Part 1: Equilibrium

10. Equilibrium electrochemistry

Bilingual Program

10. Equilibrium electrochemistry

This chapter is concerned with the description of the thermodynamic properties of reactions that take place in electrochemical cells.

There are two major topics. One is for the definition and tabulation of standard potentials; the other is for the use of these standard potentials to predict the equilibrium constants of chemical reactions.

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10.1 Thermodynamic functions of formation

1) Standard functions of formation of ions

The standard enthalpy and Gibbs energy of a reaction involving ions in solution are expressed in terms of standard enthalpies and Gibbs energies of formation, which can be used in exactly the same way as those for neutral compounds. The values of $\Delta_f H^\ominus$ and $\Delta_f G^\ominus$ refer to the formation of solutions of ions from the reference states of the parent elements. However, solutions of cations cannot be prepared without their accompanying anions.

10.1 Thermodynamic functions of formation

$$\mathrm{Ag(s)} + \tfrac{1}{2}\mathrm{Cl}_2 \rightarrow \mathrm{Ag}^{+}\mathrm{(aq)} + \mathrm{Cl}^{-}\mathrm{(aq)}$$

$$\Delta_r H^{\ominus} = \Delta_f H^{\ominus}(\mathrm{Ag}^{+},\mathrm{aq}) + \Delta_f H^{\ominus}(\mathrm{Cl}^{-},\mathrm{aq})$$

But the enthalpies of the individual formation reactions are not measurable.

The problem is solved by defining one ion, conventionally the hydrogen ion, to have zero standard enthalpy and Gibbs energy of formation at all temperatures:

$$\Delta_f H^{\ominus}(\mathrm{H}^{+},\mathrm{aq}) = 0 \qquad \Delta_f G^{\ominus}(\mathrm{H}^{+},\mathrm{aq}) = 0$$

10.1 Thermodynamic functions of formation

$$\Delta_\mathrm{f} H^\ominus(\mathrm{H}^+, \mathrm{aq}) = 0 \qquad \Delta_\mathrm{f} G^\ominus(\mathrm{H}^+, \mathrm{aq}) = 0$$

In essence, this definition adjusts the actual values of the enthalpies and Gibbs energies of formation of ions by a fixed amount.

10.1 Thermodynamic functions of formation

In the reaction:

$$\tfrac{1}{2}\mathrm{H_2(g)} + \tfrac{1}{2}\mathrm{Cl_2(g)} \rightarrow \mathrm{H^+(aq)} + \mathrm{Cl^-(aq)} \qquad \Delta_r G^\ominus = -131.23\,\mathrm{kJmol^{-1}}$$

we can write

$$\Delta_r G^\ominus = \Delta_f G^\ominus(\mathrm{H^+, aq}) + \Delta_f G^\ominus(\mathrm{Cl^-, aq}) = \Delta_f G^\ominus(\mathrm{Cl^-, aq})$$

and hence identify $\Delta_f G^\ominus(\mathrm{Cl^-, aq})$ as $-131.23\ \mathrm{kJmol^{-1}}$. All the Gibbs energies and enthalpies of formation of ions in Tables 10.1 and 2.6 were calculated in this way.

10.1 Thermodynamic functions of formation

3) Standard entropies of ions in solution

Although the partial molar entropy of the solute in an electrolyte solution can be measured, there is no experimental way of ascribing a part of that entropy to the cations and a part of to anions. Therefore, we are forced to define the standard entropy of the H^+ ions in water is zero at all temperature, and the entropy of other ions in solution are reported on this basis

$$S^{\ominus}(\mathrm{H}^{+},\mathrm{aq})=0$$

10.1 Thermodynamic functions of formation

3) Standard entropies of ions in solution

Because the entropies of ions in water are values relative to the hydrogen ion in water, they may be either positive or negative.

A positive entropy means that the ion has a higher partial molar entropy than H^+ in water

A negative entropy means that the ion has a lower partial molar entropy than H^+ in water.

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10.2 Ion activities

1) The definition of activity

the chemical potential of a solute in a real solution is related to its activity *a* by

$$\mu = \mu^{\ominus} + RT\ln a$$

If the activity is related to the molality, *b*, then the standard state is a hypothetical solution with molality $b^{\ominus}$=1 mol kg^{-1} in which the ions are behaving ideally.

$$a = \gamma\, b / b^{\ominus}$$

10.2 Ion activities

1) The definition of activity

$$a = \gamma\, b / b^{\ominus}$$

where the activity coefficient, γ, depends on the composition, molality, and T of the solution. As the solution approaches ideality at low molalities, the activity coefficient tends towards 1:

$$\gamma \to 1 \;\; \text{and} \;\; a \to b/b^{\ominus} \;\; \text{as}\; b \to 0$$

10.2 Ion activities

Because all deviations from ideality are carried in the activity coefficient, the chemical potential can be written

$$\mu = \mu^{\ominus} + RT\ln b + RT\ln\gamma$$

$$= \mu^{\text{ideal}} + RT\ln\gamma$$

where μ^{ideal} is the chemical potential of the ideal-dilute solution of the same molality.

10.2 Ion activities

2) Mean activity coefficients

If the chemical potential of a univalent cation M^+ is denoted μ_+ and that of a univalent anion X^- is denoted μ_- , the total Gibbs energy of the ions in the electrically neutral solution is the sum of these partial molar quantities. The molar Gibbs energy of an ideal solution is

$$G_m^{ideal} = \mu_+^{ideal} + \mu_-^{ideal}$$

10.2 Ion activities

2) Mean activity coefficients

For a real solution of M^+ and X^- of the same molality

$$G_{\mathrm{m}} = \mu_+ + \mu_-$$

$$= \mu_+^{\mathrm{ideal}} + \mu_-^{\mathrm{ideal}} + RT\ln\gamma_+ + RT\ln\gamma_-$$

$$= G_{\mathrm{m}}^{\mathrm{ideal}} + RT\ln\gamma_+\gamma_-$$

All the deviations from ideality are in the last term.

