

«FUNDAMENTALS OF THERMOCHEMISTRY»

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* Lecture plan

1. Basic Definitions.
2. First law of thermodynamics.
3. Enthalpy.
4. Thermochemical equations.
5. Hess' law and its consequences.
6. Entropy and its change during a chemical reaction.
7. The second law of thermodynamics.
8. Enthalpy and entropy factors.
9. Gibbs energy.

The purpose of studying chemical thermodynamics



- 1) The quantitative determination of the energy effects attending chemical processes.
- 2) The establishment of whether processes can occur spontaneously under the given conditions.
- 3) The determination of the conditions for the spontaneous occurring of processes with a given yield of the products.



1. Basic Definitions

Chemical thermodynamics considers the mutual conversions of various forms of energy attending chemical reaction and phase transition. Chemical thermodynamics is one of the main ways of studying chemical processes.

Thermodynamic system is a body or a group of bodies separated from the surroundings by an interface (boundary).

1. Basic Definitions

THERMODYNAMIC SYSTEM:

If matter can be transferred through the boundary between the system and its surroundings, the system is classified as **OPEN**.



If matter cannot pass through the boundary the system classified as **CLOSED**.



A *thermodynamic system that can exchange neither mass nor energy with its surroundings is called **ISOLATED**.*



1. Basic Definitions

THERMODYNAMIC SYSTEM :

A part or set of parts of a thermodynamic system having identical physical and chemical properties is called **PHASE**

A system consisting of one phase is **HOMOGENEOUS.**



If a system consists of several phases separated from one another by interfaces, it is **HETEROGENEOUS.**



1. Basic Definitions

The state of a system is the totality of all the physical and chemical properties of the system.

The physical characteristics of a thermodynamic system (the mass, volume, temperature, pressure, composition, energy, heat capacity, surface tension are called ***THERMODYNAMIC PROPERTIES***

ISOTHERMAL process:

T = constant

ISOBARIC process :

P = constant

ISOCHORIC process:

V = constant

Adiabatic processes:

Q = constant

1. Basic Definitions

THERMODYNAMIC FUNCTION OF STATE OF THE SYSTEM:

- ✓ U is internal energy;
- ✓ H is enthalpy;
- ✓ S is entropy;
- ✓ G is Gibbs energy.

$\Delta U, \Delta H, \Delta S, \Delta G$ – The change of function *does not depend on the path of the process but depends only on the initial and final states of the system.*

1. Basic Definitions

The internal energy (U) is the sum of the energies of motion and interaction of the diverse particles it consists of such as molecules, ions, electrons, protons, and neutrons.

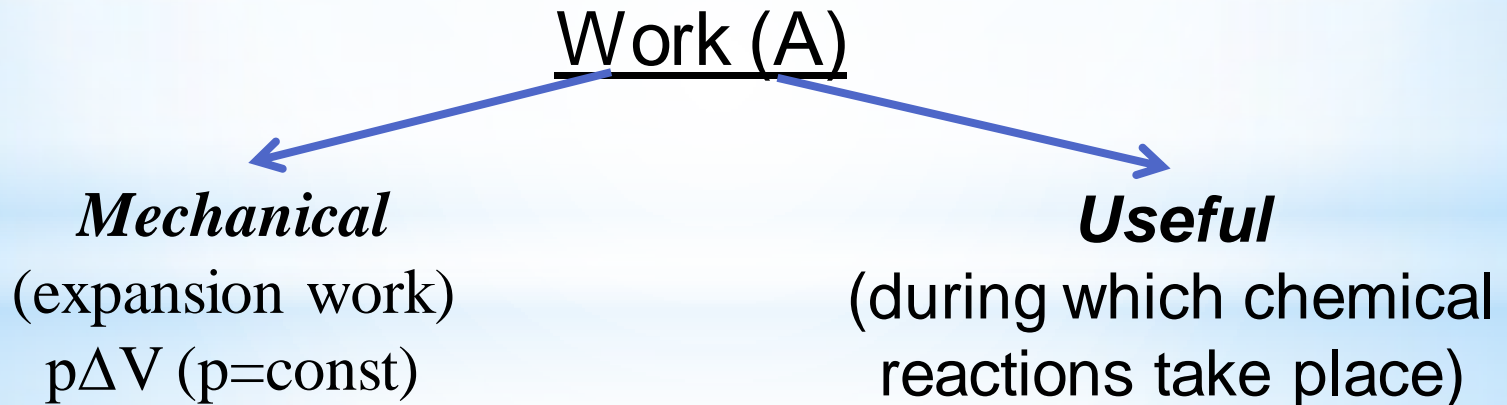
Heat (Q) is the energy transferred due to the chaotic collision of molecules on the interface between the system and the environment.

