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The atom

Historical Overview

Since ancient times, man has been keen to learn the secrets of matter. Indian philosophers have developed opinions on the nature of matter, and Greek sages have tried to explain matter. Arab schools of thought and philosophy in Iraq and Egypt have developed theories in various sciences, including medicine, mathematics, chemistry, and others. These theories were recorded and became a law after experimentation and testing. Among the great Arab chemists are Jabir ibn Hayyan, known to the West as Jabir, Al-Razi, and Ibn Sina.

The atomic idea of matter was neglected for hundreds of years until Western scientists came in the Renaissance era, where they confirmed again that matter is not continuous and that it is composed of final parts that they called atoms.

The idea of the atom continued to oscillate between theoretical philosophy and primitive experiments until the beginning of the nineteenth century, when decisive scientific evidence came at the hands of the scientist Dalton.

Atomic Dalton's Theory

It can be said that the founder of the rules of the physical construction of the modern atomic theory is the English scientist Dalton, as the scientist conducted experiments on the solubility of gases in water and other liquids, and from them he reached his theory, which can be summarized as follows:

1- Matter consists of very small particles that he called atoms.

2- A single pure substance has atoms that are similar in size, weight, and some other properties.

3- The atom cannot be destroyed or created.

4- A single pure substance has atoms that cannot be divided or converted into atoms of another substance.

5- Atoms of a pure substance differ from atoms of another pure substance in terms of weight and some properties.

6- Chemical union occurs between atoms in simple numerical ratios.

Dalton's theory created a qualitative leap in the field of science and explained many scientific phenomena that were difficult at that time, and it remained in effect for many years until the end of the nineteenth century, when scientists' research revealed the shortcomings of the theory.

Electronic constitution of atom

The old chemical analysis methods could not solve the problem of the atomic structure of matter, while the solution came by chance through experiments of electric discharge through gases under low pressures. The scientist Thomson was able to prove the electronic components of the atom as well as give the characteristic of a negative charge to the electron and give a mass equal to 0.91 * 10^{-27} grams, which is approximately 1/1838 of the mass of a hydrogen atom. The scientist Thomson opened the door for scientists to investigate the new body that he called the electron. They were able to obtain the electron in different ways, including the effect of ultraviolet rays on metals as well as heating the metal to high temperatures, which led to establishing the scientific fact that the electron is one of the basic components of the atom. Finally, the charge of the electron was known, which is equal to 1.6 * 10^{-19} coulombs.

Nucleus

The study of radio radiation of some elements gave evidence of the components of the atom. The scientist Rutherford noticed the dispersion of alpha rays at a sharp angle when they hit a thin metal wall.

After extensive study with the scientists Kayker and Marsden, Rutherford developed the theory that there is a small positive center in the middle of the atom, which he called the nucleus. The radius of the atom is 10^{-12} - 10^{-13} cm, knowing that the radius of the atom is about 10^{-8} cm. The idea of the atomic structure developed rapidly thanks to numerous experiments, and the concepts known to many people became that the atom consists of two basic parts: the nucleus and the electrons. The mass of the atom is concentrated in its nucleus, and the nucleus contains positively charged protons and neutrally charged neutrons, and the protons and electrons have charges of equal magnitude and different in properties and sign. The number of protons in the atom is equal to the number of electrons, which means that the atom is electrically neutral.

Atomic number

The number of protons in the nucleus varies when the atoms of the elements differ and this number is called the atomic number, and the atomic number of the hydrogen atom is 1 and the uranium atom is 92.

How can positively charged protons stay inside the nucleus close to each other without repelling based on the fact that similar charges repel and different charges attract?

In fact, there is no clear and complete picture of the nuclear forces now, but the prevailing agreement is that when the proton and neutron are pulled to short distances towards each other, a strong attraction occurs between them that cannot be considered electromagnetic attraction, and there is no connection due to gravity, but to the existence of short-range forces between the protons or neutrons that are the basis for maintaining the stability of the nucleus. Therefore, nuclei that have many protons, i.e. have few clusters of protons and neutrons, will not be destined to remain for long, and examples of helium nuclei with a mass number of 2 He and lithium nuclei with a mass number of 4

Mass number

It is a term used to describe the sum of protons and neutrons within a single atom.

The molecule and molecular weight

When atoms combine with each other, they sometimes produce distinct units called molecules. For example, when four hydrogen atoms combine with one carbon atom, a methane molecule is produced.

The molecular weight is the sum of the atomic weights of the components of the molecule.

Therefore, the molecular weight of methane $CH4$ is

M.W=12+(1*4)=16 gm/mole

Mole

The substance is usually measured in a model by weight, volume or number, but in chemical calculations, the substance is expressed by the number of molecular particles, by which the weight or volume of the substance can be calculated. Therefore, the carbon 12 isotope was taken as a reference for these calculations, and the mole was considered to be the number of carbon atoms of this isotope present in a mass weighing 12 grams. On this basis, the mass of one mole of any element is estimated in grams as equal to its atomic weight in grams. For example, the atomic weight of fluorine is equal to 19, so the amount of substance present in 19 grams of gas is equal to one mole.

Avogadro's number

The number of particles in one mole of any substance is constant and is $6.0221 * 10^{23}$ particles and is called Avogadro's number, meaning we can express the mole in another way, which is the amount of substance that contains the same number of atoms. The mole is used for the number of atoms, molecules, electrons, protons, neutrons, etc.

Number of moles = weight / molecular weight

Initial formula for formation

The empirical formula expresses the relative numbers of atoms of the different elements in a compound using the smallest numbers possible. The numbers are obtained by converting the mass composition to moles of each element present in the compound constant.

Example 1

A compound containing Mg 17.09%, Al 37.93% and O 44.98%. Express the empirical formula of the compound.

Solution.

If the percentages of the components of the compound are given, the total weight of the compound is considered to be 100 g.

(1) العنصر	(2) كتلة العنصر	(3) الوزن الذري	(4) عدد المولات	(5) نسبة المولات
Mg	17.09	24.31	0.703	1
Al	37.93	26.98	1.406	2
O	44.98	16	2.812	4

The second column is given in the question.

The third column is given from the table.

The fourth column: Number of moles = weight / atomic weight

(17.09/24.31=0.703)

The fifth column is calculated by dividing each cell in the fourth column by the smallest value in the column

The initial formula becomes $MgAl_2O_4$

Example 2

If you have the compound Al_2O_3, find the percentages of each of the aluminum and oxygen.

Solution

The existence of formulas for a compound means that there is a fixed relationship between the weights of any two elements in the compound or between the weight of any element and the weight of the entire compound.

1	2	3	4	5
2Al	2mole	27gm/mole	54gm	0.529
$3O_2$	3mole	16gm/mole	48gm	0.471
Sum			102 gm	1.00

That is, the compound contains

52.9% aluminum and

47.1% oxygen.

Calculations based on chemical equations

Balancing chemical equations: **The balanced equation is the basis for all calculations of the quantities of substances involved in a chemical reaction.** When substances (reactants) interact to form new substances (products), we say that a chemical reaction has occurred. The equations in a balanced equation specify the number of molecules or units of the equation of each type and the equations must comply with Dalton's condition. There is no fixed method for balancing any equation, although there is a regular algebraic method in principle, but the right-wrong method is often suitable for this.

Example 1

Balance the following equation:

$\mathbf{FeS_2+O_2 \longrightarrow Fe_2O_3+SO_2}$

Solution

1- The algebraic method

We precede each term of the equation with a coefficient, here w x y z

$\mathbf{wFeS_2+xO_2 \longrightarrow yFe_2O_3+zSO_2}$

for Fe: w=2y S: 2w=z O: 2x=3y+2z

assume y= 2
w=4
x=11 z =8
The equation becomes
$4FeS_2 + 11O_2 \longrightarrow 2Fe_2O_3 +8SO_2$

Example 1

Balance the following equation by true and false:

$C_7H_6O_2 + O_2 \longrightarrow CO_2 + H_2O$

1- To make the carbon on the right side equal to the carbon on the left, we multiply the right by *7

2- To make the hydrogen on the right side equal to the carbon on the left, we multiply the left by *3

3- To make the oxygen equal on both sides, we multiply the second term on the left side by *7.5, so the balanced equation is

$C_7H_6O_2 + 7.5O_2 \longrightarrow 7CO_2 + 3\,H_2O$
Or

$2C_7H_6O_2 + 15O_2 \longrightarrow 14CO_2 + 6\,H_2O$

Types of Chemical Reactions
1- Combustion Reactions:

Excess oxygen combines with organic compounds to form CO_2 and water.

