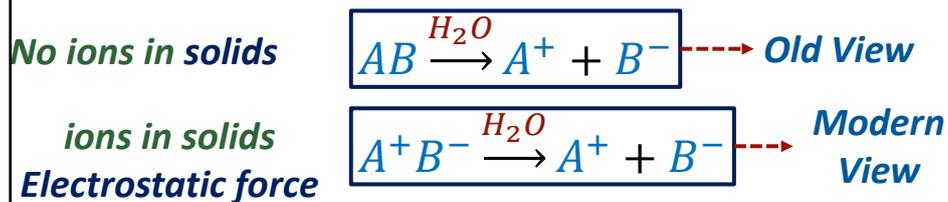*Chapter 25*

Theory of Electrolytic Dissociation

1

ARRHENIUS THEORY OF IONISATION

⚜ *After he believed that the conductivity of solutions is due to the presence of ions, Savante Arrhenius put forward in 1884 his theory of ionization which stated that:*

1) **When dissolved in water, neutral electrolyte molecules are split up "ionized" into two types of charged particles "ions". The positively charged particles were called "cations" and those having negative charge were called "anions".**

No ions in solids

$$AB \xrightarrow{H_2O} A^+ + B^-$$

‐‐‐‐▶ *Old View*

ions in solids
Electrostatic force

$$A^+B^- \xrightarrow{H_2O} A^+ + B^-$$

‐‐‐‐▶ *Modern View*

2

2) The *ions* in the solution constantly *reunite* to form neutral molecules. Thus there is a state of *equilibrium* between the undissociated molecules and the ions.

$$AB \leftrightarrow A^+ + B^- \quad \text{---------} \quad K = \frac{[A^+][B^-]}{[AB]}$$

Dissociation constant
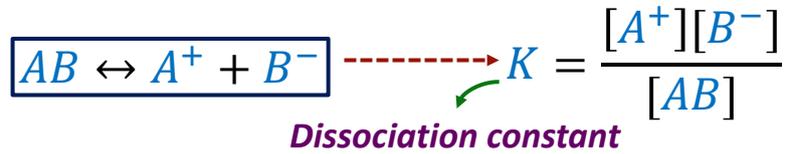
3) The charged *ions* are free to move through the solution to the oppositely charged electrode.

4) The *electrical conductivity* of an electrolyte solution depends on the *number of ions* present in solution.

3

MIGRATION OF IONS

↓ As the current is passed between the electrodes of the electrolytic cell, the ions *migrate (movement under potential difference)* with different rates to the opposite electrodes

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Prof. Ahmad Alaqraa
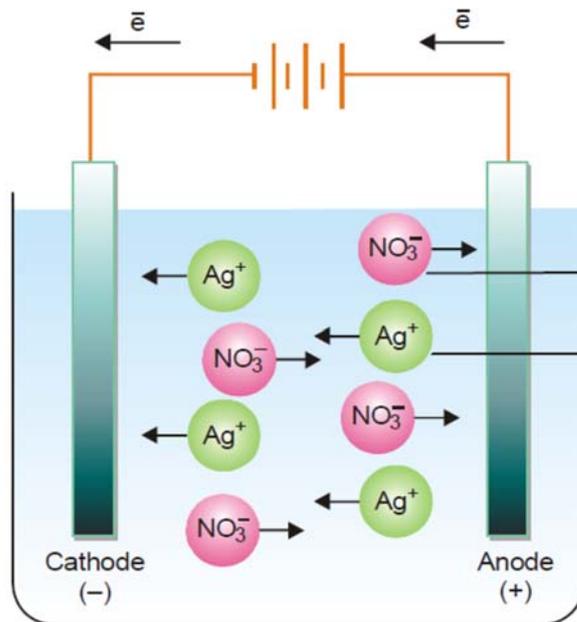
Agar-agar

