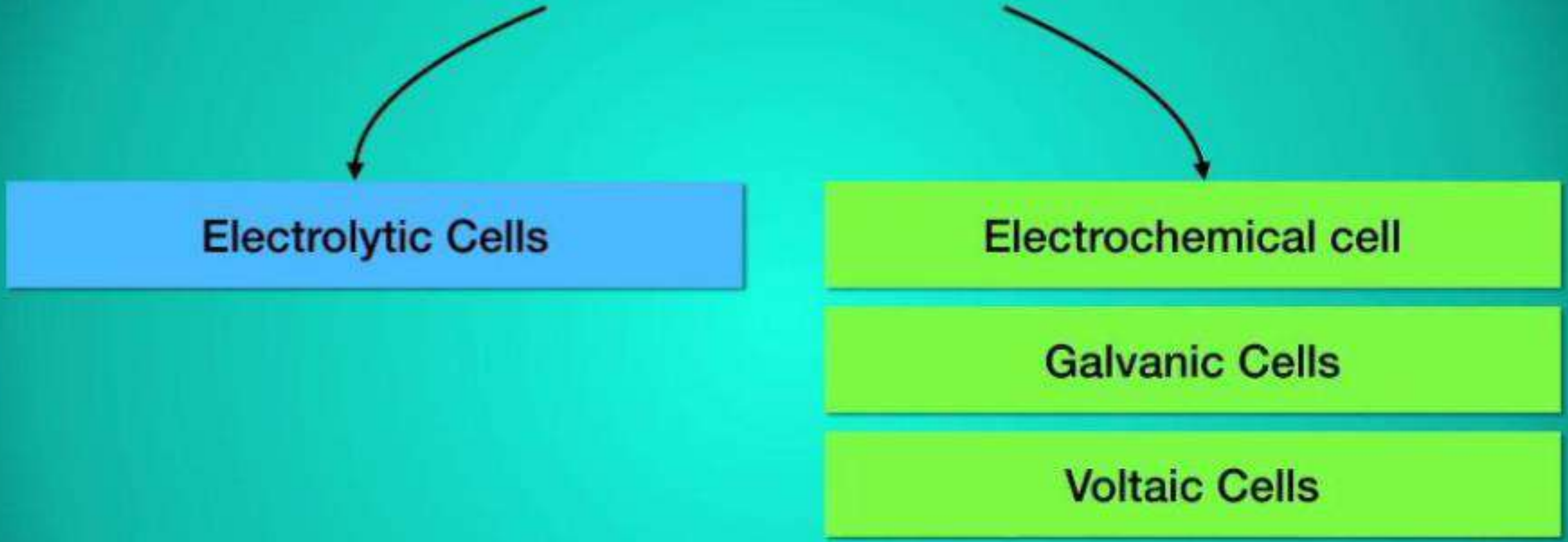
Classification of Cells



Electrolytic Cells

Electrochemical cell

Galvanic Cells

Voltaic Cells

Electrochemical cell

Chemical Cells

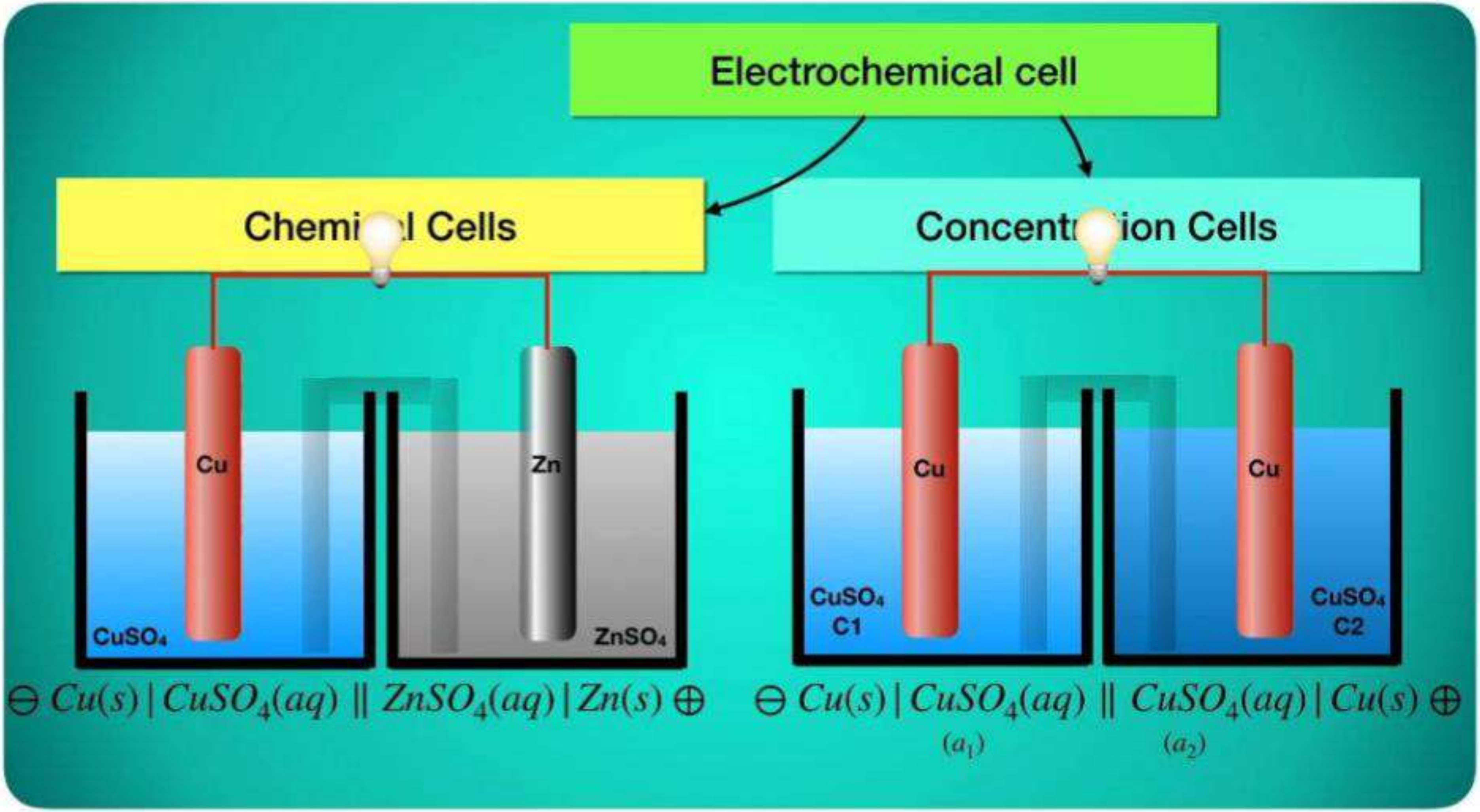
In such types of cells the two half-cell reactions involve different reactant

$\ominus\ Zn \mid ZnSO4 \parallel CuSO4 \mid Cu\ \oplus$

Concentration Cells

In such types of cells the two half-cell reactions are same, but the concentration of electrode or electrolyte are different.

