



9. **Equilibrium constants**

$$\Delta G^0 = -nFE^0; \text{ and}$$

$$\Delta G = -RT \ln K_a$$

$$\therefore E^0 = (RT/nF) \cdot \ln K_a$$

NB: can therefore calculate  $K$  from standard electrode potentials.

10. **Electrodes**

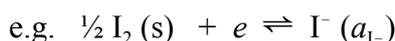
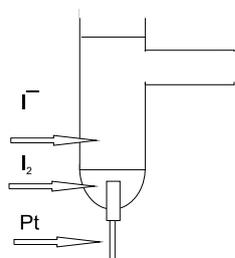
There are **five** main types to consider.

**(i) Metal – metal ion**

(e.g. for Zn, Cu, Cd)

**(ii) Amalgam**

Provides lowered activity of the metal, but more rapid establishment of equilibrium, and better reversibility. *Advantageous* in many cases, *essential* in others (e.g. Na).

**(iii) Non-metal – non-gas****(iv) Gas**

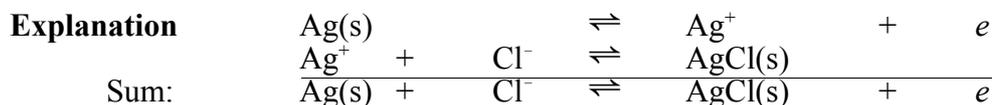
Gas bubbling around inert metal (e.g. Pt or Pd) and ions

**(v) Metal – insoluble salt**

**N.B. Read this very carefully!**

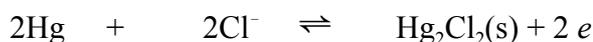
Examples: Ag|AgCl or Pb|PbSO<sub>4</sub>.

These electrodes take in or release the *anions* (Cl<sup>-</sup> or SO<sub>4</sub><sup>2-</sup>): they are *reversible* to the anions. They represent the only way to study some anions (e.g. SO<sub>4</sub><sup>2-</sup>, CN<sup>-</sup>).

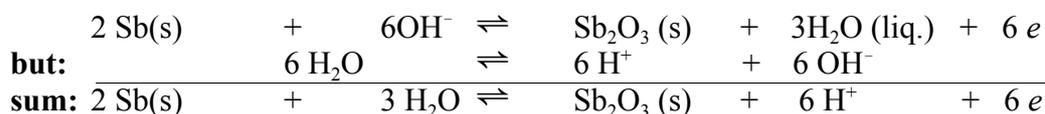


reversible to Cl<sup>-</sup>

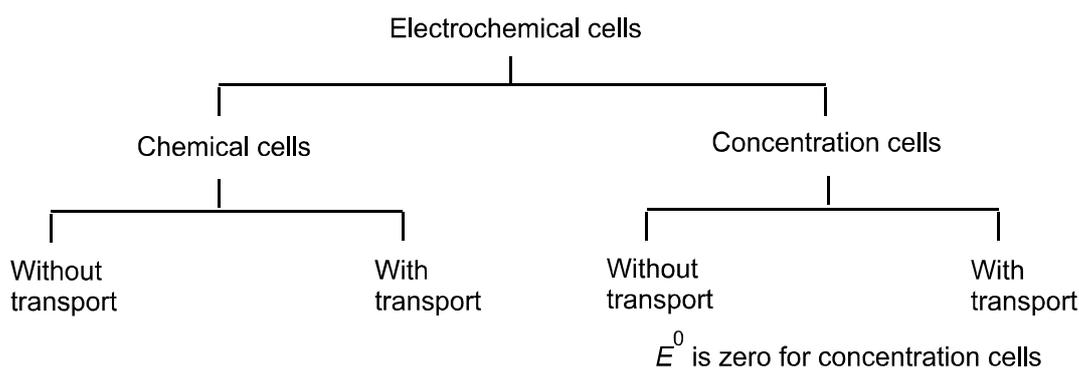
note also: *calomel electrode* (Hg|Hg<sub>2</sub>Cl<sub>2</sub>) is again reversible to Cl<sup>-</sup>.



Similarly **metal – insoluble oxide** electrodes can be reversible to **either H<sup>+</sup> or OH<sup>-</sup>**

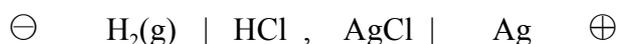


## 11. Types of cell



## 11(a). No liquid junction: chemical cell

One electrode reversible to the cation, the other to the anion of the electrolyte. E.g.



**n.b.** use to obtain *standard electrode potentials* or *activity coefficients* applying *Limiting Debye-Huckel* law, in which an extrapolation is made against  $\sqrt{I}$  to  $\sqrt{I} = 0$ .