$C_2H_6O + 3O_2 \longrightarrow 2CO_2 + 3H_2O$

2- Replacement Reaction
A more active element replaces a less active element in any compound, such as
$Zn + CuSO_4 \longrightarrow Cu + ZnSO_4$

3- Double replacement reactions

This reaction is neutral in the case of ionic reactions, as atoms or a group of atoms exchange with their partners.

$AgNO_3 + NaCl \longrightarrow NaNO_3 + AgCl$
$BaCl_2 + Na_2SO_4 \longrightarrow 2NaCL + BaSO_4$

4- Acid-base reactions. The acid that provides H+ and the base that provides OH enter into an exchange reaction to form a salt and water.

$HCl+NaOH \longrightarrow NaCl+H_2O$

5- Combination reactions Elements and compounds simply combine to form a single product such as:

$2SO_2+O_2 \longrightarrow 2SO_3$

6- Decomposition reactions: In which one reactant is converted by heat or electrolysis into two or more products, such as:

$2H_2O \longrightarrow 2H_2+O_2$

Reactions can be divided into two types depending on the state of the reactants and products:

1- Homogeneous reactions

These are reactions in which the reactants and products are of the same phase, such as

$2SO_2(gas)+O_2(gas) \longrightarrow 2SO_3 \quad (gas)$

2- Heterogeneous reactions: These are reactions that combine more than one phase at once, such as:

$4HgO(solid) \longrightarrow 2Hg_2O(solid)+O_2(gas)$

Mass Relationship from Equations

The relative numbers of molecules of reactants and products (relative moles) are shown from the coefficients in balanced chemical equations. Using molar masses, the relative masses of reactants and products from any chemical reaction can be calculated.

Example:

$4NH_3+3O_2 \longrightarrow 2N_2+6H_2O$

Solution:

$n=w/mw$
$n_{(NH3)}=10/17=0.5882$ moles
$n_{(O2)}=0.5882*3/4=0.4412$ moles
$n_{(N2)}=0.5882*2/4=0.2941$ moles
$n_{(H2O)}=0.5882*6/4=0.8823$ moles

Using molar masses (molecular weights), the weights of the reactants and products can be calculated.

Weight = number of moles * atomic or molecular weight

Weight of oxygen = 0.4412 * 32 = 14.12 g

Weight of nitrogen = 0.2941 * 28.01 = 8.238 g

Weight of water = 0.8823 * 18.02 = 15.899 g

Weight of ammonia = 10 g

Thermodynamics

Thermodynamics: It is a science concerned with studying energy changes and transformations that accompany physical and chemical processes and is concerned with determining the spontaneity or non-spontaneity of the reaction.

Thermochemistry: It is a branch of thermodynamics concerned with studying thermal changes (enthalpy) of both exothermic and endothermic types that accompany chemical reactions and physical changes.

Q // What phenomena does thermodynamics explain?

1. The reason for chemical reactions.

2. Predicting the occurrence of chemical and physical reactions when one or more substances are present under certain conditions.

3. Some reactions occur spontaneously and others never occur spontaneously under the same conditions.

4. The reason for the occurrence of energy accompanying chemical reactions, whether for the reactions themselves or in the surrounding medium.

5. Thermodynamics is not concerned with the time factor required for reactions to occur.

Type of energy

1. **Potential energy (PE):** It includes the chemical energy stored in all types of materials and all types of fuel.

2. **Kinetic energy (KE)**: It includes the energy of all moving objects such as molecules and moving water as well as cars, airplanes, etc.

Energy and temperature units

Joule J: It is the unit of energy according to the International System of Units

$$\mathbf{1J=1Kg.m^2/s^2 =1N.m}$$

Where kg: kilogram, m: meter and s: second, N: newton

Where KE kinetic energy equals the product of half the mass m and the square of the speed v $KE=1/2\ m\ v^2$

The unit of temperature in thermodynamics we use the Kelvin unit according to the following relationship $T(k)=T(C°)+273$

The first law in thermodynamics: Energy is neither created nor destroyed, but it can be converted from one form to another. For example, potential energy in water is converted into kinetic energy if the water moves from the top of the waterfall to the bottom because the resulting energy can rotate the engine to generate electrical energy.

Some thermodynamic terms

System: It is a part of the universe consisting of matter or materials involved in a chemical reaction or physical change.

The environment: It is everything that surrounds the system and affects it from physical or chemical changes.

The group: It is the system and the environment (**a pot containing water**).

The system can be divided into three types:

Type of systems

1- Open system: It is the system that allows the exchange of the system's matter and energy with the environment

Example: **A metal pot containing boiling water**, the system's matter (water vapor) rises to the environment and the water's heat (energy) leaks into the environment

2. Closed system **(pressure cooker)**: It is the system that allows the exchange of energy only and does not allow the change in the amount of the system's matter and its exchange with the environment

Example: **A closed pot containing boiling water** allows the exchange of only the water's heat (energy)

3. Isolated system: It is the system that does not allow the exchange of energy or the system's matter with the environment and is never affected by the environment

Example: Thermos.

Heat (**q**): It is the transfer of thermal energy between two bodies with different temperatures.

Temperature: It is a measure of thermal energy, and the heat lost and gained is directly proportional to the change in temperature. The change is symbolized by the symbol (Δ)

$\Delta T = T_f - T_i$

Tf: Final temperature (final)

Ti: Initial temperature (initial)

(1) $q \alpha \Delta T$ The proportionality is converted to a constant called heat capacity (C)
(2) $q = C.\Delta T$

(3) $C = \delta . m$ Capacity law

By substituting Equation 3 in Equation 2, we get the following equation

$q = \delta .m. \Delta T$

Units:

q: J Joules; Ç: J/g.c°; m:g; ΔT: C°; C: J/C°

Heat capacity (C): It is the amount of heat required to raise the temperature of a mass (g) of any substance by one degree Celsius. Its unit is J/C°.

Specific heat (δ): It is the amount of heat required to raise the temperature of one gram of any substance by one degree Celsius. Its unit is J/g.c°.

Example

What is the amount of heat produced by heating a piece of iron with a mass of 870 g from 5 to 95 C°, knowing that the specific heat of iron is 0.45 J/g.c?

Solution.

$\Delta T=Tf-Ti$
$=95-5=90$
$q=Ç*m*\Delta T$
$=0.45*870*90=35235J$

Example

The temperature of a 10-gram piece of magnesium changed from 25 to 45 C° with a heat gain of 205 J. Calculate the specific heat of magnesium.

Solution:

$\Delta T=Tf-Ti$
$=45-25=20$
$q=Ç*m*\Delta T$
$Ç = q/(m*\Delta T)$
$Ç=205/10*20=1.025J/g.C$

Heat of reaction or change in enthalpy ΔH

ΔH represents the amount of heat absorbed or released measured at constant pressure, i.e. the reaction is endothermic or exothermic.

$\Delta H=qp$

qp (heat at constant pressure)

ΔHr (change in reaction heat)

$0C°>\Delta Hr$ (Exothermic reaction)

$\Delta Hr>0C°$ (Endothermic reaction)

$\Delta Hr=\Delta HP-\Delta HR$

ΔHP (Products heat)

ΔHR (Reactant heat)

State function: It is the property or quantity that depends on the initial state of the system before the change and the final state of the system after the change regardless of the path or path through which the change occurred.

Example: Enthalpy is a state function because it has an initial state (reactants) and a final state (products).

There are other functions such as entropy and compression energy.

As for heat or work, they are not considered state functions because their values change greatly with the change in the experimental conditions and depend on the steps and path through which the change occurred.

