# General Chemistry

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# Chemical Thermodynamics
# (Ch.TD)

In the living organisms, the chemical energy is transformed to other forms of energy.

- Bioenergetics studies the transformation of different kinds of energy in the living organisms.

Chemical thermodynamics is the base of bioenergetics.

- Thermodynamics is the science about mutual conversions of different kinds of energy and transmission of energy in the form of heat and work .

# There are three problems of chemical thermodynamics

1. Determination the energy effects of the chemical and physico-chemical processes.
2. Determination the possibility, direction and limits of spontaneous processes under given conditions.
3. Determination the conditions of the systems equilibrium.

# Terminology of Chemical Thermodynamics(TD)

*A* thermodynamic system is a body or group of interacting bodies which we consider apart from its surroundings. For example, a gas in a vessel, a cell ,a plant, an organ, etc .

## The following thermodynamic systems are known according to the character of interactions with surroundings.

1. An *isolated system* is one which cannot exchange energy or matter with its surroundings. There are no such systems in the nature.
2. A *closed system* is one which can exchange energy but not a matter with its surroundings. For example, an electric lamp.
3. An *opened system* is one which can change energy and matter with its surroundings. For example, a living organism.

- A *homogeneous system* is one consisting of a single phase, has no any boundary surfaces, all parts of the system have the same physical and chemical properties. For example, the mixture of gases, the solutions.
- A *heterogeneous system* is one consisting of several phases, has boundary surfaces and different physical and chemical properties. For example, an ice and water, liquid and vapour.
- A *phase* is the part of the system with the same physical and chemical properties . For example, ice-water (an ice is the first phase, water is the second phase).

# The thermodynamic quantities of the system. (TDQ)

The change of such quantities (TDQ) in a process depends only on the initial and final states of the system, it doesn’t depend on the path by which the system is brought from one state to another.

2 groups of TDQ

1. The *independent thermodynamic quantities* can be measured. They are: temperature, pressure, mass, volume, density, etc.
2. Thermodynamic quantities whose value can not be measured and depends on the first group of TDQ and state of the system are called *state functions*.

The state functions are:

U–the internal energy;
H–the enthalpy;
S–the entropy;
G–the Gibb`s free  energy.

# Thermodynamic processes.

Any change in the state of the system is a thermodynamic process.

Two types of thermodynamic processes are distinguished.

A *reversible thermodynamic process* is defined as a process in which the system *reverts* to its initial state without having caused any changes in its surroundings.

If changes do take place in the surroundings, then the process is *irreversible*.

# Types of TD processes:

1. Processes which are carried out at constant temperature are called *isothermal*.

   (T=const, **Δ**T=0)
2. If a reaction proceeds at constant volume (V=const, **Δ** V=0), the process is *isochoric*.
3. Chemical reactions proceed more frequently at constant pressure. The process is *isobaric* (p=const, **Δ**p=0).
4. *Adiabatic* processes are those in which the system neither absorbs nor gives up heat on its surroundings (**Δ**Q=0).

# Energy

The quantitative measure of motion of matter is energy.

The forms of energy are:

mechanical, electric, chemical, etc.

The joule (J) is a unit of energy.

1J=1Nm (Newton-meter).

One calorie is equivalent to 4.184 joules (J).

1kcal=4,18kJ

# Internal Energy

*The internal energy U* of a substance (or system) is the total energy of the particles which are forming the substance (atoms, molecules, ions, electrons).

It consists of the kinetic and potential energies of the particles.

$$U=E_{kin}+E_{\mathbf{pot}}$$

It is impossible to determine the absolute value of a system internal energy at present. But changes in internal energy can be determined for various processes.

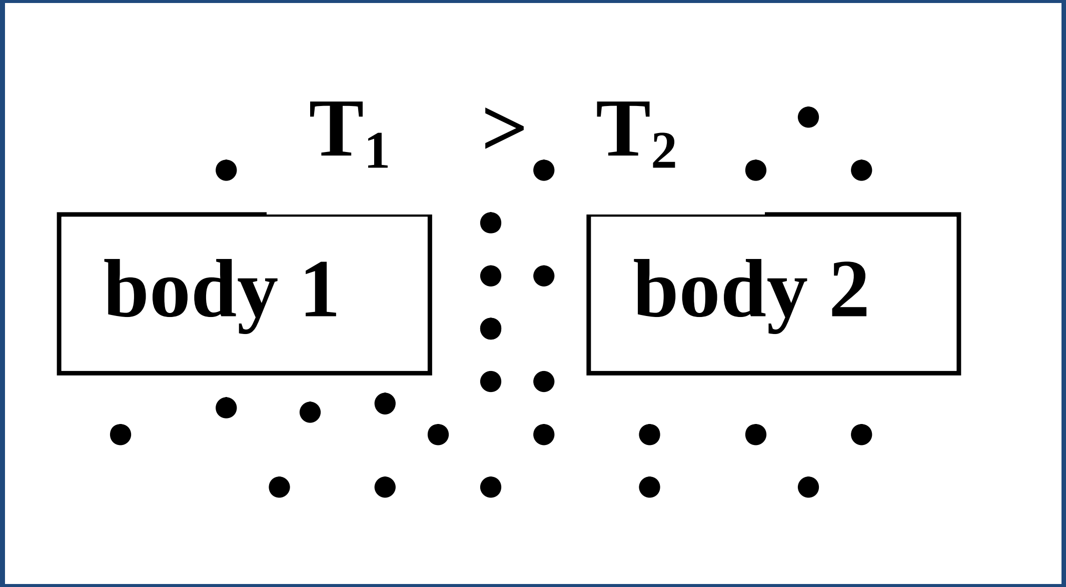
$$\Delta U = U_2 - U_1$$

Where $U_1$ and $U_2$ are the internal energy of the system in the initial (1) and the final (2) state, respectively. The quantity $\Delta U$ is considered positive if the internal energy of the system increases as a result of the given process.

