UNIT-I (SEM-II)

Chemical energy is the energy of chemical substances that is released when the substances undergo a chemical reaction and transform into other substances. Some examples of storage media of chemical energy include batteries,[1] food, and gasoline (as well as oxygen gas, which is of high chemical energy due to its relatively weak double bond [2] and indispensable for chemical-energy release in gasoline combustion).[3][4] Breaking and re-making chemical bonds involves energy, which may be either absorbed by or evolved from a chemical system. If reactants with relatively weak electron-pair bonds convert to more strongly bonded products, energy is released.[5] Therefore, relatively weakly bonded and unstable molecules store chemical energy.[2]

Energy that can be released or absorbed because of a reaction between chemical substances is equal to the difference between the energy content of the products and the reactants, if the initial and final temperature is the same. This change in energy can be estimated from the bond

energies of the reactants and products. It can also be calculated from , the internal

energy of formation of the reactant molecules, and , the internal energy of formation of the product molecules. The internal energy change of a chemical process is equal to the heat exchanged if it is measured under conditions of constant volume and equal initial and final temperature, as in a closed container such as a bomb calorimeter. However, under conditions of constant pressure, as in reactions in vessels open to the atmosphere, the measured heat change is not always equal to the internal energy change, because pressure-volume work also releases or absorbs energy. (The heat change at constant pressure is equal to the enthalpy change, in this case the enthalpy of reaction, if initial and final temperatures are equal).

A related term is the heat of combustion, which is the energy mostly of the weak double bonds of molecular oxygen[4] [6] released due to a combustion reaction and often applied in the study of fuels. Food is similar to hydrocarbon and carbohydrate fuels, and when it is oxidized to carbon dioxide and water, the energy released is analogous to the heat of combustion (though assessed differently than for a hydrocarbon fuel—see food energy).

Chemical potential energy is a form of potential energy related to the structural arrangement of atoms or molecules. This arrangement may be the result of chemical bonds within a molecule or interactions between them. Chemical energy of a chemical substance can be transformed to other forms of energy by a chemical reaction. For example, when a fuel is burned, the chemical energy of molecular oxygen and the fuel is converted to heat.[4] Green plants transform solar energy to chemical energy (mostly of oxygen) through the process of photosynthesis, and electrical energy can be converted to chemical energy and vice versa through electrochemical reactions.

The similar term chemical potential is used to indicate the potential of a substance to undergo a change of configuration, be it in the form of a chemical reaction, spatial transport, particle exchange with a reservoir, etc. It is *not* a form of potential energy itself, but is more closely related to free energy. The confusion in terminology arises from the fact that in other areas of physics not dominated by entropy, all potential energy is available to do useful work and drives the system to spontaneously undergo changes of configuration, and thus there is no distinction

between "free" and "non-free" potential energy (hence the one word "potential"). However, in systems of large entropy such as chemical systems, the total amount of energy present (and conserved according to the first law of thermodynamics) of which this chemical potential energy is a part, is separated from the amount of that energy—thermodynamic free energy (from which chemical potential is derived)—which (appears to) drive the system forward spontaneously as the global entropy increases (in accordance with the *second* law).

In a chemical reaction, **chemical equilibrium** is the state in which both the reactants and products are present in concentrations which have no further tendency to change with time, so that there is no observable change in the properties of the system.[1] This state results when the forward reaction proceeds at the same rate as the reverse reaction. The reaction rates of the forward and backward reactions are generally not zero, but they are equal. Thus, there are no net changes in the concentrations of the reactants and products. Such a state is known as dynamic equilibrium.[2][3]

Historical introduction

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The concept of chemical equilibrium was developed in 1803, after Berthollet found that some chemical reactions are reversible.[4] For any reaction mixture to exist at equilibrium, the rates of the forward and backward (reverse) reactions must be equal. In the following chemical equation, arrows point both ways to indicate equilibrium.[5] A and B are reactant chemical species, S and T are product species, and α, β, σ, and τ are the stoichiometric coefficients of the respective reactants and products:

$$\alpha\ \mathrm{A} + \beta\ \mathrm{B} \rightleftharpoons \sigma\ \mathrm{S} + \tau\ \mathrm{T}$$

The equilibrium concentration position of a reaction is said to lie "far to the right" if, at equilibrium, nearly all the reactants are consumed. Conversely the equilibrium position is said to be "far to the left" if hardly any product is formed from the reactants.

Guldberg and Waage (1865), building on Berthollet's ideas, proposed the law of mass action:

where A, B, S and T are active masses and k_+ and k_- are rate constants. Since at equilibrium forward and backward rates are equal:

and the ratio of the rate constants is also a constant, now known as an equilibrium constant.

