V. V. KHRUSTALEV, O. V. KANTSIAVA,
S. R. KAZULEVICH

CHEMICAL THERMODYNAMICS AND KINETICS FOR PHARMACISTS

Practical book

Репозиторий БГМУ

Minsk BSMU 2017

МИНИСТЕРСТВО ЗДРАВООХРАНЕНИЯ РЕСПУБЛИКИ БЕЛАРУСЬ
БЕЛОРУССКИЙ ГОСУДАРСТВЕННЫЙ МЕДИЦИНСКИЙ УНИВЕРСИТЕТ
КАФЕДРА ОБЩЕЙ ХИМИИ

В. В. Хрусталёв, О. В. Контява, С. Р. Казюлевич

ХИМИЧЕСКАЯ ТЕРМОДИНАМИКА И КИНЕТИКА ДЛЯ ПРОВИЗОРОВ

CHEMICAL THERMODYNAMICS AND KINETICS FOR PHARMACISTS

Практикум

Репозиторий БГМУ

Минск БГМУ 2017

УДК 544.3:615.1(076.5)(075.8)-054.6
ББК 28.071я73
Х95

Рекомендовано Научно-методическим советом университета в качестве практикума 21.06.2017 г., протокол № 10

Рецензенты: канд. фарм. наук, доц. Н. Д. Яранцева; канд. хим. наук, доц. Ф. Ф. Лахвич; канд. мед. наук, доц. И. Л. Котович

Хрусталёв, В. В.
Х95 Химическая термодинамика и кинетика для провизоров = Chemical thermodynamics and kinetics for pharmacists : практикум / В. В. Хрусталёв, О. В. Контява, С. Р. Казюлевич. – Минск : БГМУ, 2017. – 115 с.

ISBN 978-985-567-757-5.

Содержит теоретический материал, описание лабораторных работ, задачи по химической термодинамике и кинетике.

Предназначен для студентов 2-го курса медицинского факультета иностранных учащихся, обучающихся на английском языке по предмету «Физическая и коллоидная химия».

УДК 544.3:615.1(076.5)(075.8)-054.6
ББК 28.071я73

ISBN 978-985-567-757-5

© Хрусталёв В. В., Контява О. В., Казюлевич С. Р., 2017
© УО «Белорусский государственный медицинский университет», 2017

репозиторий БГМУ

PREFACE

Chemical thermodynamics and kinetics make together the basement of all other subdisciplines of physical and colloid chemistry. The main idea of this book is to show how thermodynamics and kinetics are connected with each other with the help of logic and mathematics. The founders of both thermodynamics and kinetics lived in the end of XIX century and the beginning of XX century when philosophical conceptions trying to explain the sensce of the whole creation were as trendy as higher mathematics dealing with derivatives, logarithms and integrals. Since those days of revelative ideas, thermodynamics and kinetics became applied disciplines: they formed an apparatus for investigations and practical approaches.

Each chapter of the book contains equations describing such models as ideal gas, isolated system, ideal solution, as well as the simplest processes occurring in and with those systems. With the help of those equations one should be able to solve problems that can be found in the end of each chapter and test the ideas behind the equations in laboratory works described in the end of the book.

The book is necessary for pharmacy students from the 2nd year of study: it contains the material that is used during the first semester and in the end of year exam in the discipline of “Physical and Colloid Chemistry”. Students studing the discipline of “General Chemistry” may also use this book as a supplementary material.

репозиторий БГМУ

CHAPTER 1
THE FIRST LAW OF THERMODYNAMICS

Main topics of the chapter:

1. *The first law of thermodynamics.*
2. *Isochoric and isobaric heat effects of a process.*
3. *Hess law.*
4. *Heat capacity.*
5. *Kirchhoff's equation.*

The first law of thermodynamics described the connection between the heat supplied to a system (Q), the work done by a system (A) and the change in inner energy of a system (ΔU). The most important idea underlying the first law of thermodynamics is that we can measure the work in the same units as heat (in Joules). According to that law, the heat absorbed by a system may be transformed into the work and the increase of an inner energy of a system.

$Q = A + \Delta U$

In the real life we cannot transform all the energy supplied to any system into the work completely. There is always a loss of energy in each step of the process. This observation has been expressed mathematically in the first law of thermodynamics.

The temperature of a real gas decreases during its expansion. So, we can say that a real gas loses a certain amount of heat when it occupies a new volume. If we measure the amount of heat released (Q) in such process and the actual change in volume (ΔV) at a constant pressure, we will see that there is a difference between the heat released and the work done by a gas. That difference is nothing but the change in inner energy (ΔU).

$Q = \Delta U + p\Delta V$ and $\Delta U = Q - p\Delta V$

If we deal with some big differences in inner energy, we use a symbol "Δ" to show it. If we deal with such parameters as heat and work, we cannot say that "a difference in work is equal to 5 kJ". We should say that the amount work is equal to 5 kJ. Because of this a symbol like "Δ" is not used in the integral form of the equation of the first law of thermodynamics.

If we deal with minimal possible changes in parameters, then we should use symbol "d" for parameters like inner energy and symbol "δ" for parameters like work and heat. A minimal possible change of a parameter is called a differential. So, here is a differential form of the same equation of the first law of thermodynamics.

$\delta Q = \delta A + dU$

If we consider that all the work of a process is a work of expansion, then $A = p \cdot \Delta V$. In the differential form it means that $\delta A = pdV$. So, we can rewrite the equation in the following way.

$\delta Q = pdV + dU$

репозиторий ВГМУ

If the process is isothermic, then there will be no change in the inner energy of a system. In this case all the heat supplied will turn to the work (in our case it will turn just to the work of expansion). To highlight that we are talking about isothermic process, a subscript capital letter “T” must be written before the letter Q.

$\delta Q_T = pdV$

Generally speaking, the first law of thermodynamics says that the heat cannot be turned into the work completely in the real life, but if we consider an ideal (model) process, then we can still use the expression written above. Of course, an isothermic transfer of heat is hard to imagine. However, we can keep the temperature of a system during a certain process relatively constant with the help of a calorimeter. In this case we can claim that our process was conducted in (almost) isothermic conditions.

If the process is isochoric (the volume is constant), but the only one possible work of a system is the work of expansion, then Q = U, and δQ = dU. It means that all the supplied heat increased the inner energy of a system. To highlight that we are talking about isochoric heat effect of a process a subscript capital letter “V” must be written before the letter Q.

$Q_V = \Delta U$

In the isobaric process (the pressure is constant) which can make only one kind of work (the work of expansion) we can introduce another parameter to make its difference equal to the heat effect. This parameter is called enthalpy (H). If the change in enthalpy is equal to the isobaric heat effect of a process, then it must be also equal to the sum of a difference in inner energy and the multiple of pressure and the difference in volume.

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

In the differential form we can write the following line.

$\delta Q_p = dU + pdV = dU + d(pV) = d(U + pV) = dH$

Actually, isobaric heat effect considers both the change in inner energy and the work of expansion.

If we perform the same process in isochoric and isobaric conditions, then isobaric heat effect is equal to the isochoric heat effect plus the work of expansion. When we say “the same process” we mean that the change in inner energy is the same in both conditions: at constant volume and at constant pressure. If it so, we can prove that statement mathematically.

$Q_p = \Delta U + p \cdot \Delta V = Q_V + p \cdot \Delta V$

If we assume that the change in volume of a system is only due to the difference in the number of moles of gases, then we can use the ideal gas equation to modify the previous equation.

If $p \cdot \Delta V = \Delta n \cdot R \cdot T$, then

$Q_p = Q_V + \Delta n \cdot R \cdot T$, or

$\Delta H = \Delta U + \Delta n \cdot R \cdot T$

репозиторий БГМУ

If the number of moles of gases increases in a given process, then isobaric heat effect is higher than isochoric heat effect ($\Delta H > \Delta U$). In contrast, if the number of moles of gases decreases in a given process, then isobaric heat effect is lower than isochoric heat effect ($\Delta H < \Delta U$). If the number of moles of gases in a given process stays the same, then isobaric heat effect is equal to isochoric heat effect ($\Delta H = \Delta U$).

Gas constant (R) is one of the most useful multiples in thermodynamic equations. Physical sense of R can be understood from the ideal gas equation:

$R = (p \cdot \Delta V) / (n \cdot T)$

If we say that $p \cdot \Delta V$ is a work of expansion, then the last equation may be re-written.

$R = A / (n \cdot T)$

Finally, gas constant is equal to the work of expansion of 1 mole of an ideal gas in case of the increase in temperature equal to 1 K. It means that R has a value of 8.31 J/mole·K. The multiple of R and T is expressed in the same units as energy and work (J/mole). So, we can multiply any dimensionless number (like ratio or its natural logarithm) by $R \cdot T$ and convert it to energy.

The heat effect of a chemical reaction can be measured in the calorimeter. The process may be conducted at the constant pressure. In this case the heat effect will be equal to the change in enthalpy with an opposite sign. If the process is conducted at the constant volume, then the heat effect will be equal to the change in the inner energy with an opposite sign. Traditionally, the heat effect reflects the change in the energy of an environment, while the difference in enthalpy and inner energy reflect the change in the energy of a system.

The Hess' law postulates that the heat effect of a chemical reaction conducted in isothermal conditions at either constant pressure, or volume, does not depend on the concrete mechanism of a process, but it depends only on the nature and state of reactants and the nature and state of products. In other words, there may be different intermediate substances, but the overall ΔH or ΔU will be exactly the same. Indeed, thermodynamics usually describes only initial and final states of a system.

There are numerous tables with the enthalpies of formation (from pure chemical elements) for each substance. These enthalpies of formation are referred to as standard, since they are measured in "STP" (standard temperature and pressure: 298 K and 1 atmosphere). A symbol representing the standard enthalpy of formation for a given substance is "ΔH_f^0". A symbol representing the standard enthalpy of combustion (with a formation of highest oxides) for a given substance is "ΔH_c^0".

To calculate the enthalpy of a chemical reaction in standard conditions (ΔH_r^0) one needs to minus the sum of ΔH_f^0 of all the reactants from the sum of ΔH_f^0 for all the products (products minus reactants). The values of ΔH_f^0 must be multiplied by stoichiometric coefficients before corresponding substances. It is logical to assume that for any pure chemical element ΔH of formation from pure chemical elements is equal to 0.

$\Delta H^0_r = \sum \Delta H^0_f \text{ (products)} - \sum \Delta H^0_f \text{ (reactants)}$

Репозиторий БГМУ

An alternative way to calculate ΔH_r^0 is to minus the sum of ΔH_c^0 of all the products from the sum of ΔH_c^0 of all the reactants (reactants minus products). It is logical to assume that for any highest oxide ΔH of its combustion to the highest oxides is equal to 0.

$\Delta H^0_r = \sum \Delta H^0_c$ (reactants) – $\sum \Delta H^0_c$ (products)

A classic example of the application of Hess's law is the calculation of the enthalpy of hydration for a dry (anhydrous) salt. We can measure ΔH^0 of the dissolving of 1 mole of an anhydrous salt in water and ΔH^0 of the dissolving of 1 mole of a hydrate of the same salt in water. Since hydration is a part of the dissolving of an anhydrous salt, but in the hydrate a salt is already hydrated (at least, we assume that it is hydrated completely), we can use the following equation.

$\Delta H^0_{\text{dry salt dissolving}} = \Delta H^0_{\text{hydrate dissolving}} + \Delta H^0_{\text{hydration}}$

A lot of chemical reactions are not even possible at STP. Because of this we need to know how to calculate ΔH_r in non-standard conditions. The key parameter for such calculations is a heat capacity (C).

The molar heat capacity is equal to the amount of heat that one needs to supply to 1 mole of a substance to increase its temperature by 1 K. The units of molar heat capacity are J/mol·K. Specific heat capacity is measured in J/g·K. Sometimes specific heat capacity is more useful for calculations than molar heat capacity. However, if we use a term "heat capcity" in this book, we mean molar heat capacity.

If we deal with some definite changes in temperature and the absorbance of big amount of heat, we can use the following equation to calculate an average heat capacity.

$C_{av} = Q/(T_2 - T_1)$

If we deal with minimal possible amount of heat and minimal change in temperature, then we can write the same equation in differential form.

$C = \delta Q/dT$

The ratio between two differentials is nothing but a derivative. In a given case, heat capacity is a derivative of the amount of heat per temperature.

Heat capacity depends not just on the nature of a substance, but also on temperature and other conditions. Let us define heat capacity in isochoric conditions.

We know that $\delta Q_V = dU$ and $C_V = \delta Q_V/dT$. So, we can substitute heat effect by the value of the minimal change of inner energy in the process. Since the process is isochoric, C_V is called a partial derivative (because the volume is constant). To highlight this fact, a symbol "∂" is used instead of "d" and the whole derivative is written in brackets with a subscript letter "V" behind them.

$C_V = (\partial U/\partial T)_V$

At a constant pressure $\delta Q_p = dH$ and $C_p = \delta Q_p/dT$. Obviously:

$C_p = (\partial H/\partial T)_p$

Actually, the last equation can be rearranged with the aim to express how the change in temperature influences the enthalpy of a process. The equation written below is known as Kirchhoff's equation.

$\partial\Delta H = \Delta C_p \partial T$

For ideal monoatomic gases we can calculate the common value of an isochoric heat capacity from the kinetic theory of ideal gases. According to that theory each degree of freedom increases C_V by R/2 value. Monoatomic gases can move in three dimensions in the space (they have 3 degrees of freedom). So, for ideal monoatomic gases:

$C_V = 3R/2$

Since $Q_p = Q_V + RT$ for 1 mole of an ideal gas, then $C_p = C_V + R$. So, for a monoatomic ideal gas:

$C_p = 3R/2 + R = 5R/2$

Unlike monoatomic gas, diatomic gas has 5 degrees of freedom: each molecule can move in three dimensions, and it also can rotate (you need 5 coordinates to identify its position in the space). The formulas for C_V and C_p calculation are as follows for ideal diatomic gases.

$C_V = 5R/2$ and $C_p = 5R/2 + R = 7R/2$

Interestingly, these formulas work relatively good for the most of gases at standard temperature and pressure. Remember that, whenever you use the gas law ($pV = nRT$) in derivations, you assume that you deal with an ideal gas.

The difference in heat capacity between the final and initial states of a system determines the difference in the enthalpy (isobaric heat effect) of a process with the increase of temperature. In other words, ΔC_p is a temperature coefficient of enthalpy.

The difference in heat capacity can be calculated for a chemical reaction in the way that is similar to the ΔH^0_r calculation. One needs to minus the sum of molar heat capacities for reactants from the sum of molar heat capacities for products. Isobaric heat capacities of all the substances must be multiplied by corresponding stoichiometric coefficients.

$\Delta C_p = \sum C_p \text{ (products)} - \sum C_p \text{ (reactants)}$

In isochoric conditions Kirghoff's equation is as follows.

$\Delta C_V = (\partial\Delta U/\partial T)_V$ or $\partial\Delta U = \Delta C_V \partial T$

In general, a temperature coefficient of the heat effect of a process is equal to the change in heat capacity of a system in that process.

If the overall heat capacity of the products is higher than the overall heat capacity of reactants ($\Delta C > 0$), the products will absorb the bigger amount of heat at higher temperature. The higher the temperature, the more endothermic the process.

If the overall heat capacity of the products is lower than the overall heat capacity of reactants ($\Delta C < 0$), the reactants will release the bigger amount of heat at higher temperature. The higher the temperature, the more exothermic the process.

Репозиторий БГМУ

If the overall heat capacity of the products is exactly the same as the overall heat capacity of the reactants, the heat effect of a chemical reaction shows no dependence on temperature.

To calculate the difference in the enthalpy of a chemical reaction one has to use an integral form of Kirchhoff's equation.

$$\Delta H = \int_{298}^{T} dH = \int_{298}^{T} \Delta C_p dT$$

If the heat capacity does not depend on temperature, or if we decide to ignore that dependence, we can assume that ΔC_p is a constant. In this case we can continue the integration in the following way.

$$\Delta H = \Delta C_p \cdot \int_{298}^{T} dT = \Delta C_p \cdot (T - 298)$$

For the calculation of exact enthalpy at a given temperature (T) we must calculate a sum of standard enthalpy and the difference between exact enthalpy and standard enthalpy.

$$\Delta H_T = \Delta H_{298} + \Delta C_p \cdot (T - 298)$$

If we want to consider the dependence between heat capacity and temperature, we should try to describe it by an equation. Traditionally this dependence is described by a trend of a squared equation: $y = a + bx + cx^2$. Instead of "x" we should use the temperature: $a + bT + cT^2$. There are special tables with values of a, b and c for each substance. If we know the values of a, b and c for reactants and products we can calculate the differences in them in the way similar to the ΔH^0_r calculation (considering stoichiometric coefficients in the equation of chemical reaction).

$\Delta a = \sum \Delta a$ (products) – $\sum \Delta a$ (reactants)

$\Delta b = \sum \Delta b$ (products) – $\sum \Delta b$ (reactants)

$\Delta c = \sum \Delta c$ (products) – $\sum \Delta c$ (reactants)

The difference in heat capacity can be calculated from the known values of a, b and c:

$\Delta C_p = \Delta a + \Delta bT + \Delta cT^2$.

Then the value of ΔC_p can be inserted in the same form of Kirchhoff's equation.

However, the most accurate calculation requires the usage of an integral of the "$\Delta a + \Delta bT + \Delta cT^2$" expression from 298 K until the temperature of interest.

$$\Delta H_T = \Delta H_{298} + \int_{298}^{T} (\Delta a + \Delta bT + \Delta cT^2)dT = \Delta H^\circ_{298} + \Delta a(T - 298) + {}^1/_2\Delta b(T^2 - 298^2) + {}+ {}^1/_3\Delta c(T^3 - 298^3)$$

Taken together, there are 3 ways to find the enthalpy of a chemical reaction using Kirchhoff's equation: 1) when we ignore the dependence of ΔC_p on temperature; 2) when we calculate ΔC_p from the differences of a, b and c values; 3) when we integrate the whole expression "$\Delta a + \Delta bT + \Delta cT^2$" into the equation.

Sometimes equations of a different form than $C_p = a + bT + cT^2$ are used in physical chemistry to describe the dependence of heat capacity on temperature. To calculate the values of ΔH at different temperatures one should use Kirchhoff's equation, but integrate the exact equation (instead of "$a + bT + cT^2$") from 298 K to the needed temperature.

репозиторий БГМУ

Typical tasks

1. Calculate the standard ΔH^0_r of a chemical reaction.

$CO_{(g)} + 1/2O_{2(g)} = CO_{2(g)}$

The values of ΔH^0_f are, respectively, equal to (kJ/mole):

–110.5 0 –393.5

2. Calculate the standard ΔH^0_r of a chemical reaction.

$CH_{4(g)} + 2O_{2(g)} = CO_{2(g)} + 2H_2O_{(g)}$

The values of ΔH^0_f are, respectively, equal to (kJ/mole):

–74.81 0 –393.5 –241.8

3. Calculate the standard ΔH^0_r of a chemical reaction.

$H_2S_{(g)} + Cl_{2(g)} = 2HCl_{(g)} + S_{(s)}$

The values of ΔH^0_f are, respectively, equal to (kJ/mole):

–20.15 0 –92.3 0

4. Calculate the standard ΔH^0_r of a chemical reaction.

$H_2O_{(g)} + CO_{(g)} = CO_{2(g)} + H_{2(g)}$

The values of ΔH^0_f are, respectively, equal to (kJ/mole):

–241.8 –110.6 –393.5 0

5. Calculate the standard ΔH^0_r of a chemical reaction.

$4NH_{3(g)} + 5O_{2(g)} = 4NO_{(g)} + 6H_2O_{(g)}$

The values of ΔH^0_f are, respectively, equal to (kJ/mole):

–46.19 0 90.37 –241.8

6. Calculate the standard ΔH^0_r of a chemical reaction.

$2Cl_{2(g)} + 2H_2O_{(g)} = 4HCl_{(g)} + O_{2(g)}$

The values of ΔH^0_f are, respectively, equal to (kJ/mole):

0 –241,8 –92,3 0

Репозиторий БГМУ

7. Find the value of ΔU in the process of gas expansion from 10 to 16 L, at a constant pressure equal to 101.3 kPa, if 126 kJ of heat have been released in that process.

8. In the reaction of carbon dioxide formation from carbon monoxide and oxygen at a constant pressure and temperature equal to 298 K the heat effect is equal to –283 kJ/mol. Calculate the isochoric heat effect of the same reaction at the same temperature.

9. In the reaction of liquid water formation from gaseous oxygen and hydrogen at a constant volume and temperature equal to 298 K the heat effect is equal to –285.8 kJ/mol. Calculate the isobaric heat effect of the same process at the same temperature.

10. Find the value of ΔH^0_r for a chemical reaction written below at 600 K:

$CH_{4(g)} + 3Cl_{2(g)} = CHCl_{3(g)} + 3HCl_{(g)}$

Substances	CH_4	Cl_2	$CHCl_3$	HCl
ΔH^0_{298f}, kJ/mol	–74.9	0	–100.4	–92.3
C_p, j/(mol·K)	17.5	36.7	81.4	26.5

11. Calculate the value of ΔH^0_r for a given chemical reaction at the temperature of 400 K:

$2N_{2(g)} + 6H_2O_{(g)} = 4NH_{3(g)} + 3O_{2(g)}$

Use the following data to consider the dependence between heat capacity of each substance on temperature ($C_p = a + bT$).

Substances	N_2	H_2O	NH_3	O_2
ΔH^0_{298f}, kJ/mol	0	–241.88	–45.94	0
C_p, J/(mol·K)	29.12	33.57	35.65	29.37
a, J/(mol·K)	27.88	30.00	29.80	31.46
$b \cdot 10^3$, J/(mol·K)	4.27	10.71	25.48	3.31

Репозиторий БГМУ

12. Calculate the value of ΔH^0_r of the reaction of benzene hydrogenation at 1000 K:

$C_6H_{6(g)} + 3H_{2(g)} = C_6H_{12(g)}$

Use the following data to consider the dependence between heat capacity of each substance on temperature ($C_p = a + bT + cT^2$).

Substances	C_6H_6	H_2	C_6H_{12}
ΔH^0_{298f}, kJ/mol	82.89	0	–123.08
C_p, J/(mol·K)	81.67	28.83	106.27
a, J/(mol·K)	–33.90	29.08	–67.66
$b \cdot 10^3$, J/(mol·K)	471.87	–0.84	679.45
$c \cdot 10^6$, J/(mol·K)	–298.34	2.01	–380.76

13. Standard enthalpy of a reaction $CH_{4(g)} + CO_{2(g)} = 2CO_{(g)} + 2H_{2(g)}$ in the gas phase at 900 K is equal to 260.119 kJ. We know heat capacities of substances at 800 K and 1000 K (in J/mol·K):

		800 K	1000 K
CH_4	....	63.18	72.00
CO_2	....	40.21	42.77
CO	....	29.81	30.36
H_2	....	28.96	29.15

Find the standard enthalpy of the same reaction at 800 K, if we know that:

$\Delta C^0_{p(900)} = {}^1/_2\,(\Delta C^0_{p(800)} + \Delta C^0_{p(1000)})$.

Репозиторий БГМУ

14. Find the value of ΔH for a process of isobaric expansion of 1 mole of monoatomic ideal gas from 5 to 10 L at the pressure equal to 196 kPa.

15. Find the value of ΔU for an isochoric process in which the pressure of 3 mol of ideal diatomic gas that occupies 7 m^3 increased from 73.4 kPa to 31.2 kPa.

16. One mole of CH_2F_2 (assume that it is an ideal gas), taken at 0 °C and 1 atmosphere of pressure, has been heated at a constant pressure until the moment when its volume has become 3 times higher. Find ΔH and ΔU of that process, if you know how exactly the heat capacity depends on temperature:

$C_p = 20.26 + 7.59 \cdot 10^{-2}\ T$

17. Find the value of ΔH^0_r for a reaction:

$C_{(graphite)} + 0.5O_{2(g)} = CO_{(g)}$,

using the values of ΔH^0_r for two other reactions:

$C_{(graphite)} + O_{2(g)} = CO_{2(g)}$, $\Delta H^0_r = -393.5$ kJ

$CO_{(g)} + 0.5O_{2(g)} = CO_{2(g)}$, $\Delta H^0_r = -283.0$ kJ

18. Standard enthalpy of liquid water formation is equal to –285.8 kJ/mol. Standard enthalpy of gaseous water formation is equal to –241.8 kJ/mol. Find the standard enthalpy of vaporization for water.

репозиторий БГМУ

19. If you dissolve 1 mole of $Na_2SO_4 \cdot 10H_2O$ in water, 78.7 kJ of heat will be absorbed. To dehydrate that salt completely you need to spend 81.6 kJ of heat. Calculate the value of ΔH^0 of the dissolving of 1 mole of a dry salt (Na_2SO_4) in water.

20. During the dissolving of 1 mole of an anhydrous salt 25 kJ of heat are released, while during the dissolving of 1 mole of its hydrate 67 kJ of heat are absorbed. Calculate the value of ΔH^0 of hydration (kJ/mol) for an anhydrous salt.

21. Calculate the heat effect of the transition from amorphous silicon to crystalline silicon, if ΔH^0_c for amorphous silicon is equal to –867.3 kJ/mol, while for crystalline silicon it is equal to –850.6 kJ/mol. The product of combustion of both modifications of silicon is the same: SiO_2.

22. The values of ΔH^0_r for reactions $CO_{(g)} + {}^1/_2O_{2(g)} \rightarrow CO_{2(g)}$ and $H_{2(g)} + {}^1/_2O_{2(g)} \rightarrow H_2O_{(g)}$ are equal to –283 kJ/mol and –241.8 kJ/mol, respectively. Calculate the value of ΔH^0_r for the reaction written below in the same conditions:

$CO_{(g)} + H_2O_{(g)} = CO_{2(g)} + H_{2(g)}$

репозиторий БГМУ

CHAPTER 2
THE SECOND AND THE THIRD LAWS OF THERMODYNAMICS

Main topics of the chapter:

1. *Reversible and irreversible processes from the point of view of thermodynamics.*
2. *The conception of a useful work.*
3. *The second law of thermodynamics.*
4. *The calculation of the change in entropy in typical processes.*
5. *The calculation of the absolute entropy.*
6. *Thermodynamic potentials.*

From the point of view of thermodynamics, reversible processes are those that can be conducted in the forward and the backward directions through the same intermediated states without any changes in the environment. As usual, there are no such ideal processes in the real life, while we can assume that some of the real processes are very close to thermodynamically irreversible ones. Such processes are very slow and they are conducted through the uncountable number of intermediate states. In each intermediate state the change in thermodynamic parameters must be as close to zero, as it is possible. In the most of relatively simple calculations we assume that our process is thermodynamically reversible. Please, notice that from the point of chemical kinetics, reversible process is the process that doesn't go up to the completion: dynamic equilibrium is the final state of such process.

Thermodynamically irreversible processes result in such changes in the environment that cannot disappear if we conduct the backward process. In other words, thermodynamically irreversible processes "leave traces" in the environment. The faster the process, and the higher the difference in thermodynamic parameters between the initial and the final state of a system, the more irreversible that process.

If the process is thermodynamically irreversible, a system can produce the maximal possible work. If we assume that a system can produce some other types of work, except the work of expansion, then we can collect all those types of work under the common name "a useful work". Actually, all types of energy exchange other than the work of expansion (mechanical work) and the energy transfer with the help of heat are considered as the work against different forces like electric or magnetic. The transfer of energy in the form of heat has different definitions, but from the point of view of physics, this is the form of energy transfer with the help of such mechanisms as conduction (when the surfaces of two bodies are in the direct connection with each other), convection (when two bodies are connected with the help of the molecules of an air between them) and radiation (when one body releases photons mostly in infrared part of a spectra which are absorbed by another body). In the initial conception of the first law of thermodynamics there was no such term as "useful work". The division of the whole work into the work of expansion and the useful

Репозиторий БГМУ

work is really very useful for calculations. However, historically only mechanical work could have been used somehow. Back in XIX century Gibbs wondered that sometimes in a future mankind will learn how to use other types of work than a mechanical one. That is why he introduced a term “useful work” in thermodynamics.

Useful work is designated by a symbol “A’”. Mathematically we can write the following expressions in integral and differential forms.

$A'_{max} = A_{max} - p\Delta V$, and $\delta A'_{max} = \delta A_{max} - pdV$

The second law of thermodynamics states that there is a special parameter that is called “entropy”, which is used with the aim to determine, whether a given process in isolated system is spontaneous or nonspontaneous. According to the second law of thermodynamics, if a spontaneous process happens in an isolated system, then entropy of that system is increasing. So, if according to calculations, the total entropy in the isolated system increases due to the given process $\Delta S > 0$ ($dS > 0$), then we can be sure that such process will be spontaneous (it will happen by itself). A process is going on until the moment when total level of entropy in an isolated system reaches its maximum. So, if for a given process $\Delta S = 0$ ($dS = 0$), then we can postulate that an isolated system is in the state of equilibrium. A process that leads to the decrease of entropy in an isolated system is completely impossible according to the second law of thermodynamics. However, there are many spontaneous processes with $\Delta S < 0$ ($dS < 0$) if we calculate dS not for the whole isolated system, but just for a certain part of that system (closed or open system). In such case, the increase in entropy for the remaining part of an isolated system (in the environment) must be higher than the decrease of entropy in the closed or open system that we are interested in.

The “thermodynamic” mathematical interpretation of the second law of thermodynamics has been given by Clausius in the middle of XIX century.

$\Delta S = Q_{reversible}/T$ or $dS = \delta Q_{reversible}/T$

This equation works only if a process of heat transfer in the isolated system is reversible. For irreversible processes this equation turns to inequality.

$\Delta S > Q_{irreversible}/T$ or $dS > \delta Q_{irreversible}/T$

If we combine the equation and the inequality together, then a well known form of the mathematical expression of the second law of thermodynamics can be written.

$\Delta S \geq Q/T$ or $dS \geq \delta Q/T$

Using the Clausius equation we can calculate the change in entropy for some simple thermodynamically reversible processes. The first sample is the isothermic expansion of the volume of an ideal gas. The first law thermodynamics can be written in the differential form.

$\delta Q = dU + pdV$

Since we know the dU is equal to $C_V dT$, we can replace dU by $C_V dT$ in the above written equation.

$\delta Q = C_V dT + pdV$

репозиторий БГМУ

If the process is isothermic, then $dT = 0$.

So, we can write that:

$\delta Q = pdV$

From the gas law we know that $pV = RT$, and $p = RT/V$.

Finally we can modify the expression in the form where the difference in volume is connected with the amount of heat.

$\delta Q = RT \cdot dV/V$

This equation can be easily re-written in the integral form.

$Q = {}_{V_1}^{V_2} RT \cdot dV/V = RT\ln(V_2/V_1)$

From the second law of thermodynamics we know that $\Delta S = Q/T$. So, we can divide both parts of the equation by T and get the equation for calculation of the change in entropy caused by the increase of a volume of an ideal gas.

$\Delta S = R \ln(V_2/V_1)$

According to this equation, if the volume of a gas is increasing, then the entropy of a system is growing. It means that the expansion of a gas is a spontaneous process in an isolated system. Entropy is measured in J/mol·K, as well as the gas constant (R). That is how we can convert a dimensionless thing (natural logarithm of the ratio between final and initial volumes) into units of entropy. It is important to highlight that the larger the volume, the higher the entropy, but this dependence is not direct, but logarithmic. If a number of moles of a gas is different from 1 mole, we need to use the following equation.

$\Delta S = n \cdot R\ln(V_2/V_1)$

If two gases are mixed together by the way of the opening of the partition between two vessels, we also can use the abowe written formula to calculate the entropy of that process. First, we need to consider the increase of the entropy for the first gas (it occupied the volume of “$V_1 + V_2$” instead of V_1), and then we need to consider the increase of the entropy for the second gas (it occupied the volume of “$V_1 + V_2$” instead of V_2). If both gases were ideal, the total enropy of the mixing is equal to the sum of the entropies of the volume expansion for two gases.

If the temperature is constant, but we know the values of initial pressure (p_1) and final pressure (p_2), we can simply derive the needed equation for ΔS calculation using the formula $V = (RT)/p$.

$\Delta S = n \cdot R\ln((RT \cdot p_1)/(RT \cdot p_2)) = n \cdot R\ln(p_1/p_2)$

If the volume is constant, but the temperature is growing, we need to derive another formula for the calculation of the change in entropy of an ideal gas.

Since $\delta Q = C_V dT$, then we can divide both parts of this expression by T and create a differential form of the needed equation.

$dS = C_V dT/T$

In the integral form (from T_1 to T_2) we have the following equation.

$\Delta S = {}_{T_1}^{T_2} C_V dT/T = C_V\ln(T_2/T_1)$

репозиторий БГМУ

Notice that in this case we assume that the heat capacity does not depend on temperature. Indeed, entropy is expressed in the same units as heat capacity (J/mol · K). The higher the temperature, the higher the entropy.

In case if we know how exactly the heat capacity depends on temperature, we should integrate a given function divided by T. For example, if $C_V = \Delta a + \Delta bT + \Delta cT^2$, then:

$\Delta S = {}_{T_1}^{T_2} C_V dT/T = {}_{T_1}^{T_2} (\Delta a + \Delta bT + \Delta cT^2)dT/T$

$\Delta S = {}_{T_1}^{T_2} (\Delta a \cdot dT/T + \Delta b \cdot T \cdot dT/T + \Delta c \cdot T^2 \cdot dT/T)$

After the crossing out T and separate integration we have the following equation.