Energy can be transferred from one part of a system to another in the form of heat or work.

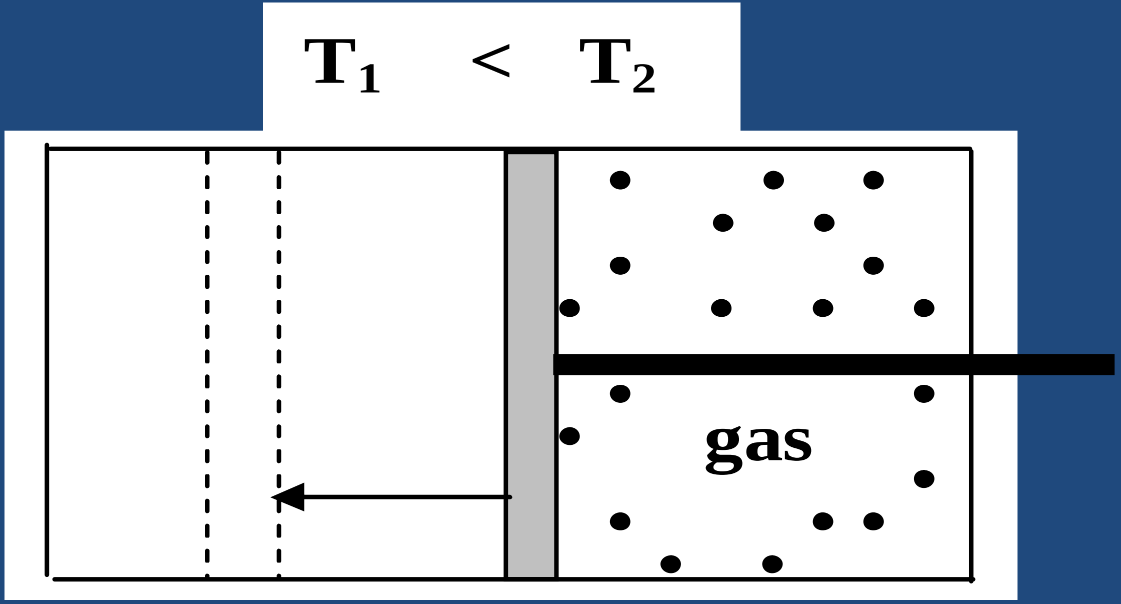
Heat and work are not state functions, they are forms of energy transfer.

The heat (Q) is the form of energy transfer which is carried out as disordered motion of matter under the temperature's gradient.



The molecules move disorderly, collide with body 1, gain an excess of energy and then give to another molecules and at last to body 2.

The work (A) is the form of energy transfer which is carried out as ordered motion of matter. The work is connected with overcoming the force of friction and the movement of bodies in space.



The expansion of a gas makes piston to move.

# The First Law of Thermodynamics(TD)

The heat energy (Q) flowing into a system can be used to change the internal energy of the system (**Δ**U) and allow the system to perform work (A) on its surroundings.

This statement can be written in equation form as $Q = \Delta U + A$,

where A is the work of expansion ($A = p\Delta V$).

# The application of the first law of thermodynamics to various processes:

*1. An isochoric process*.

$V=const$, $\Delta V=0$, $A=p\Delta V$, $A=0$.

The mathematical expression for the first law of thermodynamics at the isochoric process is

$Q_v = \Delta U$, where $Q_v$ is the heat absorbed by the system in conditions of a constant volume.

The heat effect of a reaction at constant volume and temperature corresponds to the change in the internal energy of the system during the reaction.

## 2. *An isobaric process*

$p=\text{const}$ and $\Delta p=0$, $A=p\Delta V$.

$Q_p=\Delta U+p\Delta V$;

$Q_p=U_2-U_1+pV_2-pV_1$, where $Q_p$ is the heat absorbed by the system at constant pressure.

Then we write $Q_p=(U_2+pV_2)-(U_1+pV_1)$.

The function $U+pV=H$ is called the enthalpy.

The enthalpy has the dimension of energy.

$Q_p=H_2-H_1=\Delta H \Rightarrow Q_p=\Delta H$.

The heat effect of a reaction at constant pressure and temperature corresponds to the change in the enthalpy of the system during the reaction.

The enthalpy characterizes energy content of the system.

## 3. *An isothermal process.*

T=const and then $\Delta U=0$, and $Q_T=A$ i.e. heat transforms into the work of expansion $A=p\Delta V$.

## 4. *An adiabatic process*.

An adiabatic process is one in which the system doesn't exchange heat with its surroundings, the work is performed according to the decreasing of the internal energy of the system i.e.

$Q = 0$, $Q = \Delta U + A$, $A = -\Delta U$.

Thermochemistry is the branch of chemical thermodynamics devoted to a quantitative study of the energy effects of chemical and physico-chemical processes.

The heat effect of a reaction is the amount of heat evolved or absorbed in a reaction.

Thermodynamic quantities are generally determined at standard temperature and pressure STP: T=298K (more exactly, 298.15K);

p=101kPa (more exactly, 101.325kPa).

The heat effect of a reaction is measured at STP for the formation of one mole of the product is called the standard heat effect of reaction.

Chemical equations in which the amount of liberated or absorbed heat is indicated are known as thermochemical equations.