10.2 Ion activities

2) Mean activity coefficients

There is no experimental way of separating the product $\gamma_+ \gamma_-$ into contributions from the cations and the anions. we introduce the mean activity coefficient $\gamma_\pm$:

For a 1,1−electrolyte:

$$\gamma_\pm = (\gamma_+ \gamma_-)^{1/2}$$

The individual chemical potentials of the ions is

$$\mu_+ = \mu_+^{\text{ideal}} + RT \ln \gamma_\pm \qquad \mu_- = \mu_-^{\text{ideal}} + RT \ln \gamma_\pm$$

10.2 Ion activities

2) Mean activity coefficients

It can be generalized to the case of a compound M_pX_q that dissolves to give a solution of p cations and q anions, If introduce the mean activity coefficient

$$\gamma_{\pm} = (\gamma_{+}^{p}\gamma_{-}^{q})^{1/s} \qquad s = p + q$$

The chemical potential of each ion is

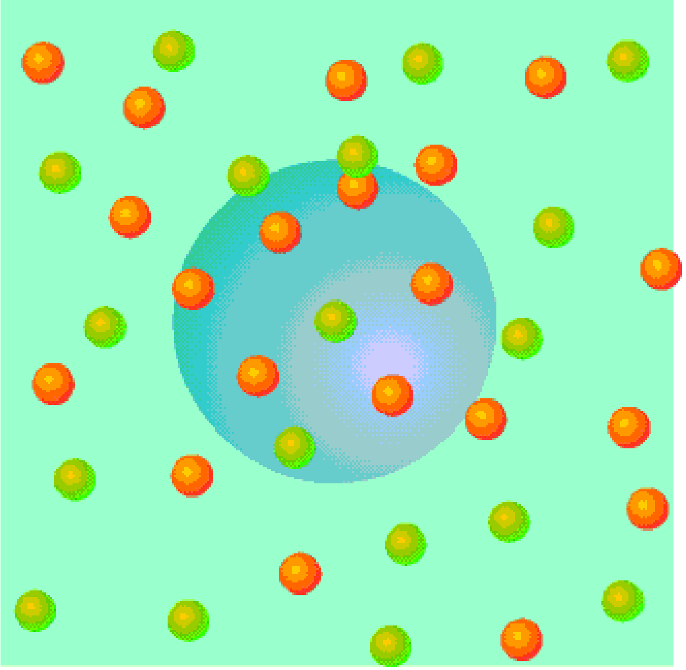
$$\mu_i = \mu_i^{\text{ideal}} + RT\ln\gamma_{\pm}$$

10.2 Ion activities

3) The Debye−Huckel limiting law

The long range and strength of the Coulombic interaction between ions means that it is likely to be primarily responsible for the departures from ideality in ionic solutions and to dominate all the other contributions to nonideality. This domination is the basis of the Debye-Huckel theory of ionic solutions.

10.2 Ion activities



The picture underlying the Debye -Hückel theory is of a tendency for anions to be found around cations, and of cations to be found around anions.

Oppositely charged ions attract one another. As a result, anions are more likely to be found near cations in solution, and vice versa. Overall the solution is electrically neutral but near any given ion there is an excess of counter-ions. Averaged over time, counter-ions are more likely to be found near any given ion. This time-averaged, spherical haze, is called its ionic atmosphere.

10.2 Ion activities

3) The Debye−Huckel limiting law

The energy, and therefore the chemical potential, of any given central ion is lowered as a result of its electrostatic interaction with its atmosphere. This lowering of energy appears as the difference between the molar Gibbs energy G_m and the ideal value G_m^{ideal} of the solute, and hence can be identified with $sRT\ln\gamma_{\pm}$.

The model leads to the result that at very low concentrations, the activity coefficient can be calculated from the Debye-Huckel limiting law

10.2 Ion activities

3) The Debye–Huckel limiting law

$$\log\gamma_{\pm} = -\left|z_{+}z_{-}\right| A I^{1/s}$$

where I is the dimensionless ionic strength of the solution:

$$I = \frac{1}{2}\sum_{i} z_i^2 (b_i / b^{\ominus})$$

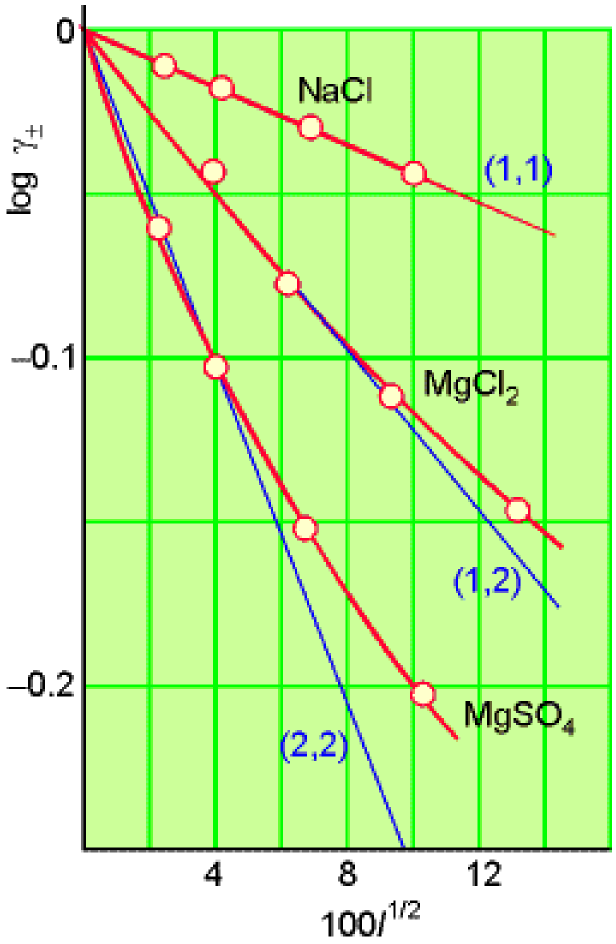
where z_i is the charge number of an ion I (positive for cations and negative for anions) and b_i is its molality.

$$A = \frac{F^3}{4\pi N_A \ln 10}\left(\frac{\rho b^{\ominus}}{2\varepsilon^3 R^3 T^3}\right)^{1/2}$$

where $A = 0.509$ for an aqueous solution at 25℃.

10.2 Ion activities

3) The Debye−Huckel limiting law



An experimental test of the Debye-Hückel limiting law. Although there are marked deviations for moderate ionic strengths, the limiting slopes as $I \rightarrow 0$ are in good agreement with the theory, so the law can be used for extrapolating data to very low molalities.

10.2 Ion activities

4) The extended Debye-Huckel law

When the ionic strength of the solution is too high for limiting law to be valid, it is found that the activity coefficient may be estimated from the extended Debye-Huckel Law:

$$\log \gamma_{\pm} = -\frac{A\left|z_{+}z_{-}\right|I^{1/2}}{1+BI^{1/2}}$$

where *B* is another dimensionless constant. Although *B* can be interpreted as a measure of the closest approach of the ions, it is best regarded as an adjustable empirical parameter.