$\Delta S = \Delta a \cdot \ln(T_2/T_1) + \Delta b \cdot (T_2 - T_1) + \Delta c \cdot {}^1/_2 \cdot (T_2^2 - T_1^2)$

If two parameters have been changed in the process independently, we may assume that we deal with two different processes in each of which just a single parameter has been changed. For example, if both temperature and pressure of an ideal have been changed, then we should calculate ΔS of an isothermic process in which the pressure was changed, ΔS of an isobaric process in which the temperature was changed, and make a sum of them.

In isobaric conditions we deal with isobaric heat capacity, instead of isochoric heat capacity.

$\Delta S = {}_{T_1}^{T_2} C_p dT/T = C_p \ln(T_2/T_1)$

The equation written above can be used with the aim to approve that a hot body can spontaneously heat up a cold body, and never vice versa.

If we have two identical pieces of the same metal, and their initial temperatures are 100 K and 200 K, then if we make a contact between them, their temperatures will become identical (150 K). If we believe that the heat capacity is the same at 100 K and 200 K, then we can calculate the change in entropy of each of these two pieces of a metal.

$\Delta S_{hot} = C_p \ln(T_2/T_1) = C_p \ln(150/200)$

$\Delta S_{cold} = C_p \ln(T_2/T_1) = C_p \ln(150/100)$

Total change of entropy for both pieces of a metal is nothing but the sum of ΔS_{hot} and ΔS_{cold}.

$\Delta S_{total} = \Delta S_{hot} + \Delta S_{cold}$

$\Delta S_{total} = C_p \ln(150/200) + C_p \ln(150/100) = C_p \ln((150 \cdot 150)/(200 \cdot 100))$

$\Delta S_{total} = C_p \ln(225/200)$

Since the number under the logarithm is higher than 1, the total change in entropy will be positive (it works if we take any two random temperatures for a hot and a cold body). It means that the process of heat transfer is spontaneous only in one direction (from hot body to cold body). Also it means that entropy is growing because of the transfer of heat in an isolated system. From this point of view, all the processes in such an isolated system as our Universe should end in the moment when the entropy will reach its maximal value. This conception is known as the heat death of the Universe. This conception is in the conflict with the law of the conservation of energy and mass. The energy just cannot be wasted or

репозиторий БГТУ

useless. The energy in the form of heat or work of expansion is always converting to other types of energy (or the work against different forces). Moreover, according to the Einstein's theory, the energy can be converted to mass, and the mass can be converted to energy. One more important fact is that the second law of thermodynamics has a "statistical" nature. It works perfectly only for systems made from a huge number of particles.

According to the statistical interpretation of entropy, the higher the thermodynamic probability (W), the higher the entropy of a system. Mathematically this dependence is direct and logarithmic. To convert the natural logarithm of thermodynamic probability into J/mol·K the gas constant is used.

$S = R \cdot \ln W$

The above written formula works for 1 mol of a substance.

To find the entropy per 1 particle of a substance we need to divide both parts by an Avogadro's number.

$S_{\text{per particle}} = (R/N_A) \cdot \ln W = k \cdot \ln W$

The change in entropy for 1 mole of a substance can be calculated as the ratio between thermodynamic probabilities in the initial and the final states.

$\Delta S = S_2 - S_1 = R \cdot \ln(W_2/W_1)$

Thermodynamic probability is the number of microstates which are possible for a given macrostate of a system. The meaning of a microstate is the combination of the positions of all the particles in a system, as well as their speeds of movement and interactions with each other. Thermodynamic probability obviously cannot be measured directly. However, this conception is useful for understanding of such processes, as mixing. As we know, two gases will spontaneously mix with each other, but gases in the mixture will never be separated from each other on their own. It happens because the number of microstates becomes much higher in any mixture of gases than in two separate gases taken together. One should understand that the mixture of two gases cannot be separated back (on its own) only if the number of gas molecules is big enough. For very small systems two gases can be occasionally separated for a moment due to chaotic movement of molecules.

The statistical conception of entropy (suggested by Boltzmann) helps to explain why the entropy of a gas is always much higher than the entropy of a liquid, and why the entropy of a liquid is always higher than the entropy of a solid substance. If we use the Boltzmann's equation for gaseous water, knowing that its absolute entropy in STP is equal to 180 J/mol·K, then we will calculate a thermodynamic probability for 1 mole.

W(for gaseous H_2O) = $e^{S/R} = e^{180/8.31} = 2.6 \cdot 10^9$

The same calculation for 1 mole of liquid water at STP shows much lower thermodynamic probability, since the absolute entropy is equal to 70 J/mol·K.

W(for liquid H_2O) = $e^{S/R} = e^{70/8.31} = 4.6 \cdot 10^3$

So, there are just about 5000 possible microstates for $6.2 \cdot 10^{23}$ molecules of liquid water.

The third law of thermodynamics is the direct consequence of the statistical interpretation of the second law of thermodynamics. If we believe that at absolute zero there is just one possible microstate for a given macrostate, then $W = 1$ and $\ln W = \ln 1 = 0$, and $S = 0$. In other words, the entropy of an ideal crystal at 0 K is equal to 0. This statement provides an opportunity to calculate an absolute entropy of any substance just because in this case we have a common starting point.

To calculate an absolute entropy at STP for a given substance we need to know how exactly its heat capacity depends on the temperature.

We know that $\delta Q_p = C_p dT$ from the first law of thermodynamics, and $dS = \delta Q_p/T$ from the second law of thermodynamics. After the substitution we obtain a combined equation in the differential form.

$dS = C_p \cdot dT/T = C_p \cdot d\ln T$

From the third law of thermodynamics we know that at 0 K $S = 0$. Using this assumption we can integrate the above written equation from 0 K to 298 K (25 °C).

$S^0_{298} = \int_0^{298} C_p \cdot d\ln T$

If there are no phase transitions for a given substance in the range of temperatures from 0 to 298 K, the above written formula is enough for the calculation of absolute standard entropy. From the graphical point of view, integral is the undercurve area for a given dependence. In our case, the natural logarithm of temperature must be placed on X axis, and the heat capacity must be placed on Y axis. Then we can simply calculate the undercurve area from 0 to 298 K, that is equal to absolute standard entropy. If we can describe the dependence between C_p and lnT by a polynomial function (like $y = a + bx + cx^2$), then we can find the integral of this function from 0 to 298 K according to the rules of integration.

If there are phase transitions in the rage of temperatures from 0 K to 298 K, we must consider ΔS for each phase transition. Since each phase transition is an isothermic process, we can use the second law of thermodynamics to calculate ΔS from ΔH.

$\Delta S_{\text{phase transition}} = \Delta H_{\text{phase transition}} / T_{\text{phase transition}}$

It is important to highlight that the dependence of heat capacity on temperature (and natural logarithm of temperature) is much different for any substance in solid, liquid and gaseous states, as well as for its different polymorphic (or allotropic) modifications. Because of this a curve of the dependence between C_p and lnT must be experimentally built for each state (and modification) separately. Then all the curves may appear on the same graph (figure 1).

So, theoretically, the calculation of absolute entropy is a routine procedure performed with the help of special calorimeters (in such calorimeters one can set an initial temperature, provide a certain amount of heat and measure the increase in temperature to find current heat capacity, as well as heat effects of all phase transitions). Once again, to find the standard absolute entropy one should make a sum of the changes in entropy due to

репозиторій БДМУ

the heating of a substance in all of its phases (and modifications), and the changes in entropy due to phase transitions.

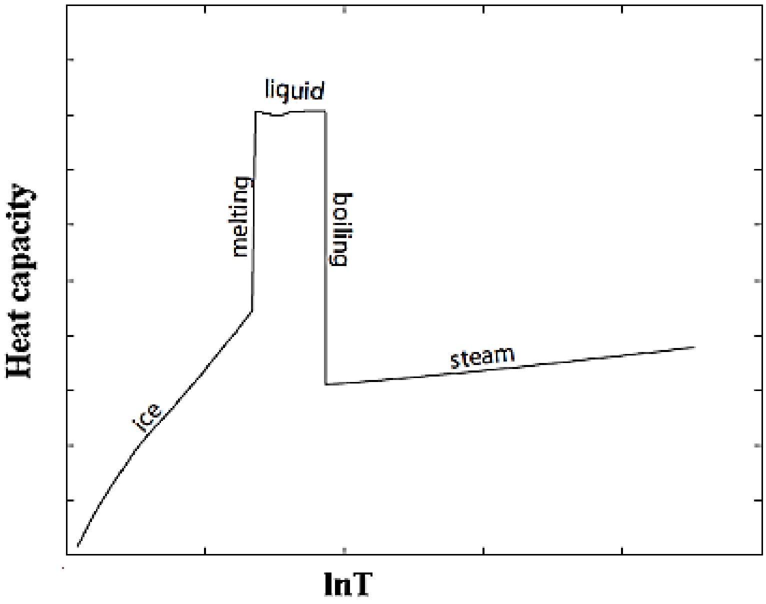


Figure 1. Dependence between the isobaric heat capacity (C_p) and natural logarithm of temperature (lnT) for water

It is hard to measure heat capacity at very low temperatures. Because of this the entropy from 0 to 5–15 K is calculated using an equation: $C_p = k \cdot T^3$. The equation for entropy calculation can be written as follows.

$$S = \int_0^{10} (C_p/T)dT = {}^1/_3kT^3$$

One can get the value of k for a given substance using an equation for C_p calculation: $C_p = a + bT + cT^2$. Values of a, b and c can be found in reference books.

Even though at temperatures close to absolute zero there are no ideal crystals, but there is a specific state of matter known as Bose-Einstein condensate, the calculation of the absolute entropy doesn't suffer much from the approximation written above. It is thought that in Bose-Einstein condensate (at temperatures very close to absolute zero) a large fraction of bosons occupy the lowest (the same) quantum state. And if they all have the same quantum state at absolute zero, then, probably, that is how a single possible microstate should really look like.

Thermodynamic potential is a function that is used for determination of the possibility of a spontaneous process, and for the estimation of the order of concurrent processes. In different conditions different thermodynamic potentials must be used.

Entropy is a thermodynamic potential for *isolated systems.*

Gibbs energy is a thermodynamic potential for processes that are both *isobaric and isothermic*.

Helmholtz energy is a thermodynamic potential for processes that are both *isochoric and isothermic*.

Репозиторий ВГУ

Inner energy is a thermodynamic potential for processes that are both *isochoric and isoentropic*.

Enthalpy is a thermodynamic potential for processes that are both *isobaric and isoentropic*.

If entropy is increasing in the isolated system, then the process is spontaneous. Entropy is growing until it reaches its maximal possible level in an isolated system.

For all other thermodynamic potentials the situation is opposite. If a thermodynamic potential is decreasing in respective conditions, then the process is spontaneous. Each thermodynamic potential (except entropy in an isolated system) is decreasing until it reaches its minimal possible level.

The most widely used thermodynamic potentials are Gibbs energy and Helmholtz energy. First we will derive Helmholtz energy.

According to the first law of thermodynamics:

$\delta Q = dU + \delta A'_{max} + pdV$

According to the second law of thermodynamics (for thermodynamically reversible processes):

$\delta Q = TdS$

So, we can substitute δQ by TdS in the first equation and obtain a combined equation of the first and second laws of thermodynamics.

$TdS = dU + \delta A'_{max} + pdV$

From this expression we can calculate a maximal useful work ($\delta A'_{max}$) of a closed system.

$\delta A'_{max} = –dU + TdS – pdV$

In case if a process is isochoric ($dV = 0$), the work of expansion is equal to zero.

$\delta A'_{max} = –dU + TdS$

Since a process is also isothermic, we can modify the last equation once again.

$\delta A'_{max} = –dU + dTS = –d(U – TS) = –F$

$A'_{max} = –\Delta F$

Helmholtz energy (F) is equal to U – TS. This parameter is equal to the maximal useful work of an isochoric isothermal process, but has an opposite sign. So, if ΔF is negative, the amount of useful work is positive (a closed system can do that useful work with the environment), and the process is spontaneous.

It is important to find partial derivatives of Helmholtz energy, because they are used in many thermodynamic calculations. In the integral form we have the following equation for Helmholtz energy calculation.

$F = U – TS$

In the differential form the same equation is re-written in the following way.

$dF = dU – TdS – SdT$

репозиторий БГМУ

From the first law of thermodynamics for an isochoric isothermic process which can make the work of expansion only ($\delta Q = dU + pdV$), and from the second law of thermodynamics for reversible process ($\delta Q = TdS$) we can get the following expression.

$TdS = dU + pdV$

It means that $dU = TdS – pdV$. This expression should be inserted into the equation $dF = dU – TdS – SdT$ instead of dU.

$dF = TdS – pdV – TdS – SdT = – SdT – pdV$

So, the final expression is:

$dF = – SdT – pdV$

If the volume is constant, then $dF = –SdT$. From this expression we can get the value of entropy with a minus sign.

$(\partial F/\partial T)_V = –S$

So, in fact, entropy (with a minus sign) is a derivative of Helmholtz energy per temperature at a constant volume.

If the temperature is constant, then $dF = –pdV$. From this expression we can get the value of pressure with a minus sign.

$(\partial F/\partial V)_T = –p$

Actually, the pressure (with a minus sign) can be described as a derivative of Helmholtz energy per volume at a constant temperature.

If a process is isobaric and isothermic, we must use another thermodynamic potential known as Gibbs energy. To start its derivation we must come back to the combined equation of the first and second laws of thermodynamics.

$\delta A'_{max} = –dU + TdS – pdV = –dU + d(TS) – d(pV) = –d(U – TS + pV)$

$\delta A'_{max} = –d(U + pV – TS) = –d(H – TS)$

Enthalpy (H) is a sum of inner energy (U) and work of expansion (pV). Gibbs energy (G) is equal to the difference between enthalpy and the multiple of temperature and entropy. So, finally we can write that:

$\delta A'_{max} = –d(H – TS) = –dG$

In the integral form:

$A'_{max} = \Delta H – T\Delta S = –\Delta G$

The maximal useful work of a closed system in isobaric and isothermic conditions is equal to the change in the Gibbs energy with an opposite sign.

$\Delta G = \Delta H – T\Delta S$

This equation is the most popular one in thermodynamics, since the most of the processes proceed at constant pressure (atmospheric pressure) and constant temperature (the temperature of the environment).

Let’s find partial derivatives of Gibbs energy from the expression $G = H – TS$ that turns to the following equation in the differential form:

$dG = dH – TdS – SdT$

репозиторий БГМУ

Since we know that $H = U + pV$, then $dH = dU + pdV + Vdp$. The last expression must be inserted in the equation $dG = dH – TdS – SdT$ instead of dH.

$dG = dU + pdV + Vdp – TdS – SdT$

From the first law of thermodynamics we know that $dU = TdS – pdV$. So, we can cross out dU, – TdS and pdV. The final expression is:

$dG = Vdp – SdT$

If temperature is constant, this expression turns to $dG = Vdp$. From this expression we can get volume.

$(\partial G/\partial p)_T = V$

If you still don't know what is volume, then we can help you with the definition. Volume is a derivative of Gibbs energy per pressure at the constant temperature.

If pressure is constant, then $dG = –SdT$. From this expression we can get entropy with a negative sign.

$(\partial G/\partial T)_p = –S$

So, the derivative of Gibbs energy per temperature at the constant pressure is nothing but entropy with a negative sign.

Indeed, when we are talking about a closed system, we mean that this system is a part of the Universe (which is thought to be an isolated system). If a spontaneous process happens in the closed system, then the entropy in the whole Universe must grow. So, each thermodynamic potential tells us about the situation in the whole Universe without the usage of parameters of the Universe itself. In isobaric and isothermic conditions ΔH is nothing but the heat effect of a reaction. It can be measured with the help of calorimeter, or it can be calculated using the Hess law. The difference in entropy for a process can be calculated from standard absolute entropies for products and reactants. Absolute entropy is calculated by the way of the measuring of the heat capacity and heat effects of phase transitions for each substance. Actually, $T\Delta S$ is a heat effect of a process calculated from heat capacities, while ΔH is a heat effect of a process calculated from heat effects of formation measured directly. If the real heat effect is lower than the predicted one, then some part of energy should escape a system in the forms which are different from the work of expansion and heat transfer. If this really happens, than the process must be spontaneous. If a system can make a useful work, then it will make it on its own.

If we divide $\Delta G = \Delta H – T\Delta S$ expression by T, then we will see that the outcome is determined by two entropies. Remember that $\Delta S = Q/T$, and $Q = –\Delta H$.

$\Delta G/T = \Delta H/T – \Delta S = –\Delta S$ of the environment $–\Delta S$ of the closed system

According to this equation, if the total difference in entropy for both closed system and the environment is positive, than the process is spontaneous.

The Gibbs energy of a chemical reaction at standard conditions can be calculated in two ways. One can just use standard Gibbs energies of formation from pure chemical elements from a special table for each compound and calculate the difference between the values for products and reactants. As usual, each value of ΔG^0_f must be multiplied by a stoichiometric coefficient for a given compound.

$\Delta G^0_r = \sum \Delta G^0_f$ for products – $\sum \Delta G^0_f$ for reactants

If the values of ΔG^0_f are not given, one can calculate them from ΔH^0_r and ΔS^0_r. The last values may be calculated from respective standard enthalpies of formation and absolute standard entropies for all substances participating in a given reaction.

If you want to calculate ΔG_r at the temperature that is different from 298 K, you should use the same formula of the combined equation of the first and the second laws of thermodynamics, but with different ΔH_r and ΔS_r values.

$\Delta G_r = \Delta H_r - T\Delta S_r$

If we assume that the heat capacities of products and reactants show no dependence on temperature, we can use Kirchhoff's equation in the form written below to calculate ΔH_r at nonstandard temperature.

$\Delta H_r = \Delta H^0_{298} + \Delta C^0_{p,\,298} \cdot (T - 298)$

The same assumption allows us to calculate ΔS_r using the following equation.

$\Delta S_r = \Delta S^0_{298} + \Delta C^0_{p,\,298} \cdot \ln(T/298)$

If we know that $G = H - TS$, while $F = U - TS$, and $H = U + pV$, than we can find a simple connection between Gibbs energy and Helmholtz energy.

$G = U + pV - TS$, and $G = F + pV$

If the pressure is constant, we can say that $dG = dF + pdV$.

So, for a given process at constant pressure and temperature we calculate ΔG from the known value of ΔF for the same process conducted at the constant volume and the amount of the work of expansion.

$\Delta G = \Delta F + p\Delta V$

If a process that we are talking about is a chemical reaction with gaseous products or reactants, we can replace the work of expansion by ΔnRT expression taken from the gas law.

$\Delta G = \Delta F + \Delta nRT$

It is obvious, that for a chemical reaction in which the number of moles of gases doesn't change ($\Delta n = 0$), the value of ΔG is equal to the value of ΔF. Indeed, in such processes the work of expansion is equal to zero.

Typical tasks

1. There are two vessels separated by a valve. One of them contains 1 mole of an ideal gas. Another one is empty. Calculate the change in entropy in the whole system after the opening of a valve.

репозиторий ВГМУ

2. Calculate the change in entropy in the reversible isothermic contraction of a) 1 mole of oxygen from the pressure of 0.001 to the pressure of 0.01 atmosphere; b) 1 mole of methane from the pressure of 0.1 to the pressure of 1 atmosphere. In both cases assume that the gas is ideal.

3. There are two vessels of the same volume separated by a valve. In one vessel we have 18 g of water vapor, in another vessel we have 40 g of argon. Calculate the change in entropy in the whole system after the opening of a valve. Assume that both water vapor and argon behave like ideal gases.

4. Calculate the molar entropy of neon (ideal monoatomic gas) at 500 K, if at 298 K and the same volume its entropy is equal to 146.2 J·mol^{-1} · K^{-1}.

5. Calculate ΔS of the process of a) isobaric, and b) isochoric heating up 10 g of N_2 from 0 °C until 100 °C. Assume that C_p of nitrogen (as a diatomic gas) is equal to 7R/2, and it is constant, while $C_V = 5R/2$.

6. Calculate ΔS of boiling of 1 mol of liquid ethyl chloride ($t_{boiling}$ = 12.3 °C), if the value of ΔH of heating is equal to 3765.6 J/g.

репозиторий БГМУ

7. Calculate the value of ΔS in the process of heating up 0.7 mol of monoclinic sulfur from 25 °C to 200 °C at the constant pressure of 1 atmosphere.

Molar heat capacity of monoclinic sulfur $C_p(S_{(s)}) = 23.64$ J/(mol · K).

Molar heat capacity of liquid sulfur is calculated with the help of the following formula: $C_p(S_{(l)}) = 35.73 + 1.17 \cdot 10^{-3}T$ J/(mol · K).

Melting point of sulfur is at 119 °C, ΔH of melting is 45.2 J/g.

8. Calculate the value of ΔS in the process of heating up 100 g of liquid water taken at 0 °C until 120 °C, at which it exists in the state of vapor. Heat capacity of liquid water is 4.19 J/(g · K), heat capacity of water vapor is 1.91 J/(g · K). The enthalpy of boiling for water is 2258 J/g at 100 °C.

9. Calculate the value of ΔS in the reaction between 1-butene and hydrogen, in which octane is formed: $2C_4H_8 + H_2 = C_8H_{18}$ at 700 K and atmospheric pressure. Use the following data for calculations.

Substances	C_4H_8	H_2	C_8H_{18}
S^0_{298}, J/(mol·K)	307.4	130.6	463.7
a, J/(mol·K)	2.54	27.28	6.91
$b \cdot 10^3$, J/(mol·K^2)	344.9	3.26	741.9
$c \cdot 10^6$, J/(mol·K^3)	–191.28	2.01	–397.3

репозиторий БГМУ

10. Calculate the value of ΔS in the process of heating up 11.2 L of nitrogen (ideal gas) from the temperature of 0 °C until the temperature of 50 °C, if in the same time the pressure has been decreased from 1 atmosphere to 0.01 atmosphere.

11. Calculate the value of ΔS in the process of heating up 0.4 mol of sodium chloride from the temperature of 20 °C until the temperature of 850 °C. The molar heat capacity of solid sodium chloride depends on temperature according to the following equation: $C_p = 45.94 + 16.32 \cdot 10^{-3} \cdot T$. The molar capacity of liquid sodium chloride is constant and equal to 66.53 J/(mol·K). The temperature of melting of sodium chloride is 800°C, and ΔH of melting is 31.0 kJ/mol.

12. For gaseous benzene C_p depends on temperature according to the following equation $C_p = -8.10 + 112.78 \cdot 10^{-3} \cdot T - 71.31 \cdot 10^{-6} \cdot T^2$. Find the value of ΔS for 1 mole of benzene in the process of its isobaric heating up from the temperature of 300 K to the temperature of 1000 K.

13. Calculate the value of $\Delta G^0_{r\,298}$ for the reaction:
$4HCl_{(g)} + O_{2(g)} = 2H_2O_{(g)} + 2Cl_{2(g)}$.
Is it spontaneous at 298K and standard pressure?
Use the following data for calculations.

Substance	$\Delta H^0_{f\,298}$, kJ/mol	S^0_{298}, J/mol
$HCl_{(g)}$	–92.4	186.9
$O_{2(g)}$	0	205.2
$H_2O_{(g)}$	–242	188.9
$Cl_{2(g)}$	0	223.0

репозиторий БГМУ

14. Calculate the value of $\Delta G^0_{r\ 298}$ for the reaction of gaseous and liquid water formation from oxygen and hydrogen at 298 K.

Use the following data for calculations.

Substance	$H_2O_{(g)}$	$H_2O_{(l)}$	$H_{2(g)}$	$O_{2(g)}$
ΔH^0_{f298}, kJ/mol	–241.8	–285.6	0	0
ΔS^0_{298}, J/(mol·K)	188.5	69.8	130.6	205.0

15. Calculate ΔG^0_r at 25°C for a given chemical reaction:

$CO_{2(g)} + 4H_{2(g)} = CH_{4(g)} + 2H_2O_{(l)}$.

Use the following data for calculations.

Substance	$CO_{2(g)}$	$H_{2(g)}$	$CH_{4(g)}$	$H_2O_{(l)}$
ΔH^0_{f298}, kJ/mol	–393.5	0	–74.81	–285.8
ΔS^0_{298}, J/(mol·K)	213.7	130.7	186.3	69.91

Репозиторий БГМУ

CHAPTER 3
THERMODYNAMICS OF CHEMICAL EQUILIBRIUM

Main topics of the chapter:

1. *The conception of chemical equilibrium.*
2. *Chemical equilibrium from the point of view of kinetics.*
3. *Chemical potential.*
4. *Chemical equilibrium from the point of view of thermodynamics.*
5. *Equation of the isotherm of a chemical reaction.*
6. *Equations of the isobar and isochore of a chemical reaction.*

As we know from the second law of thermodynamics, each process can go on until the moment when an appropriate thermodynamic potential stops its decrease. In other words, when the amount of free energy in a system reaches its minimal possible value, chemical equilibrium establishes in that system. All the spontaneous processes lead to the decrease of the free energy (an appropriate thermodynamic potential) in a given system.

From the point of view of kinetics, a reversible process is a process that doesn't go up to the completion. If we conduct a reversible reaction in a closed container, then after some period of time a chemical equilibrium between reactants and products will be established. Both reactants and products co-exist in the same container in the state of chemical equilibrium. Chemical equilibrium is usually described as dynamic equilibrium. Indeed, both forward and backward reactions proceed in such state, but the rate of the forward reaction is exactly the same as the rate of the backward reaction. Because of this, equivalence concentrations of all the substances stay the same. However, if we change any external parameter or a concentration of one of the reactants or products in a system, the rate of one of the processes may become faster than the rate of another process. This stress causes a shift in equilibrium. The rates of forward and backward reactions will become equal to each other again, but the concentrations of products and reactants will not be the same as before the stress.

Let us consider a schematic reaction between gases.

$aA + bB \leftrightarrow cC + dD$

The constant of equilibrium for this reaction should be written as follows, if we assume that this reaction is a one-step process (elementary reaction).

$K_{eq} = (C^c_C \cdot C^d_D) / (C^a_A \cdot C^b_B)$

The value of the constant of equilibrium depends on the properties of reactants and products, as well as on temperature, but it doesn't depend on concentrations of substances.

According to the law of mass action, the ratio between the multiple of concentrations of products (in certain powers) and the multiple of concentrations of reactants (in certain powers) is a constant value at a given temperature. If we deal with a reaction that is a one-step process, then the powers upon concentrations are equal to stoichiometric coefficients

репозиторий ВГМУ

from the equation of chemical reaction. If we deal with a multiple-step process, then each power must be determined experimentally (and it is usually not equal to the stoichiometric coefficient).

The rate of a forward reaction is equal to the product of a rate constant (k_f) and the multiple of concentrations of all the reactants in certain powers.

$r_f = k_f \cdot C^a{}_A \cdot C^b{}_B$

The rate of the backward reaction is equal to the product of a rate constant (k_b) and the multiple of concentrations of all the products in certain powers.

$r_b = k_b \cdot C^c{}_C \cdot C^d{}_D$

Rate constants for forward and backward reactions are rarely equal to each other. In the state of chemical equilibrium the rates of forward and backward reactions are equal to each other. So, we can write the following equation.

$k_f \cdot C^a{}_A \cdot C^b{}_B = k_b \cdot C^c{}_C \cdot C^d{}_D$

Then we can divide both part of that equation by K_b and $C^a{}_A \cdot C^b{}_B$. As you can see, the resulting equation is nothing but the equation for the constant of equilibrium.

$k_f/k_b = (C^c{}_C \cdot C^d{}_D) / (C^a{}_A \cdot C^b{}_B) = K_{eq}$

So, the constant of equilibrium is a ratio between the rate constant for the forward reaction and the rate constant for the backward reaction.

The value of the constant of equilibrium shows how “deep” is the process. If K_{eq} has a big value, then the forward reaction proceeds almost to the completion and the amounts of reactants at the equilibrium are low. If K_{eq} has a low value, then the amounts of products are close to zero. However, we cannot ignore many processes with very law values of K_{eq} like electrolytic dissociation of weak electrolytes, dissolving of hardly soluble salts, decomposition of stable complex compounds.

The constant of equilibrium for reactions between gases can be calculated both from concentrations of gases and from their partial pressures. It is important to say that the constant of equilibrium calculated from concentrations (K_C) is not equal to the constant of equilibrium calculated from partial pressures (K_p). We can derive the equation connecting K_p and K_C from the gas law.

from $pV = nRT$ and $C = n/V$

we can say that $C = p/(RT)$

and insert this ratio into the equation for K_C calculation.

$K_C = (C^c{}_C \cdot C^d{}_D) / (C^a{}_A \cdot C^b{}_B) = (p^c{}_C \cdot p^d{}_D) / (p^a{}_A \cdot p^b{}_B) \cdot (RT^{a+b}) / (RT^{c+d})$

$K_C = K_p \cdot RT^{a+b-c-d}$

In case if we deal with a one-step reaction, the powers from the above written equation are equal to stoichiometric coefficients. It means that “a+b-c-d” is nothing but the difference between the number of moles of gases among reactants and the number of moles of gases among products (-Δn). So, finally we can write that:

$K_C = K_p \cdot (RT)^{-\Delta n}$ and $K_p = K_C \cdot (RT)^{\Delta n}$

репозиторий БГМУ

For one-step processes K_p is higher than K_C if the number of moles of gases is growing. If the number of moles of gases is decreasing in an elementary reaction, then we can be sure that K_C is higher than K_p.

For real processes in water solutions activities are used instead of concentrations in equations for the constant of equilibrium calculation. Activity (a) is a multiple of concentration (C) and the coefficient of activity (f_a) for a given ion. The coefficient of activity shows the fraction of active ions: its maximal value is 1. In the same manner, for real processes with gases fugacities are used instead of partial pressures.

To understand thermodynamics of chemical equilibrium one should be familiar with a term “chemical potential”. This thermodynamic potential is necessary to use when the amount of substance in a given open system is changing (because of addition or removal). The amount of substance can also be changed in a closed system because of the chemical reaction. It is clear that the increase or decrease of the amount of substance in a system leads to the change in its total free energy. So, we can introduce a new parameter that determines a change of a complete thermodynamic potential of a system in case of the increase of the amount of a given substance by 1 mole. All other parameters should be constant in this case, including concentrations of all other substances in a system. Since this situation is hard to imagine, there is another definition of chemical potential. We can say that a chemical potential is equal to the change in an appropriate thermodynamic potential of a system caused by a minimal increase in the amount of a certain substance if all other parameters are constant. Mathematically chemical potential of a substance “i” (μ_i) can be calculated in the following way in isobaric and isothermic conditions.

$(\partial G/\partial n_i)_{T,p,j\neq i} = \mu_i$

In other words, chemical potential in this case is a molar Gibbs energy.

The derivation of the equation describing the last definition of a chemical potential is based on the calculation of the complete differential of a parameter as a sum of all its partial differentials.

$dG = (\partial G/\partial p)_{T,n1,n2,\ldots nk} \cdot dp + (\partial G/\partial T)_{p,n1,n2,\ldots nk} \cdot dT + \sum(\partial G/\partial n_i)_{T,p,j\neq i} \cdot dn_i$

Complete differential of Gibbs energy is a sum of the partial differential of Gibbs energy per pressure at constant temperature and the content of a system, the partial differential of Gibbs energy per temperature at constant pressure and the content of a system, and the partial differentials of Gibbs energy per amounts of each component at constant temperature, pressure and amounts of all other components.

From the first and the second law of thermodynamics we know that:

$dG = Vdp - SdT$

From the above written equation we can get partial derivatives of Gibbs energy per pressure (at constant temperature and content of a system) and per temperature (at constant pressure and content of a system) and insert them in the equation for the complete differential of Gibbs energy calculation.

Репозиторий БГМУ

$(\partial G/\partial p)_{T,n1,n2,\ldots nk} = V$ and $(\partial G/\partial T)_{p,n1,n2,\ldots nk} = -S$

So, $dG = Vdp - SdT + \sum(\partial G/\partial n_i)_{T,p,j\neq i} \cdot dn_i$

and $dG = Vdp - SdT + \sum\mu_i \cdot dn_i$

In isobaric and isothermic conditions ($dp = 0$ and $dT = 0$) the differential of Gibbs energy depends only on the sum of multiples of chemical potentials and differentials of the amounts of each substance.

$dG = \sum\mu_i \cdot dn_i$

The integral form of the same equation is as follows.

$G = \sum n_i \cdot \mu_i$

Let us see what happens if we conduct a process at the constant temperature and content of a system, but the pressure is not constant.

$dG = Vdp$ and $\Delta G = \int_{p^0}^{p} Vdp$

From the gas law we know that $V = (RT)/p$ for 1 mole of an ideal gas. So, since R and T are constants, we can re-write the equation in the following way.

$\Delta G = RT \int_{p^0}^{p} dp/p = RT \cdot \ln(p/p^0)$

From the gas law ($pV = nRT$) we now can express pressure through the concentration ($C = n/V$) and modify the equation once again ($p = CRT$).

$\Delta G = RT \cdot \ln(CRT/C^0RT) = RT \cdot \ln(C/C^0)$

If the initial concentration (C^0) was 1 mol/L, the above written equation turns to the following form.

