PEOPLE'S DEMOCRATIC REPUBLIC OF ALGERIA

MINISTRY OF HIGHER EDUCATION AND SCIENTIFIC RESEARCH

University Ferhat Abbas Setif-1

Faculty of Natural and Life Sciences

Thermodynamics and chemistry of mineral solutions

- ✓ *Acid-Base*
- ✓ *Oxidation-Reduction*
- ✓ *Chemical kinetics*
- ✓ *Thermodynamics*

Common base L1: Natural and Life Sciences

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Foreword

The real objective of this course is to study chemistry in solution. Indeed, by reading this manual, the student will be able to make all the calculations and interpretations necessary for a good understanding of the phenomena in solution. It will also enable him to acquire a basis to understand the mechanisms governing the equilibria in aqueous solutions.

When a chemical transformation takes place, the transition from the initial state to the final state occurs more or less low rate depending on the nature of the reaction chemical and the experimental conditions in which it is achieved. Thermodynamics is the branch of physics that deals with the dependence of properties physics of substances at temperature, phenomena where heat exchanges occur, and transformations of energy between different forms.

Chapter I: discusses in detail acidic and basic solution, the strength of acids and bases and pH calculations.

Chapter II: discusses in detail, redox reactions, electrode balance and Nernst's law and measurement of an electrode potential.

Chapter III: define all the quantities and laws relating to kinetics of a chemical reaction.

The last chapter introduces fundamental notions and first definitions used in thermodynamics. He also develops the different forms of energy, their transfers, the statement of the first principle and the second principle of thermodynamics, the notions and the different expressions of entropy, it is devoted to thermochemistry and the application of the first law of thermodynamics in chemistry.

Contents

Chapter I: Acid-Base

Chapter II: Oxidation-Reduction

Chapter III: Chemical kinetics........

Chapter IV: Thermodynamics

Chapter I: Acid-Base

I.1. Acid–Base Concepts

I.1.1. Brønsted–Lowry Concept of Acids and Bases

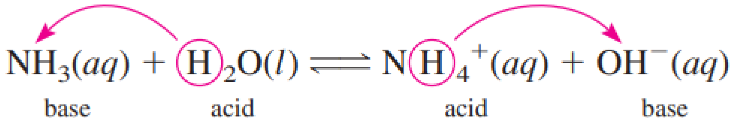
- ✓ An acid is a chemical species (molecule or ion) capable of giving up a proton.

$$AH = A^- + H^+$$

- ✓ A base is a chemical species (molecule or ion) capable of capturing a proton.

$$B + H^+ = BH^+$$

A conjugate acid–base pair consists of two species in an acid–base reaction, one acid and one base, that differ by the loss or gain of a proton. The acid in such a pair is called the conjugate acid of the base, whereas the base is the conjugate base of the acid.



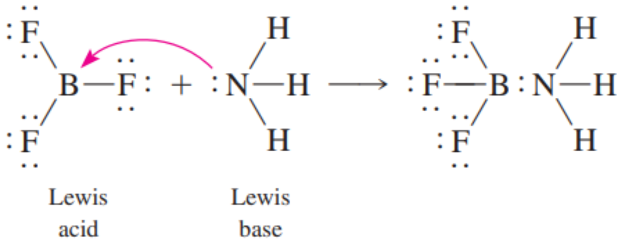
The species NH_4^+ and NH_3 are a conjugate acid–base pair.

I.1.2. Arrhenius Concept of Acids and Bases

- ✓ An acid is a substance that, when dissolved in water, increases the concentration of hydronium ion, H_3O^+.
- ✓ A base, in the Arrhenius concept, is a substance that, when dissolved in water, increases the concentration of hydroxide ion, OH^-.

I.1.3. Lewis Concept of Acids and Bases

According to this concept, a Lewis acid is a species that can form a covalent bond by accepting an electron pair from another species; a Lewis base is a species that can form a covalent bond by donating an electron pair to another species.



Boron trifluoride accepts the electron pair and so is a Lewis acid. Ammonia donates the electron pair and so is a Lewis base.

There are special cases:

- **Polyacid**

It is a species capable of releasing several protons (H_2SO_4, H_2CO_3, H_2S, H_3PO_4)

$$H2SO4 + H2O \rightleftarrows HSO4^{-} + H3O^{+} \quad (H2SO4/ HSO4^{-})$$

$$HSO4- + H2O \rightleftarrows SO4^{2-} + H3O^{+} \quad (HSO4^{-}/ SO4^{2-})$$

- **Polybase**

It is a species capable of capturing several protons (CO_3^{2-}, SO_4^{2-}…)

$$CO3^{2-} + H2O \rightleftarrows H\ CO3^{-} + OH^{-} \quad (HCO3^{-} / CO3^{2-})$$

$$HCO3^{-} + H2O \rightleftarrows H2CO3 + OH^{-} \quad (H2CO3 / HCO3^{-})$$

- **An ampholyte (or an amphoteric species)**

It is a species capable of playing both the role of an acid in a couple and a base in another couple. HSO_4^- (H_2SO_4/ HSO_4^-) et (HSO_4^-/SO_4^{2-})

I.2. Self-Ionization of Water

Although pure water is often considered a nonelectrolyte (nonconductor of electricity), precise measurements do show a very small conduction. This conduction results from self-ionization (or autoionization), a reaction in which two like molecules react to give ions. In the case of water, a proton from one H_2O molecule is transferred to another H_2O molecule, leaving behind an OH^- ion and forming a hydronium ion, H_3O^+ (aq).

$$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

You can see the slight extent to which the self-ionization of water occurs by noting the small value of its equilibrium constant Kc.

$$K_c = \frac{[H_3O^+][OH^-]}{[H_2O]^2}$$

Because the concentration of ions formed is very small, the concentration of H_2O remains essentially constant, about 56 M at 25°C. If you rearrange this equation, placing $[H_2O]_2$ with Kc, the ion product $[H_3O^+][OH^-]$ equals a constant.

We call the equilibrium value of the ion product $[H_3O^+][OH^-]$ the ion-product constant for water, which is written Kw.

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14} \text{ at } 25°C$$

$$pKw = -\log Kw = 14 \ (25°C)$$

Note: Kw only depends on temperature and is dimensionless.

Using Kw, you can calculate the concentrations of H_3O^+ and OH^- ions in pure water.

These ions are produced in equal numbers in pure water, so their concentrations are equal

$[H_3O^+]$ eq = $[OH^-]$eq $[H_3O^+]$eq = $[OH^-]$eq

$$= \sqrt{Kw} = 10^{-7} \, mol.\, L^{-1}$$

A weak acid (or base) is any acid (or base) that partially reacts with water.

An acid-base couple is characterized by an acidity constant Ka which is the constant of the following equilibrium:

$$AH\ (aq) + H_2O\ (l) = A^-\ (aq) + H_3O^+\ (aq)$$

$$Ka = \frac{[H3O^+]\,[A^-]}{[AH]} \quad \text{et } pKa = -\log Ka$$

Ka only depends on the temperature (and the solvent if we do not work in an aqueous medium) and is dimensionless.

The stronger the acid, the more it is dissociated into A^-, the larger Ka and the smaller pKa.

Symmetrically, it is possible to define the basicity constant Kb characterizing the following equilibrium:

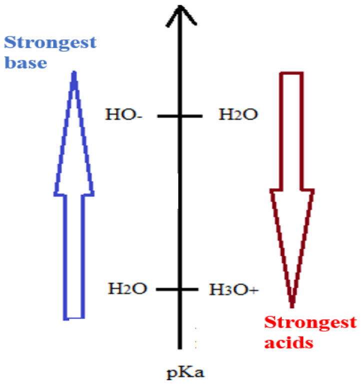
$$A^-(aq) + H_2O\ (l) = HA\ (aq) + HO^-\ (aq)$$

$$Kb = \frac{[HO^-][AH]}{[A^-]} \quad \text{et } pKb = -\log Kb$$

For the same acid/base pair, the equilibrium constants Ka and Kb are not independent:

$$\mathbf{Ka.\ Kb} = [H3O^+]\ [OH^-] = \mathbf{Kw} = 10^{-14}\ \mathbf{(25°C)}$$

$$\mathbf{pKa + pKb = pKw = 14\ (25°C)}$$



-The conjugate base of a strong acid is weak and that of a weak acid is strong.

-The conjugate acid of a strong base is weak and that of a weak base is strong.

	Acid	Base
Strong	pKa Low	pKb Low
Weak	pKa Large	pKb Large

I.3. Calculating the pH of acids and bases

I.3.1. Definition of pH

You see that whether an aqueous solution is acidic, neutral, or basic depends on the hydronium-ion concentration. You can quantitatively describe the acidity by giving the hydronium-ion concentration. But because these concentration values may be very small, it is often more convenient to give the acidity in terms of pH, which is defined as the negative of the logarithm of the molar hydronium-ion concentration: This notion was defined by Sörensen in 1909 to evaluate the acidity of a solution.

$$\mathbf{pH = - \log [H_3O^+]}$$

For a solution in which the hydronium-ion concentration is 1.0 x 10^{-3} M, the pH is:

$$pH = -\log (1.0 \times 10^{-3}) = 3.00$$

- A neutral solution, whose hydronium-ion concentration at 25°C is $[H_3O^+] = [OH^-]$, has a pH of 7.00.
- For an acidic solution, $[H_3O^+] > [OH^-]$, so the pH is less than 7.00.
- Similarly, a basic solution, $[H_3O^+] < [OH^-]$ has a pH greater than 7.00.

I.3.2. Strong acid pH

An HA acid is called a strong acid when its reaction with water is quantitative:

$$\mathbf{HA\ (aq) + H_2O\ (l) = A^-\ (aq) + H_3O^+\ (aq)}$$

A strong acid put into solution is therefore quantitatively converted into oxonium ions.

The conjugate base of a strong acid is an indifferent base. (Cl^-, Br^-, NO_3^-)

- The electro neutrality equation, applied to the solution:

$$[H_3O^+] = [OH^-] + [A^-] \qquad (1)$$

Since it is a strong acid, we neglect the concentration of hydroxide ions in relation to the concentration of oxonium ions: $[H_3O^+] >> [OH^-]$

Equation (1) becomes: $[H_3O^+] = [A^-]$ (2)

Conservation of matter: $C_a = [A^-] = [AH]$

with (Ca the initial acid concentration).

From equation (2) we derive: $C_a = [H_3O^+]$

$$\boxed{\mathbf{pH = -\log [H_3O^+] = -\log C_a}}$$

I.3.3. pH of a strong base

A base B is called a strong base when its reaction with water is quantitative:

$$\mathbf{B + H_2O\ (l) = BH^+\ (aq) + HO^-\ (aq)}$$

A strong base put into solution is therefore quantitatively converted into hydroxide ions.

The conjugate acid of a strong base is an indifferent acid. (NH_3)

- The electro neutrality equation, applied to the solution:

$$[OH^-] = [H_3O^+] + [BH^+] \qquad (1)$$

Since it is a strong base, we neglect the concentration of oxonium ions in relation to the concentration of hydroxide ions: $[OH^-] >> [H_3O^+]$

Equation (1) becomes: $[OH^-] = [BH^+]$ (2)

- Conservation of matter: $Cb = [OH^-] = [BH+]$

with (Cb: the initial concentration of the base).

