

COURSE CODE: SC202(CHEMISTRY)
COURSE INSTRUCTOR: DR. DEBARATI MITRA &
DR. SANGITA TALUKDAR
DEPT. OF SCIENCE AND MATHEMATICS
IIITG, GUWAHATI
LECTURE- CHEMICAL EQUILIBRIUM
DATE: 11.01.2023 & 12.01.2023

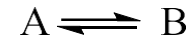
Chemical Equilibrium

(a) The reaction Gibbs energy is the slope of the plot of Gibbs energy against extent of reaction.

(b) Reactions are either exergonic (release of energy) or endergonic (absorption of energy).

(a) The reaction Gibbs energy

Consider the equilibrium



Suppose an infinitesimal amount $d\xi$ of A turns into B; then the change in the amount of A present is $dn_A = -d\xi$ and the change in the amount of B present is $dn_B = +d\xi$. **The quantity ξ (xi) is called the extent of reaction; it is reported in moles.** When the extent of reaction changes by a finite amount $\Delta\xi$, the amount of A present changes from $n_{A,0}$ to $n_{A,0} - \Delta\xi$ and the amount of B changes from $n_{B,0}$ to $n_{B,0} + \Delta\xi$.

The **reaction Gibbs energy**, $\Delta_r G$, is defined as **the slope of the graph of the Gibbs energy plotted against the extent of reaction:**

$$\Delta_r G = \left(\frac{\partial G}{\partial \xi} \right)_{p,T} \longrightarrow (1)$$

Here, Δ signifies a *derivative*, the slope of G with respect to ξ . The corresponding change in Gibbs energy is

$$dG = \mu_A dn_A + \mu_B dn_B = -\mu_A d\xi + \mu_B d\xi = (\mu_B - \mu_A) d\xi$$

This equation can be reorganized into

$$\left(\frac{\partial G}{\partial T}\right)_{p,T} = \mu_B - \mu_A$$

That is,

$$\Delta_r G = \mu_B - \mu_A \longrightarrow (2)$$

$\Delta_r G$ can be interpreted as the difference between the chemical potentials (the partial molar Gibbs energies) of the reactants and products *at the composition of the reaction mixture*.

The spontaneous direction of reaction lies in the direction of decreasing G (that is, down the slope of G plotted against ξ). Thus we see from eqn (2) that the reaction $A \rightarrow B$ is spontaneous when $\mu_A > \mu_B$, whereas the reverse reaction is spontaneous when $\mu_B > \mu_A$. The slope is zero, and the reaction is at **equilibrium and spontaneous in neither direction**, when

$$\Delta_r G = 0$$

**Condition of
equilibrium**

This condition occurs when $\mu_B = \mu_A$. **It follows that, if we can find the composition of the reaction mixture that ensures $\mu_B = \mu_A$, then we can identify the composition of the reaction mixture at equilibrium.**

(b) Exergonic and endergonic reactions

The spontaneity of a reaction **at constant temperature and pressure** can be expressed in terms of the reaction Gibbs energy:

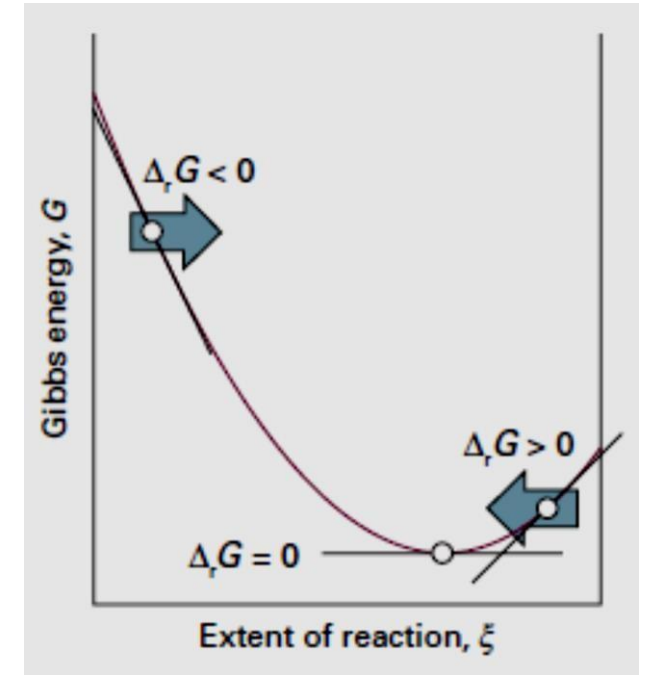
If $\Delta_r G < 0$, the forward reaction is spontaneous.

If $\Delta_r G > 0$, the reverse reaction is spontaneous.

If $\Delta_r G = 0$, the reaction is at equilibrium.

A reaction for which $\Delta_r G < 0$ is called **exergonic**. The name signifies that, because the process is spontaneous, it can be used to drive another process, such as another reaction, or used to do non-expansion work.

A reaction for which $\Delta_r G > 0$ is called **endergonic** (signifying work-consuming). The reaction can be made to occur only by doing work on it, such as electrolyzing water to reverse its spontaneous formation reaction.



As the reaction advances (represented by motion from left to right along the horizontal axis) the slope of the Gibbs energy changes. Equilibrium corresponds to zero slope, at the foot of the valley.