$\Delta G = RT \cdot \ln C$

Resulting expression can be used if the change in concentration occurred not because of the increase or decrease of pressure, but because of the increase or decrease of the amount of substance. If we accept this fact, we can write an equation for the calculation of a chemical potential for a substance at a given concentration.

$\Delta G = \mu_i - \mu^0_i$

$\mu_i = \mu^0_i + RT\ln C$

Indeed, μ^0_i is a standard chemical potential for 1 mole of a substance (in 1 litter), while $RT\ln C$ shows what happens with molar Gibbs energy when the concentration changes. If a concentration is higher than 1 mol/L, $\ln C$ has a positive value, and the total chemical potential is higher than μ^0_i. In contrast, if a concentration is lower than 1 mol/L, $\ln C$ has a negative value, and the total chemical potential is lower than μ^0_i.

Let us come back to the schematic chemical reaction at equilibrium and assume that in this state (in isothermic and isobaric conditions) the total Gibbs energy of reactants is equal to the total Gibbs energy of products, ΔG of the process is equal to 0.

$aA + bB \leftrightarrow cC + dD$

$G_A + G_B = G_C + G_D$

The last equation can be re-written with chemical potentials.

$a\mu_A + b\mu_B = c\mu_C + d\mu_D$

репозиторий БГМУ

Since chemical potential depends on concentration, we can continue re-writing of the same equation.

$a(\mu^0_A + RT\ln C_A) + b(\mu^0_B + RT\ln C_B) = c(\mu^0_C + RT\ln C_C) + d(\mu^0_D + RT\ln C_D)$

The next mathematical action is a regrouping: now chemical potentials multiplied by coefficients are in the left side, while logarithms of concentrations are in the right side.

$c\mu^0_C + d\mu^0_D - a\mu^0_A - b\mu^0_B = RT(-c\ln C_C - d\ln C_D + a\ln C_A + b\ln C_B)$

Then we should replace multiples of chemical potentials and stoichiometric coefficients by Gibbs energies. After that the left part of the equation will become nothing but the difference between total Gibbs energy of products and total Gibbs energy of reactants.

$(G^0_C + G^0_D) - (G^0_A + G^0_B) = -RT(\ln C^c_C + \ln C^d_D - \ln C^a_A - \ln C^b_B)$

$G^0_{products} - G^0_{reactants} = \Delta G^0 = -RT\ln[(C^c_C \cdot C^d_D)/(C^a_A \cdot C^b_B)]$

In the right side of the equation we can turn stoichiometric coefficients into the powers upon concentrations under the logarithms. Then we can move the whole expression in brackets under the logarithm.

As you remember, $(C^c_C \cdot C^d_D)/(C^a_A \cdot C^b_B) = K_{eq}$

So, the final expression about the connection between the equilibrium constant and the difference of Gibbs energy in the reaction is as follows.

$\Delta G^0 = -RT\ln K_{eq}$

It is important to state that ΔG^0 from the last equation is not equal to the ΔG^0_r calculated as the difference between the sum of ΔG^0_f values for products and the sum of ΔG^0_f values for reactants. Indeed, ΔG^0_f is the change of Gibbs energy on the way from reactants to products (when reactants are converted to products completely). In contrast, ΔG^0 is the change of Gibbs energy on the way from a system containing just reactants to a system at equilibrium between reactants and products (when reactants cannot be converted to products spontaneously anymore).

Let us derive the equation of the isotherm of chemical reaction. That equation shows the dependence between the actual concentrations of reactants and products and ΔG of the reaction. Once again we have to consider chemical potentials of all the substances participating in a reaction and their concentrations (not equilibrium concentrations, but actual concentrations). So, ΔG is a sum of chemical potentials for all substances. For 1 mole of each substance its chemical potential is equal to the sum of μ^0 and RTlnC. For a given number of moles we need to multiply μ by that number.

$\Delta G = \sum(n_i[\mu^0_i + RT\ln C_i]) = \sum n_i\mu^0_i + \sum n_i RT\ln C_i = \sum n_i\mu^0_i + \sum RT\ln C_i^{ni}$

For a schematic chemical reaction aA + bB ↔ cC + dD the sum of logarithms of concentrations in powers equal to the numbers of moles is replaced by the expression: $(C^c_C \cdot C^d_D)/(C^a_A \cdot C^b_B)$.

$\Delta G = \sum n_i\mu^0_i + RT\ln(C^c_C \cdot C^d_D)/(C^a_A \cdot C^b_B)$

Репозиторий БГМУ

The expression $\sum \mu_i \cdot n_i$ is replaced by ΔG^0.

$\Delta G = \Delta G^0 + RT\ln[(C^c_C \cdot C^d_D)/(C^a_A \cdot C^b_B)]$

As we already found out, $\Delta G^0 = -RT\ln K_{eq}$, so we can continue the derivation.

$\Delta G = -RT\ln K_{eq} + RT\ln[(C^c_C \cdot C^d_D)/(C^a_A \cdot C^b_B)]$

$\Delta G = RT(\ln[(C^c_C \cdot C^d_D)/(C^a_A \cdot C^b_B)] - \ln K_{eq})$

The sense of the isotherm is easy to understand. If the amount of products is high enough, than the value of $(C^c_C \cdot C^d_D)/(C^a_A \cdot C^b_B)$ is higher than the value of K_{eq}. As a result, ΔG becomes positive and the forward reaction cannot be spontaneous anymore, unlike the backward reaction. If the amount of reactants is high enough, than the value of $(C^c_C \cdot C^d_D)/(C^a_A \cdot C^b_B)$ is lower than the value of K_{eq}. As a result, ΔG becomes negative and the forward reaction is spontaneous, while the backward reaction is nonspontaneous. It is clear that if $(C^c_C \cdot C^d_D)/(C^a_A \cdot C^b_B)$ is equal to K_{eq}, ΔG is equal to zero, and there is a chemical equilibrium in a system.

There is an interesting question from the thermodynamics of chemical equilibrium: why a process that has (in general) negative ΔG value doesn't go up to the completion? When we calculate ΔG^0_r we operate with just initial and final states of a closed system. However, during a chemical reaction the number of components in a system is usually higher than in the initial or in the final state. So, chemical potentials of reactants are decreasing with each run of that reaction, since their concentrations are going down (see this equation: $\mu_i = \mu^0_i + RT\ln C$). Chemical potentials of products are growing with each run of a reaction, while still their concentrations are low, the overall sum of chemical potentials for both reactants and products is decreasing (figure 2). Once the sum of chemical potentials of products becomes the same as the sum of chemical potentials for reactants, the equilibrium is established. At higher concentrations of products a backward process becomes spontaneous, while a forward process is already nonspontaneous.

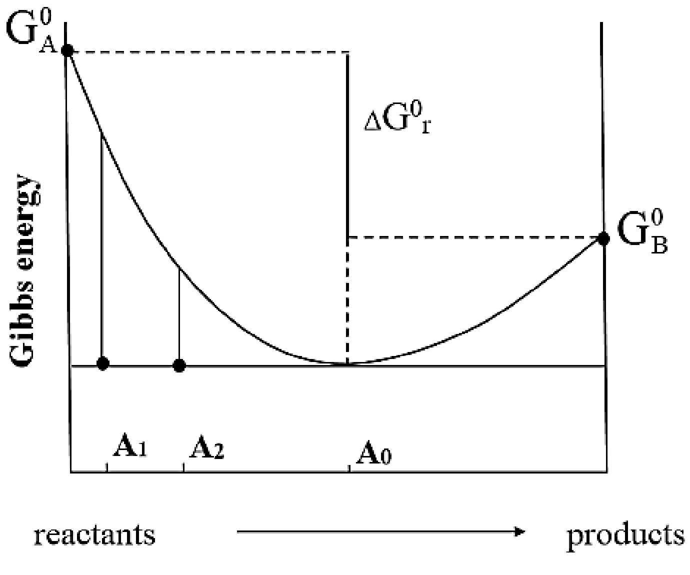


Figure 2. Dependence of Gibbs energy on the number of runs of a chemical reaction

Репозиторій БГМУ

Since chemical potential is a molar Gibbs energy in isobaric and isothermic conditions, it is built up from molar enthalpy and molar entropy. As you can understand, for ideal gases and solutions just molar entropy depends on concentration. That value includes not just an absolute molar entropy of a given substance, but also an entropy of mixing of a given substance with other components of the mixture. If we consider any chemical reaction, we must understand that on one hand it is a chemical process, but on the other hand it is a also a physical process of making a mixture between reactants and products. The entropy of mixing is always positive.

Imagine two gases separated by a partition. If we mix two gases together by the way of the removal of the partition, than each of them will occupy a new volume (V_2) instead of the initial one (V_1).

In isothermic conditions the increase in entropy of this process is calculated as follows.

$\Delta S = R\ln(V_2/V_1)$

Since $V = (RT)/p$ we can re-write the equation as:

$\Delta S = R\ln(p_1/p_2)$

We also know that $p = CRT$. It means that:

$\Delta S = R\ln(C_1/C_2) = -R\ln(C_2/C_1)$

If the initial concentration is exactly 1 mol/L, than ΔS of its mixing with another gas until a new concentration (C) is equal to $-R\ln C$.

Since the enthalpy of mixing of ideal gases is equal to zero, we can calculate the Gibbs energy of mixing for a given gas through the entropy of mixing.

$\Delta G_{mixing} = \Delta H_{mixing} - T \cdot \Delta S_{mixing} = -T \cdot \Delta S_{mixing} = RT\ln C$

So, in the equation for the chemical potential calculation ($\mu = \mu^0 + RT\ln C$) the second component ($RT\ln C$) is nothing but the entropy of mixing itself multiplied by absolute temperature.

The equation connecting Gibbs energy of a process and the constant of chemical equilibrium is widely used in molecular docking. So, you can use a special software to make thousand models of a ligand a receptor. That software is able to calculate ΔG of the formation of a complex from the sum of ΔH values for each new bond formation and each old bond destruction, as well as from the value of ΔS for a complex (it is calculated as a sum of bonds which lost their flexibilities due to the complex formation). Each software uses its own empiric coefficients to convert distances between atoms and angles between bonds into the values of energy. Finally, from the ΔG of the complex formation one can calculate K_{eq} of the complexation and the constant of inhibition (K_i). The last one is equal to the concentration of ligands when exactly one half of receptors are bound.

$\ln(K_{eq}) = -\Delta G^0 / (RT)$

$K_{eq} = e^{-\Delta G^0 / (RT)}$

$K_{eq} = C_{complex} / (C_{ligand} \cdot C_{receptor})$

$K_{eq} = 1 / C_i$ and $C_i = 1 / K_{eq}$

репозиторий ВГМУ

Using molecular docking one can check which ligand has the lowest constant of inhibition with a given receptor. Moreover, one can observe the most energetically favorable pose of a ligand on the receptor and suggest biochemical mechanisms of the receptor activation.

To derive an isobar of a chemical reaction we must write the equation $\Delta G^0 = -RT\ln K_p$ in the differential form and then divide both parts by dT.

$d\Delta G^0 = -R\ln K_p dT - RTd\ln K_p$

$(\partial \Delta G^0 / \partial T)_p = -R\ln K_p - RT(\partial \ln K_p / \partial T)_p$

Since we know that $(\partial \Delta G^0 / \partial T)_p = -\Delta S^0$, and, occasionally, $\Delta G^0 = -RT\ln K_p$, we can re-write the same equation with some familiar functions.

$-\Delta S^0 = \Delta G^0/T - RT(\partial \ln K_p / \partial T)_p$

Then we can multiply both part of the equation by T.

$RT^2(\partial \ln K_p / \partial T)_p = \Delta G^0 + T\Delta S^0 = \Delta H^0$

The final differential form of isobar is as follows.

$(\partial \ln K_p / \partial T)_p = \Delta H^0/(RT^2)$

The sign of a slope of the dependence of the natural logarithm of the constant of equilibrium on temperature is determined by the value of enthalpy of a given process. If the process is exothermic ($\Delta H^0 < 0$), the higher the temperature, the lower the constant of equilibrium: the higher the concentration of reactants in the mixture. If the process is endothermic ($\Delta H^0 > 0$), the higher the temperature, the higher the constant of equilibrium: the higher the concentration of products in the mixture. We can say that the isobar equation is a mathematical justification of the Le'Chatelier's law regarding the influence of the temperature on a system in equilibrium. The above written equation is also known as Van't Hoff's equation.

Isochore of a chemical reaction is derived from the same equation, but this time volume is constant, instead of pressure. So, the constant of equilibrium for isochoric process is connected with an appropriate thermodynamic potential that is called Helmholtz energy ($\Delta F = \Delta U - T\Delta S$).

$\Delta F^0 = -RT\ln K_V$

$d\Delta F^0 = -R\ln K_V dT - RTd\ln K_V$

$(\partial \Delta F^0 / \partial T)_V = -R\ln K_V - RT(\partial \ln K_V / \partial T)_V$

$-\Delta S^0 = \Delta F^0/T - RT(\partial \ln K_V / \partial T)_V$

$RT^2(\partial \ln K_V / \partial T)_V = \Delta F^0 + T\Delta S = \Delta U$

$(\partial \ln K_V / \partial T)_V = \Delta U^0/(RT^2)$

In isochoric conditions the sign of ΔU^0 of a process determines whether the constant of equilibrium will grow with the increase of temperature, or decline.

Let us come back to the isobar equation in the differential form and rewrite it in the integral form.

$(\partial \ln K_p / \partial T)_p = \Delta H^0/(RT^2)$

репозиторий БГМУ

If we are going to integrate above written equation from T_1 to T_2, and if we assume that the enthalpy doesn't depend on temperature, then it will look like that.

$${}_{T_1}^{T_2}\ (\partial \ln K_p/\partial T)_p = (\Delta H^0/R)\ {}_{T_1}^{T_2}\ (1/T^2)$$

$$\ln(K_2/K_1) = (\Delta H^0/R) \cdot (1/T_1 - 1/T_2)$$

According to the isobar equation in integral form, we can calculate a constant of chemical equilibrium at any temperature, if we now its value at another temperature. Also we can calculate a temperature at which the constant has a specific value. To make such calculations we need to know a value of ΔH^0. Moreover, if we know two values of the constant of equilibrium at two different temperatures, then we can calculate ΔH^0. However, two points are usually not enough to get a reliable value of ΔH^0.

One of the applications of the isobar equation is the calculation of the enthalpy of a structural shift, for example, for a peptide. On the graph with the dependence between such physical parameter as the intense of fluorescence and temperature (figure 3) we can see a plate. This almost horizontal line occurred because of a structural shift caused the increase of fluorescence (while, normally, fluorescence decreases with the growth of temperature). To calculate several values of the constant of equilibrium between initial and final forms of a peptide we need to continue two lines and find out the ratios between vertical lines, as it is shown in figure 3.

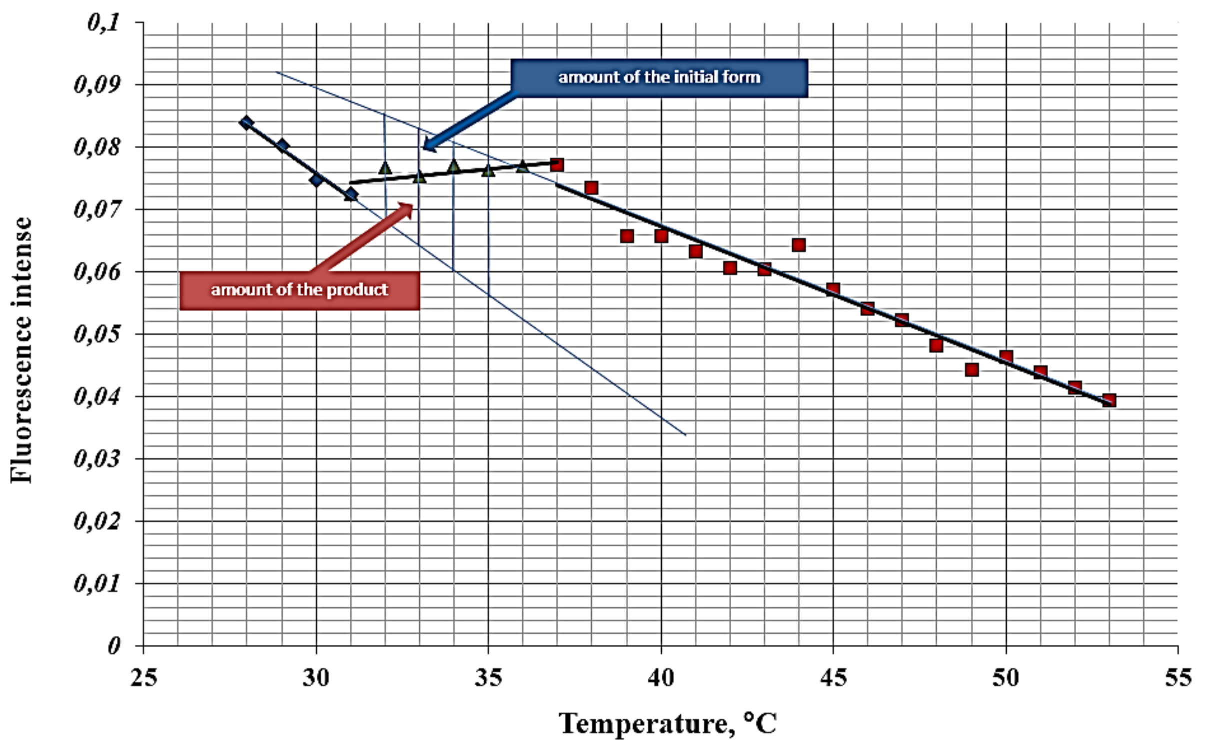


Figure 3. Dependence between the temperature and the fluorescence intense of tryptophan residue from the CC36 peptide

Then we must put a natural logarithm of those constants on the Y axis, and the value of "1/T" on the X axis (figure 4). That is how a Van't Hoff's plot looks like.

In the differential form of the isobar equation we can substitute ∂T by "$-\partial(1/T)\cdot T^2$" and get the equation describing the plot.

$(\partial \ln K_p/\partial T)_p = \Delta H^0/(RT^2)$ turns to

$-(\partial \ln K_p/(\partial(1/T)\cdot T^2))_p = \Delta H^0/(RT^2)$

After the multiplication by T^2 we got an equation describing the plot.

$(\partial \ln K_p/\partial(1/T))_p = -\Delta H^0/R$

So, the actual slope of the line in Figure 4 is equal to "$-\Delta H^0/R$". That is how we can measure a slope on the Van't Hoff's plot and get the value of ΔH^0.

We can also get the value of entropy (ΔS) from the same graph. If $\Delta G = \Delta H - T\Delta S$, and $\Delta G = -RT\ln K_{eq}$, then we can write that:

$RT\ln K_{eq} = -\Delta H + T\Delta S$

Then both parts of the equation should be divided by "RT".

$\ln K_{eq} = -\Delta H/RT + \Delta S/R$ and $\ln K_{eq} = (-\Delta H/R)\cdot(1/T) + \Delta S/R$

Now the equation has the same form as $y = kx + b$, in which y is $\ln K_{eq}$, k is "$-\Delta H/R$", x is "$1/T$", and b is "$\Delta S/R$".

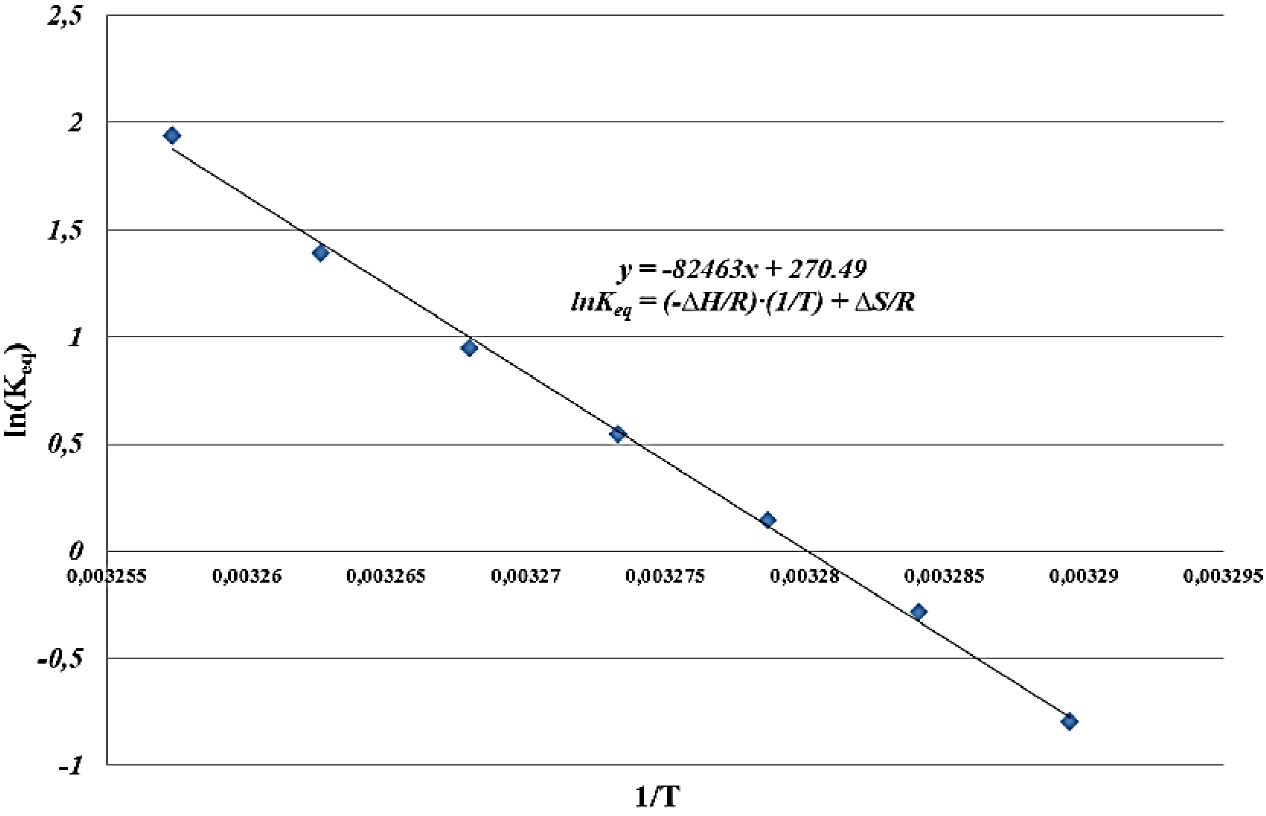


Figure 4. Vant' Hoff's plot (isobar) for the structural shift of the CC36 peptide

In the concrete case described here ΔH was equal to 685.266 kJ/mol, while ΔS was equal to 2.247 kJ/mol. Such a high value of enthalpy is an evidence that the process we observed was a dissociation of an oligomer of a peptide associated with the destruction of numerous intermolecular bonds and the increase of entropy in a system.

When we know the dependences of logarithms of constants of equilibrium for two reactions ($\ln K_1$ and $\ln K_2$), then we can calculate the dependence of the logarithm of the constant of equilibrium for a third reaction that is a sum two previous reactions. To make this action one should make a sum of $\ln K_1$ and $\ln K_2$.

Typical tasks

1. Calculate the constant of equilibrium for the following reaction at 298 K:

$NO_{2(g)} + NO_{2(g)} = N_2O_{4(g)}$

We know that ΔG^0_f (NO_2) = 51.84 kJ/mol and ΔG^0_f (N_2O_4) = 104.2 kJ/mol at the temperature of 298 K.

2. Calculate the constant of equilibrium for the following reaction at 500 K:

$CO_{(g)} + 2H_{2(g)} = CH_3OH_{(g)}$.

ΔG^0_f for $CO_{(g)}$ and $CH_3OH_{(g)}$ at 500 K are equal to: –155.4 and –134.2 kJ/mol, respectively.

3. Calculate the constant of equilibrium for the following reaction at 298 K:

$CH_3OH_{(g)} = HCHO_{(g)} + H_{2(g)}$

We know the following data:

$\Delta H^0_{f\,298}(CH_3OH) = -201.2$ kJ/mol; S^0_{298} (CH_3OH) = 239.0 J/(K·mol).

$\Delta H^0_{f\,298}(HCHO) = -115.0$ kJ/mol; S^0_{298} (HCHO) = 218.8 J/(K·mol).

$\Delta H^0_{f\,298}(H_2) = 0$ kJ/mol; S^0_{298} (H_2) = 130.6 J/(K·mol).

4. Calculate the constant of equilibrium for the following reaction at 298 K:

$CO_{(g)} + 2H_{2(g)} = CH_3OH_{(g)}$

We know the following data:

$\Delta H^0_{f\,298}(CH_3OH) = -201.2$ kJ/mol; S^0_{298} (CH_3OH) = 239.0 J/(K·mol).

Репозиторий БГМУ

$\Delta H^0_{f\,298}(CO) = –105.6$ kJ/mol; $S^0_{298}(CO) = 198.2$ J/(K·mol).
$\Delta H^0_{f\,298}(H_2) = 0$ kJ/mol; $S^0_{298}(H_2) = 130.6$ J/(K·mol).

5. For the reaction $C_2H_{4(g)} + H_{2(g)} = C_2H_{6(g)}$ at 873 K the value of $K_p = 2.864 \cdot 10^{-4}$. Determine the direction of the process at the following partial pressures of reactants and products:

for ethylene $p = 4.56 \cdot 10^4$ Pa,
for hydrogen $p = 5.07 \cdot 10^4$ Pa,
for ethane $p = 5.07 \cdot 10^4$ Pa.

6. For the reaction $2Cl_{2(g)} + 2H_2O_{(g)} = 4HCl_{(g)} + O_{2(g)}$ at 1000 K the value of $K_p = 7.9$. Determine the direction of the process at the following numbers of moles of reactants and products:

$n(Cl_2) = 1$ mol, $n(H_2O) = 2$ mol, $n(HCl) = 1$ mol, $n(O_2) = 1$ mol.

7. Calculate the constant of equilibrium at 273 K for the following reaction:

$2NO_{(g)} + O_{2(g)} = 2NO_{2(g)}$.

We know that ΔH = 294.1 kJ at 273 K, while at T = 298 K the constant of equilibrium is equal to 450.

Репозиторий БГМУ

8. Calculate the constant of equilibrium at 700 K for the following reaction

$SO_{2\,(g)} + 1/2O_{2\,(g)} = SO_{3\,(g)}$

We know that at 500 K $K_p = 588.9$, and ΔH_r of that reaction is constant and equal to –99.48 kJ.

9. Calculate ΔH_r for the following reaction at constant pressure:

$2CO_{(g)} + O_{2(g)} = 2CO_{2(g)}$.

Assume that ΔH_r is constant at different temperatures. The constant of equilibrium at 2000 K is equal to $3.97 \cdot 10^{-1}$, while at 2500 K it is equal to $2{,}29 \cdot 10^{-5}$.

10. For the reaction $N_{2(g)} + 3H_{2(g)} = 2NH_{3(g)}$ at 298 K the value of K_p is $6.0 \cdot 10^5$, and $\Delta H^0_f\,(NH_3) = –46.1$ kJ/mol. Calculate the value of the constant of equilibrium at 500 K.

11. The dependences of logarithms of constants of equilibrium for two reactions are known.

$2H_{2(g)} + HCOOCH_{3(g)} = 2CH_3OH_{(g)}$, $\lg K_p = 3149/T – 5.43$

$CH_3OH_{(g)} + CO_{(g)} = HCOOCH_{3(g)}$, $\lg K_p = 1835/T – 6.61$

Calculate the value of ΔH^0_r for a reaction:

$CO_{(g)} + 2H_{2(g)} = CH_3OH_{(g)}$.

репозиторий БГМУ

CHAPTER 4

THERMODYNAMICS OF PHASE TRANSITIONS IN ONE-COMPONENT SYSTEMS

Main topics of the chapter:

1. *Classification of phase transitions.*
2. *The number of independent components.*
3. *The phase rule of Gibbs.*
4. *Clayperon-Clausius equation.*
5. *Phase diagram of water.*
6. *The usage of phase diagrams of one-component systems.*

Phase transition is a process in which a substance turns from one phase to another. Phase transition may be caused by the change in pressure, temperature or other external parameters. Phase transitions are classified into the transitions of the first order and transitions of the second order. We can say that transitions of the first order are "major" phase transitions like: melting and freezing; boiling and condensation; sublimation and desublimation; as well as evaporation. During those phase transitions of the first order extensive parameters are changing rapidly, the differences in them are big for a system before and after the transition. Of course, such transitions of the first order are associated with the absorption or release of a big amount of heat. In contrast, during a phase transition of the second order extensive parameters are not changing, but their first derivatives per temperature (like heat capacity: $C_V = (\partial U/\partial T)_V$) or per pressure are changing. One of the popular samples of phase transitions of the second order is a transition from ferromagnetic (when the piece of a metal has its own magnetic field) to paramagnetic (when the piece of a metal has no its own magnetic field but can acquire it in the presence of a magnet) occurring at a certain temperature.

Systems are classified into homogeneous and heterogeneous ones. In the homogeneous system there is just a single phase. In the heterogeneous system there are at least two phases. The definition of the term "phase" is as follows. Phase has identical physical and chemical properties throughout its volume. In the heterogeneous system each phase has its surface separating it from other phases. Remember that all the gases are mixable with each other at any proportion. So, there may be just one gas phase in any heterogeneous system. Liquids and solids may be completely mixable with each other (in this case they form the same phase) or partially mixable (in this case they can form either the same phase, or different phases). An equilibrium between different phases is known as heterogeneous equilibrium or phase equilibrium.

The components of a system are usually defined as substances which can be extracted from a system, exist on their own for a long period of time and make the same system once again. This strange (at the first look) definition has been developed to overcome some

Репозиторий БГМУ

difficulties with water solutions. For example, in water solution of NaCl there are hydrated Na^+ and Cl^- ions, free water molecules and H_3O^+ and $H_3O_2^-$ ions as well, while we should say that there are just two components of such system: water and sodium chloride.

The total number of components in a system may be higher than the number of independent components. When some components interact with each other and form other components, we can say that the concentration of one of the components can be expressed trough the concentration of another component and the respective equilibrium constant. In this case the number of independent components is less than the number of components, and the difference between them is equal to the number of equations connecting concentrations of different components.

From this point of view, we can create a system from the minimal number of components, and this number is the number of independent components. For example, we can make a three-component system made from H_2, I_2 and HI from just one independent component (HI). In this case concentrations of H_2 and I_2 will be equal to each other. Exact concentrations can be calculated from the value of the constant of equilibrium for $2HI \leftrightarrow H_2 + I_2$ reaction. We also can make a system containing H_2, I_2 and HI from two independent components (H_2 and I_2 in different concentrations), while the concentration of HI will be determined with the help of the constant of equilibrium.

The number of the degrees of freedom for a system is equal to the number of parameters that we can change independently (in certain diapasons) without any changes in the number and the nature of phases.

According to the Gibbs phase rule, the number of the degrees of freedom for a given system is equal to the difference between the number of the independent components and the number of phases plus the number of external parameters that can cause the change in the number and nature of phases. If we assume that just temperature and pressure are those meaningful external parameters, the rule is expressed by the following equation.

$N_{\text{(degrees of freedom)}} = N_{\text{(independent components)}} - N_{\text{(phases)}} + 2$

In internationally accepted symbols this equation is writtem as follows.

$F = C - P + 2$

If the number of components is equal to one, then the above written equation turns to the simplified form:

$F = 3 - P$

So, if deal with a monocomponent system with a single phase, then the number of the degrees of freedom is equal to two. If such system has two phases, then the number of the degrees of freedom is equal to one. If there are three phases in the same monocomponent system, then the number of the degrees of freedom is equal to zero.

In Figure 5 one can see a simplified phase diagram of water built in p-T coordinates (external pressure is on the Y-axis, temperature is on the X-axis). There are three areas in this diagram representing the parameters at which water exists as a gaseous (g), liquid (l)

Репозиторий БГМУ

and solid (s) substance. For example, at the temperature of 20 °C and the pressure of 1 atmosphere, water should be liquid (the point on the cross fold of 20 °C on X-axis and 1 atmosphere on Y-axis is situated inside the area “l” of the diagram). It means that in the closed container with a pure water (and no other substances) at the pressure of 1 atmosphere and the temperature of 20 °C all the water molecules exist in the liquid phase. If we independently change temperature and pressure (a little), the situation will not be changed. It means that inside each area on the phase diagram we have two degrees of freedom (F = 1 – 1 + 2 = 2). From our everyday’s life we know that at 20 °C water is really liquid. Since the nature is an open multycomponent system, at this temperature liquid water co-exists with its vapor, but the equilibrium of the evaporation/condensation process is shifted towards liquid water. The synonymous terms “evaporation” and “vaporization” are used for the process of liquid to gas transition occurring from the surface of a liquid at temperature that is lower than the boiling point at a given pressure. In contrast, boiling means the complete transition of liquid to gas at a certain temperature (boiling point) at the given pressure. Liquid boils when the pressure of its vapor is equal to the external pressure. During the process of boiling bubbles of gas are formed inside the liquid.