From equation (2) we derive: $C_b = [OH^-]$

-The ion-product constant for water: $Kw = [OH^-]\ [H3O^+] = 10^{-14}$

$$[H_3O+] = \frac{10^{-14}}{OH^-} \quad pH = \log\frac{10^{-14}}{OH^-} = -\log 10^{-14} + \log OH^-$$

$$\boxed{\mathbf{pH = 14 + \log Cb}}$$

I.3.4. pH of weak acid

$$HA + H_2O \rightleftharpoons A^- + H_3O^+$$

- The electro neutrality equation, applied to the solution:

$$[H_3O^+] = [OH^-] + [A^-] \qquad (1)$$

Since it is an acid, we neglect the concentration of hydroxide ions in relation to the concentration of oxonium ions: $[H_3O^+] >> [OH^-]$

Equation (1) becomes : $[H_3O^+] = [A^-]$ (2)

- Conservation of matter: $C_a = [A^-] + [AH]_r$ at equilibrium ([AH]r >>[A-]) with (Ca: the initial acid concentration and [AH]r remaining acid concentration).

$$C_a = [H_3O^+] + [AH]_r$$

- The law of mass action: $Ka = [A^-] [H3O^+]/[AH] = [H3O^+]^2/[AH]$

$\log Ka = -\log [H3O^+]^2 /[AH]$

$- \log Ka = -\log [H3O^+]^2 /[AH]$

$pKa =$

$-(\log [H_3O^+]^2 – \log[AH])pKa$

$= -2\log [H3O^+] + \log [AH]$

$pKa = 2pH + \log Ca$

$$\boxed{pH = \frac{1}{2} (pKa - \log C_a)}$$

I.3.5. pH of a weak base

A base B is called a **weak base** when its reaction with water is partial:

$$\mathbf{B + H2O\ (l) = BH^+\ (aq) + HO^-\ (aq)}$$

- The electro neutrality equation, applied to the solution:

$$[OH^-] = [H_3O^+] + [BH^+] \qquad (1)$$

Since it is a strong base, we neglect the concentration of oxonium ions in relation to the concentration of hydroxide ions: $[OH^-] >> [H_3O^+]$

Equation (1) becomes : $[OH^-] = [BH^+]$ (2)

- Conservation of matter: $C_b = [B] = [B]_r + [BH^+]$ at equilibrium ([[B]r >> [BH+]) with (Cb: the initial concentration of the base and [B]r concentration of the remaining base).

- The law of mass action: $K_b = [OH^-][BH^+]/[B] = [HO^-]^2/[B]$

$-\log K_b = -\log [HO^-]^2/[B]$ $pK_b = -(\log [HO^-]^2 - \log [B])$

$pK_b = 2pOH + \log C_b$ $pK_b = 2(14 - pH) + \log C_b$ $14 - pH = 1/2\,(pK_b - \log C_b)$

$$\boxed{pH = 14 - \tfrac{1}{2}(pK_b - \log C_b)}$$

$pK_a + pK_b = 14$ (25°C)

$$\boxed{pH = \tfrac{1}{2}(14 + pK_a + \log C_b)}$$

Chapter II: Oxidation-Reduction

II.1. Definition

An oxidant: is a species capable of gaining one or more electrons.

A reductant: is a species likely to lose one or more electrons.

$$\mathrm{Ox} + n.e^- \underset{\xleftarrow{\text{Oxidation}}}{\overset{\xrightarrow{\text{Reduction}}}{=}} \mathrm{Red}$$

Ox and Red are said to be conjugated. They form an Ox/Red oxidation-reduction couple called redox couple.

Oxidation: oxidation is a loss of electrons.

$Na \longrightarrow Na^+ + 1e^-$

Reduction: reduction is a gain of electrons.

$Fe^{3+} + 1e^- \longrightarrow Fe^{2+}$

The one that loses electrons is the reducing agent Red.

The one that gains electrons is the oxidizing agent Ox.

For there to be an exchange of electrons, at least one constituent element of the species must change its oxidation number.

II.2. Oxidation number (on)

The oxidation number (or degree of oxidation) of an atom corresponds to the difference in valence electrons between the isolated atom and the atom when the structure is formed, all bonds being considered purely ionic.

The sum of the oxidation numbers is equal to the charge of the species.

In the vast majority of compounds, no (H) = +I and no (O) = -II. We deduce the number of the other atoms using the fact that the sum of the oxidation numbers is equal to the charge of the species.

Example: hydrogen sulfate ion HSO_4^-

on (S) + on (H) + 4× on (O) = -1

Let on (S) + 1 – 8 = -1

Hence on (S) = + VI

Depending on the compound in which it is considered, an element can take on many values of on.

on	-III	-II	-I	0	+I	+II	+III	+IV	+V
Nitrogen. (N)	NH_3, NH_4^+	H_2N-NH_2	H_2NOH	N_2	N_2O	NO	HNO_2, NO_2^-	NO_2	HNO_3, NO_3^-

When the number of an element increases, it undergoes **oxidation** (therefore it loses electrons).

When the number of an element decreases, it undergoes **reduction** (therefore it gains electrons).

The absolute value of the variation of on is equal to the number of electrons transferred.

II.3. Oxidation-reduction reactions

II.3.1 Skeleton Oxidation–Reduction Equations

To tackle more complex oxidation–reduction reactions in acidic and basic solutions, we need to review and discuss the essential information required to describe an oxidation–reduction reaction, which is called a skeleton equation. To set up the skeleton equation and then balance it, you need answers to the following questions:

1. What species is being oxidized (or, what is the reducing agent)? What species is being reduced (or, what is the oxidizing agent)?

2. What species result from the oxidation and reduction?

3. Does the reaction occur in acidic or basic solution? For example, iron (II) ion may be oxidized easily by a number of oxidizing agents to yield the iron (III) ion.

Permanganate ion in acidic, aqueous solution is a strong oxidizing agent and can oxidize Fe^{2+} to Fe^{3+}. In the process of oxidizing the iron (II) ion, the permanganate ion (MnO_4^-) is reduced to manganese (II) ion (Mn^{2+}). We can express these facts in the following skeleton equation:

$$Fe^{2+}(aq) + MnO_4^{-}(aq) \longrightarrow Fe^{3+}(aq) + Mn^{2+}(aq) \qquad \text{(acidic solution)}$$

no (+II) no (+VI) no (+III) no (+III)

Oxidation

Reduction

We have written oxidation numbers over the appropriate atoms. Note that the skeleton equation is not balanced. Nor is it complete; in an acidic, aqueous solution, H_3O^+(aq) and H_2O(l) may be possible reactants or products in the equation. (If this were a basic solution, OH^- ion would replace the H_3O^+ ion.)

II.3.2 Obtaining redox half-equations

Complete and balance each half-reaction.

a. Balance all atoms except O and H.
b. Balance O atoms by adding H2O's to one side of the equation.
c. Balance H atoms by adding H_3O^+ ions to one side of the equation.
d. Balance electric charge by adding electrons (e) to the more positive side.

$Fe^{3+} + 1.e^- \longrightarrow Fe^{2+}$ Couple (Fe^{3+}/ Fe^{2+})
(+III) (+II)

$Cl2 + 2.e^- \longrightarrow 2Cl^-$ Couple ($Cl2/ Cl^-$)
2x (0) 2x (-I)

In the two half-reactions the **on** decreases so we have a reduction.

$Cr_2O_7^{2-}$					Cr^{3+}			
$Cr_2O_7^{2-}$					$2.Cr^{3+}$			Cr atom balance
$Cr_2O_7^{2-}$					$2.Cr^{3+}$	+	$7.H_2O$	O atom balance
$Cr_2O_7^{2-}$			+	$14.H^+$ (aq)	$2.Cr^{3+}$	+	$7.H_2O$	H atom balance
$Cr_2O_7^{2-}$	+	**$6.e^-$**	+	$14.H^+$ (aq)	$2.Cr^{3+}$	+	$7.H_2O$	Electron balance

II.3.3 Half-Reaction Method in Acidic and Basic Solutions

Although the preceding skeleton equation is not complete, it does give the essential information about the oxidation–reduction reaction. Moreover, given the skeleton equation, you can complete and balance the equation using the half-reaction method. Let us see how to do that. We first look at balancing oxidation–reduction equations in acidic solution. To balance such equations in basic solution requires additional steps.

II.3.4 Steps in Balancing Oxidation–Reduction Equations in Acidic Solution

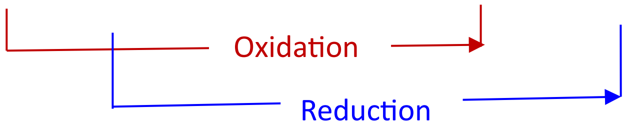
Example 1: Reaction of the oxidation of Fe^{2+} ions by $Cr_2O_2^-$ ions.

$Fe^{2+} \longrightarrow Fe^{3+} + 1.e^-$ Half-equation A

$Cr_2O_7^{2-} + 6.e^- + 14.H^+(aq) \longrightarrow 2.Cr^{3+} + 7.H_2O$ Half-equation B

$6.Fe^{2+} + Cr_2O_7^{2-} + 14.H^+\ (aq) \longrightarrow 6.Fe^{3+} + 2.Cr_3^+ + 7.H_2O$ A x (6) + B x (1)

on (+II) no (+VI) on (+III) no (+III)



Example 2:

$SO_3^{2-} + H_2O \longrightarrow SO_4^{2-} + 2H^+ + 2.e^-$ Half-equation A

$MnO_4^- + 3.e^- + 4.H^+ \longrightarrow MnO_2 + 2.H_2O$ Half-equation B

$3.SO_3^{2-} + 2.\ MnO_4^- + 2.H^+ \longrightarrow 3.SO_4^{2-} + 2.\ MnO_2 + H_2O$ A x (3) + B x (2)

no (+IV) no (+VII) no (+VI) no (+IV)

II.3.5 Steps in Balancing Oxidation–Reduction Equations in Basic Solution

Step 1: Write the half-equation of the couple in an acid medium.

$3.SO_3^{2-} + 2.\ MnO_4^- + 2.\ H^+ \longrightarrow 3.SO_4^{2-} + 2.\ MnO_2 + H_2O$

Step 2: Note the number of H^+ ions in the equation. Add this number of OH^- ions to both sides of the equation.

$3.SO_3^{2-} + 2.MnO_4^- + 2.H^+ + 2.OH^- \longrightarrow 3.SO_4^{2-} + 2.\ MnO_2 + H_2O + 2.\ OH^-$

Step 3: Simplify the equation by noting that H^+ reacts with OH^- to give H_2O. Cancel any H_2O's that occur on both sides of the equation and reduce the equation to simplest terms.

$3.SO3^{2-} + 2.\ MnO4^- + 2.H2O \longrightarrow 3.SO4^{2-} + 2.\ MnO2 + H2O + 2.\ OH^-$

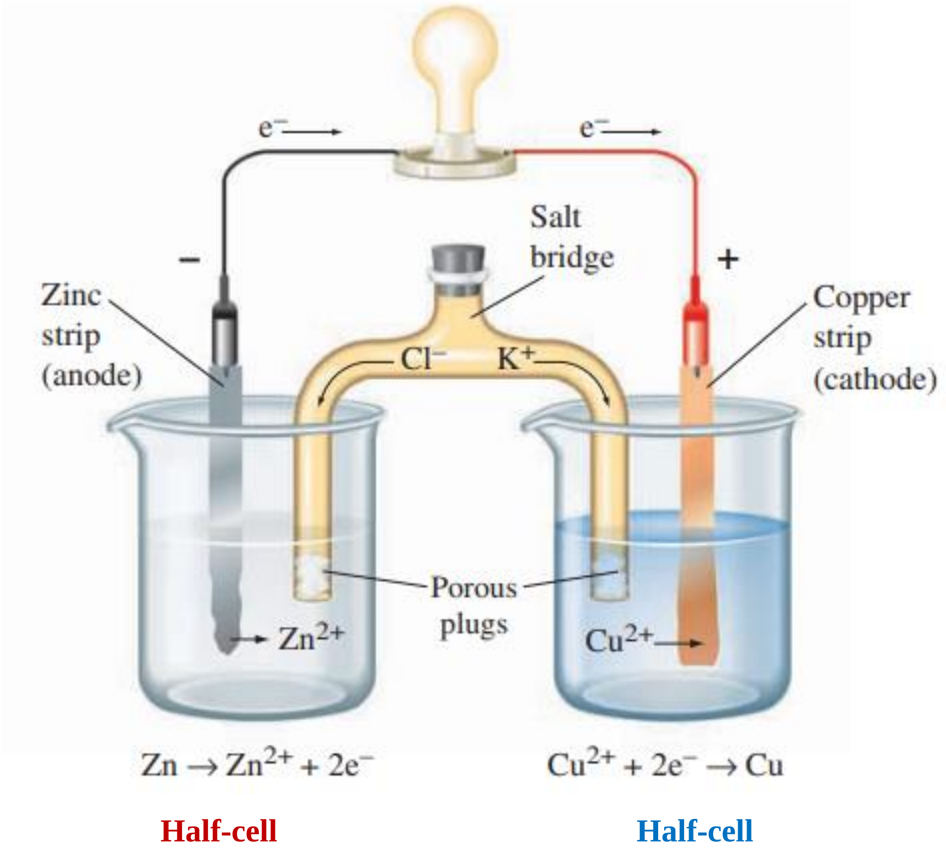
$3.SO3^{2-} + 2.\ MnO4^- + H2O \longrightarrow 3.SO4^{2-} + 2.\ MnO2 + 2.\ OH^-$

II.4 Voltaic cells

The next several sections describe battery cells, or voltaic cells (also called galvanic cells). These are a kind of electrochemical cell.