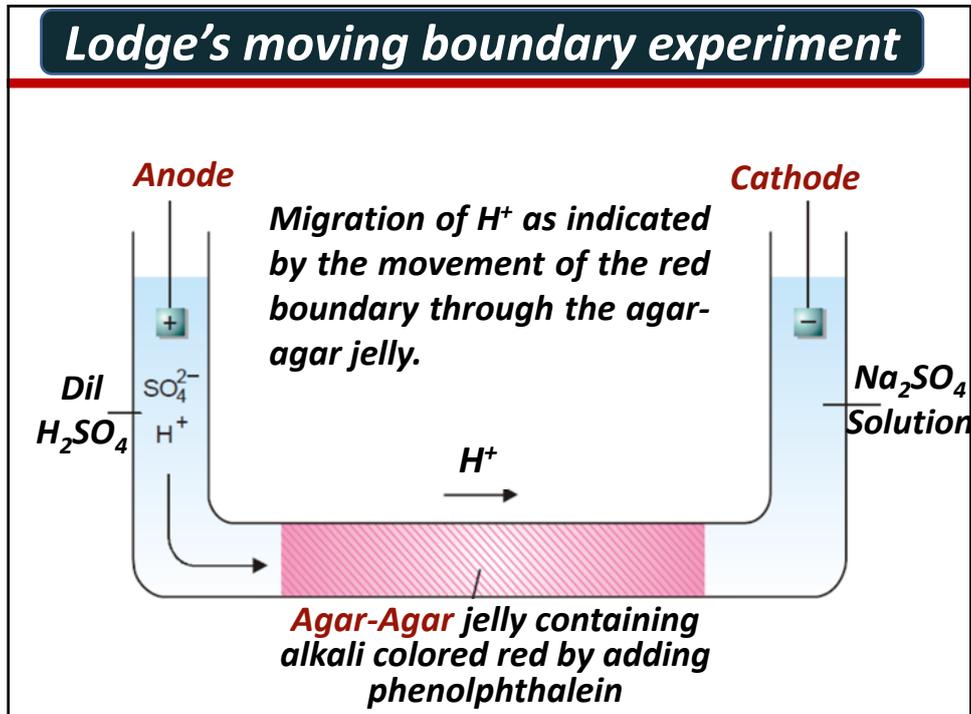- ↓ *is a mixture of 2 polysaccharides: agarose (70 %) and agaropectin.*
- ↓ *Agarose is a linear polymer, made up of repeating units of agarobiose, a disaccharide made up of D-galactose and 3,6-anhydro-L-galactopyranose.*

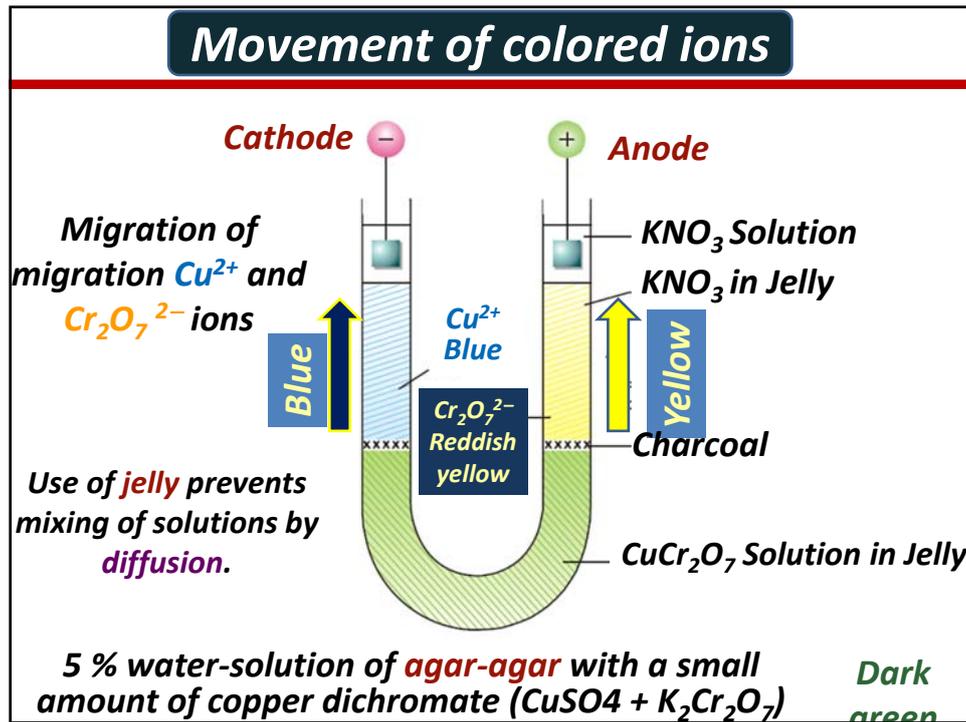- ↓ *Why do we use agar agar in the salt bridge of a voltaic cell?*
- ↓ *Agar-agar can remain in the gelly (hydrated suspension) form & thus providing an easy medium for transport of ions across it without actual movement of solvent on either side of the electrolyte solutions of the electrochemical cell & thus maintaining electrical contact only; a must for proper functioning of cell*

5

Lodge's moving boundary experiment

Anode   **Cathode**

Migration of H^+ as indicated by the movement of the red boundary through the agar-agar jelly.

Dil H_2SO_4 SO_4^{2-} H^+

Na_2SO_4 Solution

H^+

Agar-Agar jelly containing alkali colored red by adding phenolphthalein

6

Movement of colored ions

Cathode ⊖   **Anode** ⊕

Migration of migration Cu^{2+} and Cr$_2$O$_7$$^{2-}$ ions

Cu^{2+} Blue

Cr$_2$O$_7$$^{2-}$ Reddish yellow

Blue   **Yellow**

KNO$_3$ Solution
KNO$_3$ in Jelly

Charcoal

CuCr$_2$O$_7$ Solution in Jelly

Use of jelly prevents mixing of solutions by diffusion.

