

Transport number (τ)

Transport number (τ) which is defined as the fraction of total current carried by the ions of a specified type.

$$I_+ = C_+ \cdot Z_+ \cdot V_+ \cdot F \cdot A \dots\dots\dots 1$$

I_+ = current carried by cation

C_+ = concentration of cation

Z_+ = charge of cation

V_+ = velocity of cation

F = Fariday's number (constant)

A = the area (constant)

While

$$I_- = C_- \cdot Z_- \cdot V_- \cdot F \cdot A \dots\dots\dots 2$$

I_- = current carried by anion

$$I \text{ total} = I_+ + I_- \dots\dots\dots 3$$

$$\tau_+ = \frac{I_+}{I \text{ total}} = \frac{c_+ \cdot Z_+ \cdot V_+ \cdot F \cdot A}{c_+ \cdot Z_+ \cdot V_+ \cdot F \cdot A + c_- \cdot Z_- \cdot V_- \cdot F \cdot A} \dots\dots 4$$

$$\tau_- = \frac{I_-}{I \text{ total}} = \frac{c_- \cdot Z_- \cdot V_- \cdot F \cdot A}{c_+ \cdot Z_+ \cdot V_+ \cdot F \cdot A + c_- \cdot Z_- \cdot V_- \cdot F \cdot A} \dots\dots\dots 4$$

Where

τ_+ and τ_- are fraction of the current carried by the cation and inion respectively.

as

F and A are constant

So

$$\tau_+ = \frac{c_+ \cdot Z_+ \cdot V_+}{c_+ \cdot Z_+ \cdot V_+ + c_- \cdot Z_- \cdot V_-} \dots\dots\dots 5$$

As

C and Z are considered constant for symmetric electrolytes

$$C_+ = C_- = C$$

$$Z_+ = Z_- = Z$$

$$\tau_+ = \frac{V_+}{V_+ + V_-} \dots\dots\dots 6$$

As

$$V = U.E \dots\dots\dots 7$$

$$V_+ = U_+ E \dots\dots\dots 7$$

$$V_- = U_- E \dots\dots\dots 7$$

When compensation in an equation 6

$$\tau_+ = \frac{u_+ E}{u_+ E + u_- E} \dots\dots\dots 8$$

as E is still constant , therefore, E deleted from the equation.

$$\tau_+ = \frac{u_+}{u_+ + u_-} \dots\dots\dots 9$$

as

$$\mathbf{u} = \frac{\lambda}{FZ}$$

so

$$\tau_+ = \frac{\frac{\lambda_+}{FZ_+}}{\frac{\lambda_+}{FZ_+} + \frac{\lambda_-}{FZ_-}} \dots\dots\dots 10$$

As

F and Z are constant

$$\tau_+ = \frac{\lambda_+}{\lambda_+ + \lambda_-} \dots\dots\dots 11$$

As

$$\lambda_o = \lambda_+ + \lambda_-$$

So

$$\tau_+ = \frac{\lambda_+}{\lambda_o} \dots\dots\dots 12$$

Note/

$$\tau_+ + \tau_- = 1$$

Q1/ the transport number of silver ion is 0.466 and that of nitrate ion is 0.533 at 18 C°, the molar conductivity at infinity dilution is 115.8 ohm⁻¹ cm² mole⁻¹ at the same temperature.

Calculate:-

a- The ionic conductance of silver and nitrate ions

b- The ionic mobilities of the two ions

a-

$$\tau_{+} = \frac{\lambda_{+}}{\lambda_{0}}$$

$$\lambda_{Ag^{+}} = \tau_{+} \times \lambda_{0}$$

$$= 0.466 \times 115.8 = 53.8962 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$$

$$\lambda_{NO_3^{-}} = \tau_{-} \times \lambda_{0}$$

$$= 0.533 \times 115.8 = 61.837 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$$

b-

$$U_{Ag^{+}} = \frac{\lambda_{+}}{FZ}$$

$$= \frac{53.8962}{96485 \times 1} = 000559 \text{ V}^{-1} \text{ cm Sec}^{-1}$$

$$U_{NO_3^{-}} = \frac{\lambda_{-}}{FZ}$$

$$= \frac{61.837}{96485 \times 1} = 000640 \text{ V}^{-1} \text{ cm Sec}^{-1}$$

Hittorf's method for the determination of transport number

The method is based upon the principle that the fall in concentration around an electrode is proportional to the speed of the ion moving away from it.

$$\frac{\text{Fall in conc. around cathode}}{\text{Fall in conc. around anode}} = \frac{\text{Speed of anion}}{\text{Speed of cation}} = \frac{U_a}{U_c}$$

Adding 1 to both sides, we get

$$1 + \frac{\text{Fall in conc. around cathode}}{\text{Fall in conc. around anode}} = \frac{U_a}{U_c} + 1$$

Or

$$\frac{\text{Fall in conc. around anode} + \text{Fall in conc. around cathode}}{\text{Fall in conc. around anode}} = \frac{U_a + U_c}{U_c}$$

or

$$\frac{\text{Total Fall in conc. around both the electrodes}}{\text{Fall in conc. around anode}} = \frac{U_a + U_c}{U_c}$$

or

$$\frac{\text{Fall in conc. around anode}}{\text{Total Fall in conc. around both the electrodes}} = \frac{U_c}{U_a + U_c} = \tau_c$$

if the concentrations are expressed in terms of gram equivalents, the above expression may be written as

$$\tau_c = \frac{\text{Number of gram equivalents lost from the anodic compartment}}{\text{Number of gram equivalents lost from both the compartment}}$$

It may be seen that number of gram equivalents lost from both the compartments is equal to the number of gram equivalents discharged on each electrode.

