ELECTROCHEMISTRY.

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Contents of Electrochemistry.
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(1) Concept of pH & pOH.

(2) Buffer soln.

(3) Solubility product.

(4) Common ion effect.

(5) Conductance of soln.

(i) specific (ii) molar and equivalent conductance.

(6) Variation of molar conductance with dilution for strong and weak electrolyte.

(7) Kohlrausch law of independent migration of ion.

(8) Ostwald dilution law.

(9) Nernst Equation for single electrode.

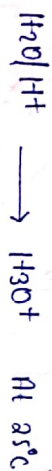(10) Numericals based on pH & pOH, Buffer soln, solubility product etc.

Home Task: for next class.

concept of p^H & pOH

Buffersolution. & common ion effect.

Concept of p^H & pOH.

p^H value of a solution is defined as the negative of logarithm of Hydrogen-ion concentration, & expressed in mol/ltr.

$$H_2O \longrightarrow H_3O^+$$

$$H_2O \rightleftharpoons H^+ + OH^-$$

$$k_D = \frac{[H^+][OH^-]}{[H_2O]}$$

Thus $p^H = -log_{10}[H^+]$

$$k_D[H_2O] = [H^+].[OH^-]$$

$$p^H = log_{10}\frac{1}{[H^+]}$$

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

ionic product of water.

or
ionisation of water = k_w = $k_D.[H_2O]$
constant.

At $25^\circ c$ $[H^+] = [OH^-] = 10^{-7}$ innentral soln

$$k_w = 10^{-7} \times 10^{-7} = 10^{-14}$$

$$p^H + pOH = \frac{k_w}{p}$$

$$pk_w = 7+7 = 14.$$

$$[H^+][OH^-] = 10^{-14} \Rightarrow p^H + pOH = 14.$$

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① 10^{-1} N HCl.
$$p^H = 1.$$

② 10^{-1} M H_2SO_4
$$p^H = -log[H^+]   \qquad [H^+] = \frac{10^{-1}}{2} \times 2 \, N = 10^{-1} N.$$
$$[H^+] = -log \, 10^{-1} = 1.$$

③ 10^{-1} N H_2SO_4.
$$[H^+] = 2 \times 10^{-1}   \quad so \quad p^H = -log_{10} 10^{-1} \times 2 = 1 - log_{10} 2 = 1-0.301 = 0.699$$

④ 10^{-8} N HCl.
$$[H^+] = 10^{-7}$$

COMMON ION EFFECT.

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$
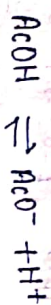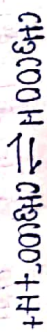
$$CH_3COONa \longrightarrow CH_3COO^- + Na^+$$
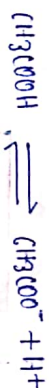
common ion occurs in weak electrolytes. not in .strong
.electrolytes

dueto common ion effect dissociation of electrolyts
decreases.

OSTWALD DILUTION LAW.

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+ \qquad NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

$$AcOH \rightleftharpoons AcO^- + H^+$$

$$Ka = \frac{[AcO^-][H^+]}{[AOH]}$$

	AcOH				NH₄OH		
at t=0	1	0	0	at t=0	1	0	0
at t=t	1-d	d	d	at t=t	1-d	d	d

d = degree of dissociation.

if at t=0   c   0   0
then at t=t   c-cd   cd   cd .

Kb = dissociation constant for base.

Ka = dissociation constant for acid.

$$Ka = \frac{cd \times cd}{c-cd} = \frac{cd^2}{1-d}$$

$$Kb = \frac{cd \times cd}{c(1-d)}$$

$d <<1$

hence $1-d \simeq 1$

then

$$Ka = \frac{cd^2}{1} = cd^2$$

$$\boxed{d = \sqrt{\frac{Ka}{c}}}$$

$$\boxed{d = \sqrt{Kb/c}}$$

BUFFER SOLUTION.

definition
example.
establishment of Handerson eqn.
Buffer action.

(a) HCl + CH3COONa.