There are two forms of writing thermochemical equations. The first form of writing is:

I. $2H_2+O_2=2H_2O+Q$; $Q= +571.6$ kJ

$H_2+1/2O_2=H_2O+Q$; $Q= +285.8$ kJ

where Q is the thermochemical heat effect of reaction which characterizes the energy change in the surroundings. If energy flows from a system to the surroundings this process is called exothermic and $Q>0$. If energy flows into the system from its surroundings this process is called endothermic and $Q < 0$.

II. $H_2+1/2O_2=H_2O$; $\Delta H= -286$ kJ/mol

where **Δ**H is the thermodynamic heat effect of the reaction which reflects the energy change in a reaction system. When **Δ**H < 0, a reaction is *exothermic* and energy decreases in a system. When **Δ**H > 0, a reaction is *endothermic* and energy increases in a system.

In any case Q = – **Δ**H.

The fundamental principle on which all thermochemical calculations are based

is known as Hess's law:

The isochoric and isobaric heat effect of a reaction depends only on the initial and final state of substances and does not depend on the intermediate stages of the process.

Hess's law allows us to calculate the heat effects of reactions when for some reason or other they cannot be measured directly.

To calculate the heat of formation of CO, we shall write reaction as two stages and summarize the thermochemical equations corresponding to these stages

1. $C(graphite)+1/2O_2(g) \rightarrow CO(g);$ $\Delta H_1=?$
2. $\underline{CO(g)+1/2O_2(g) \rightarrow CO_2(g);}$ $\Delta H_2= -283$ kJ

   $C(graphite)+O_2(g) \rightarrow CO_2(g);$ $\Delta H= -393$ kJ

By Hess's law: $\Delta H=\Delta H_1+\Delta H_2$.

This enables us to find the value of $\Delta H_1$, which doesn't lend itself to experimental measurement, namely,

$\Delta H_1 = \Delta H - \Delta H_2 = -393 - (-283) = -110$kJ.

Hess's law is strictly valid only for constant-volume processes (the isochoric processes) or for constant-pressure processes (isobaric processes). For these processes it is easily deduced from the first law of thermodynamics.

$Q_V$=**Δ**U. ΔU doesn't depend on the path by which the system is brought from one state to the other. ΔU is a state function. In this case $Q_V$ doesn't depend on intermediate stages of process as well.

$Q_p$=**Δ**H, but ΔH doesn't depend on intermediate stages of process. ΔH is a state function. In this case $Q_p$ doesn't depend on intermediate stages of process too.

$Q_T$=A, but work is not a function of state, it is a function of process.

The standard enthalpy of formation **($\Delta H^\circ_f$)** is the one mole compound formation from its elements under standard conditions (T=298 K, p=101,3 kPa).

Standard enthalpies of formation for the elements are defined as zero.

Standard enthalpy of combustion **($\Delta H^\circ_{com}$)** is the heat effect of oxidation of one mole of a compound by oxygen to the higher oxides.

Standard enthalpies of combustion of the higher oxides and oxygen are defined as zero.

It follows from Hess’s law that:

1. The enthalpy of formation of substance is equal to the enthalpy of decomposition of substance but opposite in sign (Law of Lavoisier and Laplace).

$$\Delta H_f = -\Delta H_{decomp}$$

2. The heat effect of a reaction equals to the sum of the standard enthalpies of formation of the products minus the sum of the standard enthalpies of formation of the reactants taking into account the proper stoichiometric coefficients.

$$\Delta H^\circ_{rxn} = \sum(m\Delta H^\circ_f)\text{prod.} - \sum(n\Delta H^\circ_f)\text{ react.},$$

where m and n are the coefficients in the equation of the reaction.

3. The heat effect of a reaction equals to the sum of the standard enthalpies of combustion of the reactants minus the sum of the standard enthalpies of combustion of the products taking into account the stoichiometric coefficients.

$$\Delta H^{\circ}_{rxn}=\sum(m\Delta H^{\circ}_{com})\ \text{react.} - \sum(n\Delta H^{\circ}_{com})\ \text{prod.},$$

subscript “rxn” is an abbreviation for “reaction”.

# Thermochemical Calculations and Their Usage for Characteristics of Biochemical Processes

The values of the standard enthalpies is in the reference books.

We can obtain the enthalpy change for any reaction (real or hypothetical) without carrying out any experiments, merely by using the tabulated data on heats of formation.

Example:

calculate the heat effect of the reaction of glucose oxidation, if

$\Delta H^\circ_f[C_6H_{12}O_6(s)] = -1260$ kJ/mol;

$\Delta H^\circ_f[CO_2(g)] = -393.5$ kJ/mol;

$\Delta H^\circ_f[H_2O(l)] = -285.8$ kJ/mol;

$\Delta H^\circ_f[O_2(g)]=0.$

Solution:

$C_6H_{12}O_6+6O_2 \rightarrow 6CO_2+6H_2O$ oxidation of glucose,

$$\Delta H^\circ_{rxn}=[6\Delta H^\circ_f\,(CO_2)+6\Delta H^\circ_f\,(H_2O)]-[\Delta H^\circ_f(C_6H_{12}O_6)+6\Delta H^\circ_f\,(O_2)],$$

$$\Delta H^\circ_{rxn} = [6\Delta H^\circ_f\,H_2O(l)] + 6\Delta H^\circ_f\,CO_2(g)]-[\Delta H^\circ_f C_6H_{12}O_6(s)]=$$
$$= [6\,(-285.8)+6\,(-393.5)-(-1260)]= 2815.8 kJ/mol.$$

It is known, the oxidation of one mole of glucose is attended by evolving of ~2800kJ of energy in the process of vital activity of organism. The ≈80% of this energy distributes into the surroundings in the form of heat, the ≈20% of this energy is consumed for work (electrical, chemical, etc).

Thermochemistry is a theoretical base for a dietology.