II.4.1 Construction of Voltaic Cells

A voltaic cell consists of two half-cells that are electrically connected. Each half-cell is the portion of an electrochemical cell in which a half-reaction takes place.



Salt bridge is a tube of an electrolyte in a gel that is connected to the two half-cells of a voltaic cell.

The electrode at which oxidation occurs is called the **anode**.

The electrode at which reduction occurs is called the **cathode.**

Note that the sum of the two half-reactions: $Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$

II.4.2 Notation for Voltaic Cells

It is convenient to have a shorthand way of designating particular voltaic cells. The cell described earlier, consisting of a zinc metal–zinc ion half-cell and a copper metal–copper ion half-cell, is written

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

In this notation, the anode, or oxidation half-cell, is always written on the left; the cathode, or reduction half-cell, is written on the right. The two electrodes are electrically connected by means of a salt bridge, denoted by two vertical bars.

$$\underset{\text{anode}}{Zn(s)|Zn^{2+}(aq)} \qquad \underset{\text{salt bridge}}{\|} \qquad \underset{\text{cathode}}{Cu^{2+}(aq)|Cu(s)}$$

II.4.2 Standard Cell Potentials and Standard Electrode Potentials

A cell potential (E) is a measure of the driving force of the cell reaction. This reaction occurs in the cell as separate half-reactions: an oxidation half-reaction and a reduction half-reaction.

The cell potential equals the difference between the two electrode potentials. You can think of the electrode potential as the electric potential on the electrode, and you obtain the cell potential as a potential difference in which you subtract the anode potential from the cathode potential. E cell = E cathode – E anode

- **Standard potential E^0**

The cell potential of a voltaic cell depends on the concentrations of substances and the temperature of the cell. For purposes of tabulating electrochemical data, it is usual to choose thermodynamic standard-state conditions for voltaic cells.

By convention, and for any temperature: E^0 (H^+ (aq) / H_2 (g)) = 0V.

Ox/Red	$F_2(g)/F^-$	H_2O_2/H_2O	MnO_4^-/Mn_2^+	$Cr_2O_7^-/Cr^{3+}$	$O_2(g)/H_2O$	$H^+/H_2(g)$
E^0(V)	+2,87	+1,77	+1,51	+1,33	+1,23	0,00
Ox/Red	Pb^{2+}/Pb	Ni^{2+}/Ni	Fe^{2+}/Fe	Al^{3+}/Al	Mg^{2+}/Mg	Li^+/Li
E^0(V)	-0,13	-0,26	-0,44	-1,68	-2,36	-3,04

II.5. Nernst formula

Allows you to access, through calculation, the value of the redox potential of a couple under given conditions.

$$a.Ox \ + n.e^- \longrightarrow b.Red$$

$$E_{Ox/Red} = E^0_{Ox/Red} + \frac{RT}{nF} \ln \frac{[Ox]^a}{[Red]^b}$$

$E^0_{Ox/Red}$: Standard Potential.

R: Ideal gas constant. 8.314 J/K/mol.

T: Temperature in Kelvin.

n: Number of electrons exchanged.

F: Faraday constant 1F = 96500 C /mol.

[Ox]: Concentration of the oxidant.

[Red]: Concentration of the reducer. At 25°C (298K)

$$E_{Ox/Red} = E^0_{Ox/Red} + \frac{0{,}0256}{n} \ln \frac{[Ox]^a}{[Red]^b}$$

$$\ln(x) = \ln 10 \times \log(x) \approx 2{,}3 \times \log(x).$$

$$E_{Ox/Red} = E^0_{Ox/Red} + \frac{0{,}059}{n} \log \frac{[Ox]^a}{[Red]^b} \approx E^0_{Ox/Red} + \frac{0{,}06}{n} \log \frac{[Ox]^a}{[Red]^b}$$

Example:

$Fe^{3+} + 1.e^- = Fe^{2+}$ $\quad E = E^0_{Fe3+/Fe2+} + 0{,}06 \log \frac{[Fe^{3+}]^1}{[Fe^{2+}]^1}$

$Cu^{2+} + 2.e^- = Cu\ (s)$ $\quad E = E^0_{Cu2+/Cu} + \frac{0{,}06}{2} \log [Cu^{2+}]$

$Cl_2\ (g) + 2.e^- = 2Cl^-$ $\quad E = E^0_{Cl2(g)/Cl-} + \frac{0{,}06}{2} \log \frac{P_{Cl2}}{[Cl^-]^2}$

$Cr_2O_7^{2-} + \mathbf{6.e^-} + 14.H^+\ (aq) \rightarrow 2.Cr^{3+} + 7.H_2O$

$$E = E^0_{Cr_2O_7^{2-}/Cr^{3+}} + \frac{0{,}06}{6} \log \frac{[Cr_2O_7^{2-}]^1 X [H^+]^{14}}{[Cr^{3+}]^2}$$

II.5.1 Application of Nernst's law to the voltaic cell

$E^0_{Zn2+/Zn} = -0{,}76\ V$

$E^0_{Cu2+/Cu} = +0{,}34\ V$

$E^0_{Cu2+/Cu} > E^0_{Zn2+/Zn}$

$Zn \longrightarrow Zn^{2+} + 2.e^-$ Oxidation **Anode (-)**

$Cu^{2+} + 2.e^- \longrightarrow Cu$ Reduction **Cathode (+)**

The Nernst equation:

$$E^{\oplus} = \mathrm{E}^{0}_{\mathrm{Cu2+/Cu}} + \frac{0{,}06}{2}\log\left[Cu^{2+}\right]$$

$$E^{\oplus} = 0{,}34 + 0.03\log\left[Cu^{2+}\right]$$

$$E^{\ominus} = \mathrm{E}^{0}_{\mathrm{Zn2+/Zn}} + \frac{0{,}06}{2}\log\left[Zn^{2+}\right]$$

$$E^{\ominus} = -0{,}76 + 0{,}03\log\left[Zn^{2+}\right]$$

II.5.2 Electromotive force (emf)

The maximum potential difference between the electrodes of a voltaic cell is referred to as the cell potential or electromotive force (emf) of the cell, or Ecell. It can be measured by an electronic digital voltmeter.

$$\mathrm{a.Ox1} + \mathrm{n.e^{-}} \longrightarrow \mathrm{b.Red1} \qquad \mathrm{c.Red2} \longrightarrow \mathrm{d.Ox2} + \mathrm{n.e^{-}}$$

$$E^{\oplus} = \mathrm{E}^{0}_{\oplus} + \frac{0{,}06}{\mathrm{n}}\log\frac{[\mathrm{Ox1}]^{\mathrm{a}}}{[\mathrm{Red1}]^{\mathrm{b}}} \qquad E^{\ominus} = \mathrm{E}^{0}_{\ominus} + \frac{0{,}06}{\mathrm{n}}\log\frac{[\mathrm{Ox2}]^{\mathrm{d}}}{[\mathrm{Red2}]^{\mathrm{c}}}$$

$$\mathrm{a.Ox1} + \mathrm{c.Red2} \longrightarrow \mathrm{d.Ox2} + \mathrm{b.Red1}$$

$$\mathrm{emf} = \Delta E = E^{\oplus} - E^{\ominus} = \mathrm{E}^{0}_{\oplus} - \mathrm{E}^{0}_{\ominus} + \frac{0{,}06}{\mathrm{n}}\log\frac{[\mathrm{Ox1}]^{\mathrm{a}}[\mathrm{Red2}]^{\mathrm{c}}}{[\mathrm{Red1}]^{\mathrm{b}}[\mathrm{Ox2}]^{\mathrm{d}}}$$

II.5.3 Equilibrium Constants from Cell Potentials

At equilibrium the battery stops working: emf = 0

$$\mathrm{a.Ox1} + \mathrm{c.Red2} \longrightarrow \mathrm{d.Ox2} + \mathrm{b.Red1}$$

$$K = \frac{[\mathrm{Ox2}]^{\mathrm{d}}[\mathrm{Red1}]^{b}}{[\mathrm{Red2}]^{\mathrm{c}}[\mathrm{Ox1}]^{\mathrm{a}}}$$

$$\Delta E = E^{\oplus} - E^{\ominus} = 0 = \mathrm{E}^{0}_{\oplus} - \mathrm{E}^{0}_{\ominus} + \frac{0{,}06}{\mathrm{n}}\log\frac{[\mathrm{Ox1}]^{\mathrm{a}}[\mathrm{Red2}]^{\mathrm{c}}}{[\mathrm{Red1}]^{\mathrm{b}}[\mathrm{Ox2}]^{\mathrm{d}}}$$

$$0 = \mathrm{E}^{0}_{\oplus} - \mathrm{E}^{0}_{\ominus} - \frac{0{,}06}{\mathrm{n}}\log\frac{[\mathrm{Ox2}]^{\mathrm{d}}[\mathrm{Red1}]^{b}}{[\mathrm{Red2}]^{\mathrm{c}}[\mathrm{Ox1}]^{\mathrm{a}}}$$

$$0 = \mathrm{E}^{0}_{\oplus} - \mathrm{E}^{0}_{\ominus} - \frac{0{,}06}{\mathrm{n}}\log K$$

$$\mathrm{E}^{0}_{\oplus} - \mathrm{E}^{0}_{\ominus} = \Delta E^{0} \rightarrow \Delta E^{0} = \frac{0{,}06}{\mathrm{n}}\log K \rightarrow \log K = \frac{n.\Delta E^{0}}{0{,}06}$$

$$K = 10^{\frac{n.\Delta E^{0}}{0{,}06}}$$

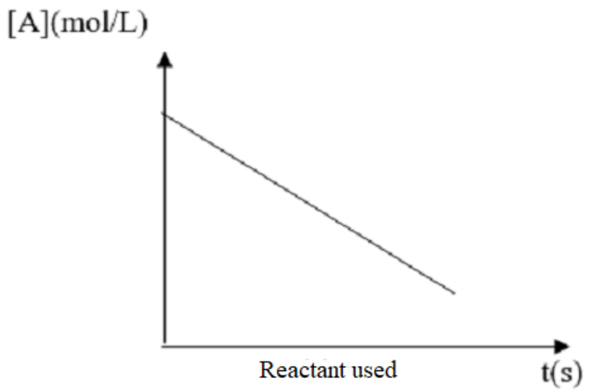
Equilibrium Constant

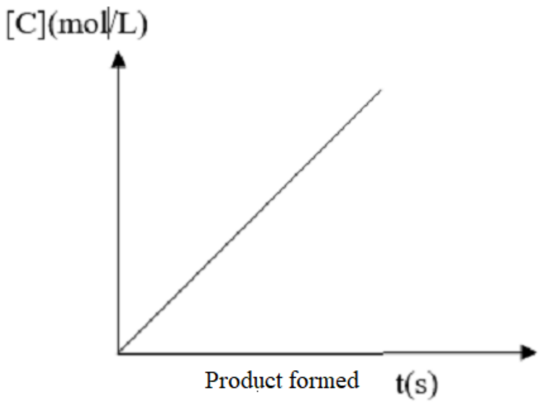
$$\mathrm{emf} = \Delta E^{0} - \frac{0{,}06}{\mathrm{n}}\log K$$