(b) CH3COOH + NaCl

(c) CH3COOH + KOH

√(d) CH3COOH + CH3COONa. Buffer solution.

NH4Cl + CH3COONa is also a buffer solution.

ACIDIC BUFFER.

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

$$CH_3COONa \longrightarrow CH_3COO^- + Na^+.$$

(i) $\underset{\substack{\text{added} \\ \text{(from outside)} \\ \text{(strong acid)}}}{H^+} + CH_3COO^- \longrightarrow \underset{\text{(weak acid)}}{CH_3COOH}$

(ii) $OH^- + CH_3COOH \longrightarrow CH_3COO^- + H_2O$
(added from outside)
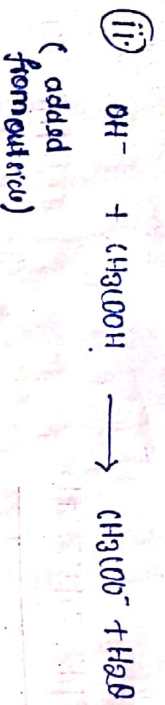
H^+ react with OH^- due to more ionic mobility and less size than Na^+.

$OH^- + H^+/Na^+/x \longrightarrow H_2O$

pH of ACIDIC BUFFER.
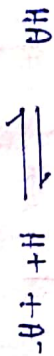
$HA \rightleftharpoons H^+ + A^-$
(weak acid)

$Ka = \dfrac{[H^+][A^-]}{[HA]}$

or $[H^+] = \dfrac{Ka\,[HA]}{[A^-]}$ - - - - ①

$BA \longrightarrow B^+ + A^-$

$[A^-] = [BA]$

$[H^+] = Ka \cdot \dfrac{[HA]}{[BA]}$

$pH = -\log[H^+] = -\log Ka + \log[BA] - \log[HA]$

$pH = -\log Ka + \log \dfrac{[BA]}{[HA]}$

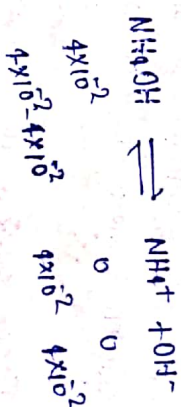$\boxed{pH = pKa + \log \dfrac{[salt]}{[acid]}}$ henderson equation.

(1) Calculate the pH of (i) 0.001 (M) HCl
(ii) 0.04 (M) NH₄OH, assuming complete dissociation.

Ans. (i) $[H^+] = 10^{-3}$

$pH = -\log[H^+] = 3.$

(ii) $[OH^-] = 4\times10^{-2}$

$NH_4OH \rightleftharpoons NH_4^+ + OH^-$
4×10^{-2} 0   0
$4\times10^{-2}-4\times10^{-2}$ 4×10^{-2} 4×10^{-2}

$pOH = -\log[OH^-]$

$pH = 14-pOH = 14 + \log 4\times10^{-2}$

$pH = 14 + 2\times0.301 -2.$

$pH = 12+0.602$

$pH = 12.602.$

or $[H^+] = \dfrac{10^{-14}}{4\times10^{-2}}$

(1) What is common ion effect? when and why this type of effect are observed? Explain by giving a suitable example. (1+2+2).

$NH_4OH \rightleftharpoons \boxed{NH_4^+} + OH^-$
weak

$NaCl \longrightarrow Na^+ + Cl^-$
strong electrolyte.
salts are always strong electrolyte.

$NH_4Cl \longrightarrow \boxed{NH_4^+} + Cl^-$
(salt)
...(added).

due to increase in NH_4^+ concentration to manage equilibrium, reaction move to backward direction.

(2) Calculate the pH of 0.002 N NH₄OH having 2.3% dissociation.?

Ans: α = 0.023
$[OH^-] = C\alpha = 0.002 \times 0.023 = 0.002 \times 0.023$

$pOH = -\log[OH^-] = -\log 4.6 \times 10^{-6} = 5 - \log 4.6.$

$pH = 14 - 5 + \log 4.6 = 9 + \log 4.6 = 9 + 0.663 = 9.663.$

(3) when a solution of propanoic acid is half neutralise with NaOH the pH = 4.87 calculate the dissociation constant of acid.