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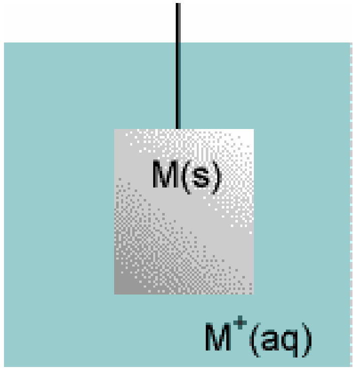
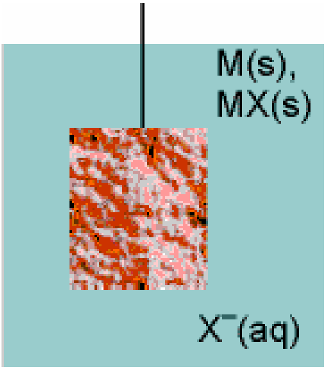
10.3 Half-reactions and electrodes

Introduction

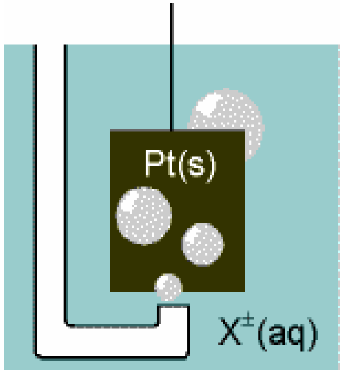
An **electrochemical cell** consists of **two electrodes** in contact with an electrolyte, an ionic conductor. An electrode and its electrolyte comprise an **electrode compartment**. The two electrodes may share the same compartment. Typical electrode types are as following:



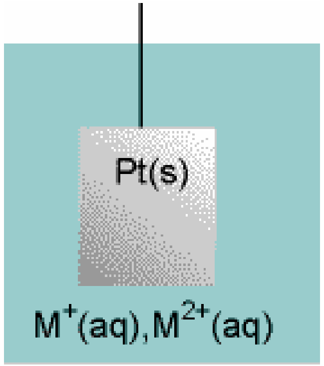
(a) metal/ metal ion



(b) metal/insoluble salt

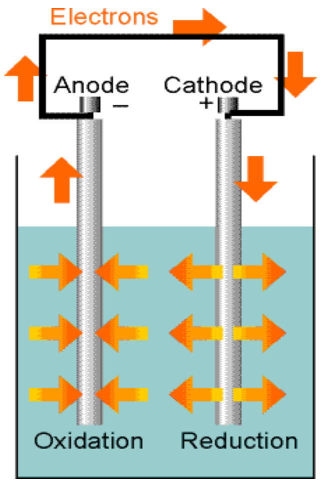


(c) gas



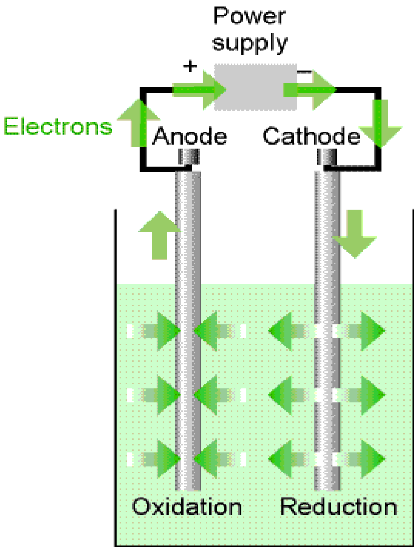
(d) redox electrodes

10.3 Half-reactions and electrodes



□ Electrochemical cells

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 nonspontaneous reaction is driven by an external source of current.

10.3 Half-reactions and electrodes

Oxidation is the removal of electrons from a species,

Reduction is the addition of electrons to a species.

A redox reaction is a reaction in which there is a transfer of electrons from one species to another. The net effect is electron transfer and hence a change in oxidation number of an element.

The reducing agent (or 'reductant') is the electron donor;
The oxidizing agent (or 'oxidant ') is the electron acceptor.

10.3 Half-reactions and electrodes

1) Half-reactions

Any redox reaction may be expressed as the difference of two reduction half-reactions, which are conceptual reactions showing the gain of electrons. For example, the reduction of Cu^{2+} ions by zinc can be expressed as the difference of the following two half-reactions:

$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ $\quad$ $Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$

The difference of the two (copper−zinc) is

$$Cu^{2+}(aq) + Zn(s) \rightarrow Cu(s) + Zn^{2+}(aq)$$

Example

Expressing a reaction in terms of half-reactions

Express the dissolution of silver chloride in water as the difference of two reduction half–reactions.

Method: First, write the overall chemical equation. Then select one of the reactants, and write a half-reaction in which it is reduced to one of the products. Next, subtract that half-reaction from the overall reaction to identify the second half-reaction. Finally, write the second half-reaction as a reduction.

Example

Answer:

The chemical equation of the overall reaction is

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

We select as one half-reaction the reduction of AgCl:

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

Subtraction of this equation from the overall reaction leaves

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

There is no net change of oxidation number in dissolution of AgCl. so it is not a redox reaction.

10.3 Half-reactions and electrodes

□ the reaction quotient, *Q*

The oxidized and reduced substances in a half-reaction form a redox couple, denoted Ox/Red. The corresponding reduction half-reaction as

$$\mathrm{Ox} + \nu e^- \rightarrow \mathrm{Red}$$

the reaction quotient, *Q*, for the half-reaction, is defined like the reaction quotient for the overall reaction, but the electrons are ignored.

10.3 Half-reactions and electrodes

□ the reaction quotient, *Q*

For the copper half-reaction

$$\mathrm{Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s)}$$

$$Q = \frac{1}{a_{\mathrm{Cu^{2+}}}}$$

Here, we have used the fact that the pure metal (the standard state of the element) has unit activity.

Example

Write the half-reaction and the reaction quotient for the reduction of oxygen to water in dilute acidic solution.

Method: **The first step is a simple balancing exercise: use H^+ ions to balance the H atoms and electrons to balance the charge. For the reaction quotient, include activities of products in the numerator and reactants (other than electrons) in the denominator.**

Example

Answer:

The reduction of O_2 in acidic solution produces H_2O according to the half-reaction

$$O_2\,(g) + 4H^+\,(aq) + 4e^- \rightarrow 2H_2O\,(aq)$$

The reaction quotient for the half-reaction is therefore

$$Q = \frac{a^2_{H_2O}}{a^4_{H^+}(f_{O_2}/p^\ominus)} \approx \frac{p^\ominus}{a^4_{H^+}\,p_{O_2}}$$

The approximations used in the second step are that $a_{H_2O} = 1$ and the oxygen behaves like a perfect gas.

10.3 Half-reactions and electrodes

2) Reactions at electrodes

In an electrochemical cell, the reduction and oxidation processes responsible for the overall reaction are separated in space: they take place in their own electrode compartment as the reaction proceeds, the electrons released in the oxidation at one electrode:

$$\mathrm{Red}_1 \rightarrow \mathrm{Ox}_1 + \nu\ \mathrm{e}^-$$

Traveling through the external circuit, the electrons reenter the cell through the other electrode and bring about reduction:

$$\mathrm{Ox}_2 + \nu\ \mathrm{e}^- \rightarrow \mathrm{Red}_2$$

10.3 Half-reactions and electrodes

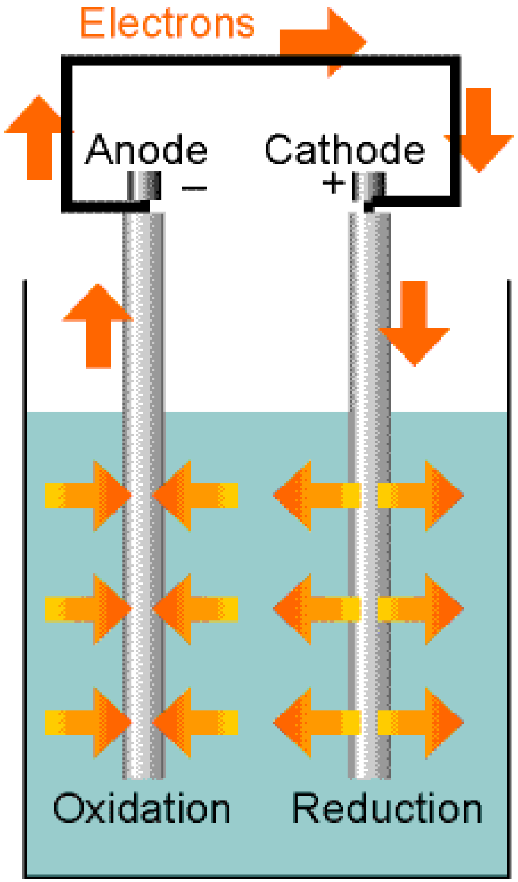
2) Reactions at electrodes

Anode The electrode at which oxidation occurs;

Cathode The electrode at which reduction occurs.

10.3 Half-reactions and electrodes

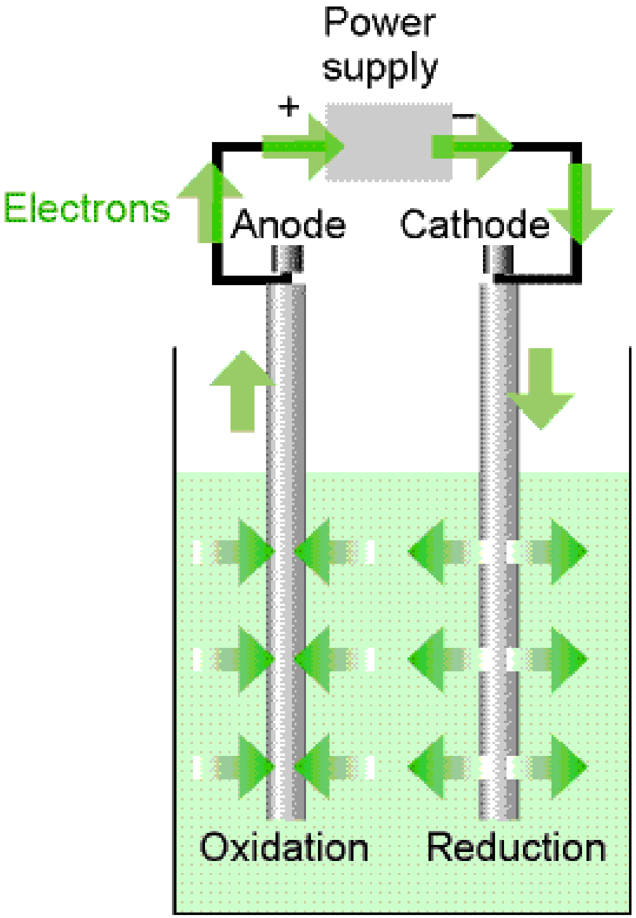
In a galvanic cell, the cathode has a higher potential than the anode.



Undergoing reduction, The species Ox_2 withdraws electrons from the cathode, and leaves a relative positive charge on it (corresponding to a higher potential). At the anode, oxidation results in the transfer of electrons to the electrode, so giving it a relative negative charge (corresponding to a lower potential).

10.3 Half-reactions and electrodes

In an electrolytic cell the anode must be made relatively positive to the cathode



The anode is still the location of oxidation, but now electrons must be withdrawn from the species in that compartment because oxidation does not occur spontaneously, and at the cathode there must be a supply of electrons to drive the reduction.

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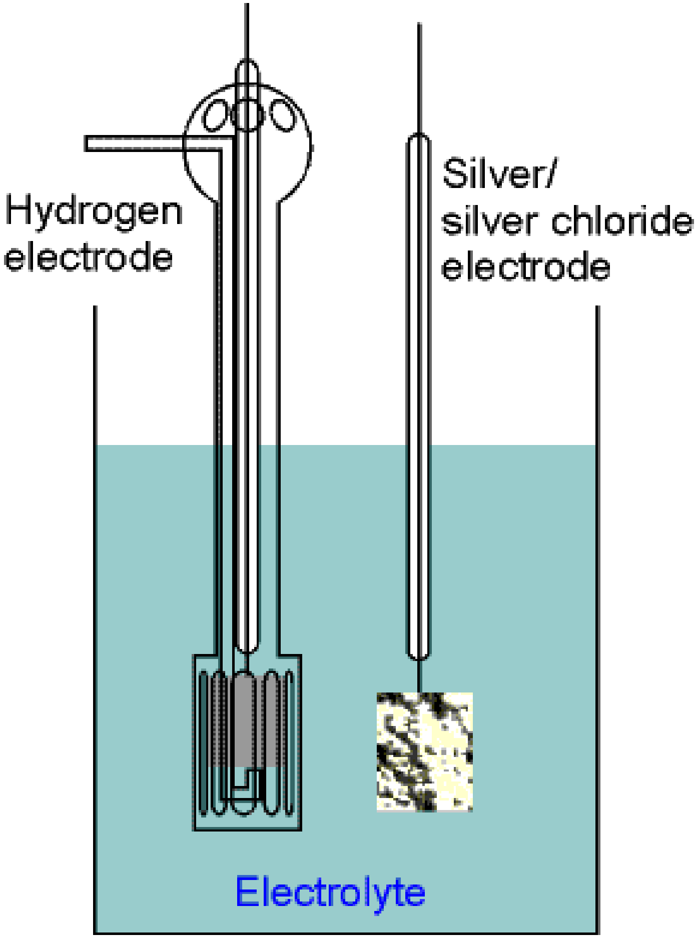
10.4 Varieties of cells

In this section, we will concentrate on:

- **Notation** ▶
- **Liquid conjunction potentials**
- **The cell reaction**
- **The cell potential**
- **The relation between E and $\Delta_r G$**
- **The Nernst equation**
- **Concentration cells**
- **Cells at equilibrium**