The thermochemical properties of foods are discussed in terms of their *specific enthalpy,* the magnitude of the enthalpy of combustion per gram of matter.

The specific enthalpy of:

carbohydrates 16.7 kJ/g,
lipids 37.6 kJ/g,
proteins 16.7 kJ/g.

Various foods have different compositions and hence different energy contents. Many labels on food packages show the calorie content of the food.
1 cal = 4.184 J (1 kcal = 4.184 kJ).

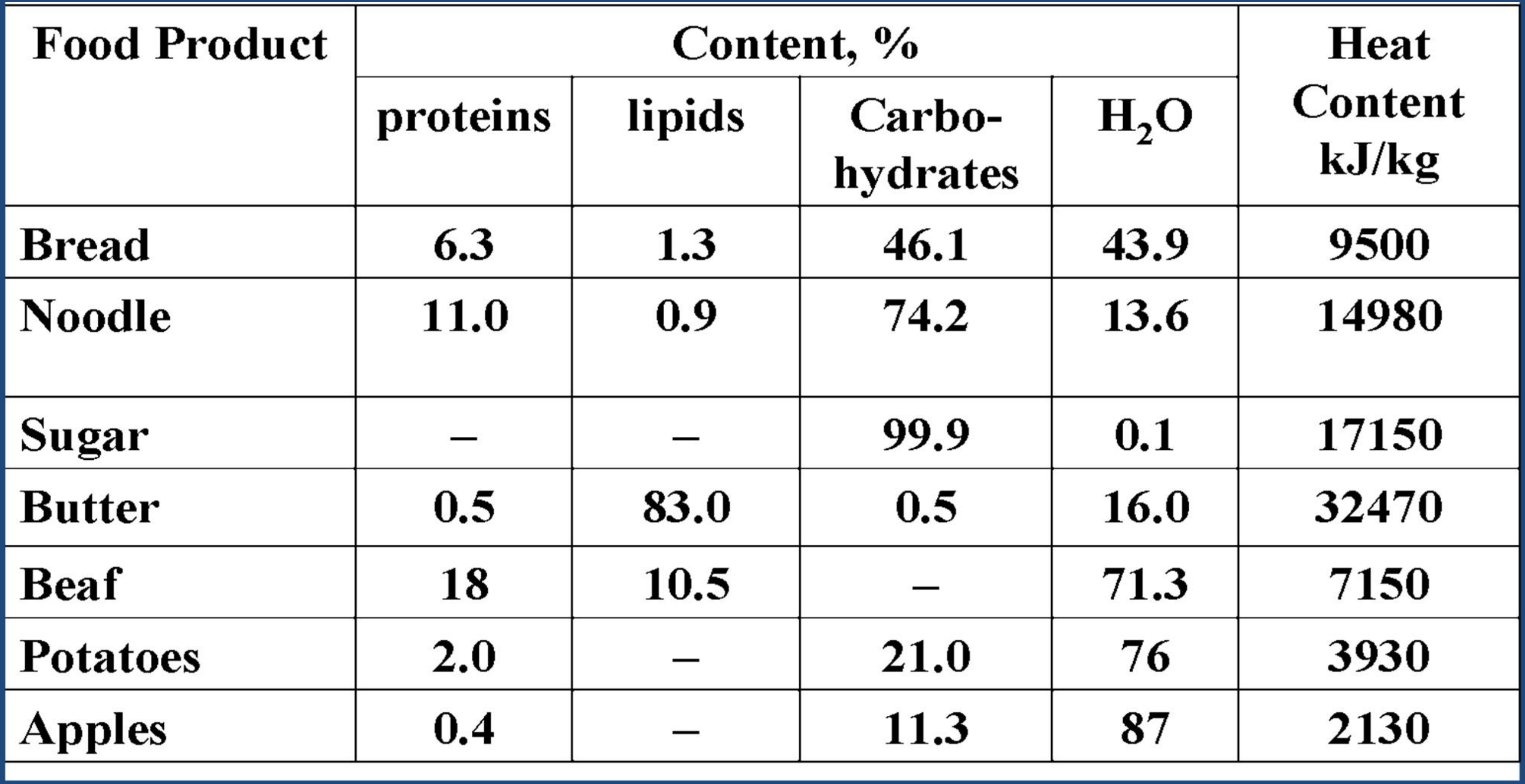
Daily Requirements in Energy depend upon muscle activity of a person:

1. Easy muscle work– 2500 kcal,
2. Average muscle work (students, doctors and some others) – 3500 kcal,
3. Hard muscle work– 4500 kcal,
4. Especially hard muscle work (sportsmen) – 7000 kcal.

High muscle activity increases energy requirements by 30-50%.

High mental activity doesn’t require increase in energy. Brain constantly oxidizes 5-6 g of glucose.

# Fuel values of food products



| Food Product | Content, % | | | | Heat Content kJ/kg |
|---|---|---|---|---|---|
| | proteins | lipids | Carbo-hydrates | $H_2O$ | |
| Bread | 6.3 | 1.3 | 46.1 | 43.9 | 9500 |
| Noodle | 11.0 | 0.9 | 74.2 | 13.6 | 14980 |
| Sugar | – | – | 99.9 | 0.1 | 17150 |
| Butter | 0.5 | 83.0 | 0.5 | 16.0 | 32470 |
| Beaf | 18 | 10.5 | – | 71.3 | 7150 |
| Potatoes | 2.0 | – | 21.0 | 76 | 3930 |
| Apples | 0.4 | – | 11.3 | 87 | 2130 |

# The Second Law of Thermodynamics

The multitude of different processes which take place in the world about us – in nature, technology, etc. – can be divided in two groups:

spontaneous and non-spontaneous processes.

