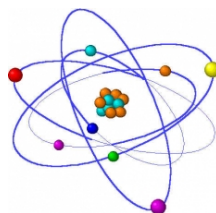


Kaplaushenko A.G., Iurchenko I.A.,  
Varinskiy B.A., Shcherbak M.A., Kucheryavyi Yu.N., Samelyuk Yu.G.



# **THE STUDY ABOUT SOLUTIONS. COLLIGATIVE PROPERTIES OF SOLUTIONS**

*Teaching and methodical manual  
for foreign students of Zaporozhye State Medical University*



Zaporozhye, 2015

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**UDC 541.1(075.8)**

**S90**

It is recommended by Methodic commission on chemical sciences as a textbook for students of medical faculty (Minutes №3, 27.11.2014)

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## PREFACE

Medicinal Chemistry is one of the most rapidly developing areas within the discipline of Chemistry, both globally and locally. It is the study of the design, biochemical effects, regulatory and ethical aspects of drugs for the treatment of disease.

The aim of this discipline is to produce graduates with an appropriate background in biology and pharmacology, built upon a strong chemistry foundation.

Methodical recommendation of Medicinal Chemistry is designed to equip students with strong grounding in biological and chemical technique which is relevant to the pharmaceutical world.

The discipline gives an in-depth coverage of the chemical techniques required and relates these to the relevant pharmacology, anatomy, biochemistry and molecular biology.

The whole course of Medical chemistry which consists of ten topics is studied by students-physicians during the first year. Lecturer staff of department has prepared an educational and methodical recommendation in which the theoretical material is stated in the concise and available form.

The distribution of material on each of ten topics that are studied is set according to training program, the thematic plan of lectures and practical training.

The material of each topic is stated in such way that performance of practical work and the solution of situational tasks are preceded by theoretical part in which questions of medicine and biological value and also connection with other disciplines (biological chemistry, normal physiology, pathophysiology and others) are included.

Offered laboratory works and situational tasks will give students the chance to understand theoretical material fully and to use this knowledge in practice.

The experience of teaching medical chemistry shows that it is not always possible to coordinate an order of laboratory works realization with sequence of lecture course statement. That is why students usually have to prepare for practical work performance independently before the lesson. Therefore the theoretical part (in which the necessary volume of knowledge for conscious performance of experiment is given) precedes to each section of these Methodical recommendations.

Increasing of level of seminar and laboratory works is reached by use of such forms of occupations which open and consolidate theoretical knowledge, train scientific thinking, develop creative initiative and impart skills of handling devices and chemicals, chemical ware.

The structures, figures and schemes are clear and easy to follow and color is used well, highlighting main points without being distracting.

Chapters are helpfully signposted throughout, informing the reader how topics are related, which is especially important in such a multidisciplinary subject.

Topics are also presented clearly and with a logical progression culminating in the main points, questions and reading sections at the beginning of each chapter.

An assortment of case studies is provided and the authors work through each one in great detail, giving an overall perspective on the science.

Finally, very useful and informative appendices and a glossary are provided together with a comprehensive index that is good enough to rival any search engine!

There are many books that describe medicinal chemistry and its uses, but these methodological recommendations present medicinal chemistry and its related topics in a clear, informative and interesting way that really demonstrates the application and impact of this fundamental subject in society.

## INTRODUCTION

**Purpose:** to form a system of knowledge of students about the solutions, their classification, ways to express concentrations, properties; Learn how to use the laws of Raoul, Vant-Goff for the calculation of relevant parameters of diluted solutions, including biological fluids

**Targets:**

- to define solutions, their classification and properties;
- to master the theoretical material on collegiate properties of diluted solutions;
- to learn how to prepare solutions and to carry out appropriate calculations;
- to learn how to use formulas and use them to solve situational problems on training;
- to get practical skills in experimental work with solutions and elementary cryometric.
- to master the methods of determining the molecular weight of cryoscopic method;
- to learn how to assess the reliability of the results;
- to learn a test material on the topic.

*The student should know:*

- classification of solutions;
- the theory that describes the process of dissolution;
- factors influencing solubility of gases and solids;
- formula for calculating the concentrations of solution;
- the law of Raoul and collegiate properties solutions, Vant-Hoff-Pfefera;
- field of application solubility and solutions in medicine.