10.4 Varieties of cells

1) Notation

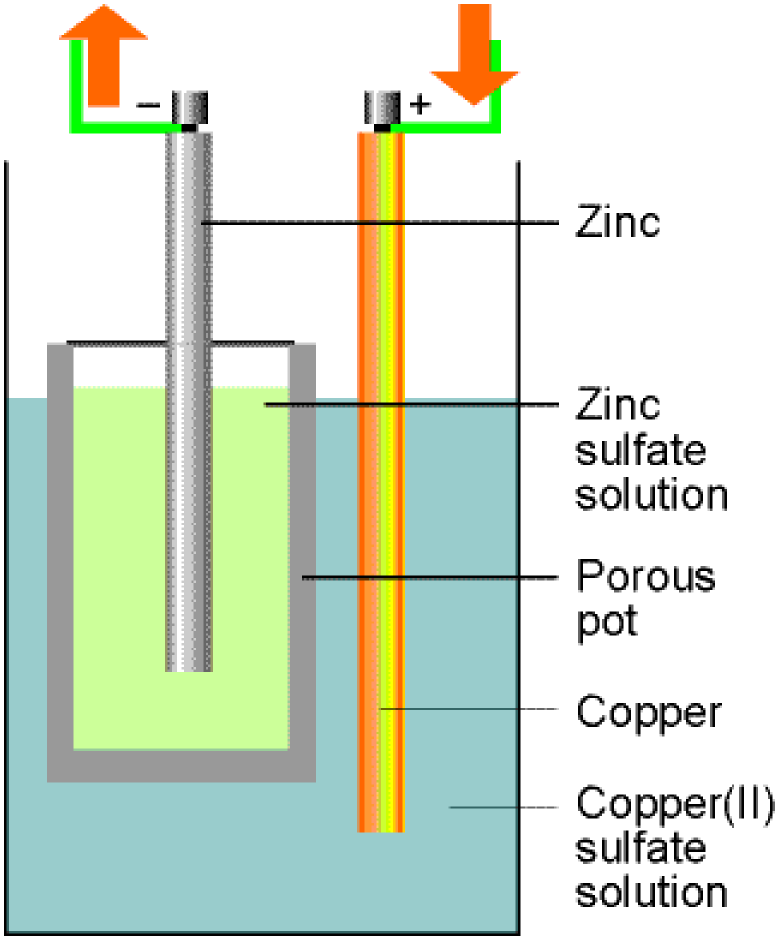


$Pt|H_2(g)|HCl(aq)|AgCl(s)|Ag(s)$

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

10.4 Varieties of cells

1) Notation

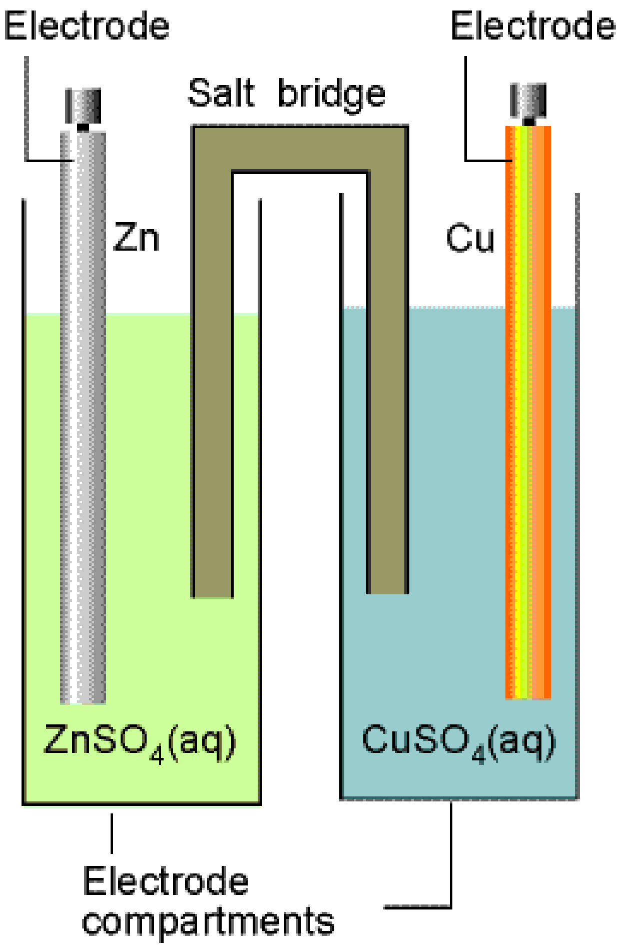


$\mathrm{Zn(s)|ZnSO_4(aq)} \vdots \mathrm{CuSO_4(aq)|Cu(s)}$

A liquid junction is denoted by $\vdots$,

10.4 Varieties of cells

1) Notation



$Zn(s)|ZnSO_4(aq)||CuSO_4\ (aq)|Cu(s)$

A double vertical line, ||, denotes an interface for which it is assumed that the junction potential has been eliminated.

10.4 Varieties of cells

2) Liquid conjunction potentials

In a cell with two different electrolyte solutions in contact, there is an additional source of potential difference, the liquid junction potential, E_{lj}, across the interface of the two electrolytes. Another liquid junction potential exist in the electrolyte concentrations cell.

10.4 Varieties of cells

2) Liquid conjunction potentials

For example, between different concentration of hydrochloric acid. At the junction, the mobile H^+ ions diffuse into the more dilute solution. The bulkier Cl^- ions follow, but initially do so more slowly, which results in a potential difference at the junction. The potential then settles down to a value such that, after that brief initial period, the ions diffuse at the same rates.

10.4 Varieties of cells

3) The cell reaction

The current produced by a galvanic cell arises from the spontaneous chemical reaction taking place inside it. The cell reaction is written on the assumption that the right-hand electrode is the cathode, and hence that the spontaneous reaction is one in which reduction is taking place in the right-hand compartment; if it is, then the cell reaction is spontaneous as written. If the left-hand electrode turns out to be the cathode, then the reverse of the cell reaction is spontaneous.

10.4 Varieties of cells

To write the cell reaction corresponding to a cell diagram, we first write the right-hand half-reaction as a reduction. Then we subtract from it the left-hand reduction half-reaction. Thus, in the cell

$$Zn(s)|ZnSO_4(aq)||CuSO_4\ (aq)|Cu(s)$$

the two electrodes' reduction half-reactions are

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

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

the overall cell reaction is the difference:

$$Cu^{2+}(aq) + Zn(s) \rightarrow Cu(s) + Zn^{2+}(aq)$$

10.4 Varieties of cells

4) The cell potential

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. This potential difference is called the cell potential and is measured in volts, V.

A cell in which the overall reaction is at equilibrium can do no work, and then the cell potential is zero.

10.4 Varieties of cells

4) The cell potential

The maximum electrical work that a system can do is given by the value of ΔG, for a spontaneous process at constant temperature and pressure:

$$w_{\mathrm{e,max}} = \Delta G$$

To make thermodynamic measurements on the cell by measuring the work it can do, we must ensure that it is operating reversibly. Only then it is producing maximum work and can be relate that work to ΔG;

10.4 Varieties of cells

Moreover, to measure $\Delta_r G$ we must ensure that the cell is operating reversibly at a specific, constant composition. Both these conditions are achieved by measuring the cell potential when it is balanced by an exactly opposing source of potential so that the cell reaction occurs reversibly and the composition is constant. The resulting potential difference is called the zero-current cell potential, E (formerly, and still commonly, the 'electromotive force', or emf, of the cell).

