] = \sqrt{K_a \times c}$ or, $pH = \log[H^+] = \frac{1}{2} pK_a - \frac{1}{2} \log c$.

From the problem, $(pH)_{300K} - (pH)_{310K} = \frac{1}{2} (pK_a)_{300K} - \frac{1}{2} (pK_a)_{310K}$

$$\text{or, } 0.1 = \frac{1}{2} [-\log(K_a)_{300K} + \log(K_a)_{310K}] = \log \left[\frac{(K_a)_{310K}}{(K_a)_{300K}} \right] = \frac{1}{2} \times \frac{\Delta H}{R \times 2.303} \times \frac{10K}{300K \times 310K}$$

or, $\Delta H = 0.1 \times 2 \times 2.303 \times 2 \text{ cal mol}^{-1} K^{-1} \times 300K \times 310K / 10K = 8567 \text{ cal mol}^{-1}$.

[Burdwan Univ. 2003]

Q 1(b). When does solubility decreases with temperature? [1]

Ans. When the dissolution of the substance is an exothermic process, then the solubility of that substance decreases with temperature increase.

(q). How does K_w changes with temperature? [1]

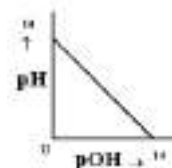
Ans. Dissociation of water is an endothermic process & so K_w increases with increasing temperature.

(r). What pH range is suitable for acetic acid/acetate buffer? [1]

Answer: the suitable P^H range for acetic acid/acetate is $pK_a - 1$ to $pK_a + 1$ or, $4.76 - 1$ to $4.76+1$ or 3.76 to 5.76 since pK_a of acetic acid is 4.76 at $25^\circ C$.

(t). For aqueous solution of varying pH, plot pH vs. pOH at a given temperature. [1]

Ans. At a given temperature, in aqueous solution $pH + pOH = pK_w = \text{Constant}$
or $pH = pK_w - pOH$, so the plot of pH vs. pOH is a straight line with negative slope.



Q 2(d). The solubility product of a sparingly soluble salt MA_3 is 2.7×10^{-7} .

Find its solubility assuming complete dissociation. [2]

Ans. For the salt MA_3 , $K_{SP} = (x^x y^y) s^{x+y} = 27s^4$ and $27s^4 = 27 \times 10^{-8}$ or $s = 1 \times 10^{-2} (M)$.

Q 4(b)(i). Derive an expression for the pH of a salt of a weak acid and weak base dissolved in water. [5]

Ans. See P15. $pH = 7 + \frac{1}{2}(pK_a - pK_b)$.

(ii) Find the pH and degree of hydrolysis of a salt of a weak acid ($K_a = 1.8 \times 10^{-5}$) and strong base if the concentration of the salt is $0.01 M$ in an aqueous solution. [5]

Ans. $pH = 7 + (1/2) pK_a + (1/2) \log c = 7 + (1/2)(-\log 1.8 \times 10^{-5}) + (1/2) \log (0.01) = 10.74$.

Again, $x^2 c \approx K_h = \frac{K_w}{K_a} = 1.0 \times 10^{-14} / 1.8 \times 10^{-5}$ so, $x = \sqrt{\frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5} \times 0.01}}$ or $x = 2.35 \times 10^{-4}$.

Q 3(e). If 0.25 moles of NH_4Cl is added to a litre of $0.1(M)$ NH_4OH solution, find the degree of dissociation of NH_4OH ($K_b = 1.8 \times 10^{-5}$ approx.) [5]

Ans. $K_b = \frac{[NH_4^+][OH^-]}{[NH_4OH]} = \frac{0.25 \times \alpha c}{(1-\alpha)c} \approx 0.25\alpha = 1.8 \times 10^{-5}$ or, $\alpha = 7.2 \times 10^{-5}$.

[Calcutta Univ.91]

Q 10(a). The solubility of a sparingly soluble salt AB_2 in water at $18^\circ C$ is $10^{-4} (M)$. Calculate its solubility in $0.01(M)$ NaB solution at this temperature. [2]

Ans. $K_{SP} = 4s_0^3 = s(s+c)^2 \approx sc^2$, since $s \ll c$ or, $s = \frac{4s_0^3}{c^2} = 4 \times \frac{(10^{-4})^3}{(0.01)^2} = 4 \times 10^{-8} (M)$.

Thus, the solubility of AB_2 in $0.01(M)$ is $4 \times 10^{-8} (M)$

[Calcutta Univ. 92]

Q 10(b). The pH of a $10^{-3} M$ aqueous solution of weak acid was found to be 4.0 at $25^\circ C$. Find the degree of dissociation of the acid at this temperature. [4]

Ans. $pH = -\log[H^+] = -\log(\alpha c)$ or, $\alpha c = 10^{-pH} = 10^{-4}$, but $c = 10^{-3} (M)$ so, $\alpha = \frac{10^{-4}}{10^{-3}} = 0.10$.

[Calcutta Univ. 95]

Q 10(c). $50 ml$ of a $0.1 N$ acetic acid is titrated with $0.1 N NaOH$ solutions. Calculate the pH of the solution at the start and at the half neutralisation point (given, $K_a = 1.75 \times 10^{-5}$). [4]

Ans. pH at the start: $[H^+] = \sqrt{K_a c} = \sqrt{1.75 \times 10^{-5} \times 0.1} = 1.32 \times 10^{-3}$ (M). Hence, $pH = 2.88$ at the start
at the half neutralization, $pH = pK_a = -\log(1.75 \times 10^{-5}) = 4.75$.

[Calcutta Univ. 97]

Q 9(d). Calculate the pH of the solution obtained on titrating a solution of decinormal acetic acid and decinormal NaOH at the equivalent point and half equivalent point. (pK_a of HAc=4.75) [4]

Ans. At the equivalent point, the salt Sodium Acetate of conc. $0.1/2=0.05$ (M) is formed. So, pH at the equivalent point is given by $pH = 7 + (1/2)pK_a + (1/2)\log c = 7 + (1/2)(4.75) + (1/2)\log(0.05) = 8.72$
at the half equivalent point using Henderson equation, $pH = pK_a = 4.75$.

[Calcutta Univ. 98][WBCS'95]

Q 10(a). Define buffer capacity. Find the condition when it has the maximum value. You are supplied with 0.1(N) NH_4OH and 0.1(N) HCl solutions show how you will use these solutions to prepare 100 ml buffer solution of $pH = 9.0$ (Given K_b for $NH_4OH = 2 \times 10^{-5}$). [1+3+3=7]

Ans. 3rd part: Henderson equation is, $pOH = pK_b + \log \frac{[salt]}{[base]}$ or, $\log \frac{[salt]}{[base]} = pOH - pK_b = 5 - 4.7 = 0.3$

or, $\frac{[salt]}{[base]} = 10^{0.3} = 2$, since $pOH = 14 - pH$ or, $\frac{[salt]}{[base]} = 2.0$ and total volume of the buffer = 100ml

Let x ml of 0.1N HCl is taken. Then $[salt] = x$ and $[base] = 100 - 2x$, since x ml HCl neutralise x ml

salt, Thus $\frac{x}{100 - 2x} = 2$ or $5x = 200$, or, $x = 40$ ml.

Hence 40 ml HCl and 60ml NH_4OH each of 0.1N concentration are to be taken to prepare 100 ml buffer solution of $pH = 9$.

Q 10(c). The solubility product of PbI_2 is 7.47×10^{-9} at $15^\circ C$ and 1.39×10^{-8} at $25^\circ C$. Calculate molar heat of solution of PbI_2 . [3]

Ans. Using van' Hoff reaction isochore, we have $\log \left(\frac{K_{s_2}}{K_{s_1}} \right) = \frac{\Delta H}{R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$

or, $\log \left(\frac{K_{s_2}}{K_{s_1}} \right) = \frac{\Delta H}{R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$ or, $\ln \left(\frac{1.39 \times 10^{-8}}{7.47 \times 10^{-9}} \right) = \frac{\Delta H}{2} \times \frac{10}{298 \times 288}$

or, $\Delta H = \left(\frac{2 \times 298 \times 288}{10} \right) \ln \left(\frac{1.39}{7.47} \right) cal mol^{-1} = 10659 cal mol^{-1} = 10.659 kcal/mol$

[Calcutta Univ. 99]

Q 9(d). Calculate pH of the solution prepared by mixing 15ml of 0.2N NH_4OH solution and 10ml of 0.15N HCl solution at $25^\circ C$. [K_b of $NH_4OH = 1.8 \times 10^{-5}$]. [2]

Ans. 10ml of 0.15N = 1.5 ml of 1N HCl and 15 ml of 0.2 N = 3.0 ml of 1N NH_4OH
Excess $NH_4OH = 3.0 - 1.5 = 1.5$ ml of 1N and salt NH_4Cl formed = 1.5 ml of 1N.

Thus $pOH = pK_b + \log \frac{[salt]}{[base]} = (-\log 1.8 \times 10^{-5}) + \log \frac{1.5}{1.5} = 4.75$

so, $pH = 14 - pOH = 14 - 4.75 = 9.25$

Q 9(e). Calculate the maximum solubility of CaF_2 in 0.1M NaF solution at 25°C.

Solubility product of $CaF_2 = 3.2 \times 10^{-11}$ at 25 °C. [2]

Ans. $K_{sp} = s(2s + c)^2$ but $s \ll c$ so, $K_{sp} = sc^2$ or, $s = \frac{K_{sp}}{c^2}$. Putting the value $c = \frac{3.2 \times 10^{-11}}{(0.1)^2} = 3.2 \times 10^{-9} M$.

[Burdwan Univ. 2004]

Q 1(x). Remark on the statement; Solubility increases with temperature. [1]

Ans. If the process of dissolution is endothermic ($\Delta H > 0$), solubility increases with temperature But if the process is exothermic ($\Delta H < 0$), the solubility decreases with temperature.

Q 2(e). What would roughly be the pH of a $10^{-7} M$ aqueous HCl solution? [2]

Ans. $pH = -\log([H^+]_{acid} + [H^+]_{water}) = -\log(10^{-7} + 10^{-7}) = -\log(2 \times 10^{-7}) = 7 - \log 2 = 7 - 0.3 = 6.7$.

4(d)(i). Starting from Ostwald's dilution law, find an approximate expression for the pH of 1 M acetic acid solution.

When is your expression likely to work poorly and why? [10]

Ans. For acetic acid dissociating as $HAc \rightleftharpoons H^+ + Ac^-$, let c is the molar concentration of HAc and α the degree of dissociation at this concentration then $[HAc] = (1 - \alpha)c$ and $[H^+] = [Ac^-] = \alpha c$.

The dissociation constant of HAc is $K_a = \frac{[H^+] \times [Ac^-]}{[HAc]} = \frac{\alpha^2 c}{1 - \alpha}$, however, $\alpha \ll 1$ hence,

$$K_a = \alpha^2 c = \frac{(\alpha c)^2}{c} = \frac{[H^+]^2}{c} \text{ or, } [H^+] = \sqrt{K_a \times c} \text{ but } c = 1M \text{ and } K_a = 1.8 \times 10^{-5} \text{ at } 25^\circ C, \text{ or,}$$

$$pH = \frac{1}{2} pK_a - \frac{1}{2} \log c. \text{ But } pK_a \text{ of HAc} = 4.7 \text{ so } pH = \frac{1}{2} \times 4.7 = 2.35.$$

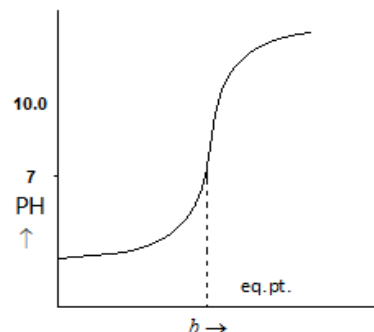
Since concentration of HAc is very high, use of concentration term is only approximate and so poor result of the expression yields.

(ii). If NaOH solution is gradually added to a solution of acetic acid, what will be the buffer capacity just at the neutralisation point and why?

Ans. The pH jumps from 7.0 to 10.0 at the neutralisation point of the above

reaction. Since, the buffer capacity (β) is defined as $\beta = \frac{db}{d(pH)} = \frac{1}{\text{slope}}$

but the slope is maximum at the neutralisation point. So, the buffer capacity becomes minimum.



[Burdwan Univ. 2005]

Q 1(c). During an acid base titration, when is the buffer capacity of the system under titration minimum? [1]

Ans. At the neutralization point, see Burdwan Univ. 2004, Q 4(d)(ii).

(d). An aqueous solution of Mohr's salt gradually becomes turbid, why? [2]

Ans. Hydrolysis of $FeSO_4$ forming $Fe(OH)_3$ which makes the solution turbid.

(p). Criticize: pH of a $10^{-8} M$ HCl solution (aq) is 8. [1]

Ans. Wrong, it is approximately 6.96, see page 6.

Q 3(e). A salt of a strong acid HA and strong base BOH shows pH = 6.2 when dissolved in water to make a 0.1(N) solution. Find the dissociation constant of BOH and explain why that of HA cannot be determined from this observation. [5]

Ans. The pH-value shows that acid HA is stronger than the base BOH. The equation for pH of such salt solution is

$$pH = 7 - \frac{1}{2} pK_b - \frac{1}{2} \log c \text{ or, } 6.2 = 7 - \frac{1}{2} pK_b - \frac{1}{2} \log 0.1$$

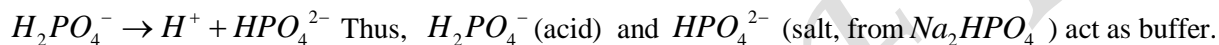
$$\text{or, } \frac{1}{2} pK_b = 7 - 6.2 - \frac{1}{2} \times (-1) = 7 - 6.2 + 0.5 = 1.3 \text{ or, } pK_b = 2.6 \text{ or, } K_b = 10^{-2.6} = 2.5 \times 10^{-3}.$$

HA is strong acid and so its conjugate base A^- is very weak. The A^- from the salt cannot produce HA so the ionic equilibrium $HA \rightleftharpoons H^+ + A^-$ does not exist and thus K_a of the acid HA is not determined.

Burdwan Univ. 2006

Q 1(ix). Explain why a mixture of aqueous solutions of NaH_2PO_4 and Na_2HPO_4 can act as a buffer, although both are acids.

Ans. NaH_2PO_4 dissociates as $Na^+ + H_2PO_4^-$ but $H_2PO_4^-$ acts as an acid, dissociating as



Q 2(d). Derive the expression for pH of an aqueous NH_4Cl solution of molar concentration c . [2]

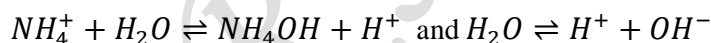
Ans. See the text to derive $pH = \frac{1}{2} pK_w - \frac{1}{2} pK_b - \frac{1}{2} \log c$.

Q 3(d). Derive the expression for buffer capacity of a solution prepared by mixing solution of weak acid and strong base. Find also the condition under which the buffer capacity is maximum. [5]

Ans. See the Text to derive, buffer capacity, $\beta = [2.303 \frac{b(a-b)}{a}]$ and find the condition for β_{\max} when $b = \frac{a}{2}$.

Q 4(a)(i). "Salt hydrolysis is in fact a manifestation of the Le-Chatelier's principle on the dissociation equation of water." - Explain. [3]

Ans. Let us consider the two equilibrium that exist in the solution of NH_4Cl .



When NH_4^+ of the salt takes up OH^- , equilibrium of H^+ & OH^- water is disturbed H^+ Conc. is increased due to forward process of ionization of H_2O process. The solution becomes acidic.

$K_w = [H^+][OH^-]$ = constant at a given temperature. When OH^- is removed by NH_4^+ , H_2O is further dissociated to keep the value of K_w constant. $[H^+]$ is increased in solution.

(ii). Calculate the pH of a 0.1 N aqueous solution of NH_4Cl , given K_b of $NH_4OH = 1.5 \times 10^{-5}$ at the experimental temperature. [3]

$$\text{Ans. } pH = 7 - \frac{1}{2} pK_b - \frac{1}{2} \log c = 7 - \frac{1}{2} \log(1.5 \times 10^{-5}) - \frac{1}{2} \log(0.1) = 7 - \frac{1}{2} \times 4.824 - \frac{1}{2} \times (-1)$$

$$= 7 - 2.412 + 0.5 = 5.088.$$

(iii). Show quantitatively that the degree of dissociation (α) of weak acid increases with dilution and $\alpha \rightarrow 1$ as $c \rightarrow 0$. [4]

Ans. See the Text for the answer. [Hints: $K_a = \frac{\alpha^2 c}{1-\alpha}$ or, $\alpha^2 c = K_a(1-\alpha)$. When $c \rightarrow 0$, $\alpha \rightarrow 1$.

(Old Registration)

Q 1(e). By raising the temperature of water, its PH can be lowered but still it remains non-acidic. Why? [1]

Ans. When temperature is raised, K_w is increased & hence $[H^+]$ is increased resulting the lowering of pH.

But by dissociation of H_2O , it produces equal conc. of H^+ & OH^- and water remains neutral.

(k). What happens to degree of hydrolysis (α) and hydrolysis const. (K_h) of aniline hydroxide in its aqueous solution when a few drops of aniline are added to the solution? [1]

Ans. The deg. of hydrolysis (α) is suppressed but hydrolysis constant (K_h) remains unchanged.

(x). A mixture contains a equivalent of HCl and b equivalent ($a > b$) of $NaOH$ in a total volume of 1 dm^3 . What is the expression for buffer capacity of the mixture? [1]

Ans. See the Text for the expression of $\beta = 2.303 \times b \frac{(a-b)}{a}$.

Q 3(d). Derive an expression relating the pH of an aqueous solution of a weak acid with its conc. Hence discuss how the pH changes with conc. and temperature of solution. [5]

Ans. See the text, $pH = \frac{1}{2} pK_a - \frac{1}{2} \log c$. As conc. (c) is increased, pH is decreased. Again with rise of temperature, K_a is increased, pK_a is decreased and pH is decreased. Again, with rise of T, K_a is increased, pK_a is decreased and pH is decreased.

Burdwan Univ. 2007

Q 1(g). 'pH of $10^{-2} (M)$ aqueous solution of acetic acid is greater than 2.0' - Comment. [2]

Ans. Acetic acid is weak electrolyte and so it is partially dissociated in aqueous solution.

$HAc \rightleftharpoons H^+ + Ac^-$ so, conc. of $[H^+] < 10^{-2} (M)$ and hence $pH > 2.0$.

(j). Draw the pH titration curve of strong acid with a weak base and indicate in it, the color change interval of an indicator with $pK_{in} = 9.1$. [2]

Ans. Color change interval of the indicator is 8.1 to 10.1 pH but pH jump for the above titration is 4.0 to 7.0 pH. See the Text for the titration curve of strong acid with a weak base.

Q 2(e). Deduce the expression of pH of a solution of a salt of weak acid and strong base. [6]

Ans. Deduce the expression $pH = \frac{1}{2} pK_w + \frac{1}{2} pK_a + \frac{1}{2} \log c$ [See the Text].

Burdwan Univ. 2008

Q A(vi). An aqueous solution of KHF_2 can act as buffer. - Justify or criticize. [2]

Ans. The aqueous solution of KHF_2 is the mixture of weak acid HF and its salt KF.

$KHF_2 \rightarrow KF + HF$. So the solution acts as buffer.

Q B(ii)(a). From the concept of molecularity in chemical kinetics explains why the degree of dissociation of a weak electrolyte increases with dilution. [4]

Ans. The weak electrolyte HA dissociates as; $HA \rightleftharpoons H^+ + A^-$ and if c is the molar conc. of HA taken and α is the degree of dissociation then $[H^+] = \alpha c$, $[OH^-] = \alpha c$ and $[HA] = (1-\alpha)c$.

The forward process is unimolecular and so first order the rate of forward reaction

$R_f = k_f[HA] = k_f c(1-\alpha)$. The rate of the backward process is kinetically bimolecular and hence 2nd order so, $R_b = k_b \times [H^+][A^-] = k_b \times \alpha c \times \alpha c$. When the two rates are equal, equilibrium is set up and $R_f = R_b$
 or, $\frac{k_f}{k_b} = \frac{(\alpha c)^2}{c(1-\alpha)}$ or, $K_a = \frac{\alpha^2 c}{1-\alpha}$, where K_a is constant and independent of conc.

Thus, when electrolyte solution is diluted, c is decreased so to keep K_a constant, the degree of dissociation (α) is increased.

(b). A reaction is giving out H_3O^+ and a product, which is stable only at $pH = pK_a$ of acetic acid. Explain why a mixture of ammonium acetate and acetic acid is best suited as medium to carry out the reaction. [6]

Ans. When the acetic acid HAc and ammonium acetate NH_4Ac are taken in the medium, pH of the solution is given by Henderson equation, $pH = pK_a + \log \frac{[salt]}{[acid]}$, where $pK_a = -\log K_a$ and K_a is the dissociation const. of acetic acid. If equal conc. of NH_4Ac and HAc are taken, then $pH = pK_a$. Thus the reaction product is stable in the medium which contains equal conc. of NH_4Ac and HAc

(c). What is the limitation of human eye that makes the color change interval of an acid-base indicator $pK_{in} \pm 1$.

Ans. The limitation of human eye is explained as follows: $ln_A \xrightarrow{K_{in}} ln_B + H^+$ and this follows that

$pH = pK_{in} + \log \frac{[ln_B]}{[ln_A]}$. The human eye can recognize the color of ln_B when $\frac{[ln_B]}{[ln_A]} \geq 10$, $pH > pK_{in} + 1$.

Again, when $\frac{[ln_B]}{[ln_A]} \leq \frac{1}{10}$, $pH < pK_{in} - 1$. The color of ln_A is seen.

So, pH-range of color change of acid-base indicator is $pK_{in} \pm 1$.

(Old registration)

Q 1(r). Why does K_w change with temperature?

[1]

Ans. Dissociation of water $H_2O \rightleftharpoons H^+ + OH^-$ is endothermic process and so with rise of T, K_w will increase.

(s). Aqueous solution of ammonium acetate is neutral. Why? [1]

Ans. For the hydrolysis of salt of weak acid and weak base, $pH = \frac{1}{2} pK_w + \frac{1}{2} (pK_a - pK_b)$.

But pK_a of acetic acid is equal to the pK_b of ammonium hydroxide. Hence $pH = \frac{1}{2} pK_w = 7$, neutral at 25°C.

Q 2(g). The pH of a buffer solution containing a weak acid and its salt should be closed to pK_a of the acid. When and under what condition? [2]

Ans. Henderson equation states that $pH = pK_a + \log \frac{[salt]}{[acid]}$. But $pH = pK_a$ of the acid when $[Salt] = [Acid]$.

Q 4(c)(ii). Calculate the pH of a mixture of 50cc 0.2(N) acetic acid and 100 cc of 0.1(N) NaOH. [2]
 (Given K_a for HAc = 1.8×10^{-5})

Ans. 50cc 0.2 (N) HAc is completely neutralized by 100 cc 0.1 (N) NaOH.

$[NaAc] = (50 \times 0.2) / 150 = 0.2/3 (N)$. $pH = 7 + \frac{1}{2} pK_a + \frac{1}{2} \log c = 8.78$

[Burdwan Univ. 2009]

Q 2(iii). Explain whether ionic product of water changes with temperature. [2]

Ans. K_w is also an equilibrium constant for the equation of the process, $H_2O \rightleftharpoons H^+ + OH^-$
All equilibrium constant depends on temperature, except only for ΔH of the process is zero.
This process is endothermic so, K_w increases of temperature.

Q 2 (b)(i). Derive an experiment for the pH of an aqueous solution of a salt BA (where BOH is a strong base and HA is a weak acid) and hence explain whether the solution will be acidic or alkaline. [6]

Ans. See the Text, for the process $A^- + H_2O \rightleftharpoons HA + OH^-$ (anionic hydrolysis), $pH = 7 + \frac{1}{2} pK_a + \frac{1}{2} \log[salt]$

Q 2(c)(iii). The pH of an acid buffer does not change with dilution. Explain. [2]

Ans. pH of acid buffer solution is calculated by Henderson equation, $pH = pK_a + \log \frac{[salt]}{[acid]}$

Thus with dilution, both [salt] and [acid] change by the same ratio and hence $[salt]/[acid]$ remains fixed so, pH is unchanged.

But if we consider for more accuracy, then $pH = pK_a + \log \frac{[A^-]}{[HA]} + \log f_{A^-}$. With dilution, f_{A^-} increases and approaches to the value of 1 and so pH is slightly increased by dilution.

Q 3(v). Starting from Ostwald's dilution law, find an approximate expression for pH of 1 M acetic acid solution. When is your approximation likely to work poorly and why? [6]

Ans. For acetic acid dissociated as The weak electrolyte HA dissociates as; $HA \rightleftharpoons H^+ + A^-$ and if c is the molar conc. of HA taken and α is the degree of dissociation then $[H^+] = \alpha c$, $[OH^-] = \alpha c$ and $[HA] = (1 - \alpha) c$.

Conc. of the acid is taken c (M) and $K_a = \frac{\alpha^2 c}{1 - \alpha}$. For approximate value of pH, α is neglected in the denominator as $\alpha \ll 1$.

Thus, $K_a \approx \alpha^2 c = \frac{(\alpha c)^2}{c} = \frac{[H^+]^2}{c}$ or, $[H^+] = \sqrt{K_a \times c}$ or, $pH = -\log[H^+] = -\log \sqrt{K_a \times c}$

or, $pH = \frac{1}{2} pK_a - \frac{1}{2} \log c$. But c = 1 M hence, $pH = \frac{1}{2} pK_a$, since c = 1 (M) so $\log c = 0$.

[Burdwan Univ. 2010]

Q 1(v). Aqueous solution of 1 (M) NH_4Cl and 1 (M) $(NH_4)_2SO_4$ do not have exactly the same pH- Justify or criticize. [2]

Ans. The statement is correct.

1 (M) NH_4Cl when hydrolyzed gives $NH_4Cl + H_2O \rightleftharpoons NH_4OH + HCl$

Or, $NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+$

But when 1 (M) $(NH_4)_2SO_4$ is hydrolyzed it gives

$(NH_4)_2SO_4 + 2H_2O \rightleftharpoons 2NH_4OH + H_2SO_4$ or, $2NH_4^+ + 2H_2O \rightleftharpoons 2NH_4OH + 2H^+$

Thus 1 (M) $(NH_4)_2SO_4$ produces more H^+ so the solution have less pH than the 1 (M) NH_4Cl solution.

Q 2(i)(b). The hydrolysis constant of KCN is 1.39×10^{-5} . Calculate the degree of hydrolysis of KCN in $10^{-1}(M)$ and $10^{-2}(M)$ solution of KCN. [4]

Ans. For the hydrolysis of KCN, $K_h = \frac{x^2 c}{1-x} \approx x^2 c$ or, $x = \sqrt{K_h/c}$. Thus, in $10^{-1}(M)$ solution of KCN,
 $x = \sqrt{1.39 \times 10^{-5} / 10^{-1}}$ or, $x = 1.8 \times 10^{-2}$. In $10^{-2}(M)$ solution, $x = \sqrt{1.39 \times 10^{-5} / 10^{-2}} = 3.7 \times 10^{-2}$.