Работа (A или W) is energy transferred from one system to another due to the movement of matter under the action of various forces (for example, gravitational).

2 First Law of Thermodynamics

THE HEAT RECEIVED BY A SYSTEM IS SPENT ON INCREASING ITS INTERNAL ENERGY AND DOING WORK ON THE SURROUNDINGS

$$Q = \Delta U + A$$



3. ENTHALPY (H)

is form of energy of a system exchanging both energy and matter with its surroundings

$$\Delta H = \Delta U + p \cdot \Delta V$$

The change in enthalpy is the change in the internal energy of the system and the completion of the work of expansion

$$\Delta H = \Delta U \quad (V, T = \text{const})$$

$$Q_p = H_2 - H_1 = \Delta H \quad (p = \text{const})$$

Heat Effect of a Reaction (ΔH) by $P = \text{const}$ equal change of enthalpy.

EXOTHERMIC reaction: $Q > 0, \Delta H < 0$

ENDOTHERMIC reaction: $Q < 0, \Delta H > 0$

3. ENTHALPY

standard heat effect of a reaction ($\Delta_f H^\circ$)

is called the heat of a chemical process occurring at standard temperature and pressure (298 K and 101 kPa) with the formation of one mole of the product.

Standard conditions

- ✓ Pressure $1,013 \cdot 10^5$ Pa
- ✓ Temperature 298 K
- ✓ Concentration 1 mol/L

$[\Delta_f H^\circ] = \text{kJ/mol}$, reference value.

3. ENTHALPY

The enthalpy of formation of simple substances that are stable at 298 K and a pressure of 100 kPa is taken equal to zero.

$$\Delta_f H^\circ (\text{O}_2, \text{C}_{\text{графит}}, \dots) = 0 \text{ kJ/mol}$$

4. Thermochemical equations

is process equations in which thermal effects are indicated.



Features when writing thermochemical equations:

- the aggregate state of substances (**gas, liquid, solid**) is indicated;
- the sign and value of ΔH° are indicated;
- **fractional coefficients** are possible.

5. Hess's Law and its Corollaries

«The thermal effect of the reaction depends on the nature and state of the reactants and products, but does not depend on the reaction path, i.e. on the number and nature of intermediate stages».

1841 г.

5. Hess's Law and its Corollaries

1. The heat effect of a reaction equals the sum of the heats of formation of the products less the sum of the heats of formation of reactants.

$$\Delta_r H^\circ = \sum n \Delta_f H^\circ (\text{products}) - \sum n \Delta_f H^\circ (\text{reagents})$$

where $\Delta_r H^\circ$ is the standard enthalpy of reaction;

$\Delta_f H^\circ$ are the standard enthalpy values of formation of products and reagents;

n are the stoichiometric numbers.

6. Entropy and its change during a chemical reaction

Entropy (S) – system state function that characterizes the degree of system disorder.

Boltzmann equation

$$S = R \cdot \ln W$$

R is the universal gas constant
(8,314 J/mol·K)

W is thermodynamic probability.