By convention, the products form the numerator. However, the law of mass action is valid only for concerted one-step reactions that proceed through a single transition state and is **not valid in general** because rate equations do not, in general, follow the stoichiometry of the reaction as Guldberg and Waage

had proposed (see, for example, nucleophilic aliphatic substitution by S_N1 or reaction of hydrogen and bromine to form hydrogen bromide). Equality of forward and backward reaction rates, however, is a necessary condition for chemical equilibrium, though it is not sufficient to explain why equilibrium occurs.

Despite the limitations of this derivation, the equilibrium constant for a reaction is indeed a constant, independent of the activities of the various species involved, though it does depend on temperature as observed by the van 't Hoff equation. Adding a catalyst will affect both the forward reaction and the reverse reaction in the same way and will not have an effect on the equilibrium constant. The catalyst will speed up both reactions thereby increasing the speed at which equilibrium is reached.[2][6]

Although the macroscopic equilibrium concentrations are constant in time, reactions do occur at the molecular level. For example, in the case of acetic acid dissolved in water and forming acetate and hydronium ions,

$$CH_3CO_2H + H_2O \rightleftharpoons CH_3CO^{-}_2 + H_3O^{+}$$

a proton may hop from one molecule of acetic acid onto a water molecule and then onto an acetate anion to form another molecule of acetic acid and leaving the number of acetic acid molecules unchanged. This is an example of dynamic equilibrium. Equilibria, like the rest of thermodynamics, are statistical phenomena, averages of microscopic behavior.

Le Châtelier's principle (1884) predicts the behavior of an equilibrium system when changes to its reaction conditions occur. *If a dynamic equilibrium is disturbed by changing the conditions, the position of equilibrium moves to partially reverse the change*. For example, adding more S (to the chemical reaction above) from the outside will cause an excess of products, and the system will try to counteract this by increasing the reverse reaction and pushing the equilibrium point backward (though the equilibrium constant will stay the same).

If mineral acid is added to the acetic acid mixture, increasing the concentration of hydronium ion, the amount of dissociation must decrease as the reaction is driven to the left in accordance with this principle. This can also be deduced from the equilibrium constant expression for the reaction:

If $\{H_3O^{+}\}$ increases $\{CH_3CO_2H\}$ must increase and $CH_3CO^{-}_2$ must decrease. The H_2O is left out, as it is the solvent and its concentration remains high and nearly constant.

A quantitative version is given by the reaction quotient.

J. W. Gibbs suggested in 1873 that equilibrium is attained when the Gibbs free energy of the system is at its minimum value (assuming the reaction is carried out at a constant temperature and pressure).

What this means is that the derivative of the Gibbs energy with respect to reaction coordinate (a measure of the extent of reaction that has occurred, ranging from zero for all reactants to a maximum for all products) vanishes (because dG = 0), signaling a stationary point. This derivative is called the reaction Gibbs energy (or energy change) and corresponds to the difference between the chemical potentials of reactants and products at the composition of the reaction mixture.[1] This criterion is both necessary and sufficient. If a mixture is not at equilibrium, the liberation of the excess Gibbs energy (or Helmholtz energy at constant volume reactions) is the "driving force" for the composition of the mixture to change until equilibrium is reached. The equilibrium constant can be related to the standard Gibbs free energy change for the reaction by the equation

where R is the universal gas constant and T the temperature.

When the reactants are dissolved in a medium of high ionic strength the quotient of activity coefficients may be taken to be constant. In that case the **concentration quotient**, K_c,

where [A] is the concentration of A, etc., is independent of the analytical concentration of the reactants. For this reason, equilibrium constants for solutions are usually determined in media of high ionic strength. K_c varies with ionic strength, temperature and pressure (or volume). Likewise K_p for gases depends on partial pressure. These constants are easier to measure and encountered in high-school chemistry course

In enzymology, an **alkylhalidase** (EC 3.8.1.1) is an enzyme that catalyzes the chemical reaction

bromochloromethane + H_2O formaldehyde + bromide + chloride

Thus, the two substrates of this enzyme are bromochloromethane and H_2O, whereas its 3 products are formaldehyde, bromide, and chloride.

This enzyme belongs to the family of hydrolases, specifically those acting on halide bonds in carbon-halide compounds. The systematic name of this enzyme class is **alkyl-halide halidohydrolase**. Other names in common use include **halogenase**, **haloalkane halidohydrolase**, and **haloalkane dehalogenase**.

alkylhalidase

Identifiers	
EC no.	3.8.1.1
CAS no.	9025-22-3
Databases	
IntEnz	IntEnz view
BRENDA	BRENDA entry
ExPASy	NiceZyme view
KEGG	KEGG entry
MetaCyc	metabolic pathway
PRIAM	profile
PDB structures	RCSB PDB PDBe PDBsum
Gene Ontology	AmiGO / QuickGO

$$2\ H_2O \rightleftharpoons H_3O^+ + OH^-$$

$$2\ CO \rightleftharpoons CO_2 + C$$

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