Q 2(i)(c). Explain briefly and qualitatively the mechanism of action of a mixture of CH_3COONa and acetic acid solution as a buffer. [4]

Ans. See the buffer action of the two solutions.

Q 2(iii)(c). Aqueous solution of two salts AB and $A'B'$ at equal molar concentration has equal pH. The acid HA and base $B'OH$ are strong while the acid HA' and base BOH are weak. Establish a relation between pK values of the weak acid and weak base in terms of salt conc.

Ans. The two salts AB and $A'B'$ are hydrolyzed as $AB + H_2O \rightleftharpoons HA + BOH$ and $pH = 7 - \frac{1}{2} pK_b - \frac{1}{2} \log c$,
 and $A'B' + H_2O \rightleftharpoons HA' + B'OH$ So for this solution $pH = 7 + \frac{1}{2} pK_a + \frac{1}{2} \log c$,
 but both solutions have same pH and have same c, so $7 - \frac{1}{2} pK_b - \frac{1}{2} \log c = 7 + \frac{1}{2} pK_a + \frac{1}{2} \log c$,
 or, $\frac{1}{2} (pK_b + pK_a) + \log c = 0$ or, $(pK_a + pK_b) + 2 \log c = 0$ or, $(pK_a + pK_b) = -2 \log c$
 This is the required relation between pK-values of weak acid and weak base in terms of salt conc. (c).

[Burdwan Univ. 2011]

Q 1(v). "The degree of dissociation of weak acid increases with dilution but its H^+ ion conc. decreases." Comment on the statement. [2]

Ans. Formulate $K_a = \frac{\alpha^2 c}{(1-\alpha)}$. When the solution is diluted, conc. c is lowered and $\frac{\alpha^2}{(1-\alpha)}$ is increased.

So, α is increased as K_a is constant at a given temperature.

Again, $K_a \approx \alpha^2 c = \frac{[H^+]^2}{c}$ or, $[H^+] = \sqrt{c \times K_a}$ when c is lowered $[H^+]$ is also decreased.

Q 2(i)(b). Explain why the color change interval of an indicator is $pK_{in} \pm 1$, where K_{in} the indicator is constant. [4]

Ans. For indicator $In_A \xrightleftharpoons{K_{in}} H^+ + In_B$ or, $K_{in} = \frac{[H^+][In_B]}{[In_A]}$ or, $[H^+] = K_{in} \times \frac{[In_A]}{[In_B]}$ or, $pH = pK_{in} + \log \frac{[In_B]}{[In_A]}$.

But when $\frac{[In_A]}{[In_B]} \geq 10$, human eye can recognize the acid color of the indicator. So to view the acid color.

$pH = pK_{in} - 1$ and less. When $\frac{[In_A]}{[In_B]} \geq \frac{1}{10}$, base color is recognized and for that $pH = pK_{in} + 1$ and above.

Thus pH range for color change of the indicator is $pK_{in} \pm 1$.

Q 3(ii)(a). Calculate the pH of a buffer solution containing 0.2 M acetic acid and 0.02 M sodium acetate. What will be the change in pH when 1 ml of 1 N HCl is added to litre of this buffer? ($K_a = 1.85 \times 10^{-5}$) [4]

Ans. Henderson equation for acid buffer, $pH = pK_a + \log \frac{[salt]}{[acid]}$, where $pK_a = -\log(1.85 \times 10^{-5}) = 4.73$

thus, $pH = 4.73 + \log\left(\frac{0.02}{0.2}\right) = 3.71$.

When 1 ml of 1 N HCl is added to 1 lit of this buffer solution $[H^+]$ added, H^+ reacts with Ac^- of the salt.

$[H^+] = 1 \times \frac{1(N)}{1000} = 1 \times 10^{-3} (N)$ and $[acid] = 0.2 + 1 \times 10^{-3} = 0.201(N) = 0.201M$

and $[salt] = 0.02 - 1 \times 10^{-3} = 0.019M$. Thus $pH = 4.73 + \log\left(\frac{0.019}{0.201}\right) = 3.706$,

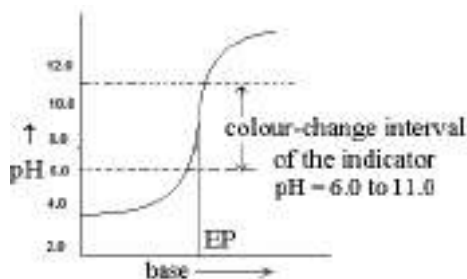
so the change of pH by the addition of 1 ml of 1 N HCl = $3.71 - 3.706 = 0.004$.

[Burdwan Univ. 2012]

Q 1(ii). An acid-base titration curve shows inflexion from pH = 6.0 to pH = 11.0. Draw the curve for pH against volume of added alkali and indicate in the diagram the color change interval of the indicator which is most suitable for the titration: Choose the indicator from the list: Methyl Orange ($pK_{in} = 3.7$),

Methyl Red ($pK_{in} = 5.1$), Phenolphthalein ($pK_{in} = 9.6$) [2]

Ans.



Phenolphthalein is the most suitable indicator.
The pH range of color change of the indicator is 8.6 to 10.6.

Q 2(d)(ii). How buffer capacity of a solution is described? Show that buffer capacity is maximum when $pH = pK_a$.

Ans. See the Text. [6]

Q 3(c)(ii). What are redox indicators? Give an example. [2]

Ans. The redox indicators are used to indicate the end point of the redox titration. They are usually organic compound which shows different contrasting colors in the reduced and oxidized forms.

One example is barium biphenyl amine sulphonate (BDS). It is colorless in the reduced form but violet in the oxidized form.

Q 3(e)(ii). Calculate the pH of a 0.02 (M) aqueous solution of NH_4Cl (Given that K_b of $NH_4Cl = 1.85 \times 10^{-5}$) [2]

Ans. The pH of the solution is $pH = 7 - \frac{1}{2} pK_b - \frac{1}{2} \log c$. But $pK_b = -\log K_b = -\log(1.85 \times 10^{-5}) = 4.73$

Thus, $pH = 7 - \frac{1}{2} \times 4.73 - \frac{1}{2} \log(0.02) = 5.48$.

[Burdwan Univ. 2013]

Q 1(iii). Estimate the pH of a solution obtained by mixing 5 gm of acetic acid and 7.5 gm of solution acetate per 500 ml of solution at 25 °C. (Given, $K_a = 1.85 \times 10^{-5}$ at 25 °C) [2]

Ans. The Henderson equation is $\text{pH} = \text{p}K_a + \log \left(\frac{[\text{salt}]}{[\text{acid}]} \right)$, here $\text{p}K_a = -\log(1.85 \times 10^{-5}) = 4.73$.

$$[\text{salt}] = \left(\frac{7.5}{82} \right) \times \left(\frac{1000}{500} \right) = 0.183(M) \quad \text{and} \quad [\text{acid}] = \frac{5}{60} \times \frac{1000}{500} = 0.167(M).$$

Putting the values in the equation, $\text{pH} = 4.73 + \log \frac{0.183}{0.167} = 4.77$.

Q 3(a)(i). State Ostwald's dilution law. Show that degree of dissociation of a weak electrolyte approaches unity as conc. tends to zero. [1+2]

Ans. See the Text.

(ii). Calculate the pH of a 0.1 (M) solution of ammonium lactate at 25 °C .

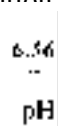
[$\text{p}K_a$ of lactic acid = 3.86, K_b of $\text{NH}_4\text{OH} = 1.8 \times 10^{-5}$] [2]

Ans. Ammonium lactate is salt of weak acid and weak base, so the pH of the salt solution, $\text{pH} = 7 + \frac{1}{2}(\text{p}K_a - \text{p}K_b)$.

$\text{p}K_a$ of $\text{NH}_4\text{OH} = -\log(1.8 \times 10^{-5}) = 4.74$. So $\text{pH} = 7 + \frac{1}{2}(3.86 - 4.74) = 6.56$.

(iii). Proof the variation of pH with conc. of ammonium lactate is an aqueous solution [1]

Ans. pH of aqueous solution of ammonium lactate is independent of salt conc. So the plot of pH vs. conc. is straight line parallel to conc. axis.



[Burdwan Univ. 2014]

Q 1(v). Calculate the percentage of ionization of an acid-base indicator (HIn) at $\text{pH} = \text{p}K_{in} + 1$. [2]

Ans. HIn dissociates as, $\text{HIn} \xrightleftharpoons{K_a} \text{H}^+ + \text{In}^{*-}$. The Henderson equation is

$$\text{pH} = \text{p}K_{in} + \log \frac{[\text{In}^{*-}]}{[\text{HIn}]}, \text{ comparing with the problem, } \log \frac{[\text{In}^{*-}]}{[\text{HIn}]} = 1 \text{ or, } \frac{[\text{In}^{*-}]}{[\text{HIn}]} = 10.$$

If α = degree of dissociation of HIn, then $\frac{\alpha c}{(1-\alpha)c} = 10$ or, $\alpha = 0.909$ or percentage of ionization of HIn = 90.9 %.

Q 2 (d)(i). What is the pH of 0.1 M solution of acetic acid? [$K_a = 1.85 \times 10^{-5} M$]. [2]

Ans. $[\text{H}^+] = \sqrt{K_a \times c} = \sqrt{1.85 \times 10^{-5} \times 0.1} = 1.36 \times 10^{-3} (M)$. Or, $\text{pH} = -\log[\text{H}^+] = -\log(1.36 \times 10^{-3}) = 2.87$.

(ii). Prove that the buffer capacity is maximum when the acid and the salt are present in equal conc. [2]

Ans. See Text.

Q 3(f). A buffer solution is 0.1(M) in acetic acid and 0.1(M) in solution acetate. Calculate the change in pH upon adding 2 ml 5(N) NaOH solution to 1 liter of buffer solution ($\text{p}K_a$ of acetic acid = 4.8) [3]

Ans. pH of buffer initially = $pK_a + \log \frac{[salt]}{[acid]} = 4.8 + \log \frac{0.1}{0.1} = 4.8$

When 2 ml of 5 (N) NaOH is added to 1 lit buffer $[OH^-] = 2 \times \frac{5}{100} = 0.01(N)$, when strong alkali is added,

$HAc + OH^- \rightleftharpoons H_2O + Ac^-$ reaction occurs. $[salt] = 0.1 + 0.01 = 0.11(M)$ and

$$[acid] = 0.1 - 0.01 = 0.09(M)$$

$$pH = 4.8 + \log \left(\frac{0.11}{0.09} \right) = 4.887. \text{ Change of } pH = 4.887 - 4.8 = 0.087.$$

Thus, change of pH by addition of 2 ml 5 (N) NaOH to 1 lit buffer of pH 4.8 is 0.0087 only.

[Burdwan Univ. 2015]

Q 1(iii). An aqueous solution of KHF_2 can act as buffer– Justify or criticize. [2]

Ans. The statement is correct. KHF_2 is HF and KF in which HF is weak acid and KF, the salt of the acid. Thus it can act as buffer.

When H^+ is added to the solution, it is neutralized by F^- as H^+ (added) + F^- (buffer) \rightarrow HF

Again when OH^- from strong base is added, it is neutralized by HF.



Q 2(b)(i). Show that $[H_3O^+]$ of a solution containing two weak monoprotic acids of conc. c_1 and c_2 is given by

$$[H_3O^+] = \sqrt{K_1c_1 + K_2c_2} . \quad [5]$$

Ans. The two monoprotic acids are dissociating as $H_2O + HA_1 \rightleftharpoons H_3O^+ + A_1^-$ and $K_1 = \frac{[H_3O^+][A_1^-]}{[HA_1]}$

but $[HA_1] = c_1(1-\alpha) \approx c_1$. Thus, $[H_3O^+][A_1^-] = K_1c_1$

Similarly for the 2nd acid, $[H_3O^+][A_2^-] = K_2c_2$ (1)

So, $\frac{[A_1^-]}{[A_2^-]} = \frac{K_1c_1}{K_2c_2}$ and $[H_3O^+] = [A_1^-] + [A_2^-]$ (2)

or, $[A_1^-] = [A_2^-] \times \frac{K_1c_1}{K_2c_2}$ (3)

as the dissociation is small, especially in the presence of $[H_3O^+]$ of the other acid which acts as common ion.

Putting equation (2) in equation (3), we have $[H_3O^+] = [A_2^-] \times \frac{K_1c_1}{K_2c_2} + [A_2^-]$

or, $[H_3O^+] = [A_2^-] \left(1 + \frac{K_1c_1}{K_2c_2} \right) = [A_2^-] \times \left(\frac{K_1c_1 + K_2c_2}{K_2c_2} \right)$, Now from (1) $[A_2^-] = \frac{K_2c_2}{[H_3O^+]}$. Or,

$$[H_3O^+] = \left(\frac{K_2c_2}{[H_3O^+]} \right) \times \left(\frac{K_1c_1 + K_2c_2}{K_2c_2} \right) \text{ or, } [H_3O^+]^2 = K_1c_1 + K_2c_2 \text{ or, } [H_3O^+] = \sqrt{K_1c_1 + K_2c_2} .$$

Q 2(b)(ii). For the indicator thymol blue, the value of pH is 2.0 when half of the indicator is present in the unionized form. Calculate the percentage of the indicator in the unionized form in a solution of 4.0×10^{-3} M hydrogen ion conc. [4]

Ans. Let the indicator is represented as $HIn \rightleftharpoons H^+ + In^-$ and $pH = pK_{In} + \log \frac{[In^-]}{[HIn]}$

Thus, But at pH = 2, $[In^-] = [HIn]$. Thus, $2.0 = pK_{In}$. Now at the $[H^+] = 4.0 \times 10^{-3}$ (M),

$$pH = -\log(4.0 \times 10^{-3}) = 2.398, \text{ so we have } 2.398 = 2.0 + \log \frac{[In^-]}{[HIn]}$$

$$\text{or, } \log \frac{[In^-]}{[HIn]} = 2.398 - 2.0 = 0.398 \quad \text{or, } \frac{[In^-]}{[HIn]} = 10^{0.398} = 2.5 \quad \text{or, } \frac{[HIn] + [In^-]}{[HIn]} = 2.5 + 1 = 3.5$$

$$\text{or, } \frac{[HIn]}{[HIn] + [In^-]} = \frac{1}{3.5} = 0.2857 \text{ so, percentage of the indicator in the unionized form, } [HIn] = 28.57.$$

Q 3(f)(i). Calculate the pH of a 0.01(M) sodium solution ($K_{acetic\ acid} = 1.8 \times 10^{-5}$ and $pK_a = 4.74$). [2]

Ans. Sodium acetate undergoes hydrolysis in aqueous solution and its pH is given as $pH = 7 + \frac{1}{2} pK_a + \frac{1}{2} \log[salt]$

$$\text{so, } pH = 7 + \frac{1}{2} \times 4.74 + \frac{1}{2} \log(0.01) = 7 + 2.37 - 1.0 = 8.37 \quad \text{at } 25^\circ\text{C}.$$

ELECTROCHEMISTRY

PROPERTIES OF IONIC SOLUTIONS – PART II

(CONDUCTANCE)

[Syllabus of BU: Specific conductance, equivalent conductance and molar conductance – variation with temperature, Kohlrausch's law; Walden rule; transport number and ionic nobilities (definition and properties). Conductance measurements and solubility products. Principle of conductometric titrations]

INTRODUCTION:

Conductance provides the evaluation of various properties of electrolyte solution.

This chapter deals with conductance of electricity by electrolyte solutions. This conducting ability of the electrolyte solutions is a direct proof of existence of ions in solution. The experimental determination of conductance provides the behavior of ions in solution and this helps to determine various physical quantities like solubility product of sparingly soluble salt, ionic product of water, dissociation constant of weak acids or bases, hydrolysis constant of salt etc. It also provides the basis of conductometric titration.

ELECTRICAL CONDUCTORS:

Conductors are the substances that allow the flow of electric current through it. It is classified as

Types of conductors

Metallic or electronic conductors	Electrolytic conductors
(1) Electrons are responsible for the conductance (2) Electrons move from higher potential to lower potential. (3) No chemical change occurs of the conductor. (4) Conductance decreases with the increase of temperature. This occurs due to the resistance offered to the moving electrons by the vibration of atoms or ions comprising the conductor. At very low temperature 3 – 4K, many conductors behave as super conductor.	(1) Ions are responsible for the conductance. (2) Ions move towards the oppositely charged electrodes. (3) Chemical change of the electrolyte occurs at the electrodes. (4) Conductance increases with the increase of temperature. This is due to increase of velocity of ions in solution.

ELECTROLYSIS → FARADAY'S LAWS:

Chemical changes that occur at the electrodes due to passage of electricity through the electrolyte solution is called electrolysis. It follows Faraday's laws.

1st law: The amount of decomposition at the electrodes (w) is directly proportional to the quantity of electricity passed (Q).

i.e. $w \propto Q$, or $w = ZQ$, or $w = ZIt$, where 'Z' is electrochemical equivalent of the decomposing substance,

'I' is the current strength i.e. amount of electricity passing in unit time and 't' is time flow of electricity.

Definition and value of one faraday.

The amount of electricity required to decompose one gram equivalent of a substance is called one faraday (F). Its value is 96,496 coulomb/gm equiv. We take approximately, $1 F = 96,500 \text{ coulomb/gm equiv.}$

This is why, one faraday is called one gm equivalent electricity.

It is not easy to keep 'I' constant so the charges ($Q = I \times t$) is difficult to measure flowing in a circuit. A good way to measure Q is to put an electrolytic cell in series in the circuit. Q is calculated from the weight of the metal deposited (w) using the relation,

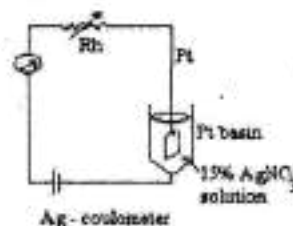
Measurement of electric charge → Ag-Coulometer

$Q = \frac{w}{Z}$ where, the electrochemical equivalent of the metal, $Z = \frac{M}{z \cdot F}$

Such a device is called coulometer. Ag is the metal commonly used. 15% solution of AgNO_3 in a platinum basin is inserted in the circuit.

The basin acts as cathode and Ag is deposited on the basin when the electricity is passed in the circuit.

$$Z_{\text{Ag}} = 0.001118 \text{ gm/C and } Q = w_{\text{Ag}} / Z_{\text{Ag}}$$



2nd law: Weight of different substances (w) decomposed at the different electrodes by a given amount of electricity are proportional to their equivalent weights (E).

$$\text{i.e. } \frac{w_1}{w_2} = \frac{E_1}{E_2}$$

Faraday's experiments showed that these rules were followed with great accuracy. So far we know these laws are exact.

Calculation of Avogadro number (N_A)

This law helps determine Avogadro's Number (N_A).

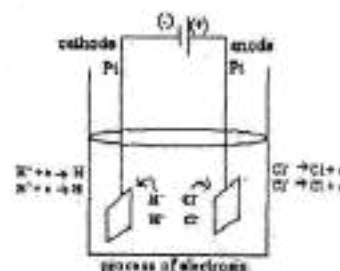
For decomposition of 1 gm ion (mole) substance at the electrode, zF electricity is required. Again 1 mole of the ion carries zeN_A amount of charge.

Therefore, we have, $zeN_A = zF$ or, $N_A = F/e$, where $z = \text{valence of decomposing ion.}$

The numerical value of Avogadro's number, $N_A = \frac{96,500 \text{ C mol}^{-1}}{1.6 \times 10^{-19} \text{ C}} = 6.023 \times 10^{23} \text{ mol}^{-1}$.

PROCESS OF ELECTROLYSIS AND MECHANISM OF ELECTROLYTIC CONDUCTANCE:

Let us take the electrolysis of HCl solution through Pt electrodes. As seen in the figure, there is surplus of electrons at the cathode and deficit of electrons at the anode. H^+ ion in solution moves towards cathode by Coulombic force and receives one electron from it and thus forms H-atom.



One electron is transported with the help of one H^+ ion and Cl^- ion

On the other hand, Cl^- ion in solution moves towards

anode, departs one electron to it and forms neutral

Cl -atom. One electron is transported from cathode to anode by H^+ and Cl^- in solution.

But due to such transport of electricity, the ions are decomposed at the electrodes. Two H-atoms form a H_2 molecule and escapes from the solution and two Cl-atoms also at the same time form Cl_2 molecule and liberates from the solution. This mechanism can thus explain also Faraday's two laws of electrolysis.

ELECTRODES:

These are electronic conductors partly immersed in solution and impart electrons or receive electrons from the solution. We may consider two types of electrodes.

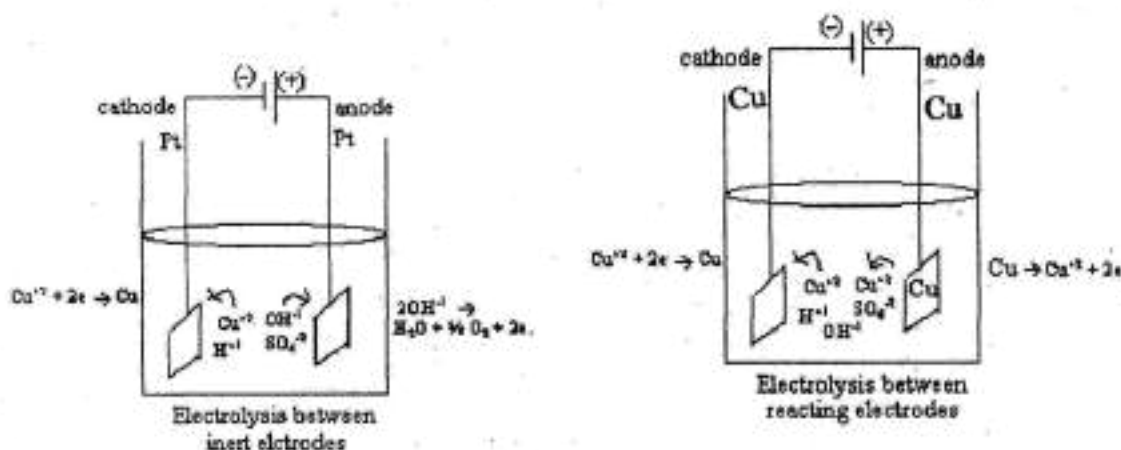
(1) Inert electrodes:

These electrodes do not participate in the electrode reactions. They merely help in the transfer of electrons to and from the solution. Pt, Au etc. are such type of electrodes.

When CuSO_4 solution is electrolyzed between Pt electrodes, Cu is deposited at the cathode by receiving two electrons.



SO_4^{-2} will not discharge at the anode due to its high deposition potential. OH^- ion present in the solution is discharged at the anode as its deposition potential is lower than SO_4^{-2} ion.



(2) Reacting electrodes: These electrodes participate in the electrode reactions either by contributing ions to the solution or accepting the discharged ions from the solution.

When CuSO_4 solution is electrolysed between two Cu electrodes, Cu is deposited at the cathode as usual but equivalent amount of Cu is dissolved at the anode.

(Note: This process is commonly used to produce pure Cu from impure Cu.)

Main points in this connection may be noted:

- (1) Current carrying ions are discharged at the electrodes.
- (2) In aqueous solution, when (-)ve ions are difficult to be discharged due to high potential, OH^- ions get discharged.
- (3) When (+)ve ions are difficult to be discharged, H^+ ions are discharged from the solution.

Problem – Calculate the quantity of electricity which would be required to reduce 9.84gm nitrobenzene to aniline. If the voltage across the electrolyte will be 2.4 volt, what energy would be consumed in the process?

Answer - The solution reaction can be written as, $\text{C}_6\text{H}_5\text{NO}_2 + 6\text{H} = \text{C}_6\text{H}_5\text{NH}_2 + 2\text{H}_2\text{O}$.

So the equivalent weight of nitrobenzene is $\frac{6 \times 12 + 5 + 14 + 32}{6} = 20.5$.

9.84 gm of nitrobenzene is thus equivalent to $9.84/20.5 = 0.48$ gm equiv.

The electrical energy would be consumed in the reduction process

$$= 0.48 \times 96500 \times 2.4 \text{ Joule} = 111.168 \text{ kJ}.$$

The quantity of electricity would be required = $0.48 \times 96500 = 46320$ Coulombs.

Definition of transport number of an ion and its relation with velocity.

TRANSPORT NUMBER (t):

We have seen that ions are current-carriers & equivalent amount of ions are discharged at each electrode by passage of electricity. But fraction of total current carried by cations and anions may not necessarily be the same. For example, in dilute solution of HNO₃ acid, 84% of current is carried by H⁺ and only 16% is carried by NO₃⁻. This is due to the fact that H⁺ moves faster than NO₃⁻.

Contribution to the transport of electricity of an ion is quantified by a term, called transport number. The fraction of total current carried by an ion is called the transport number of that ion (t). Thus,

$t_+ = \frac{I_+}{I}$ and $t_- = \frac{I_-}{I}$, so $t_+ + t_- = 1$, where I_+ and I_- are the current carried by the cations and anions respectively. The transport number of an ion signifies its contribution to the transport of charge from one electrode to the other. It is directly related to the velocity of the concerning ion and its co-ion in solution.

The exact relation between the transport number and velocity is formulated below

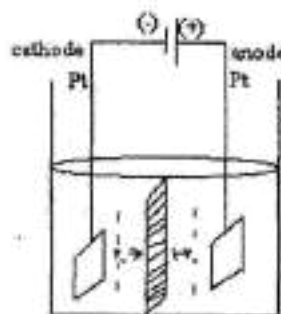
TRANSPORT NUMBER AND VELOCITY OF IONS:

Let us build up a relation between the transport number and velocity of an ion. For the purpose, an electrolyte solution is taken between two inert electrodes under an electric field E.

The following notations are used in this formulation.

- n_+ = number of cations per unit volume.
- n_- = ----- anions -----
- z_+ = valence of cation of the electrolyte.
- z_- = ----- anion -----
- v_+ = velocity of cation under electric field E.
- v_- = ----- anion -----

The symbols of the terms used in the formulation.



Migration of ions across a plane

Let us imagine a plane of surface area 'a' and see how much charge is passing through the plane in one second time. In one second, cation moves from v_+ distance and anion moves from v_- distance of the imaginary plane.

I_+ = charge passed through the plane in unit time by the cation = $(a \times v_+) n_+ z_+ e$, and
 I_- = ----- anion ----- = $(a \times v_-) n_- z_- e$.

Thus the transport number of cation, $(t_+) = \frac{I_+}{I_+ + I_-} = \frac{(a \times v_+) n_+ z_+ e}{(a \times v_+) n_+ z_+ e + (a \times v_-) n_- z_- e}$

Since the solution is electrically neutral, $n_+ z_+ e = n_- z_- e$.