$\ominus\ Cu \mid CuSO4\ (C1) \parallel CuSO4\ (C2) \mid Cu\ \oplus$



Electrochemical cell

Chemical Cells

Concentration Cells

$$\ominus\ Cu(s)\,|\,CuSO_4(aq)\,\|\,ZnSO_4(aq)\,|\,Zn(s)\ \oplus$$

$$\ominus\ Cu(s)\,|\,\underset{(a_1)}{CuSO_4(aq)}\,\|\,\underset{(a_2)}{CuSO_4(aq)}\,|\,Cu(s)\ \oplus$$

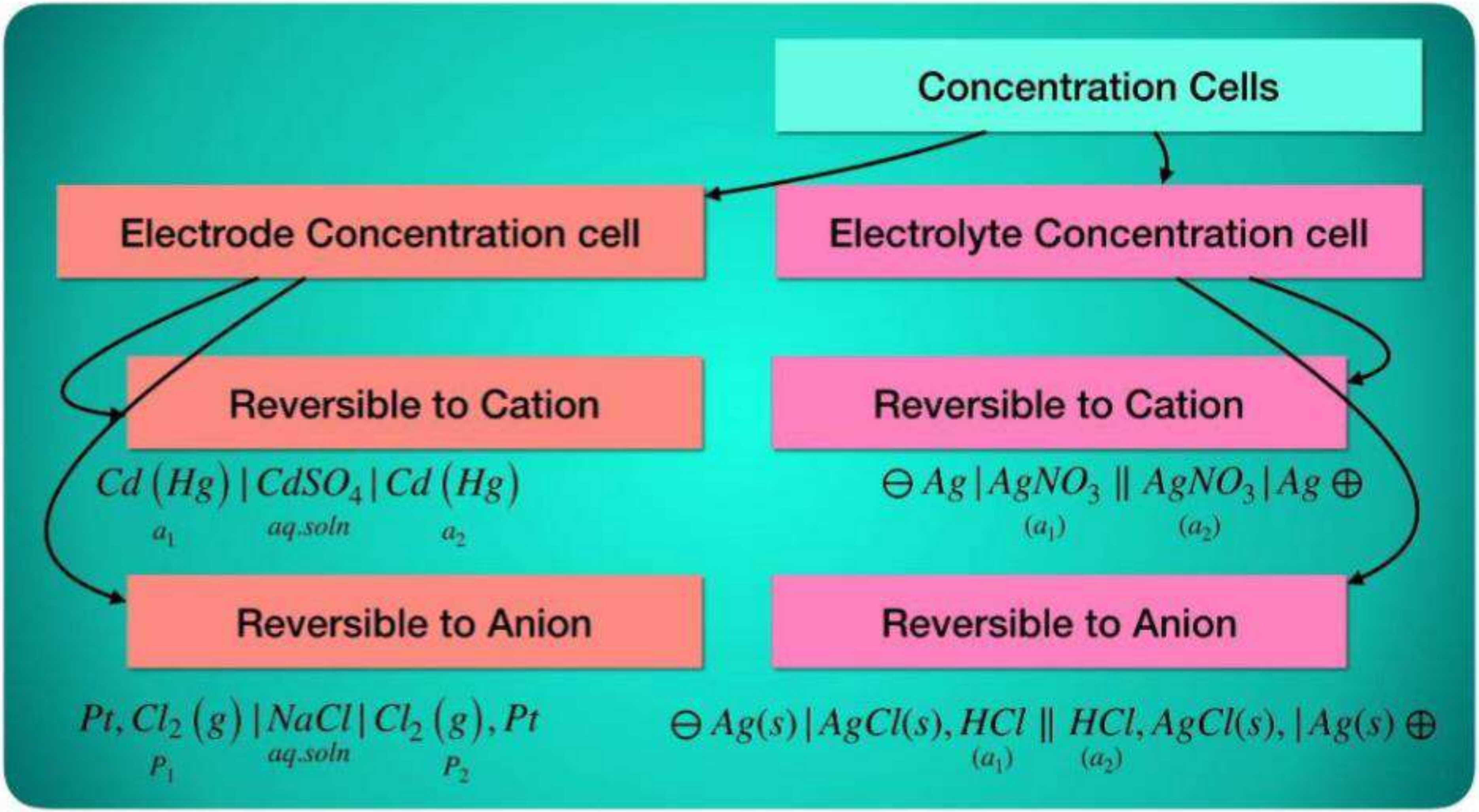
Concentration Cells

Electrode Concentration cell

$$Pt, \underset{P_1}{H_2\left(g\right)} \mid \underset{aq.soln}{HCl} \mid \underset{P_2}{H_2\left(g\right)}, Pt$$

Electrolyte Concentration cell

$$\ominus\, Ag \mid \underset{(a_1)}{AgNO_3} \parallel \underset{(a_2)}{AgNO_3} \mid Ag\, \oplus$$



Concentration Cells

Electrode Concentration cell

Reversible to Cation

$$\underset{a_1}{Cd\left(Hg\right)} \mid \underset{aq.soln}{CdSO_4} \mid \underset{a_2}{Cd\left(Hg\right)}$$

Reversible to Anion

$$Pt, \underset{P_1}{Cl_2\left(g\right)} \mid \underset{aq.soln}{NaCl} \mid \underset{P_2}{Cl_2\left(g\right)}, Pt$$

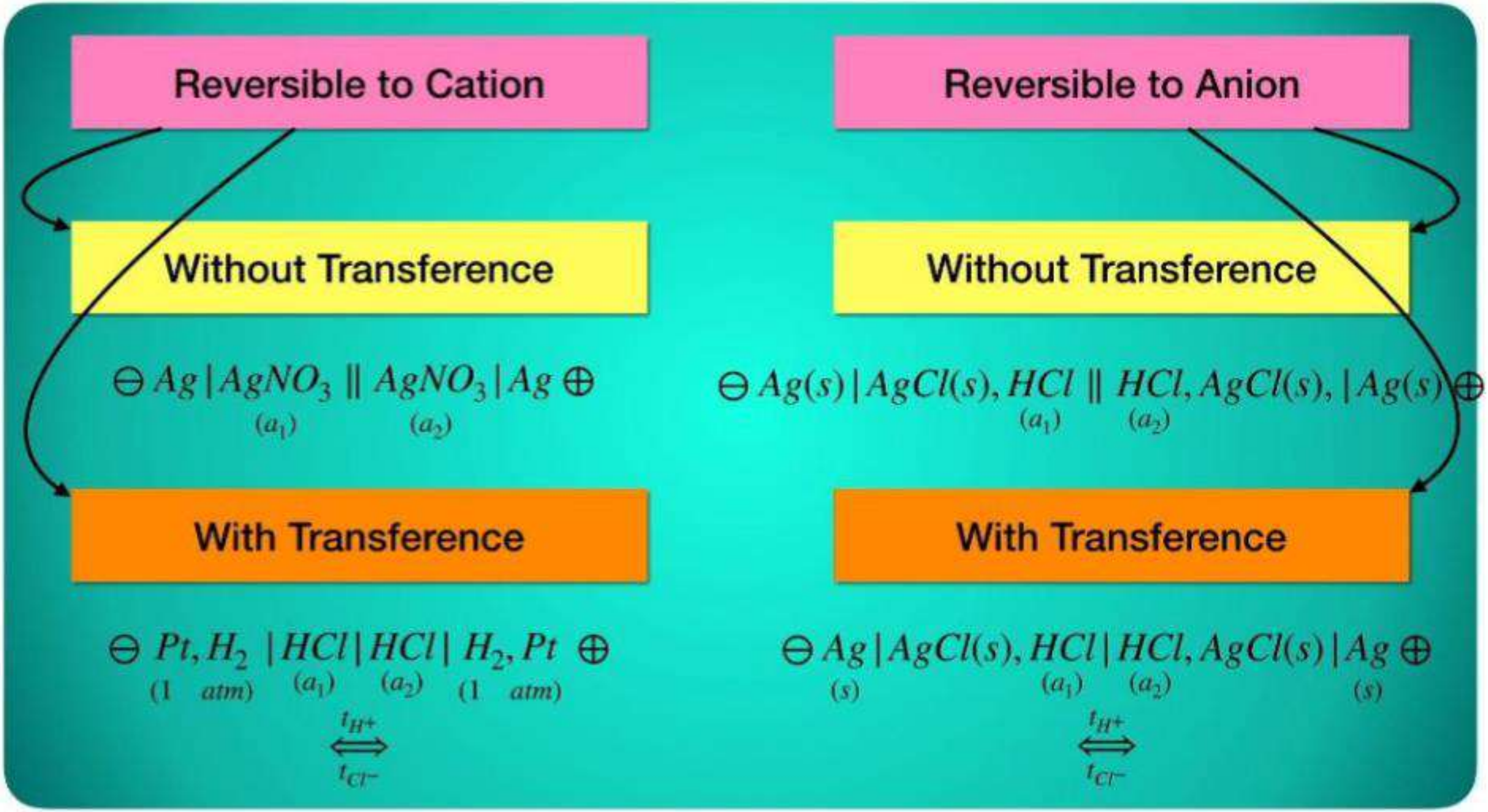
Electrolyte Concentration cell

Reversible to Cation

$$\ominus\, Ag \mid \underset{(a_1)}{AgNO_3} \parallel \underset{(a_2)}{AgNO_3} \mid Ag \,\oplus$$

