Chemical Thermodynamics

Review questions:

1. What does thermodynamics study?
2. Define the terms “system” and “surroundings”.
3. What kinds of system do you know? Give a few examples of a close, open and isolated system. What kind of system is living organism?
4. Give the definition of extensive and intensive parameters of a system and note a few examples of them. Is the volume, pressure, temperature, density extensive or intensive parameters of a system?

5. Define the following terms: internal energy, work and heat. How does a system exchange energy with surroundings? What is the difference between work and heat in meaning of molecules motion?
6. Write the expression of work for isobaric and isochoric processes. Explain the physical meaning of the ideal gas constant (R) using one of these equations.
7. Explain the meaning of the reversible process in thermodynamics. Why does it have an ideal meaning?
8. Formulate the zeroth law of thermodynamics. What thermodynamic pa-rameter is common to systems in thermal equilibrium?

9. Give a few formulations of the first law of thermodynamics. Write the common expression of the law and its expressions under different conditions of the process: isochoric, isobaric, isothermic and adiabatic. Which of them has ideal meaning and why?
10. What is enthalpy and what is its difference from heat of the process?
11. Give the formulation of heat capacity. What types of it do you know?
12. What is the difference between C_P and C_V and why? What is equal to this difference for ideal gas?

13.Kirchhoff’s law

Physical chemistry studies chemical processes along with their physical ef-fects. It establishes connection between chemical and physical properties of the matter. Physical chemistry joins chemistry, physics and mathematics that allow creating mathematical models of the biological systems and making quantitative accounts to carry out of the process.

Thennodynamies studies heat, work, energy and their changes during a process, occurred in the system. In a broader sense, thermodynamics studies the relationships between macroscopic properties of a system.

Chemical Thermodynamics deals with the transformation between chemical energy and other forms of energy. It studies direction and possibility of the chemical process and calculates heat effect of the reaction.

Basic Definitions

The system *is a body or a group of interacting bodies that we consider apart from its surrounding*. It may be a reaction vessel, an engine, a biological cell, and so on.

A chemical system exchanging neither matter nor energy with its surroundings is an **isolated system.**

A chemical system exchanging energy but not matter with its surroundings is a **closed system**. For example, if the flask is closed so that water vapor cannot escape from it or is condensed in the flask.

A chemical system exchanging both energy and matter with its surroundings is an **open system**. For example, a cup of tea, or an animal organism, or an open flask with solution in it

An adiabatic system *cannot exchange the heat with its surroundings*.

The term phase is used for that portion of the investigated system volume in which its properties are constant or continuously changing in space.

Homogenous system does not contain different parts of the system with different properties, i.e. there is no boundary surface (interface) between them. If the system has boundary surface (interface) between different parts of the system, it's called ***heterogeneous***.

The state of the system is described by its properties, the so called parameters of the system. There are two types of parameters – extensive and intensive. ***Intensive parameters*** *do not depend on the quantity of substance* and are the same as for the whole system and as for its parts (for example, temperature, densi-ty, viscosity). Properties such as enthalpy, entropy, free energy that *depend on the quantity of substance* are called e***xtensive parameters*** of the system.

When a state of a thermodynamic system is changed, we say a *thermodynamic process* occurs in a system**.** ***Spontaneous process*** *takes place without work being done on the system*. In other words, such a process occurs only at the expense of the own energy reserve of the system (without energy entry from the surroundings). It happens naturally: a gas expands to fill the available volume, a hot body cools to the temperature of its surroundings, a body falls from a higher level to a lower one, etc. ***Non-spontaneous process*** *must be brought about by doing work to the system*: compres-sion a gas to a smaller volume, cools an object with a refrigerator, etc. In closed system every spontaneous process finishes in equilibrium state. *A state of a system that remains constant in time without the intervention of any external process* is called ***an equilibrium state. Reversible process*** in thermodynamics has some other meaning, than in chemistry, where it means only that the process occurred in two opposite directions.

Internal energy, work, heat

The internal energy (U) *is total kinetic and potential energy of the particles (molecules, at-oms etc.) composing the system*. It does not include the kinetics of motion of the whole system or its potential energy. The internal energy depends both on the amount of the substance and on the conditions under which the process takes place. It's a state function and an extensive property of a system.

Heat and work are forms of energy transfer. ***Heat, q****, is an energy transfer between the system and surroundings due to a tem-perature difference and be realized by chaotic motion of molecules.* ***Work, W****, is an energy transfer between the system and surroundings due to macroscopic force acting through a distance and is realized by organized motion of molecules.*

Internal energy, heat and work are measured in the same units, the joule (J). Changes in molar internal energy are expressed in kilojoules per mole (kJmol–1).

For an <u>*isobaric* (constant pressure) *process*</u> integration of the work equation:

$$W = pdV$$

gives $W = p\ (V_2\text{-}V_1)$

Using the equation of ideal gas state for one mol ideal gas:

$$pV = RT$$

allow to obtain the following expression:

$$W = R(T_2\text{-}T_1)$$

<u>*Isothermal process* (T=const)</u>

$$p = nRT/$$

$$W = nRT\frac{dV}{V}.$$

$$W = nRT\int\frac{dV}{V} \text{ and } W = 2.303\ nRT\ lg\frac{V_2}{V_1} \text{ or } W = 2.303\ nRT\ lg\frac{P_1}{P_2}$$

In an *adiabatic process* (q=const) a gas does not absorb heat from its sur-roundings

$$W = C_v\,(T_1 - T_2)$$

For an *isochoric* (constant volume) *process* $dV = 0$, consequently $W = 0$. In this case, a system isn't able to do expansion work.

The Zeroth Law of thermodynamics

two systems each of them are found to be in thermal equilibrium with the third system, it is in thermal equilibrium with each of them.