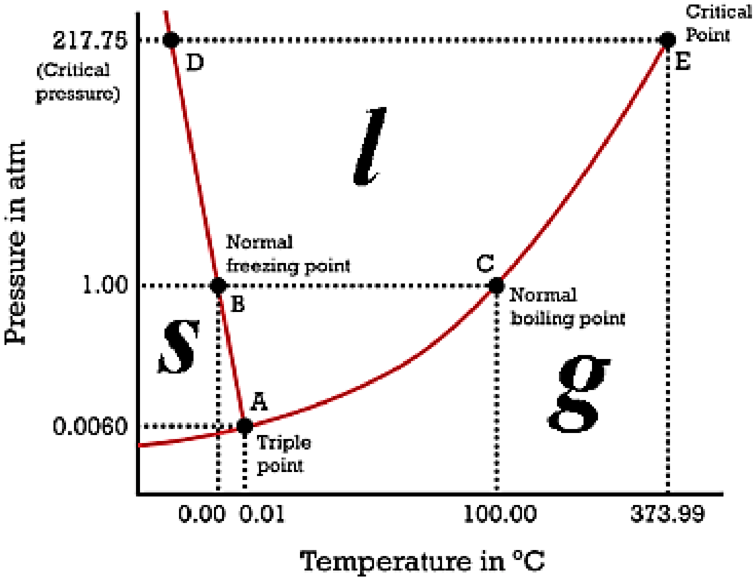


Figure 5. Schematic phase diagram of water

Also, from everyday’s life we know the ice cannot exist at 20 °C and the pressure of 1 atmosphere in nature for a long period of time: even though not immediately, but it is melting away.

There are three lines in the simplified water phase diagram. Those lines separate three areas. There is a vaporization (evaporation) curve (see the line AE in the figure 5) between the area of a gas water existence and the area of a liquid water existence that can also be called (more logically) a boiling curve. This line shows the dependence between the external pressure at which the vapor condensates and the temperature. In the closed system containing just water, vapor can co-exist with liquid water only if the values of pressure (external pressure) and temperature are situated on the vaporization curve. To keep two phases in the system one can randomly change just pressure, or just temperature. In both cases the second parameter must be changed non-randomly to keep the dot on the same curve. It means that when two phases co-exist together, there is just one degree of freedom ($F = 1 – 2 + 2 = 1$).

Since a liquid boils when the pressure of its vapor is equal to external pressure, the vaporization curve is really a curve of the dependence between the vapor pressure and the temperature. So, we can say that the Y-axis for vaporization curve combines both external pressure and vapor pressure.

The line separating the area of gaseous water (vapor) existence and the area of the solid water (ice) existence is called a sublimation curve. That curve reflects the dependence of the external pressure at which the vapor sublimates on the temperature. In the same time, sublimation curve is nothing but the dependence between the vapor pressure upon a solid substance and temperature. So, for sublimation curve we also have both external pressure and vapor pressure on the Y-axis.

The line separating the area of the liquid water existence and the area of the solid water existence is know as the melting curve (see the line AD in the figure 5). That curve shows the dependence of the melting point (the temperature at which the ice is melting) on the external pressure. It is known that a solid substance melts when the vapor pressure upon it is the same as the vapor pressure upon a liquid.

In the middle of the diagram all the three curves meet each other in a single point (see the point A in the figure 5). That point is called the triple point. Only in the triple point all three phases (vapor, liquid and ice) can co-exist in the state of equilibrium in the closed monocomponent system. Notice that triple point has two certain coordinates on the p-T diagram of water: 0.06 atmospheres of pressure (very low external pressure) and 0.01 °C. Of course, the number of degrees of freedom for a system in a triple point is equal to 0 ($F = 1 – 3 + 2 = 0$).

The curves on each phase diagram contain a lot of useful information about thermodynamic parameters describing each phase transition. With the help of Clayperon-Clausius equation we can describe those curves and calculate the missing parameters.

Each phase transition is an isobaric and isothermic process. In the state of equilibrium between two phases chemical potentials of a substance in two phases are identical. In those conditions chemical potentials are molar Gibbs energies. So, we can start from the following equation in which we deal with molar Gibbs energy, molar volume and molar entropy for a substance in two phases.

$$dG_{m1}=V_{m1}dp – S_{m1}dT$$

$$dG_{m2}=V_{m2}dp – S_{m2}dT$$

$$dG_{m1} = dG_{m2} \quad \text{and} \quad V_{m1}dp – S_{m1}dT = V_{m2}dp – S_{m2}dT$$

Then we can rearrange the equation.

$$(S_{m2} – S_{m1})dT = (V_{m2} – V_{m1})dp$$

After that we can express the value of a derivative of pressure per temperature for a phase transition as the ratio between ΔS of phase transition and the difference in molar volume (ΔV_m).

$dp/dT = \Delta S_{\text{phase transition}} / \Delta V_{\text{m phase transition}}$

For a phase transition (as for thermodynamically reversible isothermic process) ΔS is equal to ΔH/T. So, we can replace the entropy in the above written equation by enthalpy divided by temperature.

$dp/dT = \Delta H_{\text{phase transition}} / (T \cdot \Delta V_{\text{m phase transition}})$

Since the value of ΔH for such processes as sublimation and boiling is always positive (those processes are endothermic), and the molar volume of a gas is always higher than the molar volume of a solid or liquid substance, the value of dp/dT is always positive for sublimation and vaporization curves. It means that those curves have positive slopes (they are “going up”) on phase diagrams. If we assume that a vapor behaves as an ideal gas, we can express a molar volume of a gas through its temperature and pressure.

$pV = nRT$ and $V_m = V/n = (RT)/p$

The last expression is inserted in the Clayperon-Clausius equation instead of ΔV_m. This action is possible if we assume that the molar volume of a gas is much higher than the molar volume of a liquid. In this case ΔV_m is approximately equal to the molar volume of a gas.

$Dp / dT = \Delta H / [T \cdot (RT / p)] = (\Delta H \cdot p) / (RT^2)$

Then we can remove the pressure from the left part of the equation.

$Dp / (pdT) = \Delta H / (RT^2)$

Since we know that dp/p = dlnp, we can obtain the most simple form a differential form of the Clayperon-Clausius equation for vaporization curve.

$Dlnp / dT = \Delta H / (RT^2)$

ΔH of vaporization is decreasing with the growth of temperature. At a certain temperature known as critical temperature ΔH of vaporization turns to zero. Actually, we cannot continue the vaporization curve after that critical point, because vapor becomes undistinguishable from liquid in those conditions. For water the coordinates of the critical point are at 218 atmospheres of pressure (at very high pressure) and 374 °C.

One can notice that the derivative of either p per T, or lnp per T is becoming lower with the growth of temperature (since the higher the temperature, the higher the value of T^2, and the lower the value of ΔH). Because of this reason if you move from left to right on the phase diagram, the curve of vaporization should has become less steep (but it really doesn’t).

Indeed, if we use the realistic phase diagram (figure 6), then we will be able to observe that the boiling curve is becoming steeper at higher temperatures. It means that the boiling curve behaves in the different way than it is predicted by the Clayperon-Clausius equation. It happens mostly because thermodynamic derivation of the equation is based on

Репозиторий БГМУ

the assumption that the boiling process is thermodynamically reversible, and that the vapor is an ideal gas. Anyway, we can use the Clayperon-Clausius equation at relatively low temperatures and pressures.

In the narrow range of temperatures we can use an integral form of the same equation, assuming that ΔH of vaporization is constant.

$$\int_{T_1}^{T_2} d\ln p/dT = (\Delta H/R) \int_{T_1}^{T_2} (1/T^2)$$

Integration leads to the following equation, in which two values of pressure correspond to two temperatures of boiling.

$$\ln(p_2/p_1) = (\Delta H/R) \cdot (1/T_1 - 1/T_2)$$

If we know ΔH of boiling and the temperature at which water boils at a certain external pressure, we can calculate the temperature at which it will boil in case of a small change in pressure (or what external pressure should we apply to make it boil at a different temperature).

The melting curve is usually represented by a straight line. Indeed, the difference in molar volume between solid and liquid phase doesn't show a strong dependence on temperature. The direction of the melting curve is determined by the actual sign of ΔV_m.

$$dp/dT \approx \Delta p/\Delta T \approx \Delta H_{melting} / (T \cdot \Delta V_{m\ melting})$$

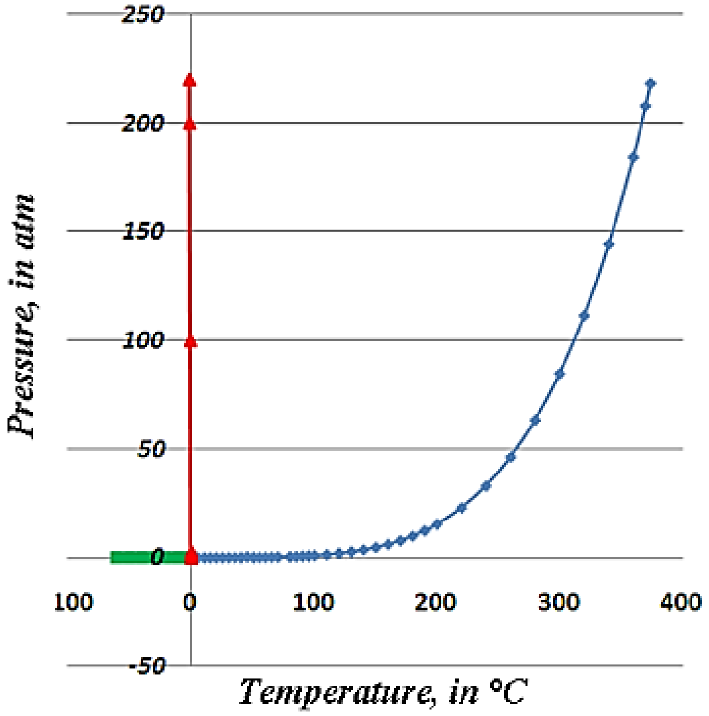


Figure 6. Realistic phase diagram of water

If the molar volume of a liquid is higher than the molar volume of a solid, then the higher the temperature, the higher the pressure at which melting occurs. For water (in contrast to the most of substances), the molar volume of liquid is lower than the molar volume of solid. Because of this reason, the slope of the melting curve is negative:

the higher the temperature, the lower the pressure at which water is melting. However, this dependence is not very noticeable. The increase in pressure equal to 1 atmosphere makes the temperature of water melting just 0.0075 K lower. In the realistic water phase diagram the melting curve is almost perpendicular to the X-axis (figure 6).

Using the phase diagram one can determine which state is thermodynamically favorable for a given substance at certain temperature and pressure. Once again, notice that this diagram works well for one-component closed systems only. Even for water there are some deviations from the behavior represented on the phase diagram. For example, pure water can be overcooled down to –48 °C at atmospheric pressure, and it will not turn to ice, until the starting point for nucleation will be provided. At the temperature lower than –48 °C nucleation points are formed spontaneously. Also, on the real phase diagram of water one can find several polymorphic modifications of ice. It means that there are several triple points on the diagram.

On the phase diagram of carbon (figure 7) one can find the same areas of vapor, liquid and solid phase existence. The area of the solid phase existence is divided into several parts. The highest part belongs to the area of the existence of diamonds (at high pressure). The lower part belongs to the area of the existence of graphite (at low pressure). Notice that the pressure is given in GPa and not in atmospheres. According to that diagram carbon must exist just in the form of graphite at atmospheric pressure and room temperature. However, diamonds do exist in normal conditions and they are not turning into graphite with the course of time. There are so-called kinetic restrictions for some processes like diamond to graphite transition that must be spontaneous from the point of view of thermodynamics. So, the phase diagram of carbon represents well the consequences of the increase in pressure, but not the consequences of its decrease.

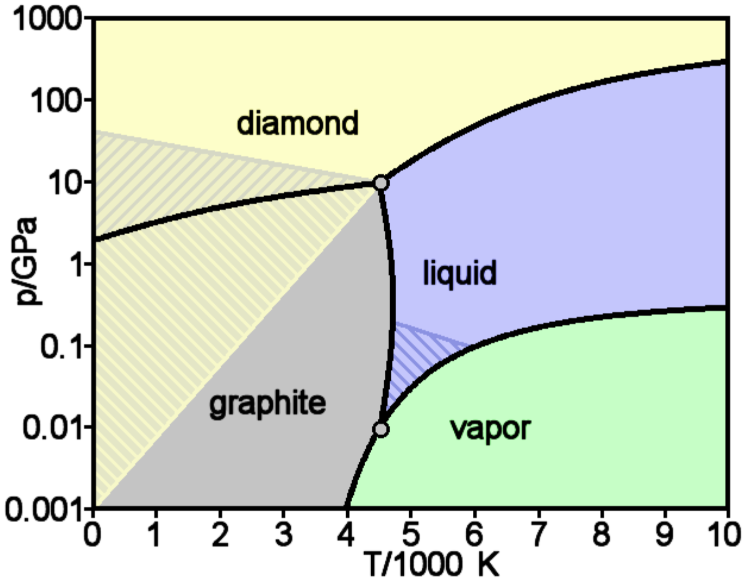
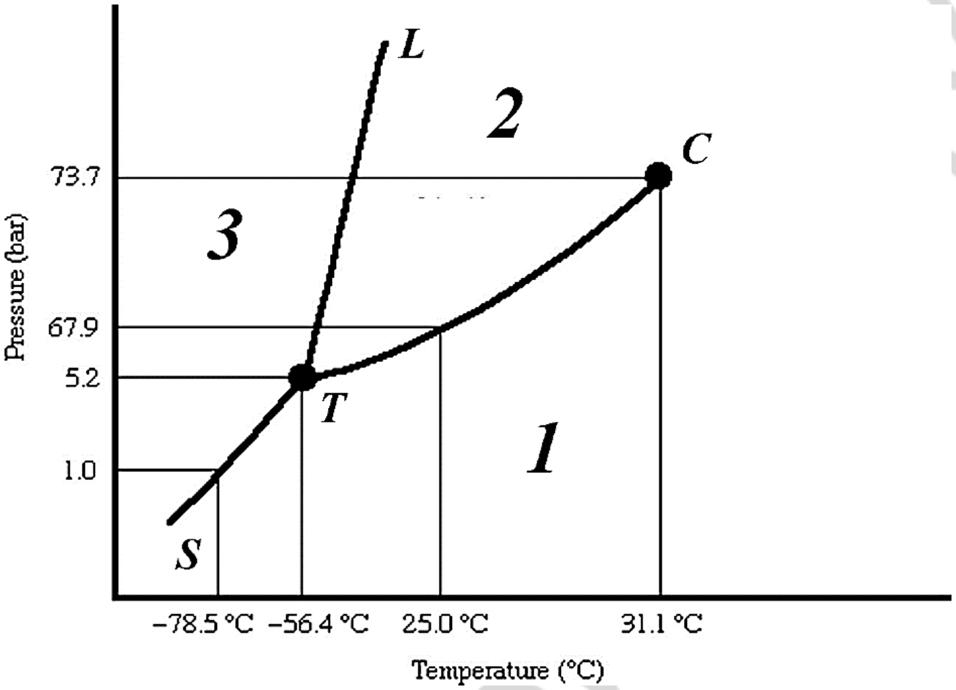


Figure 7. Phase diagram of carbon

Репозиторій ВГМУ

Typical tasks

1. Analyze the phase diagram for one-component system (CO_2). Give the names for all the lines and points, write the number and the nature of phases and the number of the degrees of freedom for all lines, points and areas.



Area 1: ____

____

Area 2: ____

____

Area 3: ____

____

Line TC: ____

____

Line TL: ____

____

Line TS: ____

____

Point T: ____

____

Point C: ____

____

Репозитор

CHAPTER 5
PHASE EQUILIBRIUM IN TWO-COMPONENT SYSTEMS

The main topics of the chapter:

1. *Description of two-component systems.*
2. *T-X melting phase diagrams for two-component systems.*
3. *p-X boiling phase diagrams for two-component systems.*
4. *T-X boiling phase diagrams for two-components systems.*
5. *Principles of distillation and rectification.*
6. *Miscibility gaps on T-X phase diagrams for two liquids.*

Phase equilibrium is a condition that is reached in case if temperatures, pressures and chemical potentials of two phases are identical. In any one-component system the number and the nature of phases depends on two external parameters: temperature and pressure. In any two-component system there is an additional parameter that determines the number and the nature of phases (together with temperature and pressure). That parameter is the content of a system. Usually such parameter as mole fraction is used to describe the content of a system. However, one may use mass fraction, volume fraction or even molarity instead of mole fraction. Since we have three variables, phase diagram should be built in three-dimensional space (with X-axis, Y-axis, and Z-axis). It is not very easy to usage such 3D-diagram. Because of this reason, two types of 2D-diagrams are used: T-X diagram in which the pressure is constant, and p-X diagram in which the temperature is constant.

Each phase diagram represents either the process of melting (and freezing) of a two-component system (melting diagram), or the process of boiling (and condensation) of a two-component system (boiling diagram). Substances in solid and liquid phases may be either completely soluble, of partially soluble. If the levels of solubility are very low, we can assume that the substances are insoluble in each other. Moreover, some substances may react with each other at least in one of the phases. So, there many different types of phase diagrams for two-component systems. In this chapter we will describe just several types. For all of them the Gibbs phase rule is written in the following manner.

$F = C – P + 1$

Indeed, in isobaric conditions (for T-X diagram) there is just one external parameter (pressure), and in isothermic conditions (for p-X diagram) there is also just one external parameter (temperature).

The first type of a phase diagram for a two-component system is a melting T-X diagram for a system with substances that are completely soluble in liquid phase and insoluble in solid phase. To build such diagram one should perform a thermal analysis of pure components and different mixtures of two substances. Thermal analysis means that one has to either heat or cool a system and measure a certain parameter of that system over time. The simplest type of thermal analysis is based on the measurement of temperature over

Репозиторий ВГМУ

time. If we slowly heat up a closed system made from a pure solid substance, then first the temperature depends on time linearly, at a certain point in time temperature stops growing (this is called temperature arrest), and then it starts growing again but at a different slope than before. The temperature arrest corresponds to the process of melting: some amount of heat is absorbed by a system during the melting process, and the temperature of a system doesn't grow even though we heat it up. However, the process of freezing is monitored more frequently than the process of melting. In such case a closed system with a pure substance should be heated up until a certain temperature and then it should be cooled down under the control of thermometer. Typical cooling curves for pure substances are shown in figure 8, *a* (lines 1 and 5).

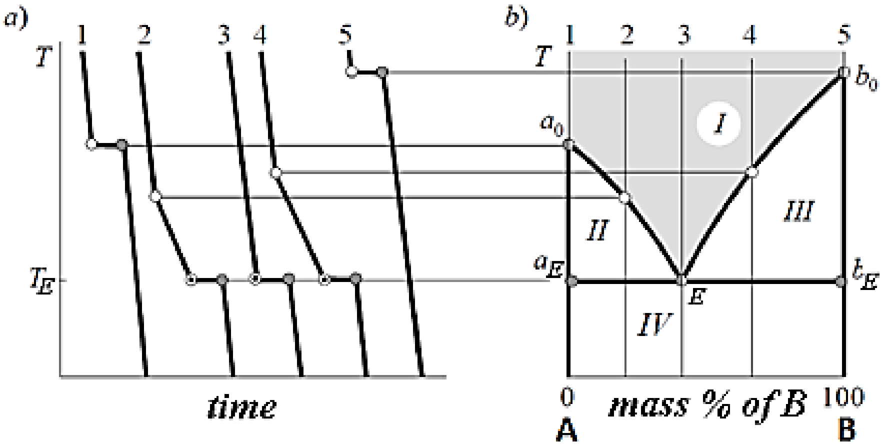


Figure 8. Cooling curves (*a*) and T-X melting phase diagram for a two-component system

As one can see in figure 8, there is a thermal arrest on the cooling curve of a pure substance. The thermal arrest starts in the point of the start of crystallization and ends in the point of the end of crystallization. Notice that these two points are always situated on the line that is parallel to the X-axis. In other words, the temperature of the start of crystallization is the same as the temperature of the end of crystallization for a pure substance. The slope of the cooling curve depends on the speed of the cooling process and the heat capacity of a substance. Heat capacities of the same substance in solid and liquid states are different, as well as the slopes of a cooling curve before and after the thermal arrest. The length of the thermal arrest depends on the speed of cooling. The temperature stops its decrease because a certain portion of heat is released during the process of crystallization. The linear shape of the thermal arrest may turn to a peak in case of the high (by module) value of $\Delta H_{freezing}$, slow speed of cooling and the overcooling of a sample. With the help of the described method one can determine the melting point for a pure substance. Usually the building of a phase diagram for two-component (binary) system starts from the determination of melting points for two pure components. These values are plotted as the leftmost (when the mole fraction of one of the components is equal to 0 %) and rightmost (when the mole fraction of the same component is equal to 100 %) points, as it is shown in figure 8, *b*.

Cooling curves for mixtures of two substances are different from those for pure substances. Indeed, in figure 8, *a* one can see that curves 2 and 4 have specific points at which the slope of the dependence between the temperature and time becomes lower. Such point is the point of the start of crystallization. Starting from this point, one of the components (component A for the curve 2, and component B for the curve 4) starts its crystallization. Because of this reason, releasing heat slows down the cooling process. The second component stays completely liquid until the start of the thermal arrest. The point of the start of crystallization of an eutectic mixture is situated in the beginning of the thermal arrest, and the point of the end of crystallization of an eutectic mixture is situated in the end of the thermal arrest. After that point both components are completely frozen. Notice that curve 3 for an eutectic mixture has the same shape as the curve for a pure substance, but the thermal arrest is situated at the lower temperature than freezing points for both pure substances. Actually, all the mixtures have the same temperature for the crystallization of an eutectic mixture, but different points of the start of crystallization. The points of the start of crystallization and the points at which eutectic mixture is crystallized are plotted on the phase diagram against the mole fraction of substance B (figure 8, *b*).

As a result, we can observe two lines of the phase diagram (figure 8, *b*). The upper one is called “liquidus” (see the line a_0Eb_0 in figure 8, *b*). This line connects the point of the start of crystallization for all the mixtures and for both pure substances. If we move from left to right, first liquidus goes down from the melting point of the substance A until the eutectic point, and then it grows up to the melting point of the substance B. This kind of shape can be explained with the help of a basic knowledge on the freezing point depression phenomenon. It is known that the higher the concentration of a substance in a solution, the lower the temperature of its freezing (i. e. the start of crystallization). This dependence is close to the linear dependence. However, this rule works for both the solution of substance B in substance A, and the solution of substance A in substance B. If we build two linear dependences of the freezing point depression on concentration for these two solutions on the same graph, they will obviously cross each other at a certain ratio between substance A and substance B. The point of their cross fold is the eutectic point. The slope of the dependence between the freezing point and the concentration depends on thermodynamical properties of a solvent (ΔH and T of melting) only, if a solution is ideal. For real solutions the nature of bonds between two substances should also be considered. So, the slopes of the descending and the ascending parts of liquidus are always different, and the eutectic point is never in the point of 1 : 1 molar ratio between substance A and substance B.

Solidus line (see the $a_0A_EEb_Eb_0$ line in figure 8, *b*) connects the points of the end of crystallization for all the mixtures and two pure substances. Solidus has three parts: it starts from the point of substance A crystallization, goes vertically down until the temperature of eutectic mixture crystallization, connects all the points of the end of eutectic mixture crystallization for mixtures (this part is a parallel line to the X-axis), and then goes vertically up to the point of substance B crystallization.

Liquidus and solidus lines break the phase diagram into four areas. The lowest area is an area of the existence of two unmixable solid substances. It means that two solid substances exist in their own crystals, but those crystals are mixed together. So, we should say that there are two solid phases in the discussed area of phase diagram from figure 8, *b*. Formally, the phase rule gives us one degree of freedom. Indeed, if we change the temperature (but doesn't reach the solidus line), there will be no effect on the amounts and nature of phases. In contrast, if we change the molar ratio between components, the amounts of phases become different. In the upper area of the phase diagram there is just a single phase, since both liquids are completely soluble in each other. The phase rule gives us two degrees of freedom inside that area, but anyway we have just one external parameter. The change in temperature has no effect on the content and nature of phases for a liquid mixture, if the temperature is higher than liquidus line. In the areas between liquidus and solidus we have two phases: the mixture of two liquids and crystals of one of the components. So, the number of the degrees of freedom in these areas is equal to one. The change in temperature cannot change the qualitative content of phases (there will be crystals of one the of the pure substance, and a liquid mixture of both substances), but it will change the quantitative content of phases (the higher the temperature, the lower the amount of crystals of one of the components, and the higher the mole fraction of that component in the liquid phase). On the solidus line we have and equilibrium between three phases: crystals of substance A, crystals of substance B, and the liquid made from both substances. On the liquidus line we have an equilibrium between two phases: crystals of one of the substances and the liquid made from both substances.

Let us consider the process of cooling down a liquid mixture with a high amount of substance A. First, a mixture will be cooled down without any changes in the number and the content of phases. When its temperature crosses the liquidus line, the changes are starting: the crystals of a pure component A are forming, while the mole fraction of a component A in the liquid phase is decreasing. For each point inside the area between liquidus and solidus we can build a parallel line to the X-axis (the node) and calculate the mole fraction of substance B in the liquid phase from the point of the cross fold between that line and liquidus. In other words, the content of a liquid phase is changing along the liquidus line. The content of a solid phase is represented by a solidus line (the same parallel line crosses solidus at the point of 0 % fraction of a component B). When the temperature crosses the solidus line, the mole fraction of component B in the liquid phases becomes equal to the one in the eutectic mixture. So, at that temperature substances A and B both turn to a solid eutectic mixture. At lower temperatures the content of a solid phase is the same as the overall content of a system. From this paragraph one can understand that the process of cooling down of a binary system with complete solubility in

Репозиторій ВНМУ

the liquid phase and insolubility in the solid phase can be used to purify one of the components. Phase diagram helps to conduct that kind of purification.

Eutectic mixture of two liquid substances freezes completely at a certain temperature. The nature of the eutectic mixture of solid substances is something to discuss. If we say that two substances are insoluble in each other in the solid phase, they are not forming any new substances or complex compounds in the eutectic solid state. They also cannot form the common crystal lattice (since they are insoluble in each other). However, in the eutectic state the seeds of each component are taking the lowest possible size, and different interactions (including hydrogen bonds formation) appear between those seeds. These specific interactions are responsible of the stoichiometry of eutectic mixture formation. For substances that are soluble in each other eutectic state in the solid phase is explained in easier way: the individual units (molecules, atoms or ions) form complexes with each other at certain stoichiometric ratios. Interestingly, for some mixtures there are numerous eutectic ratios (if they can form different complexes).

Now we can consider the process of heating up a mixture of two solids insoluble in each other. Until the temperature is below the solidus, there are no changes in the number and content of phases. At the point of the eutectic mixture crystallization substances A and B melt together and form an eutectic liquid. If the amount of substance A is higher in the whole system, than in the eutectic liquid, crystals of a pure substance A will co-exist with the eutectic liquid of both substances. The further increase in temperature leads to the partial melting of substance A and the enrichment of a liquid phase by that component. When the temperature crosses the liquidus line, substance A completely melts away and the content of a liquid phase becomes the same as the content of the whole system. The process of heating up can also be used with the aim to purify a portion of one of the substances in the form of solid.

The melting T-X diagram is useful for drug designers. Nowadays, almost each drug is really a mixture of different components. So, it is important to know the real melting point of such mixture. Another application is in the fact that two substances with close melting points form eutectic mixtures with the third substance at different temperatures. That is how one can indentify the substance using just thermal analysis.

Also with the phase diagram one can calculate the ratio between the quantity of solid and liquid phases using the rule of the lever. In figure 9 one can see that the figurative point is inside the area of co-existence of a solid substance B and a liquid mixture of substances A and B. We can build a node (a parallel line to the X-axis) through that point and measure the lengths of lines between the cross fold of the node and the liquidus and the figurative point (it represents the amount of a solid substance B), and between the figurative point and the cross fold of the node and the solidus (it represents the amount of a liquid phase). The ratio between the lengths of those lines is the same as the ratio between the amounts of solid and liquid phases, if we plot the mole fraction of substance B on the X-axis. If we plot

Репозиторий БГМУ

the mass fraction of substance B on the X-axis, the ratio between the lengths of the mentioned lines is the same as the ratio between the masses of solid and liquid phases. In general, the rule of the lever can be memorized as the vise versa relationship. The line that touches liquidus represents a solid phase, while the line that touches solidus represents a liquid phase.

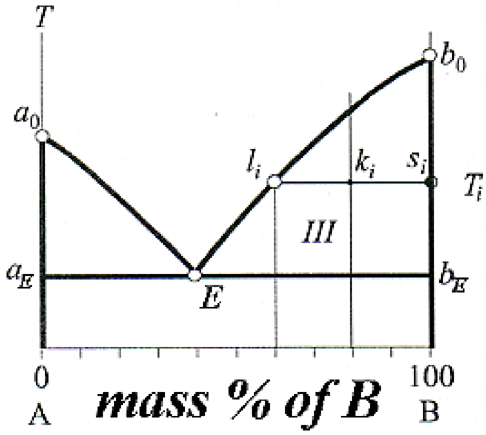


Figure 9. Phase diagram of a two-component system with the illustration of the lever rule

The next type of the phase diagram to describe is the p-X boiling diagram for binary system made from volatile components with the complete solubility in liquid phase (figure 10). First we consider that the mixture of two components in the liquid phase behaves as an ideal solution, while the mixture of vapors behaves as an ideal gas. On the X-axis of such phase diagram we should plot the mole fraction of substance B in the system. On the Y-axis we should plot the external pressure. There is an equilibrium between the process of vaporization and the process of condensation. At low external pressure both substances are gases, at high external pressure both substances are liquids. To understand what happens at average pressures we should review the Raoult’s law.

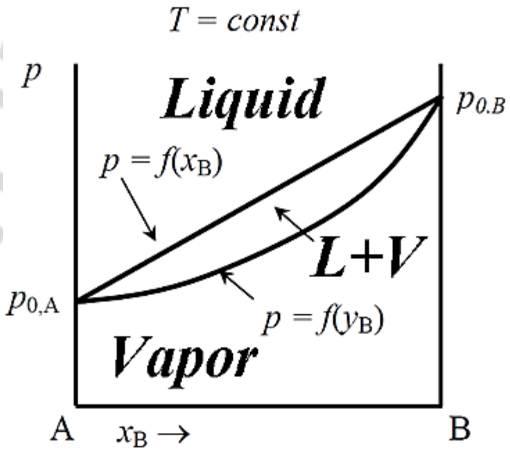


Figure 10. Schematic boiling p-X phase diagram of a two-component system

According to the Raoult’s law, the partial vapor pressure of a component of a mixture directly and linearly depends on its mole fraction in the liquid phase. The coefficient of

Репозиторий БГМУ

proportionality between partial vapor pressure (P) and the mole fraction in liquid phase (X) is nothing but the vapor pressure upon the pure liquid substance (P^0). This law works in the same manner for each component. In the binary system we can calculate the total vapor pressure as the sum of two partial vapor pressures. See the mathematical expressions below.

$P_A = P^0_A \cdot X_A$ and $P_B = P^0_B \cdot X_B$,

$P_{total} = P^0_A \cdot X_A + P^0_B \cdot X_B = P^0_B \cdot X_B + P^0_A \cdot (1 - X_B) = X_B \cdot (P^0_B - P^0_A) + P^0_A$

So, the dependence between the mole fraction of component B in the liquid phase and the total vapor pressure is really linear ($y = kx + b$). The slope is equal to the difference between the vapor pressure upon pure component B and the vapor pressure upon pure component A. The line starts from P^0_A and ends at the P^0_B. In other words, the higher the amount of more volatile component in the liquid phase, the higher the total vapor pressure upon the solution. Since liquid boils when the external pressure is equal to the vapor pressure, the straight line on the figure 10 is called the bubble curve. That curve shows the values of external pressure at which boiling starts (if we are decreasing the external pressure) for a mixture with a given mole fraction of a component B.

The mole fraction of a component B in the vapor is never equal to its mole fraction in the liquid phase. If we make some simple calculations, we will express the dependence between the mole fraction of a component B in the vapor (Y_B) and the total vapor pressure (P_{total}).

$P_A = P^0_A \cdot X_A$ and $P_B = P^0_B \cdot X_B$,

$Y_B = P_B / (P_A + P_B) = (P^0_B \cdot X_B) / P_{total}$

$P_{total} = (P^0_B \cdot X_B) / Y_B$

$P_{total} = X_B \cdot (P^0_B - P^0_A) + P^0_A$

$X_B = (P_{total} - P^0_A) / (P^0_B - P^0_A)$

$P_{total} = (P^0_B(P_{total} - P^0_A)) / (Y_B(P^0_B - P^0_A))$

$P_{total} \cdot Y_B(P^0_B - P^0_A) - P^0_B \cdot P_{total} = -P^0_B \cdot P^0_A$

$P_{total}(Y_B(P^0_B - P^0_A) - P^0_B) = -P^0_B \cdot P^0_A$

$P_{total} = (P^0_A \cdot P^0_B) / (P^0_B + Y_B(P^0_A - P^0_B))$

The last equation shows that the difference between P^0_A and P^0_B determines the direction of the curve: if P^0_B is higher than P^0_A, the curve is growing with the increase of Y_B. However, this dependence is not linear (see figure 10). If we plot the dependence of the total vapor pressure on the mole fraction of a substance B in liquid phase (a straight line), and the dependence of the vapor pressure on the mole fraction of a substance B in the vapor (a curve) on the same graph, the phase diagram will be completed. Notice that we have two variables (mole fraction of a substance B in liquid and in the vapor) on the same X-axis, and two variables (external pressure and vapor pressure) on the same Y-axis.

