Lecture Contents

7. Chemical equilibrium

Equilibrium electrochemistry

Basic Concepts

- ► **"Electrochemical method"** : The ability to make precise measurements of currents and potential differences (voltages)
- ► **"Electrochemical cell"** : Consists of two electrodes contact with an electrolyte
- ► **"Galvanic cell"** : An electrochemical cell that produces electricity as a result of the spontaneous reaction
- ► **"Electrolytic cell"** : An electrochemical cell in which a non-spontaneous reaction is driven by an external source of current

7.5 Half-reactions and electrodes

Oxidation : The removal of electrons from a species

Reduction : The addition of electrons to a species

Redox reaction : Transfer of electrons from one species to another.

Reducing agent =The electron donor, **Oxidizing agent** = the electron acceptor

Redox couple : Expressed by the reduced and oxidized species in a half-reaction

Ex) $\mathrm{Ox} + \nu \mathrm{e}^- \rightarrow \mathrm{Red}$, The redox couples : Ox/Red

Illustration 7.7 *(Expressing a reaction in terms of half-reactions)*

$$\mathrm{AgCl(s)} \rightarrow \mathrm{Ag^+(aq)} + \mathrm{Cl^-(aq)}$$

A redox reaction can be expressed as the difference of the following two reduction half reactions.

$$\mathrm{AgCl(s)} + \mathrm{e}^- \rightarrow \mathrm{Ag(s)} + \mathrm{Cl^-(aq)}$$

$$\mathrm{Ag^+(aq)} + \mathrm{e}^- \rightarrow \mathrm{Ag(s)}$$

The redox couples : AgCl/Ag,$\mathrm{Cl^-}$ and $\mathrm{Ag^+}$/Ag

7.5 Half-reactions and electrodes

The reduction and oxidation processes responsible for the overall reaction in a cell.

Oxidation : Electrons are released, $\mathrm{Red}_1 \rightarrow \mathrm{Ox}_1 + \nu e^-$ (at anode)

Reduction : Electrons are entered, $\mathrm{Ox}_2 + \nu e^- \rightarrow \mathrm{Red}_2$ (at cathode)

In a galvanic cell (See Fig7.11)

Cathode : Higher potential than the anode

(reduction)

Anode : Oxidation results in the transfer of

electrons to the electrode. (Oxidation)

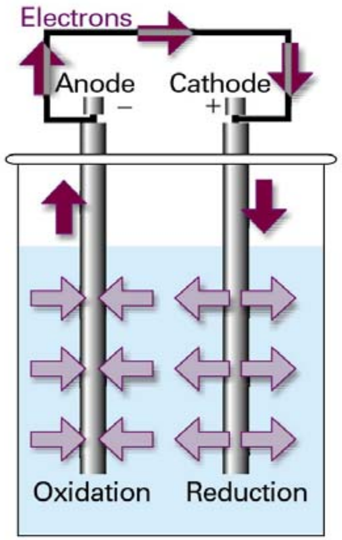


Fig. 7.11 When a spontaneous reaction takes place in a galvanic cell, electrons are deposited in one electrode (the site of oxidation, the anode) and collected from another (the site of reduction, the cathode), and so there is a net flow of current which can be used to do work. Note that the + sign of the cathode can be interpreted as indicating the electrode at which electrons enter the cell, and the – sign of the anode is where the electrons leave the cell.

7.6 Varieties of cells

► Immerse the electrodes in different electrolytes, as in the **'Daniell cell'**

: The redox couple, Cu^{2+}/Cu and Zn^{2+}/Zn (see Fig7.12)

► Electrolyte concentration cell

: The electrode compartments are identical except for the concentrations of the electrolytes.

► Electrode concentration cell

: The electrodes themselves have different concentrations ex) Gas electrodes,

Amalgams (solutions in mercury)

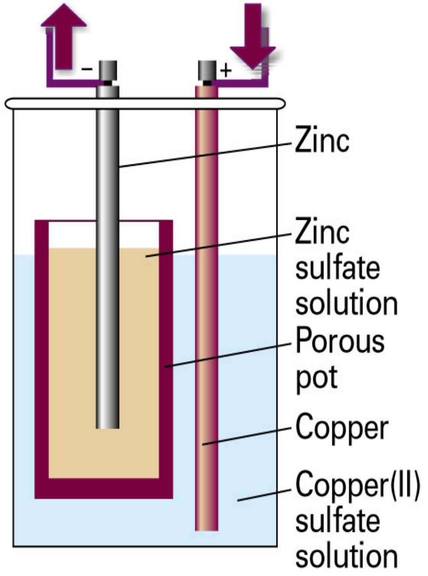


Fig. 7.12 One version of the Daniell cell. The copper electrode is the cathode and the zinc electrode is the anode. Electrons leave the cell from the zinc electrode and enter it again through the copper electrode.