Ans.

$CH_3CH_2COOH \rightleftharpoons CH_3CH_2COO^- + H^+$

c	0	0
c-cα	cα	cα
c-c/2	c/2	c/2

$Ka = \dfrac{(c\alpha)^2}{c-c\alpha} = \dfrac{c\alpha^2}{(1-\alpha)}$

$Ka = \dfrac{c/2 \cdot c/2}{c/2} = c/2.$

$pH = 4.87 = -\log[H^+] = -\log \dfrac{c}{2} = -\log c + 0.301$

$-\log c = 4.87 - 4.57. \Rightarrow \log c = -4.57.$

$c = antilog(-4.7) = antilog(-4.57)$

$c/2 = 1.34 \times 10^{-5}$

$c = 2 \times 1.34 \times 10^{-5}$

$Ka = c/2 = 1.34 \times 10^{-5}$

(4) 50 ml of 0.2M acetic acid are mixed with some of 0.2M CH₃COONa solution what will be the pH of the mixture.? (Ka = 1.85×10⁻⁵)
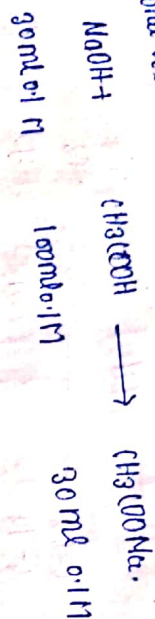
Ans: $pH = pKa + \log \dfrac{[salt]}{[acid]}$

$pH = -\log 1.85 \times 10^{-5} + \log \left[\dfrac{50 \times 0.2/(50+50)}{50 \times 0.2/(50+50)} \right]$

$pH = 5 - \log 1.85 = 5 - 0.27 = 4.73.$

⑤ 30 ml of 0.1 M NaOH is added to 100 ml of 0.1 M solution of acetic acid. calculate the pH of buffer solution. $(Ka = 1.89 \times 10^{-5})$

Ans. $[CH_3COOH] = \dfrac{100\times0.1}{(130)}$
Total volume of solution = 100+30 = 130 N.

$$NaOH + CH_3COOH \longrightarrow CH_3COONa.$$
$$\begin{array}{ccc} 30ml\,0.1N & 100ml\,0.1M & 30\,ml\,0.1M \\ & 70ml\,0.1M. \end{array}$$

$[CH_3COOH] = 70\times0.1/(70+30+30) = 7/130$

$[CH_3COONa] = 30\times0.1/(130) = 3/130$

volume of 0.1(M) CH_3COOH left unreacted
$= 100-30 = 70ml$

$pH = pKa + \log \dfrac{[salt]}{[acid]} = -\log Ka + \log \dfrac{[CH_3COONa]}{[CH_3COOH]}$

$pH = -\log 1.8\times10^{-5} + \log \dfrac{3}{7}$

$pH = 5 + \log\left(\dfrac{3}{7}/1.8\right) = 5 + \log\dfrac{3}{7}$

$pH = 5 + \log\left(\dfrac{3}{7}/1.8\right) = 5 + \log\left\{\dfrac{5}{21}\right\}$

$pH = 5 + \log 5 - 0.0921$

$pH = 5 + 0.7 - 1.32 = 5.7 - 1.32$

$pH = \boxed{4.38}$

⑥ calculated the pH of 0.005 (aOH)? assuming complete dissociation.