In the upper part of the phase diagram (figure 10) there is an area of liquid solution existence (at high pressure). In the lower part of the p-X phase diagram there is an area of the mixture of gases existence (at low pressure). In the middle of the diagram, between two

репозиторий БГМУ

lines, there is an area of co-existence for liquid and gaseous phases. If we increase the pressure for a certain mixture of two components, then at the point of the cross fold between the line parallel to the Y-axis and the curve of the dependence between the mole fraction of a component B in vapor and the pressure of the vapor, first drops of liquid will appear. Because of this reason, that (lower) curve is called the dew curve. With the increase of pressure the amount of liquid phase will grow. On the cross fold with the bubble curve all the vapor will turn to liquid. If a figurative point is situated between bubble and dew curves, we can draw a node using that point and find out the content of liquid phase (at the point of the cross fold between node and bubble curve) and gaseous phase (at the point of the cross fold between node and dew curve).

Phase p-X diagrams for real solutions can be divided into four groups. In figure 11, *a* one can see such diagram for a system with weak positive deviations from the behavior of ideal solutions. In figure 11, *b* one can see the diagram for a system with weak negative deviations from the behavior of ideal solutions. The bubble line is no longer a line, but a curve. The curve is concave downwards if the deviations are positive, but it is convex downwards if the deviations are negative.

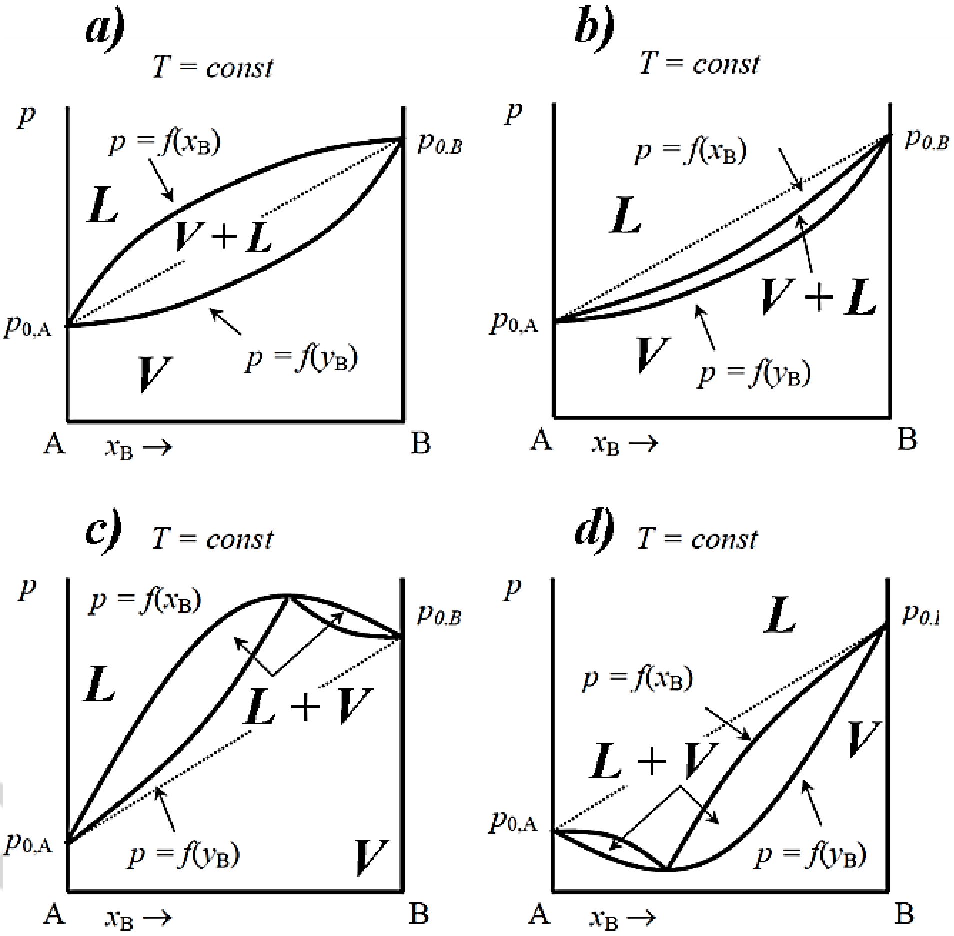


Figure 11. Schematic p-X boiling phase diagram for two-component systems with (*a*) weak positive deviations from Raoult's law; (*b*) weak negative deviations from Raoult's law; (*c*) strong positive deviations from Raoult's law; (*d*) strong negative deviations from Raoult's law

Positive deviations mean that the vapor pressure under the real solution is higher than if it was an ideal solution. That is why liquid mixture starts to boil at higher external pressure than it should (according to the Raoult's law). The physical cause of this deviation is in the fact that two substances are interacting with each other worse than they do with themselves. In other words, if the bonds (physical bonds) between molecules of two different liquid substances are weak, they are moving from liquid to vapor better than if those bonds are the same as between themselves. Notice that bubble line is concave downwards on the figure 11, *a*, while there are no points higher than the boiling point of the more volatile substance. The area of co-existence of liquid and gaseous phases is larger in figure 11, *a* than on figure 10.

Negative deviations mean that the vapor pressure under the real solution is lower than if it was an ideal solution. Mixtures with weak negative deviations from Raoult's law start to boil at the higher external pressure than it is expected according to the mentioned law. This kind of deviation happens if the physical bonds between molecules (or units) of two different substances are stronger than the bonds that exist between identical molecules (or units). In this case the molecules "prefer" to stay in the liquid state. The vapor pressure upon such solution is lower than for an ideal solution of the same content. As one can see if figure 11, *b*, the area of the co-existence of liquid and gaseous phases becomes smaller if the deviations from Raoult's law are negative but weak.

Strong deviations from Raoult's law lead to the appearance of peaks in phase diagrams. If there is a point on the bubble curve that is situated higher than the boiling point of the more volatile substance, then we deal with the phase p-X diagram with strong positive deviations from the behavior of an ideal solution. Actually, it means that a vapor will be especially hard to condensate at a certain ratio of components. Notice that the dew curve meets the bubble curve for such mixture (figure 11, *c*). The content of vapor produced due to the boiling of such mixture is exactly the same as the content of liquid that has been boiled. So, the mixture like this is called a constant boiling mixture, or "azeotrope". There is no area of co-existence of vapor and liquid for an azeotrope mixture, but just a single point.

If we deal with a system with strong negative deviations from Raoult's law, then we will observe an azeotrope mixture that has a boiling point at the pressure that is lower than that for the less volatile pure substance. At a certain molar ratio molecules of two substances make a "perfect" pattern of bonding with each other (once again, just physical bonds are discussed now). So, under such azeotrope the vapor pressure decreases largely.

Diagrams in p-X coordinates are not as useful as diagrams in T-X coordinates. Indeed, we may assume that the pressure is constant if we are heating up a mixture of liquids on the open air. If a substance demonstrates a higher vapor pressure, then it will boil at lower temperature than a substance with a lower vapor pressure. Indeed, more volatile substance requires the less increase in temperature to make its vapor pressure equal to 1 atmosphere (or another external pressure). In general, each T-X phase diagram is a mirror reflection of a corresponding p-X phase diagram in the up to down direction. However, that “mirror” is a little false. As you remember, the dependence between vapor pressure and temperature of boiling is direct, but it is not linear (see Chapter 4). For ideal solutions the curve of the dependence between vapor pressure and temperature at the boiling point is described by the Clayperon-Clausius equation. Such curve (for ideal solutions) must have a derivative that is decreasing with the growth of temperature. So, the bubble curve on the T-X diagram is convex downwards (figure 12). Notice that in these coordinates bubble curve is situated below dew curve (the last one is concave downwards). The sense of the T-X phase diagram is clear. If you know the temperature and the mole fraction of your mixture, then you can estimate the number and the nature of phases in a system. Notice that the area of the liquid mixture existence is situated in the lower part of the diagram, while the area of the mixture of vapor is situated in the upper part of the diagram. In the middle we can observe an area of co-existence for liquid and vapor phases.

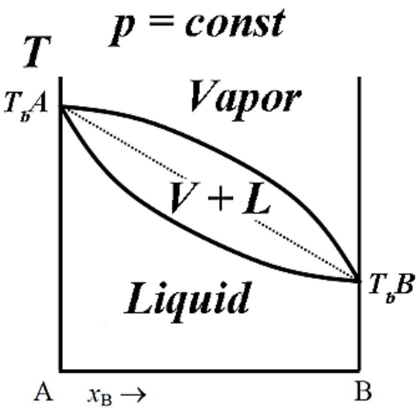


Figure 12. Schematic T-X boiling diagram for two-component system. Ideal solution

If a system demonstrates weak positive deviations from the Raoult’s law, the area of co-existence will be larger than in figure 12 (but bubble curve will not have any peaks). If the deviations are negative but weak, the area of co-existence will be smaller (but, again, without peaks).

T-X phase diagrams are useful for the explanation of the mechanism of distillation. If we heat up a mixture of two liquids with different boiling temperatures that demonstrates weak deviations from Raoult’s law, then at a certain temperature the boiling will start. In that moment the content of a vapor will be determined with the help of a node: one need to estimate a point at which it crosses a dew curve. Of course, a vapor will be enriched by a more volatile component. Then, with the growth of temperature, the content of liquid phase will be changing towards the increase of the content of a less volatile component (it will be changing along the bubble curve), as well as the content of a vapor (it will be changing along the dew curve). In the end (when the temperature is equal to the boiling point of less volatile component) we will obtain almost completely pure liquid of a less volatile component. However, we will not obtain a pure more volatile component. So, with the help of distillation we can purify just the less volatile component from the more volatile one.

With the aim to purify both components in the mixture of two liquid substances soluble in each other one can use a technique called fractional distillation. When the first portion of vapor is formed, it should be taken away from a system and cooled down with the aim to obtain a new liquid mixture with the increased fraction of a more volatile component. Then that new mixture must be boiled in its turn. The next portion of vapor will be enriched by a more volatile component to the higher extent then in the previous round. After several rounds an almost pure more volatile component will be obtained. One should not forget to cope with liquids left from each round of boiling. So, in general, the procedure fractional distillation is time consuming. The automatic procedure for the same kind of purification is called rectification.

In the process of rectification a vapor formed in the boiling process is going to the rectification column (figure 13). That column has numerous horizontal plates for condensation. In the middle of each plate there is a hole. So, a vapor (a mixture of two components) goes up until its temperature falls down and condensates on a plate. Then liquid flows down through the hole in the plate back into the initial boiling mixture. Only the most volatile vapor reaches the top of the rectification column and goes inside the next tube with a condenser (a vapor turns to almost pure liquid of a more volatile component inside the condenser). After all, only a less volatile component remains in the initial boiling liquid. A more volatile component will be finally collected in another flask connected to the condenser.

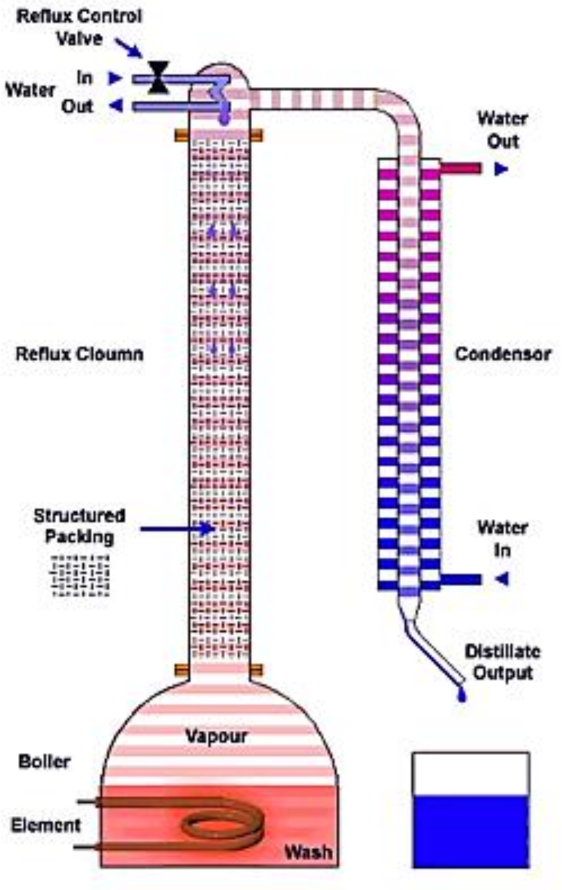


Figure 13. Scheme of the rectification column and the process of rectification

It is possible to purify both components of a mixture with the help of rectification only if the deviations from Raoult's law are weak. In case of strong positive deviations from the behavior of an ideal solution, there will be an azeotrope with the boiling point lower than that for a more volatile component (figure 14, *a*). In this case rectification will be finished at the point of separation between a pure less volatile component and an azeotrope, if the initial mixture contained a higher mole fraction of a less volatile component than that in the azeotrope. If the mole fraction of a less volatile component is higher than that in azeotrope, rectification will lead to the formation of a pure more volatile component and an azeotrope.

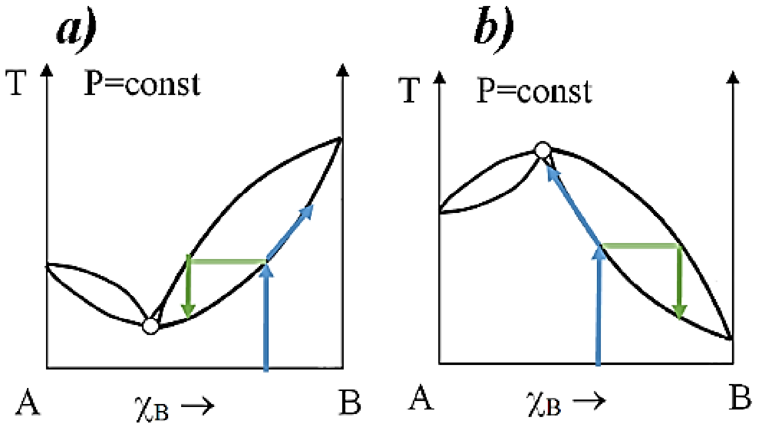


Figure 14. Schematic T-X boiling phase diagram for two-component system with (*a*) an azeotrope with low boiling point; (*b*) an azeotrope with high boiling point

If we deal with a system with strong negative deviations from Raoult's law, there will be an azeotrope with the higher boiling point than that for a less volatile component (figure 14, *b*). As in the previous case, it is possible to purify just one of the components by the way of rectification in a system represented in figure 14, *b*.

If two liquids are insoluble in each other, the Raoult's law doesn't work. The vapor pressure upon the mixture of two liquids insoluble in each other should be equal to the sum of their vapor pressures in the pure state. It means that the boiling temperature for a mixture of two insoluble liquids may be lower than that for each of the pure liquids. At a certain ratio between insoluble components the boiling temperature will reach its lowest point. This phenomenon is used in the process of distillation with water vapor for mixtures made from hydrophobic organic substances. As a result, organic components will not be decomposed at high temperature. However, there are no completely insoluble liquids. Some amount of a liquid can be dissolved in another liquid. At a higher mole fraction there will be a "cocktail" with two separate layers: a saturated solution of component A in component B, and a saturated solution of component B in component A.

If two liquids are just partially soluble in each other, there will be a miscibility gap on a phase diagram. The miscibility gap area is characterized by a presence of two separated liquids (two different phases). We can say that such phase diagram is a solubility diagram, since one can find exact temperatures and mole fractions of components at which the process of separation of two liquids takes place. There may be four different variants of the shape of the miscibility gap: with the lowest temperature of the unlimited solubility (figure 15, *a*); with the highest temperature of the unlimited solubility (figure 15, B); with both highest and lowest temperatures of the unlimited solubility (figure 15, *c*); and without highest and lowest temperatures of the unlimited solubility (figure 15, *d*). When there is just an upper point of the miscibility gap, it means that at high temperatures (lower than those at the boiling point) liquids are completely soluble in each other, while at lower temperatures they are insoluble in each other at average mole fractions.

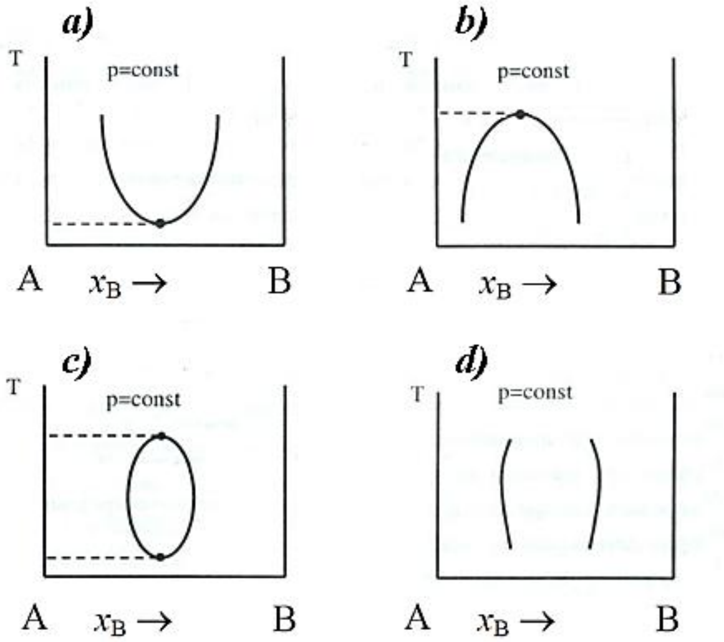
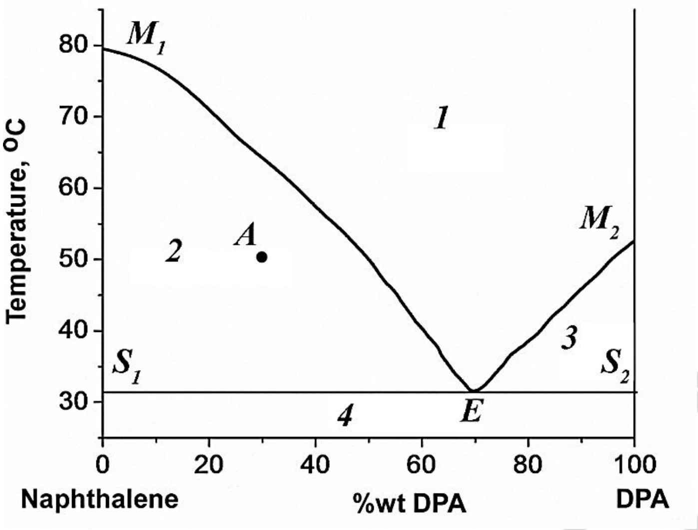


Figure 15. T-X miscibility phase diagram with (*a*) the lower point comlete miscibility; (*b*) higher point of complete miscibility; (*c*) with both higher and lower points opf complete miscibility; (*d*) without points pf complete miscibility

When there is just a lower point in the miscibility gap, then two liquids are completely soluble in each other at low temperatures (higher than those at the freezing point), but they are insoluble in each other at high temperatures. If there are both highest and lowest points on the miscibility gap area, then two liquids are not completely soluble in each other at some temperatures that are lying inside the interval between the boiling and the freezing points. For some mixtures there are no such points, and they boil and crystallize as two unmixable liquids at certain mole fractions.

Typical tasks

1. Analyze the melting phase diagram for two-component system (naphthalene and diphenylamine). Give the names for all the lines and points, write the number and the nature of phases and the number of the degrees of freedom for all lines, points and areas.



Area 1: ____

____

Area 2: ____

____

Area 3: ____

____

Area 4: ____

____

Line M_1E: ____

____

Line M_2E: ____

____

Line M_1S_1: ____

____

Line M_2S_2: ____

____

Line S_1E: ____

____

Line S_2E: ____

____

Point E: ____

____

Point M_1: ____

____

Point M_2: ____

____

Point S_1: ____

____

Репозиторий БГМУ

Point S_2: ____

____

Find the overall content of a system, the content of a solid phase and the content of a liquid phase for a figurative point A:

____

____

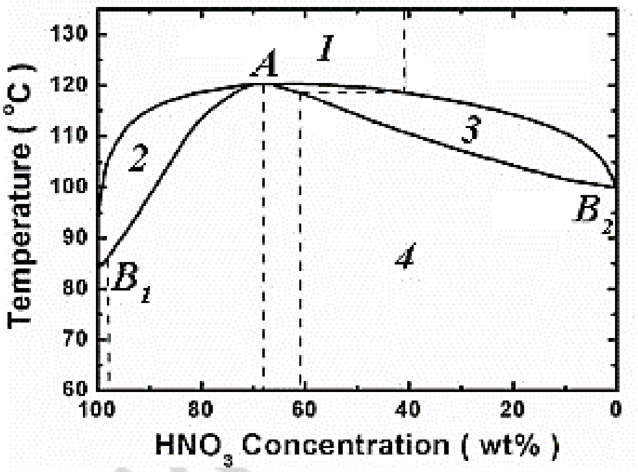
____

Find the ratio between the masses of a solid phase and a liquid phase for a system in the figurative point A:

____

____

2. Analyze the boiling T-X phase diagram for two-component system (water and nitric acid). Give the names for all the lines and points, write the number and the nature of phases and the number of the degrees of freedom for all lines, points and areas.



Area 1: ____

____

Area 2: ____

____

Area 3: ____

____

Area 4: ____

____

Line B_1A higher: ____

____

Line B_2A higher: ____

____

Line B_1A lower: ____

____

Репозиторий БГМУ

Line B_2A lower:

Point A:

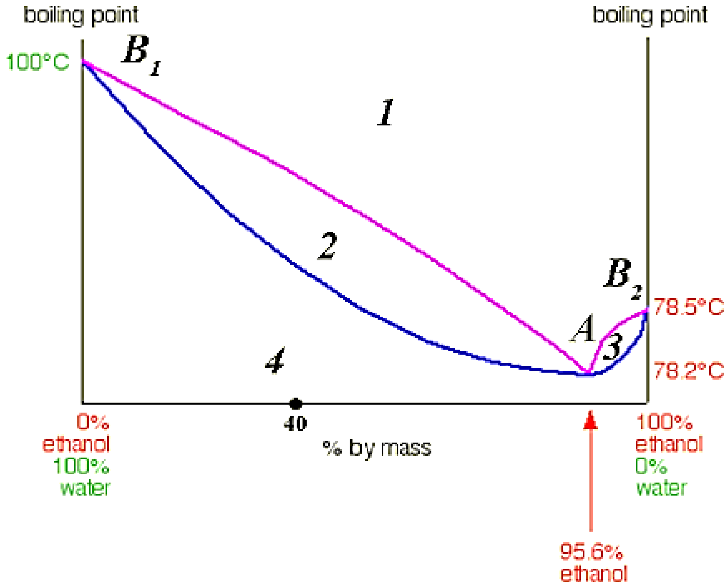
Point B_1:

Point B_2:

Find the mass composition of vapor if we boil the mixture with a mass percentage of HNO_3 equal to 61 %.

Describe the deviations from Raoult's law in the given system.

3. Analyze the boiling T-X phase diagram for two-component system (water and ethanol). Give the names for all the lines and points, write the number and the nature of phases and the number of the degrees of freedom for all lines, points and areas.



Area 1:

Area 2:

Area 3:

Area 4:

ре й БГМУ

Line B_1A higher:

Line B_2A higher:

Line B_1A lower:

Line B_2A lower:

Point A:

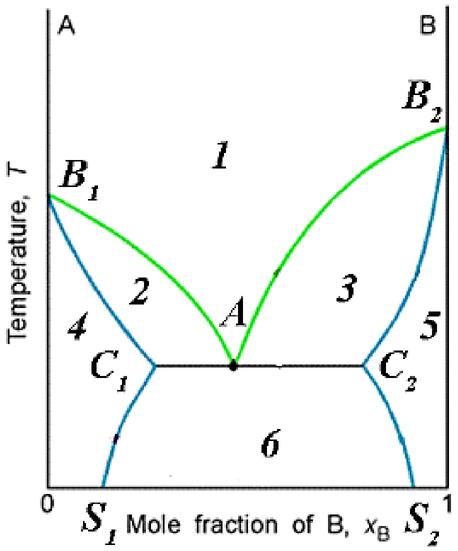
Point B_1:

Point B_2:

Find the mass composition of vapor if we will boil the mixture with a mass percentage of C_2H_5OH equal to 40 %.

Describe the deviations from Raoult's law in the given system.

4. Analyze the boiling T-X phase diagram for two-component system (substance A and substance B) with incomplete miscibility in the liquid state. Give the names for all the lines and points, write the number and the nature of phases and the number of the degrees of freedom for all lines, points and areas.



Area 1:

репозиторий БГМУ

Area 2: ____

Area 3: ____

Area 4: ____

Area 5: ____

Area 6: ____

Line B_1A: ____

Line B_2A: ____

Line B_1C_1: ____

Line B_2C_2: ____

Line C_1AC_2: ____

Line C_1S_1: ____

Line C_2S_2: ____

Point A: ____

Point B_1: ____

Point B_2: ____

Point C_1: ____

Point C_2: ____

Репозиторий БГМУ

CHAPTER 6
THREE-COMPONENT SYSTEMS

Main topics of the chapter:

1. *The constant of distribution.*
2. *The coefficient of distribution.*
3. *The coefficient of extraction.*
4. *The process of extraction.*
5. *The chemical nature of the coefficient of distribution.*

The process of extraction is widely used in pharmacy. Using this process one can extract some biologically active substances from the source into the suitable solvent. The basis of this method can be explained from the point of view of physical chemistry. If there are two liquids which are almost insoluble in each other, a third substance will be distributed among them according to the law of distribution. That law is based on the assumption that chemical potentials of a third component in both unmixable liquids will be identical in the state of equilibrium.

$\mu_3^{I} = \mu_3^{II}$

As you remember from Chapter 3, chemical potential is equal to the sum of a molar Gibbs energy (in isobaric and isothermic conditions) of a pure substance and $RT\ln a$, where “a” is an activity of a given substance in a given mixture. In the three-component system we must deal with levels of μ_3^{0} in two different mixtures. So, we can say that μ_3^{0I} is the chemical potential of 1 mole of the third component in the unlimited amount of the first component, while μ_3^{0II} is the chemical potential of 1 mole of the third component in the unlimited amount of the second component. The final formula is as follows.

$\mu_3^{0I} + RT\ln a_3^{I} = \mu_3^{0II} + RT\ln a_3^{II}$

From that formula we can express a logarithm of a ratio between two activities.

$\ln(a_3^{I}/a_3^{II}) = (\mu_3^{0II} – \mu_3^{0I}) / (R \cdot T)$

As one can see, the ratio between activities of a substance in two phases depends only on the values of its chemical potential in the unlimited amount of those substances and temperature. So, that ratio is a constant value that depends on the types of interactions between a substance and each of the two phases. Of course, the stronger the interactions of a substance with one of the phases, the higher the amount of a substance inside that phase.

The ratio between a_3^{I} and a_3^{II} is known as thermodynamic distribution (partition) constant (K^0).

The law of the distribution (partition) can be formulated in the following way. A third component that is added to a system made from two immiscible liquids is distributed between two liquids at a certain ratio, that is constant at a given temperature.

Activity is equal to the product of multiplication of molar concentration (C) and the coefficient of activity (f_a). So, we can introduce another parameter that is equal to

репозиторий ВГМУ

the ratio between concentrations (and not activities) of the same substance in two phases. This parameter (D) is called the coefficient of distribution (partition).

$D = C_3^{I} / C_3^{II}$

It is clear that the thermodynamic distribution constant and the coefficient of distribution are connected with each other by actual levels of activities.

$K^0 = D \cdot (f_{a3}^{I}/f_{a3}^{II})$

If we assume that solutions of a third component in each of the liquids are ideal, than activities are equal to concentrations and the thermodynamic distribution constant is equal to the coefficient of distribution. This assumption is somehow valid if the concentrations of a third component are very low in both of the phases.

Usually in the process of extraction a third component is moving from water to an organic solvent. In this case we can calculate the ratio between the amount of a substance in the organic phase and the overall amount of that substance using the coefficient of distribution. The above mentioned ratio is known as the coefficient of extraction (α).

$\alpha = n_{(\text{in organic phase})} / (n_{(\text{in water})} + n_{(\text{in organic phase})})$

$\alpha = C_{org} \cdot V_{org} / (C_{org} \cdot V_{org} + C_{water} \cdot V_{water})$

Than we can continue some mathematical rearrangements with the coefficient of distribution.

$\alpha = C_{org} \cdot V_{org} / C_{org} \cdot V_{org}(1 + C_{water} \cdot V_{water}/C_{org} \cdot V_{org})$

$\alpha = 1 / (1 + V_{water} / (D \cdot V_{org}))$

From the last formula it is clear that the higher the volume of an organic phase, the higher the coefficient of distribution, the higher the amount of a substance in the organic phase. To save the organic liquid, one can perform a fractional extraction. The procedure of extraction can be repeated several times using low volumes of an organic liquid.

Every time we make an extraction, the coefficient of extraction can be calculated with the following equation.

$\alpha = 1 / ((D \cdot V_{org} + V_{water}) / D \cdot V_{org}) = D \cdot V_{org} / (D \cdot V_{org} + V_{water})$

The portion of a substance that remains in the water phase is equal to 1 – α. That portion can be calculated with another equation.

$1 - \alpha = 1 - (D \cdot V_{org} / (D \cdot V_{org} + V_{water}))$

$1 - \alpha = (D \cdot V_{org} + V_{water} - D \cdot V_{org}) / (D \cdot V_{org} + V_{water})$

$1 - \alpha = V_{water} / (D \cdot V_{org} + V_{water})$

Each next round of extraction with the same volume of an organic substance makes the value of 1 – α lower. If we repeat an extraction z times, than the amount of substance that remains in water phase can be calculated with the following equation.

$n_w = n^0 \cdot (1 - \alpha)z = n^0 \cdot [V_{water} / (D \cdot V_{org} + V_{water})]^z$

The total amount of a substance that has been extracted during z rounds of extraction is calculated with the equation given below.

$n_{org} = n^0 - n_w = n^0(1 - [V_{water} / (D \cdot V_{org} + V_{water})]^z)$

Репозиторий БГМУ

Extraction can be made with the help of a separatory funnel. This funnel has a stopper at the top and stopcock at the bottom. One has to pour a water solution containing a substance that should be extracted in the funnel. Then one has to add a certain volume of an organic liquid to the funnel, close it and mix, but do not shake it. Otherwise, an emulsion will be formed. During the process of mixing a stopper may be opened to let the vapor out. Emulsion may be stable for several days. So, if it has occasionally been formed, it is better to centrifuge a funnel to separate the phases again.

After the complete separation of two phases, one has to determine which one is water phase, and which one is an “oil” phase. Usually the bottom of a meniscus is looking inside the water phase. Then one has to open up a stopcock at the bottom and collect one of the phases. Collected solution usually requires filtration.

An automatic extractor is known under the name Soxhlet extractor. With the help of this equipment one can extract substances from solid phases. A principle is as follows. A liquid phase is boiling and producing a vapor. That vapor goes up where it is cooled down by a condenser. Then a newly condensed liquid gets in the container with a material. Only when the container is fulfilled with a liquid, it starts flowing from that container back into the boiling liquid phase. If a substance that we are trying to extract is less volatile than a liquid phase, after some period of time a boiling liquid will become enriched by a substance of interest.

As one can understand, the coefficient of distribution is yet another type of a constant that describes chemical equilibrium. For example, if a substance makes bonds with several molecules of an organic phase and cannot make bonds with water molecules, we can write the following equation for an equilibrium state.

$A + nS \leftrightarrow AS_n$

A constant of equilibrium for the process of the destruction of a complex is easy to express through the concentrations.

$K_{eq} = ([A] \cdot [S]^n) / [AS_n]$

Since the coefficient of distribution is equal to $[AS_n]$ over [A], we can rewrite the last equation.

$K_{eq} = [S]^n / D$

If we have a big excess of an organic solvent (S), the value of $[S]^n$ will stay the same, and the partition low will obey.

Using the obtained equation we can calculate the coordination number of our substance in the organic phase. Indeed, if we decrease a concentration of an extragent, the value of D will be different.

$D = [S]^n \cdot (1/K_{eq})$

In the logarithmic coordinates we have a linear dependence between lgD and lg[S] in which n is the slope of the dependence.

$\lg D = n \cdot \lg[S] + \lg(1/K_{eq})$

Репозиторий БГМУ

In the same manner we may try to characterize the nature of different processes occurring in one of the phases using the coefficient of distribution. One more example is about the case in which a substance makes associates (oligomers) in one of the phases. The constant of equilibrium for the process of dissociation of oligomers is calculated from the equation of oligomerization.

$NA \leftrightarrow A_n$

$K_{eq} = [A]^N / [A_n]$

In the logarithmic form:

$lg[A_n] = N \cdot lg[A] - lgK_{eq}$

$lg(D \cdot [A]) = N \cdot lg[A] - lgK_{eq}$

$lgD + lg[A] = N \cdot lg[A] - lgK_{eq}$

$lgD = (N - 1)lg[A] - lgK_{eq}$

Using either the dependence between the logarithms of concentrations of a substance in water and organic phase, or the dependence between the coefficient of distribution and the concentration of a substance in water phase one can find the degree of oligomerization (the number of monomers in the oligomer).