Reversible to Anion

$$\ominus\, Ag(s) \mid AgCl(s), \underset{(a_1)}{HCl} \parallel \underset{(a_2)}{HCl}, AgCl(s), \mid Ag(s) \,\oplus$$



Reversible to Cation

Without Transference

$$\ominus\, Ag\,|\,\underset{(a_1)}{AgNO_3}\,\|\,\underset{(a_2)}{AgNO_3}\,|\,Ag\,\oplus$$

With Transference

$$\ominus\, \underset{(1\quad atm)}{Pt, H_2}\,|\,\underset{(a_1)}{HCl}\,|\,\underset{(a_2)}{HCl}\,|\,\underset{(1\quad atm)}{H_2, Pt}\,\oplus$$

$$\underset{t_{Cl^-}}{\overset{t_{H^+}}{\Longleftrightarrow}}$$

Reversible to Anion

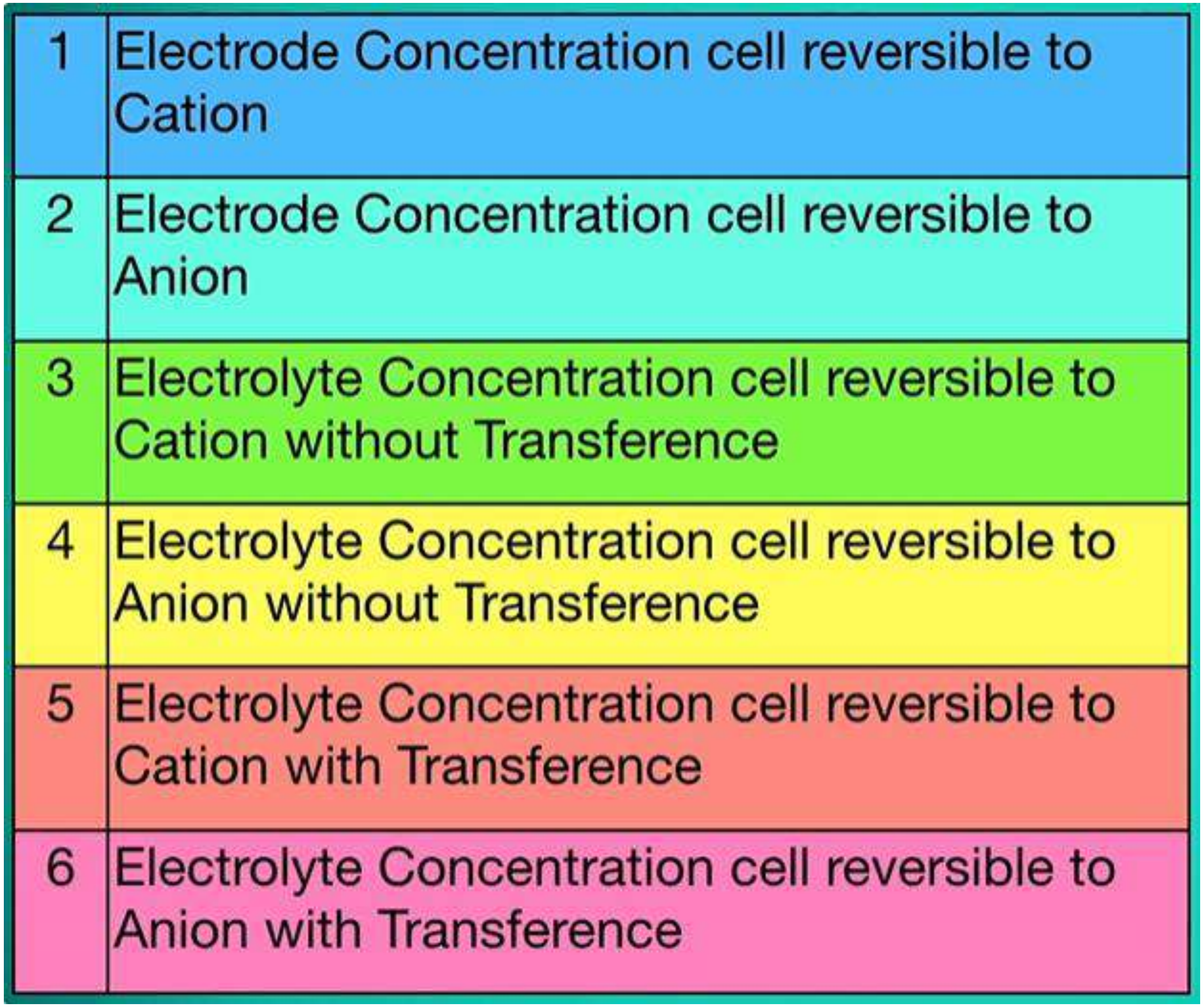
Without Transference

$$\ominus\, Ag(s)\,|\,AgCl(s), \underset{(a_1)}{HCl}\,\|\,\underset{(a_2)}{HCl}, AgCl(s), |\,Ag(s)\,\oplus$$

With Transference

$$\ominus\, \underset{(s)}{Ag}\,|\,AgCl(s), \underset{(a_1)}{HCl}\,|\,\underset{(a_2)}{HCl}, AgCl(s)\,|\,\underset{(s)}{Ag}\,\oplus$$

$$\underset{t_{Cl^-}}{\overset{t_{H^+}}{\Longleftrightarrow}}$$



1	Electrode Concentration cell reversible to Cation
2	Electrode Concentration cell reversible to Anion
3	Electrolyte Concentration cell reversible to Cation without Transference
4	Electrolyte Concentration cell reversible to Anion without Transference
5	Electrolyte Concentration cell reversible to Cation with Transference
6	Electrolyte Concentration cell reversible to Anion with Transference

1 Electrode Concentration cell reversible to Cation

Q. Derive an expression for the EMF of Electrode Concentration Cell Reversible to Cations (cell with amalgam electrode).

$$\underset{a_1}{Cd(Hg)} \mid \underset{aq.soln}{CdSO_4} \mid \underset{a_2}{Cd(Hg)}$$

Ans:

Such a cell is formed by two metal amalgam electrodes of different metal activity dipping into a common solution of a soluble salt of the metal. e.g.

$$\underset{a_1}{Cd(Hg)} \mid \underset{aq.soln}{CdSO_4} \mid \underset{a_2}{Cd(Hg)}$$

This cell is reversible to cations Cd^{2+} *ions.*

Let the activity of Cd^{2+} ions in solution be a_+. The cell reactions are as follows:

At L.H.E oxidation, $$\underset{a_1}{Cd(Hg)} \Longleftrightarrow \underset{a_+}{Cd^{2+}} + 2e^-$$

At R.H.E reduction, $$\underset{a_+}{Cd^{2+}} + 2e^- \Longleftrightarrow \underset{a_2}{Cd(Hg)}$$

∴ Net cell reaction $$\underset{a_1}{Cd(Hg)} \Longleftrightarrow \underset{a_2}{Cd(Hg)}$$

This reaction is independent of the concentration of the electrolyte. The Nernst equation for the above cell may be written as

$$E_{cell} = E^0_{cell} - \frac{RT}{nF} \ln\frac{a_2}{a_1}$$

$$E_{cell} = E^0_{cell} - \frac{2.303RT}{2F} \log\frac{a_2}{a_1}$$

(Here, the number of electrons involved in the electrode reactions. $n=2$)

Since, for concentration cells, $E^{0}_{cell} = 0V$

$$E_{cell} = -\frac{2.303RT}{2F}\log\frac{a_2}{a_1}$$

At 298K, $\frac{2.303RT}{F} = 0.0591$

$$\therefore E_{cell} = -\frac{0.0591}{2}\log\frac{a_2}{a_1}$$

i.e. $\boxed{\mathbf{E_{cell} = \frac{0.0591}{2}\log\frac{a_1}{a_2}}}$

For spontaneous cell reaction (i.e. to have positive cell e.m.f), $a_1 > a_2$.