*The student should be able to:*

- prepare solutions with specified concentration;

-play math expressions that bind the parameters of a solution and its components;

-practically use skills calculations (mass, volume, density, concentration) solution;

-play the phrase and the mathematical expressions of the laws that describe the colligative properties for parameters calculation solutions (boiling and freezing temperature, osmotic pressure);

- determine molecular weight substances cryoscopic method;

- to determine the osmotic pressure of solutions;

- to determine the reliability of the measurements and calculations.



## CONCISE THEORETICAL MATERIAL

### 1 Introduction. Basic concepts and definitions

Solutions play an important role in animate and inanimate nature, as well as science and technology.

Physiological processes in animals and in plants, all kinds of industrial processes, the formation of sedimentary rocks and the like for the most part taking place in solutions. The ubiquity of solutions is due, in particular, and that the process of dissolution of spontaneous, that is, accompanied by a decline of the Gibbs energy. So find a pure substance in the wild, or cook them in the laboratory, it is extremely difficult.

For a long period of development of the chemistry of the main objects of study substance permanent membership from some rational and strictly fixed stoichiometric ratio of components that constitute the so-called "privilege of discretion" in chemistry. Phase, not obeying the laws and have variable stoichiometric composition (including solutions) were excluded from consideration under the classical chemistry.

The rapid development of chemistry in the late 19th and early 20th century, especially the teachings on chemical equilibrium, theory of solutions (Gibbs, Vant-Goff, Le Chatelier, D.I. Mendeleev, D.P. Kononov, N.S. Kurnakov); the most common case of chemical interaction — continuity of composition changes depending on conditions. And discreteness of interaction, manifested in the formation of phases of permanent membership, is an example, albeit a very common.

The study of the solutions currently has a very special meaning because the patterns of their formation and properties, in a sense, applied to examine the nature of chemical interaction with common positions.

There are several formulations of solutions:

- Solutions are homogeneous thermodynamically stable systems consisting of 2 or more substances, the ratio of which is determined by their mutual solubility.

- A solution is a homogeneous system, consisting of two or more components: solvents, soluble substances and the products of their interaction.

- Solutions are homogeneous system of variable composition, are in a State of chemical equilibrium.

Solutions is at least two-component system. Usually the solvent considered component, which in this context is the same whether the resulting solution.

This definition substantially only when the dissolved substances are found in a different aggregate State (for example, dissolution of salts and gases in water to form liquid solutions). If the components that make up the solution, are the same whether the notion of the solvent and the solute become somewhat conditional. In this case, the solvent is referred to as the substance which by mass or volume.

## **2. Theory of education solutions.**

In the course of the development of science, two points of view were expressed on the nature of the solutions:

Physical theory (S. Arrhenius, Ostwald, Vant-Goff) considered the process of dissolution as a mechanical process of equal distribution of solute particles throughout the volume of the solvent.

The solvent was taken for indifferent environment. In other words, solutions were considered as a mechanical mixture.

Using physical theory able to explain some of the properties of diluted solutions (increasing the boiling point, lower freezing temperature, vapor pressure over water, etc.), i.e. properties that depend on their nature.

At the same time, the physical theory could not explain the properties of concentrated solutions.

Chemical theory (D.I. Mendeleev, I.A. Kablukov, N.S. Kurnakov, 1887) considers solutions, as a system, formed by particles of the solute and the solvent, volatile chemical compounds that are formed between them.