1.The physical and chemical processes that occur without the outside energy are called spontaneous processes.

Examples: the mixing of gases, the neutralization of a strong acid by a strong base, the rusting of iron, etc.

2. The physical and chemical processes that occur with the outside energy are called

non-spontaneous processes.

Examples of non-spontaneous processes are: a separation of a mixture of gases, the dissociation of water by an electric current, etc.

Changes that are spontaneous in one direction are non-spontaneous in the opposite direction.

The first law states a relation between the change in the internal energy of a system, the amount of heat supplied to it, and the work performed. The first law, however, says nothing about the character, permissibility or direction of the processes by which the various conversions of energy are brought about.

The second law specifies what processes can occur spontaneously (i.e. without work being done on the system), what amount of work can be obtained from such processes, and what is the limit of the spontaneous process, i.e, to what state of equilibrium the system tends under the given conditions.

The spontaneous processes lead to an equilibrium in a system as the final result.

The quantitative measure of approach of the system to the equilibrium is entropy (S).

Entropy is a measure of the degree of a system disorder.

When disorder increases, entropy also increases. The S, like the H and U, is a state function of a system, hence the change in the entropy $\Delta S$ during the transformation of a system is determined only by the initial and final states of the system and does not depend on the path of the process.

## By the second law of thermodynamics

- ✓ *in isolated systems the entropy of a spontaneous process increases:*

$$\Delta S>0;$$

- ✓ *when the entropy is maximum the system is in condition of complete thermodynamic equilibrium:*

$$\Delta S = 0.$$

Unlike H and U, we can determine the absolute values of the entropy.

By the third law of thermodynamics, the entropy of pure substances existing in the form of perfect crystals is zero at 0K.

The *standard entropy* of pure substances is determined for one mole of a substance at standard conditions (p=101.325 kPa and T=298K).

It is designated by $S^0{}_{298}$ or $S^0$.

The unit of the entropy is J/mol·K.

The standard entropy of simple substances does not equal zero.

The greater the disorder or randomness in a system, the larger the entropy.

Gaseous state is the most disordered and so has the highest entropy. Liquid state is less ordered and so has less entropy than the gaseous state. Solid state is the most ordered and so has the lowest entropy.

$$S\,(solid) < S\,(liquid) < S\,(gas).$$

Since the entropy is a state function, $\Delta S$ of a chemical reaction equals the difference between the values of the absolute entropies of the products and reactants. For a chemical reaction at STP we have:

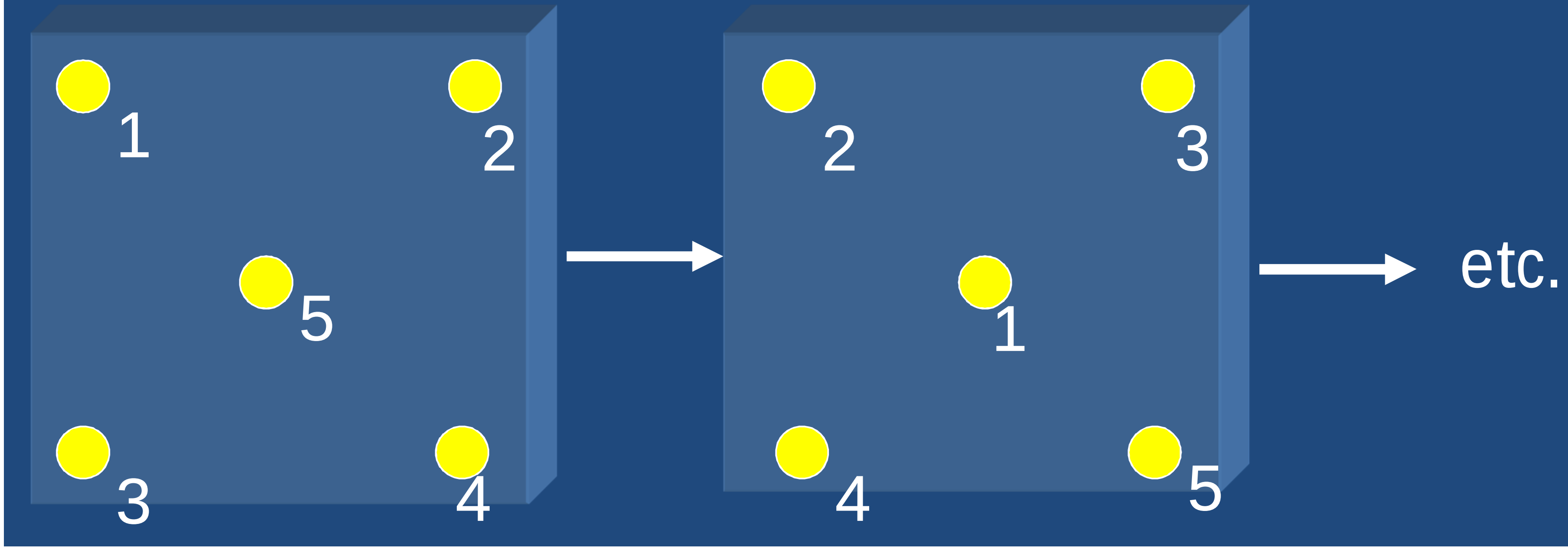
$$\Delta S^0_{rxn} = \Sigma\, m\, S^0 \text{ prod.} - \Sigma\, n\, S^0 \text{ react,}$$

where *m* and *n* are the number of moles of products or reactants, respectively.

# The Statistical Interpretation of Entropy

- It is based on the kinetic theory of gases.

Consider a system containing about five molecules. Every molecule has its own number. Take photograph of this system and have a photo. Then, take another photograph of this system and have another photo, etc.