Chapter III: Chemical kinetics

III.1 Definition of Reaction Rate

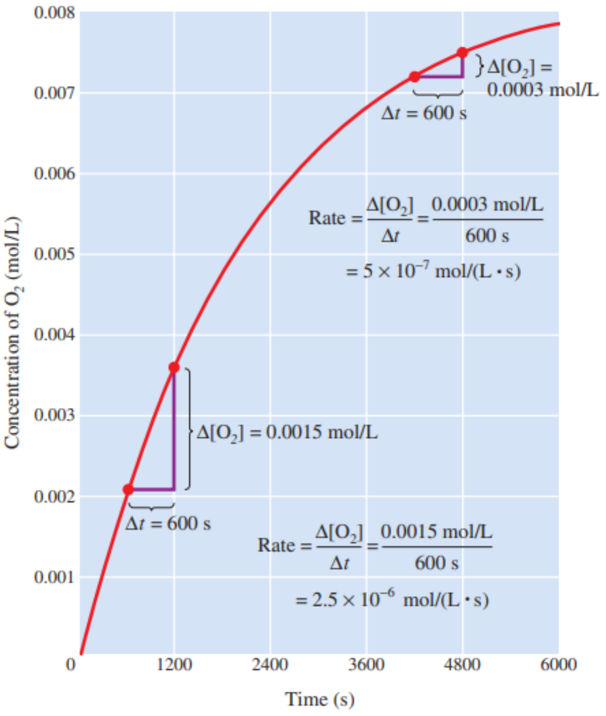
The rate of a reaction is the amount of product formed or the amount of reactant used up per unit of time. So that a rate calculation does not depend on the total quantity of reaction mixture used, you express the rate for a unit volume of the mixture. Therefore, the reaction rate is the increase in molar concentration of product of a reaction per unit time or the decrease in molar concentration of reactant per unit time. The usual unit of reaction rate is moles per liter per second, mol/(Ls).

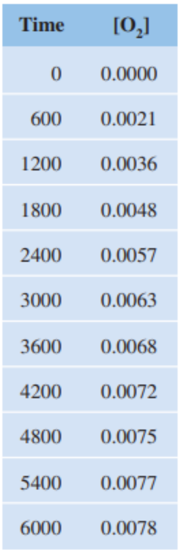




Example: Consider the gas-phase reaction.

$$2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$$





Time	$[O_2]$
0	0.0000
600	0.0021
1200	0.0036
1800	0.0048
2400	0.0057
3000	0.0063
3600	0.0068
4200	0.0072
4800	0.0075
5400	0.0077
6000	0.0078

III.1.1 Dependence of Rate on Concentration

Experimentally, it has been found that a reaction rate depends on the concentrations of certain reactants as well as the concentration of catalyst, if there is one.

$$\boldsymbol{\alpha}\,A + \boldsymbol{\beta}\,B \longrightarrow \gamma\,C + \boldsymbol{\delta}\,D$$

$$V = -1/\boldsymbol{\alpha}\ d[A]/dt = -1/\boldsymbol{\beta}\ d[B]/dt = 1/\gamma\ d[C]/dt = 1/\boldsymbol{\delta}\ d[D]/dt$$

Example:

$$2NO_2(g) + F_2(g) \longrightarrow 2NO_2F(g)$$

The rate of this reaction is observed to be proportional to the concentration of nitrogen dioxide. When the concentration of nitrogen dioxide is doubled, the rate doubles.

III.1.2 Factors affecting the rate of a reaction

The rate of a chemical reaction is influenced by the following factors:

- ✓ The nature of the reagents.
- ✓ The concentration of the reagents.
- ✓ Temperature.
- ✓ The effect of a catalyst.

III.2 Reaction Order

You can classify a reaction by its orders. The reaction order with respect to a given reactant species equals the exponent of the concentration of that species in the rate law, as determined experimentally.

$$\boldsymbol{\alpha}\,A + \boldsymbol{\beta}\,B \longrightarrow \gamma\,C + \boldsymbol{\delta}\,D$$

Rate of formation of products C and D (mol/l.s)

$$\boldsymbol{V_C = +\frac{1}{\gamma}\frac{d[C]}{dt}} \qquad \boldsymbol{V_D = +\frac{1}{\delta}\frac{d[D]}{dt}}$$

Rate of disappearance of reagents A and B (mol/l.s)

$$\boldsymbol{V_A = -\frac{1}{\propto}\frac{d[A]}{dt}} \qquad \boldsymbol{V_B = -\frac{1}{\beta}\frac{d[B]}{dt}}$$

$$\mathbf{V\ (reaction) = V_A = V_B = V_C = V_D}$$

The rate law is a mathematical relationship between the reaction rate and the concentrations of different species.

The rate can be expressed in the following form:

$$\mathbf{V = k\ [A]^{\alpha}.\ [B]^{\beta}}$$

K: Reaction rate constant.

α and β: Partial orders of the reaction.

The sum of α and β is the overall order of the reaction.

Note: Reaction orders can only be determined experimentally.

III.2.1 Zero-Order Reactions

$A \rightarrow$ product

Definition of rate: $v = -(d[A]/dt)$

Rate law: $v = k[A]^0 = k$

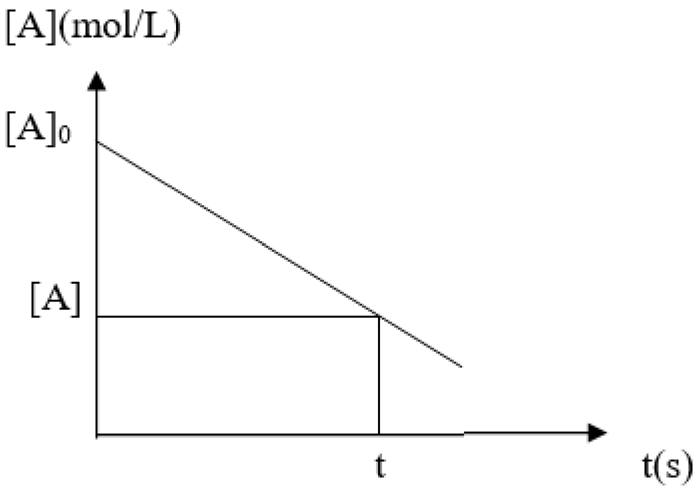
Kinetic equation: $-d[A]/dt = k$

Integrated rate law: $\int_{[A]0}^{[A]} d[A] = -\int_0^t k.dt$ $[A] - [A]_0 = -kt$

$$[A] = [A]_0 - kt$$

Unit of K = mol. l^{-1}. s^{-1}

tg α = K Slope = $[A]_0 - [A] / 0 - t$



Half-Life of a Reaction

As a reaction proceeds, the concentration of a reactant decreases, because it is being consumed. The half-life, $t_{1/2}$, of a reaction is the time it takes for the reactant concentration to decrease to one-half of its initial value.

if $t = t_{1/2}$ = **Half-Life** $[A] = [A]_0 / 2$

$[A]_0 /2 = [A]_0 - k\,t_{1/2}$ $k.t_{1/2} = [A]_0 - [A]_0 / 2$

Solving for the half-life, t1/2, you get:

$$t_{1/2} = [A]0 / (2k)$$

III.2.2 First-Order Reactions

A → product

Definition of rate: $v = -(d[A]/dt)$

Rate law: $v = k\,[A]^1$

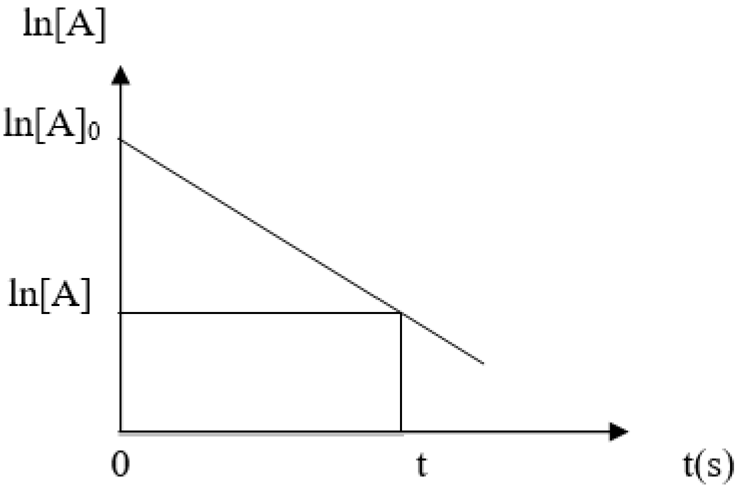
Kinetic equation: $-d[A]/dt = k[A]^1$ $d[A]/[A] = -k.\,dt$

Integrated rate law: $\int_{[A]0}^{[A]} d[A]/[A] = -\int_0^t k.\,dt$ $\ln([A]/[A]_0) = -kt$

$$\ln[A] = \ln[A]_0 - kt$$

$\mathrm{tg}\,\alpha = -K$ Slope $= \ln[A]_0 - \ln[A] / 0 - t$

Unit of $K = s^{-1}$



Half-Life of a Reaction

$\ln([A]_0/[A]_0/2) = -k.t_{1/2}$ $\ln 2 = k.\,.t_{1/2}$

$$t_{1/2} = \ln 2/k$$

III.2.3 Second-Order Reactions

A → product or A + B → product

Definition of rate: $v = -(d[A]/dt)$

Rate law: $v = k\,[A]^2$

Kinetic equation: $-(d[A]/dt) = k\,[A]^2$ $d[A]/[A]^2 = -k.t$

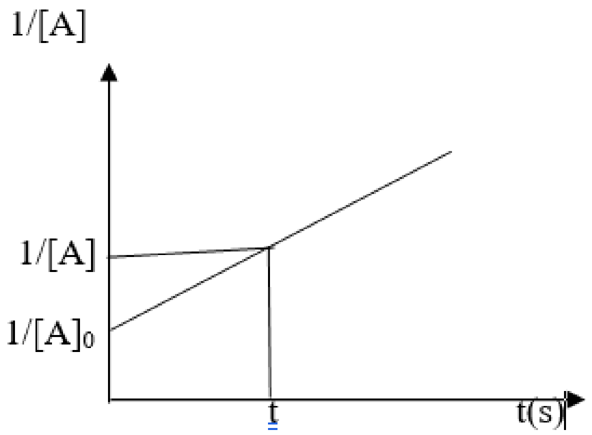
Integrated rate law: $\int_{[A]0}^{[A]} d[A] \big/ [A]^2 = -\int_0^t k.\,dt$

$(-1/[A]) - (-1/[A]_0) = -k.t$ $1/[A] - 1/[A]_0 = k.t$

$$1/[A] = k.t + 1/[A]_0$$

$$\text{tg}\ \alpha = K = \frac{\frac{1}{[A]}-\frac{1}{[A]0}}{t-0}$$

Unit of K = **mol^{-1}. l. s^{-1}**

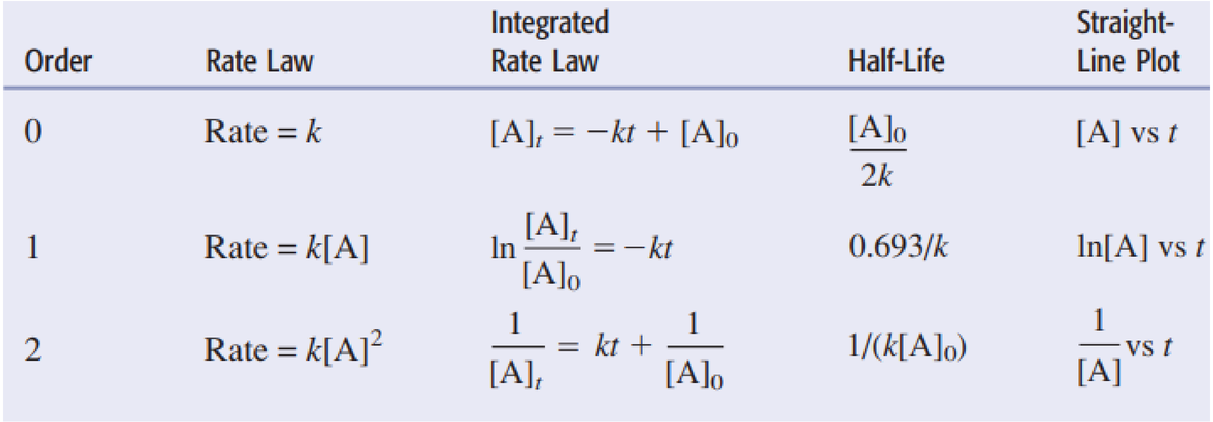


Half-Life of a Reaction

$1/[A] - 1/[A]_0 = k.t$ $\qquad$ $1/[A]_0/2 - 1/[A]_0 = k.t_{1/2}$

$2/[A]_0 \ - \ 1/[A]_0 = k.t_{1/2}$ $\qquad$ $1/[A]_0 = k.t_{1/2}$

$$t_{1/2} \quad = 1/\ k.\ [A]_0$$



Order	Rate Law	Integrated Rate Law	Half-Life	Straight-Line Plot
0	Rate = k	$[A]_t = -kt + [A]_0$	$\frac{[A]_0}{2k}$	[A] vs t
1	Rate = $k[A]$	$\ln \frac{[A]_t}{[A]_0} = -kt$	$0.693/k$	ln[A] vs t
2	Rate = $k[A]^2$	$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$	$1/(k[A]_0)$	$\frac{1}{[A]}$ vs t

Chapter IV: Thermodynamics

IV.1 Introduction

Thermodynamics is the study of the relationship between heat and other forms of energy involved in a chemical or physical process. With only heat measurements of substances, you can answer the questions just posed. You can predict the natural direction of a chemical reaction, and you can also determine the composition of a reaction mixture at equilibrium.