The absolute value of state functions cannot be measured, but the amount of change can be measured in enthalpy, which is equal to

$\Delta H = \Delta Hf - \Delta Hi$

The general properties of materials are divided into:

1- **Extensive properties**: These are properties that depend on the amount of matter present in the system, such as mass, volume, thermal capacity, enthalpy, entropy, and free energy.

2- **Intensive properties**: These are properties that do not depend on the amount of matter present in the system, such as pressure, temperature, and density.

Thermochemistry

1- Exothermic reaction (ΔHr=-): It is the chemical reaction that is accompanied by the release of heat because the energy of the reactants is greater than the energy of the products and the value of the change in enthalpy is negative.

$$\underset{g}{2H_2}+\underset{g}{O_2}=\underset{L}{2H_2O}+\underset{\text{number}}{\text{ENERGY}}$$

2- Endothermic reaction (ΔHr=+): It is the chemical reaction that is accompanied by the absorption of heat because the energy of the reactants is less than the energy of the products and the value of the change in enthalpy is positive.

$$\underset{s}{2HgO}+\underset{\text{number}}{\text{ENERGY}}=\underset{L}{2Hg}+\underset{g}{O_2}$$

Note: When the energy is on the side of the reactants, the reaction is endothermic, and when the energy is on the side of the products, the reaction is exothermic.

Measuring the enthalpy of reaction using the calorimeter

The calorimeter is used to measure the heat of reaction (enthalpy of reaction) absorbed or released, as known quantities of reactants are placed in the reaction vessel that is immersed in a certain amount of water in a well-insulated vessel. Since the heat released from the reaction raises the temperature of the water and the calorimeter, its quantity can be measured from the increase in temperature if the heat capacity of the calorimeter and its contents are known. When calculating the enthalpy of reaction using this method, pay attention to the following notes.

1- It gives a known mass of a chemical compound that is placed in the calorimeter and burned.

2- It gives the mass of water, from which we calculate q for water, which also represents the heat of the chemical compound, but this heat represents the number of moles burned according to the given mass n=w/mw, if the heat of the compound is required to be calculated in moles different from the moles of the question, we work on a ratio and proportion, and the negative sign means that the reaction is exothermic.

Example /

3 g of glucose compound $C_6H_{12}O_6$ with a molecular weight of 180 g/mole were placed in the reaction vessel, then the reaction vessel was filled with oxygen gas and this vessel was placed inside the insulated vessel that was filled with 1200 g of water (the specific heat of water is 4.2 J/g.c) and the initial temperature was 21°C. The mixture was burned and when the temperature was measured, it was found that the reaction raised the temperature of the calorimeter and its contents to 25.5°C. Calculate the amount of heat released in KJ as a result of burning 1 mole of glucose, assuming that the heat capacity of the calorimeter is negligible.

Solution:

$\Delta T=\Delta Tf - \Delta Ti$
$25.5-21=4.5$ C°
$q=Ç * m * \Delta T$

$= 4.2*1200*4.5= -22680$J Since the heat was released, a negative sign is given to it.

$n=w/mw$
$=3/180=0.017$mole
(Required for one mole)

Mole	q
0.017	-22680
1	x

$X=1*22680/0.017=-1334118$J/mole

Since the heat is under constant pressure

$\Delta H = qp = -1334118$J/mole

Example/2

If 3 grams of hydrazine N_2H_4 (molar mass of 32 g/mol) are burned in an open calorimeter containing 1000 grams of water (the specific heat of water is 4.2 J/g.C°), the temperature rises from 24.6°C to 28.2°C. Calculate the heat released as a result of the combustion of 1 mole of hydrazine in KJ/mole, assuming that the heat capacity of the calorimeter is negligible.

Solution

$\Delta T = \Delta Tf - \Delta Ti$
28.2-24.6=3.6C°
q=Ç *m*ΔT
= 4.2*1000*3.6= -15120J negative sign means that the heat was released

ΔH=qp= 15120J/mole
n=w/mw=3/32=0.094 mole

Mole	q
0.094	-15120
1	x

X=1*15120/0.094=-160851J/mole

Thermochemical equation

When writing thermochemical equations, we must show the following:
1- The sign of the change in enthalpy accompanying the chemical reaction. When writing the value of ΔH with the reactants, this means that **the reaction is endothermic, i.e. it is positive**, such as

$$\underset{S}{H_2O} + 6KJ/mole \longrightarrow \underset{L}{H_2O} \qquad \Delta H=6KJ/mole \text{ (endothermic)}$$

When writing the value of ΔH with the resulting materials, this means that **the reaction is exothermic, i.e. it is negative**, such as:

$$\underset{g}{CH_4} + \underset{g}{2O_2} \longrightarrow \underset{g}{CO_2} + \underset{L}{2H_2O} + 890KJ/mole \quad \Delta H=-890KJ/mole$$

2- The physical state of the materials entering into the reaction and resulting from it must be mentioned, because the amount of heat absorbed or released changes with the change in the physical state of the reaction materials, such as:

$H_2+1/2O_2 \longrightarrow H_2O$ ΔH=-286KJ/mole
g g L

$H_2+1/2O_2 \longrightarrow H_2O$ ΔH=-242KJ/mole
g g L

3- If the process of the reaction is reversed, the enthalpy sign changes to the opposite of what it was (Hess applications)

$H_2O \longrightarrow H_2O$ ΔH=6KJ/mole (endothermic)
s L

$H_2O \longrightarrow H_2O$ ΔH=-6KJ/mole (exothermic)
L S

4- When multiplying or dividing both sides of the equation by a specific numerical coefficient, the same operation must be performed on the value of ΔHr°.

$H_2O \longrightarrow H_2O$ ΔH=6KJ/mole
S L

*2

$2H_2O \longrightarrow 2H_2O$ ΔH=2*6 KJ/mole
S L

$C_5H_{12} + 8O_2 \longrightarrow 5CO_2 + 6H_2O$ ΔHr°= -3523 KJ/ Standard

Enthalpy of reaction (ΔHr°)

It means measuring the enthalpy at standard conditions, which are: 25°C (298K) and pressure (1 atm). It is symbolized by (ΔHr°)

It differs from STP for gases, which is 0°C (273) and pressure (1 atm)mol

$C_5H_{12} + 8O_2 \longrightarrow 5CO_2 + 6H_2O \qquad \Delta Hr° = -3523\ KJ/mol$

Types of enthalpy

1- **Standard enthalpy of formation (ΔHf°)**
2- **Standard enthalpy of combustion (ΔHc°)**
3- Enthalpy of physical changes.

1- Standard enthalpy of formation (ΔHf°): It is the heat required to form one mole of any compound from its basic elements present in their most stable form at standard conditions (1atm. 25C°).

*(Elements in their most stable forms are always stable) at standard conditions = (0) zero.

For example: gaseous H2. Liquid mercury. Solid magnesium is the most stable because it represents the states that exist under standard conditions (25C°). (1atm)

*Some elements have more than one form under standard conditions: -

For example 1- Carbon has two forms (graphite gr) which is the most stable. (And diamond)

2- Sulfur has: rhombic form which is the most stable. (and prismatic).

3- Unstable elements have ΔHf° ≠ zero such as C diamond and S prismatic and Fe liquid.

How to write the formation equation: -

1- The substance is placed on the products side, and on the reactants side the elements that make up the substance are placed (all elements are written individually except CL_2)-Br_2-O_2-H_2-F_2-N_2-2I-)).

2- The value of ΔHf° for the substance is the same as ΔHr° for the equation written for that substance when writing the equation **(in one mole)**. If the substance is more than one mole, then (ΔHr° = mole number * ΔHf°).