6. Entropy and its change during a chemical reaction

Standard entropy S° is the entropy of matter in the standard state (absolute value)

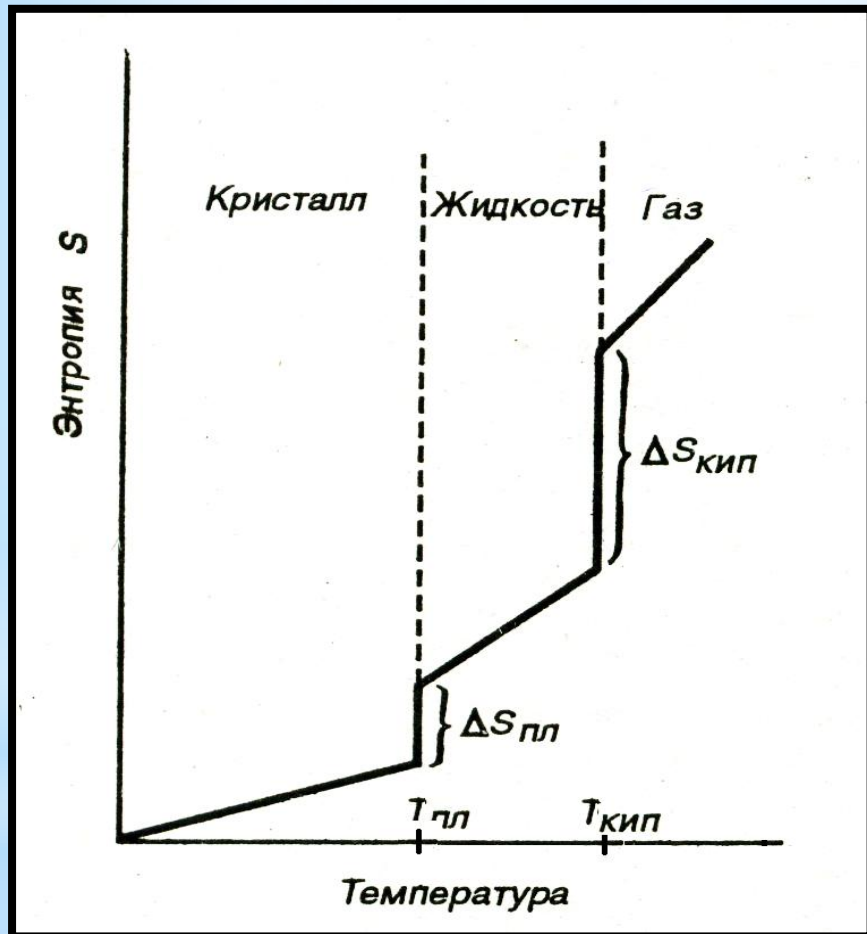
ΔS° change in entropy during a chemical reaction:

$$\Delta S^\circ = \sum n S^\circ (\text{products}) - \sum n S^\circ (\text{reagents})$$

$$[S^\circ] = \text{J}/(\text{mol}\cdot\text{K})$$

S° is reference value.

6. Entropy and its change during a chemical reaction



Substances	S° , J/K·mol
H_2O (s)	39,0
H_2O (l)	70,8
H_2O (g)	188,7

Change in the entropy of a substance with increasing temperature

7. Second Law of Thermodynamics

Processes proceed spontaneously in isolated systems if they are accompanied by an increase in entropy.

For an isolated system :

$\Delta S > 0$ the process is spontaneous;

$\Delta S < 0$ the process does not proceed spontaneously

$\Delta S = 0$ – spontaneous flow of the process is possible only with a decrease in enthalpy $\Delta H < 0$

8. Enthalpy and entropy factors

Two factors simultaneously affect the spontaneity of a chemical isobaric-isothermal process:

1) **Enthalpy factor (ΔH)** is the tendency of the particles of the system to form strong bonds, accompanied by a decrease in the energy of the system.

2) **Entropy ($T \cdot \Delta S$)** - the tendency of particles to increase disorder, separation, to increase entropy.

The Gibbs energy reflects the combined effect of two driving forces under standard conditions.

9. Gibbs energy(ΔG)

- is a function of the state of the system, which characterizes the possibility of a spontaneous occurrence of a chemical process.

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

In closed systems (with $T, P = \text{const}$) processes occur that are accompanied by a decrease in the Gibbs energy.