Utilizing the condition, we get, the transport number, $t_+ = \frac{v_+}{v_+ + v_-}$ and $t_- = \frac{v_-}{v_+ + v_-}$.

Transport number of an ion is not its absolute property.

These are the required relations. It is seen that transport number of any ion depends on the velocity of that ion and also that of other ion with which the ion is associated in solution.

Hence transport number is not an absolute property of an ion. In general, transport number of an ion depends also on the velocity of other ions present in the solution.

Problem: The speed ratio of silver and nitrate ions in an aqueous solution of AgNO_3 has been found to be 0.92. Calculate the transport number of these two types of ions. [VU'87].

Answer: Transport number of $\text{Ag}^+ = 0.48$ and that of $\text{NO}_3^- = 0.52$.

DETERMINATION OF TRANSPORT NUMBER :

(A) Hittorf Method:

Hittorf (1853 - 59) made significant contribution to build up concept of transport number of ions in electrolyte solution. For this reason transport number is some times called Hittorf number to show the honor to the scientist.

Hittorf rule:

This rule acts as principle for determination of transport number of an ion. Due to different speed of cation and anion of an electrolyte solution, the conc. around the electrodes changes when electrolysis occurs. This difference in conc. around cathode and anode is taken advantage to determine transport number of the ions.

To explain the principle, let us divide the solution into three imaginary compartments — anode, cathode and middle compartments. Let us take each compartment contains equal amount of the electrolyte.

Before passing electricity, each compartment let contains five equivalent of cations and anions.

Now after passing two faraday electricity, electrolysis occurs. Let the velocity ratio of cation and anion is one i.e., when cation moves one step towards the cathode, anion also moves one step towards the anode.

Fall in equivalent conc. in the cathode and anode compartment is equal and it is one equivalent.

When the velocity ratio of cation and anion is $3/2$, i.e. in a

given time when the cation moves 3 steps, the anion moves 2 steps to the respective electrodes, the fall in conc. in each cathode and anode compartment is not equal after passing 5F electricity. Though 5 equivalent cations and 5 equivalent anions are deposited in each electrode. the fall in conc. in cathode compartment is 2 equivalent and in anode compartment is 3 equivalent.

Taking various cation-anion velocity ratios, we can come to the following conclusions.

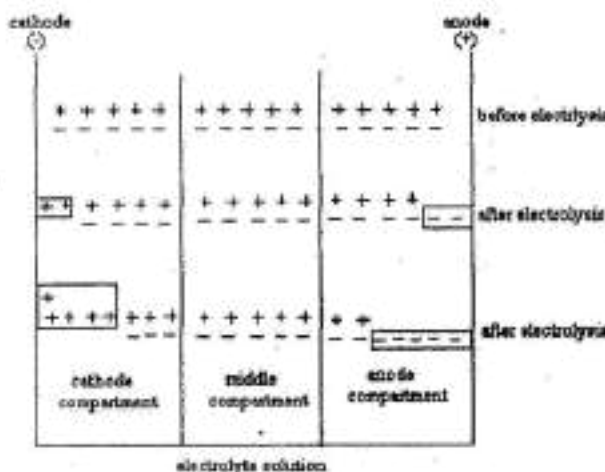
- (i) Fall in equivalent conc. around any compartment \propto velocity of the ion leaving that compartment.
- (ii) Total equivalent of ion deposited in each electrode \propto sum of velocity of cation and anion ($v_+ + v_-$).

Therefore, transport number of cation (t_+)

$$= \frac{v_+}{v_+ + v_-} = \frac{\text{Fall in equivalent conc. of the anode compartment}}{\text{Total equivalent of ion deposited at any electrode}}$$

Fall in conc. around an electrode is directly related with ionic velocity

Experimental data is utilized to formulate the Hittorf rule



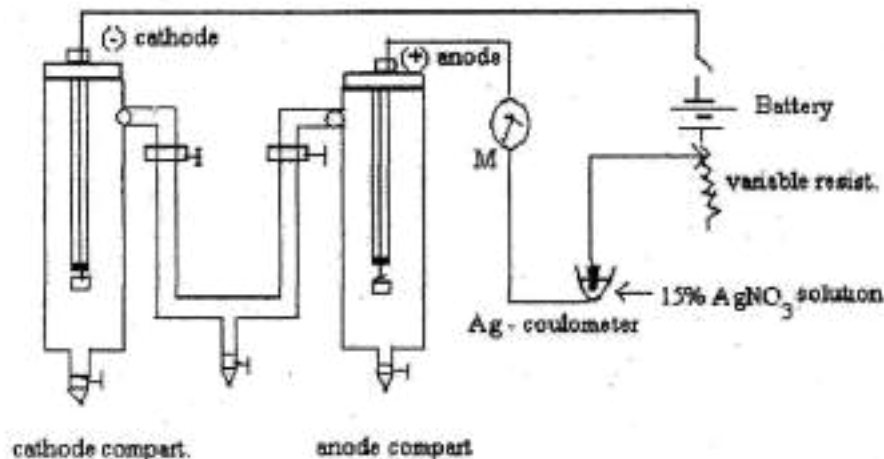
The Hittorf principle

And the transport number of anion ($t_- = 1 - t_+$).

Hittorf used the above principle to determine the transport number of ions. The apparatus consists of three compartments. The conc. of electrolyte in each compartment is determined before and after electrolysis. Analysis of the middle compartment is used to check up any interfering effect that may occur during the experiment.

Experimental precautions

A current of about 10-20 milliamps is usually passed for 2-3 hours to get an appreciable change in conc. in the anode and cathode compartment. Low current strength is used to avoid heating effect (heat produced by passing of current = $I^2 R t$)



The junction of the compartments is kept narrow to avoid mass diffusion.

(a) When the electrodes are reacting:

Let an approximate (N/10) AgNO_3 solution is electrolysed using Ag electrodes. Let the anode electrolyte (anolyte) solution is analyzed after electrolysis. Let c_i is the initial conc. (in gm equiv.) of the anolyte solution that is taken for experiment and c_f is the final conc. (in gm equiv.) of the anolyte solution after electrolysis. c_d gm equiv. of Ag is deposited in the coulometer connected in series with the circuit.

Then c_d gm equiv. of Ag is also dissolved in the anolyte solution. If c_m gm equiv. of Ag is migrated out from the anode compartment, then considering the mass-balance of the anolyte solution, we get, $c_i + c_d - c_m = c_f$ or, $c_m = c_i + c_d - c_f$.

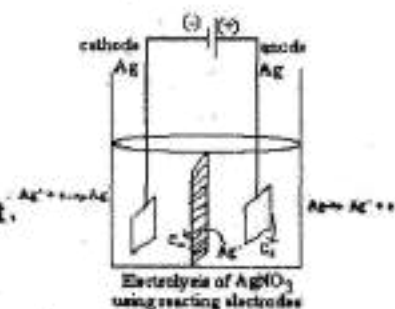
As c_m is directly proportional to the velocity of Ag^+ ion, the transport number of Ag^+ ,

$$t_{\text{Ag}^+} = \frac{c_m}{c_d} \quad \text{or,} \quad t_{\text{Ag}^+} = \frac{c_i + c_d - c_f}{c_d}$$

(b) When the electrodes are inert:

The same solution may be electrolysed using Pt electrodes which remain inert during the electrolysis. In this case, c_d in the numerator

Calculation for transport number when the electrodes are reacting



of the above equation is equal to zero, since there would be no dissolution of Ag^+ ion from Pt electrodes. Thus, the transport number of Ag^+ is given as,

$$t_{\text{Ag}^+} = \frac{c_i - c_f}{c_d} \text{ and } t_{\text{NO}_3^-} = (1 - t_{\text{Ag}^+}).$$

(B) Moving boundary method:

This method directly measures the velocity of the ions

Direct method

by noting the movement of boundary under an applied electric field.

The apparatus consists of a long but narrow vertical tube of uniform cross-section of area 'a' cm^2 . It is fitted with two inert electrodes at the two ends. The principal electrolyte, BA (here, HCl) is kept at the cathode end and the indicator electrolyte, $B'A$ (here, CdCl_2) is kept at the anode end of the tube. The conditions of the indicator electrolyte are:

Conditions of the following ion

- (i) velocity of B is greater than that of B' so that B' only follows B when the two move under electric field, hence B' is called following ion.
- (ii) The two electrolyte solutions are taken in increasing density downwards so the mixing is avoided.

These two solutions form a boundary in the narrow tube.

Let on passing Q faraday of electricity through the solution, the boundary moves the distance 'l' cm due to movement of ions B and B' .

Calculation of transport number

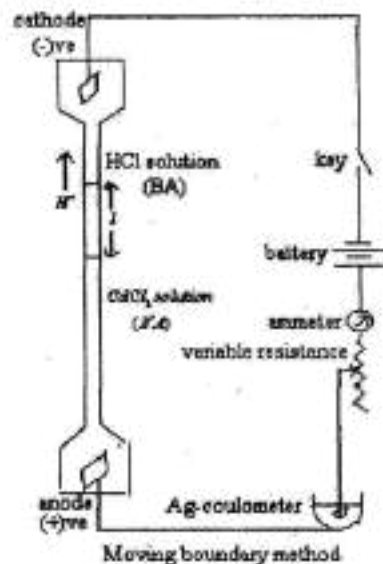
The gm equiv. of B' moves towards cathode

$$= \frac{c \times l \times a}{10^3}, \text{ where, } c = \text{conc. of BA solution}$$

in normality. Thus, charge carried by B'

$$= \frac{c \times l \times a}{10^3} \text{ faraday. Hence, } t_{B'} = \frac{c \times l \times a}{10^3 \times Q}.$$

The result obtained by this method is very accurate and the experiment is quick and easy to handle.



TRANSPORT NUMBER AND HYDRATION:

The transport number of an ion is closely related with its hydration in solution. We may discuss the effect of hydration on the alkali metal ions. :

The expected values of transport number of alkali metal ions = $t_{\text{Li}^+} > t_{\text{Na}^+} > t_{\text{K}^+}$.

Greater the hydration of an ion, lower will be its transport number.

But experimentally observed values = $t_{\text{Li}^+} < t_{\text{Na}^+} < t_{\text{K}^+}$.

It is expected that small size Li^+ ion would have high velocity and hence high transport number. But the experimental results are just opposite to the expected one.

The explanation of this anomaly is that cations are heavily hydrated; different ions have different extent of hydration. Due to small size of Li^+ , its ionic potential, φ (= charge / radius) is large and extent of hydration is also large. Thus, hydrated size of the ions are $\text{Li}^+ > \text{Na}^+ > \text{K}^+$. Since higher the size results in lower velocity and hence smaller is its transport number. This explains the anomaly of transport number of alkali metal ions.

$$(\text{Hydration number of } \text{Li}^+ = 6, \text{Na}^+ = 4, \text{K}^+ = 2, \text{Rb}^+ = 1)$$

Cause for
apparent
transport
number

APPARENT TRANSPORT NUMBER (t') AND TRUE TRANSPORT NUMBER (t):

As the ions are hydrated to large extent due to ion-dipole interaction, the transport number determined by Hittorf method is only apparent. When a cation moves under potential towards the cathode, it carries with it some water molecules from the anode. Similar results occur for the anions also. The migration of water with the ions makes an additional change in conc. of the anode and cathode compartments. But this has not been considered in Hittorf method. Thus, relation between true (t) and apparent (t') transport number of a cation is given as,

$$t_+ = t'_+ + x \frac{w_2}{W}$$

When w_2 gm equiv. of the electrolyte is present in W moles of water, and x mole of water is migrated out (net loss of water) of anode compartment

This relation shows that $t'_+ < t_+$, as 2nd term of the right hand side is generally (+)ve

We know that $t'_+ = \frac{c_a}{c_d} = \frac{c_i - c_f}{c_d}$ but due to migration of water from the anode

compartment, conc. in gm equiv. of cation is increased by $x \frac{w_2}{W}$.

Thus, c_f is apparently increased and so t'_+ is apparent transport number and it is less.

$$\text{Similarly, for anions, } t_- = t'_- - x \frac{w_2}{W}$$

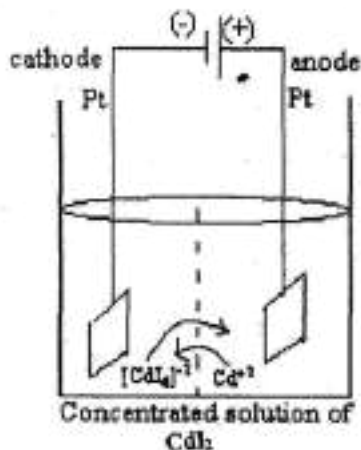
ABNORMAL TRANSPORT NUMBER :

Example of
abnormal value
of transport
number

In some electrolyte solutions, experimental value of transport number of ions is found abnormal. For example, in very dilute solution of CdI_2 , $t_{\text{Cd}^{+2}} \approx 0.4$ but with increasing conc. of the solution, $t_{\text{Cd}^{+2}}$ drops sharply below 0.4, becomes zero and even negative at very high conc. At the same time, t_{I^-} apparently increases beyond 0.6, becomes one and eventually exceeds unity. This abnormality in transport number is explained by complex formation at high conc.



The equil^m. exists largely in right hand side at concentrated solution. Thus, Cd^{+2} ions exist partly in complexed and partly as simple. These two ions move towards opposite electrodes when electricity is passed.



The transport number of Cd^{+2} ion is $t_{\text{Cd}^{+2}} = \frac{c_a}{c_d}$.

As the conc. increases, the formation of complex ion, $[\text{CdI}_4]^{-2}$ is also increased. Now when electricity is passed, Cd^{+2} ion migrates out of the anode compartment, while $[\text{CdI}_4]^{-2}$ ion enters into the compartment simultaneously. Thus, conc. of cadmium ion in anolyte solution is compensated to a large extent.

The value of c_a decreases and so $t_{\text{Cd}^{+2}}$ decreases.

When conc. is high, coming of $[CdI_4]^{-2}$ into the anode compartment compensates fully the loss of Cd^{+2} due to migration away, $c_m = 0$ and $t_{Cd^{+2}} = 0$.

Still at larger conc. of CdI_2 in solution, more of $[CdI_4]^{-2}$ ion comes to the anolyte than Cd^{+2} ion leaves it due to its higher velocity of $[CdI_4]^{-2}$. $c_m = (-)$ ve and so $t_{Cd^{+2}} = (-)$ ve.

Similar phenomenon occurs for $AgCN$ in KCN solution.

TRANSPORT NUMBER AND TEMPERATURE:

With rise in temperature, the transport number of cation and anion of an electrolyte solution try to be equalized.

Thus, when transport number > 0.5 , it decreases with increase of temperature.

and when transport number < 0.5 , it increases with rise in temperature.

TRANSPORT NUMBER AND DILUTION:

Since the velocity of cation and anion depend on conc. and they do not necessarily change at the same rate as c changes, transport number depends on conc. Transport number bears a linear relationship with \sqrt{c} . The relation may be given as

$$t_c = t_0 + k\sqrt{c}$$

where, t_c and t_0 are the transport number of an ion at conc. 'c' and at infinite dilution.

When $t_0 = 0.5$, $k = 0$, when $t_0 > 0.5$, $k = (+)$ ve and when $t_0 < 0.5$, $k = (-)$ ve.

It means that if the transport number is greater than 0.5, it increases with increase of conc.

If the transport number is less than 0.5, it decreases with increase of conc.

However variation of transport number with conc. is small.

The observed t_0 -values lies between 0.3 and 0.7 for most of the ions. H_3O^+ and OH^- have unusually high t_0 -values in aqueous solution, because of their high velocities. Some values of t_0 in aqueous solution at $25^\circ C$ and 1 atm are given.

in HCl solution, $t_{H^+}^0 = 0.82$ and $t_{Cl^-}^0 = 0.18$, in KCl solution, $t_{K^+}^0 = 0.49$ and $t_{Cl^-}^0 = 0.51$,

in $CaCl_2$ solution, $t_{Ca^{+2}}^0 = 0.44$ and $t_{Cl^-}^0 = 0.56$.

TRANSPORT NUMBER OF AN ION IN MIXTURE:

Transport number of an i th kind ion in a solution

containing a mixture of electrolytes is given by, $t_i = \frac{c_i \lambda_i}{\sum c_i \lambda_i}$

where, c_i and λ_i are the conc. and ionic equivalent conductance of the i th kind of ion.

Problems:

- (1) A solution of $AgNO_3$ was electrolysed with Ag electrodes. 0.174 g Ag was deposited on the cathode. The amount of Ag present in the anode solution before and after electrolysis were 0.5200 g and 0.6290 g respectively. What is the transport number of Ag^+ ion.

Solution: $t_{Ag^+} = \frac{c_i + c_d - c_f}{c_d} = \frac{(0.5200 + 0.174 - 0.6290) \text{ g of } Ag}{0.174 \text{ g of } Ag} = 0.373$

- (2) A moving boundary experiment is done to measure the transference number of Li^+ ion in 0.01 mol L^{-1} of $LiCl$ solution. In a tube having a cross sectional area 0.125 cm^2 , the boundary moves 7.3 cm in 1490 sec. Using a current of $1.8 \times 10^{-3} \text{ A}$, calculate t_+ .

Solution: $t_+ = \frac{a \times l \times c}{10^3 \times Q} = \frac{0.125 \text{ cm} \times 7.3 \text{ cm} \times 0.01 \text{ mol L}^{-1}}{10^3 \text{ cm}^3 \text{ L}^{-1} \times (1.8 \times 10^{-3} \text{ A} \times 1490 \text{ sec} / 96500 \text{ C mol}^{-1})} = 0.328$

- (3) A 2 molal solution of FeCl_3 is electrolyzed between Pt electrodes. After electrolysis, the cathode compartment solution weighing 20 g is found to be 1.15 molal in FeCl_3 and 1 molal in FeCl_2 . Calculate the transport number of Fe^{+3} and Cl^- ions. [CU'99].

Solution: The loss of gm equivalent of Cl^- ion in the cathode compartment after electrolysis = $2 \times 3 - (1.15 \times 3 + 1 \times 2) = 6 - 5.45 = 0.55$.

1 molal FeCl_3 is converted to 1 molal FeCl_2 in the experiment.

So the total gm equivalent change occurs in the cathode compartment = 1.

$$\text{So, } t_{\text{Cl}^-} = \frac{c_i - c_f}{c_d} = \frac{0.55}{1} = 0.55. \text{ And } t_{\text{Fe}^{+3}} = 1 - 0.55 = 0.45.$$

- (4) A 4 molal FeCl_3 solution is electrolyzed between platinum electrodes.

After the electrolysis the cathode solution weighing 30 gm is 3.15 molal in FeCl_3 and 1 molal in FeCl_2 . What is the transport number of Fe^{+3} and Cl^- ions? [WBCS'95]

(Answer: $t_{\text{Fe}^{+3}} = 0.45$ and $t_{\text{Cl}^-} = 0.55$.)

- (5) In a moving boundary experiment, the boundary of a dilute KCl solution moved through a capillary of a radius 2.073 mm under a constant current 1.82 milliamp. The boundary moved through 20 mm in 25 min. The specific conductivity is 0.2788 Sm^{-1} . Calculate the mobility of the K^+ ion.

$$\text{Solution: } t_{\text{K}^+} = \frac{Iac}{10^3(I/F)}, \text{ but } \lambda_{\text{K}^+} = t_{\text{K}^+} \times \lambda_{\text{KCl}}^0 = \frac{IacF}{10^3 It} \times \frac{10^3 \kappa}{c} \text{ or, } \frac{\lambda_{\text{K}^+}}{F} = \frac{Ia\kappa}{It}$$

$$\text{The mobility of } \text{K}^+, u_{\text{K}^+} = \frac{Ia\kappa}{It} = \frac{20 \times 10^{-3} \text{ m} \times 3.14 (2.073 \times 10^{-3} \text{ m})^2 \times 0.2788 \text{ Sm}^{-1}}{1.82 \times 10^{-3} \times 25 \times 60 \text{ C}}$$

$$= 2.75 \times 10^{-8} \text{ Sm}^2 \text{ C}^{-1} = 2.75 \times 10^{-8} (\text{ohm As})^{-1} \text{ m}^2 = 2.75 \times 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}.$$

- (6) In a moving boundary method, 33.27 (mM) solution of GdCl_3 is taken with LiCl as the following solution. A constant current of 5.594 mA is passed for 4406 s and the boundary travels between two marks on the tube; the volume between these two marks is 1.111 cm^3 . Find the cation and anion transport number in the GdCl_3 solution.

Solution: Conc. of GdCl_3 solution in normality = $3 \times 33.27 \times 10^{-3} = 9.981 \times 10^{-2} \text{ (N)}$.

The transport number of Gd^{+3} ion in the solution,

$$t_{\text{Gd}^{+3}} = \frac{(a) c F}{10^3 (It)} = \frac{1.111 \text{ cm}^3 \times 9.981 \times 10^{-2} \text{ gm equiv. L}^{-1} \times 96500 \text{ C (gm equiv.)}^{-1}}{10^3 \text{ cm}^3 \text{ L}^{-1} (5.594 \times 10^{-3} \text{ A} \times 4406 \text{ s})}$$

$$= 0.434 \text{ and transport number of } \text{Cl}^- \text{ is } 1 - 0.434 = 0.566.$$

- (7) A 0.14941 wt % aqueous KCl solution at 25°C is electrolyzed in a Hittorf apparatus using two Ag - AgCl electrodes. The cathode reaction is $\text{AgCl(s)} + e \rightarrow \text{Ag(s)} + \text{Cl}^- \text{(aq)}$; the anode reaction is the reverse of this. After the experiment, it is found that 160.24 mg of Ag has been deposited in a coulometer connected in series with the apparatus. The cathode compartment contains 120.99 g of solution that is 0.19404 % KCl by weight. Calculate t_+ and t_- in the KCl solution used in the experiment.

$$\text{Solution: Final conc. of KCl} = \frac{0.19404}{100 - 0.19404} \times 120.99 = 0.2348 \text{ g} = \frac{0.2348}{74.55} \text{ g equiv.} \\ = 3.15 \times 10^{-3} \text{ g equiv.}$$

$$\text{Ag deposited in g equiv.} = 160.24 \times 10^{-3} / 107.87 = 1.485 \times 10^{-3}.$$

$$\text{Initial conc. of KCl in gm equiv.} = \frac{0.14941}{100 - 0.14941} \times \frac{120.99 - 0.2345}{74.55} = 2.424 \times 10^{-3}.$$

$$t_{\text{Cl}^-} = \frac{c_i + c_d - c_f}{c_d} = \frac{(2.424 + 1.485 - 3.15) \times 10^{-3}}{1.485 \times 10^{-3}} = 0.511 \text{ and } t_{\text{K}^+} = 1 - 0.511 = 0.489.$$

Resistance of a conductor (R) is defined by the Ohm's law,

$$R = \frac{\Delta\phi}{I}$$

Ohm's law and its applicability.

Ohm's law is equally applicable to both electronic conductor and electrolytic conductor, provided potential difference is not extremely high and thus steady state is maintained.

In case of electrolyte solution, $\Delta\phi$ is the potential difference of the two electrodes and I is the current flowing through the solution.

R is the resistance of the solution that obstructs the flow of current.

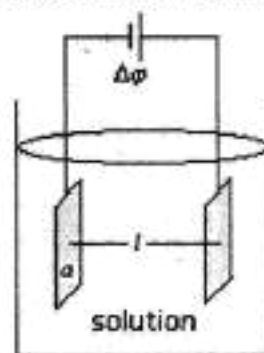
Unit of resistance (R) is ohm (Ω), given in honor of the German scientist, G. S. Ohm.

Factors on which resistance depends.

Resistance of a solution depends on the nature of the electrolyte solution (ρ), and the distance of separation of the two electrodes (l) and the area of the electrode (a) within which the solution is enclosed.

The exact dependence is given by the relation, $R = \rho \left(\frac{l}{a} \right)$.

ρ is the specific resistance of the solution.



Conductance and resistance are reciprocally related.

Reciprocal of resistance is called conductance (C), i.e. $C = \frac{1}{R}$

so conductance is the property of an electrolyte solution that helps to conduct electricity in the solution.

Similarly, specific conductance (κ) is the reciprocal of

specific resistance i.e. $\kappa = \frac{1}{\rho}$. Since ρ is constant of a solution,

so κ is also constant for a solution and does not depend on the cell constant, $\frac{l}{a}$.

Specific conductance (κ):

The above relation of resistance when expressed in terms of conductance gives

$$\frac{1}{C} = \frac{1}{\kappa} \left(\frac{l}{a} \right) \text{ or, } \kappa = C \left(\frac{l}{a} \right)$$

When $l = 1 \text{ cm}$ and $a = 1 \text{ cm}^2$, $\kappa = C$. Thus, specific conductance is the conductance of the solution enclosed between two electrodes 1 cm apart and 1 cm² area.

In other words, the specific conductance (κ) may be defined as the conductance of 1 cc solution enclosed between electrodes 1 cm apart.

Unit of specific conductance:

Unit of conductance (C) is ohm⁻¹ or mho.

Thus, the unit of specific conductance (κ) = ohm⁻¹ × $\frac{\text{cm}}{\text{cm}^2}$ = ohm⁻¹ cm⁻¹.

In SI system, unit of conductance is siemen in honor of the scientist, Sir William Siemen.

The unit of specific conductance in SI system is siemen meter⁻¹ (S m⁻¹).

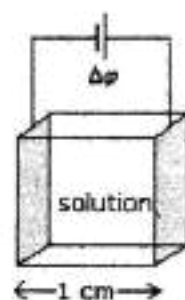
Effect of dilution on specific conductance (κ):

Specific conductance is conductance between the two faces of a unit cube.

Thus, specific conductance depends on (1) number of ions per cc of the solution, (2) charge of the ions and (3) velocity of the ions in the solution.

In case of dilution of strong electrolyte solution, number of ions per cc decreases while the velocity of the ions increases due to less interionic attraction.

Factors on which κ depends.



Specific conductance decreases with dilution.

But the 1st factor dominates over the 2nd factor and net result is the decrease of specific conductance with dilution of the solution.

But in case of dilution of weak electrolyte solution, though the dissociation is enhanced, yet net number of ions decreases per cc of the solution. Velocity of the ions is not affected with dilution as numbers of ions present are small and interionic attraction is insignificant. Thus, in this case also, the specific conductance decreases with dilution.

It also depends on temperature (T) of the solution. Specific conductance (κ) increases by 2% per degree rise in temperature. This is due to lowering of viscosity of the medium that facilitates the higher velocity of the ions.

Equivalent conductance (λ):

Definition of equivalent conductance.

It is defined as the conductance of the solution that contains 1 gm equivalent electrolyte and the solution is enclosed between two parallel electrodes of 1 cm apart.

Relation with specific conductance (κ):

Let the conc. of the electrolyte solution is $c(N)$.