**5 % water-solution of agar-agar with a small amount of copper dichromate (CuSO4 + K$_2$Cr$_2$O$_7$)**   *Dark green*

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RELATIVE SPEED OF IONS

- *Under the influence of electric field, cations migrate toward the cathode and anions toward the anode with specific speeds that are not necessarily to be the same.*

- *The speed of a migrating cation/anion is proportional to the fall of its concentration at the anode/cathode.*

Hittorf's Rule
- *states that: "the loss of concentration around any electrode is proportional to the speed of the ion moving away from it"*

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I. 13 ion-pairs: 4 +5+4
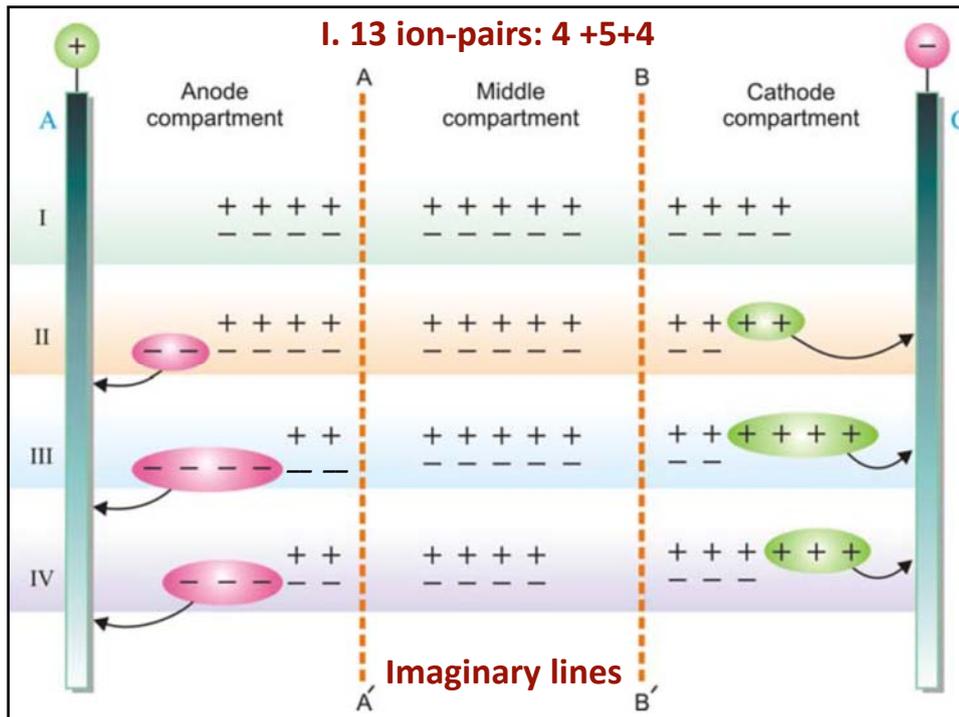
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II. **Anions alone be capable of movement:**
- Cations are not moving.
- The number of discharged anions and cations is the same (2)
- The concentration in the anode compartment, does not change
- The concentration in the cathode compartment is fallen by *two ion-pairs*.

III. **Cations and anions move at same rate:**
- Cations and anions are not moving.
- The number of discharged anions and cations is the same (4).
- The concentration of both the anode and the cathode compartments has fallen to the same extent viz, by two ion-pairs.

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III. Cations move at twice the speed of the anions:
- If *two* **cations** *moved from the anodic side, only one* **anion** *moves from the cathodic side.*
- *The total number of discharged anions and cations is again the same (3).*
- *Although the concentration in the cathode compartment has fallen by* **one ion-pair**, *the concentration in the anode compartment decreases by* **two ion-pairs**.

Generally, ions are always discharged in equivalent amounts on the opposite electrodes