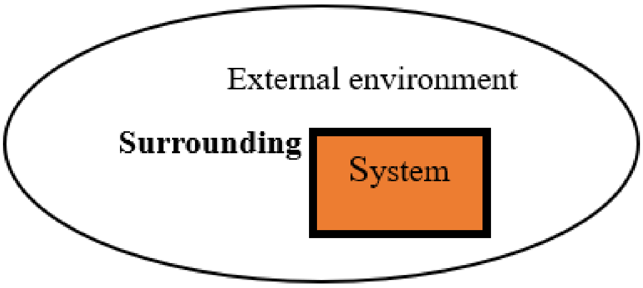
IV.2. Thermodynamic systems and equilibrium states

IV.2.1. System definition

To describe a system thermodynamically, it is necessary to:

- Define the system by delimiting its borders in relation to the external environment.
- Determine the state of the system defined by its variables.

The system is defined as a part of matter (of given mass) delimited in relation to the external environment. The external environment is the rest of the space surrounding the system.



IV.2.2 Different types of systems

Depending on the nature of the boundary between the system and the external environment, different systems are distinguished:

IV.2.2.1. Closed system

It does not exchange matter with the outside world.

Example: Electric batteries; fridge.

IV.2.2.2. Open system

It exchanges matter and energy with the outside world.

Example: Boiling water.

IV.2.2.3. Isolated system

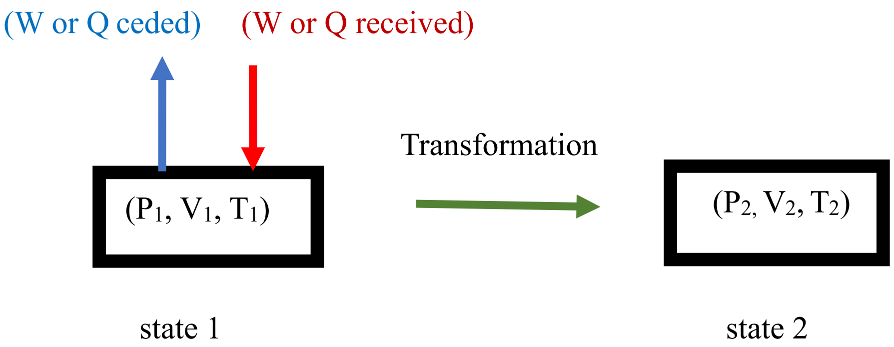
No transfer with the outside world (neither energy nor matter).

Example: sealed ampoule (thermally insulated), Thermos.

IV.2.3 Evolution or transformation of the system

The state of the system is defined or described by quantities called macroscopic variables (m, P, T, V, etc.) also called state variables.

Under the influence of exchanges or transfer of energy between the system and the external environment, the system evolves and the state variables of the system are modified. We say that the system transforms or changes state by passing from an initial equilibrium state (1) to another final equilibrium state (2).



Transformation of the system by exchange of energy (Q or W) with the external environment.

During a transformation, the state variables of the system vary to reach another equilibrium state. The transition from the equilibrium state (1) to the equilibrium state (2) generally takes place out of equilibrium. We then distinguish between:

- **Reversible** or (ideal) transformations: the system can return to all equilibrium states but by modifying all the parameters in the opposite direction. We can return, via the same path, going from the final state to the initial state.
- **Irreversible** (real) transformations: its flow over time can only happen in one direction: it is impossible to go back.

Spontaneous natural transformations are irreversible; they can only evolve in one direction.

- **Cyclic transformation**: it is a transformation where the final state coincides with the initial state after passing through several successive equilibrium states.

IV.3. Ideal gas law

The ideal gas is a thermodynamic model used to describe the behavior of real gases at low pressure; this is expressed by the ideal gas law; a simple relation which links the volume

(V); the pressure (P) and temperature (T) of a gas: This property is explained by the fact that when the pressure is low, the gas particles are sufficiently far from each other to be able to neglect order interactions electrostatic. Many real gases satisfy the ideal gas model with an excellent approximation, under normal conditions. This is the case for the main gases: air, dinitrogen and dioxygen.

$$\mathbf{PV = nRT}$$

With:

- P: pressure in pascal (Pa).
- V: the volume in m3.
- T: the temperature in °K.
- R: the ideal gas constant in $J.mol^{-1}. K^{-1}$

This relationship is only valid for low pressures where the interactions between the constituent molecules of the gas are very weak.

Under normal conditions, that is to say under a pressure of 1 bar (105 Pa), at T = 273°K, 1 mole of gas occupies 22.4 L: this is the molar volume of gases.

The ideal gas constant R;

R = 8.314 in $N. m. mol^{-1}. K^{-1}$ for: n =1 mole; P=101325 Pa=101325 (N/m^2); V = 22.4 L=0.00224 m^3; T=273°K.

1J=1 N. m therefore: R = 8.314 in $J.mol^{-1}. K^{-1}$

R= 0.082 L. atm/mole. °K

1cal=4.18J therefore: R= 2 Cal/mole. °K

IV.3.1. Three basic transformations

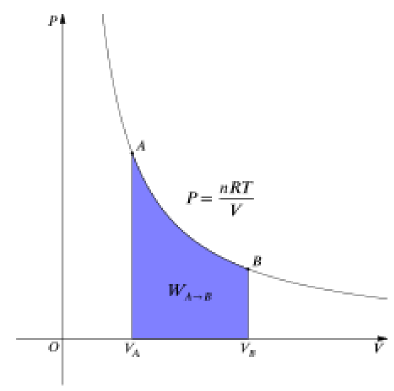
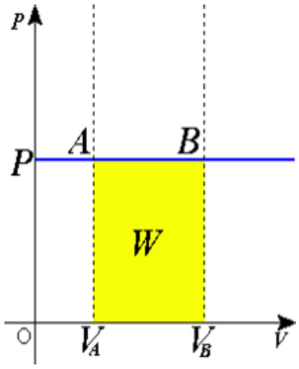
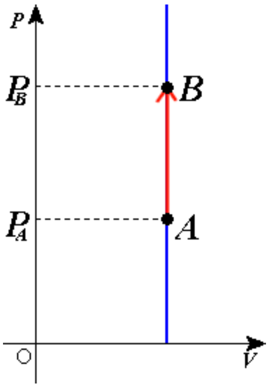
Real transformations, generally complex, can be broken down into a succession of elementary, simple or even basic transformations. This decomposition makes it possible to carry out elementary calculations of heat transfer, work, temperature variation, etc. in order to predict, with a good approximation, the result of a real transformation (explosion of an air-fuel mixture in a cylinder for example) three of these basic transformations retain a constant state variable P, V or T: these are (respectively) the isobaric, isochoric then isothermal transformation.

Isobaric transformation: the system pressure remains constant during the transformation.

Isochoric transformation: the volume of the system remains constant during the transformation.

Isothermal transformation: the temperature of the system remains constant during the transformation.

IV.3.2. Clapeyron diagram

		
Isothermal transformation	**Isochoric transformation**	**Isochoric transformation**

IV.4. First law of thermodynamics

We call internal energy U, an extensive quantity defined as the sum of all the energies exchanged between the system and the external environment. These energies are of two types:

- ✓ The work of the forces (W) which are exerted on the system.
- ✓ The quantities of heat (Q) which are exchanged.

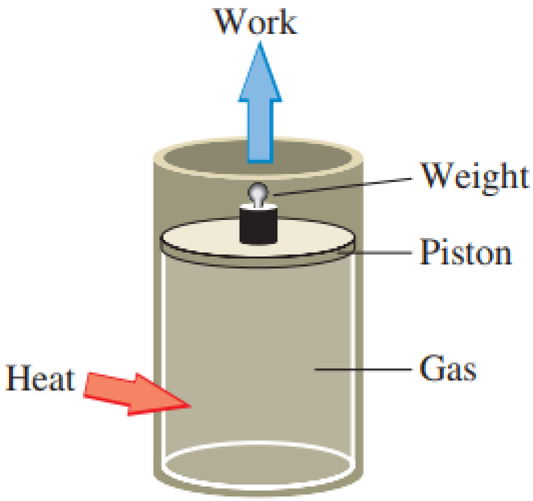


Figure 1: Exchanges of heat and work with the surroundings.

Internal energy is a state function. That is, it is a property of a system that depends only on its present state, which is completely determined by variables such as temperature and pressure.

Thus, 1 mol of water at 0°C and 1 atm pressure has a definite quantity of energy. When a system changes from one state to another, its internal energy changes from one definite value to another. You can calculate the change in internal energy, ΔU, from the initial value of the internal energy, U_i, and the final value of the internal energy, U_f.

$$\Delta U = U_{\text{final}} - U_{\text{initial}}$$

The system in Figure 1 gains internal energy from the heat absorbed and loses internal energy via the work done. In general, the net change of internal energy equals heat plus work.

$$\mathbf{\Delta U = W + Q}$$

IV.4.1 Heat (Q)

Heat is a special form of energy:

- It is an energy expressed in [J] or [kcal].
- It is exchanged on the microscopic scale in disordered form by molecular agitation (i.e. by collision between moving molecules.
- It always flows from a hot source to a cold source.
- Heat is not a state function, i.e. depends on the path followed.

It is linked to a variation in temperature (ΔT) of the system following heating or cooling of the latter. It is proportional to the quantity of the material (mass or number of moles) and to the temperature difference (ΔT).

- For an infinitesimal transformation:

$$Q = m.\, C.\, \Delta T \quad \text{or} \quad Q = n.C.\, \Delta T$$

Or:

m: The mass of the matter in the system.

n: The number of moles of the system.

C: The mass or molar heat capacity of the material expressed respectively in

[$J.\ Kg^{-1}.\ K^{-1}$] or [$J.\ mol^{-1}.\ K^{-1}$]. It can be at constant pressure (Cp) or at constant volume (C v).

IV.4.2 Work (W)

Work is another form of energy (mechanical energy):

- It is an energy expressed in [J] or [Cal].
- On the microscopic scale; it is energy exchanged in an orderly manner (thanks to the movement, for example, of a piston which gives a certain direction to the atoms.

- This is not a state function.