Examples of some substances and writing their formation equation: -

$\underset{g}{H_2} + 1/2O_2 \longrightarrow \underset{L}{H_2O}$ ΔHf°=-286KJ/mol

$\underset{(g)}{3/2H_2} + 2O_2 + 1/4P_4 \longrightarrow \underset{S}{H_3PO_4}$ ΔHf°=ΔHr°= - 128kJ/mol

$\underset{s}{Mg} + Cl_2 \longrightarrow \underset{s}{MgCl}$ ΔHf°=ΔHr°= -642KJ/mol

$\underset{Gr}{C} + \underset{g}{O2} \longrightarrow \underset{g}{CO2}$ ΔHf°=ΔHr°= -394KJ/mol

$\underset{g}{H_2} + \underset{g}{Br_2} \longrightarrow \underset{g}{2HBr}$ للحامض ΔHf° = -36KJ/mol

But (ΔHr°) for the equation becomes 72- =2*36- because the substance is two moles

*And so for any equation ((be careful))

*And ΔHr° may be given and we can find ΔHf° from it.

Explain / Fractions appear in the thermal equation?

Answer / Because of writing the thermochemical equation that represents the formation of one mole of the compound to be formed, so we resort to changing the number of moles.

Example / If you know that the standard enthalpy of formation of benzene C6H6 is equal to 49KJ/mol, write the thermochemical equation for the reaction so that ΔHr°=ΔHf° for benzene.

The answer / *The equation must be written with one mole of benzene.

$6C_{(Gr)} + 3H_2 \longrightarrow C_6H_{6(L)}$ ΔHf°=ΔHr° = 49KJ/mol

Example / Which of the following reactions has a standard enthalpy of reaction value ΔHr = a standard enthalpy of formation value ΔHf° for the following compounds.

1- $4Fe_{(S)} + 3O_{2(g)} \longrightarrow 2Fe_2O_{3(S)}$ ΔHr°=1625Kj/mol

2- $C_{(gr)} + O\ 2_{(g)} \longrightarrow CO_{2(g)}$ ΔHr°=-394KJ/mol

3- $CO_{(g)} + 1/2O_{2(g)} \longrightarrow CO_{2(g)}$ ΔHr°= 283KJ/mol

Answer /

1- The first reaction / The value of ΔHr° for this reaction does not equal ΔHf° for the substance because the substance formed (2 mol).

2- The second reaction / ΔHr°=ΔHf° because the equation fulfills two conditions, the formation of one mole of CO2 and its basic elements in their most stable form.

3- The third reaction / ΔHr°≠ΔHf° for CO2 because the reactants are not elements in their most stable form.

Example: If you know that the heat of formation of sulfuric acid ((H_2SO_4)

ΔHf°=-822KJ/mol)) write the thermochemical equation for the reaction such that

ΔHr°=ΔHf° for H_2SO_4.

Answer

$H_2 + S + 2O_2 \longrightarrow H_2SO_4$ ΔHr°=ΔHf°= -811KJ/mol

Example / Calculate the standard reaction enthalpy ΔHr° for the following reaction if you know that

$H_2 + F_2 \longrightarrow 2HF$ ΔHf°=-271Kj/mol

solution

ΔHr°= 2*-271=-542KJ/mol

2- Standard enthalpy of combustion (ΔHc°)

It is the heat released (emitted) from burning one mole of any substance (element or compound) completely with an abundance of oxygen at standard conditions of temperature (25°C) and pressure (1 atm).

• The importance of the heat of combustion: 1- Determining the calorific value of fuel and food materials

2- Finding the enthalpy of formation for some complex compounds

• All combustion reactions are exothermic reactions (the question may mention the phrase heat released or emitted and give a positive number for it, so be careful to always use a negative sign).

• ΔHr°=ΔHc° if the combusted substance reacts with (one mole) with oxygen. (If it is more than one mole then (ΔHc°*mole number = ΔHr°))

How to write the combustion equation:-

1- The element is written with oxygen in the reactions and the result is the oxide of that element, for example

$\underset{(gr)}{C} + \underset{(g)}{O_2} \longrightarrow \underset{(g)}{CO_2}$ ΔHc°=-394Kj/mol (C)

$H_2 + 1/2\, O_2 \longrightarrow H_2O$ ΔHc°=-286Kj/mol (H)

$S + O_2 \longrightarrow SO_2$ $\Delta HC^\circ=-298KJ/mole$
(rhombic) (g) S

The substance, especially organic substances, reacts with oxygen and the result is always $H_2O + CO_2$

$C_4H_{10} +13/2O_2 \longrightarrow 4CO_2 +5H_20$ $\Delta HC^\circ=-2873KJ/mole$
BUTANE(g) (g) (g) (L) butane

$C_8H_{18} +25/2O_2 \longrightarrow 8CO_2 +9H_20$ $\Delta HC^\circ=-5471KJ/mole$
OCTANE(L) (g) (g) (L) octane

$C_2H_5OH +3O_2 \longrightarrow 2CO_2 +3H_20$ $\Delta HC^\circ=-1367KJ/mole$
ETHANOL(L) (g) (g) (L) ETHANOL(L)

$C_6H_{12}O_6 +6O_2 \longrightarrow 6CO_2 +6H_20$ $\Delta HC^\circ=-2808KJ/mole$
KLOCOUZE(S) (g) (g) (L) KLOUKOZE

Q) For the following reaction under the same conditions, the numerical value of ΔHr° is the same as ΔHf° for CO2 and the same as ΔHc° for carbon.

$C + O_2 \longrightarrow CO_2$

(gr) (g)

ΔHr° is the same as ΔHf° for carbon dioxide because the product is single and of one mole and is one of the most stable basic elements and ΔHr° is the same as ΔHc° for carbon because it burns with one mole and in abundance of oxygen.

Example) Write the thermochemical equation for the burning of liquid ethyl alcohol if you know that ΔHc° (C_2H_5OH) =-1367KJ/mole

solution

$C_2H_5OH +3O_2 \longrightarrow 2CO_2 +3H_20$ $\Delta Hc^\circ=-1367KJ/mole=\Delta Hr^\circ$
ETHANOL(L) (g) (g) (L) ETHANOL(L)

Example) Write the combustion reaction of propane gas (C_3H_8) if you know that ΔHc°=-2219 Kj/mol

$$\underset{(g)}{C_3H_8}+\underset{(g)}{5O_2} \longrightarrow 3CO_2+4H_2O$$

$\Delta Hc° = \Delta Hr° = -2219$ KJ

Example) The following reaction $4Al+3O_2 \longrightarrow 2Al_2O_3$ has

ΔHr° =-3340KJ/mol find:

1- ΔHf° for Al_2O_3
2- ΔHc° for Al

Solution

1- ΔHf °=ΔHr°/2 -3340/2= -1670 KJ/mol
2- ΔHc°= ΔHr°/4 -3340/4=-835 KJ/mol

3- **Enthalpy of physical changes**: It is the process of transforming a chemical substance from one phase to another phase of the same substance. Its types are:

1- Evaporation process (ΔHvap): Transforming a substance from a liquid to a vapor.
2- Condensation process (ΔHcond): Transforming a substance from a vapor to a liquid.

The evaporation process is the opposite of the condensation process

$\Delta H_{vap} = -\Delta H_{cond}$

3- Melting process ΔHfus (Fusion): The material changes from solid to liquid.
4- Freezing process ΔHcryst (Crystallization): The material changes from liquid to solid. It is the opposite of the melting process.

$\Delta H_{fus} = -\Delta H_{cryst}$

The enthalpy of vaporization and the enthalpy of fusion are positive, while the enthalpy of condensation and the enthalpy of freezing are negative.

$$H_2O_{(L)} \xrightarrow{vap} H_2O_{(g)} \qquad \Delta H_{vap} = 44KJ/mole$$

$$H_2O_{(g)} \xrightarrow{cond} H_2O_{(L)} \qquad \Delta H_{cond} = -44KJ/mole$$

$$H_2O_{(S)} \xrightarrow{fus} H_2O_{(L)} \qquad \Delta H_{fus} = 6KJ/mole$$

$$H_2O_{(L)} \xrightarrow{cryst} H_2O_{(s)} \qquad \Delta H_{cryst} = -6KJ/mole$$

Example 1:

If you know that the enthalpy of vaporization of ammonia is 23 KJ/mole, calculate the enthalpy of condensation of ammonia.