$$\frac{Fall\ around\ anode}{Fall\ around\ cathode} = \frac{speed\ of\ cation}{speed\ of\ anion} = \frac{v_+}{v_-}$$
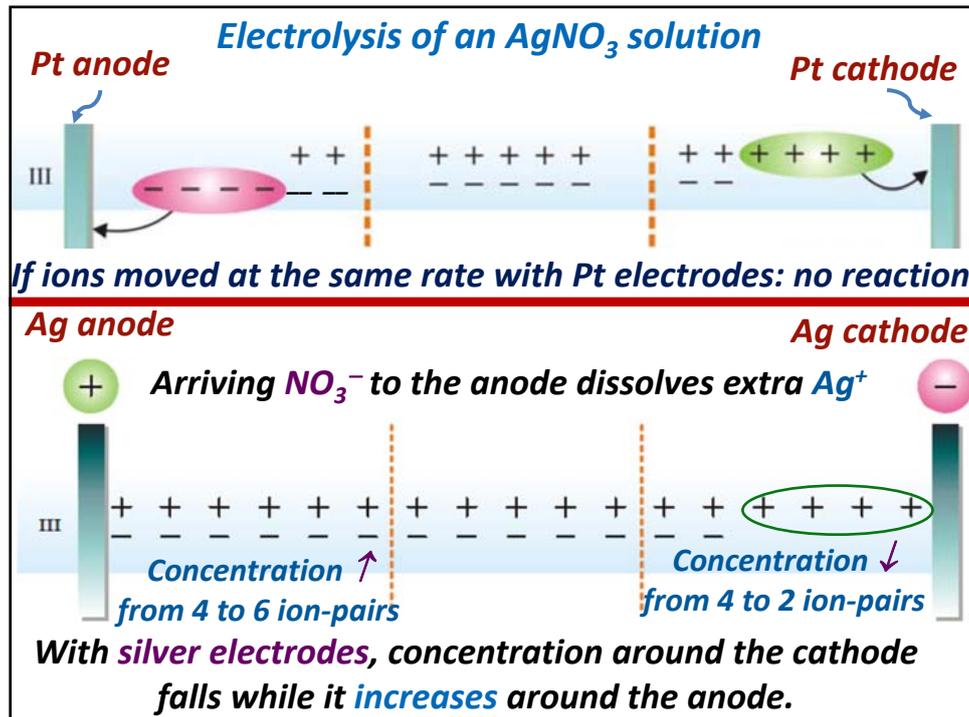
11

- *In the derivation of* **Hittorf's Rule** *the discharged ions are assumed to involve in* **no reaction** *with the* **electrodes' material**.

- *However, in many cases they* **combine (react)** *with the material of the electrodes rather than depositing on it, e.g., instead of discharging nitrate at Ag anode, it inspires its dissolution to form AgNO₃.*

$$Ag^+ + NO_3^- \rightarrow AgNO_3$$

- *This results in an increase in concentration around such an electrode instead of a decrease.*

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Electrolysis of an AgNO₃ solution

Pt anode   *Pt cathode*

If ions moved at the same rate with Pt electrodes: no reaction

Ag anode   *Ag cathode*

Arriving NO_3^- to the anode dissolves extra Ag^+

Concentration ↑ from 4 to 6 ion-pairs   *Concentration ↓ from 4 to 2 ion-pairs*

With silver electrodes, concentration around the cathode falls while it increases around the anode.

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Ag Coulometers

✦ *The speed ratio of Ag ions in this case (considering Ag⁺ dissolution at the anode and migration to the cathode) can be compared to the case of a Ag coulometer where no migration of Ag⁺ is considered (using perhaps a salt bridge). This would calculate the total current passed or increase in concentration around the anode as if no silver ions had migrated toward the cathode.*

✦ *The difference of the total increase and the actual increase around the anode would give the fall in concentration around the anode due to the migration of silver ions.*

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Problem

In an experiment, the increase in concentration of $AgNO_3$ around the silver anode was 5.6 mg of silver. 10.73 mg of silver were deposited by the same current in the silver coulometer placed in series. Find the speed ratio of Ag^+ and NO_3^- ions?

Solution

- Fall of concentration around cathode (= rise of concentration around anode) correspond to 5.6 mg Ag
- If no Ag^+ ions had migrated from the anode, the increase in concentration around the anode would have been 10.73 mg silver but the actual increase is 5.6 mg.
- Fall around anode due to Ag^+ migration = (10.73 − 5.6) = 5.13 g

$$\frac{speed\ of\ Ag^+}{speed\ of\ NO_3^-} = \frac{Fall_+}{Fall_-} = \frac{5.13\ g}{5.6\ g} = 0.916$$

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TRANSPORT NUMBER

- During electrolysis the current is carried by the anions and the cations.
- The fraction of the total current carried by the cation or the anion is termed its **Transport number (t)** or **Hittorf's number.**
- If v_+ represents the speed of migration of the cation and v_- that of the anion,

$$Transport\ number\ of\ cation, t_+ = \frac{v_+}{v_+ + v_-}$$

Unitless

$$Transport\ number\ of\ cation, t_- = \frac{v_-}{v_+ + v_-}$$

Let

$$\frac{t_+}{t_-} = \frac{v_+}{v_-} = \frac{v_+}{1 - v_+} = r$$

$$t_+ + t_- = 1$$

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$$r = \frac{t_+}{t_-} = \frac{1 - t_-}{t_-} = \frac{1}{t_-} - 1 \qquad \Rightarrow \qquad \frac{1}{t_-} = 1 + r$$

$$t_- = \frac{1}{1 + r} \qquad \textbf{Also} \qquad t_+ = \frac{r}{1 + r}$$

Problem

↓ *The speed ratio of silver and nitrate ions in a solution of silver nitrate electrolyzed between silver electrodes is 0.916. Find the transport number of the two ion.*