10.4 Varieties of cells

5) The relation between E and $\Delta_r G$

The relation between the reaction Gibbs energy and the zero-current cell potential is

$$-\nu FE = \Delta_r G$$

where F is the Faraday constant. This equation is the key connection between electrical measurements on the one hand and thermodynamic properties on the other.

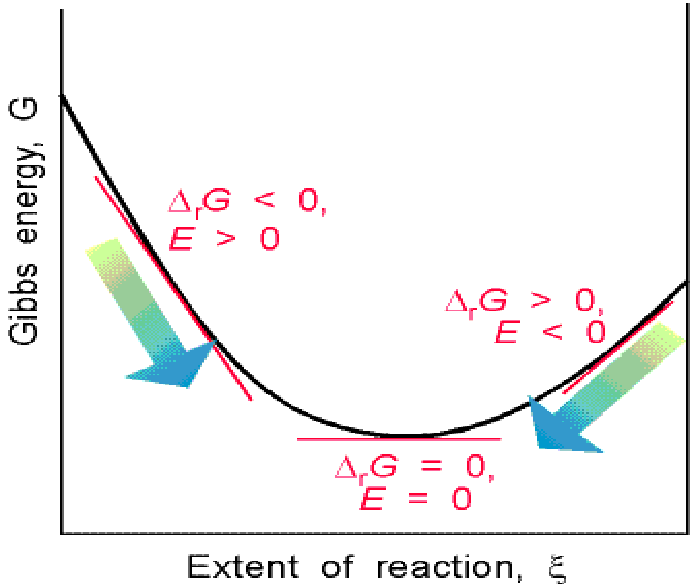
10.4 Varieties of cells

5) The relation between E and $\Delta_r G$

$$-\nu FE = \Delta_r G$$

By knowing the reaction Gibbs energy at a specified composition, we can state the zero-current cell potential at that composition. Note that a negative reaction Gibbs energy, corresponding to a spontaneous cell reaction, corresponds to a positive zero-current cell potential. The driving power of a cell is proportional to the slope of the Gibbs energy with respect to the extent reaction.

10.4 Varieties of cells



$E > 0$, the slope is steep, far from equilibrium, spontaneous reaction;

$E \to 0$, the slope is close to zero;

$E = 0$, the slope is zero, $\Delta_r G = 0$;

$E < 0$, the reverse reaction is spontaneous

10.4 Varieties of cells

6) The Nernst equation

Generally, the change in reaction Gibbs energy is related to the composition of the reaction mixture by

$$\Delta_r G = \Delta_r G^\ominus + RT\ln Q$$

with Q the reaction quotient. It follows from

$$-\nu FE = \Delta_r G$$

⇓

$$E = -\frac{\Delta_r G^\ominus}{\nu F} - \frac{RT}{\nu F}\ln Q \qquad E^\ominus = -\frac{\Delta_r G^\ominus}{\nu F}$$

10.4 Varieties of cells

6) The Nernst equation

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

This equation for the cell potential in terms of the composition is called the Nernst equation. $E^{\ominus}$ is called the standard cell potential, which can be interpreted as the zero-current cell potential when all the reactants and products are in their standard states for then all activities are 1, so $Q = 1$ and $\ln Q = 0$.

10.4 Varieties of cells

7) Concentration cells

For the potential of an electrolyte concentration cell

$$\mathrm{M} \mid \mathrm{M}^{+}(\mathrm{aq},L) \parallel \mathrm{M}^{+}(\mathrm{aq},R) \mid \mathrm{M}$$

where the solutions *L* and *R* have different molalities. The cell reaction is

$$\mathrm{M}^{+}(\mathrm{aq},L) \rightarrow \mathrm{M}^{+}(\mathrm{aq},R) \qquad Q = \frac{a_L}{a_R} \qquad \nu = 1$$

The standard cell potential is zero, and the cell potential is

$$E = -\frac{RT}{F}\ln\frac{a_L}{a_R}$$

10.4 Varieties of cells

$$E = -\frac{RT}{F}\ln\frac{a_L}{a_R} \approx -\frac{RT}{F}\ln\frac{b_L}{b_R}$$

If *Right* is the more concentrated solution, $E > 0$. Physically, the positive potential arises because positive ions tend to be reduced, so withdrawing electrons from the electrode. This process is dominant in the more concentrated right-hand electrode compartment.

10.4 Varieties of cells

8) Cells at equilibrium

A special case of Nernst equation has great importance in electrochemistry. Suppose the reaction has reached equilibrium, then $Q = K$. A chemical reaction at equilibrium cannot do work, and hence it generates zero potential difference between the electrodes of a galvanic cell.

If set $E = 0$ and $Q = K$ in the Nernst equation it gives

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

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10.5 Standard potentials

A galvanic cell is a combination of two electrodes, and each one can be considered as making 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 having a zero potential and then assign values to others on that basis. The specially selected electrode is the standard hydrogen electrode (SHE):

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

at all temperatures: $E^\ominus = 0$

10.5 Standard potentials

1) The standard potential of a cell in terms of individual standard

The standard potential of another couple is then assigned by constructing a cell in which it is the right-hand electrode and the standard hydrogen electrode is the left-hand electrode.

The value can be calculated by taking the difference of their standard potentials. This rule follows from the fact that a cell such as

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

10.5 Standard potentials

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

is equivalent to two cells joined back-to-back:

$$\mathrm{Ag(s)|Ag^{+}(aq)||H^{+}\,(aq)|H_2(g)|Pt} \text{ — } \mathrm{Pt|H_2(g)|H^{+}\,(aq)Cl^{-}(aq)|AgCl(s)|Ag(s)}$$

The overall potential of this composite cell is:

$$E^{\ominus} = E^{\ominus}(\mathrm{AgCl/Ag, Cl^{-}}) - E^{\ominus}(\mathrm{Ag^{+}/Ag}) = 0.58\,\mathrm{V}$$

Example

Identify the spontaneous direction of a reaction

One of the reactions important in corrosion in an acidic environment is

$$Fe(s) + 2H^{+}(aq) + \frac{1}{2} O_2(g) \rightarrow Fe^{2+}(aq) + H_2O(l)$$

Does the equilibrium constant favor the formation of Fe^{2+}(aq).

Example

Method: We need to decide whether the standard potential for the reaction as written is positive, for a positive value would imply that $\Delta_r G^\ominus < 0$ and hence that $K > 1$, The sign of the cell potential is found by identifying the half-reactions that make up the overall reaction, and then taking their standard potentials from the table.

Example

Answer: **The two reduction half−reactions are**

(a) $Fe^{2+}(aq) + 2e^{-} \rightarrow Fe(s)$ $\qquad E^{\ominus} = -0.44\ V$

(b) $2H^{+}(aq) + \frac{1}{2} O_2 + 2e^{-} \rightarrow H_2O(l)$ $\qquad E^{\ominus} = +1.23\ V$

The difference (b) - (a) is

$$Fe(s) + 2H^{+}(aq) + \frac{1}{2} O_2 + \rightarrow Fe^{2+}(aq) + H_2O(l)$$

$$E^{\ominus} = +1.67V$$

Because $E^{\ominus} > 0$, $K > 1$, the reaction favor products.