After all we conclude that:

a macrostate is the state of substance characterized by definite values of its macroscopic properties (temperature, pressure, volume, etc.);

a microstate is the state of substance characterized by a definite state of each particle (molecule, atom).

The same macrostate corresponds to a great number of various microstates.

The number of microstates that form given macrostate of the system is called

*the thermodynamic probability* (W).

There is a relation between entropy and thermodynamic probability of the system *(Boltzmann's equation)*:

$$S = k \ln W,$$

where *k* is Boltzmann's constant .

Greater the thermodynamic probability of the given system, greater will be entropy.

# The Thermodynamic Interpretation of Entropy

If the statistical interpretation of entropy is given by L.Boltzmann, the thermodynamical interpretation of one is given by Clausius.

We know the entropy of a pure perfectly ordered crystalline substance is zero at the absolute zero of temperature (S=0).

In this case one macrostate corresponds to one microstate (W=1), that is S=0 and a system is in equilibrium (ΔS=0).

With elevation of the temperature the entropy increases, the thermodynamic probability increases but the order decreases in the system. So the entropy of an isolated system depends on quantity of energy (Q) put into a system and temperature (T) at which the process is carried out.

The change in entropy is related to the heat absorbed by the equation:

$$\Delta S_{sys} \geq Q_{sys} / T.$$

It is a mathematical expression

of the second law of thermodynamics !

*For processes with the system at equilibrium:*

$$\Delta S_{sys} = Q_{sys} / T$$

- ✓ In reversible isothermal processes the entropy change is equal to the heat of the process divided by the absolute temperature.

*For a spontaneous process:*

$$\Delta S_{sys} > Q_{sys} / T$$

- ✓ This equation makes an important distinction between equilibrium and non-equilibrium systems; spontaneously changing systems experience greater disorder than they would if the change were made under equilibrium conditions.

# The Gibbs Free Energy

In order to know about direction and limit of the processes in opened and closed systems it is necessary to take account of change in entropy of surroundings. It is very complex and sometimes impossible task.

The possibility of processes occurring in closed and opened systems is determined by the change in a thermodynamic state function called

the *Gibbs free energy* ***Δ****G*, which is related to the enthalpy and entropy by the equation:

$$G=H-TS.$$

# The Gibbs equation: $\Delta G = \Delta H - T\Delta S$

The notion about the Gibbs energy was introduced on the basis of equations of the first law and second law of thermodynamics.

The equation for the first law of thermodynamics is

$$Q=\Delta U+A \quad (1).$$

The equation for the second law of thermodynamics is $\Delta S=Q/T$, or $Q=T\Delta S$ (2).

Inserting in the expression (1) the value $Q= T\Delta S$ from (2) we obtain:

$$T\Delta S=\Delta U+A_{max}$$

The system can perform not only the work of expansion ($p\Delta V$) but perform another forms of work (electric, chemical, osmotic, etc.) – $A_u$ – is the useful work.

$$A_{max} = p\Delta V + A_u$$

$$T\Delta S = \Delta U + p\Delta V + A_u$$

$$-A_u = \Delta U + p\,\Delta V - T\Delta S$$

$$-A_u = U_2 - U_1 + pV_2 - pV_1 - TS_2 + TS_1$$

$$-A_u = (\underbrace{U_2 + pV_2}_{H_2} - TS_2) - (\underbrace{U_1 + pV_1}_{H_1} - TS_1)$$

$$-A_u = (H_2 - TS_2) - (H_1 - TS_1) \quad \longleftrightarrow \quad H - TS = G$$

$$-A_u = G_2 - G_1 = \Delta G$$

$$-A_u = \Delta G$$

$\Delta G$ is equal in magnitude, but opposite in sign to the maximum useful work that the system does in the given process.

It follows from equation $A_u = - \Delta G$ that:

1) if a system performs work spontaneously

$A > 0$ and $\Delta G < 0$.

*It is a criterion of a spontaneous process.*

2) if the system doesn’t perform work

$A = 0$ and $\Delta G = 0$.

It is *a criterion of equilibrium state.*

The unit of the Gibbs free energy is J/mol.

# The enthalpy and entropy factors and direction of a process.

# The analysis of Gibbs equation.

$$\Delta G = \Delta H - T\Delta S.$$

The sign and the magnitude of $\Delta G$ are determined by two factors: entropy ($T\Delta S$) and enthalpy ($\Delta H$).

The enthalpy factor defines the tendency of a system to its minimum of energy.

The entropy factor defines the tendency of a system to its disorder.

The Gibbs free energy is an integral state function of a system.

1. The exothermic reactions attended by an increase in the entropy can proceed spontaneously always!

If $\Delta H<0$, $\Delta S>0$, then $\Delta G<0$

2. The endothermic reactions attended by a decrease in the entropy can't proceed spontaneously!

If $\Delta H>0$, $\Delta S<0$, then $\Delta G>0$

3. If $\Delta H = T\Delta S$, then $\Delta G=0$ and the equilibrium is settled in the system.

4. At low temperatures, the spontaneous proceeding of exothermic reactions ($\Delta H<0$) is most probable even if the entropy of the system diminishes ($\Delta S<0$).

5. At high temperatures, reactions attended by a growth in the entropy ($\Delta S>0$) are most probable, including endothermic reactions ($\Delta H>0$).