In the work of a pharmacists a word "extraction" has a wider sense that a process of a distribution of a substance between two immiscible liquids. It also includes all the preparatory steps (like grinding the raw material from plants and preparing an extragent), and the forthcoming steps (like filtration, evaporation or drying of the obtained organic solution, standardization and packaging). Moreover, the process in which some substances are moving from grinded parts of plants into the water is also called extraction, even though we deal with just a single solvent. Sometimes a mixture of two completely soluble liquids (like water and ethanol) are used for the extraction. If a raw material is boiled for 15 minutes in a bain-marie, the final product is called infusion. If a raw material is boiled for 30 minutes in a bain-marie, the final product is called decoction.

Typical tasks

1. At 25 °C phenol solution in amyl alcohol has a concentration of 10.53 g/L. This solution is in the equilibrium with phenol solution in water. In the last solution a concentration of phenol is 0.658 g/L. Assume that there are no processes of association or dissociation in both solutions. Find the mass of phenol that can be obtained from 0.5 L of its water solution with a concentration of 37.6 g/L with the help of two rounds of extraction by amyl alcohol. The volume of amyl alcohol is equal to 0.1 L in both rounds.

репозиторий БГМУ

2. The coefficient of distribution between amyl alcohol and water is equal to 16 for phenol. Calculate the mole fraction of phenol that has been extracted from water solution (C = 0.4 mol/L) to amyl alcohol after 3 rounds of extraction. The volume of amyl alcohol was equal to 0.1 L in each round.

3. Calculate the mass fraction of iodine that will be left in 1 L of water solution after its extraction from the saturated solution by 0.1 L of carbon sulfide. Solubility of iodine in water at a given temperature is 1 g per 3.616 L of water. The coefficient of distribution for iodine between carbon sulfide and water is 590. Assume that association and dissociation are not happening in this experiment.

4. Compare the mass of extracted penicillin after one and after three rounds of extraction. Penicillin has been extracted from water solution (1 L) by amyl acetate (0.3 L). The coefficient of distribution of penicillin between amyl acetate and water is equal to 25. The initial mass of penicillin was 0.5 g.

репозиторий БГМУ

CHAPTER 7
CHEMICAL KINETICS

Main topics of the chapter:

1. *Terminology of chemical kinetics.*
2. *Half-elimination period.*
3. *The methods for calculation of the order of the reaction.*
4. *Arrhenius equation.*
5. *Thermodynamics of the transition complex formation.*
6. *Homogeneous and heterogeneous catalysis.*
7. *Enzymatic catalysis.*
8. *Classification of non-elementary reactions.*

The main problems that can be solved with the help of chemical kinetics include the determination of factors that can influence the rate of a given reaction, and the determination of a mechanism of a given reaction.

The most of the chemical reactions that you can see in chemistry textbooks are not one-step processes. In the equation of such chemical reactions we write the initial set of substance and the final set of substances. All the intermediate substances are just ignored (or you can say they are hidden behind the arrow). For chemical thermodynamics those intermediate substances are not very important, since the pathway should not influence thermodynamic parameters (if our reaction is close to the thermodynamically irreversible process). The pathway of a process strongly determines the rate of the whole reaction. So, if we know how the rate of a process depends on external parameters, we can describe the mechanism of a given reaction.

However, some reactions really don't have any intermediate substances. Such one-step processes are referred to as elementary reactions. It is important to highlight that the absence of intermediate substances doesn't mean that there is no transition state complex. Transition state complex is not a substance at all. A good example of an elementary reaction is the process of nitrogen dioxide dimerization: $NO_2 + NO_2 = N_2O_4$.

Reactions that proceed in two or more steps are referred to as non-elementary reactions. Under the term "mechanism of a chemical reaction" we mean the description of all the elementary acts of a given reaction with all the intermediate substances.

Homogeneous reactions proceed in the same phase (throughout the whole volume of a system), while heterogeneous reactions proceed on the border between two phases (throughout the whole contact area or on some specific active sites of that area).

The average rate of a chemical reaction is calculated as the ratio between the difference in concentration of one of the substances and the period of time.

$r_{av} = \Delta C / \Delta\tau$

Репозиторий БГМУ

So, the rate of a chemical reaction is measured in mol/(L·sec) — in moles per liter in second, or any other unit of time (minute, hour, moth or year). In practice one has to start a reaction and measure a concentration of one of the reactants or products consequently during the process. If the concentration is measured with the help of titration, then it is called a direct measurement. However, it is very hard to arrange such an experiment. Usually one of the physical parameters that depends linearly on the concentration of one of the substances is measured. Such parameter may be an optical density at a given wavelength (figure 16). That measurement is called an indirect one.

As one can see in figure 16, the concentration of a reactant is not decreasing linearly over time. The trend of the dependence between optical density and time is curvy. If we divide the differential of concentration (or a parameter that depend linearly on it) by the differential of time, then we will calculate a momentary rate of a chemical reaction that is nothing but a derivative of concentration over time in a given moment in time.

$r_{momentary} = dC / d\tau$

Graphically one can draw a derivative for a given point on a graph and calculate the value of a slope of that line. So, usually momentary rate is not equal to the average rate (figure 16).

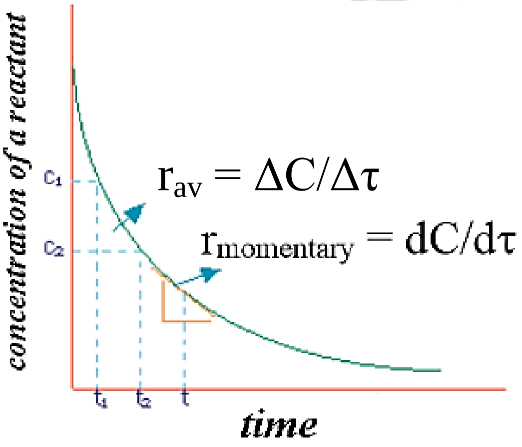


Figure 16. Dependence of the concentration of a reactant on time

Among the factors that can influence the rate of a chemical reaction we can mention: the nature of reactants, the concentrations of reactants, the temperature, the pressure (especially for gases), the presence of a catalyst, and the dispersion degree (for solid substances). First of all, we have to repeat how the concentration influences the rate of a chemical reaction. Momentary rate of a chemical reaction at a constant temperature is directly proportional to the multiple of concentrations of all the reactants in powers that must be determined experimentally. For a hypothetical reaction between substance A and substance B ($aA + bB \rightarrow \ldots$) the rate is calculated according to the following formula.

$r = k \cdot [A]^a \cdot [B]^b$

In the above written formula k is the coefficient that is constant at a given temperature, the powers (“a” and “b”), as we already said, are determined experimentally. The power upon the concentration of a substance A is called the order of the reaction according to the substance A. The power upon the concentration of a substance B is called the order of the reaction according to the substance B. The sum of “a” and “b” is known as the overall order of a reaction.

The coefficient “k” is equal to the momentary rate of a given reaction in case if the concentrations of all reactants are equal to 1 mol/L. The higher the value of k, the higher the ability to react for given substances.

For an elementary reaction the power upon a concentration (the order according to a given substance) is exactly the same as the coefficient before that substance in the balanced equation of chemical reaction. For non-elementary reactions the order is rarely equal to the coefficient. To measure the order of the reaction one has to conduct an experiment described below.

If there are two reactants (substance A and substance B), one first has to measure the rate of the reaction during a certain period of time starting from a low concentration of a substance A and the big excess of a substance B, and then to measure the rate of the reaction during a certain period of time starting from a low concentration of a substance B and the big excess of a substance A. As a result, there will be two plots: the dependence of the rate of the reaction on the concentration of a substance A, and the dependence of the rate of the reaction on the concentration of a substance B. If there is no dependence of a rate of chemical reaction on a concentration of a given substance, then the order of the reaction is equal to zero ($y = k$). If a dependence like this is described by a straight line ($y = kx$), then the order of the reaction per given substance is equal to 1. If a dependence is described by a curvy line that follows an equation like $y = kx^2$, then the order of the reaction per given substance is equal to 2. The sum of the orders for two substances gives the total order of the whole reaction. It is important to highlight that the power upon a concentration of a given substance in the equation $r = kx^n$ (that is the order of the reaction per given substance) may be fractional or even negative.

There is an important parameter for pharmacy that is called half-elimination (half-life) period. During that period of time the concentration of a given substance becomes two times lower. If the metabolization of a given substance follows the rate equation of the reaction of the ***zero order***, then:

$r = k$, $dC / d\tau = \Delta C / \Delta\tau = 0.5C / 0.5\Delta\tau = k$, $\tau_{1/2} = C / 2k$

If the metabolization follows the equation for the reaction of the ***first order***, the half-elimination period is calculated in another way.

$r = kC$, $dC / d\tau = kC$, $dC / C = k \cdot d\tau$, ${}_{C}^{C/2}\, dC/C = {}_{0}^{\tau/2}\, k \cdot d\tau$,

$\ln(1/2) = k(0 - \tau/2)$, $\ln(1/2) = -k\cdot\tau_{1/2}$, $\tau_{1/2} = -\ln(1/2)/k$,

$\tau_{1/2} = \ln 2/k$, $\tau_{1/2} \approx 0.693 / k$

It means that the half-elimination period for the reaction of the first order does not depend on the initial concentration of a reactant.

репозиторий БГМУ

In case if the metabolization follows the equation for the reaction of the ***second order***, we need to use another formula for the expression of half-elimination period.

$r = kC^2$, $dC / d\tau = kC^2$, $dC / C^2 = k \cdot d\tau$, ${}_{C}^{C/2}\ dC/C^2 = {}_{0}^{\tau/2}\ k \cdot d\tau$,

$-1/C = k(0 - \tau/2)$, $-1/C = -k \cdot \tau_{1/2}$, $\tau_{1/2} = 1/(k \cdot C)$

One can roughly estimate the order of the reaction by the way of the calculation of the rate constant at different concentrations of the same substance, or using the data on half-elimination periods at different initial concentrations. One should calculate the values of k using the equation for the reactions of the zero, first and second order and then compare them. The values of k should be equal to each other at different concentrations of a reactant in case if we used an equation of the reaction of an appropriate order. For such calculations it is better to use the equations for calculation of k from time and concentration.

For reactions of the ***zero order*** $r = k$, and

$k = dC / d\tau = \Delta C / \Delta\tau$

For reactions of the ***first order*** $r = kC$, and

$dC / d\tau = kC$, $dC / C = k \cdot d\tau$, ${}_{C_1}^{C_2}\ dC/C = {}_{\tau_1}^{\tau_2}\ k \cdot d\tau$,

$\ln(C_2/C_1) = k(\tau_2 - \tau_1)$, $\ln(C_2/C_1) = k \cdot \Delta\tau$, $k = (1 / \Delta\tau) \cdot \ln(C_2 / C_1)$

For reactions of the ***second order*** in which two molecules of ***the same substance*** react with each other, ***or the initial concentrations of two different substances are identical*** ($r = kC^2$), and

$dC / d\tau = kC^2$, $dC / C^2 = k \cdot d\tau$, ${}_{C_1}^{C_2}\ dC/C^2 = {}_{\tau_1}^{\tau_2}\ k \cdot d\tau$,

$1/C_1 - 1/C_2 = k(\tau_1 - \tau_2)$, $(C_2 - C1) / (C_1 \cdot C_2) = k \cdot \Delta\tau$,

$k = (1/\Delta\tau) \cdot (C_2 - C_1) / (C_1 \cdot C_2)$

The case when ***initial concentrations*** of two reactants (substance A and substance B) in the ***second order*** reaction ***are not equal to each other*** is more complicated from the point of view of mathematics: $r = k \cdot C_A \cdot C_B$.

The concentration of substance A after some period of time is equal to "$C_A - x$", where x is the concentration of each substance that has already reacted. Then the concentration of substance B is equal to "$C_B - x$".

$r = dx / d\tau = k \cdot (C_A - x) \cdot (C_B - x)$

$dx / ((C_A - x) \cdot (C_B - x)) = kd\tau$

${}_{0}^{x}\ dx / ((C_A - x) \cdot (C_B - x)) = {}_{0}^{\tau}\ kd\tau$

$(1 / (C_B - C_A)) \cdot (\ln(C_A / (C_A - x)) - \ln(C_B / (C_B - x)) = k\tau$

This hard equation can be simplified if we change "C_A" to "C_A^0" (initial concentration) and "$C_A - x$" to "C_A" (current concentration). The same action should be done with the concentration of substance B.

$(1 / (C_B^0 - C_A^0)) \cdot \ln((C_B \cdot C_A^0) / (C_A \cdot C_B^0)) = k\tau$

Репозиторий БГМУ

So, the rate constant for the reaction of the second order with different initial concentrations of two reactants looks like this.

$k = (1 / \tau) \cdot (1 / (C_B^0 - C_A^0)) \cdot \ln((C_B \cdot C_A^0) / (C_A \cdot C_B^0))$

Molecularity of a chemical reaction is equal to the number of particles (including molecules) that really interact with each other. This term can be applied to the elementary (one-step) reaction, as well as to the elementary act of a multy-step reaction. So, there may be monomolecular reactions, bimolecular reactions and trimolecular reactions. It is important to highlight that reactions with a molecularity higher than 3 are impossible. There is no chance that four or more particles will spontaneously collide with each other. By the way, that chance is low even for trimolecular reactions.

Usually the order is equal to the molecularity of a one-step reaction. However, if one of the reactants has been taken in a big excess, then the order of the reaction per that reactant is equal to zero. As a results, the order becomes lower than the molecularity. For multy-step reactions the molecularity of a rate-limiting step determines the order of the reaction. It means that the sum of coefficients before gaseous reactants may be equal to the order of the reaction only occasionally.

The higher the temperature, the faster the rate of movement for all the particles, especially, for gaseous particles. It means that with the growth of temperature the probability to collide is growing. From this point of view, the increase in temperature must speed up each and every chemical reaction. The first equation that connects the temperature and the rate of a reaction is known as Q_{10} rule or Van’t Hoff’s rule. According to the observation of Van’t Hoff, the rate of a chemical reaction becomes from 2 to 4 times higher with the increase in temperature equal to 10 K. The exact number of times the rate is growing with each 10 K is known as Q_{10} or Van’t Hoff’s coefficient.

$r_2 / r_1 = Q_{10}^{(t_2 - t_1)/10}$

To find out how many times the rate of a reaction will grow, one has to calculate the power upon Q_{10} first (it is equal to the difference in temperatures divided by 10 K), and then find the ratio of the rates. This method works good for biochemical reactions only at temperatures that are close to 37 °C. Indeed, at low and high temperatures enzymes are unable to perform their catalytic functions.

The ratio between the rates of a chemical reaction at different temperatures is equal to the ratio between the rate constants of that chemical reaction at different temperatures (if the reactants are in the same state of matter at both temperatures).

$r_1 / r_2 = k_1 / k_2$

Since the higher the rate, the shorter the time, we can re-write the equation mentioned above.

$\tau_1 / \tau_2 = Q_{10}^{(t_2 - t_1)/10}$

Using this formula one can check the quality of products, including medicines. Any product is best before a certain date. To calculate that date faster one may keep the product at a higher temperature. According to the Q10 rule, one can check the period of time during which the product can be used safely.

Van’t Hoff’s ideas have been developed by Svante Arrhenius, who suggested more accurate way to calculate how the temperature influences the rates of a chemical reaction. Moreover, a new theory has been suggested. The name of that theory is the theory of active collisions.

So, to react with each other particles must first collide (meet with each other). However, not each and every collision leads to the chemical reaction between particles. To react with each other the particles must carry an excessive amount of energy. Moreover, two colliding particles must be oriented appropriately relative to each other to start a chemical reaction. Both factors (the energy each particle should possess and the orientation it should have) are included in the Arrhenius equation.

$k = A \cdot e^{-E_a / (R \cdot T)}$

In this equation k is the rate constant of a reaction, A is the pre-exponential factor that shows the fraction of collisions with appropriate orientation of particles, Ea is the energy of activation (J/mol), R is the gas constant, T is the temperature measured in K, and e is an exponent (≈ 2.7). The whole expression “$e^{-E_a / (R \cdot T)}$” shows the fraction of particles possessing enough energy to react (the fraction of activated particles).

Indeed, the higher the energy of activation (E_a), the lower the value of rate constant. The lower the rate constant, the lower the slope of the dependence between the concentration of a substance and the rate of a reaction. The lower the energy of activation, the higher the rate of a chemical reaction. The higher the temperature, the higher the power upon e (it becomes less by module and higher with the respect of a minus). So, to find out how many times the rate of a chemical reaction will grow after the increase in temperature, one has to calculate the ratio between two corresponding rate constants.

$r_2 / r_1 = k_2 / k_1 = A_1 \cdot e^{-E_a / (R \cdot T_2)} / A_2 \cdot e^{-E_a / (R \cdot T_1)}$

If we assume that A is approximately the same at different temperatures, then the equation will be simplified.

$r_2 / r_1 = e^{-E_a / (R \cdot T_2)} / e^{-E_a / (R \cdot T_1)} = e^{E_a((1 / (R \cdot T_1)) - (1 / (R \cdot T_2)))}$

One can calculate the Q_{10} coefficient using the above written equation: T_2 should be equal to $T_1 + 10$. It is clear that the value of Q_{10} highly depends on the initial temperature.

The energy of activation can be calculated with the help of a special plot. One should put “1/T” on the X-axis and “lnk” on the Y-axis. These coordinates are easily obtained from the Arrhenius equation.

$k = A \cdot e^{-E_a / (R \cdot T)}$, $\ln k = \ln A - E_a / (R \cdot T)$, $\ln k = -(E_a / R) \cdot (1 / T) + \ln A$

The equation describing the dependence between “lnk” and “1/T” is linear. The slope of the dependence is equal to “$-E_a/R$”. So, the value of the Ea is always positive, but the slope of the dependence is always negative (figure 17). Actually, to get the value of E_a one has to calculate the value of the rate constant at different temperatures, build the plot

Репозиторий БГМУ

in above mentioned coordinates, find the slope of the dependence, and then multiply it by "–R". To find the value of lnA one has to measure the length of the line between "0" point and the cross fold between the line of the dependence and Y-axis.

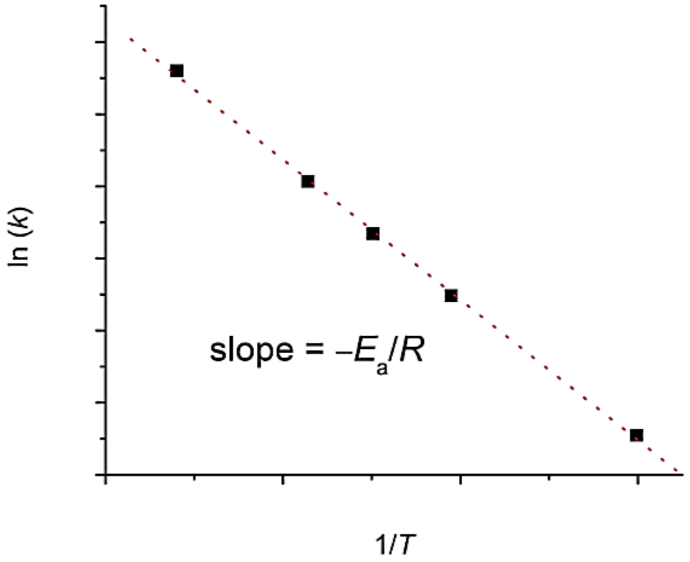


Figure 17. Arrhenius plot: natural logarithm of the rate constant against one over temperature

The theory of active collisions is mutually connected with the theory of transition state complex. According to that theory, the energy of activation is nothing but the energy that is needed to form a transition state complex in an elementary reaction. In isobaric and isothermic conditions Ea is the enthalpy of transition state complex formation. To understand it better one can see Figure 18 with so-called energetic diagrams of endothermic (*a*) and isothermic (*b*) reactions.

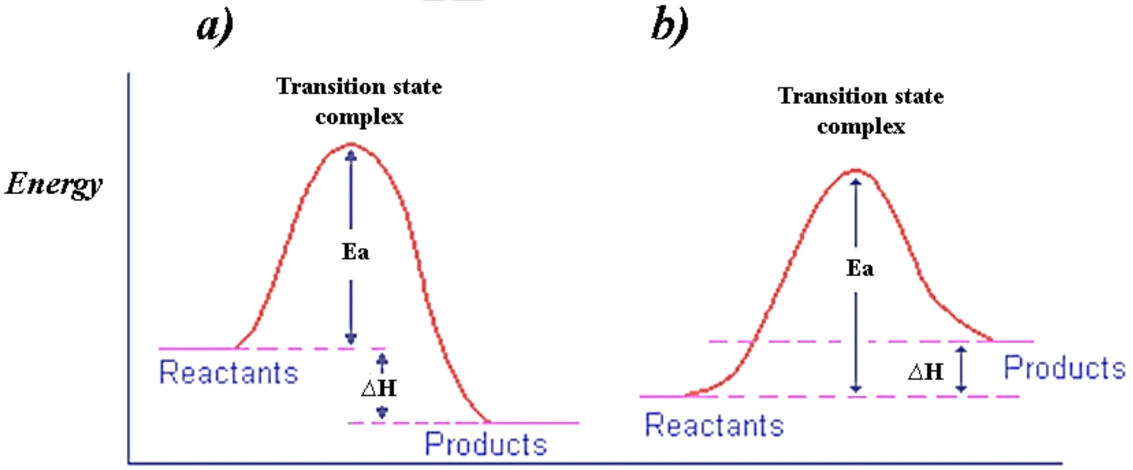


Figure 18. Energetic diagrams of exothermic (*a*) and endothermic (*b*) chemical reactions

In figure 18, *a* the overall energy of a system starts to grow up to the highest peak. Then it decreases until a certain level that is higher than the initial one. So, the difference between the initial state and the highest peak is equal to the energy of activation. At the highest peak a transition state complex is formed from reactants. That complex is described as a state in which old bonds have not been completely broken yet, but new bonds have already started to form. It is important to say that transition state complex is not a substance, its lifetime is very short. Once it is formed, it decomposes spontaneously into products of a chemical reaction and releases some energy. If the amount of energy released in the process of a transition state complex decomposition is lower than the energy of activation, the reaction is endothermic (figure 18, *a*). If the amount of energy released due to the transition state complex decomposition is higher than the amount of energy of activation, then the process is overall exothermic (figure 18, *b*).

To approve the statements made in the previous paragraph we can use some mathematical actions. Let us consider that the constant of equilibrium of the transition state complex formation is the same as the one for a regular chemical reaction: A + B = X.

$K_{eq} = [X] / ([A] \cdot [B]), \qquad [X] = K_{eq} \cdot [A] \cdot [B]$

Let us also consider the rate equation of the decomposition of the transition state complex.

$r = p \cdot [X]$

In this equation p is the rate constant for the transition state complex decomposition. So, we can combine two equations together.

$r = p \cdot K_{eq} \cdot [A] \cdot [B]$

We know that the regular rate equation for a reaction like this is written as: $r = k \cdot [A] \cdot [B]$. If the rate limiting step of the whole process is the decomposition of the transition state complex, then we can combine these equations together.

$K \cdot [A] \cdot [B] = p \cdot K_{eq} \cdot [A] \cdot [B]$

$k = p \cdot K_{eq}$

From the point of view of thermodynamics, the Gibbs energy of the formation of the transition state complex is calculated in the following way.

$\Delta G = -RT\ln K_{eq}, \qquad k_{eq} = e^{-\Delta G / (R \cdot T)}$

So, the equation to calculate the rate constant for the whole reaction is calculated as the multiple of the rate constant for transition state complex decomposition (p) and the constant of equilibrium for the transition state complex formation.

$k = p \cdot e^{-\Delta G / (R \cdot T)}$

Now we can compare that equation with the Arrhenius equation and find out that they have much in common. The next action is to define ΔG as ΔH – TΔS. So, the equation will be re-written once again.

$k = p \cdot e^{-\Delta G / (R \cdot T)} = p \cdot e^{\Delta S / R} \cdot e^{-\Delta H / (R \cdot T)}$

In this last version of the equation one can see that the pre-exponential factor from the Arrhenius equation is equal to “$p \cdot e^{\Delta S / R}$”, while the energy of activation is really equal to the enthalpy of the transition state complex formation. A factor responsible of the appropriate positioning of reactants is nothing but “$e^{\Delta S / R}$”. So, the higher the entropy of the transition state complex formation, the faster the rates of a chemical reaction.

Репозиторий БГМУ

Catalysis can be defined as a phenomenon of the change of the rate of chemical reaction in the presence of a certain substance. A substance that is able to change the rate of a given chemical reaction is called a catalyst. Even though catalyst participates in a chemical reaction and changes its mechanism, the amount of catalyst remains the same. On one of the steps of a reaction catalyst is used, while in some other step it is produced back.

According to the Arrhenius theory, a positive catalyst decreases the value of the energy of activation (and decreases the enthalpy of the transition state complex formation, as well as the structure of that complex itself), while a negative catalyst increases the value of the energy of activation. As a result, a positive catalyst increases the rate of a reaction, while a negative catalyst decreases the rate of a reaction.

Homogeneous catalysis means that all the reactants and the catalyst itself exist in the same phase. For example, the production of SO_3 from SO_2 and O_2 may be catalyzed by NO. In the first step NO reacts with O_2 and forms NO_2. In the second step NO_2 reacts with SO_2 and forms SO_3 and NO. So, NO itself is not wasted in this process. It is important to highlight that NO_2 is an intermediate substance in this pathway, but it is not a transition state complex. Homogenous catalysis is possible not only in a gas phase, but also in the water solution. Acid-base catalysis is classified as homogenous catalysis. Indeed, soluble substance and ions (like H_3O^+) exist in the same phase. Catalysis with the help of organometalic complexes is also a kind of homogenous catalysis. Those complexes consist of metal cations as central atoms and small organic molecules as ligands. The change of a ligand is possible in such complexes. So, the molecules of reactants can become ligands in such complexes. Then they will be polarized and react with each other faster. A similar type of catalysis has already been created by the nature. The most of the enzymes have certain metal cations in their active centers. However, the catalysis by metalloenzymes is on the border between homogeneous and heterogeneous catalysis. Even though both catalyst (an enzyme) and substrate are soluble in water, enzyme is usually much bigger than its substrate. Because of this reason catalysis takes place in the specific active site of an enzyme. This feature makes enzymatic catalysis close to the heterogeneous catalysis.

Heterogeneous catalysis (when a catalyst exists in a different phase than reactants) is explained by the adsorption theory. According to that theory, the concentration of reactants is increasing exactly in active centers of a catalyst. Reaction proceeds in those active sites.

Coming back to the enzymatic catalysis, we have to mention some characteristic properties of this biological catalysis. Usually, enzymes have a high specificity. They are able to bind either a single or a few similar compounds (reactants). Usually one of the possible substrates demonstrates higher affinity to the active center of an enzyme than other few similar reactants. Enzymes usually demonstrate higher catalytic activities compared to inorganic catalysts. Enzymes work in “mild” conditions (at 37 °C and atmospheric pressure), unlike the most of the inorganic catalysts. One more interesting property of enzymes is that their overall activity in a sample depends not just on

Репозиторий БГМУ

the concentration of a substrate, but also on the concentration of an enzyme itself. In any laboratory the increase of an enzymatic activity in a sample of serum is interpreted as the evidence of the growth of the concentration of that enzyme. However, the enzymatic activity may also grow because of the change of a metal cation in an active center or because of the increased concentration of a substrate. The most of the enzymes are regulated on the level of their expression and on the level of their functioning (by the way of allosteric regulation, phosphorylation, proteolysis, etc.). Usually enzymes are able to work only at a certain pH.

Kinetics of heterogeneous reactions has several distinctive features. First of all, concentrations of all the solid substances are not included in kinetic and equilibrium equations. In the same time, the rate of a reaction depends on the surface of an area of interaction between substances in different phases. The more dispersed is the solid phase, the higher the rate of a reaction. Except a chemical reaction itself, there are two more processes that influence the rate of a heterogeneous reaction: the process of the diffusion of reactants towards a solid phase, and the process of the removal of products from a solid phase.

Multy-step chemical reactions are classified into several groups. Parallel reactions are those that lead to the simultaneous formation of several products. Consequent reactions proceed in a step-by-step manner. Conjugate reactions proceed simultaneously and one of them (with $\Delta G < 0$) is the source of energy for another one ($\Delta G > 0$). So, the overall ΔG for two conjugate reactions is less than zero. Chain reactions are proceeding in such steps as the initiation of a chain, continuing of a chain and the breaking of a chain. In the first step free radicals are forming, in the second step one free radical gives rise to another free radical (a free radical attacks a molecule, makes a new compound with it but releases another free radical that was a part of the initial molecule), in the third step two free radicals form a compound with each other. In photochemical reactions light plays a role of source of energy.

Since light consists of photons, we can calculate a quantum yield of a photochemical reaction as the ratio between the number of molecules of a product and the number of absorbed photons. The number of absorbed photons can be calculated as the ratio between the absorbed energy and the energy of a single photon. The energy of a single photon is equal to the multiple of Planck's constant ($h = 6.6 \cdot 10^{-34}$ J·sec) and the frequency of the photon (ν). The frequency itself can be calculated as the ratio between the speed of light ($c = 3 \cdot 10^{8}$ m/sec) and the wavelength of photon (λ). Taken together, the energy of a single photon is calculated as follows.

$$E = h \cdot \nu = (h \cdot c) / \lambda$$

The wavelength sometimes is measured in nanometers ($1 \cdot 10^{-9}$ m), and sometimes in Angstrom ($1 \cdot 10^{-10}$ m). In the above written equation the wavelength should be measured in meters.

репозиторий БГМУ

Typical tasks

1. Estimate the order of the reaction $\mathbf{2PH_3 \rightarrow 2P + 3H_2}$ using the data on the half-elimination periods for phosphine at different initial partial pressures of that gas.

P, Pa·10^3	94.26	10.53	4.93
$T_{1/2}$, min	84	84	83

2. The rate of a chemical reaction $\mathbf{2NCl_3 \rightarrow N_2 + 3Cl_2}$ has been calculated by the way of the estimation of the volume of N_2. Using the data on the dependence the volume of N_2 on time decide whether this reaction is of the zero, firs, or second order.

Time, hour	**4**	**6**	**22**	**∞**
The volume of N_2, ml	**10**	**13**	**26**	**28.5**

3. Estimate the order of the reaction $2CO = CO_2 + C$, if in the first experiment the pressure decreased from $1.05 \cdot 10^5$ Pa to $9.24 \cdot 10^4$ Pa during 30 minutes, while in the second experiment the pressure decreased from $7.13 \cdot 10^4$ Pa to $6.24 \cdot 10^4$ Pa during the same period of time.

4. Find the order of the process $HCNO_{(g)} \rightarrow HCNO_{(s)}$. The pressure of HCNO in one of the experiments decreased from $2.25 \cdot 10^4$ Pa to $2.04 \cdot 10^4$ Pa during 23 hours, while in another experiment it decreased from $1.05 \cdot 10^4$ to $1.02 \cdot 10^4$ Pa during 21 hours.

репозиторий БГМУ

5. In the reaction of the first order the half elimination period is equal to 1000 seconds. How long does it take to eliminate 99 % of a reactant?

6. The reaction between substances A and B is the reaction of the second order. After 10 minutes from the start of the reaction 25 % of reactants reacted with each other. How long will it take for 90 % of the reactants to react? Initial concentrations of A and B are equal to each other.

7. In the enzymatic reaction of the first order 35.4 % of the substrate reacted during 60 minutes. Find the percentage of the substrate that will react during 5 hours.

8. 0.01 N solution of ethylacetate reacts with 0.05 N solution of NaOH during 30 minutes. As a result, 20 % of ethylacetate reacted. Calculate the rate constant of this process.

9. The rate constant of the reaction between ethylacetate and sodium hydroxide is 2.37. Find the time (in minutes) needed to consume 90 % of ethylacetate, if initial concentrations of ethylacetate and sodium hydroxide are 0.8 an 1 mol/L, respectively.

репозиторий БГМУ

10. 0.2 N solution of ethylacetate reacts with 0.4 N solution of NaOH during 30 minutes and the amount of ethylacetate decreased by 10 %. How long will it take for 10 % of ethylacetate to react with 0.3 NaOH solution?

11. Calculate the rate constant for HI decomposition reaction at the temperature of 647 K. At the temperature of 629 K this constant is equal to $8.09 \cdot 10^{-5}$. Q_{10} coefficient is equal to 2.

12. At 363 К a chemical reaction ends after 16 minutes. Calculate the time needed for the completion of that reaction at 413 K and 333 K, if the value of Q_{10} is 2.5.

13. The activation energy of a certain reaction is equal to 97133.8 J/mol. How many times the rate of this reaction will increase in case of the growth of temperature from 293 K to 333 K?

14. The energy of activation for the reaction of HI decomposition is equal to 184219 J/mol. Calculate the fraction of HI molecules possessing enough energy to be decomposed at 400 K and 500 K.

репозиторий БГМУ

15. The rate constant of a certain reaction at 552 K is equal to $6.09 \cdot 10^{-5}$. At 593 K the rate constant for that reaction is equal to $1.32 \cdot 10^{-3}$. Calculate the energy of activation and the rate constant of the reaction at 688 K.

16. The rate constant of a certain reaction at 574 K is equal to $8.56 \cdot 10^{-2}$. At 497 K the rate constant for that reaction is equal to $3.6 \cdot 10^{-4}$. Calculate the energy of activation and the rate constant of the reaction at 473 K.

17. At the temperature of 300 K a catalyst decreases the activation energy by 40 kJ/mol. How many times the rate of this reaction will increase after the introduction of that catalyst?

18. A catalyst decreases the energy of activation from 80 to 40 kJ/mol. Calculate how that catalyst influences the Q_{10} coefficient of the reaction at the temperature of 250 K.