The description of chemical equilibrium ($A \rightleftharpoons B$):

When A and B are perfect gases, we can use eqn ($\mu = \mu^\ominus + RT \ln p$, with p interpreted as p/p^\ominus) to write

$$\begin{aligned}\Delta_r G &= \mu_B - \mu_A = (\mu_B^\ominus + RT \ln p_B) - (\mu_A^\ominus + RT \ln p_A) \\ &= \Delta_r G^\ominus + RT \ln \frac{p_B}{p_A}\end{aligned}\longrightarrow (3)$$

If we denote the ratio of partial pressures by Q , we obtain

$$\Delta_r G = \Delta_r G^\ominus + RT \ln Q \quad Q = \frac{p_B}{p_A} \longrightarrow (4)$$

The ratio Q is an example of a **reaction quotient**. It ranges from 0 when $p_B = 0$ (corresponding to pure A) to infinity when $p_A = 0$ (corresponding to pure B). The **standard reaction Gibbs energy**, $\Delta_r G^\ominus$, is defined (like the standard reaction enthalpy) as the difference in the standard molar Gibbs energies of the reactants and products. For our reaction

$$\Delta_r G^\ominus = \Delta_f G^\ominus(B) - \Delta_f G^\ominus(A) \longrightarrow (5)$$

At equilibrium $\Delta_r G = 0$. The ratio of partial pressures at equilibrium is denoted by K , and eqn (4) becomes

$$\begin{aligned}0 &= \Delta_r G^\ominus + RT \ln K \\ RT \ln K &= -\Delta_r G^\ominus \quad K = \left(\frac{p_B}{p_A} \right)_{\text{equilibrium}}\end{aligned}\longrightarrow (6)$$

Thus, from eqn (6), when $\Delta_r G^\ominus > 0$, $K < 1$. Therefore, at equilibrium the partial pressure of A exceeds that of B, which means that the reactant A is favoured in the equilibrium. When $\Delta_r G^\ominus < 0$, $K > 1$, so at equilibrium the partial pressure of B exceeds that of A. Now the product B is favoured in the equilibrium.

Problem 1: Calculate the equilibrium constant for the ammonia synthesis reaction, $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons \text{NH}_3(\text{g})$, at 298 K.

$$\Delta_f G^\circ(\text{NH}_3, \text{g}) = -16.5 \text{ kJ mol}^{-1}$$

The standard Gibbs energy of the reaction is

$$\begin{aligned} \Delta_r G^\circ &= 2\Delta_f G^\circ(\text{NH}_3, \text{g}) - \{\Delta_f G^\circ(\text{N}_2, \text{g}) + 3\Delta_f G^\circ(\text{H}_2, \text{g})\} \\ &= 2\Delta_f G^\circ(\text{NH}_3, \text{g}) = 2 \times (-16.5 \text{ kJ mol}^{-1}) \end{aligned} \quad (\Delta_f G^\circ \text{ of any element e.g., } \text{N}_2 \text{ is zero as in standard state.})$$

Then,

$$\ln K = -\frac{2 \times (-16.5 \times 10^3 \text{ J mol}^{-1})}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})} = \frac{2 \times 16.5 \times 10^3}{8.3145 \times 298}$$

$$K = 6.1 \times 10^5.$$

Problem 2: $\text{A} \rightleftharpoons \text{B}$ Find $\log K_{\text{eq}} = ?$

If $\Delta_r H^\circ = -54.07 \text{ KJ/mol}$

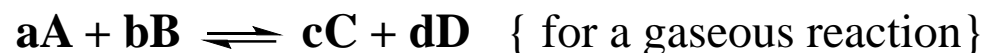
$\Delta_r S^\circ = 10 \text{ J/mol}$

$R = 8.314 \text{ J/molK}$

Relation between the equilibrium constants

Two types of Equilibrium constants

1. K_c = Active masses is expressed in molarity (n/V)
2. K_p = Active masses is expressed in partial pressures of gases



$$K_p = (P_C^c)(P_D^d) / (P_A^a)(P_B^b)$$

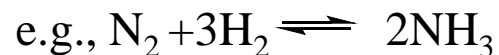
$$PV = nRT$$

$$P = nRT/V = cRT$$

$$K_p = (C_c RT)^c (C_D RT)^d / (C_A RT)^a (C_B RT)^b = [C]^c [D]^d \cdot (RT)^{(c+a)-(a+b)} / [A]^a [B]^b$$

$$\boxed{K_p = K_c (RT)^{\Delta n}}$$

$$\Delta n_g = n_p - n_R$$



$$\Delta n_g = 2 - 4 = -2; K_p = K_c (RT)^{-2}$$

Problem 3: The standard reaction Gibbs energy for the decomposition $\text{H}_2\text{O}(\text{g}) \longrightarrow \text{H}_2(\text{g}) + 1/2\text{O}_2(\text{g})$ is 118.08 KJ/mol at 2300 K. What is the degree of dissociation of H_2O at 2300 K and 1 bar?

Le Chatelier's principle

A system at equilibrium, when subjected to a disturbance, responds in a way that tends to minimize the effect of the disturbance.

The principle implies that, if a system at equilibrium is compressed, then the reaction will adjust so as to minimize the increase in pressure.