Solution

$$t_-(NO_3^-) = \frac{1}{1 + r} = \frac{1}{1 + 0.916}$$
$$= 0.521$$

$$t_+(Ag^+) = 1 - t_- = 1 - 0.521 = 0.479$$

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DETERMINATION OF TRANSPORT NUMBER

1) Hittorf's method : *t of ions is calculated from experimental concentration' changes around electrodes.*

↓ *When current (~ 0.01 A) is passed for ca. 3 h, the stopcocks at the top of the U-tube are closed.*
↓ *The liquid in the anode side is drained and weighed.*
↓ *Its Ag content is determined by titrating against a standard KSCN solution.*
↓ *The mass of Ag deposited in the Ag coulometer is also noted. (If a Cu coulometer is used instead, the mass of Ag equivalent to deposited Cu is calculated by multiplying it with 108/31.5.*
↓ *If NO_3^- attack the Ag anode, there would be an increase in [Ag⁺] ions. Same experiment can also be performed by using Pt electrodes to avoid this attack.*

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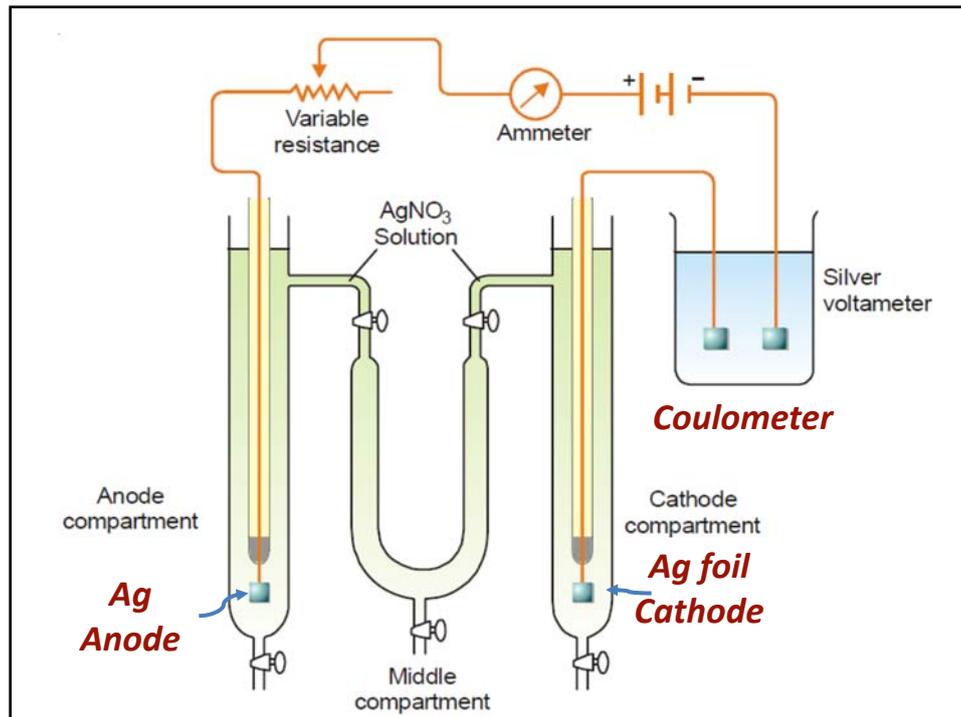
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Calculations	_Electrodes are unattackable (Pt electrodes)_

<div align="right">

Ag⁺ migration is active
</div>

<p>

- mass of anodic solution after electrolysis = a g
- mass of $AgNO_3$ in this solution (by titration) = b g
- mass of water in this solution = $a - b$ g
- Let c g represented mass of $AgNO_3$ in solution before electrolysis
</p>

$$Fall\ in\ Ag = Fall\ in\ AgNO_3 = \left(\frac{(c-b)}{170}\right) g\ equivalent$$

$$= d$$

If $w_1\ (g) = \frac{w_1}{108}\ (g\ eqvt)\ = W\ (g\ eqvt)$ of Ag was deposited in Ag coulometer

$t_+(Ag^+) = \dfrac{d}{W}$		$t_-(NO_3^-) = 1 - \dfrac{d}{W}$

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Calculations | <u>*Electrodes are attackable (Ag electrodes)*</u>