19. Calculate the quantum yield of a photochemical reaction $CO + Cl_2 = COCl_2$. $2 \cdot 10^5$ J of energy have been absorbed on the wavelength of 5100 Angstrom. The mass of the $COCl_2$ formed in this reaction is 85 g.

репозиторий БГМУ

20. A mixture of H_2 and Cl_2 is stored under the water in the vessel with a volume of $10 \cdot 10^{-3}$ m^3 at the temperature of 283 K and the pressure of $1.01 \cdot 10^5$ Pa. Under the influence of light HCl is synthesized in the vessel. Calculate the quantum yield of the reaction after the absorption of $1 \cdot 10^{-2}$ J of energy at the wavelength of 5891 A. The pressure in the vessel has decreased by $0.113 \cdot 10^5$ Pa.

репозиторий БГМУ

LABORATORY WORK 1. DETERMINATION OF THE CONCENTRATION OF ACETIC ACID SOLUTION BY THE ACID-BASE TITRATION

Objective: to determine the concentration of acetic acid in water solution with the help of titration by sodium hydroxide solution.

Reactants: acetic acid solution with unknown concentration, 0.10 M sodium hydroxide solution and phenolphthalein as an indicator.

Labware: burette with a capacity of 25 ml, Mohr's pipette, funnel, flasks for titration.

The task. Fill the burette with 0.10 M sodium hydroxide solution.

Pour 10 ml of acetic acid solution and 2–3 drops of phenolphthalein into each of the three flasks for titration. Notice that solution is colorless.

Titrate the solution of acetic acid by the alkali solution until the appearance of a permanent slightly pink color. Titration results should be immediately written down with the accuracy from 0.05 to 0.1 ml.

The second and third titration should be carried out more precisely. At first you should quickly add the titrant with the volume less than 0.5–1.0 mL of the volume previously determined during the first tentative titration in the titration flask. Then add the titrant in the drop by drop manner and try not to overlook the last drop that will change the color of the solution. Titration should be repeated till you get three similar results (i. e. they shouldn't differ more than 0.1 mL).

All the results should be written down in the table:

Titration number	C(NaOH), mol/L	V(NaOH), ml	V(CH_3COOH), ml
1	0.10		10.0
2	0.10		10.0
3	0.10		10.0

Calculations

The volume of NaOH solution used for the titration can be calculated as the arithmetic average of three similar results (V(NaOH) is calculated with the precision up to 0.01 mL):

$$V_{av}(NaOH) = (V_1(NaOH) + V_2(NaOH) + V_3(NaOH)) / 3$$

Using the titration results and the equivalence principle you can calculate the concentration of CH_3COOH solution:

$$C(CH_3COOH) \cdot V(CH_3COOH) = C(NaOH) \cdot V(NaOH)$$

$$C(CH_3COOH) = (C(NaOH) \cdot V(NaOH)) / V(CH_3COOH)$$

$C(CH_3COOH)$ = (_______ · _______) / __________ = ___________ mol/L

The value of $C(CH_3COOH)$ should be calculated with the precision up to the fourth significant digit after the point.

Conclusion: by the method of acid-base titration, using the technique of direct titration, I determined the concentration of CH_3COOH solution: $C(CH_3COOH)$ = _______________ mol/L.

Репозиторий БГМУ

LABORATORY WORK 2. DETERMINATION OF THE CALORIMETER CONSTANT

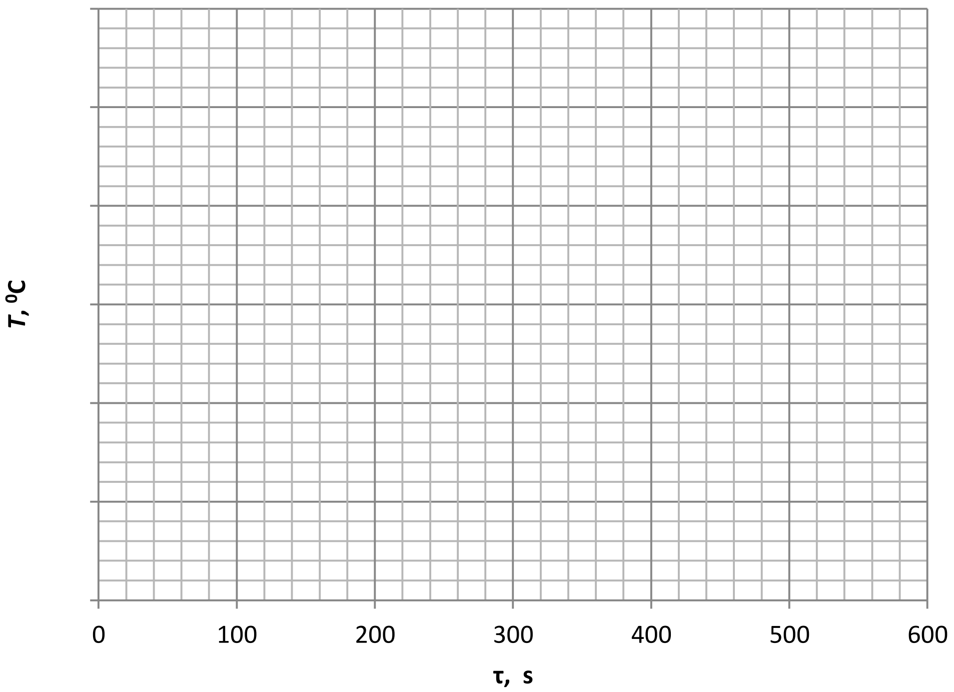
Objective: to determine the calorimeter constant with the isothermal shell according to the heat of dissolution of NH_4Cl.

Reactants: distilled water, ammonium chloride.

Labware: educational-laboratory complex “Chemistry”, computer with the program elsms2.exe, electronic scales, glass cup 150 cm^3, graduated cylinder, syringe.

The task

1. Switch on the educational-laboratory complex “Chemistry” and set the necessary settings in accordance with its instructions.
2. Add 100 ml of distilled water to the measuring glass using a graduated cylinder. Put the glass in the calorimeter and close the cover with the temperature sensor fixed in it. ***Caution !!!*** All holes in the cover must be tightly closed with stoppers.
3. Prepare a sample of NH_4Cl weighing 3,000 g on the electronic scales and transfer it quantitatively to the test syringe. Insert the syringe into the hole in the cover of calorimeter. Wait until the temperature inside the calorimeter will become constant during 5 minutes.
4. Start the recording of the data in the memory bank in accordance with the instructions of the complex “Chemistry”. Wait until the controller records 10 readings in the cells.
5. Then ***quickly (!!!)*** pour the salt from the test syringe into the water through the hole in the calorimeter box. Make measurements until all the cells in the memory bank (100) will be recorded.
6. Build a graph:



The temperature during the process of NH_4Cl dissolving in water

Calculations

According to the graph, you should determine the actual temperature change ΔT during the dissolving of the salt and calculate the calorimeter constant using the formula:

$$K = \pm\frac{Q}{\Delta T} - (m_s - m_w) \cdot c_p$$

If **ΔT** > 0, then put “+” before the formula, if **ΔT** < 0, then put “–” before the formula; **K** is the calorimeter constant; **Q** is the heat of salt dissolution, J (855 J); $\mathbf{m_s}$ is the mass of the salt, g; $\mathbf{m_w}$ is the mass of water, g; $\mathbf{c_p}$ is the heat capacity of the solution, $J \cdot K^{-1} \cdot g^{-1}$.

The heat capacities of dilute solutions of inorganic salts in water are practically the same and slightly differ from the heat capacity of water: $\mathbf{c_p} = 4.18\ J \cdot K^{-1} \cdot g^{-1}$.

Using the presented data, you should calculate the calorimeter constant:

$$K = \quad \overline{\qquad\qquad} - (\qquad - \qquad) \cdot \qquad = J \cdot K^{-1}$$

Conclusion: according to the heat of dissolution of NH_4Cl I determined the calorimeter constant with the isothermal shell: **K** = __________ $\mathbf{J \cdot K^{-1}}$.

Репозиторий БГМУ

LABORATORY WORK 3. DETERMINATION OF THE HEAT OF NEUTRALIZATION REACTION OF A STRONG ACID WITH A STRONG BASE

Objective: to determine the heat of neutralization of a strong acid by a strong base.

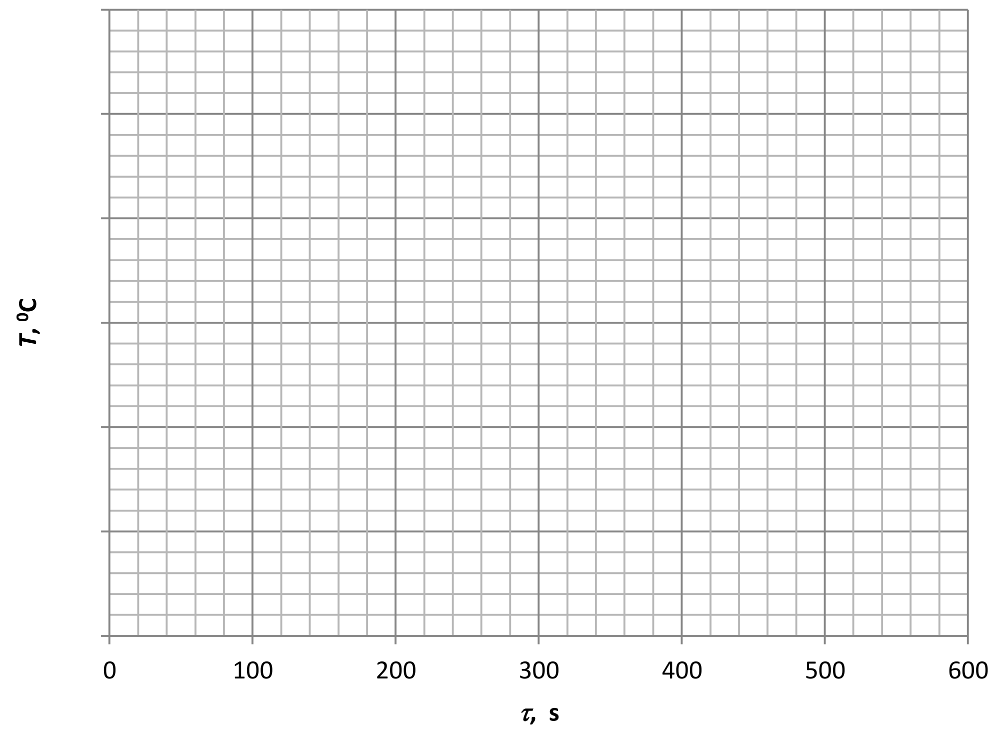
Reactants: distilled water, solution of NaOH with C(NaOH) = 0.15 mol/dm^3, solution of HCl with C(HCl) = 5 mol/dm^3 (ρ(solution) = 1 g·ml^{-1}).

Labware: educational-laboratory complex “Chemistry”, computer with the program elsms2.exe, glass cup 150 cm^3, graduated cylinder, syringe.

The task

1. Switch on the educational-laboratory complex “Chemistry” and set the necessary settings in accordance with the instructions.
2. Add 100 cm^3 of distilled water to the measuring glass using a graduated cylinder. Put the glass in the special place on the calorimeter and close the cover with the temperature sensor fixed in it. ***Caution !!!*** All holes in the cover must be tightly closed with stoppers.
3. Pour 3 ml of HCl solution into the syringe. Insert the syringe into the hole in the calorimeter cover. Wait until the temperature of the calorimetric liquid in the glass will become stable during 5 minutes.
4. Start the recording of data in the memory bank in accordance with the instructions of complex “Chemistry”. Wait until the controller records 10 readings in the cells.
5. Then ***quickly (!!!)*** pour the HCl solution from the test syringe into the water through the hole in the calorimeter box. Make measurements until all the cells in the memory bank (100) will be recorded.

ОРИЙ БГМУ



The temperature during the dilution of HCl

6. Pour the contents of the beaker into the waste container. Wash the glass with running water, and then rinse with distilled water.

7. Based on the data obtained in the experiment determine the actual temperature change during the dilution of acid solution. Draw the graph of the dependence of the temperature on time.

8. Add 100 cm^3 of NaOH solution to the measuring glass using a graduated cylinder. Put the glass in the special place on the calorimeter and close the cover with the temperature sensor fixed in it. ***Caution !!!*** All holes in the cover must be tightly closed with stoppers.

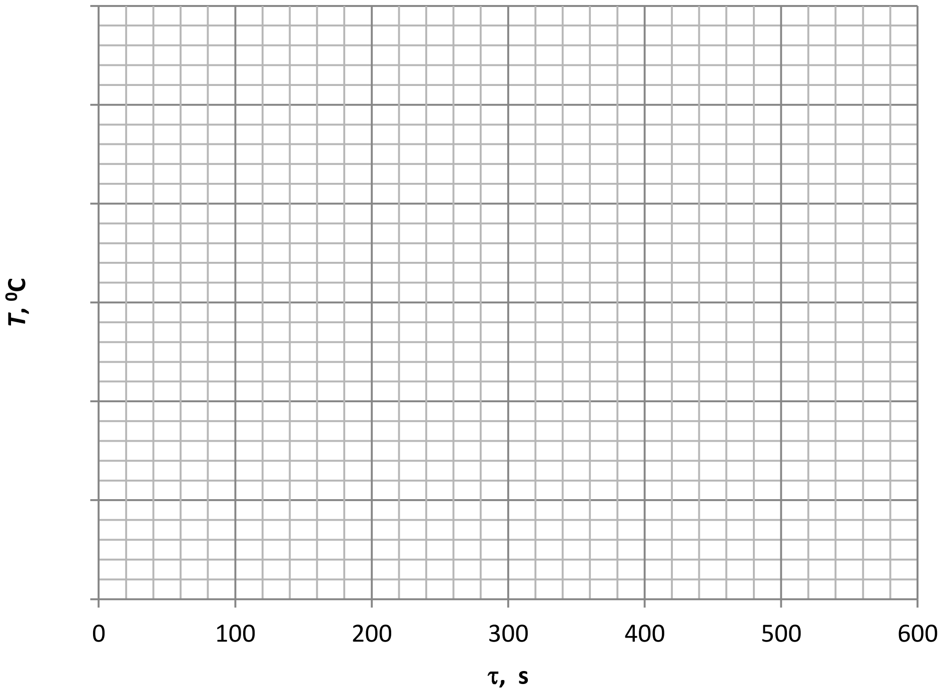
9. Put 3 ml of HCl solution into the syringe. Insert the syringe into the hole of the calorimeter cover. Wait until the temperature of the calorimetric liquid in the glass will become stable for 5 minutes.

10. Start the recording of data in the memory bank in accordance with the instructions for working with the complex “Chemistry”. Wait until the controller records 10 readings in the cells.

11. Then ***quickly (!!!)*** pour the HCl solution from the test syringe into the water through the hole in the calorimeter box. Make measurements until all the cells in the memory bank (100) will be recorded.

12. Pour the contents of the beaker into the waste container. Wash the glass with running water, and then rinse with distilled water.

13. Based on the data obtained in the experiment determine the actual temperature change of neutralization of the acid by alkali. Draw the graph of the dependence of temperature on time.



The temperature during the neutralization reaction

БГМУ

All the results should be written down in the table:

Experiment number	m(H_2O), g	m(NaOH), g	m(HCl), g	ΔT_1	ΔT_2	Q, J·mol^{-1}	q, J·g^{-1}
1	100	–	3				
2	–	100	3				

Calculations

Calculate the heat of the neutralization reaction using the experimental data according to the equation:

$$\mathbf{Q = (m_1c + m_2c + K)\cdot(\Delta T_1 - \Delta T_2)},$$

where **Q** is the heat of neutralization, J; $\mathbf{m_1}$ is the HCl mass, g; $\mathbf{m_2}$ is the NaOH mass, g; **c** is the heat capacity of the solution, J·K^{-1}·g^{-1} . The heat capacities of dilute solutions of inorganic salts in water are practically the same and slightly differ from the heat capacity of water: c = 4.18 J·K^{-1}·g^{-1}; **K** — calorimeter constant, J·K^{-1} (29.96 J·K^{-1}).

The obtained value of the heat of neutralization should be converted into the molar value for an acid:

$$q = \frac{1000 \cdot Q}{C(HCl) \cdot V(HCl)}$$

Using the obtained data, calculate the heat of neutralization:

Q = ________________________________ = _______ J;

$$q = \frac{1000 \cdot}{\qquad\qquad} = \qquad\qquad J \cdot mol^{-1}.$$

The heat of neutralization of a strong acid by a strong base is always the same, and it is equal to 55.9 kJ/mol at 298 K. Actually, it is the heat effect of the reaction of liquid water formation from H^+ (H_3O^+) and OH^- ions.

Conclusion: according to the calculated value of the heat of neutralization **q** = _________ J·mol^{-1} the reaction of neutralization is ____________________.

exo- or endothermic

Репозиторий БГМУ

LABORATORY WORK 4. DETERMINATION OF THE HEAT OF DISSOCIATION OF A WEAK BASE

Objective: to determine the heat of dissociation of a weak base $NH_3·H_2O$.

Reactants: distilled water, solution of $NH_3·H_2O$ with C = 5 mol / dm^3, solution of HCl with C(HCl) = 0.15 mol/dm^3 (ρ(solution) = 1 g·ml^{-1}).

Labware: educational-laboratory complex “Chemistry”, computer with the program elsms2.exe, glass cup 150 cm^3, graduated cylinder, syringe.

The task

1. Switch on the educational-laboratory complex “Chemistry” and set the necessary settings in accordance with its instructions.

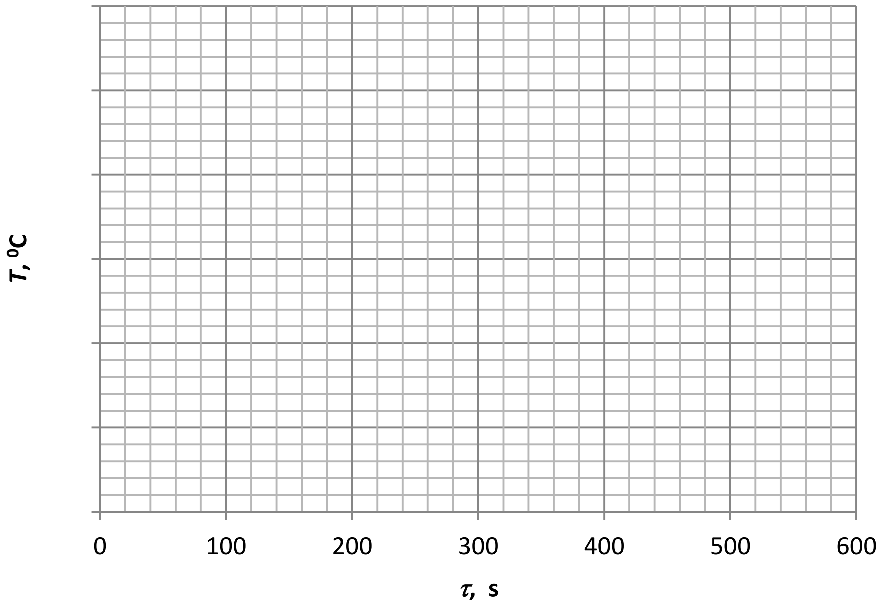
2. Add 100 cm^3 of distilled water to the measuring glass using a graduated cylinder. Put the glass in the special place on the calorimeter and close the cover with the temperature sensor fixed in it. ***Caution !!!*** All holes in the cover must be tightly closed with stoppers.

3. Put 3 ml of $NH_3·H_2O$ solution into the syringe. Insert the syringe into the hole on the calorimeter cover. Wait until the temperature of the calorimetric liquid in the glass will become stable for 5 minutes.

4. Start the recording of data in the memory bank in accordance with the instructions for working with the complex “Chemistry”. Wait until the controller records 10 readings in the cells.

5. Then ***quickly (!!!)*** pour the $NH_3·H_2O$ solution from the test syringe into the water through the hole in the calorimeter box. Make measurements until all the cells in the memory bank (100) will be recorded.

6. Pour the contents of the beaker into the waste container. Wash the glass with running water, and then rinse with distilled water.



The temperature during the dilution of $NH_3·H_2O$

7. Based on the data obtained in the experiment determine the actual temperature change of the dilution of a weak base solution. Draw the graph of the dependence of temperature on time.

8. Add 100 cm^3 of HCl solution to the measuring glass using a graduated cylinder. Place the glass in the special hole on the calorimeter and close the cover with the temperature sensor fixed in it. ***Caution !!!*** All holes in the cover must be tightly closed with stoppers.

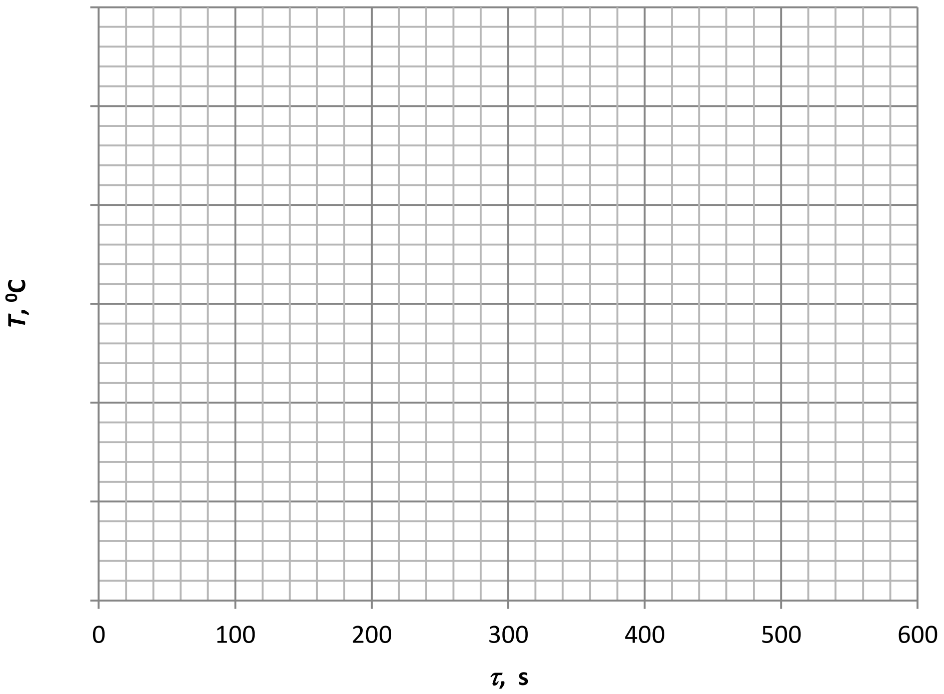
9. Put 3 ml of $NH_3{\cdot}H_2O$ solution into the syringe. Insert the syringe into the hole on the calorimeter cover. Wait until the temperature of the calorimetric liquid in the glass will become stable for 5 minutes.

10. Start the recording of data in the memory bank in accordance with the instructions for working with the complex "Chemistry". Wait until the controller records 10 readings in the cells.

11. Then ***quickly (!!!)*** pour the $NH_3{\cdot}H_2O$ solution from the test syringe into the water through the hole in the calorimeter box. Make measurements until all the cells in the memory bank (100) will be recorded.

12. Pour the contents of the beaker into the waste container. Wash the glass with running water, and then rinse with distilled water.

13. Based on the data obtained in the experiment determine the actual temperature change of the neutralization of the weak base by the strong acid. Draw the graph of the dependence of temperature on time.



The temperature during the neutralization of the weak base by the strong acid

Репозиторий БГМУ

All the results should be written down in the table:

Experiment number	$m(H_2O)$, g	m(HCl), g	$m(NH_3 \cdot H_2O)$, g	ΔT_1	ΔT_2	Q_{diss}, $J \cdot mol^{-1}$	q, $J \cdot g^{-1}$
1	100	–	3				
2	–	100	3				

Calculations

In this work, a small volume of the base solution is added to a large volume of the acid solution, so the volume of the acid solution changes just a little when the base is poured into it. The heat of dilution of the acid is small, and it can be ignored. The heat of dilution of the base solution with acid is high in this case, and it must be taken into account during the determination of the heat of neutralization. Then

$$\mathbf{Q_1 = Q_2 + Q_3 + Q_{diss}},$$

where $\mathbf{Q_1}$ is the heat of neutralization, J; $\mathbf{Q_2}$ is the heat of formation of water (see the laboratory work 3), J; $\mathbf{Q_3}$ is the heat of dilution of the base solution, J; $\mathbf{Q_{diss}}$ is the heat of dissociation, J.

Calculate the heat of dissociation using the experimental data according to the equation:

$$\mathbf{Q_{diss} = (m_1c + m_2c + K) \cdot (\Delta T_1 - \Delta T_2) - Q_2},$$

where $\mathbf{m_1}$ is the $NH_3 \cdot H_2O$ mass, g; $\mathbf{m_2}$ is the HCl mass, g; **c** is the heat capacity of the solution, $J \cdot K^{-1} \cdot g^{-1}$. The heat capacities of dilute solutions of inorganic salts in water are practically the same and slightly differ from the heat capacity of water: c = 4.18 $J \cdot K^{-1} \cdot g^{-1}$; **K** — calorimeter constant, $J \cdot K^{-1}$ (29,96 $J \cdot K^{-1}$).

The obtained value of the heat of dissociation should be converted into the molar value for 1 mole of the base:

$$q = \frac{1000 \cdot Q}{C(NH_3 \cdot H_2O) \cdot V(NH_3 \cdot H_2O)}$$

Using the presented data, calculate the heat of dissociation:

Q = ____________________________________ = _______ J;

$$q = \frac{1000 \cdot}{\qquad\qquad} = \qquad\qquad J \cdot mol^{-1}.$$

Conclusion: according to the calculated value of the heat of dissociation ***q*** = _________ $J \cdot mol^{-1}$ the reaction is _____________________.

exo- or endothermic

Репозиторий БГМУ

LABORATORY WORK 5. DETERMINATION OF THE HEAT OF THE DISSOLVING OF ANHYDROUS COPPER SULFATE IN WATER

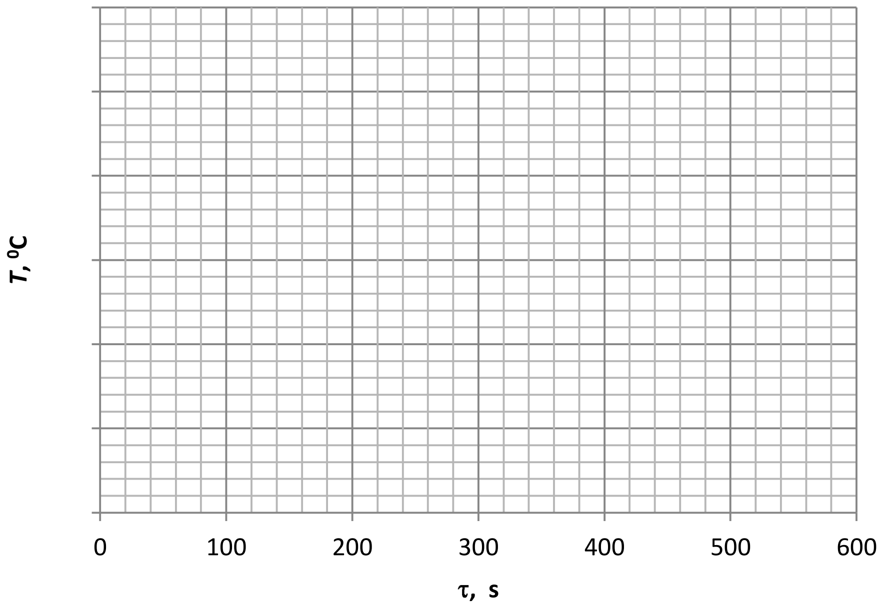
Objective: to determine the heat of the dissolving of anhydrous copper sulfate.

Reactants: distilled water (ρ(solution) = 1 g·ml^{-1}), 3 g of anhydrous $CuSO_4$.

Labware: educational-laboratory complex "Chemistry", computer with the program elsms2.exe, glass cup 150 cm^3, graduated cylinder, syringe.

The task

1. Switch on the educational-laboratory complex "Chemistry" and set the necessary settings in accordance with its instructions.
2. Add 100 cm^3 of distilled water to the measuring glass using a graduated cylinder. Put the glass in the special place on the calorimeter and close the cover with the temperature sensor fixed in it. ***Caution !!!*** All holes in the cover must be tightly closed with stoppers.
3. Put 3 g of anhydrous $CuSO_4$ into the syringe. Insert the syringe into the hole of the calorimeter cover. Wait until the temperature of the calorimetric liquid in the glass will become stable for 5 minutes.
4. Start the recording of data in the memory bank in accordance with the instructions for working with the complex "Chemistry". Wait until the controller records 10 readings in the cells.
5. Then ***quickly (!!!)*** pour out $CuSO_4$ from the test syringe into the water through the hole in the calorimeter box. Make measurements until all the cells in the memory bank (100) will be recorded.
6. Pour the contents of the beaker into the waste container. Wash the glass with running water, and then rinse with distilled water.



The temperature during the dissolving of anhydrous $CuSO_4$ in water

Репозиторий БГМУ

7. Based on the data obtained in the experiment determine the actual temperature change during the dissolving of anhydrous $CuSO_4$. Draw the graph of the dependence of temperature on time.

Calculations

The heat of the dissolving of anhydrous $CuSO_4$ you should be calculated using the experimental data according to the equation:

$$\mathbf{Q = (m_1c + m_2c + K) \cdot \Delta T},$$

where **Q** is the heat of dissolution, J; $\mathbf{m_1}$ is the mass of H_2O, g; $\mathbf{m_2}$ is the mass of $CuSO_4$, g; **c** is the heat capacity of the solution, $J{\cdot}K^{-1}{\cdot}g^{-1}$. The heat capacities of dilute solutions of inorganic salts in water are practically the same and slightly differ from the heat capacity of water: $c = 4.18\ J{\cdot}K^{-1}{\cdot}g^{-1}$; **K** — calorimeter constant, $J{\cdot}K^{-1}$ ($29.96\ J{\cdot}K^{-1}$).

The obtained value of the heat of the dissolving should be converted into the mass value — per 1 g of the salt:

$$q = \frac{Q}{m(CuSO_4)}$$

Using the presented data, calculate the heat of the dissolving:

Q = ________________________________ = _______ **J**;

$q = \frac{\qquad}{\qquad} = \qquad\qquad J \cdot g^{-1}.$

Conclusion: according to the calculated value of the heat of the dissolving **q** = _________ $\mathbf{J{\cdot}g^{-1}}$ the reaction is ____________________.

exo- or endothermic

Репозиторий ВГМУ

LABORATORY WORK 6. DETERMINATION OF THE SPECIFIC HEAT OF HYDRATION

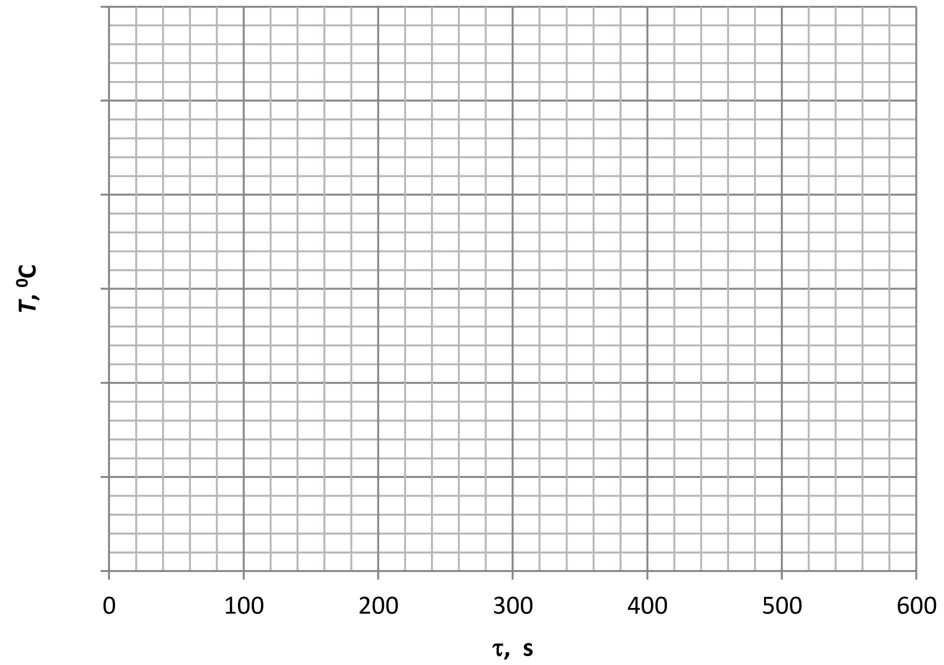
Objective: to determine the heat of hydration of $CuSO_4 \cdot 5H_2O$.

Reactants: distilled water (ρ(solution) = 1 g·ml^{-1}), 3 g of $CuSO_4 \cdot H_2O$.

Labware: educational-laboratory complex “Chemistry”, computer with the program elsms2.exe, glass cup 150 cm^3, graduated cylinder, syringe.