If the volume of the solution is V cc and it contains

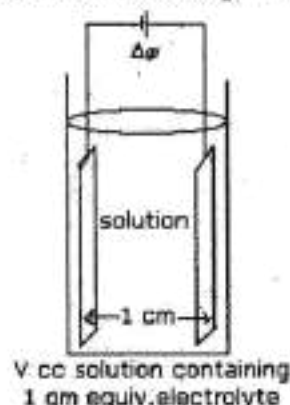
1 gm equiv. electrolyte, then, $V = \frac{1000}{c(N)}$.

Relation between sp. conduct. and equiv. conduct.

The solution is kept between two electrodes of 1 cm apart and specific conductance (κ) is the conductance of 1 cc solution placed between the electrodes of 1 cm apart, hence, the equivalent conductance (λ) = $V \times \kappa$.

Replacing V by conc. c , we get,

$$\lambda = \frac{10^3 \kappa}{c_{(N)}}$$



Unit of λ in cgs and SI systems.

Unit of equivalent conductance = $(\text{ohm}^{-1} \text{cm}^{-1}) / (\text{gm equiv. cm}^{-3}) = \text{ohm}^{-1} \text{cm}^2 \text{gmequiv}^{-1}$ and in S I system it is $\text{S m}^2 \text{gmequiv.}^{-1}$.

Among these properties, conductance (C) is extensive and other two are intensive.

Molar conductance (\wedge);

Definition and unit of molar conduct.

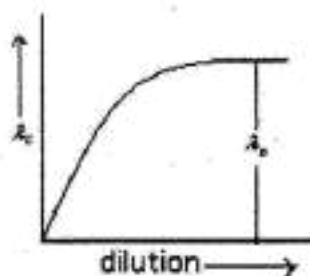
It is defined by similar fashion as the conductance of solution that contains 1 mole of an electrolyte and the solution is placed between two parallel electrodes of 1 cm apart. Its relation with specific conductance (κ) is, $\wedge = \frac{10^3 \kappa}{c_{(M)}}$.

The unit of molar conductance is $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ and in S I system is $\text{S m}^2 \text{mol}^{-1}$.
Effect of dilution on equivalent conductance:

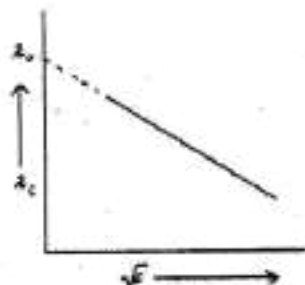
This is discussed separately for two types of electrolyte solutions.

(a) Strong electrolyte solutions: In this case the electrolyte is fully dissociated ($\alpha = 1$) so the total number of ions in 1 gm equivalent electrolyte is fixed. The total charge of the ions in solution is also fixed. Thus, with dilution, the interionic separation is increased and the ionic attraction becomes less. The velocity of the ions are increased resulting the increase of equivalent conductance of the solution. With more dilution, equivalent conductance increases more and attains a limiting value, called equivalent conductance at infinite dilution (λ_0).

Equiv. conduct. of strong electrolyte increases with dilution and attains limiting value.



Kohlrausch plot to determine λ_0 of strong electrolyte.



Strong electrolyte solutions obey Kohlrausch equation,

$$\lambda_c = \lambda_0 - k\sqrt{c}$$

This is an experimental equation, formulated by Kohlrausch from the conductance data of strong electrolyte solutions at different conc.

k = constant but it depends on temperature (T), dielectric constant and viscosity of the solution.

Thus, when λ_c is plotted against \sqrt{c} , a straight line is obtained and the extrapolated intercept gives the value of λ_0 . This is an important method to determine the equivalent conductance of a strong electrolyte at infinite dilution (λ_0).

(b) Weak electrolyte solutions: In this case the dissociation is incomplete ($\alpha < 1$) and low.

So the numbers of ions in solution are relatively few, the interionic attraction does not play any important role. The movements of the ions are free.

With dilution, numbers of ions are increased according to Ostwald dilution law and equivalent conductance (λ) increases but the effect is prominent at high dilution only. Thus, with further dilution of the solution, the resistance of the solution becomes comparable to that of water and it is not experimentally possible to reach the limiting value of equivalent conductance (λ_0).

Weak electrolyte solutions do not obey Kohlrausch equation so its λ_0 value can not be determined by the plot

λ_c vs. \sqrt{c} , as it does not produce straight line.

However, it is determined by other methods to be discussed later.

As the solution is more and more diluted, extent of dissociation is increased very rapidly and when $c \rightarrow 0$, $\alpha \rightarrow 1$.

This helps Arrhenius to formulate a relation for calculation of degree of dissociation from the measurement of equivalent conductance data of weak electrolyte in solution.

The relation is proposed as follows:

$\lambda_c \propto$ numbers of ions present in solution at conc. $c(N)$ and

$\lambda_0 \propto$ total numbers of ions present when the weak electrolyte is fully dissociated.

Therefore, the degree of dissociation at the conc. c of the solution, $\alpha_c = \frac{\lambda_c}{\lambda_0}$.

Problems: For mercury at 0°C , $\kappa = 1.062963 \times 10^6 \text{ S/m}$.

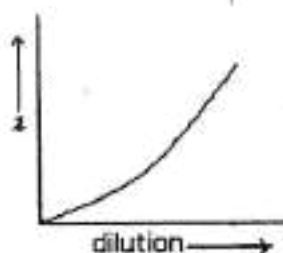
(a) If the resistance of a cell containing mercury is 0.243166Ω , what is the cell constant of the cell?

(b) If the same cell is filled with potassium chloride solution at 0°C , the resistance of the cell is $3.966 \times 10^4 \Omega$. What is the conductivity of the KCl solution?

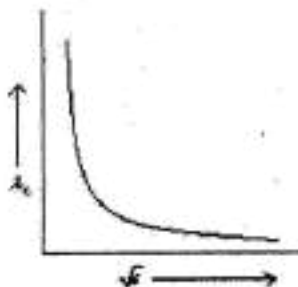
(c) If the average cross-sectional area of the cell is 0.9643 mm^2 , what is the effective distance between the electrodes?

Answer: (a) $0.258476 \times 10^6 \text{ m}^{-1}$ (b) 6.517 S/m (c) 0.2492 m .

Equiv. conduct. of weak electrolyte increases with dilution but does not reach limiting value.



Kohlrausch plot does not help to determine limiting value of equiv. conduct. (λ_0).



Arrhenius formulation of degree of dissociation (α).

DETERMINATION OF λ_0 OF A WEAK ELECTROLYTE FROM A SET OF CONDUCTIVITY DATA OF THE WEAK ELECTROLYTE ITSELF

The equivalent conductance at infinite dilution (λ_0) of a strong electrolyte is determined from the extrapolated intercept of the plot λ_c vs. \sqrt{c} according to the Kohlrausch equation, $\lambda_c = \lambda_0 - k\sqrt{c}$.

But weak electrolyte solution does not obey the above equation and λ_0 of weak electrolyte can not be determined by the above method. However, we can collect the equivalent conductivity data of a weak electrolyte solution at different conc. and these data can be used to calculate λ_0 and also dissociation constant (K) of the weak electrolyte.

Let the weak electrolyte is represented by HA which is dissociating partially in aqueous solution as,



Let the conc. of HA is c mol lit⁻¹ and α is the degree of dissociation, then, $c_{\text{HA}} = c(1-\alpha)$, $c_{\text{H}^+} = \alpha c$ and $c_{\text{A}^-} = \alpha c$.

The dissociation constant of the weak acid, $K_a = \frac{c_{\text{H}^+} \times c_{\text{A}^-}}{c_{\text{HA}}} = \frac{\alpha c \times \alpha c}{c(1-\alpha)}$ or, $K_a = \frac{\alpha^2 c}{1-\alpha}$.

But according to Arrhenius formulation, $\alpha = \frac{\lambda}{\lambda_0}$,

where λ_c is the equivalent conductance of the electrolyte at conc. c (M).

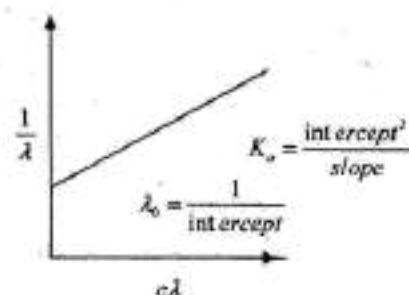
Putting this, we get $K_a = \frac{\left(\frac{\lambda}{\lambda_0}\right)^2 \times c}{1 - \left(\frac{\lambda}{\lambda_0}\right)} = \frac{\lambda^2 \times c}{\lambda_0^2 - \lambda \lambda_0}$ or, $K_a \lambda_0^2 - K_a \lambda \lambda_0 = \lambda^2 \times c$.

Dividing by $K_a \lambda_0^2 \lambda$ and rearranging, $\frac{1}{\lambda} = \frac{1}{\lambda_0} + \frac{c \times \lambda}{K_a \lambda_0^2}$.

When $\frac{1}{\lambda}$ is plotted against $c \times \lambda$, we get a straight

line and its slope = $\frac{1}{K_a \lambda_0^2}$ and intercept = $\frac{1}{\lambda_0}$.

From the slope and intercept, λ_0 and K_a can be calculated.



MEASUREMENT OF CONDUCTANCE (C), SPECIFIC CONDUCTANCE (κ) AND EQUIVALENT CONDUCTANCE (λ) OF AN ELECTROLYTE SOLUTION.

Kohlrausch modified the Wheatstone meter bridge to determine conductance (C) of an electrolyte solution.

From the conductance, the specific conductance (κ) of the solution is calculated by the

use of the equation, $\kappa = C \times \left(\frac{l}{a}\right)$ and again $\lambda_c = \frac{10^3 \times \kappa}{c_{(N)}}$ can be used to calculate the

equivalent conductance (λ_c) of the solution.

Direct current (DC) in the meter bridge is replaced by alternating current (AC). The frequency of AC is further increased to 500 – 1000 c/s through induction coil.

DC is replaced by AC.

If DC is used, resistance (R) hence conductance (1/R) can not be determined accurately due to the following two effects.

Problems occurs if DC is used.

- (1) Electrolysis occurs and so conc. of the electrolyte in solution changes and resistance does not attain steady value.
- (2) Further the products of electrolysis (specially when gaseous products are formed) accumulate at the surface of the electrodes and change the resistance of the solution. These products set up a counter emf of polarization which opposes the passage of current.

AC eliminates back emf.

To eliminate the above effects, AC is used between two platinum electrodes, coated with colloidal Pt black. In AC, the direction of current is reversed many times and polarization produced in each pulse (half cycle) of the current is neutralized by the next half cycle, provided the alteration is symmetrical.

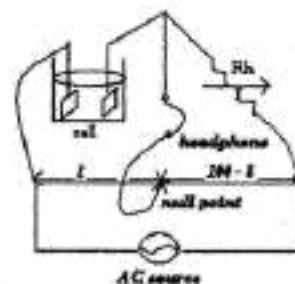
Galvanometer is replaced by headphone.

Again use of AC requires the replacement of galvanometer by a headphone or any other electronic device to detect the current-flow in the circuit. The headphone is connected to a sliding contact. On completing the circuit, a buzzing sound is produced in the headphone. The sliding contact is then moved on along until a minimum sound is obtained.

Let l is the length of the wire at which null-point is obtained,

Resistance is determined.

Then the resistance of the solution, $R = Rh \times \left(\frac{l}{100-l} \right)$, since the total length of the wire is 100 cm and resistance is directly proportional to the length of the uniform cross section wire. Rh is the variable resistance connected in the circuit.



$$\text{The conductance of the solution (C)} = \frac{1}{\text{resistance}(R)}$$

Care to be taken to eliminate temperature variation.

Care must be taken to eliminate the variation of temperature which results due to heating effect of current flowing in the solution. Accurately controlled thermostat is used otherwise resistance will vary with variation of temperature.

Water must also be taken in extremely purity form as very small impurity can produce variation of conductance. Conductivity water must be used to prepare the solution.

For calculation of specific conductance (κ) of a solution, the cell constant, $\left(\frac{l}{a} \right)$ of

Determination of cell constant.

the conductivity cell is known. This value is obtained by measuring conductance (resistance) of KCl solution of known strength whose specific conductance data is given in a table supplied by Kohlrausch himself.

The equivalent conductance (λ) of the solution is known from specific conductance (κ) of the solution using the above appropriate relation.

Problem: At 25°C, a solution of KCl having conductivity of 0.14088 S/m exhibits a resistance of 654 Ω in a particular conductivity cell. In this same cell, a 0.10 mol /L solution of NH_4OH has a resistance of 2524 Ω . The limiting molar conductance of NH_4OH is $271.85 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$. Calculate

- (a) the cell constant
- (b) the molar conductivity of the NH_4OH solution
- (c) the degree of dissociation of the 0.01 mol /L NH_4OH
- (d) the dissociation constant of NH_4OH . (Physical Chemistry – Castellan, problem 31.34)

[Ans. (a) 92.135 m^{-1} , (b) $3.65 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$ (c) 0.0134 and (d) 1.83×10^{-5}].

Statement of the law.	The law states that at infinite dilution, each ion moves independent of the influence of its co-ion and contributes a definite share to the equivalent conductance (λ_0) of the electrolyte, provided the solvent and temperature of the solution remains same.
Validity of the law.	This law is valid only when the solution is infinitely diluted. At this dilution, the electrolyte is fully dissociated ($\alpha = 1$) and interionic attraction is not operative as the distance between the ions in solution is large.
Ionic equivalent conductance.	The definite share of one gm equivalent of a type of ions is called its ionic equivalent conductance (or, simply ionic conductance) and it is dependent on the nature of this type of ion and independent of the other type of ions present in solution, provided the solution is infinitely diluted. Thus according to the law, $\lambda_{BA}^0 = \lambda_{B^+}^0 + \lambda_{A^-}^0,$ here, $\lambda_{B^+}^0$ and $\lambda_{A^-}^0$ are the ionic conductance of the cation and anion respectively.
Experimental evidence in support of the law.	Experimentally it is seen that difference of λ_0 - values of electrolytes with common ion is same and independent of the nature of the common ion. This is shown as, $\lambda_{KCl}^0 - \lambda_{LiCl}^0 = 149.9 - 115.0 = 34.9 \quad \text{and} \quad \lambda_{KNO_3}^0 - \lambda_{LiNO_3}^0 = 145.0 - 110.1 = 34.9$ again, $\lambda_{KCl}^0 - \lambda_{KNO_3}^0 = 4.9$ and $\lambda_{LiCl}^0 - \lambda_{LiNO_3}^0 = 4.9$, all are in cgs unit.
Application of the law – determination of λ_0 of a weak electrolyte.	We have seen that λ_0 of the weak electrolytes can not be determined by plotting λ_c vs. \sqrt{c} using Kohlrausch equation $\lambda_c = \lambda_0 - k\sqrt{c}$. However, λ_0 of weak electrolyte such as HAc can be calculated by using this law. $\lambda_{HAc}^0 = \lambda_{H^+}^0 + \lambda_{Ac^-}^0 = (\lambda_{H^+}^0 + \lambda_{Cl^-}^0) + (\lambda_{Na^+}^0 + \lambda_{Ac^-}^0) - (\lambda_{Na^+}^0 + \lambda_{Cl^-}^0)$ $\lambda_{HAc}^0 = \lambda_{HCl}^0 + \lambda_{NaAc}^0 - \lambda_{NaCl}^0.$ Each of the λ_0 - values of the electrolytes can be determined by using the plots of λ_c vs. \sqrt{c} , since all these in the RHS are strong electrolytes.
Values of limiting ionic conductance.	We know that ionic conductance is proportional to its velocity, so the transport number of an ion can also be expressed in terms of ionic conductance. $t_+^0 = \frac{\lambda_+^0}{\lambda_+^0 + \lambda_-^0} \quad \text{or,} \quad t_+^0 = \frac{\lambda_+^0}{\lambda_0}$ Thus, the limiting ionic conductance of an ion can be known from its transport number. $\lambda_+^0 = t_+^0 \times \lambda_0.$ Similarly for the anion, $\lambda_-^0 = t_-^0 \times \lambda_0$. For example, $\lambda_{HCl}^0 = 426.14 \text{ ohm}^{-1} \text{ cm}^2 \text{ equiv.}^{-1}$ and $t_{H^+}^0 = 0.82$ are given at 25°C. So, the ionic conductance of H^+ ion is, $\lambda_{H^+}^0 = t_{H^+}^0 \times \lambda_{HCl}^0 = 0.82 \times 426.14 \text{ ohm}^{-1} \text{ cm}^2 \text{ equiv.}^{-1}$ $= 349.82 \text{ ohm}^{-1} \text{ cm}^2 \text{ equiv.}^{-1}$ and that of Cl^- is according to Kohlrausch law, $\lambda_{Cl^-}^0 = 426.14 - 349.82$ $= 76.32 \text{ ohm}^{-1} \text{ cm}^2 \text{ equiv.}^{-1}.$
Sparingly soluble salt and its λ_0 - value	By the use of the law, it is also possible to calculate λ_0 of a sparingly soluble salt which can not be determined by the Kohlrausch plot. Thus, λ_0 of $BaSO_4$ is calculated as, $\lambda_{\frac{1}{2}BaSO_4}^0 = \lambda_{\frac{1}{2}BaCl_2}^0 + \lambda_{\frac{1}{2}K_2SO_4}^0 - \lambda_{KCl}^0.$

**ABNORMALLY HIGH CONDUCTANCE OF HYDROGEN AND HYDROXYL IONS
IN AQUEOUS SOLUTION**

Experimental values of limiting ionic conductance of different ions in aqueous solution are given in a table below for comparison. (λ_0 - values are in $\text{ohm}^{-1}\text{cm}^2\text{equiv.}^{-1}$)

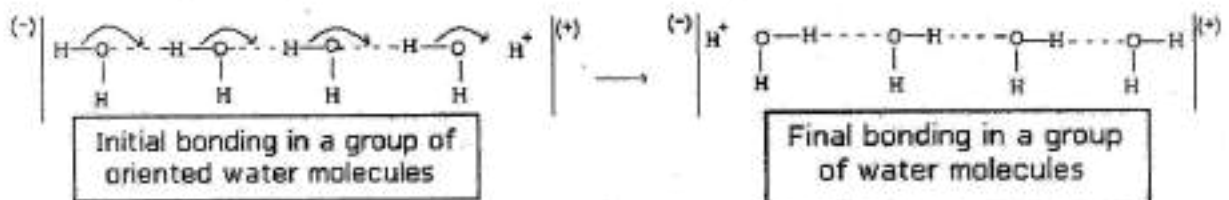
Table for showing λ_0 - values of ions for comparison.

Cations	H^+	K^+	$\frac{1}{2}\text{Ba}^{+2}$	Ag^+	$\frac{1}{2}\text{Ca}^{+2}$	$\frac{1}{2}\text{Mg}^{+2}$	Na^+
λ_0° - values	349.8	73.52	63.64	61.92	59.5	53.00	50.11
Anions	OH^-	$\frac{1}{2}\text{SO}_4^{-2}$	Br^-	Γ	Cl^-	NO_3^-	Ac^-
λ_0° - values	197.6	80.00	78.14	76.80	76.34	71.44	40.90

The λ_0 - values of H^+ and OH^- ions are abnormally high in aqueous solution.

Grotthus special jumping mechanism.

This was first explained by Von Grotthus and so the explanation is known as Grotthus special jumping mechanism. This mechanism involves the proton-jump from one water molecule to another instead of pushing the solvent molecules for its flow. Solvents, instead of creating resistance in the transport of H^+ and OH^- ions, act as bridge for them. Thus solvent H_2O helps in the conduction of electricity.



Solvent molecules require rotation and orientation for conduction of charge.

In order to another H^+ to be transferred to the left (cathode) through this group of water molecules, molecular rotations must occur to produce again a favorable orientation for charge transfer.

This mechanism is supported by the fact that NH_4^+ and NH_2^- ions in liquid NH_3 solvent have also abnormally high ionic conductance.

Again it is expected that RO^- in ROH solvent should exhibit high conductance, but this is not observed. It may be due to high energy barrier for rotation and re-orientation of the solvent ROH molecules.

These evidences support the Grotthus mechanism.

Various evidences in support of the Grotthus mechanism.

The temperature coefficient of ionic conductance is generally 2% per degree rise in temperature, i.e.

$$\lambda_{\rho c}^\circ = \lambda_{25^\circ c}^\circ [1 + 0.02(t - 25)]$$

However, the temperature coefficient of H^+ and OH^- are 14% and 16% respectively. This is probably due to the difference in conduction mechanism of these two ions.

Problem: What will be the value of λ for a 0.001M aqueous solution of ammonia?

Given, for NH_4OH , $K_b = 1.8 \times 10^{-5}$ and $\lambda_0 = 238 \text{ ohm}^{-1}\text{cm}^2\text{equiv.}^{-1}$. [CU'96]

Solution: For weak base ammonia, $K_b \approx \alpha^2 c$, now putting the values,

$$1.8 \times 10^{-5} = \alpha^2 \times 0.001 \text{ or, } \alpha = 0.134.$$

$$\text{But } \lambda = \alpha \times \lambda_0 = 0.134 \times 238 = 31.93 \text{ ohm}^{-1}\text{cm}^2\text{equiv.}^{-1}.$$

Besides other factors like conc., temperature etc, velocity of an ion depends on the potential gradient (electric field) applied to the electrolytic solution. In fact, velocity of an ion (v) \propto potential gradient applied.

or, velocity of an ion (v) = constant \times potential gradient applied.

This constant is called mobility (u) of the ion and it is defined as the velocity per unit potential gradient applied. That is,

$$\text{mobility of an ion}(u) = \frac{\text{velocity of the ion}(v)}{\text{potential gradient}(\Delta\phi / \Delta x) \text{ applied}}$$

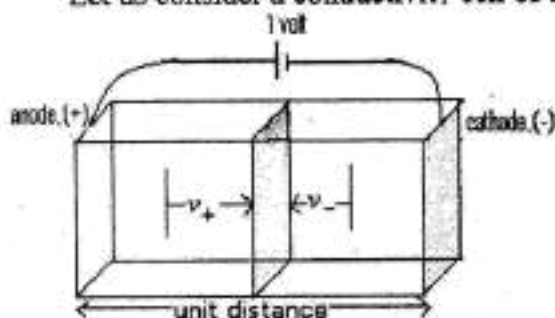
Definition of ionic mobility

Unit of ionic mobility

Unit of ionic mobility (u) = $\frac{cm \text{ sec}^{-1}}{volt \text{ cm}^{-1}} = cm^2 \text{ sec}^{-1} \text{ volt}^{-1}$ (in cgs system),
and the unit in SI system is $m^2 \text{ s}^{-1} \text{ V}^{-1}$.

Relation of ionic conductance with ionic mobility:

Let us consider a conductivity cell of the type used to define equivalent conductance.



Solution and the cell used for derivation with proper sketch

Two electrodes of 1 cm apart are inserted into a solution that contains 1 gm equiv. electrolyte.

For an applied potential difference, $\Delta\phi$, let the current, I is flowing through the cell. Since the solution obeys the Ohm's law, so

$$I = \frac{\Delta\phi}{R} \text{ or, } I = \lambda \times \Delta\phi.$$

As the solution contains 1 gm equiv.

electrolyte, so the conductance ($1/R$) is equivalent conductance (λ).

If the solution is taken very dilute so to interaction is totally absent, then $\lambda = \lambda_0$.

$$\text{Thus, } I = I_+ + I_- = \lambda_+ \times \Delta\phi = (\lambda_+^0 + \lambda_-^0) \Delta\phi = \lambda_+^0 \Delta\phi + \lambda_-^0 \Delta\phi.$$

Separating into two equations, we get, $I_+ = \lambda_+^0 \Delta\phi$ and $I_- = \lambda_-^0 \Delta\phi$.

This flow of current can be analyzed from considering the movement of ions in the cell.

For the formulation, let an imaginary wall is considered at the middle of the cell.

The solution contains 1 gm equiv. strong electrolyte which is very dilute and it is confined within the electrodes of unit distance apart. The cations which are at a maximum distance of v_+ away from the imaginary wall can cross the wall in unit time. The solution contains (N_+/z_+) number of cations and (N_-/z_-) number of anions. The charge transported by cations through the imaginary wall in unit time is

No. of cations that reach the imaginary wall in unit time

$$= v_+ \left(\frac{N_+}{z_+} \right)$$

the current carried by the cations, $I_+ = v_+ \left(\frac{N_+}{z_+} \right) \times z_+ e = v_+ (N_+ \times e) = v_+ \times F$

and, the current carried by the anions, $I_- = v_- \left(\frac{N_-}{z_-} \right) \times z_- e = v_- (N_- \times e) = v_- \times F$

The relations are

$$\lambda_+^0 = F \times u_+$$

and

$$\lambda_-^0 = F \times u_-$$

Comparing with the expression of I_+ and I_- , $\lambda_+^0 \Delta\phi = v_+ \times F$ or, $\lambda_+^0 = \left(\frac{v_+}{\Delta\phi} \right) \times F$.

But the term within the bracket is ionic mobility (u), so the relation is $\lambda_+^0 = F \times u_+$, for anion, $\lambda_-^0 = F \times u_-$. The relations are also valid approximately for dilute solutions.

Ionic mobility and transport number:

We have the limiting mobility of the cation, $u_+ = \frac{\lambda_+^0}{F}$, and $\lambda_+^0 = t_+ \lambda_0$,

$$\text{hence, } u_+ = \frac{t_+ \lambda_0}{F} \text{ and that for anion, } u_- = \frac{t_- \lambda_0}{F}.$$

At appreciable concentrated solutions, u_+ and u_- will be slightly less.

Experimental measurement of ionic mobility:

Moving boundary method is used to determine the mobility of an ion in solution.

Let us determine, for example, the mobility of K^+ ion in KCl solution. Experimental set up is that, KCl solution is placed over a solution of $CdCl_2$ solution in a narrow electrolysis tube of uniform cross section. The solution used must have common anion, here, Cl^- . When the current flows, the K^+ ions migrate upward to the cathode, and Cd^{2+} ions only follow the K^+ ions in the same direction. For the experiment to work, the cations of the lower solution must have a lower mobility than the cations of the upper solution, i.e., $u_{Cd^{2+}} < u_{K^+}$.

The velocity of K^+ is found by measuring the distance l that the boundary moves in time t . The boundary between the solutions is visible because of a difference in refractive index of the two solutions.

Thus, the velocity of K^+ ions, $v_{K^+} = \frac{l}{t}$ and its ionic mobility, $u_{K^+} = \frac{v_{K^+}}{E}$, where, $E = \frac{\Delta\phi}{\Delta x}$.

E is electric field applied which is equivalent to the potential gradient.

Problems: (1) The equivalent conductance of LiCl at infinite dilution is $115.03 \text{ ohm}^{-1} \text{ cm}^2 \text{ gm equiv.}^{-1}$. The transport number of the cation is 0.336.

