Chemical thermodynamics. Chemical equilibrium.

Chemical thermodynamics researches laws describing energy transformations during chemical processes. It allows to determine the ability, direction and limit of chemical reaction flow in different conditions.

Common measure of motion and interaction of all kinds of matter is energy E. One of fundamental laws of nature is the energy conservation law:

Energy does not arise from anything and does not disappear, it can only transform from one form to another in equivalent quantities.

Thermodynamic system – specific object of thermodynamic research, mentally isolated from the environment. It is a complex of macroscopic bodies, that can interact with each other and with external environment – exchange energy and substance with them.

Thermodynamic systems can be classified by different features:

- by state: equilibrium and non-equilibrium

- by interaction with environment: opened (substance and energy), closed (energy) and isolated (nothing).

- By the number of phases: homogeneous and heterogeneous

- By the number of components (chemical substances).

Internal energy of the system U – sum of all kinds of energy, motion and interaction of particles (molecules, atoms, ions, radicals etc.), composing the system – kinetic energy of chaotic motion of molecules relatively of mass center of the system and potential energy of molecules' interaction.

State of the system – complex of physical and chemical properties, characterizing the system. It described by state parameters – temperature T, pressure p, volume V, concentration C, etc.

Thermodynamic process – any interaction in the system, accompanied by parameters change. The motive force of processes is factors – irregularity of parameters values (temperatures, pressures, etc.). Process going in constant pressure is called isobaric, in constant temperature – isothermal, in constant value of heat – adiabatic.

Heat exchange – spontaneous irreversible transition of energy in form heat from body with higher temperature to body with lower temperature while their contact. Motive force of heat exchange – difference of bodies temperatures. Heat – form of irregular motion of particles forming body (molecules, atoms and etc.). Heat has unit Dj.

Work – form of energy transfer from one system to another, associated with action against external forces. Unit is Dj.

Heat capacity C – relation of heat quantity, absorbed by body.

Temperature T – degree of body heating, determined by the distribution of molecules and other particles by velocities of kinetic motion and degree of occupancy of higher energetic levels of molecules.

Zero law of thermodynamics

All parts of the system residing in thermodynamic equilibrium have the same temperature.

The first law of thermodynamics

In every process the change of internal energy $\Delta U = U_2 - U_1$ of some system equal to the quantity of the heat transferred to the system minus the quantity of work performed by the system.

As p and V – parameters of the state, U – function of the state, than the sum $U + pV = H$ is also the state function. This function is called **enthalpy**.

Between the change of enthalpy and the change of internal energy of the system existing the relationship, described by the equations:

$\Delta H = \Delta U + \Delta nRT$ or $\Delta U = \Delta H - \Delta nRT$,

Which is able to get using Mendeleev-Clapeyron equation:

$pV = nRT$, then $p\Delta V = \Delta nRT$.

Thermochemistry – the chapter of chemical thermodynamics, practicing the determination of heat effects of chemical reactions and evaluation of their dependencies from different conditions.

Heat effect of reaction – the value of heat, emited or absorbed by the thermodynamic system during the flow of chemical reaction in it.

Processes in which the heat is emited by the system are called exothermic; processes in which the heat is absorbed by the system are called endothermic.

Heat of combustion ΔH_c heat effect of oxidation reaction of some substance by oxygen with formation of higher oxides of appropriate elements. Unit of heat of combustion is Dj/mol.

Heats of combustion of higher oxides are equal to zero.

Heat of formation ΔH_f – heat effect of the reaction of formation of some substance from simple substances in the most stable state of appropriate elements in some temperature and pressure. Unit is Dj/mol.

Thermochemical equations contain the heat effect and aggregate states of all substances, participating in reaction.

$C_{(graphite)} + 1/2\ O_{2\ (g)} = CO_{(g)} + \Delta H_r$;

$\Delta H_r = -110,54$ kDj/mol

Hess law

The heat effect of the reaction depends only on the reagents and products states, but not on the way of the reaction.

1 consequence – heat effect of decomposition of substance to more simple substances is numerically equal, but opposite in sign to heat effect of formation of this substance from this simple substances.

Example:

$CaCO_{3\ (s)} = CO_{2\ (g)} + CaO_{(s)} + \Delta H_1$

$\Delta H_1 = +178,23$ kDj/mol.

$CaO_{(s)} + CO_{2\,(s)} = CaCO_{3\,(s)} + \Delta H_2$

$\Delta H_2 = -178{,}23$ kDj/mol.

2 consequence – If two reactions are going, leading from different beginning states to one ending, the difference between their heat effects is equal to the heat effect of transition from one beginning state to another.

3 consequence – if two reactions leading from one beginning state to different ending states are going, then the difference between their heat effects is equal to the heat effect of transition between one ending state to another.

The dependency of heat effect of reaction from temperature is described by the Kirchhoff law

$\Delta H_2 = \Delta H_1 + \Delta C_{p\,r}(T_2 - T_1)$,

<u>The second law of thermodynamics</u>

1. Heat can not be transferred from the more cold body to more heated.

2. Energy of different kinds tends to turn to heat, and heat tends to dissipate.

Entropy is the measure of disorder in the system.

$S = k \ln W$, (3.1)

where k – Bolzman's konstant.

In the system do not getting energy from the environment, spontaneous processes are going with the increase of entropy.

<u>Third law of thermodynamics</u>

In absolute zero of temperature entropy of any substance in form of ideal crystal is equal to zero.

Thermodynamic probability W is equal to 1

$S_0 = k \ln 1 = 0$

Chemical equilibrium – is a thermodynamic equilibrium in the system, in which is able direct and reverse chemical reactions (reversible).

From the kinetical point of view in chemical equilibrium velocities of all reactions going in both opposite directions are equal.

Some reversible chemical reaction can be written as:

$aA + bB \Leftrightarrow dD + eE$

According to the mass action law in the simplest case the velocity of direct reaction is associated with concentration of reagents by equation:

$$V_{dir} = k_{dir}\, C_A^{\,a}\, C_B^{\,b}\ ,$$

and the velocity of the reverse reaction – with concentrations of products by equation:

$$v_{rev} = k_{rev}\, C_D^{\,d}\, C_E^{\,e}\ .$$

In equilibrium this velocities are equal to each other

$$V_{dir} = v_{rev}$$

Equilibrium constant is a ratio of direct and reverse velocity constants.

$$\frac{k_{пр}}{k_{обр}} = K_c = \frac{C_D^{\,d}\, C_E^{\,e}}{C_A^{\,a}\, C_B^{\,b}}\ ,$$

Le-Shatele principle

When any system at equilibrium is subjected to change in concentration, temperature, volume, or pressure, then the system readjusts itself to (partially) counteract the effect of the applied change and a new equilibrium is established