The task

1. Switch on the educational-laboratory complex “Chemistry” and set the necessary settings in accordance with its instructions.
2. Add 100 cm^3 of distilled water to the measuring glass using a graduated cylinder. Put the glass in the special place on the calorimeter and close the cover with the temperature sensor fixed in it. ***Caution !!!*** All holes in the cover must be tightly closed with stoppers.
3. Put 3 g of $CuSO_4 \cdot 5H_2O$ into the syringe. Insert the syringe into the hole of the calorimeter cover. Wait until the temperature of the calorimetric liquid in the glass will become stable for 5 minutes.
4. Start the recording of data in the memory bank in accordance with the instructions for working with the complex “Chemistry”. Wait until the controller records 10 readings in the cells.
5. Then ***quickly (!!!)*** pour out $CuSO_4 \cdot 5H_2O$ from the test syringe into the water through the hole in the calorimeter box. Make measurements until all the cells in the memory bank (100) will be recorded.
6. Pour the contents of the beaker into the waste container. Wash the glass with running water, and then rinse with distilled water.



The temperature during the dissolving of $CuSO_4 \cdot 5H_2O$ in water

7. Based on the data obtained in the experiment determine the actual temperature change during the dissolving of $CuSO_4 \cdot 5H_2O$. Draw the graph of the dependence of temperature on time.

Calculations

The heat of the dissolving of $CuSO_4 \cdot 5H_2O$ should be calculated using the experimental data according to theequation:

$$\mathbf{Q = (m_1c + m_2c + K) \cdot \Delta T},$$

where **Q** is the heat of the dissolving, J; $\mathbf{m_1}$ is the mass of H_2O, g; $\mathbf{m_2}$ is the mass of $CuSO_4 \cdot 5H_2O$, g; **c** is the heat capacity of the solution, $J \cdot K^{-1} \cdot g^{-1}$. The heat capacities of dilute solutions of inorganic salts in water are practically the same and slightly differ from the heat capacity of water: $c = 4.18\ J \cdot K^{-1} \cdot g^{-1}$; **K** — calorimeter constant, $J \cdot K^{-1}$ (29,96 $J \cdot K^{-1}$).

The obtained value of the heat of the dissolving should be converted into the mass value — per 1 g of $CuSO_4 \cdot 5H_2O$:

$$q = \frac{Q}{m(CuSO_4 \cdot H_2O)}$$

Using the presented data, calculate the heat of the dissolving:

Q = ________________________________ = _______ **J**;

$$q = \frac{\qquad}{\qquad} = \qquad\qquad J \cdot g^{-1}.$$

The difference in the heats of the dissolving of anhydrous salt and salt hydrate is equal to the heat of the hydration. Calculate the heat of the hydration using the formula:

$$\mathbf{q}_{hydr} = \mathbf{q}\ (CuSO_4) - \mathbf{q}\ (CuSO_4 \cdot 5H_2O)$$

$\mathbf{q}_{hydr}$ =____________________________________**J/g**.

Conclusion: according to the calculated value of the heat of the hydration **q** = _________ $\mathbf{J \cdot g^{-1}}$ that process is ____________________.

exo- or endothermic

Репозиторий ВГМУ

LABORATORY WORK 7. DETERMINATION OF THE MELTING POINTS OF DIPHENYLAMINE AND NAPHTHALENE. THE CALCULATION OF THE ENTROPY OF MELTING

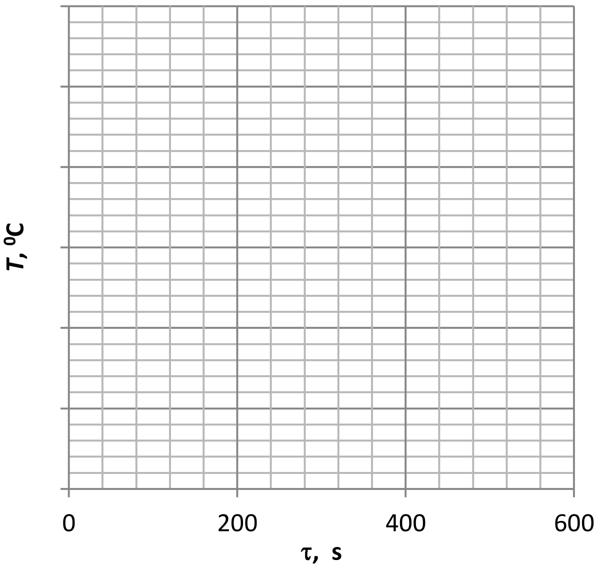
Objective: to determine the melting points of diphenylamine and naphthalene by the thermal analysis method and to calculate the entropy of the phase transition.

Reactants: ampoules with diphenylamine and naphthalene.

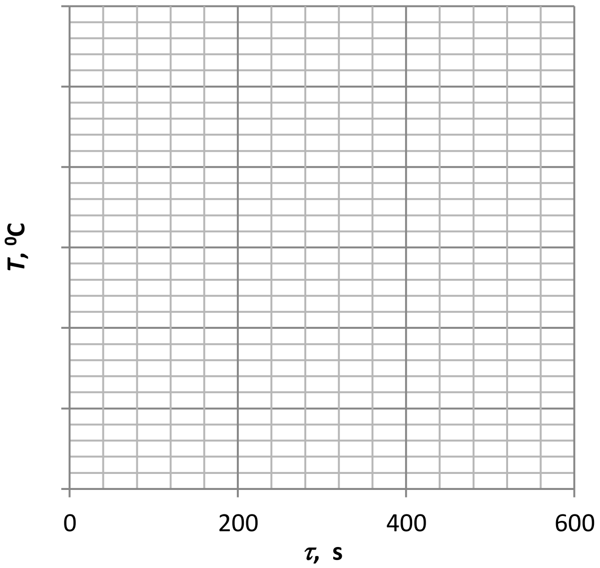
Labware: educational-laboratory complex “Chemistry”, computer with the program elsms2.exe.

The task

1. Switch on the educational-laboratory complex “Chemistry” and set the necessary settings in accordance with its instructions.
2. Place the ampoules containing pure diphenylamine (No. 10) and naphthalene (No. 0) into the “HEAT” sockets 5 and 6, respectively. Carry out the heating to the temperature of 90–95 °C. Fix the temperature every 10 seconds. To fix and process the data, use the elsms2.exe program.
3. Based on the data obtained in the experiment determine the melting points of diphenylamine and naphthalene.
4. Draw the graphs of the dependence of the temperature on time:



The temperature during the melting of naphthalene



The temperature during the melting of diphenylamine

5. Analyze the obtained heating curves and determine the melting points of diphenylamine and naphthalene:

T_m (naphthalene) = °C = K;

T_m (diphenylamine) = °C = K.

Репозиторий БГМУ

6. Calculate the entropy of melting according to the formula:

$$\Delta_m S = \frac{\Delta_m H}{T_m},$$

where Δ_m**H** is the molar enthalpy of melting: for naphthalene it is 19.29 kJ·mol^{-1}, for diphenylamine it is 17.86 kJ·mol^{-1}; **T** is the temperature of melting, K.

$$\Delta_m S(\text{naphthalene}) = \frac{\qquad\qquad}{} = \qquad\qquad \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1};$$

$$\Delta_m S(\text{diphenylamine}) = \frac{\qquad\qquad}{} = \qquad\qquad \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}.$$

Conclusion: according to the experimental data I calculated the entropies of melting for naphthalene $\Delta_m S$ = _________ **J·K^{-1}·mol^{-1}** and diphenylamine $\Delta_m S$ = ______________ **J·K^{-1}·mol^{-1}.**

репозиторий БГМУ

LABORATORY WORK 8. CONSTRUCTION OF THE T-X PHASE DIAGRAM OF MELTING FOR THE BINARY SYSTEM DIPHENYLAMINE-NAPHTHALENE

Objective: to construct the melting diagram of the diphenylamine-naphthalene system by the method of thermal analysis and to analyze it.

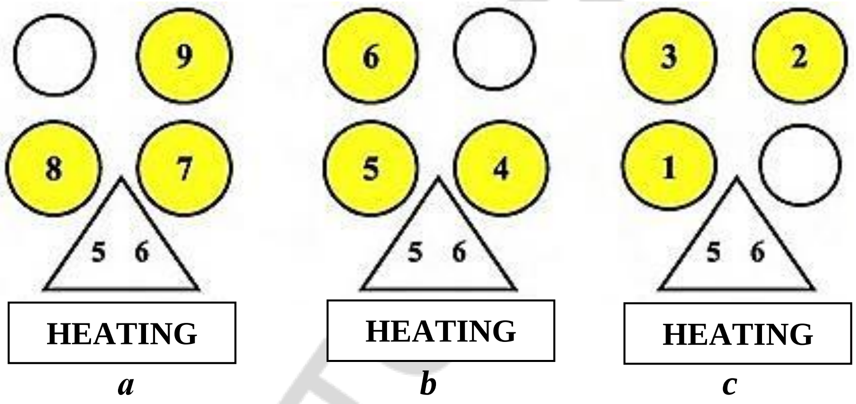
Reactants: 9 ampoules with diphenylamine and naphthalene taken at different proportions (from 10 % to 90 %).

Labware: educational-laboratory complex “Chemistry”, computer with the program elsms2.exe.

The task

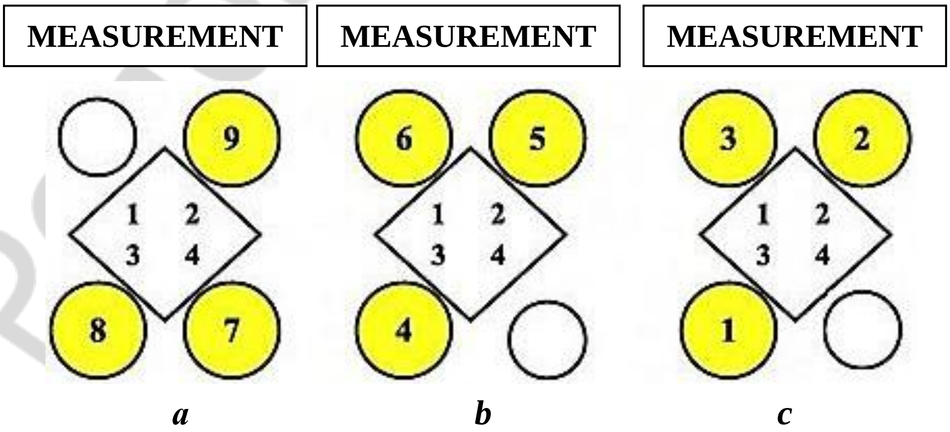
1. Switch on the educational-laboratory complex “Chemistry” and set the necessary settings in accordance with its instructions.

2. Place the ampoules No. 7–9 containing mixtures of diphenylamine and naphthalene into the “HEAT” sockets according the figure 1, *a, b*. Carry out the heating to the temperature of 90–95 °C.



Location of ampoules in nests “HEATING” in each of the experiments

3. When the heating is completed, you should hold it for at least 5 minutes. Then move the ampoules to the “MEASUREMENT” nests (according to the scheme in figure 2, *a, b*).



Location of ampoules in nests “MEASUREMENT” in each of the experiments

Репозиторий БГТУ

4. Then the ampoules are cooled down. You should fix the temperature every 20 seconds. To fix and process the data, use the elsms2.exe program.

5. After the completion of the measurements, the ampoules No. 7–9 are placed in the “STORAGE” slot group.

6. Repeat the experiment for ampoules No. 4–6, and then for ampoules No. 1–3 according to the scheme in Figures 1c and 2c, heat them to 90–95 ° C.

7. The values for ampoules No.0 and No. 10 are taken from the laboratory work 7.

All the results should be written down in the table:

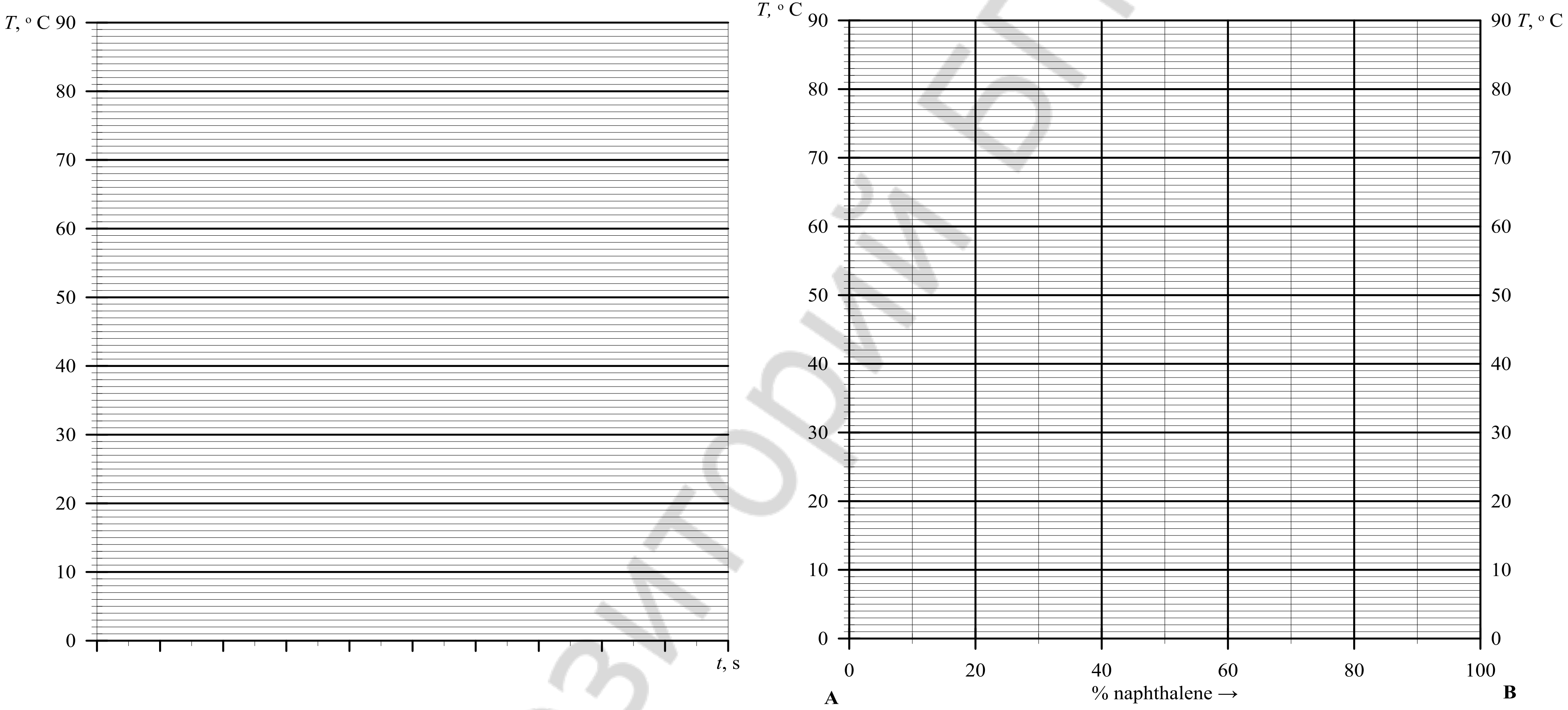
Ampoule	**Content of naphthalene, %**	**Content of diphenylamine, %**	**T_1**	**T_2**
0	100	0		-
1	90	10		
2	80	20		
3	70	30		
4	60	40		
5	50	50		
6	40	60		
7	30	70		
8	20	80		
9	10	90		
10	0	100		-

8. Based on the data obtained in the experiments construct the cooling curve (figure 3, *a*) and the phase diagram (figure 3, *b*) of the diphenylamine-naphthalene system (figure 3).

Conclusion: according to the experimental data I constructed the cooling curves and the phase diagram of the diphenylamine-naphthalene system:

- melting temperatures of diphenylamine and naphthalene are _______ °C and ________ °C respectively;
- eutectic temperature of the diphenylamine-naphthalene system is _______ °C;
- under the line of eutectic temperature the system consist of ________ (quantity) phase(-s) and _________components, therefore according to the Gibbs’ phase rule the number of the degrees of freedom is **C** = __________;
- above the liquidus line the system consist of ________ (quantity) phase(-s) and _________ components, therefore according to the Gibbs’ phase rule the number of the degrees of freedom is **C** = __________;
- between the liquidus and solidus lines the system consist of ________ (quantity) phase(-s) and _________ components, therefore according the Gibbs’ phase rule the number of the degrees of freedom is **C** = __________.

Репозиторий БГМУ



a

b

Cooling curves (*a*) and phase diagram (*b*) of the diphenylamine-naphthalene system

Репозиторий БГМУ

LABORATORY WORK 9. DETERMINATION OF THE DISTRIBUTION COEFFICIENT OF ACETIC ACID BETWEEN THE ORGANIC SOLVENT AND WATER

Objective: to study the distribution of acetic acid between two immiscible liquids (water and organic solvents: diethyl ether, toluene, xylene, etc.).

Reactants: water solutions of acetic acid with a molar concentration of 0.2, 0.4 and 0.8 mol/L, water solutions of sodium hydroxide with a molar concentration of 0.1–0.2 mol/L; organic solvents — diethyl ether, toluene, xylene, carbon tetrachloride, etc., phenolphthalein.

Labware: three tripods, three dividing funnels per 100–200 ml, graduated cylinders 50 ml or Mohr’s pipettes 25 ml, burettes 25 ml, three flasks 50–100 ml.

Instruction

Pour 25 ml of acetic acid water solution of different concentrations (0.2M, 0.4M, 0.8M) in each of the three dividing funnels. Add 25 ml of an organic solvent to each of them. Close the funnel and shake it carefully for 1–2 minutes. Then fix each funnel in its tripod and wait until the liquids will separate.

Still you wait for complete separation of liquids in funnels, titrate initial solutions of acetic acid. Use 5 ml of each solution, and dilute it by 20 ml of water. Titrate each solution with sodium hydroxide solution in the presence of phenolphthalein.

After the complete separation, pour out the lower layer of liquid (water solution) from each funnel into the corresponding glass. Keep 1 ml of watewr solution in each funnel to avoid the contamination by organic solution.

Titrate water solutions after the extraction in the same manner as the initial solutions.

Calculations:

1. Calculate the concentration of acetic acid before and after the extraction for three initial concentrations using the following formula:

$$\mathbf{C(CH_3COOH) = \frac{C(NaOH) \cdot V(NaOH)}{V(CH_3COOH)} \cdot 5},$$

2. Calculate the equilibrium concentration of acetic acid in the organic solvent using the following formula (it works when the volumes of water and organic solvents are equal to each other).

$$\mathbf{C^{organic}(CH_3COOH) = C^{water}_{initial}(CH_3COOH) - C^{water}_{final}(CH_3COOH)},$$

3. Calculate the coefficient of distribution of acetic acid between organic solvent and water:

$$\mathbf{К = \frac{C^{organic}(CH_3COOH)}{C^{water}_{final}(CH_3COOH)}},$$

Репозиторий БГМУ

Fill in the table:

№	**Before the extraction**		**After the extraction**			**К**
	$C^{water}_{initial}$ (CH_3COOH), mol/L	**V(NaOH), ml**	**V(NaOH), ml**	**C^{water}_{final} (CH_3COOH), mol/L**	**$C^{organic}$ (CH_3COOH), mol/L**	
1						
2						
3						

Conclusion: *“The coefficient of distribution between an organic solvent and water for acetic acid is equal to ______________, and it is ____________________ at a given temperature”.*

Репозиторий БГМУ

LABORATORY WORK 10. STUDY OF THE KINETICS OF THE REACTION BETWEEN ETHYL ACETATE AND ALKALI (SAPONIFICATION) WITH THE HELP OF POTENTIOMETRY

The aim of the work: to calculate the activation energy of ethyl acetate reaction with alkali.

The tasks:

1. To conduct the reaction between alkali and the excess of ethyl acetate at different temperatures.
2. To estimate the values of a rate constant at different temperatures.
3. To calculate the energy of activation using the values of a rate constant at different temperatures.

Equipment and reactants: laboratory complex “Chemistry” in the following construction: the controller; the thermostat; glass and silver chloride electrodes; glasses; the mixer; the thermometer; 0.01 M NaOH solution, ethyl acetate; distilled water; labware.

Instruction:

1. Fill the thermostat by distilled water and set the glass with 100 ml of previously prepared 0.01 M NaOH solution. Close the thermostat and set glass and silver chloride electrodes, as well as the thermometer.
2. Turn on the controller and run the program on PC.
3. Set the thermostat to maintain a certain temperature (wait until it will be changed).
4. Take a certain volume of ethyl acetate (a big excess) and pour it in the cell in the cap of the thermostat.
5. Stop mixing the solution and start the measurement of EMF (E) during 10 minutes with a step of 1 minute.
6. Fill in the table with your data:

№ of experiment	**T, K**	**T^{-1}, K^{-1}**	**tgα**	**b_0**	**k**	**lnk**
1						
2						
3						

Build the graph of the dependence between E and τ. Using the equations given below you need to find the rate constant k, and its natural logarithm (lnk).

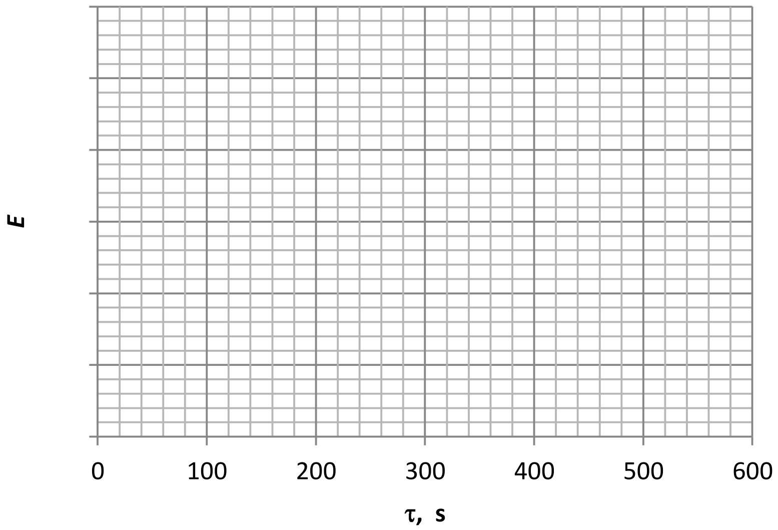
$$E_\tau = E_0 + \tau \cdot \mathrm{tg}\alpha,$$

E_τ is an EMF in a certain moment in time (τ); **E_0** is an EMF in the beginning of the experiment; **tgα** is the slope of the dependence between E and τ; **τ** is the time, sec.

Репозиторий БГМУ

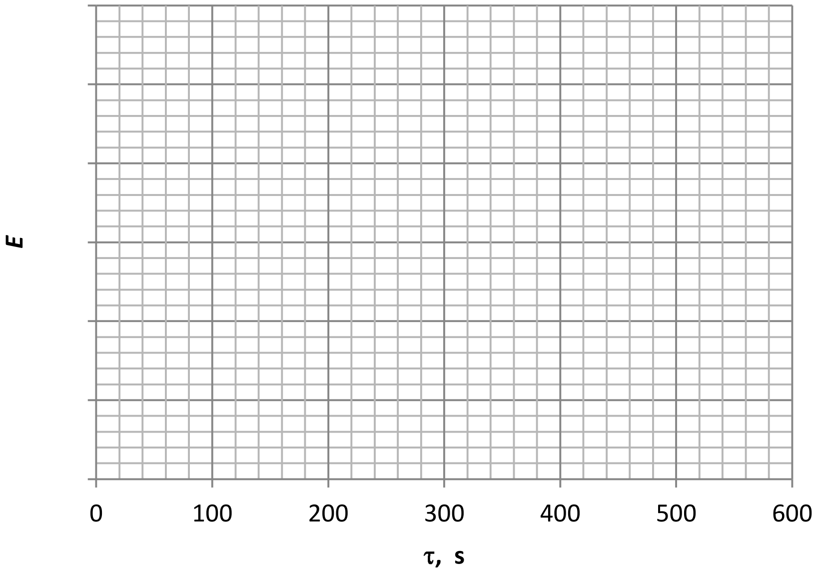
$$\mathbf{tg\alpha = k \cdot b_0 \cdot C_{ester}},$$

k is the rate constant; $\mathbf{b_0}$ is the coefficient that is equal to (RT)/F; $\mathbf{C_{estr}}$ is the concentration of the eater (9.867 mol/L); **R** is the gas constant (8.314 J/(mol·K)); **F** is the Faraday's constant (96485.3383(83) Кл·моль$^{-1}$); **T** is the temperature, K.

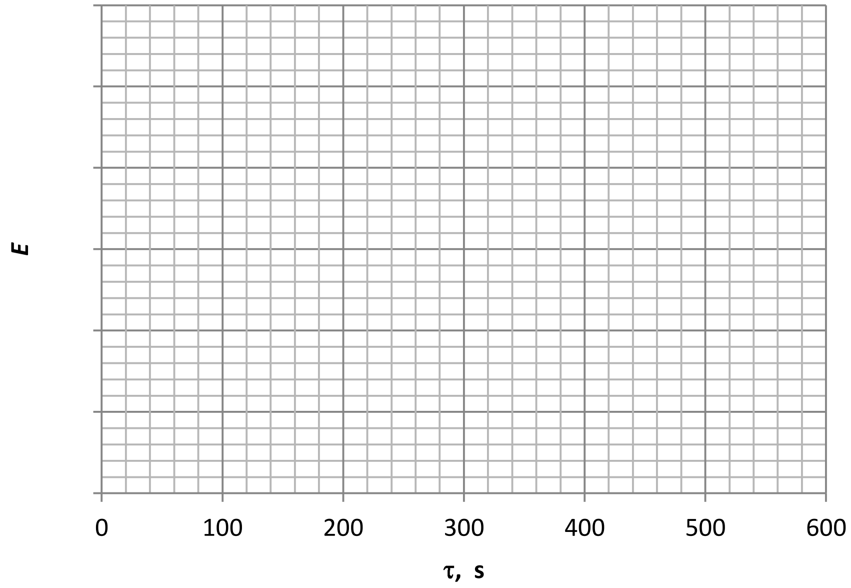


The EMF during the saponification reaction at ____ °C

7. Repeat the experiment two more times at different temperatures.

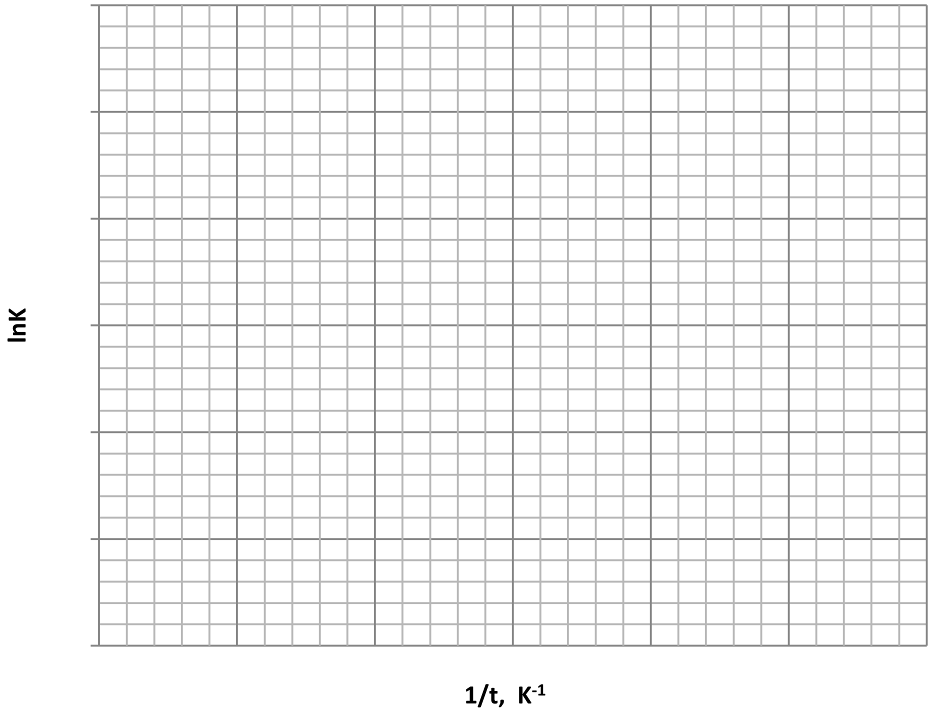


The EMF during the saponification reaction at ____ °C



The EMF during the saponification reaction at ____ °C

8. Build the Arrhenius plot in the coordinates: lnk — T^{-1} and find the slope of the dependence. Calculate the energy of activation: $\mathbf{E_a = \pm tg\alpha \cdot R}$ = ___________________ = ____________________________.



Dependence between the natural logarithm of the rate constant and one over temperature

Conclusion: *"The energy of activation for the reaction between ethyl acetate and alkali (saponification) is equal to ____________".*

LABORATORY WORK 11. STUDY OF THE EFFECT OF CATALYST ON THE RATE OF CHEMICAL REACTION

Title: the influence of a catalyst on the rate of chemical reaction.

The aim of the work: to study a catalytic influence of certain ions on the rate of chemical reactions.

Experiment 1. *Catalytic influence of* NO_3^- *ions on the reaction of potassium permanganate reduction by atomic hydrogen.*

Atomic hydrogen is produced in the reaction between zinc and dilute sulfuric acid. Then that atomic hydrogen reacts with $KMnO_4$:

$$2KMnO_4 + 10H + 3H_2SO_4 = 2MnSO_4 + K_2SO_4 + 8H_2O$$

Taken together:

$$2KMnO_4 + 5Zn + 8H_2SO_4 = 5ZnSO_4 + K_2SO_4 + 2MnSO_4 + 8H_2O$$

This reaction is slow. If you add $NaNO_3$, it becomes much faster because of the two fast reactions with nitrate anions:

$$NaNO_3 + 2H = NaNO_2 + H_2O$$

$$5NaNO_2 + 2KMnO_4 + 3H_2SO_4 = 5NaNO_3 + 2MnSO_4 + K_2SO_4 + 3H_2O$$

In the first reaction nitrate anions are reduced to nitrite anions. In the second reaction nitrites are oxidized by potassium permanganate up to nitrates. That is how nitrates are regenerated in the second reaction.

Instructions. Pour 3 ml of acidic $KMnO_4$ solution in three tubes. Add the reactants listed below in the respective tubes. Fix the time needed to change the color of the initial solution (from violet to colorless).

Tube 1: Zn (dust of granules). Time: ______________________
Tube 2: Zn and 3–5 drops of $NaNO_3$. Time: ______________________
Tube 3: 3–5 drops of $NaNO_2$ solution. Time: ______________________

Notice that in the last tube the process is finished almost immediately.

Experiment 2. *Catalytic influence of* Mn^{2+} *cations on the reaction of potassium permanganate reduction by oxalic acid in the acidic medium (autocatalysis).*

Reaction between $KMnO_4$ and $H_2C_2O_4$ (in the presence of H_2SO_4) at room temperature is very slow. Manganese (II) cations are both the products of this reaction and the catalysts for this process:

$$5H_2C_2O_4 + 2KMnO_4 + 3H_2SO_4 = 2MnSO_4 + K_2SO_4 + 10CO_2 + 8H_2O$$

Instructions. Pour 2 ml of $H_2C_2O_4$ and acidic $KMnO_4$ solutions in each of the two tubes. Add several drops of Mn^{2+} containing salt solution. Fix the time needed to change the color of the initial solution (from violet to colorless).

Tube 1: without Mn^{2+}. Time: ______________________
Tube 2: with Mn^{2+}. Time: ______________________

Conclusion: "*Catalyst changes the pathway of a process, but it does not* ____".

Репозиторий БГМУ

MAIN SOURCES OF LITERATURE

1. *Химическая* термодинамика для провизоров : учеб.-метод. пособие / Е. В. Барковский [и др.]. Минск : БГМУ, 2016. 212 с.

2. *Барковский, Е. В*. Общая химия : учеб. пособие / Е. В. Барковский, С. В. Ткачёв, Л. Г. Петрушенко. Минск : Вышэйшая школа, 2013. 639 с.

3. *Медицинская* химия = Medical Chemistry : учеб. / В. О. Калибабчук [и др.]. 3-е изд., испр. Киев : Медицина, 2015. 224 с.

4. *Atkins, P.* Atkins' Physical Chemistry / P. Atkins, J. de Paula. 10th ed. Oxford University Press, 2014. 500 p.

5. *Chandra, S.* Energy, Entropy and Engiens : An Introduction to Thermodynamics / S. Chandra. Wiley, 2016. 400 p.

Репозиторий БГМУ

CONTENTS

Репозиторий БГМУ

Учебное издание

Хрусталёв Владислав Викторович
Контява Ольга Викторовна
Казюлевич Светлана Ричардовна

ХИМИЧЕСКАЯ ТЕРМОДИНАМИКА И КИНЕТИКА ДЛЯ ПРОВИЗОРОВ

CHEMICAL THERMODYNAMICS AND KINETICS FOR PHARMACISTS

Практикум

На английском языке

Ответственный за выпуск В. В. Хрусталёв
Переводчик В. В. Хрусталёв
Компьютерный набор В. В. Хрусталёва
Компьютерная верстка Н. М. Федорцовой

Подписано в печать 21.06.17. Формат 60×84/8. Бумага писчая «Снегурочка».
Ризография. Гарнитура «Times».
Усл. печ. л. 13,48. Уч.-изд. л. 6,43. Тираж 26 экз. Заказ 459.

Издатель и полиграфическое исполнение: учреждение образования
«Белорусский государственный медицинский университет».
Свидетельство о государственной регистрации издателя, изготовителя,
распространителя печатных изданий № 1/187 от 18.02.2014.
Ул. Ленинградская, 6, 220006, Минск.

Репозиторий БГМУ