Solution.

$$NH_{3(L)} \longrightarrow NH_{3(g)} \qquad \Delta H_{vap} = 23KJ/mole$$

$$NH_{3(g)} \longrightarrow NH_{3(L)} \qquad \Delta H_{cond} = -23KJ/mole$$

Example 2:

If you know that the enthalpy of fusion of glacial acetic acid (CH_3COOH) is 5.11 KJ/mole, calculate the enthalpy of freezing of this acid.

solution.

$$CH_3COOH_{(s)} \longrightarrow CH_3COOH_{(L)} \qquad \Delta H_{fus} = +5.11KJ/mole$$

$$CH_3COOH_{(L)} \longrightarrow CH_3COOH_{(s)} \qquad \Delta H_{cryst}=-5.11KJ/mole$$

Methods for calculating reaction enthalpy:

1- Hess's Law method.

2- Method of using standard enthalpy of formation values.

1- **Hess's Law method**: When converting reactants to products, the change in reaction enthalpy is the same whether the reaction goes through one step or a series of steps.

Importance:

There are many chemical compounds that cannot be manufactured directly from their elements?

This is for many reasons, including that the reaction may proceed very slowly or form unwanted side compounds.

Hess's Law depends on the fact that (ΔHr°) is a state function, meaning that it depends on the initial and final states of the system only (i.e. on the nature of the reactants and products) and does not depend on the paths taken by the reaction to transform from reactants to products.

Hess's Law solution steps

1- The question gives two or three equations with information (ΔHr°)

2- A main goal is required to state one of the three types of enthalpies, and we may work on writing the equation or it may be written.

3- The known equations (ΔHr°) we modify them (reverse, multiply, divide) according to the question, then we put forward the similarities between the reactant, product and residue, an equation similar to the target appears.

4- We collect (ΔHr°) for the equations after the modification, so we show (ΔHr°) for the target equation, then we use it for the main requirement.

5- The rates may not be given, but we write them and then modify them, especially if the question gives two or more combustion enthalpies, as in the following example

$$\underset{(gr)}{C} + \underset{(g)}{1/2O_2} \longrightarrow \underset{(g)}{CO} \qquad \Delta Hr^\circ=?$$

يعطى التفاعلين المعلومين (ΔHr°)

1- $$\underset{(gr)}{C} + \underset{(g)}{O_2} \longrightarrow \underset{(g)}{CO_2} \qquad \Delta Hr^\circ=-393.5KJ/mol$$

2- $$\underset{(g)}{CO} + \underset{(g)}{1/2O_2} \longrightarrow \underset{(g)}{CO_2} \qquad \Delta Hr^\circ=-283KJ/mol$$

Solution:

1- Equation number one remains because (C) is similar in location and mole (reactant).
2- 2- We reverse the second equation because the location of (CO) is not similar to the location of the target equation.

So the solution is

$$\underset{gr}{C} + \underset{g}{O_2} \qquad \underset{g}{CO_2} \qquad \Delta Hr^\circ=-393.5KJ/mol$$

$$\underset{g}{\cancel{CO_2}} \longrightarrow \underset{g}{CO} + 1/2\,\underset{g}{\cancel{O_2}} \qquad \Delta Hr^\circ=+283KJ/mol$$

$$\underset{gr}{C} + \underset{g}{1/2O_2} \longrightarrow \underset{g}{CO} \qquad \Delta Hr^\circ=-110.5\ KJ/mol$$

Example / Calculate the enthalpy of formation of the compound CS_2) from its basic elements, a base image.

$$C_{(gr)}+2S_{(\text{معيني})} \qquad CS_{2(L)}$$

اذا اعطيت المعادلات التالية :-

1- $C_{(gr)} + O_{2(g)} \longrightarrow CO_{2(g)}$ $\quad \Delta Hr° = -394$ KJ

2- $S_{(\text{معيني})} + O_{2(g)} \longrightarrow SO_{2(g)}$ $\quad \Delta Hr° = -296$KJ

3- $CS_{2(l)} + 3O_{2(g)} \longrightarrow CO_{2(g)} + 2SO_{2(g)}$ $\quad \Delta Hr° = -1072$K

Solution

الحل

معالدلة رقم واحد تبقى

معادلة رقم اثنين تضرب في 2

معادلة رقم ثلاثة تقلب

1- $C_{(gr)} + \cancel{O_{2(g)}} \longrightarrow \cancel{CO_{2(g)}}$ $\quad \Delta Hr° = -394$ KJ

2- $2S_{(\text{معيني})} + \cancel{2\,O_{2(g)}} \longrightarrow \cancel{2SO_{2(g)}}$ $\quad \Delta Hr° = 2 * -296$KJ

3- $\cancel{CO_{2(g)}} + \cancel{2SO_{2(g)}} \longrightarrow CS_{2(l)} + \cancel{3O_{2(g)}}$ $\quad \Delta Hr° = +1072$K

$C_{(gr)} + 2S_{(\text{معيني})} \longrightarrow CS_{2(l)}$ $\quad \Delta Hr° = +\ 186$KJ

Example / Calculate the standard enthalpy of formation ($\Delta Hf°$) of acetylene C_2H_2 from its basic elements

$2C + H_2 \longrightarrow C_2H_2$

اذا اعطيت المعادلة التالية :-

1- $C + O_2 \longrightarrow CO_2$ $\Delta Hr° = -394$ KJ
2- $H_2 + 1/2\ O_2 \longrightarrow H_2O$ $\Delta Hr° = -286$KJ
3- $2C_2H_2 + 5O_2 \longrightarrow 4CO_2 + 2H_2O$ $\Delta Hr° = -2599$KJ

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solution

المعادلة الاولى تضرب في 2

المعادلة الثانية تبقى

المعادلة الثالثة تقلب وتقسم على 2

1- $2C + \cancel{2O_2} \longrightarrow \cancel{2\ CO_2}$ $\Delta Hr° = 2 * -394$ KJ
2- $H_2 + \cancel{1/2\ O_2} \longrightarrow \cancel{H_2O}$ $\Delta Hr° = -286$KJ
3- $\cancel{2CO_2} + \cancel{H_2O} \longrightarrow C_2H_2 + \cancel{5/2\ O_2}$ $\Delta Hr° = +2599$KJ /2

$2C + H_2 \longrightarrow C_2H_2$ $\Delta Hr° = 225.5$KJ

It is the same as ° ΔHf for C2H2 (because

(1) the product is one,

(2) one mole,

(3) it is one of its basic elements and in a stable form(

$\therefore \Delta Hf°_{C2H2} = \Delta Hr° = +225.5$KJ

Example: If you know that the enthalpy of combustion of H_2, CO and CH_3OH is -286, -284 and -727 KJ/mol respectively, calculate the enthalpy of the following reaction:

$$\underset{g}{CO} + \underset{g}{2H_2} \longrightarrow \underset{L}{CH_3OH}$$

Solution:

Using the enthalpies of combustion, we write combustion equations for one mole of the given materials in order to achieve the condition of equality of the enthalpy of reaction with the enthalpy of combustion, i.e. ($\Delta Hf° = \Delta Hr$)

Since the question informs us that there is combustion of hydrogen, oxygen and alcohol, the equations that we write are as follows:

$$\underset{g}{H_2} + \underset{g}{1/2O_2} \longrightarrow \underset{L}{H_2O} \qquad \Delta Hr° = -286\ KJ$$

$$\underset{g}{CO} + \underset{g}{1/2O_2} \longrightarrow \underset{g}{CO_2} \qquad \Delta Hr° = -284\ KJ$$

$$\underset{g}{CH_3OH} + \underset{g}{3/2O_2} \longrightarrow \underset{g}{CO_2} + \underset{L}{2H_2O} \qquad \Delta Hr° = -727\ KJ$$