Consider, for instance, the perfect gas equilibrium $A \rightleftharpoons 2 B$, for which the equilibrium constant is

$$K = \frac{p_B^2}{p_A p^\ominus} \longrightarrow (16)$$

To treat the effect of compression quantitatively, we suppose that there is an amount n of A present initially (and no B). At equilibrium the amount of A is $(1 - \alpha)n$ and the amount of B is $2\alpha n$, where α is the degree of dissociation of A into 2B. It follows that the mole fractions present at equilibrium are

$$x_A = \frac{(1 - \alpha)n}{(1 - \alpha)n + 2\alpha n} = \frac{1 - \alpha}{1 + \alpha} \quad x_B = \frac{2\alpha}{1 + \alpha} \longrightarrow (17)$$

The equilibrium constant for the reaction is

$$K = \frac{p_B^2}{p_A p^\ominus} = \frac{x_B^2 p^2}{x_A p p^\ominus} = \frac{4\alpha^2 (p/p^\ominus)}{1 - \alpha^2} \quad \text{which rearranges to, } \alpha = \left(\frac{1}{1 + 4p/Kp^\ominus} \right)^{1/2} \longrightarrow (18)$$

This formula shows that, **even though K is independent of pressure, the amounts of A and B do depend on pressure.** It also shows that, as p is increased, α decreases, in accord with Le Chatelier's principle.

Response of equilibria to changes of temperature

Le Chatelier's principle predicts that a system at equilibrium will tend to shift in the endothermic direction if the temperature is raised (energy is absorbed as heat and the rise in temperature is opposed). Conversely, an equilibrium can be expected to shift in the exothermic direction if the temperature is lowered (energy is released and the reduction in temperature is opposed). These conclusions can be summarized as follows:

Exothermic reactions: Increased temperature favours the reactants.

Endothermic reactions: Increased temperature favours the products.

The van't Hoff equation

The van't Hoff equation, is an expression for the slope of a plot of the equilibrium constant (specifically, $\ln K$) as a function of temperature. It may be expressed in either of two ways:

$$(a) \frac{d \ln K}{dT} = \frac{\Delta_r H^\ominus}{RT^2} \quad (b) \frac{d \ln K}{d(1/T)} = -\frac{\Delta_r H^\ominus}{R}$$

Van't Hoff
equation

→ (19)

Derivation

From eqn (6), we know that

$$\ln K = -\frac{\Delta_r G^\ominus}{RT} \longrightarrow (20)$$

Differentiation of $\ln K$ with respect to temperature then gives

$$\frac{d \ln K}{dT} = -\frac{1}{R} \frac{d(\Delta_r G^\ominus/T)}{dT} \longrightarrow (21)$$

To develop this equation, we use the Gibbs–Helmholtz equation in the form

$$\frac{d(\Delta_r G^\ominus/T)}{dT} = -\frac{\Delta_r H^\ominus}{T^2} \longrightarrow (22)$$

where $\Delta_r H^\ominus$ is the standard reaction enthalpy at the temperature T . Combining the two equations (21) and (22) gives the van't Hoff equation, eqn (19a). The second form of the eqn (19b) is obtained by noting that

$$\frac{d(1/T)}{dT} = -\frac{1}{T^2}, \quad \text{so} \quad dT = -T^2 d(1/T) \longrightarrow (23)$$

Thus, putting this value in eqn (22)

$$-\frac{d \ln K}{T^2 d(1/T)} = \frac{\Delta_r H^\ominus}{RT^2} \longrightarrow (24)$$

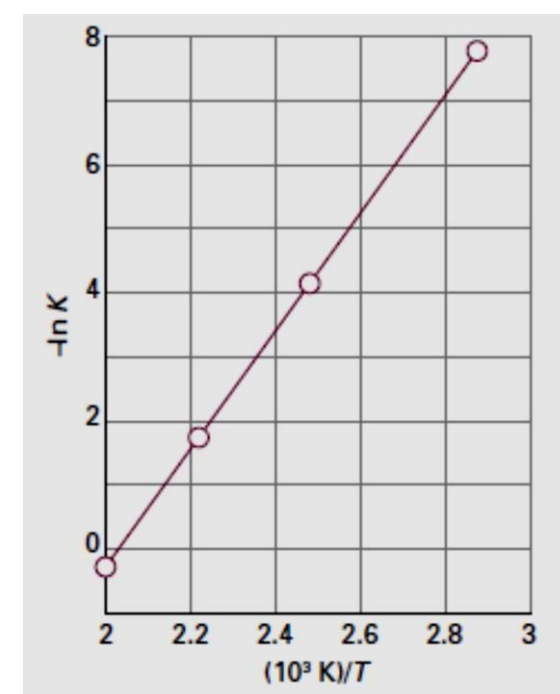


Fig 1: When $-\ln K$ is plotted against $1/T$, a straight line is expected with slope equal to $\Delta_r H^\ominus/R$

The value of K at different temperatures

To find the value of the equilibrium constant at a temperature T_2 in terms of its value K_1 at another temperature T_1 , we integrate eqn (19 b) between these two temperatures:

$$\ln K_2 - \ln K_1 = -\frac{1}{R} \int_{1/T_1}^{1/T_2} \Delta_r H^\ominus d(1/T) \longrightarrow (25)$$

If we suppose that $\Delta_r H^\ominus$ varies only slightly with temperature over the temperature range of interest, then we may take it outside the integral. It follows that

$$\ln K_2 - \ln K_1 = -\frac{\Delta_r H^\ominus}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad \boxed{\text{Temperature dependence of } K} \longrightarrow (26)$$

Problem 2: Estimate the equilibrium constant for the synthesis of ammonia at 500 K from its value at 298 K ($K_1 = 6.1 \times 10^5$).

$$\Delta_f H^\circ(\text{NH}_3) = -92.2 \text{ kJ mol}^{-1}$$

$$\ln K_2 - \ln K_1 = - \frac{\Delta_r H^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\begin{aligned} \ln K_2 &= \ln(6.1 \times 10^5) - (-92.2 \times 10^3 \text{ J mol}^{-1}) / (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) (1/500 \text{ K} - 1/298 \text{ K}) \\ &= -1.71 \end{aligned}$$

$K_2 = 0.18$, a lower value than at 298 K, as expected for this exothermic reaction.