(a) Calculate the mobility of the cation.

(b) Calculate the velocity of the cation if 6.0 volt is applied across electrodes 4.0 cm apart.

Solution: Ionic conductance of the cation = $t_+ \times \lambda_{LiCl}^0 = 0.336 \times 115.03 = 38.65 \text{ ohm}^{-1} \text{ cm}^2 \text{ gm equiv.}^{-1}$.

$$\text{Mobility of the cation} = \frac{\lambda_+^0}{F} = \frac{38.65 \text{ ohm}^{-1} \text{ cm}^2 \text{ gm equiv.}^{-1}}{96,500 \text{ C gm equiv.}^{-1}} = 4.01 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ sec}^{-1}.$$

$$\begin{aligned} \text{Velocity of the cation} &= u_+ \times \left(\frac{\Delta\phi}{\Delta x} \right) = 4.01 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ sec}^{-1} \times (6/4) \text{ V cm}^{-1} \\ &= 6.0 \times 10^{-4} \text{ cm sec}^{-1}. \end{aligned}$$

(1) At 18°C , the mobility at infinite dilution of NH_4^+ ion is $6.6 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ sec}^{-1}$, while that of chlorate ion is $5.7 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ sec}^{-1}$.

Calculate λ_0 of ammonium chlorate and transport number of the two ions. [CU'98]

Solution: $\lambda_0 = \lambda_+^0 + \lambda_-^0 = F(u_+^0 + u_-^0) = 96500 \times (6.6 + 5.7) \times 10^{-4} = 118.69 \text{ ohm}^{-1} \text{ cm}^2 \text{ equiv.}^{-1}$

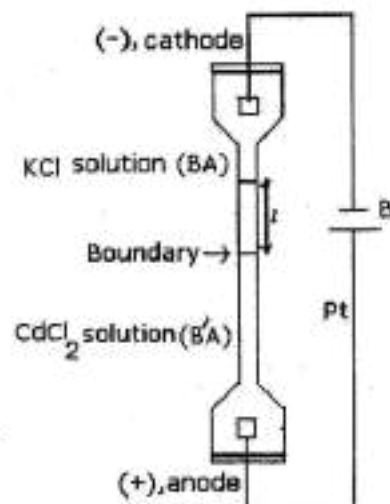
$$t_+ = \frac{6.6 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ sec}^{-1}}{(6.6 + 5.7) \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ sec}^{-1}} = 0.53 \quad \text{and} \quad t_- = 1 - t_+ = 1 - 0.53 = 0.47.$$

Experimental set up

Condition for two solutions used in the experiment

Velocity and mobility of the ion

Related two problems and their solutions



Conductance of a solution is a measure of its current carrying ability and the ions are the current carriers. Thus, measurement of conductance gives information about the ions in solution. Several physical properties of the solution could be known from this conductance measurement. We may discuss in brief the determination of various physical constants of the electrolytes.

(1) Degree of dissociation and dissociation constant of a weak electrolyte.

A weak electrolyte say, weak acid HA even in fairly dilute solution is partially dissociated and interionic force of attraction is negligible as the ions are far apart in solution.

The dissociation constant, $K_a = \frac{\alpha^2 c}{1-\alpha}$, where, $\alpha = \frac{\lambda}{\lambda_0}$, called degree of dissociation.

λ and λ_0 are the equivalent conductance of the solution at conc. c and at infinite dilution. λ is obtained from determination of specific conductance (κ) of the solution and λ_0 is obtained from ionic conductance data given in table, $\lambda_{HA}^0 = \lambda_{H^+}^0 + \lambda_{A^-}^0$.

Thus, knowing α , dissociation constant of the weak acid (K_a) can be determined.

Problem: The equivalent conductance of a 0.01(M) solution of chloroacetic acid is $110 \text{ ohm}^{-1} \text{ cm}^2 \text{ equiv.}^{-1}$. Find the dissociation constant of the acid from the following data:

$$\lambda_{HCl}^0 = 426, \lambda_{KCl}^0 = 150 \text{ and } \lambda_{CH_2ClCO_2K}^0 = 132 \text{ (in } \text{ohm}^{-1} \text{ cm}^2 \text{ equiv.}^{-1}\text{)}$$

Solution: Using Kohlrausch law, $\lambda_{CH_2ClCO_2H}^0 = \lambda_{HCl}^0 + \lambda_{CH_2ClCO_2K}^0 - \lambda_{KCl}^0$

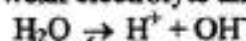
$$\text{Putting values, } \lambda_{CH_2ClCO_2H}^0 = 426 + 132 - 150 = 408 \text{ ohm}^{-1} \text{ cm}^2 \text{ equiv.}^{-1}$$

$$\text{The degree of dissociation, } \alpha = \frac{\lambda}{\lambda_0} = \frac{110 \text{ ohm}^{-1} \text{ cm}^2 \text{ equiv.}^{-1}}{408 \text{ ohm}^{-1} \text{ cm}^2 \text{ equiv.}^{-1}} = 0.27$$

$$\text{The dissociation constant of the acid, } K_a = \frac{\alpha^2 c}{1-\alpha} = \frac{0.27^2 \times 0.01}{1-0.27} = 1 \times 10^{-3}$$

(2) Ionic product of water:

Water is a very weak electrolyte and is feebly dissociated as,



The ionic product of water is, $K_w = [H^+][OH^-]$, but in pure water, $[H^+] = [OH^-] = \alpha c$.

α is the degree of dissociation of water and c is its molar conc.

$$\text{Thus, } K_w = \alpha^2 c^2, \text{ but } \alpha = \frac{\lambda}{\lambda_0} \text{ and } \lambda = \frac{10^3 \kappa}{c_{(N)}}. \text{ Putting the values, } K_w = \frac{10^6 \kappa^2}{\lambda_0^2}$$

κ is determined by measuring the conductance of pure water and λ_0 of water is obtained

from the limiting ionic conductance of H^+ and OH^- ions, $\lambda_{H_2O}^0 = \lambda_{H^+}^0 + \lambda_{OH^-}^0$.

Thus the ionic product of water can be determined by conductance measurement.

Problem: The specific conductance of water is determined as $0.58 \times 10^{-7} \text{ ohm}^{-1} \text{ cm}^{-1}$.

The limiting ionic conductance of H^+ and OH^- are 349.8 and 198 in $\text{ohm}^{-1} \text{ cm}^2 \text{ equiv.}^{-1}$ unit respectively. Find K_w of water.

$$\text{Solution: } K_w = \frac{10^6 \kappa^2}{\lambda_0^2} = \frac{10^6 \times (0.58 \times 10^{-7})^2}{(349.8 + 198)^2} = 1.0 \times 10^{-14}$$

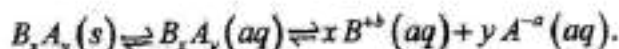
(3) Solubility(s) and solubility product (K_s) of a sparingly soluble salt.

Conc. of the solution is small.

Minute amount of these salts are soluble in water and their conc. in solution is so small that chemical analysis is not able to find the value. However, conductance measurement can be used to determine the solubility of these salts.

Let us first formulate the relation between solubility product (K_s) and solubility (s) of a sparingly soluble salt (B_xA_y). The salt remains in equilibrium in solution as follows:

Relation between the solubility product (K_s) and solubility(s).



If s moles of the salt is dissolved per litre of the solution and makes a saturated solution, then, conc. of cation = xs and that of anion = ys and the solubility product = $[B^{+b}]^x[A^{-a}]^y$ or, $K_s = (xs)^x \times (ys)^y$. So the required relation, $K_s = (x^x y^y) s^{x+y}$.

For 1-1 salt like AgCl, the relation is $K_s = s^2$, for 2-1 salt, like CaF_2 , $K_s = 4s^3$, for 2-3 salt, like $Ca_3(PO_4)_2$, $K_s = 127s^5$.

The conc. (c) of the saturated salt solution is calculated by measuring specific conductance (k) of the solution,

Measurement of specific conductance.

$$\lambda = \frac{10^3 k}{c_{(N)}} \text{ or, } c_{(N)} = \frac{10^3 k}{\lambda}$$

The solution is very dilute as the salt is only sparingly soluble, so $\lambda \rightarrow \lambda_0$ (limiting value). λ_0 of the salt is obtained from the limiting conductance of the constituent ions of the salt.

$$\lambda_0 = \lambda_+^0 + \lambda_-^0$$

Again, specific conductance of this very dilute solution is comparable with that of water, so specific conductance of water is subtracted from the measured value for the solution.

$$k = k_{\text{solution}} - k_{\text{water}}$$

Solubility of the solution.

Thus the conc. of the saturated salt solution, $c_{(N)} = \frac{10^3}{(\lambda_+^0 + \lambda_-^0)} (k_{\text{solution}} - k_{\text{water}})$

This conc. in normality is to be expressed in molarity and this gives solubility (s) of the salt.

[CU' 96]

Problem: At 25°C, specific conductance of a saturated solution of $SrSO_4$ and that of water used are 1.482×10^{-4} and $1.5 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$ respectively.

(1) Given, the ionic conductance of the strontium and sulphate ions are 59.46 and $79.8 \text{ ohm}^{-1} \text{ cm}^2 (\text{g.eq.})^{-1}$ respectively at this temperature.

Calculate the solubility of the salt in g.L^{-1} . [The formula weight of $SrSO_4 = 182$]

Solution: Putting the values given in the problem,

$$c_{(N)} = \frac{10^3(1.482 \times 10^{-4} - 1.5 \times 10^{-6})}{(59.46 + 79.8)} = 1.05 \times 10^{-3} \text{ (N)} = 1.05 \times 10^{-3} \times \frac{182}{2} = 0.096 \text{ g L}^{-1}$$

[CU' 94]

Problem: At 25°C, in a saturated solution of $BaSO_4$, Ba^{+2} and SO_4^{-2} ions take 151 sec and

(2) 121 sec respectively to cover a distance of 1 cm across which a potential difference of 10 volts is applied. The solubility product of $BaSO_4$ at 25°C is 10^{-10} (considered in gm equiv./lit). The conductance of the solution is $2.2 \times 10^{-6} \text{ ohm}^{-1}$ in a cell and in the same cell, conductance of water is $0.8 \times 10^{-6} \text{ ohm}^{-1}$ at 25°C. If in the same cell, conductance of 0.01N KCl solution be $1.40 \times 10^{-3} \text{ ohm}^{-1}$ at 25°C, what should be its specific conductance at the same temperature?

Solution: λ_0 of $BaSO_4 = 143.66 \text{ ohm}^{-1} \text{ cm}^2 (\text{g.eq.})^{-1}$, k of $BaSO_4$ soln = $1.44 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$

Cell const. = 1.03 cm^{-1} , and k of KCl soln = $1.44 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$.

(4) Degree of hydrolysis and hydrolysis constant of a salt:

Criteria of the salt for this method.

For this conductance method, one restriction is that the resulting free acid or base from the salt hydrolysis should be non-conducting. However, absolutely non-conducting acids are rare but many non-conducting bases are known. So this method is mainly applied for the salt of weak base and strong acid such as aniline hydrochloride. The salt reacts with water as,



Let c is the molar con. of the salt taken and x is the degree of hydrolysis of the salt then, $[HCl] = xc$ and $[\text{unhydrolysed salt}] = c(1-x)$.

The conductance of this solution is partly due to HCl formed as a result of hydrolysis and partly due to unhydrolysed salt. Thus conductance of the resulting solution,

$$c\lambda = c(1-x)\lambda_s + xc\lambda_{HCl}$$

Conductance of the resulting solution.

Solving the above, we get the degree of hydrolysis, $x = \frac{\lambda - \lambda_s}{\lambda_{HCl}^0 - \lambda_s}$

The degree of hydrolysis is small, so the conc. of HCl is also very small. Thus,

$$\lambda_{HCl} = \lambda_{HCl}^0 = \lambda_{H^+}^0 + \lambda_{Cl^-}^0$$

λ = equivalent conductance of the resulting solution and it is calculated from the

$$\text{measurement of specific conductance of the solution, } \lambda = \frac{10^3 \kappa}{c}$$

Measurement of equiv. conduct. of the solution in hydrolyzed and unhydrolysed state.

λ_s = equivalent conductance of the salt if it would remain unhydrolysed in the solution and it is determined from the solution in presence of excess of the base, aniline. Under this condition, hydrolysis of the salt is suppressed and equivalent conductance is taken for unhydrolysed salt in solution.

Using the above values, it is possible to find the degree of hydrolysis (x)

Hydrolysis constant (K_h).

The hydrolysis constant of the salt is also calculated by using expression, $K_h = \frac{x^2 c}{1-x}$

Problem: The equivalent conductance of 0.011(M) solution of aniline hydrochloride is $120 \text{ ohm}^{-1} \text{ cm}^2 \text{ gmequiv.}^{-1}$. When the solution is saturated with excess aniline, the equivalent conductance drops to $104 \text{ ohm}^{-1} \text{ cm}^2 \text{ gmequiv.}^{-1}$. The equivalent conductance of HCl at the same conc. is $410 \text{ ohm}^{-1} \text{ cm}^2 \text{ gmequiv.}^{-1}$.

Find the degree of hydrolysis and the hydrolysis constant.

Solution: The degree of hydrolysis, $x = \frac{\lambda - \lambda_s}{\lambda_{HCl}^0 - \lambda_s} = \frac{120 - 104}{410 - 104} = 0.052$.

$$\text{The hydrolysis constant, } K_h = \frac{x^2 c}{1-x} = \frac{(0.052)^2 \times 0.011}{1-0.052} = 3.14 \times 10^{-5}$$

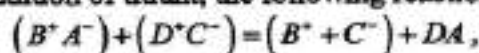
(5) Conductometric Titration:

Titration forms basis of volumetric analysis. End point of titration is located by variation of conductance.

Titration is an operation forming the basis of volumetric analysis. The addition of measured amount of a solution of one reagent from a burette (called the 'titrant') to a definite amount of another reagent (called 'titre') is done until the 2nd reagent is depleted.

When the end point of various volumetric titrations is located by conductance measurement, it is called conductometric titration. This method utilizes the variation of conductance with the progress of titration especially when it varies sharply at the end point. Let us take a titre (B^+A^-) titrated with the titrant (D^+C^-).

With the addition of titrant, the following reaction occurs.



where, DA is either weak electrolyte or an insoluble salt and it is only poor conducting.

End point is located by drawing curves.

Titrant is more concentrated.

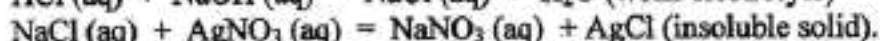
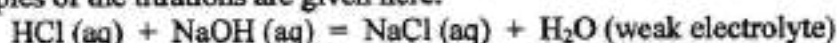
Temperature requires to be controlled.

With the addition of the titrant (D^+C^-), A^- is being replaced by C^- and if there is difference of conductance value of the two ions, the conductance of the solution changes and after the end point, conductance increases rapidly due to further addition of the titrant (D^+C^-). The conductance data at each addition are plotted against volume of the titrant added. Two straight lines with difference in slope are obtained. The volume of titrant at the point of intersection of the two straight lines gives the end point of the titration.

In order to avoid the dilution effect on conductance, the conc. of the titrant is kept at least ten times greater than that of the titre. Otherwise, C will increase with dilution.

The titre is taken in conductivity cell which is again kept in thermostat of accurately controlled temperature. Otherwise, the heat of reaction will change the temperature and thus conductance will also vary during the titration.

Some examples of the titrations are given here.



(A) Acid-base titrations: Several types of such titrations could be made by this method.

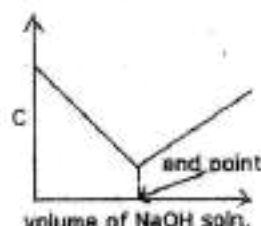
(a) Strong acid (HCl) by strong base (NaOH):

Higher conducting ion is replaced by lower conducting ion.

Before addition of NaOH solution (titrant), conductance (C) of HCl solution (titre) is very high due to high conducting H^+ ion. The reaction is, $(\text{H}^+ + \text{Cl}^-) + (\text{Na}^+ + \text{OH}^-) = (\text{Na}^+ + \text{Cl}^-) + \text{H}_2\text{O}$. With the addition of NaOH, H^+ ion is replaced by low conducting Na^+ ion i.e., $\lambda_{\text{H}^+}^0 > \lambda_{\text{Na}^+}^0$,

and so conductance falls. At the end point, all H^+ ions are replaced and conductance becomes minimum.

After end point NaOH is still added and conductance increases sharply.



(b) Weak acid (HAc) by strong base (NaOH):

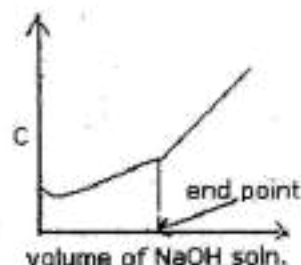
Conductance increases with a hump.

Before addition of NaOH, conductance (C) is low since it is weak electrolyte and dissociation is small. With slight addition of NaOH, conductance falls slightly due to suppression of dissociation of the weak acid in presence of common Ac^- ion, formed from the salt.

With further addition of NaOH, conductance increases due to formation of Na^+ and Ac^- ions of the salt. The reaction of the titration is,



After the end point, conductance increases sharply due to addition of NaOH.



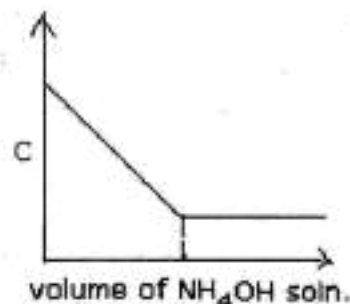
(c) Strong acid (HCl) by weak base (NH_4OH):

Conductance decreases and then remains steady after end point.

Before addition of NH_4OH , the conductance of HCl solution is high. With the addition of NH_4OH , H^+ is replaced by low conducting NH_4^+ ion and conductance falls.



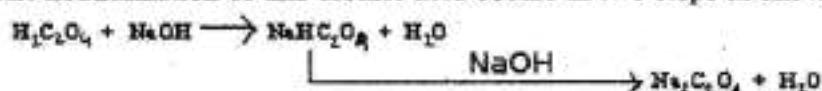
After the end point, with further addition of NH_4OH , conductance almost remains constant as the added NH_4OH is virtually not dissociated due to the common NH_4^+ ion present in the solution.



However, when a strong base (NaOH) is titrated by weak acid (HAc), the curve obtained is similar to the titration of strong acid by weak base [discussed in (c)].

(d) Dibasic acid (oxalic acid) by strong base (NaOH):

The neutralization of this dibasic acid occurs in two steps as shown below.



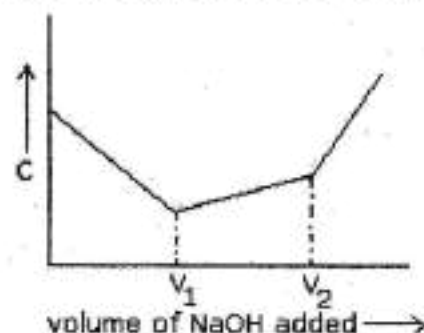
Condition for two inflexions in dibasic acid.

For this acid, $K_1 \geq 100K_2$ and so the titration with NaOH produces two inflexions.

V_1 = volume of NaOH solution required for neutralization of first dissociated H^+ ion of oxalic acid.

V_2 = total volume of NaOH solution for complete neutralization of the acid.

$V_2 - V_1$ = volume of NaOH for neutralization of second dissociated H^+ ion.



(e) Mixture of strong acid and weak acid (HCl + HAc) by strong base (NaOH):

Same type of curve as above (d) is obtained. In this case, the volume corresponding inflexions are given below.

V_1 = volume of NaOH for neutralization of strong acid (HCl) in the mixture.

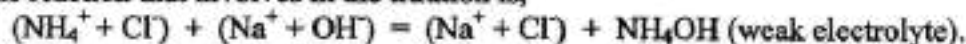
$V_2 - V_1$ = same for weak acid (HAc) in the mixture.

A mixture of HCl and HAc by NaOH

(B) Titration involving displacement reactions:

(a) Salt of strong acid and weak base (NH_4Cl) by strong base (NaOH):

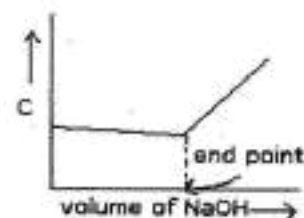
The reaction that involves in the titration is,



With the progress of the titration, NH_4^+ ions are replaced by Na^+ ions. But NH_4^+ ion is slightly more conducting than Na^+ ion,

$\lambda_{\text{NH}_4^+}^0 = 73.5$ while $\lambda_{\text{Na}^+}^0 = 50.1$ in cgs unit.

Thus, conductance of the titre is slightly decreasing and after the end point rises steeply.



NH_4Cl solution is titrated by NaOH solution.

(b) Mixture of salt of strong acid-weak base (NH_4Cl) and strong acid (HCl) by strong base (NaOH):

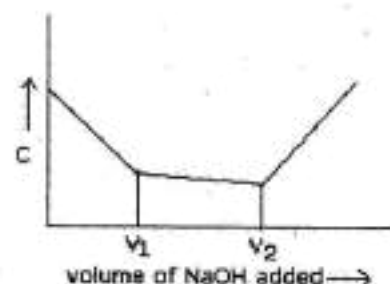
Before addition of NaOH, the conductance of the solution is high due to H^+ ions of HCl.

After addition of NaOH, H^+ ions are replaced by Na^+ ions and conductance falls sharply.

After neutralization of the HCl in the mixture, NH_4^+ ions are being replaced by Na^+ ions.

The conductance is slightly decreasing.

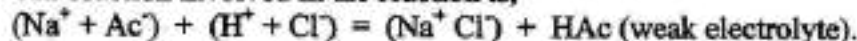
After the complete replacement NH_4^+ , conductance increases steeply due to further addition of NaOH.



A mixture of NH_4Cl and HCl is titrated by NaOH

(c) Salt of weak acid and strong base (NaAc) by strong acid (HCl):

The reaction involved in the reaction is,



NaAc is
titrated by HCl

Ac⁻ ions are replaced by slightly higher conducting Cl⁻ ions, so conductance is slightly increasing, $\lambda_{Cl}^0 = 76.34$ and $\lambda_{Ac}^0 = 40.9$ in $\text{ohm}^{-1} \text{cm}^2 \text{gm equiv}^{-1}$.

After the end point, conductance increases sharply due to high λ_0 - value of HCl. [The curve is same as in (a) only in the 1st part, conductance increases instead of decreasing].

Mixture of NaAc
and NaOH is
titrated by HCl

(d) Mixture of salt of weak acid - strong base (NaAc) and strong base (NaOH) by strong acid (HCl):

HCl first neutralizes NaOH in the mixture then it reacts with the salt, NaAc.

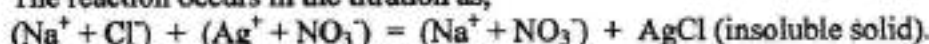
[Same as in (b), only the difference is in the 2nd part in which C increases slightly].

(C) Precipitation titrations:

In these titrations, one of the reaction products is insoluble and does not contribute to the conductance of the solution.

(a) Sodium chloride (NaCl) by silver nitrate (AgNO₃):

The reaction occurs in the titration as,



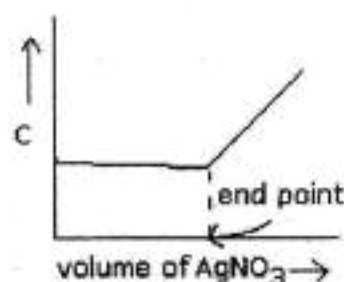
Cl⁻ ions in the titre is replaced by NO₃⁻ ions

and the two type of ions have nearly same

λ_0 - values, so the conductance remains almost

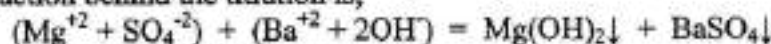
unchanged with the addition of AgNO₃.

After the endpoint, conductance increases due to further addition of AgNO₃.



(b) Magnesium sulphate (MgSO₄) by Baryta water [Ba(OH)₂ solution]:

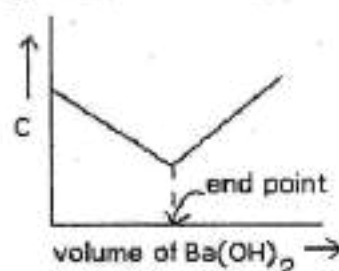
The reaction behind the titration is,



In this titration, both the reaction products are insoluble and hence conductance drops sharply.

After the end point, conductance increases

due to further addition of Ba(OH)₂ solution.



NaCl solution is
titrated by
AgNO₃ solution.

MgSO₄
solution is
titrated by
Baryta water

Advantages of the titration:

- (i) Weak acid and weak base titrations could be done by this conductometric method though the indicator method fails due to lack of suitable indicator.
- (ii) Colored solutions could be titrated though indicator method is not suitable.
- (iii) A mixture of strong and weak acid can be titrated and each strength of the acid can be determined
- (iv) This method can determine conc. of strong electrolyte solution even up to 10⁻⁴ (N).

Precautions:

- (i) Titrant must be taken at least ten times stronger than the titre in order to avoid dilution effect and to get sharp end point of the titration.
- (ii) Volume of the titre that changes due to addition of titrant may be corrected by multiplying measured conductance with $\frac{V}{V+v}$ where, V = initial volume of the titre and v = volume of titrant at each addition.

Situation created for a single ion to act independently in solution.

When an electrolyte solution is infinitely diluted, it is fully dissociated and interionic attraction is also absent. The ions move freely and independent of the influence of the other ions present. Under this situation, ions are considered independent in activity in solution. A single such independent ion in the solution is subjected to an electric field E .

Driving force on this single ion under applied electric field, E .

The electric field will exert a driving force to move the ion towards opposite electrode. This driving force on the i th ion of valence z_i , is,

$$f_{\text{driving}} = E z_i e$$

The ion also experiences a viscous force that opposes the motion of the ion. The viscous force on the ion is given by Stoke's law, assuming spherical shape of the hydrated ion,

$$f_{\text{viscous}} = 6 \pi \eta r_i v_i'$$

Opposing viscous force experienced by the ion.

r_i and v_i' are the radius and limiting velocity of the hydrated ion.

When the forces are balancing each other, the ion will move with steady velocity.

$$\text{Then, } 6 \pi \eta r_i v_i' = E z_i e$$

Rearranging the equation, dividing by E and then multiplying by faraday, F , we get

$$\frac{v_i' \times F}{E} = \frac{z_i e F}{6 \pi \eta r_i}, \text{ but } \frac{v_i' \times F}{E} = \text{limiting ionic conductance of the } i\text{th ion, } \lambda_i^\circ.$$

Formulation of Walden rule to this single ion.

Since the solution is infinitely diluted, $\eta \rightarrow \eta_0$, viscosity of the solvent used.