نحور المعادلات لكي تتماشي مع المعادلة الهدف وكما يلي:
المعادلة الاولى *2
المعادلة الثانية تبقى
المعاجدة الثالثة تقلب

$$\underset{g}{2H_2} + \underset{g}{\cancel{O_2}} \longrightarrow \underset{L}{\cancel{2H_2O}} \qquad \Delta Hr° = (-286)*2\ KJ$$

$$\underset{g}{CO} + \underset{g}{\cancel{1/2O_2}} \longrightarrow \underset{g}{\cancel{CO_2}} \qquad \Delta Hr° = -284\ KJ$$

$$\underset{g}{\cancel{CO_2}} + \underset{L}{\cancel{2H_2O}} \longrightarrow \underset{g}{CH_3OH} + \underset{g}{\cancel{3/2O_2}} \qquad \Delta Hr° = +727\ KJ$$

$$\underset{g}{2H_2} + \underset{g}{CO} \longrightarrow \underset{g}{CH_3OH} \qquad \Delta Hr° = -129\ KJ$$

2- Method of using the standard enthalpy of formation values:

A law can be used to calculate ΔHr° from the standard enthalpy of formation values ΔHf° for chemical compounds as follows:

$$\Delta Hr° = \sum n\Delta Hf°\ (products) - \sum n\Delta Hf°\ (reactants)$$

n= The factors in equalized equation

for equation below

$$aA \ + bB \longrightarrow dD + eE$$

that

$\Delta Hr° =[d^*(\Delta Hf°D) +e^*(\Delta Hf°E)] – [a^*(\Delta Hf°A) + b^*(\Delta Hf°B)]$

Important Notes:

- This law is used to find ($\Delta Hr°$) from the values of ($\Delta Hf°$) for the materials of the equation and vice versa, it may give ($\Delta Hr°$) information and ($\Delta Hf°$) for one of the materials is unknown.
- If a combustion equation is given, do not forget that $\Delta Hc° = \Delta Hr°$ for one mole. If $\Delta Hc°$ is given for a material and there is no equation, write a combustion equation.
- If the combustion of a material gives its value in mass, we do the following:-

  1- Convert the mass to moles $n=m/M$

  2- Then we calculate $\Delta Hr°$ from it by comparing it to the figure

- If he gave two equations and the common factor between them is (a substance), then $\Delta Hf°$ is considered constant for each substance. We can extract it from one equation and use it in another equation.
- If he gave $\Delta Hf°$ for two elements, remember that this element is not constant and stable, so pay attention to that.

Example: The thermite reaction involving aluminum and iron oxide Fe+3 proceeds as follows:

$\underset{s}{2Al} + \underset{s}{Fe_2O_3} \longrightarrow \underset{s}{Al_2O_3} + \underset{L}{2Fe}$, calculate $\Delta Hr°$ if:

$\Delta Hf° (Al_2O_3) =- 1670 KJ/mol$

$\Delta Hf° (Fe_2O_3) =-822 KJ/mol$

$\Delta Hf° (Fe) = 12 KJ/mol$

Solution:

$\Delta Hr° = \sum n\Delta Hf° (products) - \sum n\Delta Hf° (reactants)$

$\Delta Hr° = ((-1670) + 2(12)) - (2(0) + (-822))$

وذلك لان الالمنيوم في الحالة الصلبة $\Delta Hf° (Al) = 0$

$\Delta Hr° = (-1646)-(-822)$ $\Delta Hr° = -824kJ$

Example: Benzene (C_6H_6) burns in air to give carbon dioxide and liquid water. Calculate ΔHr° for this reaction, knowing that

$\Delta Hf° (C6H6) = 49$ KJ / mol

$\Delta Hf°(CO2) = -394$ KJ/ mol

$\Delta Hf°(H2O) = -286$ KJ/ mol

Solution

Write combustion equation

$$\underset{L}{C_6H_6} + \underset{g}{15/2O_2} \longrightarrow \underset{g}{6\,CO_2} + \underset{L}{3\,H_2O}$$

$$\Delta Hr° = \sum n\Delta Hf° \,(products) - \sum n\Delta Hf° \,(reactants)$$

$\Delta Hr° = (6(-394) + 3(-286)) - ((498) + 15/2(0))$
$= -3271KJ$

Example / Calculate (ΔHf°) for methane gas if you know:

$\Delta Hf°(H_2O) = -286KJ/mol$

$\Delta Hf°(CO_2) = -394KJ/mol$

And ΔHc° for (2g) of ($CH_4 = -111.27$ KJ) knowing that $CH_4 = 16$ g/mol

Solution

Combustion equation is $\underset{g}{CH_4} + \underset{g}{2O_2} \longrightarrow \underset{g}{CO_2} + \underset{L}{2H_2O}$

n=W/MW

n=2/16=0.125 moles

mole	heat
0.125	111.27
1	X

$X = \Delta Hr° = -890.16\ KJ$

$$\Delta Hr° = \sum n\Delta Hf°\,(products) - \sum n\Delta Hf°\,(reactants)$$

$-890.16 = ((-394)+2(-286))-((\ \Delta Hf°(\ CH_4)+2(0))$

$\Delta Hf°(\ CH_4) = -75.16\ KJ/mol$

Adsorption and Ion Exchange

Adsorption and ion exchange (IX) are treatment processes in which solutes (dissolved constituents) are removed from water by transferring them to the surface of a solid. Adsorption processes are commonly used in municipal drinking water treatment to remove synthetic organic chemicals (SOCs), taste- and odor-causing organics, color-forming organics, and disinfection by-product (DBP) precursors. Natural organic matter (NOM) and some inorganic constituents such as perchlorate, arsenic, and some heavy metals can be removed by either adsorption or ion exchange. Other inorganic constituents, such as hardness (calcium and magnesium), nitrate, iron, and manganese are effectively removed by ion exchange but not by adsorption.

The most common adsorbent material in drinking water treatment is activated carbon, which can be used in either a granular or powdered form. Granular ferric hydroxide, activated alumina, and zeolite are other available adsorbent materials.

The vast majority of IX installations in the United States are small,

point-of-use devices at individual households that are used as water softeners. Full-scale systems are in use for industrial applications, such as the demineralization of water for prevention of scale formation in power plant boilers, removal of calcium and magnesium in car-washing facilities, and production of ultrapure water for making pharmaceuticals and semiconductor materials. The application of IX to municipal water treatment has been limited.

It is appropriate to discuss adsorption and ion exchange together because they have some similarities, such as design configurations that include fixed-bed contactors and suspended-media reactors. However, they also have important differences. In ion exchange, ions participate in a two-way transfer between the water and resin; the ions transferred to the resin must be replaced by an equal amount (in equivalents) of ions transferred from the resin to the water so that electro neutrality is maintained in both phases. Adsorption has no such requirement; the target contaminants are transferred to the adsorbent with no accompanying flow of matter from the adsorbent to the water. This difference in behavior leads to important differences in the equilibrium and kinetics of the processes, even though process design tends to be similar.

Pore Size and Surface Area

The constituent that undergoes adsorption onto a surface is called the adsorbate, and the solid onto which the constituent is adsorbed is called the adsorbent. During the adsorption process, dissolved species diffuse into the porous solid adsorbent granule and are then adsorbed onto the extensive inner surface of the adsorbent. A key feature of adsorbents is a high degree of porosity within the adsorbent granules, which translates into a vast amount of interior surface area onto which adsorption can occur.

Because adsorption takes place on the surface, a large amount of surface area is an essential characteristic of an effective adsorbent. The large surface area is accomplished by using materials that have a vast number of tiny pores in the interior of a granular material. The porosity (ratio of pore volume to total volume) is often near 50 percent.

With this porosity, adsorbents can have a pore volume of 0.1 to 0.8 mL/g and an internal surface area ranging from 400 to 1500 m2/g. As a result, the adsorption capacity can be as high as 0.2 g of adsorbate per gram of adsorbent, depending on the adsorbate concentration and type. Generally, there is an inverse relationship between the pore size and surface area: the smaller the pores for a given pore volume, the greater the surface area that is available for adsorption. In addition, the size of the adsorbate that can enter a pore is limited by the size of the pore. The relationship between pore size and volume is shown in the following example:

Example-

Calculation of the internal surface area of a porous adsorbent Assume a granule of adsorbent material has cylindrical pores with diameters of either 1 or 5 nm, a porosity of 50 percent, and a particle density of 1 g/cm3. Determine the internal surface area of the adsorbent.