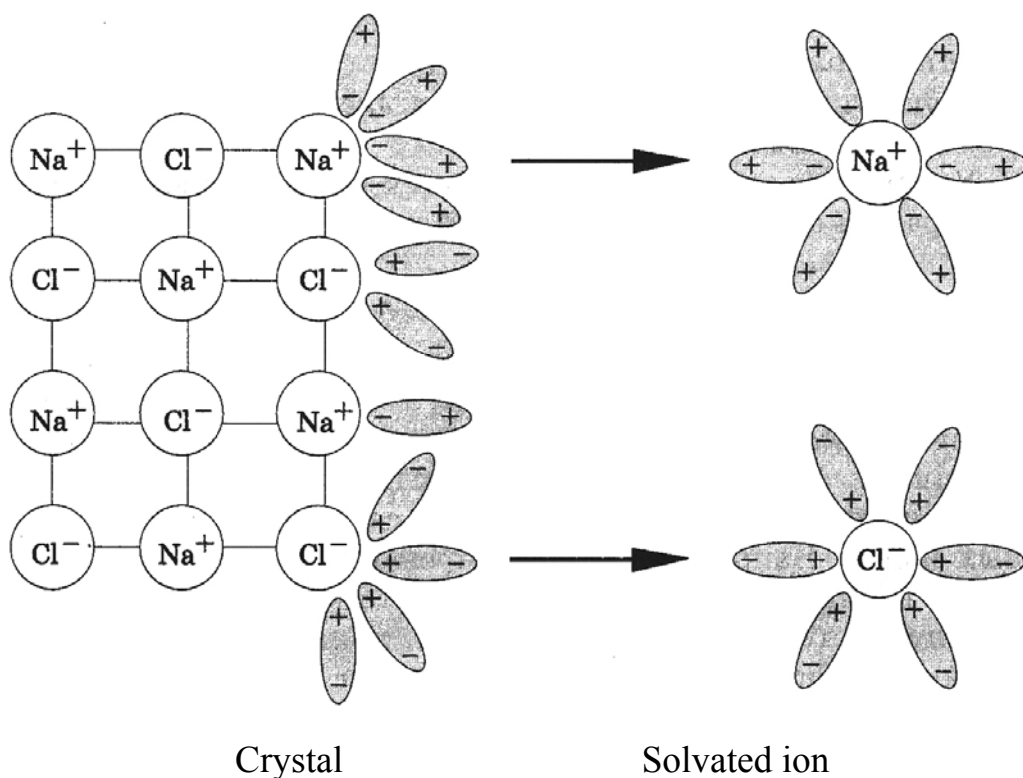
According to this theory of solute particles interact with the molecules of the solvent to form unstable compounds of variable composition called solvate (non-aqueous solvent) or hydrates (solvates), the solvent is water. Hydrates (solvate) do not occur at the expense of fundamental chemical bonds, but due to Van der Waals forces or by hydrogen bond. Because the energy of these linkages is small, the resulting compounds are fragile.

Dissolved substances with Ionic structure of solvent molecules are held around the ion by ion-dipole interaction.

Dissolved substances with the molecular structure solvates(hydrates) are produced by Dipole-Dipole interaction.

The dipoles of dissolved substances can be permanent (for substances with polar molecules) or induced, i.e. induced action of the solvent (for substances with nonpolar molecules). The cause of their formation is the hydrogen bond, as well as the interaction between a number of polar molecules.

For example, the hydrate shell, arising from the dissolution of NaCl (KCl) can be visualized as follows:



Between ions and solvent with a few extra ones thrown ion-dipole (interaction) that play a large role in the dissolution. The degree of hydration of ions, i.e. the number of water molecules associated with different ions depends on the nature of these ions.

For example:  $\text{Li}^+$  - 13 moles  
 $\text{Na}^+$  - 8 moles  
 $\text{Mg}^{2+}$  - 14 moles  
 $\text{Cl}^-$  - 3 moles  
 $\text{Br}^-$  moles

Cations hydration the more, the more their radius. Anions are less hydration than cations.

The ion-dipole, and Dipole-Dipole interaction has an electrostatic interaction of donor-acceptor mechanism (cations hydration), as well as hydrogen bond (hydration anions).

Confirmation of the theory of D. I. Mendeleev were the following factors:

And you can discover hydrates some direct supervision (copper sulfate (II)) is the anhydrous is colorless, but in solution becomes blue;

b) many hydrates can be seen in crystalline form is the so called brine rejection ( $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ;  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ;  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ , etc.);

In dissolution is often accompanied by the heat effect and change of physical properties of fluids (for example, the concentration is the change in volume).