So, $\lambda_i^\circ = \frac{e F}{6 \pi \eta_0} \left(\frac{z_i}{r_i} \right)$. From this equation we get the interpretation of λ_i° .

This relation shows that in a given solvent at a particular temperature, greater the valence and smaller the size of the ion, higher is its limiting ionic equivalent conductance (λ_i°).

Rearranging, we have Walden rule applicable to ionic conductance,

$$\lambda_i^\circ \eta_0 = \frac{e F}{6 \pi} \left(\frac{z_i}{r_i} \right)$$

Walden rule applied to ion.

For a given ion, $\lambda_i^\circ \eta_0 = \text{constant}$, independent of the nature of solvent at a given temperature and independent of temperature in one solvent.

Adding the above relation for cation and anion of an electrolyte in infinitely diluted solution, we have,

Walden rule for an electrolyte solution at infinite dilution.

$$(\lambda_+^\circ + \lambda_-^\circ) \eta_0 = \frac{e F}{6 \pi} \left(\frac{z_+}{r_+} + \frac{z_-}{r_-} \right), \text{ or, } \lambda_0 \eta_0 = \frac{e F}{6 \pi} \left(\frac{z_+}{r_+} + \frac{z_-}{r_-} \right) \text{ (Using Kohlrausch law).}$$

This is the basis of Walden rule which states that

$$\lambda_0 \eta_0 = \text{constant for a given electrolyte and is independent of temperature.}$$

At a given temperature for an electrolyte, the relation states that $\lambda_0 \eta_0 = \lambda_0' \eta_0' = \text{constant}$.

Rule is applied in different solvents at given T and also at different T in a given solvent.

Thus, at a given temperature if limiting equivalent conductance of an electrolyte (λ_0) is known in one solvent of viscosity (η_0), it is possible to know the same (λ_0') in another solvent of viscosity (η_0').

It also explains the temperature effect of equivalent conductance. With rise of one degree temperature, viscosity is decreased by 2% and so equivalent conductance is also increased by 2% per degree rise of temperature.

Solvation invalidates the rule.

Validity: This rule is valid for the electrolytes comprising of large size ions such as tetra methyl ammonium iodide, $[(CH_3)_4N^+I^-]$, picrate ion, $C_6H_2(NO_2)_3O^-$. For small ions, there occurs solvation and so radius of the solvated ions varies depending on the extent of their solvation in different solvents. This law is not applicable to H_3O^+ and OH^- in aqueous solution as viscosity of the solution does not control the movement of these ions.

This rule can be utilized to compare the radius of ions in aqueous solution.

Rule is used to compare the radius of ions.

$$\text{From the relation applied to single ion, } \frac{\lambda_i^0}{z_i} = \frac{eF}{6\pi\eta_0} \left(\frac{1}{r_i} \right) \text{ or, } \frac{1}{r_i} \propto \frac{\lambda_i^0}{z_i}$$

$$\text{Thus for, } Mg^{+2} \text{ ion, } \frac{\lambda_{Mg^{+2}}^0}{2} = 26.52 \text{ ohm}^{-1} \text{cm}^2 \text{ gm equiv.}^{-1}$$

$$\text{and for } (C_2H_5)_4N^+ \text{ ion, } \frac{\lambda_{(C_2H_5)_4N^+}^0}{1} = 23.42 \text{ ohm}^{-1} \text{cm}^2 \text{ gm equiv.}^{-1}$$

Since, R_4N^+ ion has very little hydration due to hydrophobic group R that reacts weakly with the water dipole and these R remains on the surface of the ions. But Mg^{+2} ions due to high charge and small radius are heavily hydrated and the hydrated radius is comparable to the $(C_2H_5)_4N^+$ ions.

This shows that radius of magnesium ion is comparable to that of tetra ethyl ammonium ion in aqueous solution.

Problem: Estimate the radii of $Na^+(aq)$ and $Mg^{+2}(aq)$, given that the viscosity of water at $25^\circ C$ is 0.89 cp, $\lambda_{Na^+}^0$ and $\lambda_{Mg^{+2}}^0$ are 50.1 and 53.0 in $\text{ohm}^{-1} \text{cm}^2 \text{ gm equiv.}^{-1}$.

One problem is worked out to compare the radius of ions.

Solution:

$$r_{Na^+} = \frac{eF}{6\pi\eta_0} \left(\frac{z_{Na^+}}{\lambda_{Na^+}^0} \right) = \frac{1.6 \times 10^{-19} C \times 96500 C (gm \text{ equiv.})^{-1}}{6 \times 3.14 \times 0.89 \times 10^{-2} \text{ poise}} \left(\frac{1}{50.1 \text{ ohm}^{-1} \text{cm}^2 \text{ gm equiv.}^{-1}} \right)$$

$$\begin{aligned} &= 9.2 \times 10^{-14} \times 0.01996 C \times \text{poise}^{-1} (\text{ohm} \times C) \times \text{cm}^{-2} \\ &= 1.83 \times 10^{-15} C \times (\text{dyne cm}^{-2} \text{ sec})^{-1} (V \times \text{sec}) \text{cm}^{-2} = 1.83 \times 10^{-15} \text{ J dyne}^{-1} \\ &= 1.83 \times 10^{-15} \times 10^7 \text{ cm} = 1.83 \times 10^{-8} \text{ cm.} \end{aligned}$$

$$\text{Now, } r_{Mg^{+2}} = r_{Na^+} \times \frac{z_{Mg^{+2}}}{z_{Na^+}} \times \frac{\lambda_{Na^+}^0}{\lambda_{Mg^{+2}}^0} = 1.83 \times 10^{-8} \text{ cm.} \times \frac{2}{1} \times \frac{50.1}{53.0} = 3.4 \times 10^{-8} \text{ cm.}$$

These are hydrated size of the ions. Hydration number of Na^+ is 4 and that of Mg^{+2} is 12.

Relation between equivalent conductance (λ) and molar conductance (\wedge).

For a strong electrolyte, B_xA_y dissociating as, $B_xA_y(aq) \rightarrow xB^{+z_+}(aq) + yA^{-z_-}(aq)$.

$$\text{The relation is, } \lambda = \frac{\wedge}{x z_+} \text{ or, } \lambda = \frac{\wedge}{y z_-}$$

Thus for, $Cu_3(PO_4)_2(aq)$ we have $x = 3$ and $z_+ = 2$, so equiv. conduct. (λ) = $\wedge/6$.

Table \rightarrow Specific conductance of KCl solution (k) in $\text{ohm}^{-1} \text{cm}^{-1}$

Conc. in equiv / liter	0°C	18°C	25°C
0.01	0.0007751	0.0012227	0.0014114
0.10	0.007154	0.011192	0.012886
1.00	0.06543	0.0982	0.11173

Problem: Using the above table, find the molar conductance of 1.00 mol/dm³ aqueous solution of KCl at 25°C. [Ans. 112 $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$].

Kohlrausch equation.

Dependence of equivalent conductance (λ_c) of strong electrolyte on its solution conc. (c) is formulated by Kohlrausch on the basis of experimental data. The equation is,

$$\lambda_c = \lambda_0 - k\sqrt{c}$$

When the solution is not infinitely diluted, ionic interaction operates and this results a definite pattern of arrangement of ions in solution. Debye, Huckel and later Onsagar proposed ion atmosphere model and on the basis, they explained the above equation.

Debye and Huckel proposed ion atmosphere model.

According to their proposed model, each ion is surrounded by spherical haze of ions in which the opposite charge ions dominate over the like charge ions. This spherical haze is called ion atmosphere whose net charge on a time-average is equal but opposite to that of central ion. In absence of electric field, the ion atmosphere is spherical in shape and surrounds the central ion symmetrically.

When electric field is applied, the central ion begins to move.

Now when the solution is subjected to an electric field, E, the driving force on the central ion to move towards oppositely charged electrode is,

$$f_{\text{driving}} = E z_+ e$$

When the central ion begins to move, various retarding effects acting on it are outlined below.

(1) Viscous effect: This effect retards the motion of the central ion and according to Stoke, it is

$$f_{\text{viscous}} = 6\pi\eta r_+ v_+ = k_1 v_+, \text{ where, } k_1 = 6\pi\eta r_+$$

(2) Asymmetric effect: Under the applied electric field, the central ion begins to move and its surrounding ion atmosphere does not remain symmetrical, it lags behind. More of the ion atmosphere remains behind than in front of the central ion. Oppositely charged ion atmosphere attracts the moving central ion from behind. This retards the velocity of the central moving ion. Asymmetric shape of the ion atmosphere is the cause of this retardation and so it is called asymmetric effect. In another way, it can be said that the ion atmosphere relaxes for sometimes and can not move symmetrically with the moving central ion. This is why this effect is also called 'relaxation effect'

The magnitude of this effect = $k_2 E \sqrt{c}$.

$$\text{Where, } k_2 \propto \frac{1}{(DT)^{3/2}}$$

(3) Electrophoretic effect:

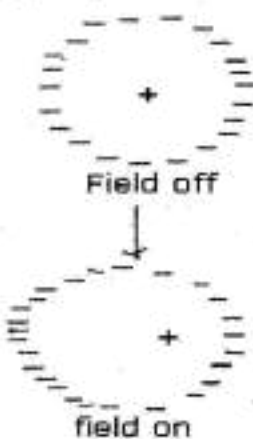
This effect arises from the motion of the solvent molecules associated with the ion atmosphere in the direction opposite to that of the central ion. Both the ion atmosphere and the central ion pull solvent with them and each is, in effect, swimming upstream against the motion of the solvent.

The magnitude of this effect = $k_3 E \sqrt{c}$

$$\text{Where, } k_3 \propto \frac{1}{\eta(DT)^{3/2}}$$

With higher viscous solvent, motion of the solvent associated with ion atmosphere is slowed down and the central ion experience less retardation while swimming upstream.

Retarding effect due to asymmetric shape of ion atmosphere.



Retarding effect due to movement of solvent molecules associated with ion atmosphere.

Effect of conc. on asymmetric retardation.

The effect of conc. (c) is that as c increases, the density of ions in the atmosphere increases and the ionic mobility is further reduced by this asymmetric effect. When the driving force on the ion is balanced by these opposing forces, the ion moves with steady velocity.

$$E z_i e = k_1 v_i + k_2 E \sqrt{c} + k_3 E \sqrt{c}$$

or,

$$\frac{v_i \times F}{E} = \frac{z_i e F}{k_1} - \frac{(k_2 + k_3) F}{k_1} \sqrt{c}$$

Outlined formulation of Debye-Huckel-Onsager equation.

but, $\frac{v_i \times F}{E} = \lambda_i$, is called ionic equivalent conductance of the ions.

Thus the equation becomes,
$$\lambda_i = \frac{z_i e F}{k_1} - \frac{(k_2 + k_3) F}{k_1} \sqrt{c}$$

Again, when the solution is infinitely diluted, $c \rightarrow 0$, $\lambda_i^0 = \frac{z_i e F}{k_1}$,

putting in the equation, we have,
$$\lambda_i = \lambda_i^0 - \frac{(k_2 + k_3) F}{k_1} \sqrt{c}$$

For the particular i th ion this equation is valid. But for an electrolyte comprising of cation and anion, the above equation can be extended to the form

$$\lambda = \lambda_0 - (A + B \lambda_0) \sqrt{c} \quad (\text{Applicable to 1-1 strong electrolyte}).$$

The term $A \sqrt{c}$ originates from electrophoretic effect, and $B \lambda_0 \sqrt{c}$ comes from

asymmetric effect. The value of $A = \frac{82.4}{\eta(DT)^{3/2}}$ and $B = \frac{8.20 \times 10^5}{(DT)^{3/2}}$.

Values of constants in the equation.

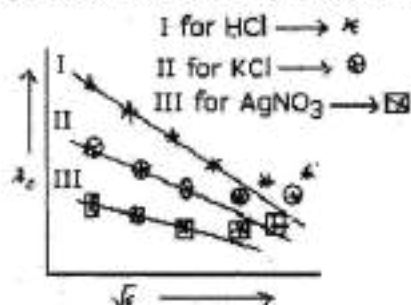
For aqueous solution at 25°C, $D = 78.6$ and $T = 298$ K, $\eta = 8.95 \times 10^{-3}$ poise, $A = 60.2$ and $B = 0.23$ and the Debye, Huckel and Onsager equation becomes

$$\lambda = \lambda_0 - (60.2 + 0.23 \lambda_0) \sqrt{c}$$

Test of the equation:

To verify the equation, λ_c vs. \sqrt{c} plot is made from the points of experimental data and also from the points obtained from Debye, Huckel and Onsager equation. These two curves coincide at low conc. of the electrolyte solution.

Experimental verification of the equation.



Solid lines represent the theoretical curves obtained from equation, and cross points represent the experimental data.

The curves show that the equation is valid only for low conc. of the electrolyte solution.

The equation is closely obeyed up to the conc. 2×10^{-3} (N).

Conceptual verification of the equation.

A further test is done by investigating what happens when the effect of the ion atmosphere is eliminated. This can be done by the experiment made by Wien and Falkenhagen.

In Wien effect, to eliminate the effect of ion atmosphere, the mobility of the ions is increased tremendously high at very high electric field so that no atmosphere has time to build up around the central ion.

Another way is to measure the conductance at very high frequencies.

Then the central ion is moved backward and forward very rapidly, and the retarding effects of ion atmosphere ought to average to zero. This is Debye Falkenhagen effect.

WIEN EFFECT:

Observation. In 1927, Wien observed that the equivalent conductance (λ_e) of strong electrolyte solution of conc. c is found to increase when field strength at about $20,000 \text{ V cm}^{-1}$ and higher is applied.

Explanation. This phenomenon is explained on the basis of ion atmosphere model of electrolyte solution. Under this high electric field, an ion moves at a velocity of about 1 meter/sec. The ion, with this high velocity, moves several times the thickness of ion atmosphere in the relaxation time (time for the ion atmosphere to rebuild around the central ion). The ion atmosphere has got no longer time to form itself around the moving ion and the ion moves virtually free from the oppositely charged ion atmosphere. The dragging effect on the moving ion is thus greatly diminished and the mobility of ions is increased. This results an increase of equivalent conductance of the electrolyte in solution due to gradual elimination of retarding asymmetric effect of ion atmosphere. This effect is more pronounced at concentrated solution of higher valence ions.

DEBYE FALKENHAGEN EFFECT:

Observation. Debye and Falkenhagen observed that when alternating current of high frequency is used, the equivalent conductance of a strong electrolyte in solution of conc. c begins to increase and at very high frequency it attains limiting value i.e., $\lambda_e \rightarrow \lambda_0$. This effect is utilized to determine λ_0 of a strong electrolyte.

Explanation. When AC of very high frequency is used, the ions in solution also oscillate with very high frequency. The time of oscillation becomes very small in comparison to the time of relaxation (θ) of the ion atmosphere. The asymmetric charge distribution has got no time to form completely around the moving central ion. It means that the central ion comes back to its original point before the ion atmosphere vanishes. The dragging force due to asymmetric effect and electrophoretic effect begins to decrease. If the oscillation frequency is very high, the ion becomes virtually stationary and the ion atmosphere remains symmetrical. Both the asymmetric and electrophoretic effect are totally eliminated and the equivalent conductance (λ_e) of the solution becomes its limiting value (λ_0).

The relaxation time (θ) for 1-1 electrolyte is about $\frac{10^{-10}}{c}$ sec.

Thus for solution of $c = 1 \times 10^{-3} (N)$, the relaxation time, $\theta = \frac{10^{-10}}{1 \times 10^{-3}} = 10^{-7}$ sec.

Minimum frequency of AC required for the effect to appear. The frequency (ν) of the AC at which the abnormal conductance is to be expected is given by

$$\nu = \frac{1}{\theta} = \frac{1}{10^{-7}} = 10^7 \text{ Hertz.}$$

This is the limiting frequency of AC at which λ_e begins to increase for the above solution.

The effect is more pronounced in concentrated solution of high valence ions.

DISSOCIATION FIELD EFFECT:

High electric field applied to weak electrolyte. Weak electrolyte is dissociated to small extent in solution. But when applied field strength (E) is raised, dissociation becomes several times greater than expected in the definite conc. of the solution. It is highly probable that the powerful electric field produces temporary dissociation into ions of the molecules of weak acids and bases. When the electric field is withdrawn, the dissociation reverts to its initial state. This phenomenon is referred to as 'dissociation field effect'.

ELECTROCHEMISTRY
PART III: ACTIVITY AND ACTIVITY COEFFICIENT
(DEBYE HUCKEL LIMITING LAW)

INTRODUCTION

Chemical potential in ideal solutions

Ideal solutions have certain criteria, one of which is that the chemical potential and other thermodynamic properties can be expressed by conc. such that

$$\mu_i = \mu_i^o + RT \ln x_i, \text{ where } x_i \text{ is molefraction of the } i \text{ th component in the mixture.}$$

Chemical potential in non-ideal solutions

But for non-ideal solutions, if conc. is used for calculation of the thermodynamic properties, much errors have crept in, and activity in stead of conc. gives better results, such that

$$\mu_i = \mu_i^o + RT \ln a_i, \text{ where } a_i \text{ is activity of the } i \text{ th component in the mixture.}$$

Non-electrolyte solutions and gaseous systems are ideal

Non-electrolytic solutions and gaseous systems behave ideally even at moderate conc. and pressure. The physical properties of these cases can be calculated by using conc. and pressure respectively. This is due to the fact that very weak van der Waals forces are operative. The effectiveness of these forces occur only when conc. of these solutions is large and pressure of the gas is high. These forces are short-range forces.

Electrolyte solutions are non-ideal

But electrolyte solutions even at low conc. behave non-ideal and activity is to be used to get accurate value of the physical properties. This is due to strong Coulombic force operating between the ions and this force is long-range one.

Relation between activity (a_i) and conc. of a species

The activity (a) of a component is related with conc. as

$$a_i = c_i f_i, \text{ where } c_i = \text{molar conc. of the } i \text{ th component and}$$

$$f_i = \text{molar-scale activity coefficient of that component in the solution.}$$

and, $a_i = m_i \gamma_i$, where m_i = molal conc. of the i the component and

$$\gamma_i = \text{molal-scale activity coefficient of that component in the solution.}$$

The example is showing the better result when activity is used instead of conc.

One example of calculation of dissociation constant of a weak electrolyte, such as acetic acid can be given below to show that activity instead of conc. gives more accurate value of the property.

DISSOCIATION CONSTANT OF ACETIC ACID AT 25 °C

conc. (molarity) $\times 10^5$	2.8	21.8	102.8	948.0	2000.0
K_a (conc.) $\times 10^5$	1.77	1.78	1.80	1.83	1.84
K_a (activity) $\times 10^5$	1.75	1.75	1.75	1.75	1.74

Question: Why do deviations from ideality begin to occur at much lower conc. for electrolytic solutions than for non-electrolytic solutions?

[Burdwan Univ. 1993]

RELATION BETWEEN ACTIVITY AND CONC. OF AN ELECTROLYTE IN A SOLUTION

Strong electrolyte, $B_x A_y$ is used in the relation

Let us take a strong electrolyte, $B_x A_y$ dissolved in a solution of activity ' a ' and molarity ' c ' dissociating completely as: $B_x A_y \rightarrow xB^{+z} + yA^{-z}$

z_+ and z_- are the magnitude of the valence of cation and anion of the electrolyte respectively.

If c mole of the electrolyte is dissolved in c_s mole of the solvent, then total free energy of the solution is

$$G = c_s \mu_s + c \mu,$$

where μ_s and μ are the chemical potential of the solvent and solute respectively.

But the electrolyte in solution remains in ionic forms and hence we can write

$$G = c_s \mu_s + c(x\mu_+ + y\mu_-), \quad (2)$$

as xc and yc are the mole of cations and anions respectively.

Comparing equation (1) and (2), we get

$$\mu = x\mu_+ + y\mu_- \quad (3)$$

Mean ionic chemical potential is defined as,

$$\mu_{\pm} = \frac{x\mu_+ + y\mu_-}{x+y} \text{ or, } (x+y)\mu_{\pm} = x\mu_+ + y\mu_- \quad (4)$$

Relation between μ of the electrolyte and the ions.

Two equations (3) and (4) are collectively written as $\mu = (x+y)\mu_{\pm} = x\mu_+ + y\mu_- \quad (5)$

Expressing chemical potential in terms of activity, we have

$$\mu^{\circ} + RT \ln a = (x+y)\left[\mu_{\pm}^{\circ} + RT \ln a_{\pm}\right] = x\left[\mu_+^{\circ} + RT \ln a_+\right] + y\left[\mu_-^{\circ} + RT \ln a_-\right]$$

$^{\circ}$ superscript denotes term at the standard state. a , a_{\pm} , a_+ and a_- are the activity of the electrolyte, mean ionic activity, activity of the cation and anion respectively.

The above equation can be written as

$$\mu^{\circ} + RT \ln a = (x+y)\mu_{\pm}^{\circ} + RT \ln a_{\pm}^{(x+y)} = (x\mu_+^{\circ} + y\mu_-^{\circ}) + RT \ln (a_+^x \cdot a_-^y) \quad (6)$$

Relation (5) holds also for standard conditions and hence, $\mu^{\circ} = (x+y)\mu_{\pm}^{\circ} = x\mu_+^{\circ} + y\mu_-^{\circ}$.

Relation between activity of electrolyte and the ions

$$\text{Inserting the above in equation (6), we have } a = a_{\pm}^{(x+y)} = a_+^x \times a_-^y \quad (7)$$

Relating with conc. terms, we have $a = a_{\pm}^{(x+y)} = (c_+ f_+)^x \times (c_- f_-)^y = (c_+^x \times c_-^y) (f_+^x \times f_-^y)$

where c_+ and c_- are molar conc. of the cation and anion respectively.

But for the electrolyte, $c_+ = xc$ and $c_- = yc$. Putting these values, we get the final relation

$$a = a_{\pm}^{(x+y)} = (xc)^x (yc)^y f_{\pm}^{x+y}$$

or,

$$a = a_{\pm}^{(x+y)} = (x^x y^y) c^{x+y} f_{\pm}^{x+y},$$

where

$$f_{\pm}^{x+y} = f_+^x \times f_-^y$$

and f_{\pm} is called molar-scale mean ionic activity coefficient of the electrolyte.

Relation between activity and conc. of a strong electrolyte

When molal conc. is used in the expression, we have

$$a = a_{\pm}^{(x+y)} = (x^x y^y) m^{x+y} \gamma_{\pm}^{x+y}$$

and γ_{\pm} is called molal-scale mean ionic activity coefficient of the electrolyte.

For uni uni valent electrolyte, $x = 1$, $y = 1$, so the relation is $a = a_{\pm}^2 = c^2 f_{\pm}^2$ and $a = a_{\pm}^2 = m^2 \gamma_{\pm}^2$.

For bi uni valent electrolyte, $x = 1$, $y = 2$ so the relation is $a = a_{\pm}^3 = 4c^3 f_{\pm}^3$ and $a = a_{\pm}^3 = 4m^3 \gamma_{\pm}^3$.

Question: Demonstrate, starting from $\mu_{M_p X_q} = p\mu_M + q\mu_X$ that the activity of a salt, $M_p X_q$ can be

$$\text{written as, } a_{M_p X_q} = (p^p q^q) m^{p+q} \gamma_{\pm}^{p+q}$$

where m is the molality and γ_{\pm} is molal-scale mean activity coefficient. [Burdwan Univ. 1996]

Question (1): How is the activity ‘ a ’ of $\text{La}_2(\text{SO}_4)_3$ related to the mean ionic activity?

Solution: For the salt, $x = 2$, $y = 3$ and so $a = a_{\pm}^5$.

[Burdwan Univ. 2008]

Question (2): Show that mean ionic activity is the geometric mean of the individual ionic activities.

Solution: We have mean ionic chemical potential (μ_{\pm}) is related with ionic chemical potentials

as $(x + y)\mu_{\pm} = x\mu_+ + y\mu_-$. Then proceed as above in the text.

Question (2): Calculate a_{\pm} for a 0.1 molal solution of H_2SO_4 at 25 °C, where $\gamma_{\pm} = 0.265$.

[Burdwan Univ. 1998]

Solution: $a_{\pm}^{(x+y)} = (x^x y^y) m^{x+y} \gamma_{\pm}^{x+y}$, but here, $x = 2$, $y = 1$, hence $a_{\pm}^3 = 4m^3 \gamma_{\pm}^3$.

Putting the values, $a_{\pm}^3 = 4(0.1)^3 \times (0.265)^3$ or, $a_{\pm} = 0.042$.

Question: Given that $\mu = \nu \mu_{\pm}$, the relation $a = a_{\pm}^{\nu}$ follows. → Justify / criticize. [Burdwan Univ. 2008]

Question: Show that mean ionic activity is the geometric mean of the individual ionic activities.

EXPERIMENTAL OBSERVATION ON ACTIVITY COEFFICIENT (γ_{\pm}) AND CONCEPT OF IONIC STRENGTH OF AN ELECTROLYTE SOLUTION

Mean activity coefficient (γ_{\pm}) of an electrolyte in solution could be experimentally determined by solubility measurements, e.m.f. measurements, etc. On studying the various results of γ_{\pm} in different electrolyte solutions, following observations have been made.

Variation of γ_{\pm} with conc. of pure electrolyte in solution

(1) In pure electrolyte solution, γ_{\pm} of an electrolyte decreases, attains minimum and then increases with the increase of conc. of the solution provided the solution is dilute.

When γ_{\pm} is plotted against \sqrt{m}

or, $-\log \gamma_{\pm}$ is plotted against \sqrt{m} ,

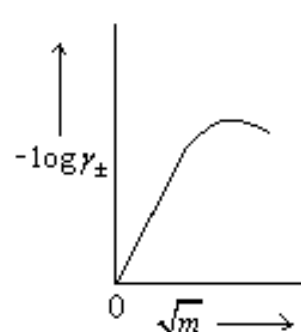
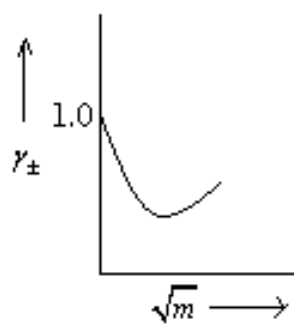
the curves are obtained as given:

The approximate relation

between γ_{\pm} and \sqrt{m} can be written as:

$$-\log \gamma_{\pm} = A\sqrt{m}.$$

Where A is constant for a given electrolyte in a given solvent at a given temperature.



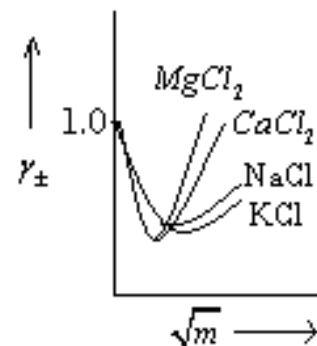
Variation of γ_{\pm} with conc. of same valence-type electrolytes in solution

For the electrolytes of same valence type

(uni-uni valent or bi-uni valent, etc.), the variation of γ_{\pm}

with \sqrt{m} is same up to certain conc. ($m = 0.01$) but

at higher conc. individual character of the ions plays its role.