⑦ find the pH of buffer soln of 0.2 mole of acetic acid per ltr and 0.1 mol of CH_3COONa per ltr $(Ka=1.8\times10^{-5})$.
   (4.47)

⑧ calculate the amount of NH_3 & NH_4Cl required to prepare a buffer of pH 9 when the total conc. of buffering reagent is 0.6 mol/ltr ($P_{kb(NH_3)} = 4.7$)
$\left\{\begin{array}{l} [NH_3]=0.2\ mol/ltr \\ [NH_4^+] = 9.4\ mol/ltr. \end{array}\right.$

SOLUBILITY PRODUCT.

$$A_xB_y \rightleftharpoons xA^{n+} + yB^{m-}$$

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

$$AgCl \rightleftharpoons Ag^+ + Cl^-$$

$$Ksp = [Ag^+][Cl^-]$$

$$Ag_2CrO_4 \rightleftharpoons 2Ag^+ + CrO_4^{2-}$$

$$Ksp = [Ag^+]^2[CrO_4^{2-}]$$

CONDUCTANCE.

$$NaCl \longrightarrow Na^+ + Cl^-$$

cathode

Na^+ Cell anode

Na^+ Cl^-

$l = 1cm$,
$a = 1cm^2$

$NaOH \longrightarrow$ molar mass / **equivalent mass** $= 40$

Equivalent conductance or
Molar conductance are equal of NaOH solution.

A solution which contain 40 g of NaOH gives
its equivalent / molar conductance.

MOLAR AND EQUIVALENT CONDUCTANCE.

SPECIFIC CONDUCTANCE.

ondilution $\longrightarrow$ specific conductance decreases.

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① CELL CONSTANT. and its unit

② What is the effect of dilution on the molar conductivity of a weak electrolyte.

③ How is molar conductivity related to the molarity.

④ Give the relationship between molar and equivalent conductivity.

⑤ What is the effect of temp. on molar conductivity

Temp↑   molar conductivity↑

⑥ How does molar conductivity of weak electrolyte vary with concentration.

⑦ Why does the equivalent conductivity of a weak electrolyte increases on dilution.

⑧ Specific conductance decreases on dilution while equivalent conductance increases. give reason.

⑨ what is the possible pH of pure water at 65°C.

⑩ What is the unit of dissociation constant

⑪ what chemicals would you use to make a buffer of pH

⑫ What is the effect of dilution on pH value of
(a) HCl (b) NaOH (c) CH₃COONH₄ solution,

① 5   ② 10

KOHLROUSCH LAW.

$$\lambda CH_3COOH = \lambda CH_3COONa + \lambda HCl - \lambda NaCl.$$

$$\lambda NH_4OH = \lambda NH_4Cl + \lambda NaOH - \lambda NaCl.$$

(iv) According to direction.

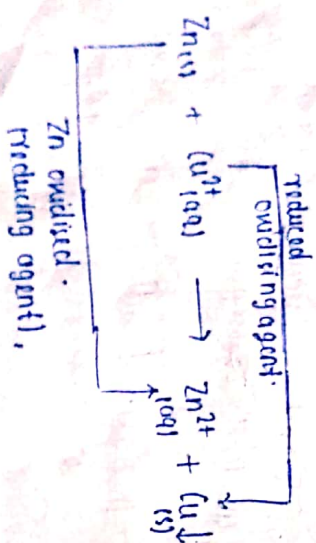## Electrochemical Cell.

(1) Galvanic Cell

(2) Electrolytic cell.

chemical energy $\xrightarrow{\text{Galvanic Cell}}$ Electrical energy.
$\xleftarrow{\text{Electrolytic Cell}}$

$$Zn_{(s)} + CuSO_{4(aq)} \longrightarrow ZnSO_{4(aq)} + Cu_{(s)}$$

$$Cu + ZnSO_4_{(aq)} \longrightarrow X.$$

$$Zn_{(s)} + Cu^{2+}_{(aq)} \longrightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$$

Zn oxidised.
(reducing agent).

reduced
oxidising agent.

Cell presentation.

$$\underset{\text{Anode}}{Zn_{(s)} | Zn^{2+}_{(aq)}} \| \underset{\text{Cathode.}}{Cu^{2+}_{(aq)} | Cu_{(s)}}.$$

$$aA + bB \rightleftharpoons cC + dD.$$

$$Q = \frac{[C]^c [D]^d}{[A]^a [B]^b}.$$

$\left(\begin{array}{c}\text{Thermodynamic} \\ \text{reaction quotient}\end{array}\right)$

$[\,] = $ concentration of reactants or products.

$$\boxed{E_{cell} = E^o_{cell} - \frac{RT}{nF} \ln Q.}$$
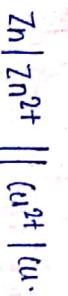
$R = $ gas constant.