This shows that the solvent does not indifferent against the dissolved substance. However, it should be noted that, because the solutions are to a certain extent, properties and mechanical mixtures and chemicals, both theories (physical and chemical) to exclude each other.

The modern theory of dissolving combines physical and chemical point of view and allows you to define the process of dissolution, as complex physical-chemical process consists of two stages:

a) stage of hydration (solvation) at which water molecules surround the molecule, forming hydrates and solvates.

Proof of this is the fact that many of the hydrates are crystallized. These are called brine rejection:  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ .  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ , etc. included in their composition of water is called crystallization.

b) dissolution phase, during which the diffusion of hydrates (solvates) in various parts of the system, making it uniform.

Stage of hydration of exothermic (which is consistent with the principle of the lowest energy) and the stage of the dissolution of endothermic. The thermal effect of the process is the sum of:  $Q_{\text{total}} = Q_{\text{hydration}} + Q_{\text{dissolving}}$

$$\Delta H_{\text{total}} = \Delta H_{\text{hydration}} + \Delta H_{\text{dissolving}}$$

1. If  $\Delta H_{\text{hydration}} > \Delta H_{\text{dissolving}}$ , so heat is generated after dissolving these substances in water.

For example: dilution of sulfuric acid in water.

2. If  $\Delta H_{\text{hydration}} < \Delta H_{\text{dissolving}}$ , so heat is devoured after dissolving these substances in water.

For example: dissolving sodium thiosulfate in water, dissolving sucrose in water.

3. If  $\Delta H_{\text{hydration}} \approx \Delta H_{\text{dissolving}}$ , so the dissolution of these substances does not depend on temperature.

For example: dissolution of sodium chloride in water.

Thus, the solutions are physical-chemical systems are intermediate between chemical and mechanical mixtures.

As the chemicals solutions:

1. uniform.
2. characterized by thermal phenomena.
3. a rebuttal (reduced when mixing liquids).

As a mechanical mixture of solutions:

- 1 Not subject to the law of definite proportions.
- 2 can be divided into parts.

### **3. Water solubility**

Solubility is the ability of a substance to dissolve in a solvent.

Quantification of solubility is expressed by the number of ounces that can be dissolved in 100 g solvent at a given temperature. In practice, the solubility of solid substances solubility coefficient =  $MV_{\text{express-VA}} \cdot 100/m$ . The solubility in water 10 g of substance;

- a) good soluble in 100 g of water dissolves more than 10 g of substance;
- b) only slightly soluble in 100 g of water is less than 1 g of substance;
- in) is almost insoluble in 100 g of water is less than 0.1 g of substance.

The solubility of a substance is a measure of the concentration of a saturated solution. Solutions are unsaturated, saturated, and overly saturated.

Called unsaturated solution, which can dissolve substance at a given temperature.

The solution is called a saturated if it is in equilibrium with the dissolved substance, i.e. in a saturated solution contains the limit under these conditions

the content of substances. It is a dynamic equilibrium system in which the speed of dissolution equals the rate of crystallization (precipitation of solute from a solution).

Supersaturated solution containing substance called more than that is determined by its solubility.

These solutions are in special circumstances, they are very unstable, quickly become saturated.

Solubility depends on:

1. the nature of the substance and the solvent.

This relationship defines the rule of thumb is "like dissolves like", that is to dissolve Ionic compounds and Covalent polar molecules, it is better to use the polar solvents (e.g., water), nonpolar substance is dissolve in polar and low-polarity solvents (benzene, petroleum ether, chloroform, etc.).

2. the temperature.

At the same time:

a) solubility of solids and liquids with a temperature increase typically increases (there may be exceptions, such as NaCl,  $\text{AlCl}_3$  is almost unchanged,  $\text{CaC}_2\text{O}_4$ ,  $\text{Li}_2\text{CO}_3$ ,  $\text{CaCl}_2$  etc.-decreases;