Example

Calculating an equilibrium constant

Calculate the equilibrium constant for the disproportionation $2Cu^{+}(aq) \rightarrow Cu(s) + Cu^{2+}(aq)$ at 298.15 K.

Method: **The strategy is to calculate the standard potential for the cell in which the reaction of interest is the cell reaction. To proceed, express the overall reaction as the difference of two reduction half-reactions and then find the corresponding standard potentials by referring to the Table.**

Use $RT/F = 0.025693$ V.

Example

Answer: **The half-reactions and standard potentials we require are**

R: Cu(s)|Cu^+(aq) $Cu^+(aq) + e^- \rightarrow Cu(s)$ $E^\ominus = +0.52\ \text{V}$

L: Pt|Cu^{2+}(aq), Cu^+(aq) $Cu^{2+}(aq) + e^- \rightarrow Cu^+(aq)$ $E^\ominus = +0.16\ \text{V}$

The standard cell potential is therefore

$$E^\ominus = 0.52\text{V} - 0.16\text{V} = 0.36\text{V}$$

Then, because $v = 1$,

$$\ln K = \frac{vFE^\ominus}{RT} = \frac{0.36\ \text{V}}{0.025693\ \ \text{V}} = 14 \qquad K = 1.2 \times 10^6$$

10.5 Standard potentials

2) The measurement of standard potentials

The procedure for measuring a standard potential is illustrated by considering the silver chloride electrode:

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

$$\tfrac{1}{2}\,\mathrm{H_2\,(g)} + \mathrm{AgCl\,(s)} \rightarrow \mathrm{HCl\,(\,aq)} + \mathrm{Ag(\,s)}$$

for which

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

since a_{Ag}, a_{AgCl} and $a_{\mathrm{H_2}}$ are equal to 1 in this case

$$E = E^{\ominus}(\mathrm{AgCl/Ag,Cl^-}) - \frac{RT}{F}\ln\left(a_{\mathrm{H^+}}a_{\mathrm{Cl^-}}\right)$$

10.5 Standard potentials

$$a_{\pm}^{2} = a_{\mathrm{H}^{+}} a_{\mathrm{Cl}^{-}} \qquad a_{\pm} = \gamma_{\pm} b$$

It follows that

$$E = E^{\ominus}(\mathrm{AgCl/Ag,Cl^{-}}) - \frac{RT}{F}\ln a_{\pm}^{2}$$

$$= E^{\ominus}(\mathrm{AgCl/Ag,Cl^{-}}) - \frac{2RT}{F}\ln \gamma_{\pm} b$$

This expression rearranges to

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

From the Debye-Hiickel limiting law for a 1,1-electrolyte

$$\ln \gamma_{\pm} \propto -b^{1/2}$$

10.5 Standard potentials

with the constant of proportionality in this relation written A'

$$E+\frac{2RT}{F}\ln b=E^{\ominus}-\frac{2RTA'}{F}\ln b^{1/2}$$

The expression on the left is evaluated at a range of molalities, plotted against $b^{1/2}$, and extrapolated to $b = 0$. The intercept at $b^{1/2} = 0$ is the value of $E^{\ominus}$.

Example

Determining the standard potential of a cell

The potential of the cell $Zn|ZnCl_2(aq,b)|AgCl(s)|Ag$ at 25℃ has the following values:

$b/(10^{-3}b^{\ominus})$	0.772	1.253	1.453	3.112	6.022
E / V	1.2475	1.2289	1.2235	1.1953	1.1742

Determine the standard potential of the cell.

Example

Method: Start by writing the Nernst equation for the cell, and then express the activities that occur in Q in terms of the mean activity coefficient. The latter can be written as proportional to $b^{1/2}$ by using the Debye-Hiickel limiting law. However, there is no need to write all the constants because the standard cell potential is obtained by extrapolation.

Example

Answer: The ionic equation for the cell reaction is

$$\mathrm{Zn(s)+2AgCl(s)} \rightarrow \mathrm{2Ag(s)\ Zn^{2+}(aq)+2Cl^{+}(aq)}$$

because all the solids are at unit activity. The Nernst equation is

$$E = E^{\ominus} - \frac{RT}{F}\ln a_{\mathrm{Zn}^{2+}} a^{2}_{\mathrm{Cl}^{-}}$$

The activities are related to the molality, b, of $\mathrm{ZnCl_2}$ by

$$a_{\mathrm{Zn}^{2+}} a^{2}_{\mathrm{Cl}^{-}} = \gamma_{\pm}^{3} b_{\mathrm{Zn}^{2+}} b^{2}_{\mathrm{Cl}^{-}} = 4\gamma_{\pm}^{3} b^{3}$$

because $b_{\mathrm{Zn}^{2+}} = b$ and $b_{\mathrm{Cl}^{-}} = 2b$ for a fully dissociated salt.

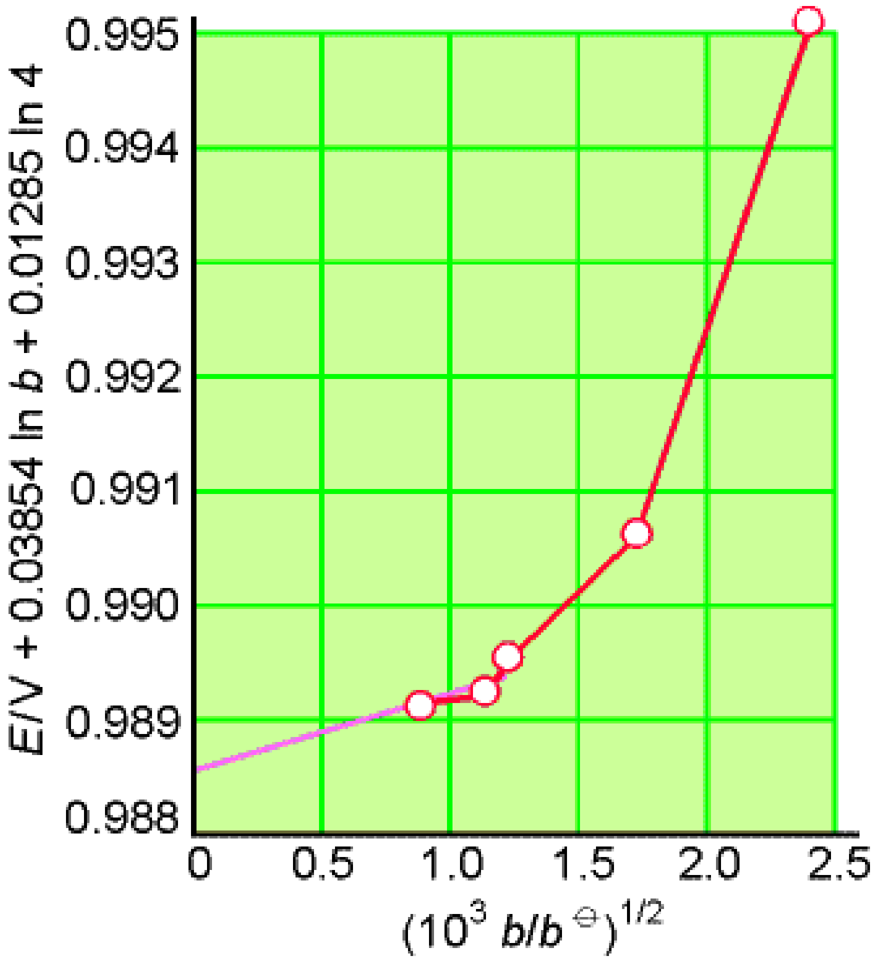
Example

$$\underline{E + \frac{3RT}{2F}\ln b + \frac{RT}{2F}\ln 4} = E^{\ominus} + \underline{Cb}^{1/2}$$