The First law of thermodynamics

The first law can be formulated in several ways:

Energy can be neither created nor destroyed and if energy disappears in one form, it reappears in another form in a strictly equivalent amount.

It is impossible to construct the first order perpetual-motion ma-chine) i.e. a machine by which we could obtain work without spending an equivalent amount of energy.

The total energy of an isolated system is constant

The mathematical expression of the first law of thermodynamics

$\Delta U = q - W$

For processes involving only infinitesimally small changes, it is written in the form:
$dU = dq - dW$

In isochoric process *($dV=0$)* the system can not do expansion work, so $dW=0$ and
$dU = dq$
In isochoric process, the heat imparted to the system is spent only to internal energy change.
In adiabatic process $dq=0$, so we can write:
$-\,dU = dW$
The system is able to do work only at the expense of internal energy.
In isothermal process, when $T=const$, U is constant too (because U for ideal gas depends only on the T), so $dU=0$ and we can write:
$dq = dW$

Under such conditions, the heat imparted to the system is spent only on carried out work. This equation has an ideal sense, because it is impossible to transform heat to work in equal amounts. ***For isobaric process p=const***, so the system is able to do the work of expan-sion and the first law has the following expression:
$dq = dU + dW$ *or* $dq = dU + pdV = dH$

Though change in enthalpy is equal to the heat effect of a process occurred in a system, their signs are opposite, because H attributes to the system and q at-tributes to the surroundings. So, in the exothermic process $dH<0$, but $dq>0$, be-cause in such process the energy of the system decreases, while the energy of the surroundings increases.

Enthalpy(H) is a thermal effect of reaction.

For ideal gases at constant temperature $p\Delta V = \Delta nRT$, so the first law we can write as:
$\Delta H = \Delta U + \Delta nRT$
where Δn is the change of moles of the gas during the reaction.

Heat capacity

When the heat flows into the system as a rule the temperature of the system is proportionally increased and we can write, that $q=C\Delta T$.
$C = dq/dT$
Heat capacity is defined as amount of heat necessary to the change of the tempera-ture of the system in one degree.
Types of capacity:
Specific heat capacity is amount of heat necessary for one gram of a matter temperature arising in one degree.
Molar heat capacity is amount of heat necessary for one mol of a material temperature arising in one degree.
Heat capacity depends on the temperature and on the conditions under which a process takes place. According to the thermodynamics first law, $dq = dH$ in iso-baric process and $dq = dU$ in isochoric process, hence the ***heat capacity at con-stant pressure***, ***Cp***, is equal to:
$Cp = dH/dT$
and ***the heat capacity at constant volume***, ***Cv***, is equal to:
$Cv = dU/dT$
From the first law $dH>dU$ ($dH=dU+pdV$), consequently $Cp>Cv$, and the difference between them is equal to the work of expansion: $Cp – Cv = pdV$. For ideal gas $Cp – Cv = R$

Hess’s Law

A difference between enthalpy value for initial and final states of the chemical system and this difference is a ***heat effect*** of a process.

In 1840 year, G.Hess formulated the fundamental law of thermochemistry, which is known by his name: *the heat effect of a chemical reaction is independent on the path of the reaction, i. e., on its intermediate stages and depends only on the initial and final states of the system.* In other words, *if from given initial substanc-es we can obtain given products in different ways, then whatever the path of the reaction, i.e., whatever its intermediate stages, the over-all heat effect of the reac-tion are the same for all the paths.*

The standard enthalpy of formation is the standard reaction enthalpy of a reaction
during which one mole of a given substance is formed from elements.

In consequence of Hess's law, the standard reaction enthalpy of every chemical reaction
equals the difference between the standard enthalpies of formation of its products and reactants
multiplied by the respective stoichiometric coefficients. For the general reaction we thus
have

$$\begin{aligned}\Delta_r H^\circ &= r\,\Delta_f H^\circ_R + s\,\Delta_f H^\circ_S + \cdots - a\,\Delta_f H^\circ_A - b\,\Delta_f H^\circ_B - \cdots \\ &= \sum^{n} \nu_i\,\Delta_f H^\circ_i\end{aligned}$$

The standard enthalpy of combustion is the standard reaction enthalpy of a reaction
during which one mole of a substance reacts with oxygen while producing defined waste
products of the reaction.
If we know the enthalpies of combustion of all substances present in the general reaction
, then for the reaction enthalpy of this reaction we write:

$$\begin{aligned}\Delta_r H^\circ &= a\,\Delta_c H^\circ_A + b\,\Delta_c H^\circ_B + \cdots - r\,\Delta_c H^\circ_R - s\,\Delta_c H^\circ_S - \cdots \\ &= -\sum_{i=1}^{n} \nu_i\,\Delta_c H^\circ_i\,.\end{aligned}$$

Kirchhoff's law—dependence of the reaction enthalpy on temperature
For the derivative of the reaction enthalpy with respect to the temperature of the reaction we have:

$$\left(\frac{\partial \Delta_r H}{\partial T}\right)_p = \Delta C_p\,,$$

Where

$$\Delta C_p = r\,C_{pm}(\mathrm{R}) + s\,C_{pm}(\mathrm{S}) + \cdots - a\,C_{pm}(\mathrm{A}) - b\,C_{pm}(\mathrm{B}) - \cdots = \sum_{i=1}^{n} \nu_i C_{pmi}\,.$$

$$\Delta_r H(T_2) = \Delta_r H(T_1) + \int_{T_1}^{T_2} \Delta C_p \, dT \, ,$$

This relation is called Kirchhoff’s law. It allows us to convert reaction enthalpies from one temperature to another if we know the dependence of the heat capacities of substances on temperature.