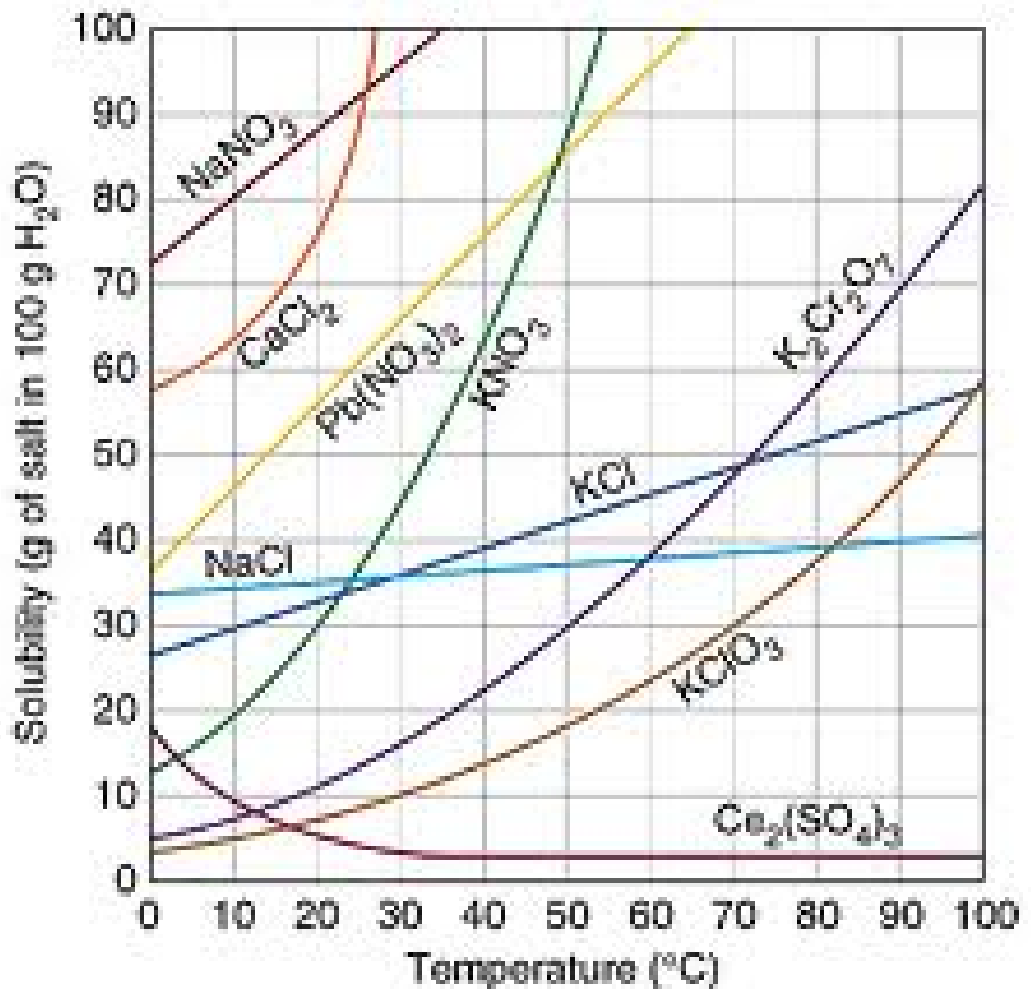


Fig. 1. The dependence of solubility on temperature

Gas solubility decreases as the temperature increases. The dependence of solubility on temperature is graphically depicted in the form of curves called the solubility curves.

The pressure depends only the solubility of gases in liquids and solubility of solids. Mutual solubility of liquids a little depends on the pressure, and increases only at very high pressures (on the order of thousands of atmospheres or 100 000 kPa).