Problem 3: The equilibrium constant for $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$ is 0.15 at 298 K. Estimate its value at 100°C.

Equilibrium Electrochemistry

An **electrochemical cell** consists of two **electrodes** or metallic conductors in contact with an **electrolyte** being an ionic conductor (which may be a solution, a liquid, or a solid).

An electrode and its electrolyte comprise **an electrode compartment**. If the electrolytes are different, the two compartments may be joined by a **salt bridge**, which is a tube containing a concentrated electrolyte solution (for instance, potassium chloride in agar jelly) that completes the electrical circuit and enables the cell to function.

A **galvanic cell** is an electrochemical cell that produces electricity as a result of the spontaneous reaction occurring inside it.

An **electrolytic cell** is an electrochemical cell in which a non-spontaneous reaction is driven by an external source of current.

Oxidation is the removal of electrons from a species, a **reduction** is the addition of electrons to a species, and a **redox reaction** is a reaction in which there is a transfer of electrons from one species to another.

The **reducing agent** (or *reductant*) is the electron donor; the **oxidizing agent** (or *oxidant*) is the electron acceptor. The reduced and oxidized species in a half-reaction form a **redox couple**.

In general we write a couple as Ox/Red and the corresponding reduction half-reaction as



Varieties of Cells

Galvanic cells are classified as electrolyte concentration and electrode concentration cells.

In an **electrolyte concentration cell**, the electrode compartments are identical except for the concentrations of the electrolytes.

In an **electrode concentration cell** the electrodes themselves have different concentrations, either because they are gas electrodes operating at different pressures or because they are amalgams (solutions in mercury) with different concentrations

Liquid junction potentials

- In a cell with two different electrolyte solutions in contact, as in the Daniell cell, there is an additional source of potential difference across the interface of the two electrolytes. This potential is called the **liquid junction potential**, E_{lj} .
- Electrolyte concentration cells **always have a liquid junction**; electrode concentration cells **do not**.

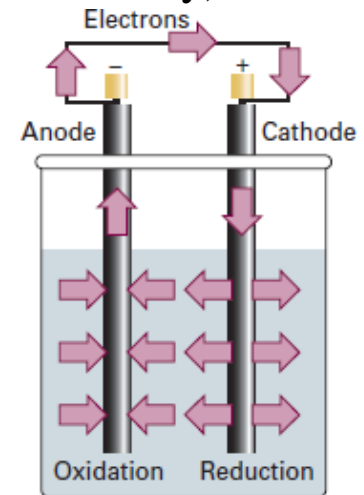


Fig 2: When a spontaneous reaction takes place in a galvanic cell, electrons are deposited in one electrode (the site of oxidation, the anode) and collected from another (the site of reduction, the cathode), and so there is a net flow of current, which can be used to do work.

The contribution of the liquid junction to the potential can be reduced (to about 1 to 2 mV) **by joining the electrolyte compartments through a salt bridge** (Fig. 4). The reason for the success of the salt bridge is that, provided the ions dissolved in the jelly have similar mobilities, then the **liquid junction potentials at either end are largely independent of the concentrations of the two dilute solutions**, and so nearly cancel.

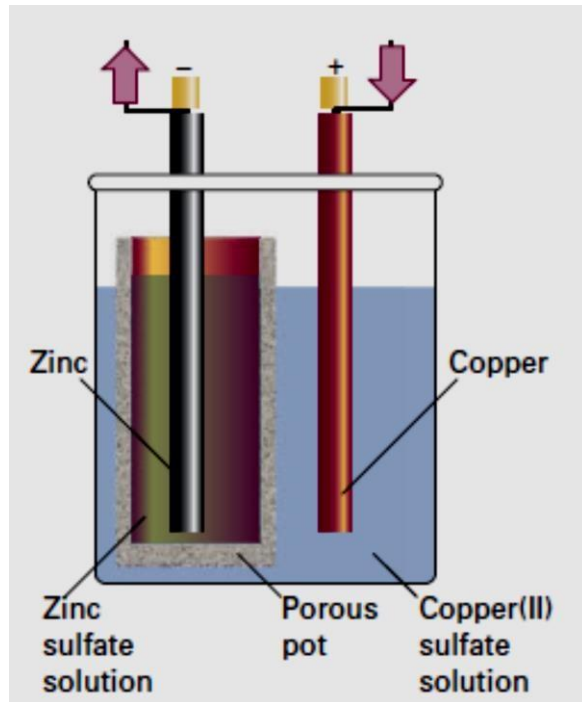


Fig 3: One version of the Daniell cell. The copper electrode is the cathode and the zinc electrode is the anode. Electrons leave the cell from the zinc electrode and enter it again through the copper electrode.