T (in K)

$n = $ no. of e^- exchange.

$$Zn_{(s)} + Cu^{+2}SO_4_{(aq)} \longrightarrow Zn^{+2}SO_4 + Cu$$

$$E_{cell} = E^o_{cell} - \frac{RT}{2F} \ln \frac{[Zn^{2+}][Cu]}{[Cu^{2+}][Zn]}$$

$$E_{cell} = E^o_{cell} - \frac{RT}{2F} \ln \frac{[Zn^{2+}]}{[Cu^{2+}]}.$$

$$\{\ [Cu_{(s)}] = 1 \ , \ [Zn_{(s)}] = 1 \ \}.$$

Zn | Zn²⁺ || Cu²⁺ | Cu.

① Calculate standard emf of the cell $Zn|Zn^{2+}(m)||$
$Fe^{3+}(m), Fe^{2+}(m)|pt.$ given $E^0_{Zn^{2+}/Zn} = -0.761$
volt & $E^0_{Fe^{3+}/Fe^{2+}} = 0.771$ volt at 298 K.

Ans $E^0_{cell} = E^0_{R.H.S.} - E^0_{L.H.S.}$

when reduction potential is given.

$$\boxed{E^0_{cell} = E^0_{cathode} - E^0_{anode}.}$$

$E^0_{cell} = E^0_{Fe^{3+}/Fe^{2+}} - E^0_{Zn^{2+}/Zn}$

$E^0_{cell} = 0.771 + 0.761$

$= 1.532$ volt.

② Write down the cell reaction and expression for emf
of the following reversible cell.

$Sn_{(s)}|Sn^{2+}_{(aq)}.||H^+_{(aq)}|H_{2(g)}$ pt.

Ans.
$Sn_{(s)} + 2H^+_{(aq)} \longrightarrow Sn^{2+}_{(aq)} + H_{2(g)}$
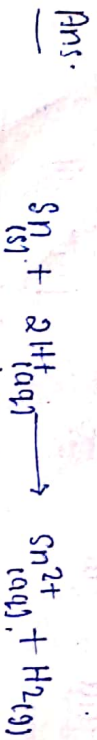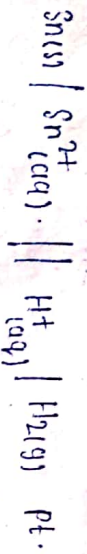
$E_{cell} = E^0_{cell} - \dfrac{RT}{2F} \ln \dfrac{[Sn^{2+}][H_2]}{[H^+]^2}.$

③ The unit of molar conductance is

    ⓐ ohm cm mol⁻¹

    ⓑ ohm⁻¹ cm² mol⁻¹ (✓)

    ⓒ ohm⁻¹ cm⁻¹ mol⁻¹

    ⓓ None of These

④ The potential at the junction of two electrolyte is
known as liquid junction potential.

⑤ The metal ions involved in the calomine electrode
is

    ⓐ Cd²⁺

    ⓑ Hg²⁺

    ✓ⓒ Hg₂²⁺

    ⓓ Pb²⁺

⑥ A conductivity cell has electrode 0.6 cm. apart and each
is of area 0.8 cm². The cell constant is ?

Ans. cell
constant $x = l/A = 0.6/0.8 = 6/8 = 3/4 = 0.75.$

⑦ find out the correct order of ionic conductance of alkali
metal ion.

    ⓐ Na⁺, K⁺, Rb⁺, Cs⁺,

    ⓐ   ⓑ   ⓒ   ⓓ

Ans: a>b>c>d.

(9) In electrochemical process the salt bridge is used.

Ans: to mantain electrical neutrality in each solution surrounding electrode.

(7) Calculate the value of $\dfrac{2.303RT}{F}$ at 298k.

Ans: 0.059.