- mass of anodic solution after electrolysis = a g
- mass of AgNO$_3$ in this solution (by titration) = b g
- mass of water in this solution = $a - b$ g
- Let c g represented mass of AgNO$_3$ in solution before electrolysis

$$increase\ in\ Ag = e = \left(\frac{(b-c)}{170}\right) g\ equivalent$$

- If Ag$^+$ didn't migrate from anodic side, $e = W$ ($g\ eqvt$)
- If Ag$^+$ migrated, Fall of [Ag$^+$] due to migration = $W - e$

$$t_+(Ag^+) = \frac{W-e}{W}$$ $$t_-(NO_3^-) = 1 - \frac{W-e}{W}$$

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Problem

- A solution of AgNO$_3$ containing 12.14 g of Ag in 50 mL solution was electrolyzed between Pt electrodes. After electrolysis, 50 mL of the anode solution was found to contain 11.55 g of silver, while 1.25 g of metallic silver was deposited on the cathode. Calculate the transport number of Ag$^+$ and NO$_3^-$ ions.

Solution

$$Fall\ in\ Ag = d = \frac{(c-b)}{108} = \frac{(12.14 - 11.55)}{108}$$
$$= 0.0055\ geqvt$$

W = Mass of Ag deposited in Ag coulom. = 1.25 g = 1.25/108 = 0.0116 g eqvt

$$t_+(Ag^+) = \frac{d}{W} = \frac{0.0055}{0.0116} = 0.474$$

$$t_-(NO_3^-) = 1 - \frac{d}{W} = 0.526$$

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Problem

In an electrolysis of $CuSO_4$ between Cu electrodes the total mass of Cu deposited at the cathode was 0.153 g and the masses of copper per unit volume of the anode liquid before and after electrolysis were 0.79 and 0.91 g respectively. Calculate the transport number of the Cu^{2+} and SO_4^{2-} ions?

Solution

$$increase\ in\ mass\ of\ Cu = e = 0.91 - 0.79$$
$$= 0.12\ g$$

W = Mass of Cu deposited in Ag coulom. = 0.153 g

$$t_+\left(Cu^{2+}\right) = \frac{W - e}{W} = \frac{0.153 - 0.12}{0.153} = 0.215$$

$$t_-\left(SO_4^{2-}\right) = 1 - \frac{W - e}{W} = 1 - 0.215 = 0.785$$

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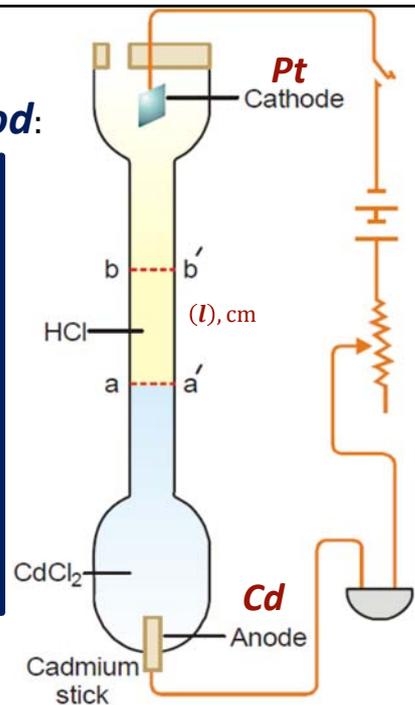
DETERMINATION OF t

2) Moving boundary method:

- On passing a current, H_2 is **evolved** at the cathode, Cl^- ions move toward the **anode** and Cd^{2+} ions toward the **cathode.**

- The **boundary line** moves upward to a **distance** (l) corresponding to the **quantity of electricity applied.**

Pt
Cathode

b --------- b′

(l), cm

HCl —

a --------- a′

CdCl₂ —

Cd
Anode

Cadmium stick

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+ *If $t_+(A^+)$ is to be determined, the electrolyte **AX** solution is taken in the upper part and a layer of another electrolyte **BX** having the common ion X^- is added in the lower part.*

+ *The electrolyte **BX** is selected so that the velocity of B^+ ion is less than that of A^+ ion.*
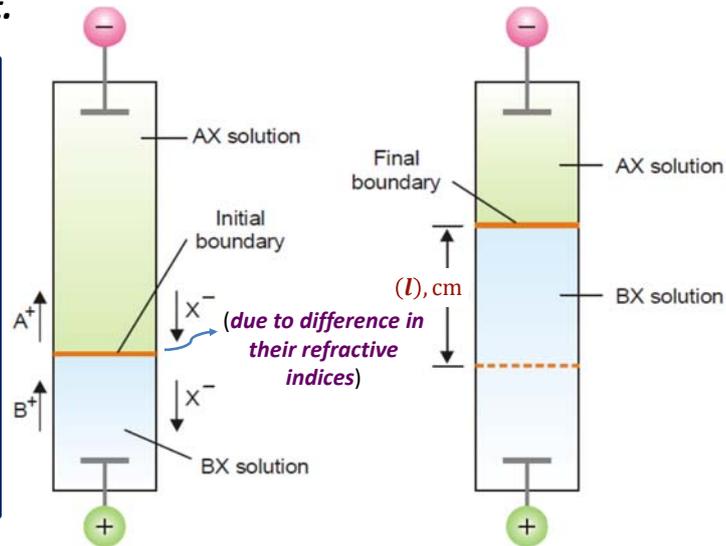
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Calculations	*Let*