As the cell reaction suggests the Cd of activity a_1 *is being transferred to Cd of activity* a_2*. That means as the time proceeds the ratio* $\frac{a_1}{a_2}$ *goes on decreasing. Thats why the emf of the cell goes on decreasing with time. When these activities become equal, the potentials of both electrodes are the same and the cell ceases to operate.*

Calculate the e.m.f. of the following electrode concentration cell at 298K.

$$\underset{a_1 = 0.1}{Cd(Hg)} \;|\; \underset{aq.soln}{CdSO_4} \;|\; \underset{a_2 = 0.05}{Cd(Hg)}$$

At L.H.E oxidation,

$$\underset{a_1}{Cd(Hg)} \Longleftrightarrow \underset{a_+}{Cd^{2+}} + 2e^-$$

At R.H.E reduction,

$$\underset{a_+}{Cd^{2+}} + 2e^- \Longleftrightarrow \underset{a_2}{Cd(Hg)}$$

$$\therefore \text{ Net cell reaction } \underset{a_1}{Cd(Hg)} \Longleftrightarrow \underset{a_2}{Cd(Hg)}$$

$$\boxed{E_{cell} = \frac{0.0591}{2} \log \frac{a_1}{a_2}}$$

$$E_{cell} = \frac{0.0591}{2} \log \frac{0.1}{0.05}$$

$$E_{cell} = 0.02955 \ \log 2$$

$$E_{cell} = 0.02955 \times 0.301$$

$$= 8.895 \times 10^{-3} V$$

Q. Derive an expression for the EMF of Electrode Concentration Cell Reversible to Cations (cell with gas electrode).

$$Pt,\ \underset{P_1}{H_2(g)}\ |\ \underset{aq.soln}{HCl}\ |\ \underset{P_2}{H_2(g)},\ Pt$$

Ans:

Such a cell consists of two hydrogen gas electrodes operating at different pressures dipping in to a common solution of hydrochloric acid e.g.

$$Pt,\ \underset{P_1}{H_2(g)}\ |\ \underset{aq.soln}{HCl}\ |\ \underset{P_2}{H_2(g)},\ Pt$$

This cell is reversible to cations H^+ *ions.*

Let the activity of H^+ *ions in solution be* a_+. *The cell reactions are as follows:*

At L.H.E oxidation, $$\frac{1}{2}H_2(P_1) \Longleftrightarrow \underset{a_+}{H^+} + e^-$$

At R.H.E reduction, $$\underset{a_+}{H^+} + e^- \Longleftrightarrow \frac{1}{2}H_2(P_2)$$

$\therefore$ *Net cell reaction* $$\frac{1}{2}H_2(P_1) \Longleftrightarrow \frac{1}{2}H_2(P_2)$$

This reaction is independent of the concentration of the electrolyte.

The Nernst equation for the above cell may be written as

$$E_{cell} = E^0_{cell} - \frac{RT}{nF} \ln\left(\frac{P_2}{P_1}\right)^{1/2}$$

$$E_{cell} = E^0_{cell} - \frac{2.303RT}{F} \log\left(\frac{P_2}{P_1}\right)^{1/2}$$

(Here, the number of electrons involved in the electrode reactions. n=1)

Since, for concentration cells, $E^0_{cell} = 0V$

At 298K, $\frac{2.303RT}{F} = 0.0591$

$$E_{cell} = - \frac{2.303RT}{F} \log\left(\frac{P_2}{P_1}\right)^{1/2}$$

$$E_{cell} = - \frac{2.303RT}{2F} \log\left(\frac{P_2}{P_1}\right)$$

$$\therefore\ E_{cell} = - \frac{0.0591}{2} \log\left(\frac{P_2}{P_1}\right)$$

i.e. $\boxed{\mathbf{E_{cell} = \frac{0.0591}{2} \log\left(\frac{P_1}{P_2}\right)}}$

For spontaneous cell reaction (i.e. to have positive cell e.m.f), $P_1 > P_2$.

Calculate the e.m.f. of the following electrode concentration cell at 298K.

$$\underset{P_1\,=\,400\text{torr}}{Pt,\ H_2} \ \Big|\ \underset{aq.soln}{HCl}\ \Big|\ \underset{P_2\,=\,200\text{torr}}{H_2,\ Pt}$$

Solution: *The cell reactions are*

At L.H.E oxidation, $\frac{1}{2}H_2(P_1) \Longleftrightarrow \underset{a_+}{H^+} + e^-$

At R.H.E reduction, $\underset{a_+}{H^+} + e^- \Longleftrightarrow \frac{1}{2}H_2(P_2)$

$\therefore$ *Net cell reaction* $\frac{1}{2}H_2(P_1) \Longleftrightarrow \frac{1}{2}H_2(P_2)$

$$\boxed{E_{cell} = \frac{0.0591}{2}\log\left(\frac{P_1}{P_2}\right)}$$

$$E_{cell} = \frac{0.0591}{2}\log\left(\frac{400}{200}\right)$$

$$E_{cell} = \frac{0.0591}{2}\log(2)$$

$$E_{cell} = 0.02955 \times 0.301$$
$$= 8.895 \times 10^{-3}V$$

2 Electrode Concentration cell reversible to Anion

Q. Derive an expression for the EMF of Electrode Concentration Cell Reversible to Anions (cell with gas electrode).

$$Pt,\ \underset{P_1}{Cl_2(g)}\ |\ \underset{aq.soln}{NaCl}\ |\ \underset{P_2}{Cl_2(g)},\ Pt$$

Ans:

Such a cell consists of two chlorine gas electrodes operating at different pressures dipping in to a common solution of sodium chloride e.g.

$$Pt,\ \underset{P_1}{Cl_2(g)}\ |\ \underset{aq.soln}{NaCl}\ |\ \underset{P_2}{Cl_2(g)},\ Pt$$

This cell is reversible to anion Cl^- *ions.*

Let the activity of Cl^- ions in solution be a_-. The cell reactions are as follows:

At L.H.E oxidation, $$\underset{a_-}{Cl^-} \Longleftrightarrow \frac{1}{2}Cl_2(P_1) + e^-$$

At R.H.E reduction, $$\frac{1}{2}Cl_2(P_2) + e^- \Longleftrightarrow \underset{a_-}{Cl^-}$$

$\therefore$ Net cell reaction $$\frac{1}{2}Cl_2(P_2) \Longleftrightarrow \frac{1}{2}Cl_2(P_1)$$

This reaction is independent of the concentration of the electrolyte.

The Nernst equation for the above cell may be written as

$$E_{cell} = E^{0}_{cell} - \frac{RT}{nF} \ln\left(\frac{P_1}{P_2}\right)^{1/2}$$

$$E_{cell} = E^{0}_{cell} - \frac{2.303RT}{F} \log\left(\frac{P_1}{P_2}\right)^{1/2}$$

(Here, the number of electrons involved in the electrode reactions. $n=1$)

Since, for concentration cells, $E^{0}_{cell} = 0V$

$$E_{cell} = - \frac{2.303RT}{F} \log\left(\frac{P_1}{P_2}\right)^{1/2}$$

$$E_{cell} = - \frac{2.303RT}{2F} \log\left(\frac{P_1}{P_2}\right)$$

At 298K, $\frac{2.303RT}{F} = 0.0591$

$$\therefore E_{cell} = - \frac{0.0591}{2} \log\left(\frac{P_1}{P_2}\right)$$

i.e. $\boxed{\mathbf{E_{cell} = \frac{0.0591}{2} \log\left(\frac{P_2}{P_1}\right)}}$

For spontaneous cell reaction (i.e. to have positive cell e.m.f), $P_2 > P_1$.

Calculate the emf of the following cell at 298K

$$\underset{P_1 = 100\ torr}{Pt,\ Cl_2(g)}\ |\ \underset{aq.soln}{NaCl}\ |\ \underset{P_2 = 200\ torr}{Cl_2(g),\ Pt}$$

The cell reactions are as follows:

At L.H.E oxidation, $\underset{a_-}{Cl^-} \Longleftrightarrow \frac{1}{2}Cl_2(P_1) + e^-$

At R.H.E reduction, $\frac{1}{2}Cl_2(P_2) + e^- \Longleftrightarrow \underset{a_-}{Cl^-}$

$\therefore$ *Net cell reaction* $\frac{1}{2}Cl_2(P_2) \Longleftrightarrow \frac{1}{2}Cl_2(P_1)$

The Nernst equation for the above cell may be written as

$$\boxed{E_{cell} = \frac{0.0591}{2}\log\left(\frac{P_2}{P_1}\right)}$$

$$E_{cell} = \frac{0.0591}{2}\log\left(\frac{200}{100}\right)$$

$$E_{cell} = 0.02955\ \log(2)$$

$$E_{cell} = 0.02955 \times 0.301$$

$$E_{cell} = 8.895 \times 10^{-3}\ V$$

Q. Derive an expression for the EMF of Electrolyte Concentration Cell Reversible to Cations.

$$\ominus\ Ag \mid \underset{(a_1)}{AgNO_3} \parallel \underset{(a_2)}{AgNO_3} \mid Ag\ \oplus$$

Ans:

Consider a cell of the type

$$\ominus\ Ag \mid \underset{(a_1)}{AgNO_3} \parallel \underset{(a_2)}{AgNO_3} \mid Ag\ \oplus$$

which consists of two silver electrodes immersed in two solutions of $AgNO_3$ *of activities* a_1 *and* a_2.