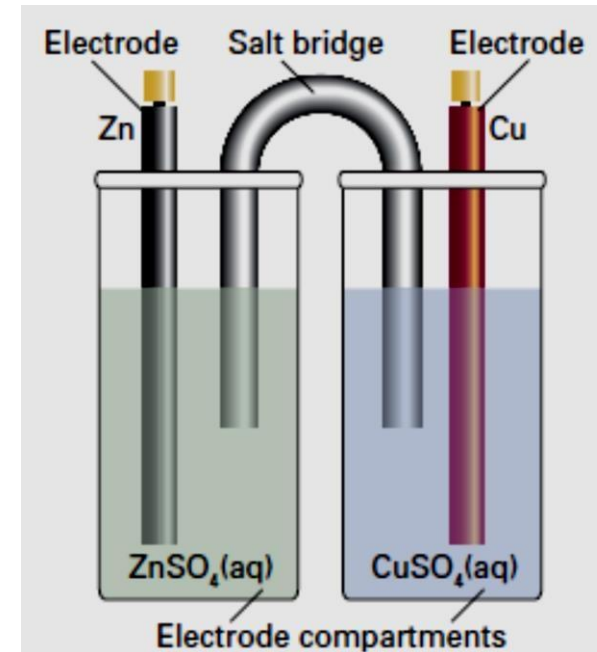
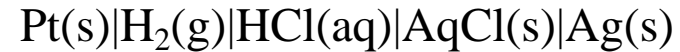
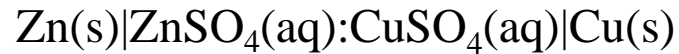


Fig 4: The salt bridge, essentially an inverted U-tube full of concentrated salt solution in a jelly, has two opposing liquid junction potentials that almost cancel.

In the notation for cells, phase boundaries are denoted by a **vertical bar**. For example,



A liquid junction is denoted by **:**, so the cell in Fig. 3 is denoted



A double vertical line, **||**, denotes **an interface** for which it is assumed that the junction potential has been eliminated. Thus the cell in Fig. 4 is denoted



An example of an electrolyte concentration cell in which the liquid junction potential is assumed to be eliminated is



The **cell reaction** is the reaction in the cell written on the assumption that the **right-hand electrode is the cathode**.

Thus, in the cell $\text{Zn(s)}|\text{ZnSO}_4(\text{aq})||\text{CuSO}_4(\text{aq})|\text{Cu(s)}$

the two electrodes and their reduction half-reactions are

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

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

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

A cell in which the overall cell reaction **has not reached chemical equilibrium can do electrical work** as the reaction drives electrons through an external circuit. The work that a given transfer of electrons can accomplish depends on the **potential difference between the two electrodes**. When the potential difference is large, a given number of electrons travelling between the electrodes can do a large amount of electrical work. When the potential difference is small, the same number of electrons can do only a small amount of work. A cell in which the overall reaction is at equilibrium can do no work, and then the potential difference is zero.

The **cell potential**, E_{cell} , is the measure of the **potential** difference between two half **cells** in an electrochemical **cell**.

The **electromotive force** of a **cell** or **EMF** of a **cell** is the maximum **potential** difference between two electrodes of a **cell**.

IUPAC prefers the term ‘cell potential’ because a potential difference is not a force.

The relation between the cell potential and the reaction Gibbs energy

We consider the change in G when the cell reaction advances by an infinitesimal amount $d\xi$ at some composition. We can write (at constant temperature and pressure)

$$dG = \Delta_r G d\xi \longrightarrow (27)$$

The maximum non-expansion (electrical) work that the reaction can do as it advances by $d\xi$ at constant temperature and pressure is therefore

$$dw_e = \Delta_r G d\xi \longrightarrow (28)$$

Suppose that the reaction advances by $d\xi$; then $\nu d\xi$ electrons must travel from the anode to the cathode. **The total charge transported between the electrodes when this change occurs is $-\nu e N_A d\xi$ (because $\nu d\xi$ is the amount of electrons and the charge per mole of electrons is $-e N_A$).**

Hence, the total charge transported is $-\nu F d\xi$ because $e N_A = F$.

The work done when an infinitesimal charge $-\nu F d\xi$ travels from the anode to the cathode is equal to the product of the charge and the potential difference E_{cell}

$$dw_e = -\nu F E_{\text{cell}} d\xi \longrightarrow (29)$$

When we equate this eqn (29) to eqn (28), the advancement $d\xi$ cancels, and we obtain eqn (30).

$$-\nu F E_{\text{cell}} = \Delta_r G \longrightarrow (30) \quad \boxed{\text{The cell potential}}$$

where F is Faraday's constant, $F = e N_A$, and ν is the stoichiometric coefficient of the electrons in the half-reactions into which the cell reaction can be divided.

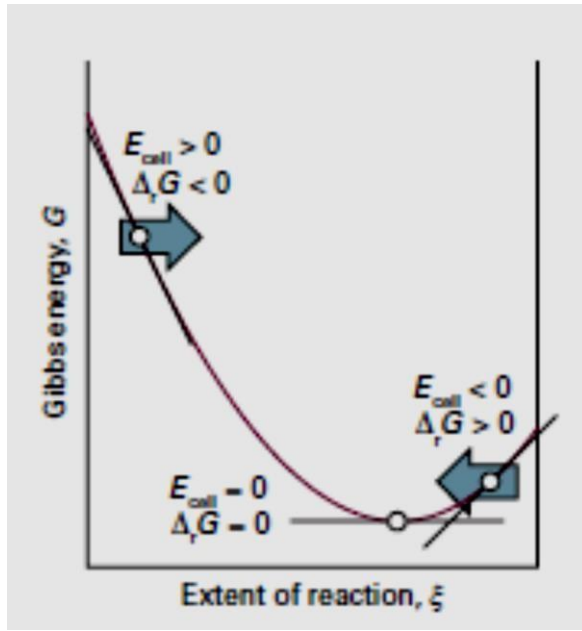


Fig 5: A spontaneous reaction occurs in the direction of decreasing Gibbs energy and can be expressed in terms of the cell potential, E_{cell} . The reaction is spontaneous as written (from left to right on the illustration) when $E_{\text{cell}} > 0$. The reverse reaction is spontaneous when $E_{\text{cell}} < 0$. When the cell reaction is at equilibrium, the cell potential is zero.