7.6 Varieties of cells

(a) Liquid junction potentials (E_{ij})

► Definition : Potential difference across the interface of the two electrolytes.

ex) Daniell cell

► Another example of junction potential

(Different concentrations of hydrochloric acid)

H^+ ions diffuse into the more dilute solution

↓

Cl^- ions follow but so slowly

↓

Results in potential difference at the junction

► A Salt bridge can reduce the potential difference between two electrolytes.

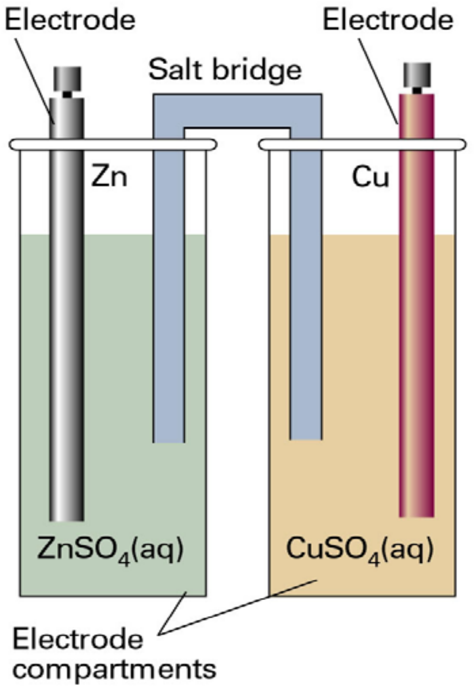


Fig. 7.13 The salt bridge, essentially an inverted U-tube full of concentrated salt solution in a jelly, has two opposing liquid junction potentials that almost cancel.

7.6 Varieties of cells

(b) Notation for cells

- Phase boundaries are denoted by a vertical bar. (see Fig 7.11)

$\mathrm{Pt(s)\,|\,H_2(g)\,|\,HCl(aq)\,|\,AgCl(s)\,|\,Ag(s)}$

- Liquid junction (see Fig 7.12)

$\mathrm{Zn(s)\,|\,ZnSO_4(aq)} \vdots \mathrm{CuSO_4(aq)\,|\,Cu(s)}$

- A double vertical line, $\|$, denotes an elimination of junction potential (see Fig 7.13)

$\mathrm{Zn(s)\,|\,ZnSO_4\,(aq)\,\|\,CuSO_4(aq)\,|\,Cu(s)}$

- Example of electrolyte concentration cell (liquid junction potential eliminated)

$\mathrm{Pt(s)\,|\,H_2(g)\,|\,HCl(aq,b_1)\,\|\,HCl(aq,\,b_2)\,|\,H_2(g)\,|\,Pt(s)}$

7.7 The electromotive force

'The cell reaction' : The reaction in the cell written on the assumption that the right-hand electrode is the cathode, so that the spontaneous reaction is one in which reduction is taking place in the right-hand compartment.

ex) $Zn(s) \mid ZnSO_4(aq) \parallel CuSO_4(aq) \mid Cu(s)$

Right-hand electrode : $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$
Left-hand electrode : $Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$

The overall cell reaction is the difference : **$Cu^{2+}(aq) + Zn(s) \rightarrow Cu(s) + Zn^{2+}(aq)$**

(a) The nernst equation

► The **cell potential** : the potential difference between two electrodes. V ($1V=1JC^{-1}s$)

A large cell potential → a large amount of electrical work can be done.

A small cell potential → only a small amount of electrical work can be done.

7.7 The electromotive force

The maximum non-expansion work (see eqn 3.38), $W_{e,max} = \Delta G$ (where, ΔG is defined with the Gibbs energy of the cell reaction, $\Delta_r G$)

To make use of $\Delta_r G$ **,** the cell is operating reversibly at a specific, constant composition.