+ $c = [A^+]_0,\ geqvt\ mL^{-1}$
+ l, cm: *the distance moved by boundary*
+ s, cm^2: *the area of cross-section of the tube*
+ n: *the number of Faradays of current passed*
+ $n, geqvt = \dfrac{Q\ (C)}{F(96500\ C\ geqvt^{-1})}$

+ *Number of A^+ equivalents moving upward* $= s \times l \times c$
+ *Fraction of A^+ that carries current* $= n \times t_+(A^+)$

$$\boxed{s \times l \times c = n \times t_+(A^+)}$$

$$t_+(A^+) = \frac{s \times l \times c}{n}$$

$$t_+(A^+) = \frac{s \times l \times c \times F}{Q}$$

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Problem

In a moving boundary experiment with 0.100 N KCl using 0.065 N LiCl as indicator solution, a constant current of 0.005893 A was passed for 2130 s. The boundary was observed to move 5.6 cm in a tube of 0.1142 cm² cross-section. Calculate the transport number of K⁺ and Cl⁻ ions.

Solution

$$t_+(K^+) = \frac{s \times l \times c \times F}{Q} =$$

$$\frac{0.1142 \ cm^2 \times 5.6 \ cm \times \frac{0.1 \ geqvt \ L^{-1}}{1000 \ mL \ L^{-1}} \times 96500 \ C}{0.005893 \ A \times 2130 \ s} = 0.492$$

$$t_-(Cl^-) = 1 - 0.492 = 0.508$$

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Problem

Calculate $t_+(H^+)$ from the following data obtained by moving boundary method:
Concentration of HCl solution = 0.10 N
Mass of Ag deposited in the coulometer = 0.12 g
Distance moved by the boundary = 7.5 cm
Cross-section of the tube = 1.25 cm²
Equivalent mass of silver =108

Solution

$$108 \ g \ eq \ Ag \ \rightarrow 1F$$
$$0.12 \ g \rightarrow n$$

$$n = \frac{0.12 \ g \times 1F}{108 \ g} = 0.00111 \ F$$

$$t_+(H^+) = \frac{s \times l \times c}{n} = \frac{1.25 \ cm^2 \times 7.5 \ cm \times \frac{0.1 \ geqvt \ L^{-1}}{1000 \ mL \ L^{-1}}}{0.00111}$$

$$= 0.852$$

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KOHLRAUSCH'S LAW

+ *The equivalent conductance of an electrolyte at infinite dilution is equal to the sum of the equivalent conductances of the component ions.*

$$\lambda_\infty(CA \text{ or } C^+A^-) = \lambda_\infty^+(C^+) + \lambda_\infty^-(A^-)$$

Problem

+ *Calculate the equivalent conductance of NaCl at infinite dilution at 25°C knowing that the equivalent conductances of Na⁺ and Cl⁻ ion are 50.11 ohm⁻¹ and 76.34 S cm^2 $eqvt^{-1}$, respectively?*

$$\lambda_\infty(NaCl) = \lambda_\infty^+(Na^+) + \lambda_\infty^-(Cl^-)$$
$$\lambda_\infty(NaCl) = 50.11 + 76.34$$
$$= 126.45 \text{ S } cm^2 \text{ } eqvt^{-1}$$

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Calculation of λ_∞ for Weak electrolytes

+ *Weak electrolytes do not ionize **completely** even at very high dilution.*
+ *Practical determination of their λ_∞ is not possible but it can be calculated from **Kohlrausch's law**.*

$$\lambda_\infty^+ = \lambda_c \propto \overset{speed}{\nu_+} \implies \lambda_c = k\nu_+$$

Also

$$\lambda_\infty^- = \lambda_a \propto \nu_- \implies \lambda_a = k\nu_-$$

$$\boxed{\lambda_\infty = \lambda_c + \lambda_a = k\nu_+ + k\nu_- = k(\nu_+ + \nu_-)}$$

$$\boxed{\frac{\lambda_c}{\lambda_\infty} = \frac{k\nu_+}{k(\nu_+ + \nu_-)} = \frac{\nu_+}{\nu_- + \nu_+} = t_+}$$

$$\boxed{\frac{\lambda_a}{\lambda_\infty} = \frac{k\nu_-}{k(\nu_+ + \nu_-)} = \frac{\nu_-}{\nu_- + \nu_+} = t_-}$$

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$$\frac{\lambda_a}{\lambda_c} = \frac{v_-}{v_+} = \frac{t_-}{t_+} = \frac{t_-}{1-t_-}$$

- The ionic mobilities of the two ions present in the weak electrolyte can be calculated.
- The equivalent conductance of the electrolyte at infinite dilution is obtained by adding up these two values.