Eqn (30) provides an electrical method for measuring a reaction Gibbs energy at any composition of the reaction mixture: we simply measure the cell potential and convert it to $\Delta_r G$. Conversely, **if we know the value of $\Delta_r G$ at a particular composition, then we can predict the cell potential.** For example, if $\Delta_r G = -1 \times 10^2 \text{ kJ mol}^{-1}$ and $\nu = 1$, then

$$\begin{aligned} E_{\text{cell}} &= -\Delta_r G / \nu F = (-1 \times 10^5 \text{ J mol}^{-1}) / 1 \times (9.6485 \times 10^4 \text{ C mol}^{-1}) \\ &= 1 \text{ V} \end{aligned}$$

where we have used $1 \text{ J} = 1 \text{ C V}$

The reaction Gibbs energy is related to the composition of the reaction mixture by eqn ($\Delta_r G = \Delta_r G^\ominus + RT \ln Q$); it follows, on division of both sides by $-vF$, that

$$E_{\text{cell}} = -\frac{\Delta_r G^\ominus}{vF} - \frac{RT}{vF} \ln Q \longrightarrow (31)$$

The first term on the right is written

$$E_{\text{cell}}^\ominus = -\frac{\Delta_r G^\ominus}{vF} \quad \boxed{\text{Definition of standard cell potential}} \longrightarrow (32)$$

and called the **standard cell potential**. That is, the standard cell potential is the standard reaction Gibbs energy expressed as a potential difference (in volts). It follows that

$$E_{\text{cell}} = E_{\text{cell}}^\ominus - \frac{RT}{vF} \ln Q \longrightarrow (33)$$

This equation for the cell potential in terms of the composition is called the **Nernst equation**.

Because $RT/F = 25.7 \text{ mV}$ at 25°C , a practical form of the Nernst equation is

$$E_{\text{cell}} = E_{\text{cell}}^\ominus - \frac{25.7 \text{ mV}}{v} \ln Q \longrightarrow (34)$$

Thus, for a reaction in which $v = 1$, if Q is increased by a factor of 10, then the cell potential decreases by 59.2 mV.

(b) Cells at equilibrium

Suppose the reaction has reached equilibrium; then $Q = K$, where K is the equilibrium constant of the cell reaction.

However, a chemical reaction at equilibrium cannot do work, and hence it generates zero potential difference between the electrodes of a galvanic cell. Therefore, setting $E_{\text{cell}} = 0$ and $Q = K$ in the Nernst equation gives

$$\ln K = \frac{vFE_{\text{cell}}^{\ominus}}{RT}$$

Equilibrium constant and
standard cell potential

—————→ (35)

Standard electrode potentials

A galvanic cell is a combination of two electrodes each of which can be considered to make a characteristic contribution to the overall cell potential. Although it is not possible to measure the contribution of a single electrode, we can define the potential of one of the electrodes as zero and then assign values to others on that basis. The specially selected electrode is the standard hydrogen electrode (SHE):



The standard potential of a couple is the cell potential in which it forms the right-hand electrode and the left-hand electrode is a standard hydrogen electrode.

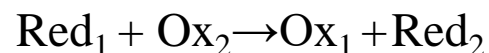
Applications of Standard Potentials

(a) The electrochemical series

We have seen that for two redox couples, Ox_1/Red_1 and Ox_2/Red_2 , and the cell

$$\text{Red}_1, \text{Ox}_1 \parallel \text{Red}_2, \text{Ox}_2 \qquad E_{\text{cell}}^{\ominus} = E_2^{\ominus} - E_1^{\ominus} \qquad \longrightarrow \qquad (36)$$

that the cell reaction



has $K > 1$ as written if $E_{\text{cell}}^{\ominus} > 0$, and therefore if $E_2^{\ominus} > E_1^{\ominus}$.

Because in the cell reaction,

Red_1 reduces Ox_2 , we can conclude that

Red_1 has a thermodynamic tendency (in the sense $K > 1$) to reduce Ox_2 if $E_1^{\ominus} < E_2^{\ominus}$.

More briefly: low reduces high.

Because $E^{\ominus}(\text{Zn}^{2+}, \text{Zn}) = -0.76 \text{ V} < E^{\ominus}(\text{Cu}^{2+}, \text{Cu}) = +0.34 \text{ V}$, the reduction of Cu^{2+} by Zn is a reaction with $K > 1$, so zinc has a thermodynamic tendency to reduce Cu^{2+} ions in aqueous solution under standard conditions.

In the **electrochemical series**, the metallic elements (and hydrogen) are arranged **in the order of their reducing power as measured by their standard potentials in aqueous solution**.

A metal low in the series (with a lower standard potential) can reduce the ions of metals with higher standard potentials. For example, to determine whether zinc can displace magnesium from aqueous solutions at 298 K, **zinc lies above magnesium in the electrochemical series**, so zinc cannot reduce magnesium ions in aqueous solution.

Zinc can reduce hydrogen ions, because hydrogen lies higher in the series. However, even for reactions that are thermodynamically favourable, there may be **kinetic factors** that result in very slow rates of reaction.