► **The electromotive force (emf), *E***

$$\boxed{-\nu FE = \Delta_r G}$$

: F = Faraday’s constant, $F = eN'_A$

ν = The stoichiometric coefficient of the electrons in the half-reactions into which the cell reaction can be divided.

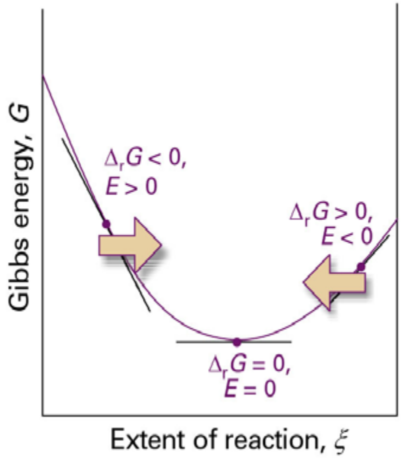


Fig. 7.14 A spontaneous reaction occurs in the direction of decreasing Gibbs energy. When expressed in terms of a cell potential, the spontaneous direction of change can be expressed in terms of the cell emf, *E*. The reaction is spontaneous as written (from left to right on the illustration) when $E > 0$. The reverse reaction is spontaneous when $E < 0$. When the cell reaction is at equilibrium, the cell potential is zero.

► The driving power of a cell (emf) is proportional to the slope of the Gibbs energy. (see Fig7.14)

If the slope is steep, the cell reaction is far from equilibrium.

If it is close to zero, the cell reaction is close to equilibrium.

7.7 The electromotive force

Relate the **emf** to the activities of the participants in the cell.

$$E = -\frac{\Delta_r G^\circ}{\nu F} - \frac{RT}{\nu F}\ln Q \,, \qquad (\Delta_r G = \Delta_r G^\circ + RT\ln Q) - \text{eqn 7.11}$$

The first term on the right is

$$E^\circ = -\frac{\Delta_r G^\circ}{\nu F} \,,$$: Standard emf of the cell

$$\boxed{E = E^\circ - \frac{RT}{\nu F}\ln Q}$$

Nernst equation

: predicts the dependence of cell potential on composition (see Fig7.15)

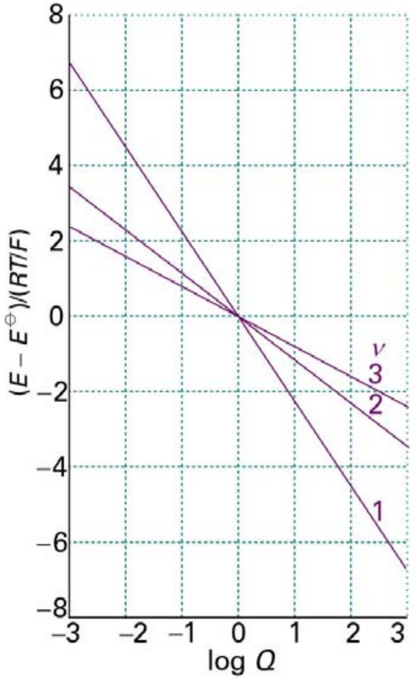


Fig. 7.15 The variation of cell emf with the value of the reaction quotient for the cell reaction for different values of ν (the number of electrons transferred). At 298 K, $RT/F = 25.69$ mV, so the vertical scale refers to multiples of this value.

► Application of Nernst equation : The determination of the pH of a solution and suitable choice of electrodes of the concentration of other ions.

► The standard emf : Interpreted as the emf when all the reactants and products in the cell reaction are in standard states. (Q=1, lnQ=0)

7.7 The electromotive force

(b) Cells at equilibrium

Suppose the reaction has reached equilibrium; $Q = K$

However, a chemical reaction at equilibrium cannot do work, and hence it generates zero potential difference between electrodes of a galvanic cell.

$$E = E^{\circ} - \frac{RT}{\nu F} \ln Q$$

Nernst equation

$$\downarrow$$

Setting, $E = 0$, $Q = K$

$$\ln K = \frac{\nu F E^{\circ}}{RT}$$

7.8. Standard potentials

We can define the potential of one of the electrodes as zero and then assign values to others on that basis

Pt(s) | H_2(g) | H^+(aq) $E^\circ = 0$ **(Standard hydrogen electrode (SHE))**

- The activity of the hydrogen ions must be 1 (pH = 0).
- The pressure of hydrogen gas must be 1 bar.