## 11(b). Liquid junction: chemical cell

$$E_{\text{total}} = E_{\text{R}} + E_{\text{L}} + E_{\text{junction}}$$

$E_{\text{junction}}$  may be small (but may not). Thus not suitable for *exact* evaluation of thermodynamic functions.

Junctions are of the types:

- (i) direct contact of electrolytes; (ii) salt bridge; (iii) flowing junction.

## 11(c). No liquid junction

## i) Electrode concentration cell



$$E = -(RT/2F) \cdot \ln(P_2/P_1)$$

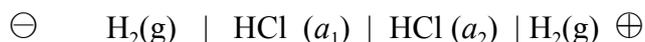
## ii) Electrolyte concentration cell

Two cells connected to oppose each other



$$\begin{aligned} E &= E_1 - E_2 \\ &= -(RT/F) \cdot \ln(a_1/a_2) \end{aligned}$$

## 11(d). Liquid junction: concentration cell with transport



overall reaction is  $\text{H}^+(a_2) \rightleftharpoons \text{H}^+(a_1)$

It can be shown (**separate sheet:** <http://rpw.chem.ox.ac.uk/coll/transport.html>) that

$$E = -t_- \cdot (RT/F) \cdot \ln(a_1/a_2)$$

where  $t_-$  is the *transport number* (see §12) of the **anion** (cell is reversible to **cation**).

## 12. Transport (or transference) numbers

The *transport number* (sometimes called *transference number*) of an ion is the fraction of charge carried in an electrolyte by that ion. Thus in a simple electrolyte containing one cation and one anion, the transport numbers are represented  $t_+$  and  $t_-$  with  $t_+ + t_- = 1$ .

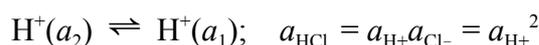
There are several ways of determining transport numbers that do not involve electrochemical cells (Hittorf's method; moving-boundary method), but comparison of §11(c)(ii) with §11(d) shows that the ratio of potentials of cells with and without transport (for the same overall reaction) is equal to the transport number (for the **anion** if the cell is reversible to the **cation**). That is

$$\frac{E_{\text{with transport}}}{E_{\text{without transport}}} = t_- \quad \text{if reversible w.r.t. cation;}$$

$$\frac{E_{\text{with transport}}}{E_{\text{without transport}}} = t_+ \quad \text{if reversible w.r.t. anion;}$$

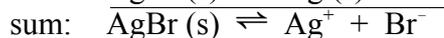
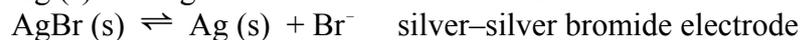
## 13. Junction potentials

In the example of §11(d), the overall reaction is



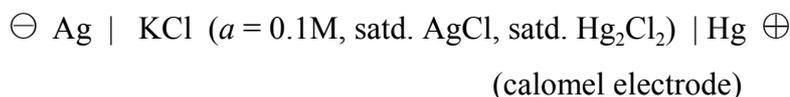
$$\begin{aligned} \text{so that} \quad E_1 + E_2 &= -(RT/F) \cdot \ln(a_{\text{H}^+1}/a_{\text{H}^+2}) \\ \text{but} \quad E_{\text{junction}} &= E - (E_1 + E_2) \\ &= t_- \cdot (RT/F) \cdot \ln(a_{\text{HCl}1}/a_{\text{HCl}2}) - (RT/F) \cdot \ln(a_{\text{H}^+1}/a_{\text{H}^+2}) \\ &= (2t_- - 1) \cdot (RT/F) \cdot \ln(a_{\text{H}^+1}/a_{\text{H}^+2}) \\ &= (t_- - t_+) \cdot (RT/F) \cdot \ln(a_{\text{H}^+1}/a_{\text{H}^+2}) \end{aligned}$$

## 14. Solubility product



$$E^0 = (RT/nF) \cdot \ln K_S$$

Less precise method (e.g. for AgCl)



$$E = E_{\text{Ag}} + E_{\text{calomel}}; \quad \text{or } E_{\text{Ag}} = E - E_{\text{calomel}}$$

but  $E_{\text{Ag}} = E_{\text{Ag}}^0 - (Rt/F) \cdot \ln a_{\text{Ag}^+}$  also, so that a value for  $a_{\text{Ag}^+}$  may be found.

$a_{\text{Cl}^-}$  can be equated to  $m_{\text{Cl}}\gamma_{\text{Cl}^-}$ , so that  $K_S = a_{\text{Ag}^+}a_{\text{Cl}^-}$  may be calculated.

## 15. Applications

pH determination; acid-base titrations; oxidation-reduction titrations; precipitation titrations.