Least strongly reducing

Gold

Platinum

Silver

Mercury

Copper

(Hydrogen)

Lead

Tin

Nickel

Iron

Zinc

Chromium

Aluminium

Magnesium

Sodium

Calcium

Potassium

Most strongly reducing

The electrochemical series of the metals

(b) The determination of equilibrium constants

The principal use for standard potentials is to calculate the standard potential of a cell formed from any two electrodes. To do so, we subtract the standard potential of the left-hand electrode from the standard potential of the right-hand electrode:

$$E_{\text{cell}}^{\ominus} = E^{\ominus}(\text{right}) - E^{\ominus}(\text{left}) \longrightarrow (37) \quad \boxed{\text{Cell convention}}$$

Because $\Delta_r G^{\ominus} = -vFE_{\text{cell}}^{\ominus}$, it then follows that, if the result gives $E_{\text{cell}}^{\ominus} > 0$, then the corresponding cell reaction has $K > 1$.

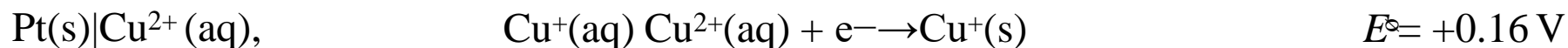
A disproportionation is a reaction in which a species is both oxidized and reduced. To study the disproportionation

$2\text{Cu}^+(\text{aq}) \rightarrow \text{Cu}(\text{s}) + \text{Cu}^{2+}(\text{aq})$ we combine the following electrodes:

Right-hand electrode:



Left-hand electrode:



where the standard potentials are measured at 298 K. The standard potential of the cell is therefore $E_{\text{cell}}^{\ominus} = +0.52 \text{ V} - 0.16 \text{ V} = +0.36 \text{ V}$

$$\text{Using the equation, } \ln K = \frac{vFE_{\text{cell}}^{\ominus}}{RT} \qquad \ln K = \frac{0.36 \text{ V}}{0.025693 \text{ V}} = \frac{0.36}{0.025693} \qquad K = 1.2 \times 10^6$$

(c) The determination of thermodynamic functions

The standard potential of a cell is related to the standard reaction Gibbs energy through eqn (30), $\Delta_r G^\ominus = -vFE_{\text{cell}}^\ominus$, therefore, by measuring E_{cell}^\ominus we can obtain this important thermodynamic quantity.

The temperature coefficient of the standard cell potential, $dE_{\text{cell}}^\ominus/dT$, gives the standard entropy of the cell reaction.

This conclusion follows from the thermodynamic relation $(\partial G/\partial T)_p = -S$ and eqn (30), which combine to give

$$\frac{dE_{\text{cell}}^\ominus}{dT} = \frac{\Delta_r S^\ominus}{vF} \quad \text{Temperature coefficient of standard cell potential} \longrightarrow (38)$$

Finally, we can combine the results obtained so far and use them to obtain the standard reaction enthalpy:

$$\Delta_r H^\ominus = \Delta_r G^\ominus + T\Delta_r S^\ominus = -vF \left(E_{\text{cell}}^\ominus - T \frac{dE_{\text{cell}}^\ominus}{dT} \right) \longrightarrow (39)$$

Problem 4. The standard potential of the cell $\text{Pt(s)}|\text{H}_2(\text{g})|\text{HBr(aq)}|\text{AgBr(s)}|\text{Ag(s)}$ was measured over a range of temperatures, and the data were found to fit the following polynomial:

$$E_{\text{cell}}^{\ominus}/\text{V} = 0.07131 - 4.99 \times 10^{-4}(T/\text{K} - 298) - 3.45 \times 10^{-6}(T/\text{K} - 298)^2$$

The cell reaction is $\text{AgBr(s)} + \text{H}_2(\text{g}) \rightarrow \text{Ag(s)} + \text{HBr(aq)}$. Evaluate the standard reaction Gibbs energy, enthalpy, and entropy at 298 K.

Answer:

$$\begin{aligned}\Delta_{\text{r}}G^{\ominus} &= -\nu FE_{\text{cell}}^{\ominus} = -(1) \times (9.6485 \times 10^4 \text{ C mol}^{-1}) \times (+0.07131 \text{ V}) \\ &= -6.880 \times 10^3 \text{ V C mol}^{-1} = -6.880 \text{ kJ mol}^{-1}\end{aligned}$$

The temperature coefficient of the cell potential is

$$\frac{dE_{\text{cell}}^{\ominus}}{dT} = -4.99 \times 10^{-4} \text{ V K}^{-1} - 2(3.45 \times 10^{-6})(T/\text{K} - 298) \text{ V K}^{-1}$$

At $T = 298 \text{ K}$ this expression evaluates to

$$\frac{dE_{\text{cell}}^{\ominus}}{dT} = -4.99 \times 10^{-4} \text{ V K}^{-1}$$

So, from eqn $\frac{dE_{\text{cell}}^{\ominus}}{dT} = \frac{\Delta_{\text{r}}S^{\ominus}}{\nu F}$, the reaction entropy is

$$\begin{aligned}\Delta_{\text{r}}S^{\ominus} &= 1 \times (9.6485 \times 10^4 \text{ C mol}^{-1}) \times (-4.99 \times 10^{-4} \text{ V K}^{-1}) \\ &= -48.1 \text{ J K}^{-1} \text{ mol}^{-1}\end{aligned}$$

$$\begin{aligned}\Delta_{\text{r}}H^{\ominus} &= \Delta_{\text{r}}G^{\ominus} + T\Delta_{\text{r}}S^{\ominus} = -6.880 \text{ kJ mol}^{-1} + (298 \text{ K}) \times (-0.0482 \text{ kJ K}^{-1} \text{ mol}^{-1}) \\ &= -21.2 \text{ kJ mol}^{-1}\end{aligned}$$