Measuring standard potential in the silver chloride electrode

Pt(s) | H_2(g) | HCl(aq) | AgCl(s) | Ag(s), $\frac{1}{2}H_2(g) + AgCl(s) \rightarrow HCl(aq) + Ag(s)$

Nernst equation

$$E = E^\circ(AgCl/Ag, Cl^-) - \frac{RT}{F}\ln\frac{a_{H^+}a_{Cl^-}}{a_{H_2}{}^{\frac{1}{2}}} \quad , \quad a_{H_2} = 1$$

7.8. Standard potentials

$$E = E^{\circ} - \frac{RT}{F}\ln a_{H^+}a_{Cl^-}\,, \qquad a_{H^+} = \gamma_{\pm}b/b \text{ and } a_{Cl^-} = \gamma_{\pm}b/b^{\circ} \quad \text{(Section 5.9)}$$

$$E = E^{\circ} - \frac{RT}{F}\ln b^2 - \frac{RT}{F}\ln \gamma_{\pm}^{\ 2}\,, \qquad \text{(Replace } \ b/b^{\circ} \text{ by } b \ \text{)}$$

$$E + \frac{2RT}{F}\ln b = E^{\circ} - \frac{2RT}{F}\ln \gamma_{\pm} \quad \longrightarrow \quad E + \frac{2RT}{F}\ln b = E^{\circ} + Cb^{\frac{1}{2}}$$

Illustration 7.12 *(Determining the standard emf of a cell)*

ex) Pt(s) | H2(g) | HCl(aq) | AgCl(s) | Ag(s) at 25°C

$b/(10^{-3}\,b^{\circ})$	3.215	5.619	9.138	25.63
$E\,/\,V$	0.52053	0.49257	0.46860	0.41824

To determine the standard emf of the cell, draw up the following table

$b/(10\text{-}3\ b^{\circ})$	3.215	5.619	9.138	25.63
$\{b/(10\text{-}3\ b^{\circ})\}^{1/2}$	1.793	2.370	3.023	5.063
E/V	0.52053	0.49257	0.46860	0.41824
$E/V + 0.051\,39 \ln b$	0.2256	0.2263	0.2273	0.2299

7.8. Standard potentials

The data of Illustration 7.12 are plotted in Fig7.16.

(The extrapolate to $E^\circ = 0.2232\ \text{V}$)

► Table7.2 lists standard potentials at 298K. If the chemical equation or a half-reaction is multiplied by a numerical factor, the standard emf and standard potentials of electrodes are unchanged.

A numerical factor increases the standard Gibbs energy, but it also increases the number of electrons transferred by the same factor and the value of E° remains unchanged. (Cell emf is an intensive property)

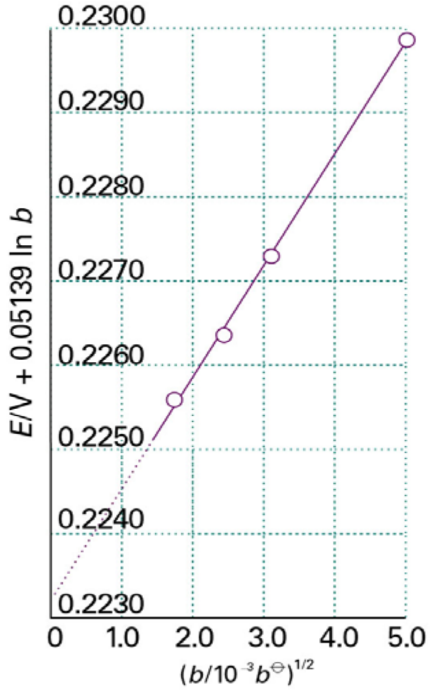
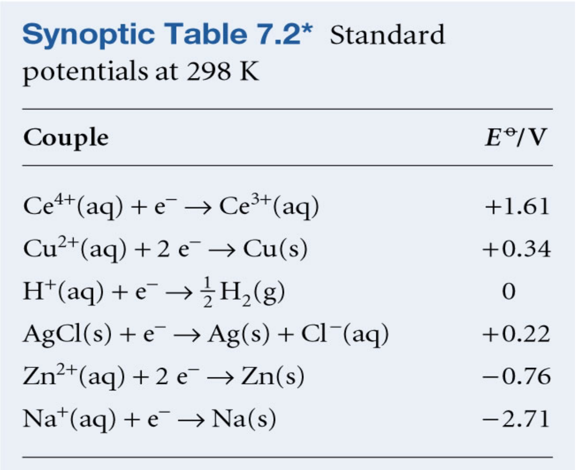


Fig. 7.16 The plot and the extrapolation used for the experimental measurement of a standard cell emf. The intercept at $b^{1/2} = 0$ is $E^\ominus$.