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Problem

- At 25°C the transport number of H⁺ ion in HCl and CH_3COO^- ion in CH_3COONa are 0.81 and 0.47 respectively. The equivalent conductances at infinite dilution of HCl and CH_3COONa are 426 and 91.0 ohm⁻¹ cm² eqvt⁻¹, respectively. Calculate equivalent conductance of acetic acid at infinite dilution?

Solution

$$\frac{\lambda_c}{\lambda_\infty} = t_+ \qquad\qquad \frac{\lambda_a}{\lambda_\infty} = t_-$$

$$\lambda_c(H^+) = t_+ \times \lambda_\infty(HCl) = 0.81 \times 426 = 345.06$$

$$\lambda_a(CH_3COO^-) = t_- \times \lambda_\infty(CH_3COONa)$$
$$= 0.47 \times 91 = 42.77$$

$$\lambda_\infty(CH_3COOH) = \lambda_c(H^+) + \lambda_a(CH_3COO^-)$$
$$= 345.06 + 42.77 = 387.83 \; S \; cm^2 \; eqvt^{-1}$$

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Problem

👍 Calculate the equivalent conductance at 20°C of NH_4OH at infinite dilution. Given these values in $S\ cm^2\ eqvt^{-1}$:

$\lambda_\infty(NH_4Cl) = 130,\quad \lambda_a(OH^-) = 174\ $ and $\ \lambda_a(Cl^-) = 66$

Solution

$$\lambda_\infty(NH_4OH) = \lambda_c(NH_4^+) + \lambda_a(OH^-) =$$
$$\lambda_\infty(NH_4Cl) + \lambda_a(OH^-) - \lambda_a(Cl^-)$$
$$= 130 + 174 - 66$$
$$= 238\ \text{S}\ cm^2\ eqvt^{-1}$$

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Absolute ionic mobility, U

👍 The velocity of an ion in cm/s under a potential gradient of 1 V/cm.

Problem

👍 Calculate the mobility of a certain anion at infinite dilution moving with a velocity V_a (cm/s) between two electrodes 20 cm apart under a voltage of 100 V?

Solution

$$U_a = \frac{V_a}{Pot.\,gradient} = \frac{V_a}{100/20} = \frac{V_a}{5}\ \text{cm}^2\,\text{V}^{-1}\text{s}^{-1}$$

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ionic mobility vs. Eq. Conductance

$$\lambda_a \propto U_a \quad \Rightarrow \quad \lambda_a = k\,U_a \quad \Rightarrow \quad \lambda_c = k\,U_c$$

$$k = \frac{\lambda_a}{U_a} = \frac{S\,cm^2\,eqvt^{-1}}{cm^2\,V^{-1}s^{-1}} = A \times s \times eqvt^{-1} = C\ eqvt^{-1} = F$$

- where k is the proportionality constant. Its value is equal to the charge on one gram-equivalent of the ion under the potential gradient of 1 V/cm, i.e., k = **96,500** coulomb (**1 Faraday**).
- The ionic mobility is obtained by dividing the ionic conductance by 96,500 coulombs.

$$U_{\mp} = \frac{\lambda_{\mp}}{96500} \qquad\qquad \lambda_{\mp} = FU_{\mp}$$

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Problem

- The molecular conductance at infinite dilution of KCl is 130.1. The Hittorf number, t_ for the chloride ion in very dilute solution is 0.505. Calculate the mobilities in cm sec^{-1} of potassium and chloride ions.

Solution

$$\frac{\lambda_a(Cl^-)}{\lambda_\infty} = t_-$$

$$\lambda_a(Cl^-) = t_- \times \lambda_\infty = 0.505 \times 130.1 = 65.7 \; S\,cm^2\,eqvt^{-1}$$

$$U_- = \frac{\lambda_-}{96500} = \frac{65.7}{96500} = 6.81 \times 10^{-4}\ cm^2\,V^{-1}s^{-1}$$

$$\lambda_c(K^+) = \lambda_\infty(1 - t_-) = 130.1(1 - 0.505) = 64.4$$

$$U_+ = \frac{\lambda_+}{96500} = \frac{64.4}{96500} = 6.67 \times 10^{-4}\ cm^2\,V^{-1}s^{-1}$$

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