Now consider a chemical system—for example, the reaction of zinc metal with hydrochloric acid. The reaction is:

$$Zn(s) + 2H_3O^+(aq) \longrightarrow Zn^{2+}(aq) + 2H_2O(l) + H_2(g)$$

When this reaction is carried out in a beaker open to the atmosphere, the reaction is exothermic, evolving 152.4 kJ of heat per mole of zinc consumed. You write Qp =-152.4 kJ, where the subscript p indicates that the process occurs at constant pressure.

The hydrogen gas that is produced increases the volume of the system. As hydrogen is evolved, work must be done by the system to push back the atmosphere. How can you calculate this work?

Imagine for the moment that the atmosphere is replaced by a piston and weights, whose downward force from gravity F creates a pressure on the gas equivalent to that of the atmosphere. The pressure P equals F divided by the cross-sectional area of the piston, A. (See Figure 2).

$$\mathbf{P = F/A}$$

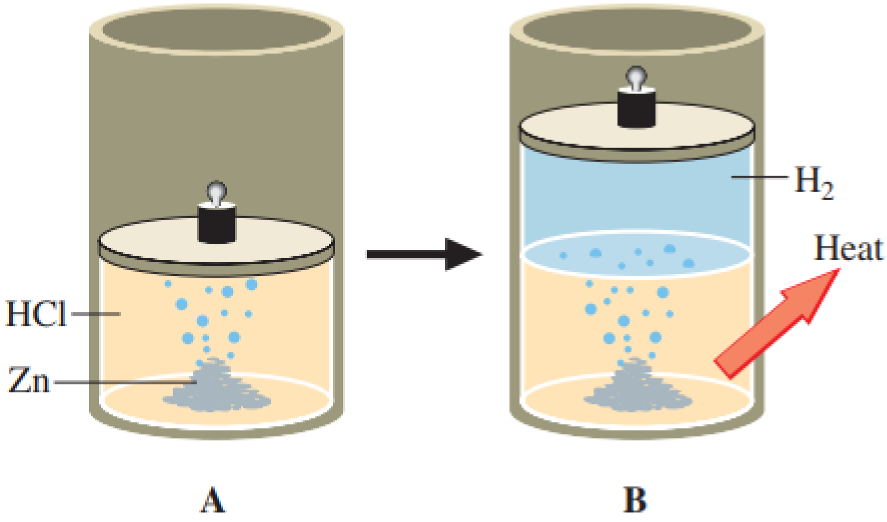


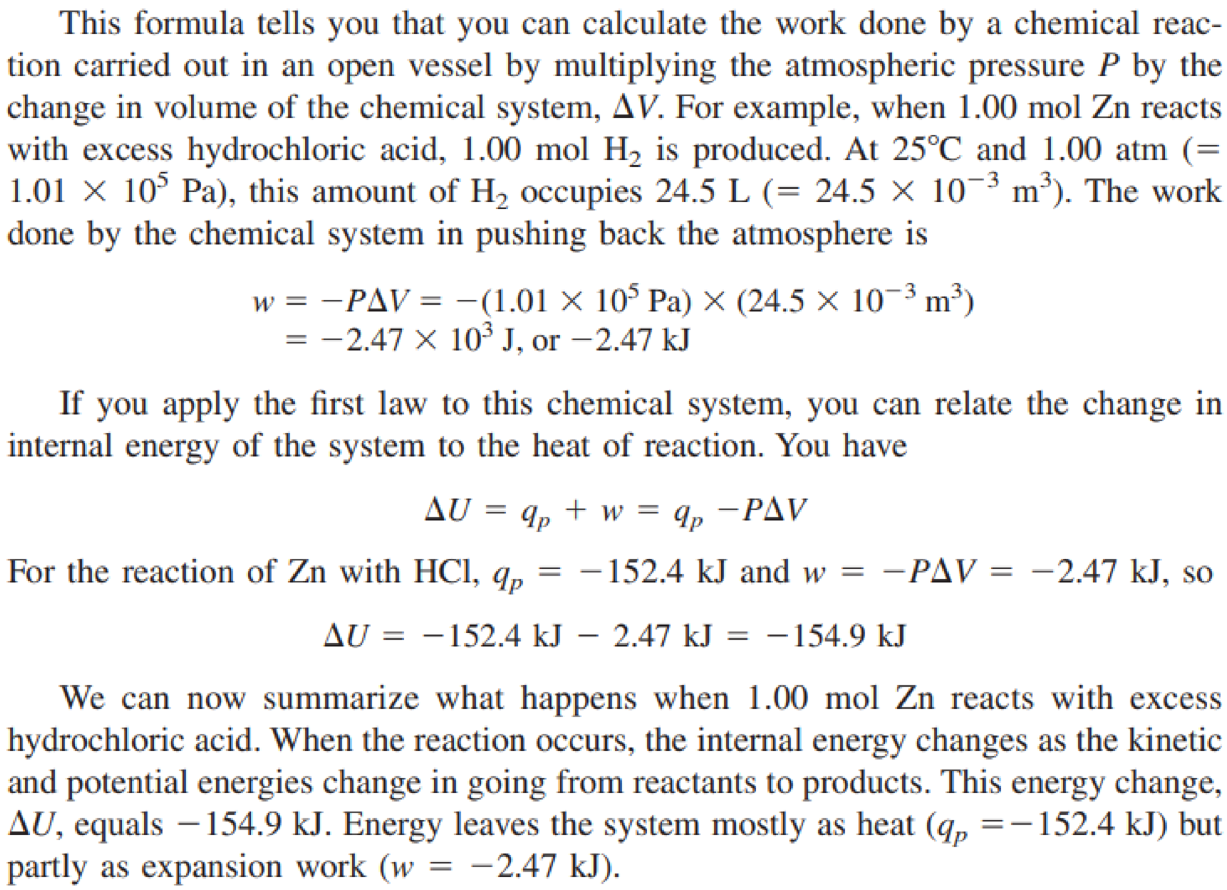
Figure 2: Reaction of zinc metal with hydrochloric acid at constant pressure.

Suppose the increase in volume of the system due to the production of hydrogen is ΔV. Because the volume of a cylinder equals its height dx times its cross-sectional area A, the change in volume is ΔV=A x dx, and dx=ΔV/A. The work done by the system in expanding equals the force of gravity times the distance the piston moves.

$$dW = -F.\ dx = -P.A.\ dx = -P.A.\ dV/S = -P.\ dV$$

The negative sign is given because w is work done by the system and represents energy lost by it. Note that F/A is the pressure, P, which equals that of the atmosphere. Therefore,

$$dW = -\ P.dV$$



This formula tells you that you can calculate the work done by a chemical reaction carried out in an open vessel by multiplying the atmospheric pressure P by the change in volume of the chemical system, ΔV. For example, when 1.00 mol Zn reacts with excess hydrochloric acid, 1.00 mol H_2 is produced. At 25°C and 1.00 atm (= 1.01×10^5 Pa), this amount of H_2 occupies 24.5 L (= 24.5×10^{-3} m^3). The work done by the chemical system in pushing back the atmosphere is

$$w = -P\Delta V = -(1.01 \times 10^5 \text{ Pa}) \times (24.5 \times 10^{-3} \text{ m}^3)$$
$$= -2.47 \times 10^3 \text{ J, or } -2.47 \text{ kJ}$$

If you apply the first law to this chemical system, you can relate the change in internal energy of the system to the heat of reaction. You have

$$\Delta U = q_p + w = q_p - P\Delta V$$

For the reaction of Zn with HCl, $q_p = -152.4$ kJ and $w = -P\Delta V = -2.47$ kJ, so

$$\Delta U = -152.4 \text{ kJ} - 2.47 \text{ kJ} = -154.9 \text{ kJ}$$

We can now summarize what happens when 1.00 mol Zn reacts with excess hydrochloric acid. When the reaction occurs, the internal energy changes as the kinetic and potential energies change in going from reactants to products. This energy change, ΔU, equals -154.9 kJ. Energy leaves the system mostly as heat ($q_p = -152.4$ kJ) but partly as expansion work ($w = -2.47$ kJ).

For a finite transformation between the initial state (1) and the final state (2); the variation of work is:

$$W_{1-2} = -\int PdV$$

We distinguish several types of transformation, where we can each time calculate the work received or transferred by the system during these evolutions:

a) For an isobaric transformation (P = Constant)

$W_{1-2} = -\int PdV = -P\int dV$ = -P (V_2-V_1)

b) For an isothermal transformation (T = Constant)

$$W_{1-2} = -\int PdV$$

P ≠ constant; ideal gas: PV= nRT

P = nRT/V

$$W_{1-2} = -\int \frac{nRTdV}{V} = -nRT\int \frac{dV}{V} = -nRT\ln {}^{V_2}/_{V_1}$$

$$W_{1-2} = nRT\ln {}^{V_1}/_{V_2}$$

On a: $P_1V_1 = nRT_1$

$P_2V_2 = nRT_2$

$P_2/P_1 = V_1/V_2$

$$W_{1-2} = nRT\ln {}^{P_2}/_{P_1}$$

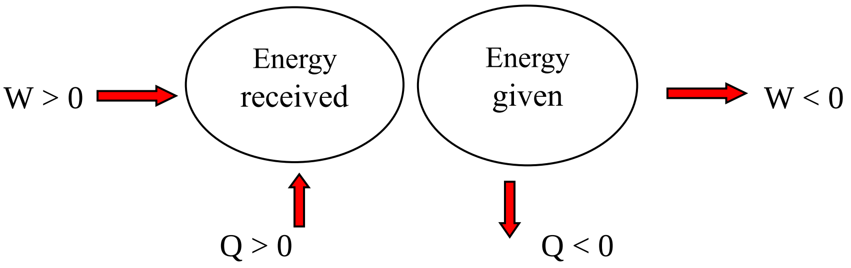
c) For an isochoric transformation (V = Constant)

No variation in volume, so dV = 0

$$W_{1-2} = -\int PdV = 0$$

IV.4.3 Energy sign convention

- The energies (W, Q) received by the system are > 0 (positive) and assigned a sign (+).
- The energies (W, Q) given up by the system are < 0 (negative) and assigned a sign (-).



The first law of thermodynamics, also known as the principle of conservation of energy, states that:

- The energy of the system is conserved during transformations of the system (i.e., does not degrade).
- The energy of the system is only transformed from one form of energy to another form (equivalence of energy forms).
- The energy of an isolated system remains constant ($\Delta U = 0$).

- The energy of a non-isolated system can vary as a result of energy exchange (Q, W) with the external environment, then the system evolves from an initial equilibrium state (1) to another state final equilibrium (2): we say that the system has undergone a transformation.
- The internal energy variation of the system during a transformation is equal to the algebraic sum of the energies exchanged W + Q.
- The internal energy of the system therefore varies during the transformation between state (1) and state (2):

$$\Delta U= U_2-U_1= \int dW + \int dQ = W+Q$$

If the transformation is elementary (infinitesimal):

$$dU= \int dW + \int dQ$$

The first law of thermodynamics is as follows:

"During any transformation of a non-isolated system, the variation of its internal energy is equal to the quantity of energy exchanged with the external environment, by thermal transfer (heat) and mechanical transfer (work)".

IV.4.4 Enthalpy (H)

The enthalpy function designated by the letter (H) corresponds to the total energy of a thermodynamic system. It includes the internal energy (U) of the system, to which is added the work that this system must exert against the external pressure to occupy its volume. Enthalpy is a thermodynamic potential. It is a state function which is an extensive quantity. Enthalpy is commonly used when studying changes in the energy of a system in many chemical, biological, and physical processes. The enthalpy change corresponds to the heat absorbed (or released), when the work is due only to pressure forces. In this case, the enthalpy change is positive or negative in the case where heat is released. The enthalpy (H) is defined by the following relationship:

$$\mathbf{H= U+PV}$$

- It is an energy expressed in [Joules] or in [calories]
- It is also a state function, like internal energy.