Synoptic Table 7.2* Standard potentials at 298 K

Couple	$E^\ominus$/V
$Ce^{4+}(aq) + e^- \rightarrow Ce^{3+}(aq)$	+1.61
$Cu^{2+}(aq) + 2\,e^- \rightarrow Cu(s)$	+0.34
$H^+(aq) + e^- \rightarrow \frac{1}{2}H_2(g)$	0
$AgCl(s) + e^- \rightarrow Ag(s) + Cl^-(aq)$	+0.22
$Zn^{2+}(aq) + 2\,e^- \rightarrow Zn(s)$	−0.76
$Na^+(aq) + e^- \rightarrow Na(s)$	−2.71

7.9 Application of standard potentials

(a) The electrochemical series

Two redox couples, Ox_1/Red_1 and Ox_2/Red_2

$Red_1, Ox_1 \parallel Red_2, Ox_2$, $E^\circ = E_2^\circ - E_1^\circ$

The cell reaction

$Red_1 + Ox_2 \rightarrow Ox_1 + Red_2$ is spontaneous if $E^\circ > 0$,

therefore $E_2^\circ > E_1^\circ$

Red_1 reduces Ox_2

Red_1 has a thermodynamic tendency to reduce Ox_2

if $E_1^\circ < E_2^\circ$

Table7.3 shows the electrochemical series

Zinc → "cannot reduce magnesium ions in aqueous solution"

Zinc → "can reduce hydrogen ions"

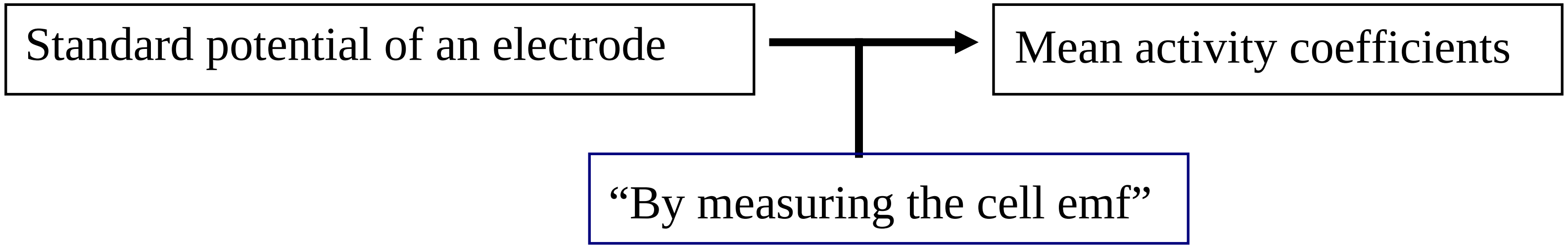
Table 7.3 The electrochemical series of the metals*

Least strongly reducing
Gold
Platinum
Silver
Mercury
Copper
(Hydrogen)
Lead
Tin
Nickel
Iron
Zinc
Chromium
Aluminium
Magnesium
Sodium
Calcium
Potassium
Most strongly reducing

* The complete series can be inferred from Table 7.2.

7.9 Application of standard potentials

(b) The determination of activity coefficients



Standard potential of an electrode

Mean activity coefficients

"By measuring the cell emf"

The mean activity coefficient of the ions in hydrochloric acid;

$$\ln \gamma_{\pm} = \frac{E^{\circ} - E}{2RT/F} - \ln b$$

, b : Molality

(c) The determination of equilibrium constants

The standard emf of a cell can be calculated by the standard potential of each electrodes.

$$\boxed{E^{\circ} = E^{\circ}(right) - E^{\circ}(left)}$$

If the result gives $E^{\circ} > 0$, the cell reaction has $K > 1$

7.9 Application of standard potentials

(d) Species-selective electrodes

► Glass electrode (see Fig7.18)

- sensitive to hydrogen ion activity, potential proportional to pH

- glass membrane : permeable to Na^+ and Li^+ ions, but not to H^+.→ **potential difference**

- Mechanism (see Fig7.19) ;

<u>Charge modification (Na^+, Li^+)</u>

\+ <u>Hydrogen ions modify hydrated silica layer</u>

► Gas-sensing electrode

- application of glass electrode.