Solution

1. Develop a relationship for the ratio of surface area to pore volume for the adsorbent.

a. The volume of cylindrical pores, Vad (m3/g), can be computed based on the number of pores n (amount/g), the pore radius R (m), and the pore length L (m):

$$V_{\mathrm{ad}} = n\pi R^2 L$$

b- The surface area of the pores, Aad (m2/g), is also determined

assuming a cylindrical pore shape:

$$A_{\mathrm{ad}} = 2n\pi RL$$

c- The surface area–pore volume ratio for the adsorbent, Aad/Vad,

can be written by combining the expressions developed in steps 1a and 1b:

$$\frac{A_{\mathrm{ad}}}{V_{\mathrm{ad}}} = \frac{2}{R}$$

2. Determine the surface area for adsorbents with pore sizes of 1 and 5nm.

a. Compute the adsorbent volume using the porosity and adsorbent density provided in the problem statement. By definition,

porosity = pore volume/total volume, so 1 g of adsorbent with a

porosity of 0.5 would have a total volume of 1 cm3 and a pore volume of 0.5cm3. Therefore Vad = 0.5cm3/g = 5 × 10−7 m3/g.

b. For a pore diameter $d_p = 1.0\ \mathrm{nm} = 10^{-9}\ \mathrm{m}$, $R = 5 \times 10^{-10}\ \mathrm{m}$, then

$$A_{\mathrm{ad}} = V_{\mathrm{ad}}\frac{2}{R} = (5 \times 10^{-7}\ \mathrm{m^3/g})\frac{2}{5 \times 10^{-10}\ \mathrm{m}} = 2000\ \mathrm{m^2/g}$$

c. For a pore diameter $d_p = 5.0\ \mathrm{nm} = 5 \times 10^{-9}\ \mathrm{m}$, $R = 2.5 \times 10^{-9}\ \mathrm{m}$, then

$$A_{\mathrm{ad}} = V_{\mathrm{ad}}\frac{2}{R} = (5 \times 10^{-7}\ \mathrm{m^3/g})\frac{2}{2.5 \times 10^{-9}\ \mathrm{m}} = 400\ \mathrm{m^2/g}$$

The porosity of adsorbents generally does not exceed 50 percent because of the manufacturing process and the skeletal strength of the adsorbent.

If the porosity is higher, adsorbents become brittle and break apart when transported into and out of adsorption vessels, which can result in significant adsorbent losses and expense.

For the purpose of classifying pore sizes (diameter dp), the International Union of Pure and Applied Chemistry (IUPAC) uses the following convention:

Micro pores $d_p<2$ nm
Meso pores 2 nm<dp<50 nm
Macro pores dp>50 nm
nm(nanometer)

Adsorption takes place in either fixed-bed or suspended-media contactors. Fixed-bed contactors consist of a bed of granular media typically 1 to 3m deep, either in a pressure vessel or an open basin. Water passes through the bed and adsorption occurs as the water contacts the media. Water flow is typically downward through the media. In some cases, the adsorption media also functions as granular filtration media , in which case the media captures particles as well as solutes. When used as a filter, the media must be backwashed to remove the particles when the head loss becomes excessive. However, fixed-bed adsorption works most effectively when the media is not disrupted by backwashing, and the media can be loaded with contaminants progressively from the top to the bottom without the media being mixed. When the adsorption capacity has been used up, the media must be replaced or regenerated. Fixed-bed contactors are typically designed to be operated for months or years before the adsorption capacity is exhausted.

In suspended-media contactors, the adsorbent is mixed directly into the process water and allowed to travel with the process stream as the water makes its way through the treatment plant. Adsorption takes place as the adsorbent travels with the water. After a sufficient period of time has been allowed for adsorption to take place, the adsorbent is separated from the water, typically by sedimentation and filtration.

Type of Adsorption

Dissolved species are concentrated on the solid surface by chemical reaction (chemisorption) or physical attraction (physical adsorption) to the surface.

Key elements of adsorption mechanisms are listed in Table 10-3

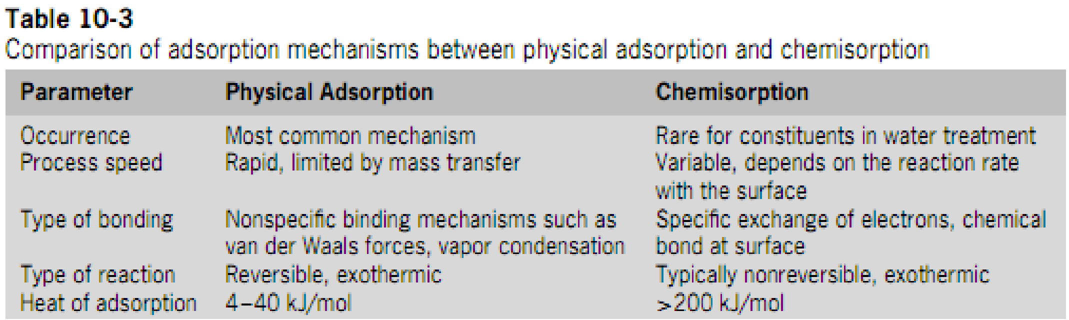

Table 10-3
Comparison of adsorption mechanisms between physical adsorption and chemisorption

Parameter	Physical Adsorption	Chemisorption
Occurrence	Most common mechanism	Rare for constituents in water treatment
Process speed	Rapid, limited by mass transfer	Variable, depends on the reaction rate with the surface
Type of bonding	Nonspecific binding mechanisms such as van der Waals forces, vapor condensation	Specific exchange of electrons, chemical bond at surface
Type of reaction	Reversible, exothermic	Typically nonreversible, exothermic
Heat of adsorption	4–40 kJ/mol	>200 kJ/mol

Therefore, there are two types of adsorption:

1- Physical adsorption is a nonspecific reversible reaction; that is, the adsorbate desorbs in response to a decrease in solution concentration or displacement by a more strongly adsorbed species. Physical adsorption is exothermic with a heat of adsorption that is typically 4 to 40 kJ/mol (about 2 times greater than the heat of vaporization or dissolution for gases and liquids, respectively).

2- Chemisorption is more specific because a chemical bond between adsorbent and adsorbate occurs. The heat of adsorption for chemisorption is typically above 200 kJ/mol. Chemisorption is usually not reversible, and desorption, if it occurs, is accompanied by a chemical change in the adsorbate.

In aqueous solution, adsorption involves three interactions:

(1) adsorbate–water interactions,
(2) adsorbate–surface interactions, and
(3) water–surface interactions.

Factors affecting adsorption

1- pH
2- the temperature
3- the dose of the adsorbent
4- the contact time
5- the concentration of the adsorbate

Thermodynamic Parameters

1- Standard Enthalpy Changes (ΔH^0) (J/mole)

If $\Delta H^0 > 0$ the reaction is endothermic

If $\Delta H^0 < 0$ the reaction is exothermic

2- Gibb's free energy change (ΔG^0) (J/mole)

Thermodynamic considerations of an adsorption process are necessary to conclude whether the process is spontaneous or not. For example, the negative values of ΔG^0 show a spontaneous and favorable process. The higher ΔG^0 magnitude, the more favorable and spontaneous the adsorption. For significant adsorption to occur, Gibb's free energy change of adsorption, ΔG^0, must be negative. A decrease in the negative value of ΔG^0 with an increase in temperature indicates that the adsorption process is more favourable at higher temperatures. On the contrary, an increase in the negative value of ΔG^0 with an increase in temperature implies that lower temperature makes the adsorption easier.

$\Delta G^0 < 0$ (spontaneous and favorable process)

$\Delta G^0 > 0$ (not spontaneous)

$$\Delta G^0 = -RT \ln(K_e)$$

where R is the universal gas constant (8.314 J/mole.K), T is the temperature, and Ke is the equilibrium thermodynamic constant.