We have already seen that for an infinitesimal transformation:

$dU = dW + dQ$ or: $dU= dQ - PdV$

$dH = dU + d(PV) = dU + PdV + VdP$

dH = dQ - PdV + PdV + VdP

Either: dH = dQ +VdP

IV.4.5 Heat capacity

The specific or molar heat or heat capacity is also called specific heat. It is determined by the quantity of energy to be provided by thermal exchange to raise the temperature of the unit mass of a system by one kelvin. It is therefore an intensive quantity which depends on the mass of the system studied. Its unit in the international system is [J/Kg.K] if it is mass or [J/mol.K] if it is molar.

a) For an isochoric transformation (V = constant)

dH = dQ (dP = 0)

Hence: $\Delta H = \Delta Q = n\ Cp\ \Delta T$

Which gives: Cp = (dH/dT) p

Cp: Heat capacity at constant pressure.

b) For an isobaric transformation (constant P)

dH = dQ (dP = 0)

Hence: $\Delta H = \Delta Q = n\ Cp\ \Delta T$

Which gives: Cp = (dH/dT) p

Cp: Heat capacity at constant pressure.

c) Relationship between Cp and Cv (MAYER relationship)

Knowing that: dH = dU + d(PV)

And that: dH = Qp = n Cp dT

And dU = Qv = n Cv dT

So, we will have: n Cp dT = n Cv dT + d(PV)

And PV = nRT

Therefore: n Cp dT = n Cv dT + d(nRT) = n Cv dT + n R dT

We will have the MAYER relation:

$$\mathbf{Cp - C\,v = R}$$

b) For an isobaric transformation (constant P)

dH = dQ (dP = 0)

Hence: $\Delta H = \Delta Q = n\ Cp\ \Delta T$

Which gives: Cp = (dH/dT) p

Cp: Heat capacity at constant pressure.

Calculation of work (W):

$dW1\text{-}2 = - P\, dV$

$W1\text{-}2 = - \int P\, dV = 0$ therefore: $W1\text{-}2 = 0$

Calculation of heat quantity (Q):

$$Q1\text{-}2 = m\, Cv\, \Delta T = Qv$$

Calculation of internal energy and enthalpy:

$\Delta U= W_{1\text{-}2}+Q_{1\text{-}2} = m\, Cv\, (T_2\text{-}T_1) = Q\, v$

$\Delta H = \Delta U + \Delta\, (PV) = m\, Cp\, (T_2\text{-}T_1) = Q\, p$

IV.4.6 Isobaric transformation (P = constant)

Either a supposedly perfect gas and enclosed in an enclosure with a deformable volume, it undergoes a transformation at constant pressure.

The equation of state of an ideal gas: $PV = n\, R\, T$

therefore: Initial state (1): $P_1V_1 = n\, R\, T_1$

Final state (2): $P_2V_2 = n\, R\, T_2$

Since: P = constant therefore; $dP = 0$ and $P_1 = P_2$,

We will have: $V_1/V_2 = T_1/T_2$

- ✓ **Calculation of work (W)**

$W1\text{-}2 = - \int P\, dV = - P \int dV = - P\, (V2\text{-}V1)$

$$W12 = - P1\, (V2\text{-}V1) = - P2\, (V2\text{-}V1)$$

Or: $W12 = - P\, (V2\text{-}V1) = - (P2V2\text{-}\, P1V1) = - (nRT2\text{-}nRT1)$

$W1\text{-}2 = - nR\, (T2\text{-}T1)$

- ✓ **Calculation of heat quantity (Q)**

$dH = dU + d(PV) = dQ – PdV + PdV + VdV$

$Q_{1\text{-}2} = \Delta H = QP = n\, Cp\, (T_2\text{-}T_1)$

- ✓ **Calculation of internal energy and enthalpy**

$$\Delta U = W1\text{-}2+Q1\text{-}2$$

So: $\Delta U = n\, Cv\, (T_2\text{-}T_1)$

And: $\Delta H = n\, Cp\, (T_2\text{-}T_1)$

IV.4.7 Isothermal transformation (T= constant)

Consider a supposedly perfect gas which undergoes a transformation at constant temperature.

Initial state (1): $P_1V_1 = n\, R\, T_1$

Final state (2): $P_2V_2 = n\, R\, T_2$

With: $T_1 = T_2$; therefore: $P_1V_1 = P_2V_2$

So, the equation of state of the isotherms is:

$P_1V_1 = P_2V_2 = \ldots\ldots\ldots = PnVn = PV = \text{constant}$

- **Work calculation**

$W_{1\text{-}2} = - \int P\, dV = - \int nRT\, dV/V = - nRT \int P\, dV/V = - nRT \ln V_2/V_1$

$$W_{1\text{-}2} = nRT \ln V_1/V_2 = nRT \ln P_2/P_1$$

- **Calculation of heat quantity**

T = constant; U = f(T); therefore: $\Delta U= 0$;

So: $Q_{1\text{-}2} = - W_{1\text{-}2} = nRT \ln P_1/P_2$

- **Calculation of internal energy and enthalpy**

$\Delta U= 0$ because $\Delta U = f(T)$

$\Delta H = 0$ because $\Delta H = f(T)$

V.4.8 Reversible adiabatic transformation (dQ= 0)

Consider a supposedly perfect gas which undergoes an adiabatic (isentropic) transformation, that is to say without change in the quantity of heat.

We have: $dU = dQ + dW$

$dU = dQ - P\, dV$

So: $dQ = dU + P\, dV$ or $(dU = n\, Cv\, dT)$

Then: $dQ = n\, Cv\, dT + P\, dV = 0$

$n\, Cv\, dT = - P\, dV$ (1)

We also have: $\Delta H = dU + d\,(PV) = dQ - P\, dV + P\, dV + VdP$

$dQ = dH - VdP$ or $(dH = n\ Cp\ dT)$

So: $dQ = n\ Cp\ dT - VdP = 0$

$$n\ Cp\ dT = VdP \quad (2)$$

We can divide equation (1) by (2):

$(n\ Cv\ dT)/(n\ Cp\ dT) = (-P\ dV)/(V\ dP)$

$(dP/P)\ (n\ Cv\ dT)/(n\ Cp\ dT) = (dP/P)\ (-P\ dV)/(V\ dP)$

$(dP/P)\ Cv/Cp = (-\ dV)/(V)$

$(dP/P)\ Cv/Cp\ (Cp/Cv) = (Cp/Cv)\ (-\ dV)/(V\ )$

$$\left(\frac{dP}{P}\right) = -\left(\frac{Cp}{Cv}\right)\frac{dV}{V}$$

We state that: $Cp/Cv = \gamma$, γ is called the adiabatic constant.

So: $$\frac{dP}{P} = -\gamma\frac{dV}{V}$$

$$\int\frac{dP}{P} = -\gamma\int\frac{dV}{V} \qquad \ln\frac{P2}{P1} = -\gamma\ln\frac{V2}{V1}$$

$$\ln\frac{P2}{P1} = \gamma\ln\frac{V1}{V2}$$

$$\ln\frac{P_2}{P_1} = \ln\left[\frac{V_1}{V_2}\right]^{\gamma}$$

So: $$\frac{P_2}{P_1} = \left[\frac{V_1}{V_2}\right]^{\gamma}$$

So, we will have this formula which describes the adiabatic equation of state, also called the LAPLACE formula:

$$\boldsymbol{P_2 * V_2^{\gamma} = P_1 * V_1^{\gamma}}$$

- ✓ **Work calculation**

$W_{1\text{-}2} = -\int P\ dV$

$dU = dQ + dW = dW$ $\quad$ **(**$dQ=0$)

So : $dW = dU = n\ Cv\ dT$

$W_{12} = \int dU = \int n\ Cv\ dT = n\ Cv \int dT = n\ Cv\ \Delta T$

$$\frac{Cp}{Cv} = \gamma \quad \text{et} \quad Cp - Cv = R$$

$\gamma\ Cv - Cv = R \qquad Cv\ (\gamma -1) = R$

$Cv = R/ (\gamma -1)$

So: $W_{1\text{-}2} = \frac{n\,R}{(\gamma -1)} (T_2 - T_1) = \frac{n\,RT2 - n\,R\,T1}{(\gamma -1)}$

$$W_{1\text{-}2} = \frac{P2\,V2 - P1V1}{(\gamma -1)}$$

- ✓ **Calculation of the amount of heat**

The transformation is adiabatic, therefore no variation in the quantity of heat.

$$Q_{1\text{-}2} = 0$$

- ✓ **Calculation of internal energy and enthalpy**

$$\Delta U = n\,Cv\,(T_2\text{-}T_1) = W_{1\text{-}2}$$

And : $\Delta H = Qp = n\,Cp\,(T_2\text{-}T_1)$

We have: $Cp/Cv = \gamma$ then: $Cp = \gamma\,Cv$

Therefore: $\Delta H = \gamma\,n\,Cv\,(T_2\text{-}T_1) = \gamma\,\Delta U$

IV.5 Entropy and the Second Law of Thermodynamics

The first law of thermodynamics help you keep track of the various forms of energy in a chemical change, using the constancy of total energy (conservation of energy). But although at one time it was thought that spontaneous reactions must be exothermic ($\Delta H > 0$), many spontaneous reactions are now known to be endothermic ($\Delta H<0$). The second law of thermodynamics, which we will discuss in this section, provides a way to answer questions about the spontaneity of a reaction. The second law is expressed in terms of a quantity called entropy.

IV.5.1 Entropy

The notion of entropy is linked to the possibilities of movements existing at the microscopic scale (vibration, rotation and translation movements). Entropy constitutes a sort of measure of the disorder reigning at the molecular scale.

Entropy = disorder

The variation in entropy, during a transformation, characterizes the order lost or gained during this transformation:

- If $\Delta S > 0$ increase in disorder on the microscopic scale.
- If $\Delta S < 0$ the order increases on the microscopic scale.

The change of entropy in the system is the entropy created during the spontaneous reaction that occurs plus the entropy change that is associated with the heat flow (entropy flow).

$$\Delta S = \textbf{Entropy created} + Q/T$$

The quantity of entropy created during a spontaneous process is a positive quantity—the entropy increases as it is created. If we delete "entropy created" from the right side of the equation for ΔS, we know that the left side is then greater than the right side:

$$\Delta S > Q/T$$

We can now restate the second law as follows:

Second Law of Thermodynamics: *For a spontaneous process at a given temperature T, the change in entropy of the system is greater than the heat divided by the absolute temperature, Q/T.*

IV.5.2 Expression of entropy for ideal gases

- ✓ **Expression as a function of T and V:**

For a reversible transformation we have: $dU = dQ_{rev} + dW_{rev}$

And $dQ = T.dS$ $dW = - P.dV$

$\Longrightarrow$ $dU = T.dS - P.dV$

The case of an ideal gas: $dU = n.Cv.dT$

$\Longrightarrow$ $n.Cv.dT = T.dS - P.dV$

$dS = n.Cv.dT/T + P.dV/T$ $PV = nRT$ $\Longrightarrow$ $P/T = nR/V$

$dS = n\,(Cv.dT/T + R.dV/V)$

$\Longrightarrow$ $\Delta S = S_2 - S_1 = n\,[Cv.\ln(T_2/T_1) + R.\ln(V_2/V_1)]$

V = constant : $\Delta S = n\,Cv.\ln(T_2/T_1)$

T = constant : $\Delta S = n.R.\ln(V_2/V_1)$

- ✓ **Expression as a function of T and P:**

$dS = n\,(Cv.dT/T + R.dV/V)$ and $PV = nRT$

$d(PV) = d\,(nRT)$ $\Longrightarrow$ $dP.V + P.dV = nR.dT$

$dP.V/P.V + P.dV/P.V = nR.dT/P.V$

$$\Longrightarrow \quad dP/P + dV/V = dT/T \Longrightarrow dV/V = dT/T - dP/P$$

$$dS = n\,(Cv.dT/T + R.dV/V)$$

$$dS = n\,(Cv.dT/T + R.(dT/T - dP/P)) \quad \Longrightarrow \quad dS = n\,[(Cv + R)\,dT/T - R\,.\,dP/P\,]$$

$$dS = n\,[Cp\,dT/T - R.\,dP/P]$$

$$\Longrightarrow \quad \Delta S = S_2 - S_1 = n\,[Cp.\ln(T_2/T_1) - R.\ln(P_2/P_1)\,]$$

T = constant : $\Delta S = -\,n\,R.\ln(P_2/P_1)$
P = constant : $\Delta S = n\,Cp.\ln(T_2/T_1)$

IV.5.3 Entropy Change for a phase transition

Certain processes occur at equilibrium or, more precisely, very close to equilibrium. For example, ice at 0°C is in equilibrium with liquid water at 0°C. If heat is slowly absorbed by the system, it remains very near equilibrium, but the ice melts. Under these essentially equilibrium conditions, no significant amount of entropy is created. The entropy changes results entirely from the absorption of heat. Therefore,

$\Delta S = Q/T$ (equilibrium process)

Other phase changes, such as the vaporization of a liquid, also occur under equilibrium conditions.