Influence of different ions on γ_{\pm} of an electrolyte in solution

(2) Lewis and Randall found that the influence of an ion in a mixture on the activity coefficient of an electrolyte depends on the conc. of the ion and square of its valence.

Thus a bivalent ion (say Ca^{+2}) influences the activity co-efficient of an electrolyte (say NaNO_3) in mixture four times that of monovalent ion (say K^+).

Definition of ionic strength (i) of an electrolyte solution

For comparing the activity coefficient of electrolyte in pure state or in mixture with other electrolytes, Lewis and Randall introduced a conc. term, called *ionic strength* of the solution. It is obtained by multiplying the conc. of each ion present in the solution with square of its valence and dividing the sum of these products by two.

Thus the ionic strength (i) of the solution is $i = \frac{1}{2}(m_1 z_1^2 + m_2 z_2^2 + m_3 z_3^2 \dots) = \frac{1}{2} \sum m_i z_i^2$

The ionic strength considers the effective influence of each ion in solution towards γ_{\pm} of an electrolyte inserting due weightage of the conc. and valence of each ion.

γ_{\pm} of an electrolyte is same in solutions of same i

(4) Lewis and Randall further observed that in very dilute solutions, γ_{\pm} of an electrolyte is same in all solutions of same ionic strength.

Some problems on the calculation of ionic strength (i)

Calculation of ionic strength of pure electrolytes in solution

(1) For pure electrolyte solutions of molality, m .

(a) uni-uni valent (1, 1) electrolyte (BA), example: NaCl, KNO₃, HCl, etc.

BA dissociates as $BA \rightarrow B^+ + A^-$, so, $i = \frac{1}{2}[m \times 1^2 + m \times 1^2] = m$

(b) bi-uni valent (2, 1) electrolyte (BA₂), such as CaCl₂, Mg(NO₃)₂, etc

$$i = \frac{1}{2}[m \times 2^2 + 2m \times 1^2] = 3m$$

(c) bi-bi valent (2, 2) electrolyte (BA), such as CaSO₄, MgSO₄, etc.

$$i = \frac{1}{2}[m \times 2^2 + m \times 2^2] = 4m$$

Short-cut way to find ionic strength of an electrolyte solution

Thus for pure electrolyte solutions, ionic strength (i) is related with molality (m) as:

$$i = k m$$

where, $k = 1$ for (1, 1) electrolytes,

$= 3$ for (2, 1) electrolytes,

$= 4$ for (2, 2) electrolytes,

$= 6$ for (3, 1) electrolytes,

$= 9$ for (3, 3) electrolytes and

$= 15$ for (3, 2) electrolytes.

(2) In mixture of electrolytes in solution:

(a) A solution containing 0.008 m BaCl₂ and 0.005 m KCl.

[Burdwan Univ. 2011, 2014]

Solution: $i = \frac{1}{2}[0.008 \times 2^2 + 0.005 \times 1^2 + (2 \times 0.008 + 0.005) \times 1^2] = 0.029 \text{ (m)}$.

(b) Calculate the ionic strength of the resulting solution obtained by mixing 25 ml 0.002 m K₄[Fe(CN)₆] solution and 75 ml 0.003 m K₃[Fe(CN)₆] solution.

Solution: Molality of K₄[Fe(CN)₆] in the resulting solution

$$= \frac{25 \times 0.002}{(75 + 25)} = 0.0005 \text{ m} \quad \text{and} \quad K_3[\text{Fe}(\text{CN})_6] = \frac{75 \times 0.003}{(75 + 25)} = 0.00225 \text{ m}$$

$$i = \frac{1}{2}[(4 \times 0.0005 + 3 \times 0.00225) \times 1^2 + 0.0005 \times 4^2 + 0.00225 \times 3^2] = 0.0185 \text{ m}$$

(c) 60 cc of 0.015 (m) BaCl₂ solution is mixed with 40 cc of 0.0125 (m) KCl solution.

Calculate the ionic strength of the solution. Consider ideal mixing of the solution.

Solution: $i = 0.032 \text{ (m)}$

[Burdwan Univ. 1990]

- (d) Assuming complete dissociation, calculate the ionic strength of a solution formed by mixing equal volumes of 0.01 m K_2SO_4 and 0.02 m $BaCl_2$ solutions. [Burdwan Univ. 1993]
Answer: $i = 0.025(m)$
- (e) Calculate the ionic strength of m molal solution of $LaCl_3$. [Burdwan Univ. 2014]
- (f) What is ionic strength? Calculate the ionic strength of a solution obtained by mixing equal volumes of 0.01 (N) $NaCl$ and 0.02 (N) Na_3PO_4 [West Bengal Civil Service Exam. 2003]
Solution: $i = 0.025 (M)$
- (g) What molality (m) of $CuSO_4$ solution has the same ionic strength as 1 m KCl solution
Solution: 0.25 m. [NET-CSIR, UGC. 2000]
- (h) Calculate the ionic strength of a solution obtained by mixing aqueous solutions of 50 ml of 0.02(M) $AlCl_3$, 25 ml of 0.04(M) K_2SO_4 and 50 ml of 0.02(M) urea at 25 °C. [Ans. 0.072(M)]
 [Calcutta Univ. 2013]

Debye Huckel Theory and limiting law

Introduction

P. Debye and E. Huckel (1923) first formulated an expression to calculate the activity coefficient (γ_{\pm}) of an electrolyte in a solution of ionic strength (i). This formulation is based on ionic atmosphere model they have proposed earlier. This is called Debye-Huckel theory and it consists of the following postulates:

Coulombic force between two ions in solution

- (1) The theory assumes strong electrolyte ($\alpha = 1$) and it is in dilute solution. It thus considers that the non-ideality of the solution is only due to long-range Coulombic force. The short-range van der Waals force is not effective in this dilute solution as the interionic distance is large.

The Coulombic force between the ions in solution is given as:

$$F = \frac{z_1 z_2 e^2}{D r^2}, \text{ terms have their usual meaning.}$$

The electrolytes of higher valence ions, low dielectric constant (D) and high concentrated solution favours the solution for being non-ideal as these factors can produce high Coulombic force among the ions in solution.

Comparison of non-ideality in different solutions

Thus, $NaCl$ in alcohol solution is more non-ideal than in water solution of same conc. as

$$D_{alcohol} < D_{water} \quad \text{[Burdwan Univ. 2002]}$$

Again, $CaCl_2$ in aqueous solution is more non-ideal than $NaCl$ in aqueous solution of same conc. as

$$z_{Ca^{+2}} > z_{Na^{+1}} \quad \text{.}$$

However when the solution is infinitely diluted, Coulombic force is negligibly small as interionic distance is very large and the solution behaves ideal.

Effects responsible for formation of ion atmosphere in solution

- (2) The arrangement of ions in electrolyte solution depends on two opposing effects.

The one effect is Coulombic potential which is trying to keep the ions in ordered state as we have seen in ionic crystal. However, the Coulombic force is D times less in solution than in air.

The other effect is due to thermal energy which tries to keep the ions in random arrangement. A comprise of these two effects result in the formation of ion atmosphere surrounding a particular ion. Thus each ion (reference ion) is surrounded by spherically symmetrical ion atmosphere that contains both cations and anions but the opposite ions to that of reference ion dominate in the ion atmosphere. The net charge of the ion atm. is equal in magnitude but opposite in sign to that of the reference ion (we call it central ion and it is taken positive ion). If the central ion has $(+z_j e)$ then the ion atmosphere has the charge $(-z_j e)$.

(3) Ion atmosphere actually screens the central ion and thus the activeness of the central ion is diminished from that when it is not screened by ion atmosphere.

The chemical potential of the central ion is also decreased due to formation of ion atmosphere.

$$\mu_j(\text{non-ideal}) = \mu_j^\circ + RT \ln a_j = (\mu_j^\circ + RT \ln m_j) + RT \ln \gamma_j$$

but,
$$\mu_j(\text{ideal}) = \mu_j^\circ + RT \ln m_j$$

so,
$$\mu_j(\text{non-ideal}) = \mu_j(\text{ideal}) + RT \ln \gamma_j.$$

Since in dilute solution, $\gamma_j < 1$, so $\mu_j(\text{non-ideal}) < \mu_j(\text{ideal})$.

Similarly, potential due to central ion at a distance r from the central ion is less than that it would be when it is not shielded by the ion atmosphere.

$$\psi(\text{shielded}) < \psi(\text{unshielded})$$

FORMULATION OF POTENTIAL DUE TO SHIELDED CENTRAL ION AT A DISTANCE, r

Formulation of charge density (ρ) of the ion atmosphere

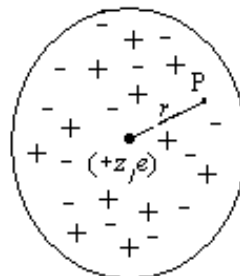
The charge density of the ion atmosphere (charge per unit volume) of the ion atmosphere at a distance r from the central ion of charge, $(+z_j e)$ is given as:

$$\rho = \sum z_i e \times n_i e^{-z_i e \psi / kT}$$

n_i = number of ions per unit volume at a distance where central ion has no influence (at infinite r)

$z_i e \psi$ = amount of work required to bring one ion of charge, $z_i e$ from infinity to the point P where ψ is the potential.

So, $n_i e^{-z_i e \psi / kT}$ = number of i th kind ions per unit volume (cc) at the point P, where each ion has excess energy $z_i e \psi$. Σ is taken to include all the ions present per cc at the point P. (Boltzmann distribution law)



Expression of charge density (ρ)

Expanding the expression of ρ and neglecting higher powers of small term, $z_i e \psi / kT$, we have

$$\rho = \sum n_i z_i e \left(1 - \frac{z_i e \psi}{kT} \right) = \sum n_i z_i e - \left(\frac{e^2}{kT} \sum n_i z_i^2 \right) \psi,$$

where ψ is the potential at the point P due to the central ion when it is shielded by the ion atmosphere. But $\sum n_i z_i e = 0$ as at the infinite distance the solution is electrically neutral.

The charge density at point P,
$$\rho = - \left(\frac{e^2}{kT} \sum n_i z_i^2 \right) \psi.$$

Poisson's equation

For finding expression of ρ and ψ , we require another relation and that is the Poisson's equation and the Poisson's equation is $\nabla^2 \psi = -\frac{4\pi}{D} \rho$, where ∇^2 (Laplacian operator) = $\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d}{dr} \right)$ as the ion atmosphere is spherically symmetrical and so independent of azimuthal angle (ϕ) and zenith angle (θ).

Expression of κ

We have
$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d\psi}{dr} \right) = \left(\frac{4\pi e^2}{DkT} \sum n_i z_i^2 \right) \psi \quad \text{or,} \quad \frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d\psi}{dr} \right) = \kappa^2 \psi,$$

where, $\kappa^2 = \frac{4\pi e^2}{DkT} \sum n_i z_i^2$, again $\sum n_i z_i^2 = \frac{N_A d}{10^3} \sum m_i z_i^2 = \frac{2N_A d}{10^3} i$,

where, m_i is molality of i th kind ion and d is density of the solvent.

Or,
$$\kappa = \left(\sqrt{\frac{8\pi e^2 d N_A}{10^3 D k T}} \right) \sqrt{i}, \quad \text{where } i = \text{ionic strength of the solution} = \frac{1}{2} \sum m_i z_i^2.$$

Evaluation of A and potential of central ion alone, $\psi_{central}$

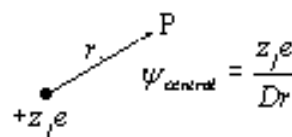
Solving the equation, $\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d\psi}{dr} \right) = \kappa^2 \psi$, we get the expression of potential, $\psi = A e^{-\kappa r}$.

At infinite dilution, ion atmosphere is not formed and $\kappa = 0$. The potential, $\psi = A$

This is the potential due to central ion alone when it is not shielded

by ion atmosphere. This is, $\psi_{central} = \frac{z_j e}{Dr}$, so $A = \frac{z_j e}{Dr}$.

Plot of potential vs. r for shielded and unshielded ion



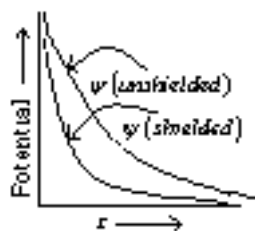
Inserting A, we have potential due to central ion surrounded by

ion atmosphere at a distance r ,
$$\psi = \frac{z_j e}{Dr} e^{-\kappa r}$$

Since, $e^{-\kappa r} < 1$, so, $\psi < \psi_{central}$

i.e. the potential at a distance, r due to central ion is less when shielded by the ion atmosphere.

ψ and $\psi_{central}$ can be plotted against r , and we have the following plots.



ψ is decreased more rapidly than $\psi_{central}$ as r increases

since, $\frac{z_j e}{Dr}$ and $e^{-\kappa r}$ both terms decrease as r increases.

As, $r = 0$, $\psi \rightarrow \infty$ and $r \rightarrow \infty$, $\psi \rightarrow 0$

Again, as, $r \rightarrow 0$, $\psi_{central} \rightarrow \infty$

and $r \rightarrow \infty$, $\psi_{central} \rightarrow 0$.

Question: What is the unit of κ in the equation, $\psi = A e^{-\kappa r}$, r being the distance. (Ans. length^{-1})

[Burdwan Univ. 2001]

Potential due to ion atmosphere ($\psi_{ion atm}$)

Expanding the expression of potential, $\psi = \frac{z_j e}{Dr} e^{-\kappa r}$ taking $\kappa r \ll 1$,

we get,
$$\psi = \frac{z_j e}{Dr} (1 - \kappa r) \quad \text{or,} \quad \psi = \frac{z_j e}{Dr} - \frac{z_j e \kappa}{D}$$

Potential, ψ consists of two parts – one for central ion and other for ion atmosphere

It could be written as

$$\psi = \frac{z_j e}{Dr} - \frac{z_j e}{D \left(\frac{1}{\kappa} \right)} = \psi_{central} + \psi_{ion atm}.$$

First term is the potential due to central ion alone at a distance, r from the central ion and it is

$\psi_{central} = \frac{z_j e}{Dr}$. Second term is the potential due to ion atmosphere and it is $\psi_{ion atm} = -\frac{z_j e \kappa}{D}$

The expression of $\psi_{ion atm}$ shows that κ has the dimension of L^{-1} and its unit is cm^{-1} or m^{-1} .

Concept of potential and thickness of ion atmosphere

Again, the above relation does not contain r and ion atmosphere has charge $(-z_j e)$, it is assumed that it is the potential due to the ion atmosphere at the central ion (assumed to be point charge) and when the whole charge of the ion atmosphere $(-z_j e)$ is assumed to be concentrated at a point, $(1/\kappa)$ distance away from the central ion. Thus $(1/\kappa)$ is assumed to be the thickness of ion atmosphere (it is sometimes called Debye length, r_D).

Expression of potential due to ion atmosphere from mathematical view point:

We have, $\psi = \psi_{central} + \psi_{ion atm}$

$$\begin{aligned} \text{Thus, } \psi_{ion atm} &= \psi - \psi_{central} = \frac{z_j e}{Dr} e^{-\kappa r} - \frac{z_j e}{Dr} = \frac{z_j e}{D} \left[\frac{1}{r} (e^{-\kappa r}) - \frac{1}{r} \right] \\ &= \frac{z_j e}{D} \left[\frac{1}{r} \left(1 - \kappa r + \frac{1}{2} (\kappa r)^2 - \dots \right) - \frac{1}{r} \right] = \frac{z_j e}{D} \left[\left(\frac{1}{r} - \kappa + \frac{1}{2} \kappa^2 r - \dots \right) - \frac{1}{r} \right] \\ &= \frac{z_j e}{D} \left[\left(-\kappa + \frac{1}{2} \kappa^2 r - \dots \right) \right]. \end{aligned}$$

The value of $\psi_{ion atm}$ at the central ion ($r = 0$), $\psi_{ion atm} = \frac{z_j e}{D} \left[\left(-\kappa + \frac{1}{2} \kappa^2 r - \dots \right) \right]_{r=0}$

or, $\psi_{ion atm} = -\frac{z_j e \kappa}{D}$. Thus, the expression of $\psi_{ion atm}$ can be formulated mathematically.

Question: According to Debye Huckel model, electrical potential at a distance r from the central positive ion is given by $\psi = \frac{z_j e}{Dr} - \frac{z_j e \kappa}{D}$. Show that κ has the dimension of L^{-1} .

Interpret the two terms in the right side of the equation. Plot ψ vs. r for two values of κ (say $\kappa = 0$ and $\kappa = 1$)

Burdwan Univ. 2001

Expression of charge density and other facets of ion atmosphere

We have already formulated the charge density as, $\rho = -\left(\frac{e^2}{kT} \sum n_i z_i^2 \right) \psi$ and potential, $\psi = \frac{z_j e}{Dr} e^{-\kappa r}$.

Replacing ψ in the expression of ρ , we get

$$\rho = -\left(\frac{e^2}{kT} \sum n_i z_i^2 \right) \frac{z_j e}{Dr} e^{-\kappa r} = -\frac{z_j e}{4\pi r} \left(\frac{4\pi e^2}{DkT} \sum n_i z_i^2 \right) e^{-\kappa r}, \text{ but } \left(\frac{4\pi e^2}{DkT} \sum n_i z_i^2 \right) = \kappa^2,$$

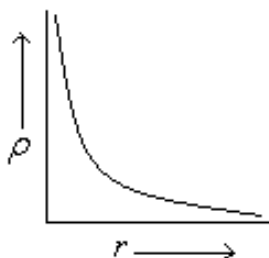
The expression of charge density of the ion atmosphere at a point r from the central ion is

$$\rho = -\frac{z_j e}{4\pi r} \kappa^2 e^{-\kappa r}.$$

A plot of magnitude of ρ vs. r is given as;

Both the factors containing r decreases with increase of r and due to the exponential term, ρ decreases very rapidly with increase of r .

When, $r \rightarrow 0$, $\rho \rightarrow \infty$ and $r \rightarrow \infty$, $\rho \rightarrow 0$.



Expression of ρ as a function of distance r

The plot of ρ vs. r

Calculation of total charge of the ion atmosphere:

Let us consider a spherical shell within the ion atmosphere of radius r from the central ion of thickness dr .

The volume of the spherical shell, $dv = 4\pi r^2 dr$.

Charge contained within the shell, $dq = \rho dv$.

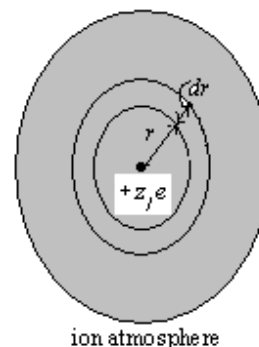
$$\text{or, } dq = \left(-\frac{z_j e}{4\pi r} \kappa^2 e^{-\kappa r} \right) \times 4\pi r^2 dr = (-z_j e) \kappa^2 r e^{-\kappa r} dr.$$

So the total charge of the ion atmosphere,

$$q_{ion\ atm} = \int_0^{\infty} (-z_j e) \kappa^2 r e^{-\kappa r} dr = (-z_j e) \int_0^{\infty} \kappa^2 r e^{-\kappa r} dr = (-z_j e) \int_0^{\infty} (\kappa r) e^{-\kappa r} d(\kappa r) = (-z_j e).$$

$$[\text{Since } \int_0^{\infty} t e^{-t} dt = 1, \text{ here, } t = \kappa r].$$

This shows that total charge of the ion atmosphere is $(-z_j e)$ which is equal but opposite in sign to the charge of the central ion, $(+z_j e)$.



Expression of thickness of the ion atmosphere:

The fraction of total charge of the ion atmosphere that is contained within the spherical shell

$$= \frac{dq}{q_{ion\ atm}} = \frac{(-z_j e) \kappa^2 r e^{-\kappa r} dr}{(-z_j e)} = \kappa^2 r e^{-\kappa r} dr = F(r) dr$$

where, $F(r) = \kappa^2 r e^{-\kappa r}$ and it is called charge distribution function of the ion atmosphere.

It may be defined as the fraction of the total charge of the ion atmosphere contained within the spherical shell of radius, r with unit thickness.

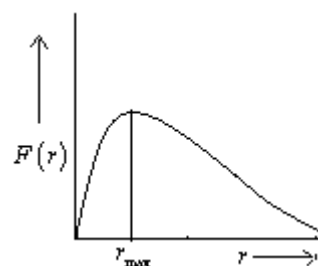
When $F(r)$ is plotted against r , the curve starts from origin and increases, attains maximum and then decreases to asymptotic value with increase of r .

This is due to the fact that the $F(r)$ consists of two terms – one is non-exponential term (r) and other is exponential term ($e^{-\kappa r}$). This type of distribution is called Gaussian distribution.

At $r = 0$, $F(r) = 0$ and now as r increases, the non-exponential term increases but exponential term decreases. At low value of r , the non-exponential term dominates over the exponential term and so value of $F(r)$ increases. But at high values of r , the exponential term dominates and $F(r)$ decreases.

When $r \rightarrow \infty$, $F(r) \rightarrow 0$.

$F(r)$ attains maximum values at a certain radius, r_{max} of the spherical shell in which the maximum fraction of charge of the ion atmosphere is present.



The expression of r_{max} can be obtained from the condition of maxima and minima, $\frac{dF(r)}{dr} = 0$.

Thus differentiating $F(r)$ with respect to r and equating to zero, we have

$$\frac{dF(r)}{dr} = \kappa^2 (e^{-\kappa r} - r\kappa e^{-\kappa r}) = 0 \quad \text{or,} \quad \kappa^2 e^{-\kappa r} (1 - r\kappa) = 0$$

(i) when $\kappa = 0$, there is no ion atmosphere, (ii) when $e^{-\kappa r} = 0$, $r = \infty$, and it is minimum point

and (iii) $1 - r\kappa = 0$, it denotes maximum point of the curve, so $r_{\max} = 1/\kappa$.

This shows that the spherical shell of radius, $(1/\kappa)$ with unit thickness contains maximum fraction of total charge of the ion atmosphere. Thus $(1/\kappa)$ is called the thickness of the ion atmosphere or called Debye length (r_D).

Putting the value of $\kappa = \left(\frac{8\pi e^2 dN_A}{10^3 DkT} \right) \sqrt{i}$ in the expression, we get the thickness or Debye length,

Expression of thickness of ion atmosphere

$$r_D = \left(\frac{1}{\kappa} \right) = \sqrt{\frac{10^3 DkT}{8\pi e^2 dN_A}} / \sqrt{i}, \text{ putting the value of universal constants, } r_D = \frac{1.987 \times 10^{-10} \sqrt{DT}}{\sqrt{i}} \text{ cm.}$$

$$\text{For aqueous solution at } 25^\circ\text{C, } D = 78.6 \text{ and } T = 298 \text{ K, } r_D = \frac{3.03}{\sqrt{i}} \text{ \AA.}$$

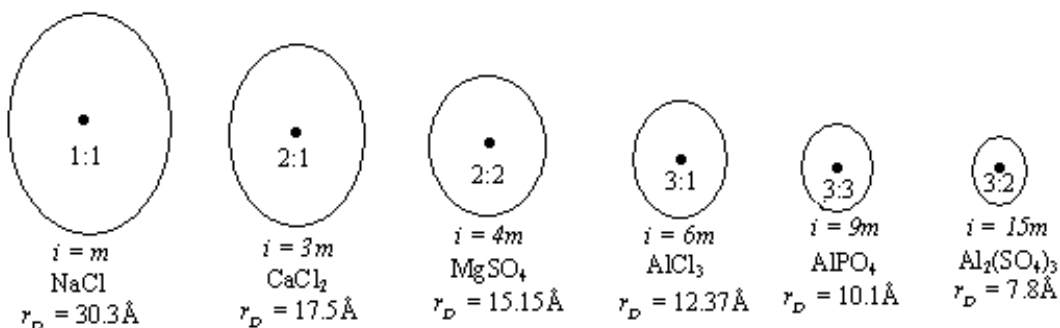
The factors that controls the size of the ion atmosphere

Thus the thickness of the ion atmosphere is of angstrom range and it depends on dielectric constant (D), temperature (T) and the ionic strength (i) of the solution. Greater the value of D and T, more diffuse is the ion atmosphere and thickness is large, while higher the ionic strength of the solution, more compact is the ion atmosphere and thickness is small.

However, it is to be noted that the thickness of ion atmosphere does not depend on the charge of the central ion and every ion is surrounded by ion atmosphere of same size in a given ionic solution.

Comparison of size of ion atmosphere of different valence type electrolytes

Comparison of thickness of ion atmosphere in different valence type electrolytes of 0.01 molal aqueous solution at 25°C are given below:



Question: The thickness of ion atmosphere Debye Huckel theory may be written as

$$b = \alpha A^m B^n C^p, \text{ where } \alpha \text{ is some constant and } A = D/e^2.$$

(D = dielectric constant; e = electronic charge), B = kT and C has the dimension of L^3 .

(i) Express the dimension of A and B in terms of M, L, T.

(Ans. $A = M^{-1} L^{-3} T^2$, $B = ML^2 T^{-2}$)

(ii) Put them in the given expression for b to find how m, n and p are related.

(Ans. $2n - 3m + 3p = 1$)

(iii) Find m if the condition $m = n = p$ holds. (Ans. $m = 1/2$)

(iv) Identify the quantity C. (Ans. C is reciprocal of ionic strength).

[Burdwan Univ. 1997, $m = 1 \times 2 + 3 + 1 + 2 = 8$]

Question: Calculate the thickness of ion atmosphere for a 0.01 (M) MgCl₂ solution at 298 K, given that the thickness of the ion atmosphere of 0.1 (M) NaCl solution is 0.96 nm at

298 K. (Ans. thickness of ion atmosphere in MgCl₂ is 1.75 nm) [Burdwan Univ. 2000]

Question: Discuss the effect of temperature and dielectric constant of the medium on the thickness of the ion-atmosphere. [Burdwan Univ.2013]

Solution: See the text as above.

Formulation of Debye Huckel limiting law

We have, chemical potential of the j th kind ions (they are taken as the reference ions around which ion atmosphere is formed)

$$\mu_j(\text{non-ideal}) = \mu_j^\circ + RT \ln a_j$$

but $a_j = m_j \gamma_j$, putting, $\mu_j(\text{non-ideal}) = (\mu_j^\circ + RT \ln m_j) + RT \ln \gamma_j = \mu_j(\text{ideal}) + RT \ln \gamma_j$.

Thus, $\mu_j(\text{non-ideal}) - \mu_j(\text{ideal}) = RT \ln \gamma_j$

or, $\Delta\mu_j = RT \ln \gamma_j$

Calculation of $(\Delta\mu_j)$ from Debye Huckel model

This decrease of chemical potential of the reference ions is due to electrical interaction in non-ideal solution. And this additional chemical potential $(\Delta\mu_j)$ originates from excess energy acquired by j th ion for its surrounding ion atmosphere.