An **ion-selective electrode** is an electrode that generates a potential in response to the presence of a solution of **specific ions**. An example is the **glass electrode** (Fig. 1), which is **sensitive to hydrogen ion activity, and has a potential proportional to pH**. It is filled with a phosphate buffer containing Cl^- ions, and conveniently has $E = 0$ when the external medium is at $\text{pH} = 6$. **It is necessary to calibrate the glass electrode before use with solutions of known pH.**

The responsiveness of a glass electrode to the hydrogen ion activity is a result of complex processes at the interface between the **glass membrane and the solutions on either side of it**. The membrane itself is permeable to Na^+ and Li^+ ions but not to H^+ ions. Each face is coated with a thin layer of hydrated silica (Fig. 2). The hydrogen ions in the test solution modify this layer to an extent that depends on their activity in the solution, and the charge modification of the outside layer is transmitted to the inner layer by the Na^+ and Li^+ ions in the glass. **The hydrogen ion activity gives rise to a membrane potential by this indirect mechanism.**

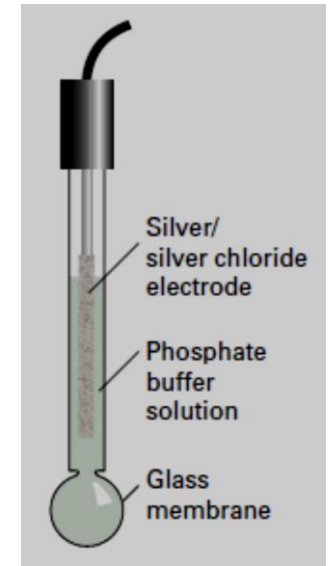


Fig 1: The glass electrode. It is commonly used in conjunction with a calomel electrode that makes contact with the test solution through a salt bridge.

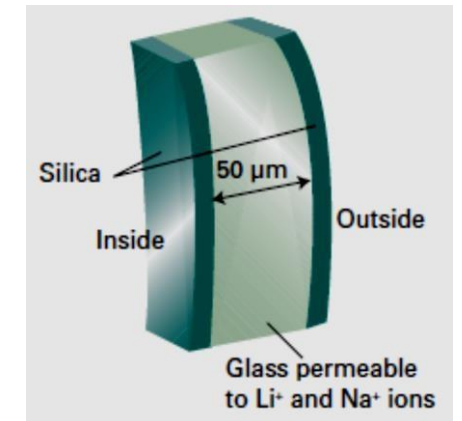


Fig 2 : A section through the wall of a glass electrode

Electrodes sensitive to hydrogen ions, and hence to pH, are typically glasses based on lithium silicate doped with heavy-metal oxides. The glass can also be made responsive to Na^+ , K^+ , and NH_4^+ ions by being doped with Al_2O_3 and B_2O_3 . A suitably adapted glass electrode can be used to detect the presence of certain gases.

A simple form of a **gas-sensing electrode** consists of a glass electrode contained in an outer sleeve filled with an aqueous solution and separated from the test solution by a membrane that is permeable to gas. When a gas such as sulfur dioxide or ammonia diffuses into the aqueous solution, it modifies its pH, which in turn affects the potential of the glass electrode.

The presence of an enzyme that converts a compound, such as urea or an amino acid, into ammonia, which then affects the pH, can be used to detect these organic compounds. Somewhat more sophisticated devices are used as ion-selective electrodes that give potentials according to the presence of specific ions present in a test solution. In one arrangement, a porous lipophilic (hydrocarbon-attracting) membrane is attached to a small reservoir of a hydrophobic (water-repelling) liquid, such as dioctylphenylphosphonate, that saturates it (Fig. 3).

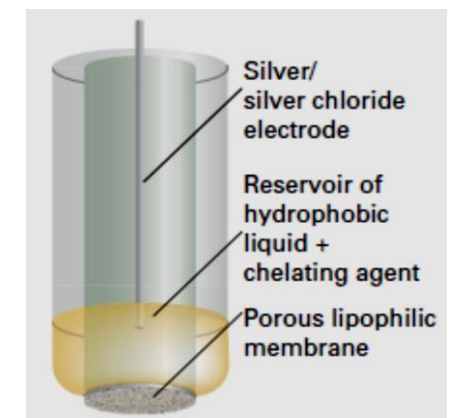


Fig. 3: The structure of an ion-selective electrode. Chelated ions are able to migrate through the lipophilic membrane.

Home Assignment

1. Find the EMF of cell at 25°C.



$$E^\circ_{\text{Zn}^{2+}/\text{Zn}} = -0.76\text{V}$$

$$E^\circ_{\text{Sn}^{2+}/\text{Sn}} = -0.14\text{V}$$

2. The equilibrium constant of a reaction is found to fit the expression $\ln K = A + B/T + C/T^3$ at 450 K with $A = -2.04$, $B = -1176\text{K}$, & $c = 2.1 \times 10^7 \text{ K}^3$. Calculate the standard reaction enthalpy & standard reaction entropy at 450K.

3. For the equilibrium, $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$, the degree of dissociation, α at 298 K is 0.201 at 1.00 bar total pressure. Calculate K.

4. Molecular bromine is 24% dissociated at 1600 K and 1 bar in the equilibrium $\text{Br}_2(\text{g}) \rightleftharpoons 2\text{Br}(\text{g})$. Calculate K at (a) 1600 K (b) 2000 K. given $\Delta_f H^\circ = 112 \text{ KJ/mol}$ over the temp range.