$\Delta G < 0$ - spontaneous process is possible

$\Delta G > 0$ the reaction does not proceed in the forward direction.

$\Delta G = 0$ the system is in equilibrium

9. Gibbs energy(ΔG)

Standard Gibbs Energy of Matter Formation ($\Delta_f G^\circ$) is change in the Gibbs energy of the system during the formation of 1 mol of a complex substance from simple substances that are stable at 298 K и 10^5 Pa.

$$[\Delta_f G^\circ] = \text{kJ/mol}$$

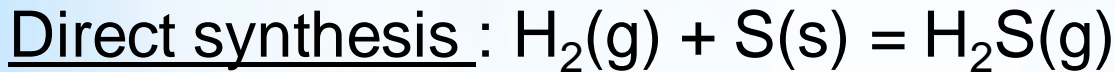
$$\Delta_f G^\circ (\text{simple substances}) = 0$$

9. Gibbs energy(ΔG)

1) $\Delta_f G^\circ < 0$

- substance is thermodynamically **stable**,
- can be obtained from simple substances (direct synthesis).

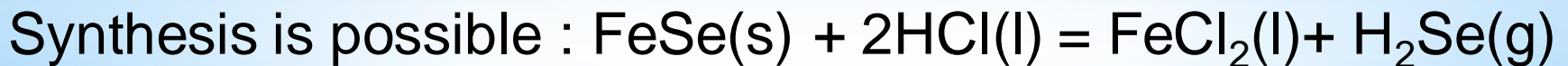
F.e.: $\Delta_f G^\circ (\text{H}_2\text{S}) = -33,8 \text{ kJ/mol}$



2) $\Delta_f G^\circ > 0$

- substance is thermodynamically **unstable**,
- can only be obtained indirectly.

F.e.: $\Delta_f G^\circ (\text{H}_2\text{Se}) = 19,7 \text{ kJ/mol}$



9. Gibbs energy(ΔG)

At any temperature is determined by the equation :

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

At standard temperature (298 K) is determined:

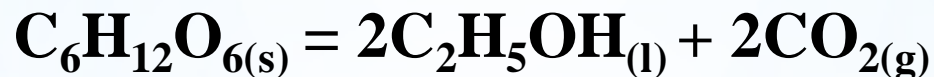
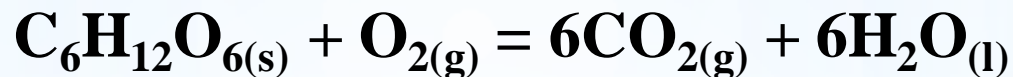
$$\Delta_r G^\circ = \sum \Delta_f G^\circ (\text{products}) - \sum \Delta_f G^\circ (\text{reagents})$$

Lecture conclusion

1. The calculation of entropy for an isolated system and the calculation of the Gibbs energy for a closed system answers the question of the possibility of a process occurring **without conducting an experiment**
2. You can evaluate the energy of the process by determining the thermal effect of a chemical reaction. The process proceeds with the release or absorption of heat.

Home task № 1.

1. Calculate the value of standard enthalpy for the reactions of glucose transformation proceeding in organism:



$$\Delta_f H^\circ [\text{CO}_{2(g)}] = -393.5 \text{ kJ/mol}$$

$$\Delta_f H^\circ [\text{H}_2\text{O}_{(l)}] = -286.0 \text{ kJ/mol}$$

$$\Delta_f H^\circ [\text{C}_2\text{H}_5\text{OH}_{(l)}] = -277.6 \text{ kJ/mol}$$

$$\Delta_f H^\circ [\text{C}_6\text{H}_{12}\text{O}_{6(s)}] = -1264.0 \text{ kJ/mol}$$

Which of these reactions supplies more energy to the organism?

Home task №2.

The reaction equation is given, for substances the corresponding thermodynamic constants are given :



$\Delta H_{298}^0,$ kJ/mol	11	0	-285,8	-207,4
$S_{298}^0,$ J/K·mol	304	205	70	147

Determine:

1. Direction of this reaction in an isolated system;
2. The direction of this reaction in a closed system at $T = 500 \text{ K}$;