Let $a_2 > a_1$. *Since the two solutions are connected by a salt bridge, there is negligible transfer of electrolyte at the liquid junction.*

The use of salt bridge is represented by the double line put between the two half cells.

This cell is reversible with cations, Ag^+ *ions.*

The cell reactions are

At L.H.E oxidation, $\underset{s}{Ag} \Longleftrightarrow \underset{a_1}{Ag^+} + e^-$

At R.H.E reduction, $\underset{a_2}{Ag^+} + e^- \Longleftrightarrow \underset{s}{Ag}$

$\therefore$ *Net cell reaction* $\underset{a_2}{Ag^+} \Longleftrightarrow \underset{a_1}{Ag^+}$

The Nernst equation for the above cell may be written as

$$E_{cell} = E^0_{cell} - \frac{RT}{nF}\ \ln\left(\frac{a_1}{a_2}\right)$$

$$E_{cell} = E^0_{cell} - \frac{2.303RT}{F}\ \log\left(\frac{a_1}{a_2}\right)$$

(Here, the number of electrons involved in the electrode reactions. n=1)

Since, for concentration cells, $E^{0}_{cell} = 0V$

$$E_{cell} = -\frac{2.303RT}{F}\log\left(\frac{a_1}{a_2}\right)$$

At 298K, $\frac{2.303RT}{F} = 0.0591$

$$\therefore E_{cell} = -0.0591\log\left(\frac{a_1}{a_2}\right)$$

i.e. $\boxed{\mathbf{E_{cell} = 0.0591}\log\left(\frac{\mathbf{a_2}}{\mathbf{a_1}}\right)}$

For spontaneous cell reaction, $a_2 > a_1$.

Now the activity of single ion is given by $a = m\gamma$

where m = *molality of ion and* γ = *activity coefficient.*

$\therefore a_1 = m_1\gamma_1$ *and* $a_2 = m_2\gamma_2$

i.e. $\boxed{\mathbf{E_{cell} = 0.0591}\log\left(\frac{\mathbf{m_2\gamma_2}}{\mathbf{m_1\gamma_1}}\right)}$

Calculate the e.m.f. of the following cell at 298K

$$\ominus\ Ag \mid \underset{(0.01m)}{AgNO_3} \parallel \underset{(0.1m)}{AgNO_3} \mid Ag\ \oplus$$

Given that 0.1m $AgNO_3$ and 0.01m $AgNO_3$ solutions are 80% and 90% dissociated.

Solution:

From the percentage dissociation of $AgNO_3$ we can first calculate the dissociation per mole.

$$\therefore \text{ Conc. of } Ag^+ \text{ ion in } 0.01m\ AgNO_3 = \frac{0.01 \times 90}{100} = 0.009m$$

$$\text{Similarly, Conc. of } Ag^+ \text{ ion in } 0.1m\ AgNO_3 = \frac{0.1 \times 80}{100} = 0.08m$$

For concentration cell without transference reversible to cations, we have

$$\boxed{E_{cell} = 0.0591 \ \log\left(\frac{a_2}{a_1}\right)}$$

$$E_{cell} = 0.0591 \ \log\left(\frac{0.08}{0.009}\right)$$

$$E_{cell} = 0.0591 \ \log(8.89)$$

$$E_{cell} = 0.0591 \times 0.949$$

$$E_{cell} = 0.056V$$

Q. Derive an expression for the EMF of Electrolyte Concentration Cell Reversible to Anions without transference.

$$\ominus\ Ag(s) \mid AgCl(s),\ \underset{(a_1)}{HCl} \parallel \underset{(a_2)}{HCl}\ AgCl(s), \mid Ag(s)\ \oplus$$

Consider a cell of the type

$$\ominus\ Ag(s) \mid AgCl(s),\ \underset{(a_1)}{HCl} \parallel \underset{(a_2)}{HCl}\ AgCl(s), \mid Ag(s)\ \oplus$$

which consists of two metal-insoluble salt type electrodes (silver-silver chloride). The two HCl solutions of activities a_1 *and* a_2 *are used.*
Let $a_1 > a_2$

Since the two solutions are connected by a salt bridge, there is negligible transfer of electrolyte at the liquid junction.

The use of salt bridge is represented by the double line put between the two half cells.

This cell is reversible with anions, Cl^- ions.

The cell reactions are

At L.H.E oxidation, $\underset{(s)}{Ag} + \underset{(a_1)}{Cl^-} \Longleftrightarrow \underset{(s)}{AgCl} + e^-$

At R.H.E reduction, $\underset{(s)}{AgCl} + e^- \Longleftrightarrow \underset{s}{Ag} + \underset{(a_2)}{Cl^-}$

∴ Net cell reaction $\underset{(a_1)}{Cl^-} \Longleftrightarrow \underset{(a_2)}{Cl^-}$

The Nernst equation for the above cell may be written as

$$E_{cell} = E^{0}_{cell} - \frac{RT}{nF} \ln\left(\frac{a_2}{a_1}\right) = E^{0}_{cell} - \frac{2.303RT}{F} \log\left(\frac{a_2}{a_1}\right)$$

(Here, the number of electrons involved in the electrode reactions. n=1)

Since, for concentration cells, $E^{0}_{cell} = 0V$

$$E_{cell} = -\frac{2.303RT}{F} \log\left(\frac{a_2}{a_1}\right)$$

At 298K, $\frac{2.303RT}{F} = 0.0591$

$$\therefore E_{cell} = -0.0591 \log\left(\frac{a_2}{a_1}\right)$$

i.e. $\boxed{\mathbf{E_{cell} = 0.0591 \log\left(\frac{a_1}{a_2}\right)}}$

For spontaneous cell reaction, $a_2 > a_1$.

Now the activity of single ion is given by $a = m\gamma$

where m *= molality of ion and* γ *= activity coefficient.*

$\therefore a_1 = m_1\gamma_1$ *and* $a_2 = m_2\gamma_2$

i.e. $\boxed{\mathbf{E_{cell} = 0.0591 \log\left(\frac{m_1\gamma_1}{m_2\gamma_2}\right)}}$

Calculate the e..m.f. of the following cell at 298K

$$\ominus\ Ag(s)\ |\ AgCl(s),\ \underset{\substack{m\,=\,0.1\\ \gamma\,=\,0.90}}{HCl}\ \|\ \underset{\substack{m\,=\,0.05\\ \gamma\,=\,0.98}}{HCl}\ AgCl(s),\ |\ Ag(s)\ \oplus$$

Solution:

The given cell is concentration cell without transference reversible to anions. Therefore,

$$\boxed{E_{cell} = 0.0591\ \log\left(\frac{m_1\gamma_1}{m_2\gamma_2}\right)}$$

$$E_{cell} = 0.0591\ \log\left(\frac{0.1 \times 0.90}{0.05 \times 0.98}\right)$$

$$E_{cell} = 0.0591\ \log\left(\frac{0.09}{0.049}\right)$$

$$E_{cell} = 0.0591\ \log(1.837)$$

$$E_{cell} = 0.0591 \times 0.264$$

$$E_{cell} = 0.0156V$$

Q. Derive an expression for the EMF of Electrolyte Concentration Cell Reversible to Cations with transference.

$$\ominus\ \underset{(1\ atm)}{Pt,\ H_2} \mid \underset{(a_1)}{HCl} \mid \underset{(a_2)}{HCl} \mid \underset{(1\ atm)}{H_2,\ Pt}\ \oplus$$

$$\overset{t_{H^+}}{\underset{t_{Cl^-}}{\Longleftrightarrow}}$$

Ans:

Consider a cell of the type

$$\ominus\ \underset{(1\ atm)}{Pt,\ H_2} \mid \underset{(a_1)}{HCl} \mid \underset{(a_2)}{HCl} \mid \underset{(1\ atm)}{H_2,\ Pt}\ \oplus$$

$$\overset{t_{H^+}}{\underset{t_{Cl^-}}{\Longleftrightarrow}}$$

which consists of two hydrogen gas electrodes in contact with HCl solutions of different concentrations or activities. The two solutions are in direct contact with each other through porous partition. This cell is reversible to cations H^+ *ions. Let* $a_2 > a_1$

As the two solutions are in direct contact, the transfer of electrolyte takes place from one compartment to another. Hence, there will be a liquid junction potential.