You can use the previous equation to obtain the entropy change for a phase change. Consider the melting of ice. The heat absorbed is the heat of fusion, ΔH_{fus}, which is known from experiment to be 6.0 kJ for 1 mol of ice. You get the entropy change for melting by dividing ΔH_{fus} by the absolute temperature of the phase transition, 273 K (0°C). Because entropy changes are usually expressed in joules per kelvin, you convert ΔH_{fus} to 6.0 x10^3 J.

$$\Delta S = \frac{\Delta H_{fus}}{T} = \frac{6.0 \times 10^3\ \text{J}}{273\ \text{K}} = 22\ \text{J/K}$$

- ✓ **Vaporization:** $\frac{\Delta H_{Vap}}{T_{Vap}}$
- ✓ **Sublimation :** $\frac{\Delta H_{Sub}}{T_{Sub}}$

IV.5.4 Entropy of solids and liquids

According to the first principle:

$dU = dQ + dW$ and we also have $dQ = T.dS$

from which: $dU = T.dS - P.dV$

On the other hand: $H = U + PV$ $dH = dU + PdV + VdP$

Hence: $dH = T.dS + VdP$

For liquids and solids, the pressure varies little, so we neglect the terms PdV and VdP hence:

$dU = T.dS$ and $dH = T.dS$ $dU = dH$ and we will have:

$$dS = dU/T = dH/T = n\ C\ dT/T$$

C: is the molar heat capacity of the system.

For liquids and solids: Cv = Cp and it is approximately constant, hence:

$$\Delta S = \int_{T1}^{T2} n\ C\ dT/T$$

$\Delta S = n\ C \ln T_2/T_1$ or $\Delta S = m\ C \ln T_2/T_1$

IV.6 Standard Entropies and the third law of thermodynamics

The third law of thermodynamics states that a substance that is perfectly crystalline at 0 K has an entropy of zero. This seems reasonable. A perfectly crystalline substance at 0 K should have perfect order. When the temperature is raised, however, the substance increases in entropy as it absorbs heat and energy disperses through it.

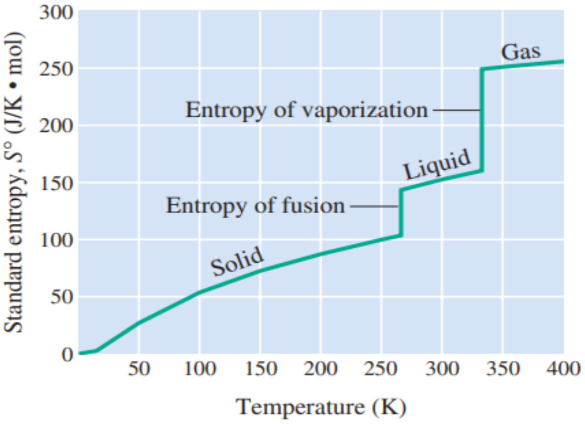


Figure 3: Standard entropy of bromine, Br2, at various temperatures.

This figure shows how the entropy of a substance changes with temperature. Note that the entropy increases gradually as the temperature increases. But when there is a phase change (for example, from solid to liquid), the entropy increases sharply.

IV.6.1 Standard Free-Energy Change

Recall that for purposes of tabulating thermodynamic data, certain standard states are chosen, which are indicated by a superscript degree sign on the symbol of the quantity. The standard states are as follows: for pure liquids and solids, 1 atm pressure; for gases, 1 atm partial pressure; for solutions, 1 M concentration. The temperature is the temperature of interest, usually 25°C (298 K). The standard free-energy change, ΔG°, is the free-energy change that occurs when reactants in their standard states are converted to products in their standard states.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

IV.6.2 Standard Free Energies of Formation

The standard free energy of formation, ΔG° f, of a substance is defined similarly to the standard enthalpy of formation.

That is, ΔG° f is the free-energy change that occurs when 1 mol of substance is formed from its elements in their stablest states at 1 atm and at a specified temperature (usually 25°C).

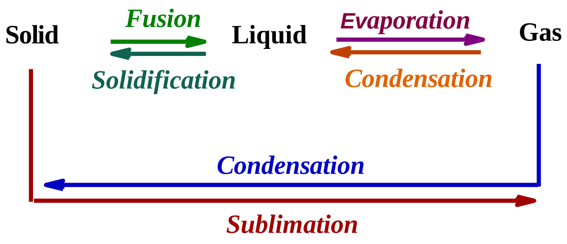
$$\Delta G^\circ = \Sigma\, n\Delta G_f^\circ(\text{products}) - \Sigma\, m\Delta G_f^\circ(\text{reactants})$$

IV.6Thermochemistry

Thermodynamics is the science of the relationships between heat and other forms of energy. Thermochemistry is one area of thermodynamics. It concerns the study of the quantity of heat absorbed or evolved (given off) by chemical reactions. An example of a heat-evolving reaction is the burning of fuel.

IV.6.1 Change in physical state

Matter appears in the form of solid, liquid or gas, it is capable of passing from one state to another under very specific temperature and pressure conditions.



IV.6.2. Hess's law

Enthalpy, you may recall, is a state function. This means that the enthalpy change for a chemical reaction is independent of the path by which the products are obtained. In 1840, the Russian chemist Germain Henri Hess, a professor at the University of St. Petersburg, discovered this result by experiment. Hess's law of heat summation states that for a chemical equation that can be written as the sum of two or more steps, the enthalpy change for the overall equation equals the sum of the enthalpy changes for the individual steps.

$$\begin{tikzcd}
C(s) + O_2(g) \arrow[rr, "\mathbf{\Delta H}"] \arrow[d, "\mathbf{\Delta H_1}"'] & & CO_2(g) \\
CO(g) + \tfrac{1}{2} O_2(g) \arrow[urr, "\mathbf{\Delta H_2}"'] & &
\end{tikzcd}$$

$\mathbf{\Delta H_1} = \Delta H_{products} - \Delta H_{reactifs} = [H_{(CO)} + 1/2\ H_{(O2)}] - [H_{(C)} + H_{(O2)}]$

$\mathbf{\Delta H_2} = H_{(CO2)} - [H_{(C)} + 1/2\ H_{(O2)}]$

$\mathbf{\Delta H} = \Delta H_1 + \Delta H_2 = H_{(CO)} + 1/2\ H_{(O2)} - H_{(C)} - H_{(O2)} + H_{(CO2)} - H_{(C)} - 1/2\ H_{(O2)}$

$$\Delta H = H_{(CO2)} – [H_{(C)} + H_{(O2)}]$$

Example:

$S(s) + O_2(g) \longrightarrow SO_2(g);\ \Delta H = -297\ kJ$ **(1)**

$2SO_3(g) \longrightarrow 2SO_2(g) + O_2(g);\ \Delta H = 198\ kJ$ **(2)**

$2S(s) + 3O_2(g) \longrightarrow 2SO_3(g)$

$$\begin{array}{lcl}
2S(s) + 2O_2(g) \longrightarrow \cancel{2SO_2(g)} & & \Delta H = (-297\ kJ) \times (2) \\
\cancel{2SO_2(g)} + O_2(g) \longrightarrow 2SO_3(g) & & \Delta H = (198\ kJ) \times (-1) \\
\hline
2S(s) + 3O_2(g) \longrightarrow 2SO_3(g) & & \Delta H = -792\ kJ
\end{array}$$

IV.6.3. Standard Enthalpies of Formation

The enthalpy of formation of a compound is the change in enthalpy which corresponds to the formation of one mole of this compound from its constituent elements. Under standard conditions, we define the "standard enthalpy of formation" which corresponds to the enthalpy of the synthesis of one mole of the compound from simple substances, taken in the standard state.

$$C(s) + O_2(g) \xrightarrow{\Delta H^\circ_R = \Delta H^\circ_f} CO_2(g)$$

$$\Delta H^\circ_f = -94.05\ Kcal.mol^{-1}$$

Note: For a simple substance $\Delta H^\circ_f = 0$

$\Delta H^\circ_f(O_2) = 0$; $\Delta H^\circ_f(N_2) = 0$; $\Delta H^\circ_f(C) = 0$; $\Delta H^\circ_f(H_2) = 0$

IV.6.4. Determination of the heat of reaction ΔH°_R from ΔH°_f

In a chemical reaction, to obtain the products we can imagine two processes:

1) Formation of products from elements: this is the direct process.
2) formation of reactants from elements then transformation of reactants into products.

$$\begin{tikzcd} \text{Eléments} \arrow[rr, "\sum \Delta H^\circ_{f(\text{produits})}"] \arrow[dr, "\sum \Delta H^\circ_{f(\text{réactifs})}"'] & & \text{Produits} \\ & \text{Réactifs} \arrow[ur, "\Delta H^\circ_R"'] & \end{tikzcd}$$

HESS's law: $\sum \Delta H^\circ_{f(\text{produits})}) = \sum \Delta H^\circ_{f(\text{réactifs})}) + \Delta H^\circ_R$

In general, you can calculate the **ΔH°_R** for a reaction by the equation:

$$\Delta H^\circ_R = \sum n\, \Delta H^\circ_{f(\text{produits})}) - \sum m\, \Delta H^\circ_{f(\text{réactifs})})$$

Here $\sum$ is the mathematical symbol meaning "the sum of," and n and m are the coefficients of the substances in the chemical equation.

Example:

$$CH_4(g) + 4Cl_2(g) \longrightarrow CCl_4(l) + 4HCl(g);\ \Delta H^\circ = ?$$

$$C(\text{graphite}) + 2H_2(g) \longrightarrow CH_4(g);\ \Delta H^\circ_f = -74.9\ \text{kJ} \qquad \textbf{(1)}$$

$$C(\text{graphite}) + 2Cl_2(g) \longrightarrow CCl_4(l);\ \Delta H^\circ_f = -135.4\ \text{kJ} \qquad \textbf{(2)}$$

$$\tfrac{1}{2}H_2(g) + \tfrac{1}{2}Cl_2(g) \longrightarrow HCl(g);\ \Delta H^\circ_f = -92.3\ \text{kJ} \qquad \textbf{(3)}$$

You now apply Hess's law. Since you want CH_4 to appear on the left, and CCl_4 and 4HCl on the right, you reverse Equation 1 and add Equation 2 and 4 x Equation 3.

$$\begin{array}{rcll}
CH_4(g) & \longrightarrow & \cancel{C(\text{graphite})} + \cancel{2H_2(g)} & (-74.9\ \text{kJ}) \times (-1) \\
\cancel{C(\text{graphite})} + 2Cl_2(g) & \longrightarrow & CCl_4(l) & (-135.4\ \text{kJ}) \times (1) \\
\cancel{2H_2(g)} + 2Cl_2(g) & \longrightarrow & 4HCl(g) & (-92.3\ \text{kJ}) \times (4) \\
\hline
CH_4(g) + 4Cl_2(g) & \longrightarrow & CCl_4(l) + 4HCl(g) & \Delta H^\circ = -429.7\ \text{kJ}
\end{array}$$

IV.6.5. Kirchhoff's law

Kirchhoff's law makes it possible to calculate the standard enthalpy of reaction at temperature T, knowing the standard enthalpy of reaction at temperature T_0.

$$\Delta H_T = \Delta H_{T0} + \int_{T0}^{T} n\Delta C_p dT \qquad \Delta U_T = \Delta U_{T0} + \int_{T0}^{T} n\Delta C_v dT$$

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