This, in turn, can be found by placing a silver or copper voltameter in series, as according to faraday's second law, when the same quantity of electricity flows through the silver voltameter, the same number of gram equivalents of Ag or Cu will be deposited. Thus the above formula reduces to

$$\tau_c = \frac{\text{Number of gram equivalents lost from the anodic compartment}}{\text{Number of gram equivalents deposited in the voltameter}}$$

So

$$\tau_a = 1 - \tau_c$$

Q/ During the electrolysis of a solution of potassium chloride between platinum electrodes, 0.0137g of the chloride was lost from the anodic compartment and 0.0857g of silver was deposited in a silver coulometer connected in series with cell. Determine the transport number of K^+ and Cl^- ions.

$$\tau_c = \frac{\text{Number of gram equivalents lost from the anodic compartment}}{\text{Number of gram equivalents deposited in coulometer}}$$

$$\text{No. of g eq of } Cl^- = \frac{0.0137}{35.5} = 0.0003859$$

$$\text{No. of g eq of Ag deposited in coulometer} = \frac{0.0857}{108} = 0.0007935$$

$$\tau_c(K^+) = \frac{0.0003859}{0.0007935} = 0.486$$

$$\tau_a(Cl^-) = 1 - \tau_c(K^+) = 0.514$$

Ionic Strength

$$I = \frac{1}{2} \sum C_i Z_i^2$$

Q1/ Calculate the ionic strength of 0.1M NaCl?



$$I = \frac{1}{2} \sum C_i Z_i^2$$

$$= \frac{1}{2} [0.1 \times 1^2 + 0.1 \times (-1)^2] = 0.1$$

Q2/ Calculate the ionic strength of 0.1M CaCl₂?



$$I = \frac{1}{2} \sum C_i Z_i^2$$

$$= \frac{1}{2} [0.1 \times 2^2 + (0.1 \times 2) \times (-1)^2] = 0.3$$

Q3/ Calculate the ionic strength of 0.1gm from NaCl dissolve in quarter liter of water?

Activity Coefficients

$$\text{Log } F_+ = -AZ_+^2\sqrt{I}$$

F_+ = Activity Coefficients of cation.

A = Constant = 0.509

I = ionic strength

Z = Charge

$$\text{Log } F_- = -AZ_-^2\sqrt{I}$$

$$F_{+-} = F_+ \cdot F_-$$

F_{+-} = mean activity

$$a = F \cdot C$$

a = Activity

Q4/ Calculate the F_{\pm} for ionic strength is equal 0.01 of CaCl_2 .

$$\text{Log } F_{+} = -AZ_{+}^2\sqrt{I}$$

$$\text{Log } F_{+} = -0.509 (2)^2\sqrt{0.01}$$

$$\text{Log } F_{+} = -0.2036$$

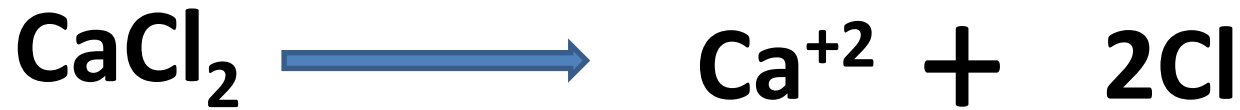
$$F_{+} = 0.626$$

$$\text{Log } F_{-} = -AZ_{-}^2\sqrt{I}$$

$$\text{Log } F_{-} = -0.509 (-1)^2\sqrt{0.01}$$

$$\text{Log } F_{-} = -0.0509$$

$$F = 0.824$$



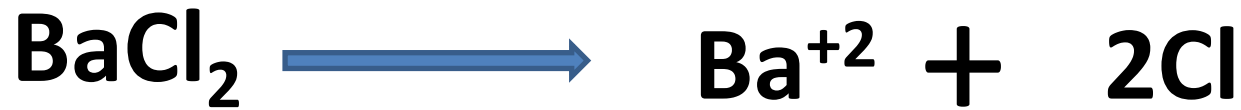
$$F_{+-} = F_+ \cdot F_-$$

$$F_{+-} = F_+ \cdot F_-^2$$

$$F_{+-} = 0.626 \cdot (0.824)^2$$

$$F_{+-} = 0.497$$

Q5/ Calculate the activity coefficients and activity for 0.02M BaCl₂ solution if the ionic strength is 0.01?



$$\text{Log } F_+ = -AZ_+^2\sqrt{I}$$

$$\text{Log } F_+ = -0.509(2)^2\sqrt{0.01}$$

$$F_+ = 0.626$$

$$\text{Log } F_- = -AZ_-^2\sqrt{I}$$

$$\text{Log } F_- = -0.509(-1)^2\sqrt{0.01}$$

$$F_- = 0.89$$

$$F_{+-} = F_+ \cdot F_-$$

$$F_{+-} = F_+ \cdot F_-^2$$

$$F_{+-} = 0.626 \cdot (0.89)^2$$

$$F_{+-} = 0.497$$

$$a = F \cdot C$$



$$a = (F \cdot C)_+ \cdot [(F^2) \cdot (2C)]_-$$

$$a = (0.497 \cdot 0.0008)$$

$$a = 0.0003976$$



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