When one faraday of electricity passes through the cell. 1gm atom of hydrogen dissolves at the L.H.E. to yield 1gm-ion of H^+ and the same amount of H^+ ions is reduced to form 1gm-atom of hydrogen gas which is liberated at the R.H.E.

Therefore, the reactions at the respective electrodes of the cell can be written as,

At L.H.E oxidation, $\frac{1}{2}H_2(g) \Longleftrightarrow \underset{(a_1)}{H^+} + e^-$

At R.H.E reduction, $\underset{(a_2)}{H^+} + e^- \Longleftrightarrow \frac{1}{2}H_2(g)$

∴ Net cell reaction $\underset{(a_2)}{H^+} \Longleftrightarrow \underset{(a_1)}{H^+}$ ....(1)

The electrons liberated move in the external circuit from L.H.E. to R.H.E. To complete the circuit similar charges must pass from right to left through the liquid junction. These charges are carried by the ions of the solution. As Cl^- ions carry negative charge they move in the direction of electrons. The H^+ ions carry positive charge and thus they move in the opposite direction. Thus, while the current is passing t_+ gm-ions of H^+ ions will migrate across the junction between the two solutions from left to right and t_- gm-ions of Cl^- ions will move in the opposite direction. Here t_+ and t_- are the transference numbers of H^+ and Cl^- ions respectively. Therefore, t_+ faraday of charge will be carried by t_+ gm-ion of H^+ from left to right and t_- faraday of charge will be carried by t_- gm-ion of Cl^- from right to left. These reactions can be written as follows:

For the transfer of H^+ ions $$t_+ \underset{(a_1)}{H^+} \Longleftrightarrow t_+ \underset{(a_2)}{H^+}$$

Since $t_+ + t_- = 1 \quad \therefore t_+ = (1 - t_-)$

Hence,

$$\boxed{(1 - t_-) \underset{(a_1)}{H^+} \Longleftrightarrow (1 - t_-) \underset{(a_2)}{H^+} \qquad \text{....(2)}}$$

For the transfer of Cl^- ions.

$$\boxed{t_- \underset{(a_2)}{Cl^-} \Longleftrightarrow t_- \underset{(a_1)}{Cl^-} \qquad\qquad ....(3)}$$

The net cell reaction is given by addition of equations (1), (2) and (3)

$$\text{i.e. } \underset{(a_2)}{H^+} + (1 - t_-) \underset{(a_1)}{H^+} + t_- \underset{(a_2)}{Cl^-} \Longleftrightarrow \underset{(a_1)}{H^+} + (1 - t_-) \underset{(a_2)}{H^+} + t_- \underset{(a_1)}{Cl^-}$$

$$\underset{(a_2)}{H^+} + \underset{(a_1)}{H^+} - t_- \underset{(a_1)}{H^+} + t_- \underset{(a_2)}{Cl^-} \Longleftrightarrow \underset{(a_1)}{H^+} + \underset{(a_2)}{H^+} - t_- \underset{(a_2)}{H^+} + t_- \underset{(a_1)}{Cl^-}$$

$$- t_- \underset{(a_1)}{H^+} + t_- \underset{(a_2)}{Cl^-} \Longleftrightarrow - t_- \underset{(a_2)}{H^+} + t_- \underset{(a_1)}{Cl^-}$$

$$t_- \underset{(a_2)}{H^+} + t_- \underset{(a_2)}{Cl^-} \Longleftrightarrow t_- \underset{(a_1)}{H^+} + t_- \underset{(a_1)}{Cl^-}$$

$$\therefore\ t_- \underset{(a_2)}{HCl} \Longleftrightarrow t_- \underset{(a_1)}{HCl}$$

From this net cell reaction, the Nernst equation for the above cell may be written as,

$$E_{cell} = E^{0}_{cell} - \frac{RT}{nF} \ln\left(\frac{a_1}{a_2}\right)^{t_-}$$

$$E_{cell} = E^{0}_{cell} - \frac{2.303RT}{F} \log\left(\frac{a_1}{a_2}\right)^{t_-}$$

(Here , n= 1)

Since, for concentration cells, $E^{0}_{cell} = 0V$

$$E_{cell} = - \frac{2.303RT}{F} \log\left(\frac{a_1}{a_2}\right)^{t_-}$$

At 298K, $\frac{2.303RT}{F} = 0.0591$

$$\therefore E_{cell} = - 0.0591 \log\left(\frac{a_1}{a_2}\right)^{t_-}$$

$$E_{cell} = - 0.0591 \times t_- \log\left(\frac{a_1}{a_2}\right)$$

i.e. $\boxed{E_{cell} = 0.0591 \times t_- \log\left(\frac{a_2}{a_1}\right)}$

Since, HCl is uni-univalent electrolyte, $a_1 = m_1^2\gamma_1^2$ *and* $a_2 = m_2^2\gamma_2^2$

where m *and* γ *represent molality and activity coefficient.*

Thus,

$$E_{cell} = 0.0591 \times t\text{-} \ \log\left(\frac{m_2^2\gamma_2^2}{m_1^2\gamma_1^2}\right)$$

$$E_{cell} = 0.0591 \times t\text{-} \ \log\left(\frac{m_2\gamma_2}{m_1\gamma_1}\right)^2$$

$$\boxed{\boldsymbol{E_{cell} = 0.0591 \times 2t\text{-} \ \log\left(\frac{m_2\gamma_2}{m_1\gamma_1}\right)}}$$

For spontaneous cell reaction, $a_2 > a_1$.

It should be noted that if the electrodes of the concentration cell are reversible with respect to cation, the transference number of the anion gets involved in the equation.

Note: If the electrolyte used in the above cell is bi-univalent or uni-bivalent, then $a_1 = 4m_1^3\gamma_1^3$ *and* $a_2 = 4m_2^3\gamma_2^3$

Hence the expression for e.mf. of this cell becomes

$$\boxed{E_{cell} = 0.0591 \times 3t\text{-}\ \log\left(\frac{m_2\gamma_2}{m_1\gamma_1}\right)}$$

The e.m.f. of the following cell at 298K is 0.0418volt.

$$\ominus\ Ag(s) \mid \underset{\substack{m\, =\, 0.02\\ \gamma\, =\, 0.90}}{AgNO_3} \mid \underset{\substack{m\, =\, 0.1\\ \gamma\, =\, 0.85}}{AgNO_3} \mid Ag(s)\ \oplus$$

Calculate the transference numbers of Ag^+ ***and*** NO_3^- ***ions in the given range of concentration.***

Solution:

The given cell is an electrolyte concentration cell with transference reversible to cations Ag^+*. Hence, its e.m.f. is given by*

$$\underset{at\ 298K}{E_t} = 0.0591 \times 2t_- \log\left(\frac{m_2\gamma_2}{m_1\gamma_1}\right)$$

substituting the data,

$$0.0418 = 0.0591 \times 2t_- \log\left(\frac{0.1 \times 0.85}{0.02 \times 0.90}\right)$$

$$0.0418 = 0.0591 \times 2t_- \log\left(\frac{0.085}{0.018}\right)$$

$$0.0418 = 0.0591 \times 2t_- \log(4.722)$$

$$0.0418 = 0.0591 \times 2t_- \times 0.674$$

$$\therefore t_- = \frac{0.0418}{0.0591 \times 2 \times 0.674}$$

$$= \frac{0.0418}{0.0797} = 0.525$$

$$\therefore t_{NO_3^-} = 0.525$$

$$\therefore t_{Ag^+} = (1 - t_{NO_3^-})$$

$$= (1 - 0.525)$$

$$= 0.475$$

Q. Derive an expression for the EMF of Electrolyte Concentration Cell with transference Reversible to Anions.

$$\ominus\ \underset{(s)}{Ag} \mid AgCl(s)\ \underset{(a_1)}{HCl} \mid \underset{(a_2)}{HCl}\ AgCl(s) \mid \underset{(s)}{Ag}\ \oplus$$

$$\underset{t_{Cl^-}}{\overset{t_{H^+}}{\Longleftrightarrow}}$$

Consider a cell of the type

$$\ominus\ \underset{(s)}{Ag} \mid AgCl(s)\ \underset{(a_1)}{HCl} \mid \underset{(a_2)}{HCl}\ AgCl(s) \mid \underset{(s)}{Ag}\ \oplus$$

$$\underset{t_{Cl^-}}{\overset{t_{H^+}}{\Longleftrightarrow}}$$

this cell consists of two metal-insoluble salt type electrodes (i.e. silver-silver chloride) in contact with HCl solutions of different concentrations or activities. The two solutions are in direct contact with each other through porous partition. This cell is reversible to anions Cl^- *ions. Let* $a_1 > a_2$

As the two solutions are in direct contact, the transfer of electrolyte takes place from one compartment to another. Hence, there will be a liquid junction potential.

When one faraday of electricity passes through the cell. The following reactions occure at the respective electrodes of the cell,

At L.H.E oxidation, $Ag(s) + \underset{a_1}{Cl^-} \Longleftrightarrow AgCl(s) + e^-$

At R.H.E reduction, $AgCl(s) + e^- \Longleftrightarrow Ag(s) + \underset{a_2}{Cl^-}$

∴ Net cell reaction $\underset{a_1}{Cl^-} \Longleftrightarrow \underset{a_2}{Cl^-}$ ....(1)

The electrons liberated move in the external circuit from L.H.E. to R.H.E. To complete the circuit similar charges must pass from right to left through the liquid junction. These charges are carried by the ions of the solution. As Cl^- ions carry negative charge they move in the direction of electrons. The H^+ ions carry positive charge and thus they move in the opposite direction. Thus, while the current is passing t_+ gm-ions of H^+ ions will migrate across the junction between the two solutions from left to right and t_- gm-ions of Cl^- ions will move in the opposite direction. Here t_+ and t_- are the transference numbers of H^+ and Cl^- ions respectively. Therefore, t_+ faraday of charge will be carried by t_+ gm-ion of H^+ from left to right and t_- faraday of charge will be carried by t_- gm-ion of Cl^- from right to left. These reactions can be written as follows:

For the transfer of H^+ ions

$$\boxed{t_+ \underset{(a_1)}{H^+} \Longleftrightarrow t_+ \underset{(a_2)}{H^+} \qquad \qquad \text{....(2)}}$$

For the transfer of Cl^- ions.

$$t_- \underset{(a_2)}{Cl^-} \Longleftrightarrow t_- \underset{(a_1)}{Cl^-}$$

For the transfer of Cl^- ions. $t_- \underset{(a_2)}{Cl^-} \Longleftrightarrow t_- \underset{(a_1)}{Cl^-}$

Since $t_+ + t_- = 1 \qquad \therefore t_- = (1 - t_+)$

Hence, $\boxed{(1 - t_+) \underset{(a_2)}{Cl^-} \Longleftrightarrow (1 - t_+) \underset{(a_1)}{Cl^-} \qquad ....(3)}$

The net cell reaction is given by addition of equations (1), (2) and (3)

$$\underset{a_1}{Cl^-} \Longleftrightarrow \underset{a_2}{Cl^-} \qquad ....(1)$$

$$\boxed{t_+ \underset{(a_1)}{H^+} \Longleftrightarrow t_+ \underset{(a_2)}{H^+} \qquad ....(2)}$$

$$\boxed{(1 - t_+) \underset{(a_2)}{Cl^-} \Longleftrightarrow (1 - t_+) \underset{(a_1)}{Cl^-} \qquad ....(3)}$$

i.e. $\underset{(a_1)}{Cl^-} + t_+ \underset{(a_1)}{H^+} + (1 - t_+) \underset{(a_2)}{Cl^-} \Longleftrightarrow \underset{(a_2)}{Cl^-} + t_+ \underset{(a_2)}{H^+} + (1 - t_+) \underset{(a_1)}{Cl^-}$

$$i.e.\ \underset{(a_1)}{Cl^-} + t_+ \underset{(a_1)}{H^+} + (1 - t_+) \underset{(a_2)}{Cl^-} \Longleftrightarrow \underset{(a_2)}{Cl^-} + t_+ \underset{(a_2)}{H^+} + (1 - t_+) \underset{(a_1)}{Cl^-}$$

$$\underset{(a_1)}{Cl^-} + t_+ \underset{(a_1)}{H^+} + \underset{(a_2)}{Cl^-} - t_+ \underset{(a_2)}{Cl^-} \Longleftrightarrow \underset{(a_2)}{Cl^-} + t_+ \underset{(a_2)}{H^+} + \underset{(a_1)}{Cl^-} - t_+ \underset{(a_1)}{Cl^-}$$

$$t_+ \underset{(a_1)}{H^+} - t_+ \underset{(a_2)}{Cl^-} \Longleftrightarrow t_+ \underset{(a_2)}{H^+} - t_+ \underset{(a_1)}{Cl^-}$$

$$t_+ \underset{(a_1)}{H^+} + t_+ \underset{(a_1)}{Cl^-} \Longleftrightarrow t_+ \underset{(a_2)}{H^+} + t_+ \underset{(a_2)}{Cl^-}$$

$$t_+ \underset{(a_1)}{HCl} \Longleftrightarrow t_+ \underset{(a_2)}{HCl}$$

From this net cell reaction, the Nernst equation for the above cell may be written as,

$$E_{cell} = E^0_{cell} - \frac{RT}{nF} \ln\left(\frac{a_2}{a_1}\right)^{t_+}$$

$$E_{cell} = E^{0}_{cell} - \frac{RT}{nF} \ln\left(\frac{a_2}{a_1}\right)^{t_+}$$

$$E_{cell} = E^{0}_{cell} - \frac{2.303RT}{F} \log\left(\frac{a_2}{a_1}\right)^{t_+} \qquad (Here\ ,\ n= 1)$$

Since, for concentration cells, $E^{0}_{cell} = 0V$

$$E_{cell} = - \frac{2.303RT}{F} \log\left(\frac{a_2}{a_1}\right)^{t_+}$$

At 298K, $\frac{2.303RT}{F} = 0.0591$

$$\therefore E_{cell} = - 0.0591 \log\left(\frac{a_2}{a_1}\right)^{t_+}$$

$$E_{cell} = - 0.0591 \times t_+ \log\left(\frac{a_2}{a_1}\right)$$

i.e. $\boxed{E_{cell} = 0.0591 \times t_+ \log\left(\frac{a_1}{a_2}\right)}$

Since, HCl is uni-univalent electrolyte, $a_1 = m_1^2\gamma_1^2$ *and* $a_2 = m_2^2\gamma_2^2$

where m and γ *represent molality and activity coefficient.*

Thus,

$$E_{cell} = 0.0591 \times t_+ \log\left(\frac{m_1^2\gamma_1^2}{m_2^2\gamma_2^2}\right)$$

$$E_{cell} = 0.0591 \times t_+ \log\left(\frac{m_1\gamma_1}{m_2\gamma_2}\right)^2$$

$$\boxed{E_{cell} = 0.0591 \times 2t_+ \log\left(\frac{m_1\gamma_1}{m_2\gamma_2}\right)}$$

For spontaneous cell reaction, $a_1 > a_2$.

It should be noted that if the electrodes of the concentration cell are reversible with respect to anions, the transference number of the cations gets involved in the equation.