# Table shows the possibility (or impossibility) of the spontaneous proceeding of a reaction with different combinations of the signs of △H and △S.

| Sing of change in function | | | Possibility (impossibility) of spontaneous proceeding of reactions |
|---|---|---|---|
| △H | △S | △G | |
| – | + | – | Possible at any temperature 1 |
| + | – | + | Impossible at any temperature 2 |
| – | – | ± | Possible at sufficiently low temperature 4 |
| + | + | ± | Possible at sufficiently high temperature 5 |

Calculation of the free energy change in chemical reactions:

at standard conditions

1. $\Delta G^0_{rxn} = \sum m \Delta G^0_f$ prod. – $\sum n \Delta G^0_f$ react., where m and n are the numbers of moles of a given product or reactant, respectively.

The standard free energy of formation $\Delta G_f^0$ is the change of free energy during the formation of a substance in its standard state from the elements in their standard states. The standard free energies of formation of elements in their standard states are zero. $\Delta G_f^0$ is tabulated data.

2. Alternatively, you can calculate the enthalpy and entropy changes for the reaction $\Delta H^0_{rxn}$ and $\Delta S^0_{rxn}$ and combine them using the Gibbs equation:

$\Delta G^0_{rxn} = \Delta H^0_{rxn}. - T\Delta S^0_{rxn}$

$\Delta H^\circ_{rxn} = \sum m\Delta H^\circ prod. - \sum n\Delta H^\circ react.$

$\Delta S^\circ_{rxn} = \sum mS^\circ prod. - \sum nS^\circ react.$

But the reactions don’t proceed at standard conditions.

# In real conditions

3.For the reaction A+B=C+D calculation of $\Delta G$ can be performed according to the equation:

$$\Delta G_{rxn} = \Delta G^0_{rxn} + RT \ln [C][D]/[A][B],$$

where *[C], [D], [A]* and *[B]* are the concentrations of the substances; $\Delta G^0_{rxn}$ is the standard change in the Gibbs energy of the reaction, *R* is the molar gas constant, R = 8.314 J/mol K; *T* is the temperature, *K*.

## Conclussion:

In the general case, the possibility (or impossibility) of a reaction is determined by the sign of $\Delta G$.

1. $\Delta G<0$ is negative,

   a process is spontaneous; it is possible;

2. $\Delta G>0$ is positive,

   a process is not spontaneous; it is impossible;

3. $\Delta G=0$, the process is at equilibrium.

# Endergonic and Exergonic Reactions

Biochemical reactions are chemical reactions which proceed in vivo. They are:

Exergonic (spontaneous) $\Delta G < 0$;

Endergonic (nonspontaneous) $\Delta G > 0$.

Many biochemical reactions are endergonic, but in some cases they can be carried out to an appreciable extent by coupling them with an exergonic reaction.

A coupled (conjugated) reaction is a process in which an endergonic reaction is made to proceed by coupling it to an exergonic reaction.

Carbohydrates and lipids metabolism involves highly spontaneous oxidation reactions:

$C_6H_{12}O_6 + 6\ O_2 \rightarrow 6\ CO_2 + 6\ H_2O, \quad \Delta G = -\ 2870\ kJ$

$C_{15}H_{31}COOH + 23\ O_2 \rightarrow 16\ CO_2 + 16\ H_2O,$

$\Delta G = -\ 9790\ kJ$

Some of this energy is released as heat that maintains constant body temperature. Another portion is stored in high-energy molecules.

The most important of these energy transport molecules is adenosine tri-phosphate (ATP).

In cells ATP production is coupled with glucose oxidation. One molecule of glucose can convert as many as 36 ADP molecules into ATP molecules as it is oxidized to $CO_2$ and water:

$C_6H_{12}O_6 + 6\ O_2 \rightarrow 6\ CO_2 + 6\ H_2O$, $\Delta G = -2870$ kJ

$36\ (ADP + H_3PO_4) \rightarrow 36\ (ATP + H_2O)$, $\Delta G = +1100$ kJ

$\Delta G$ overall = – 2870 + 1100 = – 1770 kJ

Although 1100 kJ of energy is stored in this coupled process, 1770 kJ of energy is "wasted". Efficiency of a process is: 1100/2870 = 0.38 or 38%

Thus cells harness 38% of the chemical energy stored in glucose to drive the biochemical machinery of metabolism. The remaining 62% of energy is dissipated as heat.

# Thermodynamics
# of the Chemical Equilibrium

All chemical reactions can be divided into two groups: irreversible and reversible reactions.

Irreversible reactions *proceed to the end* – until one of the reactants is completely used up.

Irreversible reactions are characterized by the formation of an insoluble substance, the formation of a gas, the formation of a week electrolyte ($H_2O$).

A reversible reaction *is the reaction which can proceed either in the forward or in the reverse direction.*

Reversible reactions are characterized by the symbol $\rightleftarrows$ between the reactants and products. When the rates of the forward ($V_f$) and reverse ($V_r$) reactions become the same, chemical equilibrium sets in, i.e. $V_f = V_r$.

The concentrations of the substances (both the reactants and the products) remain unchanged. These concentrations are called equilibrium concentrations.

Chemical equilibrium is characterized quantitatively by a quantity known as the chemical equilibrium constant.

The chemical equilibrium constant is the ratio of the product of product equilibrium concentrations to the product of reactant equilibrium concentrations.

For example, for the reaction $aA + bB \rightleftarrows cC + dD$

the chemical equilibrium constant is:

$$K = \boxed{\frac{[C]^c[D]^d}{[A]^a[B]^b}}$$

Concentrations of solids are assumed to be 1 and they can be left out of the concentration ratio without altering the value of K.

The numerical value of the equilibrium constant characterizes the yield of the given reaction.

For example, when $K>>1$, the yield of a reaction is high, because $[C]^c [D]^d >> [A]^a [B]^b$ the concentrations of the products are much greater than those of the reactants.

The larger is K, the greater is the degree of conversion of the reactants into the products.

When $K<<1$ the yield of the reaction is low.