This $(\Delta\mu_j)$ can be calculated from the work required to bring one mole j th kind ions from the ideal solution (where there is no ion atmosphere) to the non-ideal solution (where there exists ion atmosphere surrounding the ion).

This is equivalent to the difference of work required to charge one mole of the central ion in ideal solution ($\kappa = 0$) and in non-ideal solution ($\kappa \neq 0$).

Work required in charging the central ion in ideal solution, $w_{ideal} = \int_0^{z_j e} \psi dq = \int_0^{z_j e} \frac{q}{Da} dq = \frac{z_j^2 e^2}{2Da}$

In the reversible process of charging an ion, small amount of charge, dq is added to the neutral ion on the surface (where distance from the central ion is, $a =$ radius of the ion).

Work required in charging the same ion in non-ideal solution in presence of ion atmosphere

$$w_{non-ideal} = \int_0^{z_j e} \psi dq = \int_0^{z_j e} \left(\frac{q}{Da} - \frac{q\kappa}{D} \right) dq = \frac{z_j^2 e^2}{2Da} - \frac{z_j^2 e^2 \kappa}{2D}$$

The additional work required to charge the central ion is equal to the additional free energy

acquired by the central ion due to ion atmosphere and it is, $\Delta w = w_{non-ideal} - w_{ideal} = -\frac{z_j^2 e^2 \kappa}{2D}$.

For one mole (N_A number) of j th ions, the additional chemical potential, $\Delta\mu_j = N_A \times \Delta w$.

Therefore, we have $\Delta\mu_j = -\frac{z_j^2 e^2 N_A \kappa}{2D}$ but, $\Delta\mu_j = RT \ln \gamma_j$.

Equating two expressions of $\Delta\mu_j$, we have, $RT \ln \gamma_j = -\frac{z_j^2 e^2 N_A \kappa}{2D}$.

Inserting the expression of $\kappa = \left(\frac{8\pi e^2 dN_A}{10^3 DkT} \right) \sqrt{i}$, we get $\ln \gamma_j = -\frac{z_j^2 e^2 N_A}{2DRT} \left(\frac{8\pi e^2 dN_A}{10^3 DkT} \right) \sqrt{i}$.

Or, $\ln \gamma_j = -z_j^2 \left(\frac{e^2 N_A}{2DRT} \sqrt{\frac{8\pi e^2 dN_A}{10^3 DkT}} \right) \sqrt{i}$ or, $\ln \gamma_j = -z_j^2 B \sqrt{i}$ where, $B = \left(\frac{e^2 N_A}{2DRT} \sqrt{\frac{8\pi e^2 dN_A}{10^3 DkT}} \right)$.

Or, $\log \gamma_j = -z_j^2 \left(\frac{B}{2.303} \right) \sqrt{i}$ or, $\log \gamma_j = -z_j^2 A \sqrt{i}$ where, $A = B/2.303$.

Thus Debye-Huckel limiting law is given as, $\log \gamma_j = -z_j^2 A \sqrt{i}$ where, $A \propto \frac{1}{(DT)^{3/2}}$.

A is called Debye-Huckel constant and $A = 0.509 \approx 0.51$ for aqueous solution at 25 °C.

Problem (1): In a book, the following expression for the Debye Huckel limiting law has been written:

$\ln \gamma_j = * z_j^2 B \sqrt{i}$, the algebraic sign (*) being blurred by bad printing.

Put the appropriate sign giving reasons.

[Burdwan Univ. 1994]

Answer: (-)ve sign. As i increases, the γ_j of the solution decreases, hence the negative sign.

Problem (2): Explain qualitatively the effect of dielectric constant on the value of $\log \gamma_j$.

[Burdwan Univ. 2005]

Answer: D.H. constant, $A \propto \frac{1}{(DT)^{3/2}}$, hence explain the effect.

Problem (1): The value of Debye Huckel constant, $A = 0.51$ at 25 °C. Calculate its value at 30 °C.

Solution: The value of A at 303 K = 0.507.

Problem (2): If the Debye Huckel limiting law is written in the form, $f_j = \exp(-Bz_j^2 \sqrt{i})$, find B, giving the Debye Huckel constant, $A = 0.51$. [Ans. $B = 1.174$]

Problem: Calculate γ_+ , γ_- and γ_{\pm} for 0.001 m NaCl solution in water at 25 °C using Debye Huckel limiting law. [Given, $A = 0.509$]

[Burdwan Univ. 2007]

Question: Assuming free energy change of one mole of $it h$ kind ions for interionic interaction

in electrolytic solution, $\Delta G = -\frac{(z_j e)^2 N_A}{2D} \left[\left(\frac{4\pi e^2}{DkT} \right) \sum n_i z_i^2 \right]^{1/2}$. Arrive at the Debye Huckel limiting law.

[Burdwan Univ. 2007]

Question: According to Debye Huckel model, the electrical potential at a distance r from the central positive ion of charge ze is given by

$$\psi = \frac{z_j e}{Dr} - \frac{z_j e \kappa}{D}$$

Interpret the terms. Find the work done for transferring the charged ion from the solution in infinite dilution to that in a given concentration. Find the dimension of κ . [Burdwan Univ. 2008, 2015]

Expression of mean ionic activity coefficient (γ_{\pm}) of an electrolyte in solution

For an electrolyte, dissociating completely as, $B_x A_y \rightarrow xB^{+z_+} + yA^{-z_-}$,

where z_+ and z_- are the numerical value of valence of cation and anion respectively.

The mean ionic activity coefficient, $\gamma_{\pm}^{x+y} = \gamma_+^x \gamma_-^y$ or, $(x+y) \log \gamma_{\pm} = x \log \gamma_+ + y \log \gamma_-$.

Using Debye Huckel law for activity coefficient of cation and anion,

$$\begin{aligned} (x+y) \log \gamma_{\pm} &= x(-Az_+^2 \sqrt{i}) + y(-Az_-^2 \sqrt{i}) = -A[xz_+^2 + yz_-^2] \sqrt{i} \\ &= -A(xz_+ z_+ + yz_- z_-) \sqrt{i} \end{aligned}$$

But the electro neutrality condition of the electrolytic solution is $xz_+ = yz_-$

Using the above condition, we get $(x+y) \log \gamma_{\pm} = -Az_+ z_- (x+y) \sqrt{i}$

or, $\log \gamma_{\pm} = -Az_+ z_- \sqrt{i}$ or precisely it is $\log \gamma_{\pm} = -A z_+ |z_-| \sqrt{i}$, where $A \propto \frac{1}{(DT)^{3/2}}$

This is Debye-Huckel limiting law.

Significance of the term 'limiting' in the Debye Huckel law

The term 'limiting' is used as the law is valid at very low conc. of the electrolyte solution, $i \leq 0.01$. Ionic solution of moderate molalities may have activity coefficients that differ from the values given by the above expression. The law is found to give good result when $i = 0.01$ and less hence for (2, 2) electrolyte it corresponds to molality 0.0025.

Question: Starting from the relation: $\log f_j = Az_j^2 \sqrt{i}$, arrive at a formula for $\log f_{\pm}$.

Draw $\log f_{\pm}$ vs. \sqrt{i} for a (1:1) electrolyte stating clearly the value of the slope.

How does the slope vary with temperature?

[Burdwan Univ. 2005]

Question: Show schematically the plot of $\log f_{\pm}$ versus μ .

[Burdwan Univ. 2006]

Question: Arrive at the expression of mean ionic activity (a_{\pm}) in terms of activities of the individual ions of an electrolyte. Assuming $\log \gamma_j = -Bz_j^2 \sqrt{i}$, find the expression of $\log \gamma_{\pm}$ in a solution having ionic strength, i .

[Burdwan Univ. 2010]

Question: Obtain expressions for the mean activity co-efficient of a (i) uni-uni valent, (ii) uni- trivalent and (iii) bi-bi valent type of salts assuming ionic strength of the solution as i .

[Burdwan Univ. 2010]

Question: Arrive at the expression of mean ionic activity (a_{\pm}) in terms of activities of the individual ions of an electrolyte. Assume $\log \gamma_i = -B_1 z_i^2 \sqrt{\mu}$, find the expression of $\log \gamma_{\pm}$ in a solution having ionic strength μ .

[Burdwan Univ. 2013]

Question: Compare the values of mean activity co-efficient for uni-bivalent and bi- bivalent type of electrolytes having the same ionic strength in aqueous solution at the same temperature.

[Burdwan Univ. 2014]

Answer: $\frac{\log \gamma_{\pm}'}{\log \gamma_{\pm}} = 2$, where γ_{\pm}' and γ_{\pm} are the mean ionic activity coefficient of bi-bivalent and uni-bivalent type of electrolytes respectively.

Extended Debye Huckel law for moderately concentrated solution

For relatively concentrated solution $0.1 \geq i \geq 0.01$, Debye and Huckel equation is modified by considering that central ion is no longer point-charge and dielectric constant (D) will also vary from one point to another point within the medium. The potential due to ion atmosphere is modified as:

$$\psi_{\text{ion atm}} = -\frac{z_j e}{D(a + \frac{1}{\kappa})} \quad \text{where, } a = \text{radius of the central ion and } \frac{1}{\kappa} = \text{thickness of the ion atm.}$$

In concentrated ionic solution, $\frac{1}{\kappa}$ is comparable to 'a' and so it can not be neglected.

The above potential can be written as,
$$\psi_{\text{ion atm}} = -\frac{z_j e \kappa}{D(1 + a\kappa)}$$

Inserting the expression of κ and simplifying we get,

$$\log \gamma_{\pm} = -\frac{A z_+ |z_-| \sqrt{i}}{1 + aA_1 \sqrt{i}}$$

(i) For dilute solution, i is very small so the 2nd term in the denominator can be neglected in comparison to 1 and we have Debye Huckel limiting law, $\log \gamma_{\pm} = -A z_+ |z_-| \sqrt{i}$.

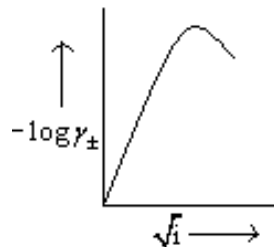
(ii) For moderate concentrated ionic solution, $0.1 \geq i \geq 0.01$, the equation is

$$\log \gamma_{\pm} = -A z_+ |z_-| \sqrt{i} (1 + aA_1 \sqrt{i})^{-1} = -A z_+ |z_-| \sqrt{i} + (aA_1 A z_+ |z_-|) i$$

or, $-\log \gamma_{\pm} = A z_+ |z_-| \sqrt{i} - C i$, where $C = (aA_1 A z_+ |z_-|)$.

The plot of $-\log \gamma_{\pm}$ vs. \sqrt{i} is given as:

At $i = 0$, $-\log \gamma_{\pm} = 0$. For low value of i , first term dominates and $-\log \gamma_{\pm}$ increases with increase of i but as i is further increased, second term dominates and $-\log \gamma_{\pm}$ is decreased after attaining maximum value.



Question: Given that $\log f_{\pm} = -A\sqrt{i} + Bi$, discuss the nature of $\log f_{\pm}$ vs. \sqrt{i} plot. (A and B are positive)

[Burdwan Univ. 2004]

Question: An extended form of Debye Huckel limit law equation

for 1:1 electrolyte is given by $\log f_{\pm} = -\frac{A\sqrt{i}}{1+B\sqrt{i}}$, where A and B are constants.

Suggest a suitable linear plot to find A and B .

[Burdwan Univ. 2006]

Answer: Hints; $\frac{1}{\log \gamma_{\pm}} = -\frac{1}{A} \frac{1}{\sqrt{i}} + \frac{B}{A}$ and $\frac{1}{\log \gamma_{\pm}}$ vs. $\frac{1}{\sqrt{i}}$ plot gives a straight line.

Verification of the law

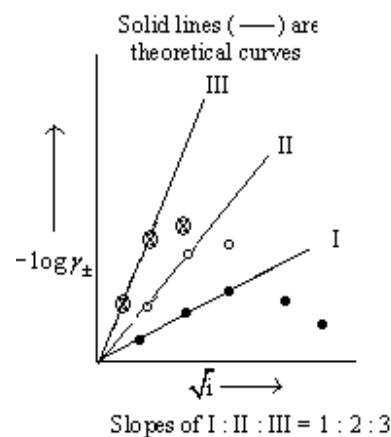
The law can be tested by using different type of salts in solutions of different ionic strength.

Cobalt amine complex salts of the following type are taken for the test.

Various valence-type cobalt amine complex salts are taken for verification

- I. (1, 1) type salt: $[Co(NH_3)_4 Cl_2] Cl$,
- II. (2, 1) type salt: $[Co(NH_3)_5 Cl] Cl_2$ and
- III. (3, 1) type salt: $[Co(NH_3)_6] Cl_3$.

Now $-\log \gamma_{\pm}$ of the above salts are plotted against \sqrt{i} from experimental data. The curves verify the Debye Huckel limiting law when the solution is very dilute within limit, $i \leq 0.01$



Problem: The experimental value of mean activity coefficient (γ_{\pm}) of 0.005 m KCl at 25 °C is 0.927. What is the % of error in the value of γ_{\pm} predicted by the Debye Huckel limiting law?

[CSIR-UGC-NET, 2000]

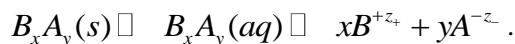
Solution: The Debye Huckel limiting law is $\log \gamma_{\pm} = -A z_+ |z_-| \sqrt{i}$ or, $\gamma_{\pm} = 10^{-A z_+ |z_-| \sqrt{i}}$

Putting the value, $\gamma_{\pm}(\text{predicted value}) = 10^{-0.51 \times 1 \times 1 \times \sqrt{0.005}} = 0.9203$.

% of error in the value of $\gamma_{\pm} = \frac{0.927 - 0.9203}{0.927} \times 100 = 0.72$.

Solubility of sparingly soluble salt and ionic strength of medium

Let us take a sparingly soluble salt, B_xA_y remaining in equilibrium in aqueous solution as:



The equilibrium of the species in different phases is represented in terms of chemical potential as

$$\mu_{B_xA_y(s)} = \mu_{B_xA_y(aq)} = x\mu_{B^{+z_+}} + y\mu_{A^{-z_-}}$$

Thus, $\mu_{B_xA_y(s)} = x\mu_+ + y\mu_-$. When expressed in terms of activities, we have

$$\mu_{B_xA_y(s)}^0 + RT \ln a_{B_xA_y(s)} = x(\mu_+^0 + RT \ln a_+) + y(\mu_-^0 + RT \ln a_-), \text{ but } a_{B_xA_y(s)} = 1, \text{ so,}$$

$$\mu_{B_xA_y(s)}^0 = x\mu_+^0 + y\mu_-^0 + RT \ln(a_+^x \times a_-^y) \text{ or, } RT \ln(a_+^x \times a_-^y) = -\left[(x\mu_+^0 + y\mu_-^0) - \mu_{B_xA_y(s)}^0\right] = -\Delta\mu$$

or, $a_+^x \times a_-^y = e^{-\Delta\mu/RT} = K_{sp}$ or, $K_{sp} = a_+^x \times a_-^y$, where K_{sp} is solubility product of the salt which is constant for the salt at a given temperature and a_+ and a_- are the activities of the cation and anion of the electrolyte in the saturated solution.

Replacing activities by molar conc., we get $K_{sp} = (c_+ f_+)^x \times (c_- f_-)^y = (c_+^x \times c_-^y) \times (f_+^x f_-^y)$.

Let s is the solubility of the electrolyte in mole / litre, then $c_+ = xs$, $c_- = ys$, and $f_+^x f_-^y = f_{\pm}^{x+y}$.

So,
$$K_{sp} = (x^x y^y) s^{x+y} f_{\pm}^{x+y} \quad (1)$$

This is relation between the solubility (s) and solubility product (K_{sp}) of the sparingly soluble salt.

For AgCl, $K_{sp} = s^2 f_{\pm}^2$, for CaF₂, $K_{sp} = 4s^3 f_{\pm}^3$ and for Ca₃(PO₄)₂, $K_{sp} = (2^2 \times 3^3) s^5 f_{\pm}^5$ etc.

The equation (1) can be written as:
$$\left(\frac{K_{sp}}{x^x y^y}\right)^{\frac{1}{x+y}} = s f_{\pm} \quad (2)$$

= constant for a given electrolyte at a given temperature.

Taking log of both sides and rearranging,
$$\log s = \frac{1}{x+y} \log\left(\frac{K_{sp}}{x^x y^y}\right) - \log f_{\pm} \quad (3)$$

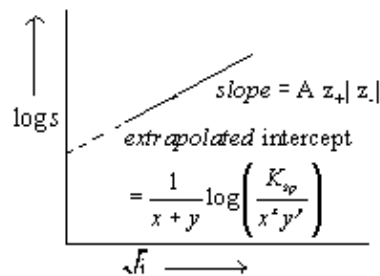
Using Debye Huckel limiting law, $-\log f_{\pm} = A |z_+ z_-| \sqrt{i}$ in the above expression, we get

$$\log s = \frac{1}{x+y} \log\left(\frac{K_{sp}}{x^x y^y}\right) + A |z_+ z_-| \sqrt{i} \quad (4)$$

Solubility (s) of the electrolyte is determined experimentally in solutions of different ionic strength. The ionic strength (i) can be varied by adding different amount of inert ions in the solution.

When $\log s$ is plotted against \sqrt{i} , a straight line is obtained.

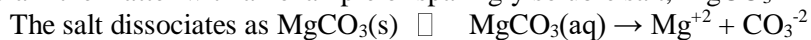
The extrapolated intercept gives the value of K_{sp} .



Further knowing the value of K_{sp} of the electrolyte, we can also determine f_{\pm} from the measurement of solubility (s) using equation (3).

Lastly, the slope provides the value of Debye Huckel constant, A. Thus Debye Huckel law is verified if 'A' comes to the value of 0.51 for aqueous solution at 25 °C.

Let us explain the matter with an example of sparingly soluble salt, MgCO_3 in aqueous solution.



The solubility product of the salt, $K_{sp} = a_+ \times a_- = c_+ f_+ \times c_- f_- = (c_+ \times c_-) f_{\pm}^2 = s^2 f_{\pm}^2$

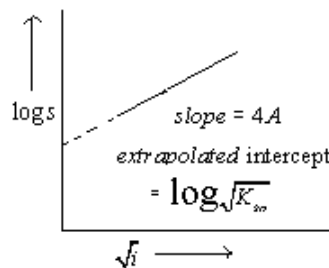
or, $sf_{\pm} = \sqrt{K_{sp}}$ = constant for the electrolyte at a given temperature.

Taking log of both sides, $\log s = \frac{1}{2} \log K_{sp} - \log f_{\pm}$.

Using the Debye Huckel limiting law, $-\log f_{\pm} = A |z_+| |z_-| \sqrt{i} = 4A \sqrt{i}$.

we have, $\log s = \frac{1}{2} \log K_{sp} + 4A \sqrt{i}$

A plot of $\log s$ vs. \sqrt{i} gives a straight line with intercept equals to $\frac{1}{2} \log K_{sp}$ and slope equals to $4A$.



Solubility product of the salt, K_{sp} and Debye Huckel constant, 'A' can be obtained.

Mean ionic activity coefficient of the salt in solution can also

be obtained by measuring the solubility of the salt (s) using the equation, $f_{\pm} = \frac{\sqrt{K_{sp}}}{s}$.

Solubility (s) of the MgCO_3 is determined by titration with standard EDTA solution using ErioChrome Black T (EBT) indicator.

The ionic strength (i) of the solutions is varied by adding some inert salt solution like KCl solution.

To summarize results of the discussion, we can mention the following points:

- (1) The thermodynamic solubility product of (K_{sp}) of a sparingly soluble salt can be experimentally determined.
- (2) Linear plot of $\log s$ vs. \sqrt{i} verifies the Debye Huckel limiting law.
The value Debye Huckel constant, A determined from the slope of the plot and it is same with that obtained from calculation of the law.
- (3) The mean ionic activity coefficient (f_{\pm}) can be obtained by measuring the solubility (s) of the sparingly soluble salt in solution.

Problem: Solubility of MgCO_3 at a particular temperature is 10^{-3} mol litre $^{-1}$. Calculate its solubility in 0.1 (M) KNO_3 solution. **[Burdwan Univ.1994]**

Solution: For a given electrolyte at a particular temperature, $sf_{\pm} = \text{constant}$.

If 'o' superscript is added to the term for aqueous solution, then $s^o f_{\pm}^o = sf_{\pm}$

or, $s = \frac{s^o f_{\pm}^o}{f_{\pm}}$, But $f_{\pm}^o = 1$, since the aqueous solution of the salt is very dilute

and $f_{\pm} = 10^{-A|z_+||z_-|\sqrt{i}} = 10^{-0.51 \times 2 \times 2 \times \sqrt{0.1}} = 0.226$, as ionic strength is contributed mainly from 0.1 (M) KNO_3 in the solution and MgCO_3 is only slightly soluble in water.

Putting the values, $s = \frac{s^o f_{\pm}^o}{f_{\pm}} = \frac{10^{-3} \times 1}{0.226} = 4.425 \times 10^{-3}$ mol litre $^{-1}$.

Problem: Show that the solubility s of (1:1) salt in water is given approximately by

$$(K_{sp})^{1/2} \exp. \left[1.172(s)^{1/2} \right], \text{ where } K_{sp} = \text{solubility product.} \quad [\text{Burdwan Univ.1996}]$$

Solution: For (1:1) salt, $K_{sp} = s^2 f_{\pm}^2$, or $s = \frac{\sqrt{K_{sp}}}{f_{\pm}}$. But, $f_{\pm} = e^{-0.51 \times 2.303 \times \sqrt{s}}$.

or, $f_{\pm} = e^{-0.51 \times 2.303 \times \sqrt{s}} = e^{-1.172 \sqrt{s}}$, since, $i = s$. Thus putting the expression of f_{\pm} ,

we have $s = \frac{\sqrt{K_{sp}}}{e^{-1.172 \sqrt{s}}}$ or, $s = \sqrt{K_{sp}} e^{1.172 \sqrt{s}}$. Thus, $(K_{sp})^{1/2} \exp. \left[1.172(s)^{1/2} \right]$.

Problem: Solubility of AgCl in pure water is 10^{-5} mol / lit. Calculate the solubility on 0.01 (M) KNO_3 solution. [Given, D.H. Constant, $A = 0.51$] [Burdwan Univ.1999]

Solution: Solubility of AgCl in the 0.01 (M) KNO_3 solution is 1.12×10^{-5} mol / lit.

Problem: An (1:1) weak electrolyte is 10 % dissociated in a 0.01 (M) solution at 298 K. Calculate the thermodynamic dissociation constant. [D.H. Constant = 0.51 at 298 K] [Burdwan Univ.2001]

Solution: The thermodynamic dissociation constant, $K_a = \frac{\alpha^2 c}{1-\alpha} f_{\pm}^2$. But $f_{\pm} = 10^{-A z_+ |z_-| \sqrt{i}}$

$$\text{and } i = \frac{1}{2} (c_+ z_+^2 + c_- z_-^2) = \frac{1}{2} (\alpha c \times 1^2 + \alpha c \times 1^2) = \alpha c = 0.1 \times 0.01$$

Putting the values, $f_{\pm} = 10^{-0.51 \times 1 \times 1 \times \sqrt{0.1 \times 0.01}} = 0.9635$.

Thus the dissociation constant, $K_a = \frac{\alpha^2 c}{1-\alpha} f_{\pm}^2 = \frac{(0.1)^2 \times 0.01}{1-0.1} (0.9635)^2 = 1.03 \times 10^{-4}$.

Problem: The resistance of a 0.05 (M) solution of a weak monobasic acid in a cell (cell constant = 1 cm^{-1}) is 500 ohm at 298 K. Calculate the thermodynamic dissociation constant of the acid. [Given, $A = 0.51$ and $\lambda_o = 400 \text{ ohm}^{-1} \text{ cm}^2 \text{ gmequiv}^{-1}$] [Burdwan Univ.2004]

Solution: Sp. conductance, $\kappa = \frac{\text{cell constant}}{\text{resistance}} = \frac{1}{500} = 0.002 \text{ ohm}^{-1} \text{ cm}^{-1}$.

Equivalent conductance, $\lambda = \frac{10^3 \kappa}{c} = \frac{10^3 \times 0.002}{0.05} = 40 \text{ ohm}^{-1} \text{ cm}^2 (\text{gmequiv.})^{-1}$.

The degree of dissociation of the weak acid, $\alpha = \frac{\lambda}{\lambda_o} = \frac{40}{400} = 0.1$.

Activity coefficient, $f_{\pm} = 10^{-A z_+ |z_-| \sqrt{i}} = 10^{-0.51 \sqrt{0.1 \times 0.05}} = 0.92$.

True or thermodynamic dissociation constant of the monobasic weak acid (K_a),

$$K_a = \frac{\alpha^2 c}{1-\alpha} f_{\pm}^2 = \frac{(0.1)^2 \times 0.005}{1-0.1} (0.92)^2 = 4.70 \times 10^{-4} \text{ at } 25^\circ \text{C.}$$

Problem: Solubility of AgCl in water is 10^{-5} M. Calculate its solubility in 0.1 M KNO_3 .

[Burdwan Univ.2005]

Solution: Solubility product of AgCl is $K_{sp} = S_0^2 f_{\pm 0}^2 = S^2 f_{\pm}^2$, where S_0 = solubility in water

= 10^{-5} M, $f_{\pm 0}$ = mean activity co-efficient of AgCl in water = 1 as the solution very dilute, S and f_{\pm} are solubility and mean activity co-efficient of AgCl in 0.1 M KNO_3 solution respectively.

Thus, $S_0 f_{\pm 0} = S f_{\pm}$ or, $S = \frac{S_0}{f_{\pm}} \cdot f_{\pm} = 10^{-0.5\sqrt{0.1}} = 0.69$. Putting the values, $s = \frac{10^{-5}}{0.69} = 1.45 \times 10^{-5}$ M

Thus the solubility of AgCl in 0.1 M KNO_3 is 1.45×10^{-5} M.

Problem: The solubility product of BaSO_4 is $9.2 \times 10^{-11} \text{ mol}^2 \text{ dm}^{-6}$. Calculate the mean activity coefficient of Ba^{2+} and SO_4^{2-} ions in a solution that is 0.05M in KNO_3 and 0.05M KCl, assuming the Debye-Huckel limiting law to apply. What is the solubility of BaSO_4 in that solution and in pure water? [Burdwan Univ.2013]

Solution: Hints; The ionic strength of the solution (i) = 0.10. Mean activity coefficient of Ba^{2+} and SO_4^{2-} ions in a solution is 0.2264. Solubility of BaSO_4 in the above solution is $4.2366 \times 10^{-5} \text{ mol/dm}^3$. The Solubility of BaSO_4 in pure water is $9.59 \times 10^{-6} \text{ mol/dm}^3$.