3- Standard Entropy Change (J/mole.K)

In relation to the ΔS^0, negative values show that the randomness decreases at the solid solution interface during the adsorption, and positive values suggest the possibility of some structural changes or readjustments in the adsorbate–adsorbent complex. The positive ΔS^0 value also corresponds to an increase in the degree of freedom of the adsorbed species. A negative value of ΔS^0 suggests that the adsorption process is enthalpy driven. A negative value of ΔS^0 also implies a decreased disorder at the solid/liquid interface during the adsorption process causing the adsorbate ions/molecules to escape from the solid phase to the liquid phase.

$\Delta S^0>0$ (Increasing randomness and irregularity of the system)

$\Delta S^0<0$ (decreasing randomness)

$$\Delta G^0 = \Delta H^0 - T\Delta S^0$$

$$\ln(K_e) = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R}$$

Ion Exchange

Ion Exchange involves the exchange of anion in the aqueous phase for anion in the solid phase. In drinking water treatment applications, the exchange media is typically a **synthetic polymeric resin**.

Polymeric ion exchange resins are composed of a three-dimensional, cross-linked polymer matrix that contains covalently bonded functional groups **with fixed ionic charges**. Vinyl polymers (typically, polystyrene and polyacrylic) are used for the resin matrix backbone. Divinylbenzene is used to crosslink the polymer backbone. **There are two major types of resins: macroreticular and gel resins**. Macrorecticular resins are solid beads and retain their size when they are dried out because they have a great deal of crosslinking. Gel-type resins contain lots of water and resemble fish scales when they are dried out.

On amicroscopic level, ion exchange resins resemble a plate of spaghetti where the spaghetti represents the polymer chains to which cationic or anionic functional groups are attached. As shown in Fig. 10-5, the charged functional groups fixed to the polymer chains have counterions associated with them (shown as A+ in Fig 10-5a), which are mobile and free to move in the pores of the polymer matrix. **Cation A+ is called the presaturant ion.**

During exchange, some of the A+ ions will move from the resin into the solution to be replaced by B+ ions. **Cation B+ is called the exchanging ion.**

Based on the functional groups bonded to the resin backbone, the four general types of exchange resins are (1) strong-acid cation (SAC), (2) weak-acid cation (WAC), (3) strong-base anion (SBA), and (4) weak-base anion (WBA).

1- STRONG-ACID CATION EXCHANGE RESIN

In SAC exchange resins, a charged sulfonate group typically acts as the exchange site. The term ''strong'' in SAC has nothing to do with the physical strength of the resin, but it originates from the ease with which the functional group will lose a proton. For strong acids such as sulfuric acid, functional groups will readily dissociate at any pH. **In other words, the resin's low pKa(< 0) implies SAC resins will readily give up a proton over a wide pH range (1 to 14)**. For the reaction shown in Eq. 10-12, based on the pKa of SAC resins and the large hydrated radius of hydrogen, SAC resins have little affinity for the hydrogen ion and will readily exchange it for another cation.

Because the hydrated radius of the H+ ion in a SAC resin is much larger than other cations, **the resin will typically shrink upon exchange (≈7 percent for a gel-type resin, 3 to 5 percent for macroreticular-type resin**). The sodium form of a SAC will also behave in a similar manner, although the shrinkage will be less than observed for the hydrogen form

2- WEAK-ACID CATION EXCHANGE RESIN

In WAC exchange resins, the functional group on the resin is usually a carboxylate, and the exchange reaction can be written with R = COO in Eqs.10-12 and 10-13. **Weak-acid cation resins have pKa values in the range of 4 to 5 and thus will not readily give up a proton unless the pH is greater than 6**. At a pH less than 6, WAC resins have a great affinity for hydrogen and will not exchange it for another cation; therefore, the apparent cation exchange capacity of a WAC resin is a function of pH, and **the effective operating range for exchange is pH > 7**. As the pH increases, **the apparent capacity increases to a maximum total capacity between pH values of 10 and 11**.

Weak-acid resins usually require alkaline species in the water to react with the more tightly bound hydrogen ions. Because WAC resins exhibit a higher affinity for H+ than SAC resins do, they exhibit higher regeneration efficiencies. WAC resins do not require as high a concentration of regenerant as that required for regenerating SAC resins to the hydrogen form. The carboxylic functional groups will utilize up to 90 percent of the acid (HCl or H_2SO_4) regenerant, even with low acid concentrations. By comparison, SAC resin regeneration requires a large excess of regenerant solution to provide the driving force for exchange to take place. Weak-acid resins have been used in water treatment to remove cations in high alkalinity water (e.g., high CO_3^{2-}, OH^-, and HCO_3^- concentrations) with low dissolved carbon dioxide and sodium.

3- STRONG-BASE ANION EXCHANGE RESIN

Strong-base anion exchange resins typically have a quaternary amine group as the fixed positive charge. **Strong-base anion resins have pKb values of 0 to 1, implying that they will readily give up a hydroxide ion if the pH value is less than 13**. The operational pH of SBA resins (pH < 13) makes the apparent anionic exchange capacity independent of pH. Strong-base anion resins in the hydroxide formwill shrink upon exchange due to other anions typically having hydrated radii smaller than hydroxide. Type 1 has a slightly greater chemical stability, while type 2 has a slightly greater regeneration efficiency and capacity. SBA resins are less stable than SAC resins and are characterized by the fishy odor of amines even at room temperature.

Strong-base resins traditionally have been used for many years to demineralize water. However, more recently, SBA resins are increasingly being used to treat waters contaminated with nitrate, arsenic, and perchlorate

4- WEAK-BASE ANION EXCHANGE RESIN

In WBA exchange resins, the exchange site is a tertiary amine group, which does not have a permanent fixed positive charge. Weak-base anion exchange resins are available in either chloride or free-base forms. The free-base designation indicates that the tertiary amine group is not ionized but has a water molecule (HOH) associated with it. The tertiary amine groups will adsorb ions without the exchange of an ion (Helfferich, 1995).

The weak-base designation is derived from the WBA resin’s pKb values of 5.7 to 7.3. Weak-base anion resins will not readily give up hydroxide ion unless the pOH is greater than the pKb of the resin (pH values less than 8.3 to 6.7 at 25◦ C); hence, **the effective operating range is pH < 6.**

$$n[R^{\pm}]A^{\pm} + B^{n\pm} \rightleftarrows [nR^{\pm}]B^{n\pm} + nA^{\pm} \quad \text{(exchange reaction)} \qquad (10\text{-}12)$$

$$[nR^{\pm}]B^{n\pm} + nA^{\pm} \rightleftarrows n[R^{\pm}]A^{\pm} + B^{n\pm} \quad \text{(regeneration reaction)} \qquad (10\text{-}13)$$

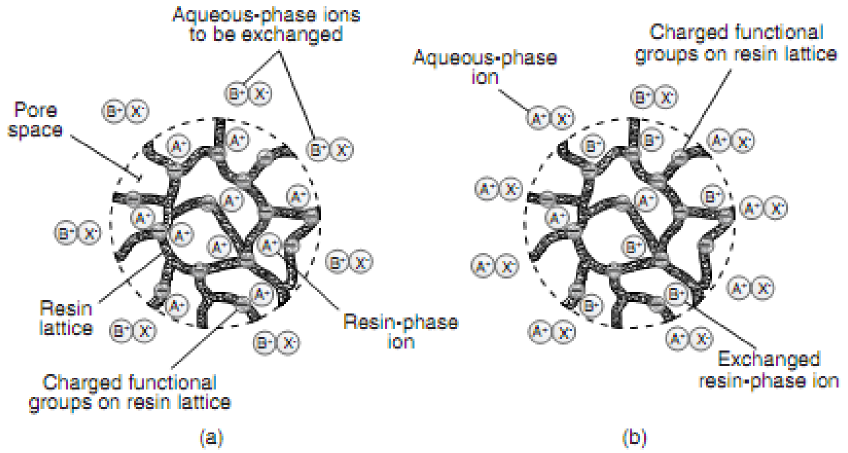

Figure 10-5
Schematic framework of a cation exchange resin: (a) resin with A+ presaturant ions initially immersed in an aqueous solution containing B+ cations and X− anions and (b) cation exchange resin in equilibrium with the aqueous solution of B+ cations and X− anions.