The magnitude of the equilibrium constant depends on the nature of the reacting substances and on the temperature.

It does not depend on the presence of catalysts. A catalyst can only accelerate or retard the setting in of equilibrium.

The ways of designation of the equilibrium constant:

1. For solutions of non-electrolytes and sufficiently dilute solutions of electrolytes the equilibrium constant $K_c$ is used (the equilibrium concentrations are expressed in mol/L in liquid phase):

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

2. For strong electrolytes the activity (a) is used:

$$K_a = \frac{a^c(C) \cdot a^d(D)}{a^a(A) \cdot a^b(B)}$$

3. Chemical equilibrium between gases at low pressures is expressed in terms of the partial pressures $p_i$ of the reactants and products:

$$H_2(g) + I_2(g) \rightleftarrows 2HI(g); \qquad K_p = \frac{p^2(HI)}{p(H_2) \cdot p(I_2)}$$

# The Isotherm Equation of a Chemical Reaction

$A + B \rightleftarrows C + D$; T=const

1. The change in the Gibbs energy of this reaction in real conditions is

$$\Delta G = \Delta G^\circ + RT \ln \frac{[C][D]}{[A][B]}$$ real concentrations

The value of the change in the Gibbs energy in a reaction depends on the temperature and also on the nature and concentrations of the reactants and products.

2. For the state of chemical equilibrium $\Delta G=0$, then we obtain:

$0 = \Delta G° + RT \ln \frac{[C][D]}{[A][B]}$ equilibrium concentrations,

but $\ln \frac{[C][D]}{[A][B]} = \ln K_c$ and $\Delta G° = -RT\ln K_c$ .

Introduce the equation $\Delta G° = -RT\ln K_c$ into the equation $\Delta G = \Delta G° + RT \ln \frac{[C][D]}{[A][B]}$ , we get

the isotherm equation of a chemical reaction

$$\Delta G = -RT \ln K_c + RT \ln \frac{[C][D]}{[A][B]}$$

where [A],[B], [C], [D] are real concentrations.

$\ln \frac{[C][D]}{[A][B]}$ is the concentration term;

$\ln K_c$ is the constant term.

The sign of $\Delta G$ depends on the real concentrations of the reactants and products for given time.

# The analysis of the isotherm equation:

1. $\ln\frac{[C][D]}{[A][B]} < \ln K_c$ and $\Delta G<0$

A spontaneous chemical reaction occurs from left to right. If we change the concentrations we can affect the direction of the spontaneous proceeding of the reaction.

2. $\ln\frac{[C][D]}{[A][B]} > \ln K_c$ and $\Delta G>0$

A spontaneous chemical reaction doesn’t occur from left to right, but the reaction is spontaneous from right to leff.

3. $\ln\frac{[C][D]}{[A][B]} = \ln K_c$ and $\Delta G=0$

The system is in an equilibrium.

# The Isobar Equation of a Chemical Reaction

In the integral form we have the equation:

$$\ln\frac{K_1}{K_2}=\frac{\Delta H}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)$$ ,p=const

where $K_1$ and $K_2$ are equilibrium constants at the different temperatures $T_1$ and $T_2$; $\Delta H$ is change in enthalpy; $R$ is the molar gas constant.

The equation is in the differential form $$\frac{d\ln K_p}{dT}=\frac{\Delta H}{RT^2}$$

The Isobar equations establish a relation between the change in the equilibrium constant with temperature and the heat of the reaction (the enthalpy change).

It relates the kinetics and thermodynamics.

The analysis of the Isobar equation of a chemical reaction:

1. $\Delta H < 0$ *exothermic reaction.*

When heat is evolved in the chemical reaction i.e.

$\Delta H<0$ and $\frac{\Delta H}{RT^2} < 0$ as well, then we conclude that $\frac{d\ln K_p}{dT} < 0$.

This denotes that the equilibrium constant decreases with rise in temperature (the numerator decreases) and equilibrium is displaced towards the left. In other words, with rise in temperature equilibrium is displaced in the direction of the endothermic process.

With lowering in temperature ($dT<0$) the equilibrium constant increases and equilibrium is displaced towards the right.

2. $\Delta H>0$ *endothermic reaction.*

When heat is absorbed in the chemical reaction, i.e. $\Delta H > 0$ and $\frac{\Delta H}{RT^2} > 0$ as well, we conclude that $\frac{d\ln K_p}{dT} > 0$.

This denotes that the equilibrium constant increases with rise in temperature and with lowering in temperature the equilibrium constant decreases.

# Le Chatelier's Principle

A change in the conditions (temperature, pressure, concentration) under which a system is in a state of chemical equilibrium disturbs equilibrium because of the different changes in the rates of the forward and reverse reactions ($V_f \neq V_r$). With time, new chemical equilibrium sets in in the system ($V_f = V_r$) that corresponds to the new conditions. The transition from one equilibrium state to another is called a shift of equilibrium.

The direction of a shift of chemical equilibrium as a result of a change in the external conditions is determined by Le Chatelier's principle:

«if any change of conditions is imposed on a system in equilibrium, equilibrium will shift in the direction of the process that counteracts the imposed change».

For instance:

- ✓ elevation of the temperature leads to the shifting of equilibrium in the direction of the reaction attended by the absorption of heat, i.e. by cooling of the system;
- ✓ an increase in the pressure causes equilibrium shift in the direction of a decrease in the total number of moles of gaseous substances, i.e. in the direction leading to lowering of the pressure;
- ✓ the removal from a system one of the products results the equilibrium being displaced in the direction of the forward reaction;
- ✓ diminishing the concentration of one of the reactants leads to shifting of equilibrium in the direction of the reverse reaction.