- sulfur dioxide or ammonia diffuse into the aqueous solution → modifies pH of solution

→ affects the potential of the glass electrodes

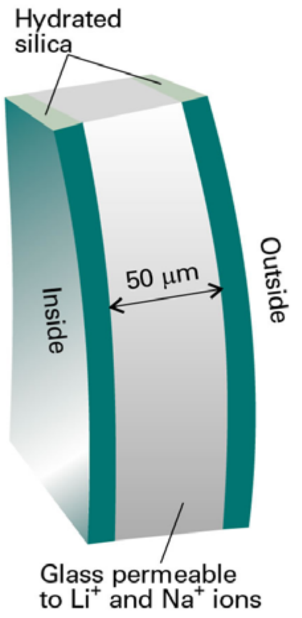


Fig. 7.19 A section through the wall of a glass electrode.

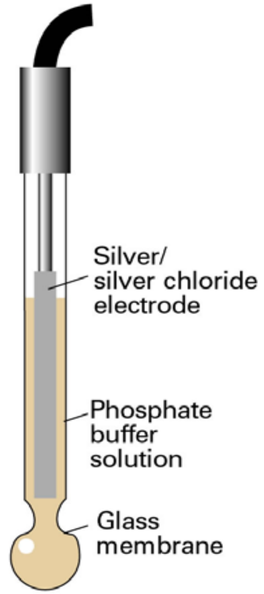


Fig. 7.18 The glass electrode. It is commonly used in conjunction with a calomel electrode that makes contact with the test solution through a salt bridge.

7.9 Application of standard potentials

► **Ion-selective electrodes.** (see Fig7.20)

- A porous lipophilic membrane is attached to the hydrophobic liquid.

(hydrophobic liquid contains $(RO)_2PO_2$ with R a C_8 to C_{18} chain → form a complex → complex's ions migrate through the lipophilic membrane → give rise to transmembrane potential→ detected by silver/silver chloride electrode)

- **In theory** : The transmembrane potential should be determined by differences in the activity of the species.

- **In practice** : Asymmetry potential is observed.

(All species-selective electrodes are sensitive to more than one species.)

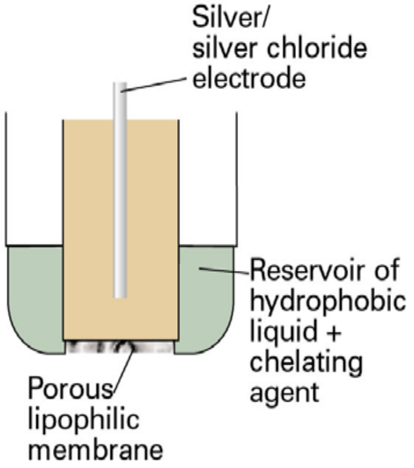


Fig. 7.20 The structure of an ion-selective electrode. Chelated ions are able to migrate through the lipophilic membrane.

$$\boxed{E = E_{ap} + \beta \frac{RT}{F} \ln(a_{X^+} + k_{X,Y} a_{Y^+})}$$

E_{ap} : the asymmetry potential

β: an experimental parameter

$K_{X,Y}$: the selective coefficient

$\beta = 1$: The electrode responds to the activity of ions in solution in a way that is consistent with the Nernst equation

7.9 Application of standard potentials

(e) The determination of thermodynamic functions

The standard emf is related to the standard reaction Gibbs energy (see eqn 7.28)

$$(\Delta_r G^\circ) = -\nu F E^\circ$$

By measuring E°, we can calculate the Gibbs energy of formation of ions. (Section 3.6)

The temperature coefficient of the standard cell emf, dE° / dT gives the standard entropy of the cell reaction.

$$(\partial G / \partial T)_P = -S \ , \qquad \frac{dE^\circ}{dT} = \frac{\Delta_r S^\circ}{\nu F}$$

E° and $\Delta_r G^\circ$ are independent of the pressure.

► Standard reaction enthalpy;

$$\boxed{\Delta_r H^\circ = \Delta_r G^\circ + T\Delta_r S^\circ = -\nu F (E^\circ - T\frac{dE^\circ}{dT})}$$