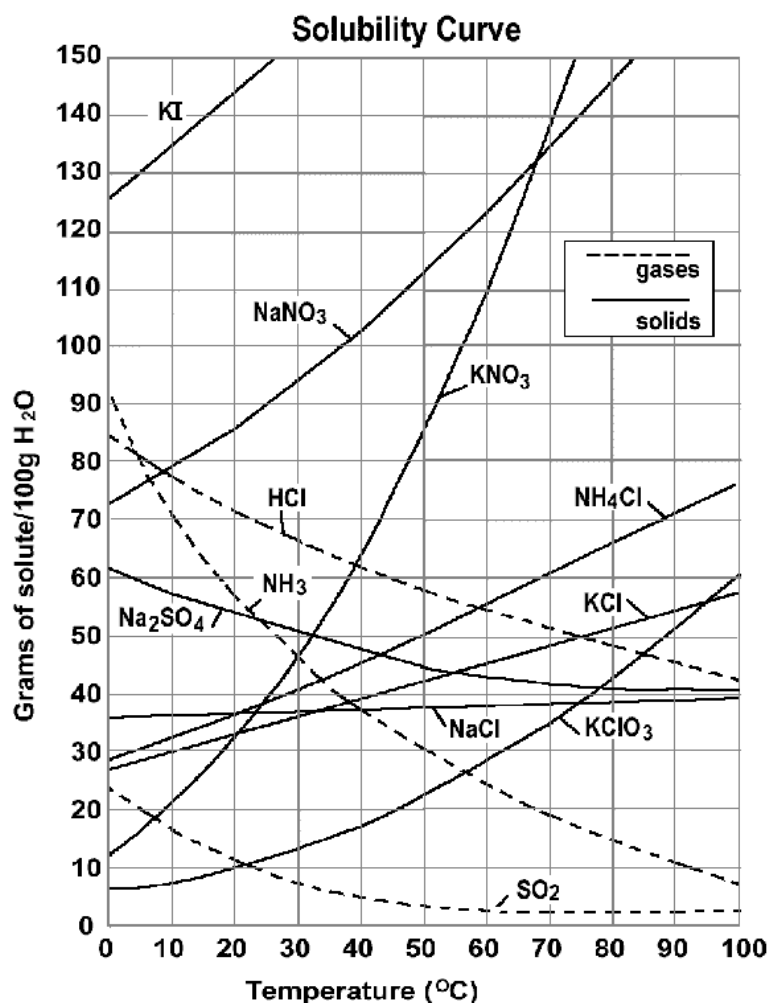
Pressure effects on the solubility of gases in liquids is Henry's law: the mass of gas, dissolved at a constant temperature in the fluid volume indices of gas partial pressures:

$$m = k \cdot p,$$

where:  $m$  is a mass concentration of gas in a saturated solution;



k is the constant of proportionality is called the constant of Henry;  
 p is partial pressure.



It should be however noted that the gases are subject to the law of Henry at not very high pressures and only if they do not enter into chemical interaction with the solvent. If the liquid is a mixture of gases, each gas is proportional to its partial pressure (Henry Dalton's law).

Distribution law characterizes the water solubility of the system consisting of two immiscible liquids: the substance can be dissolved in two immiscible liquids is distributed between them so that the ratio of its concentration in these solvents at a constant temperature remains regardless of the total amount of dissolved substances:

$$C_1/C_2 = k, \text{ where}$$

$C_1$  and  $C_2$  in the first and second phase solvent;

$K$  is coefficient of distribution.

Sechenov's law: the higher the salt concentration in the solution, the lower the solubility of the gases. For example: at a temperature of 20° c and normal pressure in 1 ml of water soluble 2.26 mL Cl<sub>2</sub>, while 26% solution of sodium chloride is only 0.3 ml. Use it when storing chlorine above the water.

This pattern is confirmed when dissolving solids and liquids. Reducing the solubility of substances in the presence of salts is called salting-out. M. Sechenov drew attention to the solubility of carbon monoxide in the blood, which decreases with increasing concentration of salts in the lymph. This technique is used for removing carbon monoxide from blood poisoning.

#### **4. The concentration of solutions and ways of expression. Molar, normal, molal concentration. Mass percent of solute.**

There are different ways of expressing the composition of a solution. The most frequent use of mass fraction of solute, molar and normal concentration.