Note: If the electrolyte used in the above cell is bi-univalent or uni-bivalent, then $a_1 = 4m_1^3\gamma_1^3$ *and* $a_2 = 4m_2^3\gamma_2^3$

Hence the expression for e.mf. of this cell becomes

$$\boxed{E_{cell} = 0.0591 \times 3t_{+} \log\left(\frac{m_1\gamma_1}{m_2\gamma_2}\right)}$$

The e.m.f. of the following cell with transference is 0.0461 volt at 298K.

$$\ominus\ Pt,\ \underset{(1\ atm)}{Cl_2(g)}\ |\ \underset{a\ =\ 0.1}{NaCl}\ |\ \underset{a\ =\ 0.01}{NaCl}\ |\ \underset{(1\ atm)}{Cl_2(g)},\ Pt\ \oplus$$

Calculate the transport numbers of Na^+ ***and*** Cl^- ***ions.***

For concentration cell with transference reversible to anions, we have

$$\underset{at\ 298K}{E_t} = 0.0591 \times 2t_+ \log\left(\frac{a_1}{a_2}\right)$$

Substituting the data,

$$0.0461 = 0.0591 \times 2t_+ \log\left(\frac{0.1}{0.01}\right)$$

$$0.0461 = 0.0591 \times 2t_+ \log(10)$$

$$0.0461 = 0.0591 \times 2t_+ \times 1$$

$$t_+ = \frac{0.0461}{0.0591 \times 2} = \frac{0.0461}{0.1182} = 0.390$$

$$\therefore t_{Na^+} = 0.390$$

$$\therefore t_{Cl^-} = (1 - t_{Na^+})$$

$$= (1 - 0.390)$$

$$= 0.61$$

Applications of EMF measurements

- Determination of solubility product constants
- Determination of pH
- Determination of activity coefficients
- Determination of transport numbers

Determination of solubility product constants

Consider the salt MX in equilibrium with its ions in a saturated solution.

$$MX(s) \rightleftarrows M^{+}(aq) + X^{-}(aq)$$

$$K_{sp} = a_{+} \times a_{-} = [M^{+}][X^{-}]$$

The above reaction is the cell reaction for the following cell

$$M(s)\,|\,M^{+}X^{-}(satd.\,solu.)\,|\,MX(s),\,M(s)$$

$$Ag(s)\,|\,Ag^{+}Br^{-}(satd.\,solu.)\,|\,AgBr(s),\,Ag(s)$$

LHE (Anode: Oxidation) $\mathrm{M}(s) + \mathrm{e}^- \rightarrow \mathrm{M}^+(aq) + \mathrm{e}^-$

RHE (Cathode: Reduction) $\mathrm{MX}(s) + \mathrm{e}^- \rightarrow \mathrm{M}(s) + \mathrm{X}^-$

Net cell reaction $\mathrm{MX}(s) \rightleftarrows \mathrm{M}^+(aq) + \mathrm{X}^-(aq)$

$$-\Delta G^0 = nFE^0 \qquad -\Delta G^0 = 2.303\ RT \log K_{sp}$$

$$E^0 = \frac{2.303\ RT}{nF} \log K_{sp} = \frac{0.0591}{n} \log K_{sp} (\text{at } 25\ {}^0\text{C})$$

Determination of pH

- By using hydrogen electrode: The electrode reaction for the hydrogen electrode

$$\mathrm{Pt}(s)\,|\,\mathrm{H_2}(g, 1\,bar)\,|\,\mathrm{H^+}(aq)$$

may be given as

$$\mathrm{H^+}(aq) + \mathrm{e^-} \rightleftarrows \frac{1}{2}\mathrm{H_2}(g)$$

Its potential is given by the Nernst equation:

$$E_{el} = E_{el}^{0} + \frac{2.303RT}{F}\log\left[\frac{H^+}{H_2^{1/2}}\right] ------(52)$$

But $E_{el}^{0} = 0$

$$E_{el} = \frac{2.303RT}{F}\log H^{+} = -0.0591\,pH \quad (\text{at } 25\ {}^{0}\text{C}) ------(53)$$

This electrode is coupled with a saturated calomel electrode (SCE).

$$\text{Pt}(s)\,|\,\text{H}_2(g, 1\,bar)\,|\,\text{H}^{+}(aq)\,||\,\text{KCl}(aq.\,sat.)\,|\,\text{Hg}_2\text{Cl}_2(s)\,|\,\text{Hg}(l)$$

$$E_{cell} = E_R - E_L = 0.2422 + 0.0591\,pH ------(54)$$

$$pH = \frac{E_{cell} - 0.2422}{0.0591} ------(55)$$

Determination of pH: Hydrogen electrode

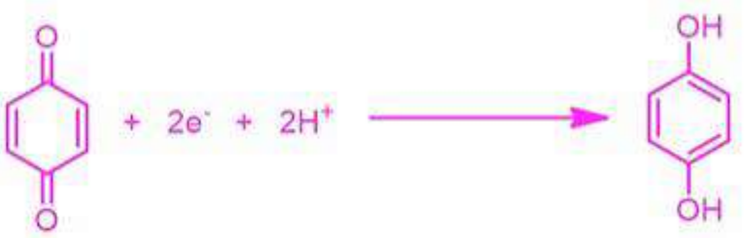
- It requires the passage of H_2 gas at 1 bar pressure
- Requires considerable volume of test solution
- Cannot be used in oxidizing solutions
- Cannot be used in the presence metal ions that poisons Pt (As, Sb)

Determination of pH

- By using quinhydrone electrode: The electrode reaction for the quinhydrone electrode

$$\mathrm{Pt}(s)\,|\,\mathrm{Q}(s),\,\mathrm{QH_2}(s)\,|\,\mathrm{H^+}(aq)$$

may be given as



Q

QH_2

Its potential is given by the Nernst equation:

$$E_{el} = E_{el}^{0} + \frac{2.303RT}{2F}\log\frac{[\mathrm{Q}]\left[\mathrm{H}^{+}\right]^{2}}{[\mathrm{QH_2}]} ------(56)$$

$$E_{el} = E_{el}^{0} + \frac{2.303RT}{2F}\log\frac{[\mathrm{Q}]}{[\mathrm{QH_2}]} + \frac{2.303RT}{F}\log\left[\mathrm{H}^{+}\right] ------(57)$$

$$E_{el} = E_{el}^{0} + \frac{0.0591}{2}\log\frac{[\mathrm{Q}]}{[\mathrm{QH_2}]} - 0.0591\,pH \ \ (\text{at } 25\,^{0}\mathrm{C}) ------(58)$$

A small amount of quinhydrone which contains equimolar amounts of Q and $\mathrm{QH_2}$ is taken

$$\therefore \frac{[Q]}{[QH_2]} = 1$$

$$E_{el} = E_{el}^{0} - 0.0591\,pH ------(59)$$

$$E_{el} = 0.6996 - 0.0591\,pH ------(60)$$

This electrode is coupled with a (SCE)

$$\mathrm{Hg}(l)\,|\,\mathrm{Hg_2Cl_2}(s)\,|\,\mathrm{KCl}(aq.\,sat.)\,\|\,\mathrm{H^+}(aq.\,sat.)\,|\,\mathrm{Q}(s),\mathrm{QH_2}(s)\,|\,\mathrm{Pt}(s)$$

$$E_{cell} = E_R - E_L = (0.6996 - 0.0591\,pH) - 0.2422 \text{ ------ } (61)$$

$$pH = \frac{0.6996 - 0.2422 - E_{cell}}{0.0591} \text{ ------ } (62)$$

- ☐ Can be set up easily
- ☐ Gives accurate results even in the presence of oxidizing agents
- ☐ Cannot be used for solutions having pH > 8
- ☐ $\mathrm{Q\text{-}QH_2}$ equilibrium is altered in strong alkaline solutions

Determination of pH

- ☐ By using glass electrode: A potential exists at the interface between glass and a solution containing H^+ ions. This potential at 25 ^{0}C is given by

$$E_G = E_G^0 + 0.0591 \log\left[\mathrm{H}^+\right] = E_G^0 - 0.0591\, pH ------(63)$$

The glass electrode is made of a special glass of relatively low melting point and high electrical conductivity. It is blown in the form of a bulb which is then sealed to the bottom of a glass tube. A solution of 0.1 M HCl is placed inside the bulb and a Pt wire is inserted to make electrical contact. Calomel electrode act as the reference electrode.