where *C* is a collection of constants come from the limiting law. We now draw up the table using *RT*/2*F*=0.01285 V

$b/(10^{-3}\,b\ \ )$	0.772	1.253	1.453	3.112	6.022
$b/(10^{-3}\,b)^{½}$	0.879	1.119	1.205	1.764	2.454
$E/\mathrm{V} + 0.03854 \ln b + 0.01285 \ln 4$	0.9891	0.9892	0.9895	0.9906	0.9950

Example



The data are plotted and extrapolate to $E^\ominus = +0.9886$ V.

10.5 Standard potentials

3) The measurement of activity coefficients

Once the standard potential of an electrode in a cell is known, the activities of the ions with respect to which it is reversible can be determined simply by measuring the cell potential with the ions at the concentration of interest.

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

$$\ln\gamma_{\pm}=\frac{E^{\ominus}(\mathrm{AgCl/Ag,Cl^-})-E}{2RT/F}-\ln b$$

10. Equilibrium electrochemistry

The thermodynamic properties of ions in solution

- 10.1 Thermodynamic functions of formation
- 10.2 Ion activities

Electrochemical cells

- 10.3 Half-reactions and electrodes
- 10.4 Varieties of cells
- 10.5 Standard potentials

Applications of standard potentials

- 10.6 The electrochemical series
- 10.7 Solubility constants
- 10.8 The measurement of pH and pK
- 10.9 Thermodynamic functions from cell potential measurements ▶

10.9 Thermodynamic functions from cell potential measurements

1) The reaction Gibbs energy

The reaction Gibbs energy is related to the zero-current cell potential by

$$\Delta_r G^{\ominus} = -\nu F E^{\ominus} \quad \textbf{and} \quad \Delta_r G = -\nu F E$$

2) The temperature coefficient of the cell potential

Since $(\partial G/ \partial T) = -S$, then

$$\left(\frac{\partial \Delta_r G}{\partial T}\right)_p = -\Delta_r S$$

10.9 Thermodynamic functions from cell potential measurements

$$-\left(\frac{\partial \Delta_r G}{\partial T}\right)_p = \nu F\left(\frac{\partial E}{\partial T}\right)_p = \Delta_r S$$

$$\frac{dE^\ominus}{dT} = \frac{\Delta_r S^\ominus}{\nu F}$$

The term ($\partial E/\partial T$) is called the temperature coefficient of the cell potential.

3) The standard reaction enthalpy

Because $\Delta_r H^\ominus = \Delta_r G^\ominus + T\Delta_r S^\ominus$, we then have

$$\Delta_r H^\ominus = -\nu F E^\ominus + \nu F T \frac{\mathrm{d}E^\ominus}{\mathrm{d}T}$$

This expression provides a noncalorimetric method for measuring $\Delta_r H$ and, through the convention $\Delta_r H\ (\mathrm{H^+aq})=0$ the standard enthalpies of formation of ions in solution. Thus, electrical measurements can be used to calculate all the thermodynamic properties of ions in solutions.

Example

Using the temperature coefficient of the cell potential

The standard cell potential of

$\mathrm{Pt}|\mathrm{H_2(g)}|\mathrm{HBr(aq)}|\mathrm{AgBr(s)}|\mathrm{Ag(s)}$

was measured over a range of temperatures, and the data were fitted to the following polynomial:

$$E^{\ominus}/\mathrm{V} = 0.07131 - 4.99\times10^{-4}(T/\mathrm{K}-298) - 3.45\times10^{-6}\,(T/\mathrm{K}-298)^2$$

Evaluate the standard reaction Gibbs energy, enthalpy, and entropy at 298 K.

Example

Method: The standard Gibbs energy of reaction is obtained by using the following equation after evaluating E at 298 K.

$$E^{\ominus} = -\frac{\Delta_r G^{\ominus}}{\nu F}$$

The standard entropy of reaction is obtained by using the following equation, which involves differentiating the polynomial with respect to T and then setting $T = 298$ K.

$$\frac{\mathrm{d}E^{\ominus}}{\mathrm{d}T} = \frac{\Delta_r S^{\ominus}}{\nu F}$$

The reaction enthalpy is obtained by combining the values of the standard Gibbs energy and entropy.

Example

Answer: At $T = 298$ K, $E^\ominus = +0,07131$V, so

$$\Delta_r G^\ominus = -\nu F E^\ominus = -(1)\times(96.485\ \text{kCmol}^{-1})\times(+0.07131\text{V})$$

$$= -6.880\ \text{kJmol}^{-1}$$

$$\frac{\mathrm{d}E^\ominus}{\mathrm{d}T} = \frac{\Delta_r S^\ominus}{\nu F}$$

$$= -4.99\times10^{-4}\ \text{VK}^{-1} - 2(3.45\times10^{-6})\ (T/\text{K}-298)\ \text{VK}^{-1}$$

At $T = 298$ K , this expression evaluates to

$$\frac{\mathrm{d}E^\ominus}{\mathrm{d}T} = -4.99\times10^{-4}\ \text{VK}^{-1}$$

Example

$$\Delta_r S^\ominus = \nu F \frac{\mathrm{d}E^\ominus}{\mathrm{d}T}$$

$$=(1)\times(96.485\ \mathrm{kC\,mol^{-1}})\times(-4.99\times10^{-4}\ \mathrm{V\,K^{-1}})$$

$$=-48.2\ \mathrm{J\,K^{-1}mol^{-1}}$$

$$\Delta_r H^\ominus = \Delta_r G^\ominus + T\Delta_r S^\ominus$$

$$=-6.880\ \mathrm{kJ\,mol^{-1}}+(298\mathrm{K})\times(-0.0482\mathrm{kJ\,K^{-1}mol^{-1}})$$

$$=-21.2\ \mathrm{kJ\,mol^{-1}}$$

Part 1: Equilibrium

1. The properties of gases
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3. The First Law: the machinery
4. The Second Law: the concepts
5. The Second Law: the machinery
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