Methods expression of concentration of solutions	Define	Formula
Molar concentration	shows the number of moles of solute per liter of solution 1 Often use symbols for example: 1 M solution (cm = 1 mol/l);	$C_M(B) = \frac{n(B)}{V(solution)}$ $n(B) = \frac{m(B)}{M(B)},$ where $C_M(B) = \frac{m(B)}{M(B) \cdot V(solution)},$ Where <b>n(B)</b> (sometimes

		denote $\nu(B)$ – the number of moles of solute; $m(B)$ - the mass of solute; $M(B)$ - the molar mass of the solute.
Molal concentration molality $C_m$ mol/kg	shows the number of moles of solute per 1 kg (or 1000 g) solvent  Often use symbols For Example: 1m –solution ( $C_m = 1$ mol/kg); 0,1m solution ( $C_m = 0,1$ mol/kg) etc.  The designation, for example, 1 m NaOH means the water is contained in kg 1 mol NaOH.	$C_m(B) = \frac{1000 \cdot n(B)}{m(solvent)}$ or  $C_m = \frac{m(B) \cdot 1000}{M(B) \cdot m(solvent)}$  $m(solvent)$ is the total mass of the solvent, kg
Molar concentration of equivalent, equivalent concentration normal concentration, normality, $C_n$ or $C_{eq}$ Mol*eq/L, mol/L, n.	shows the number of moles of solute equivalents in 1 liter of solution.	$C_{eq} = \frac{n_{eq}(B)}{V(solution)}$  $n_{eq}(B) = \frac{m(B)}{M_{eq}(B)}$  $C_{eq}(B) = \frac{m(B)}{M_{eq}(B) \cdot V(solution)}$ where $n_{eq}(B)$ (or $\nu_{eq}(B)$ )- $M_{eq}(B)$ the number of moles of solute equivalents; $M_{eq}(B)$ is the molar mass of equivalent substances

<p>Titre T, mg/mL, g/mL</p>	<p>How many grams of the substance is contained in 1 ml (CC) solution</p>	$T_B = \frac{m(B)}{V(solution)}$ <p>m(B) - the mass of a substance, mg or g</p>
<p>Mass fraction of <math>\omega</math> (Omega), if expressed in%; <math>\omega</math> if in fractions of units</p>	<p>There are a mass of solute to the mass of the solution. <math>\omega</math> indicates how many grams in 1 g in 100 g (then the result in%) solution.</p>	$\omega\%(B) = \frac{m(B)}{m(solution)} \cdot 100\%$ <p>m(solution)=m(B)+m(solvent), where from <math display="block">\omega\%(B) = \frac{m(B)}{m(B) + m(solvent)} \cdot 100\%</math></p>
<p>Volume fraction <math>\phi\%</math> is expressed percent or percentage</p>	<p>shows the number of ml in 1 ml or 100 ml. Used to characterize the composition of gas mixtures and fluids, fluids.</p>	$\phi\%(B) = \frac{V(B)}{V(p - pa)} \cdot 100\%$ <p>V(solution)=V(B) +V(solvent)</p>
<p>Mole fraction N1-Mole fraction of solvent, N2 is the mole fraction of solute is expressed as a percentage or a percentage</p>	<p>N2-the ratio of solute (mole) to the total number of mole of all components of the solution. Formulas are given for a binary solution.</p>	$N_2 = \frac{n_2}{n_1 + n_2},$ <p>where n1 is the number of moles of solvent n2 is the number of moles of solute. Suma Mole fraction of all components of the solution is equal to 1. For binary solution:<b><math>N_1 + N_2 = 1</math></b></p>

Sometimes in the medical laboratory practice have to recalculate the molar concentration in normal. If the equivalent mass of a substance is the mass of the

mole (for example, HCl, KCl, KOH), then the normal concentration equal molar concentration. So, 1 N hydrochloric acid in 1 M solution. However, for most compounds equivalent weight is mole and therefore the normal concentration of solutions of these substances does not equal molar concentration

### **5. Properties of ideal and real solutions. Cryoscopy and boiling-point elevation.**

The ideal is a solution which has the following properties:

one component of the solution between the molecules and molecules of different components apply the same force Intermolecular attraction. The molecules of one component does not facilitate or impede the transition to steam phase molecules of another component;

mixing the two components of the solution are not accompanied by changes in enthalpy;

volume of the mixture of two components (solution) is exactly equal to the amount of their levels prior to mixing.

Perfect solutions are subject to the law of Raul.

In 1887, Raul experimentally found that the partial pressure of a vapor in equilibrium with the diluted solution is proportional to the molefraction of solvent in the solution. This can be expressed as the following equation:

$$p_A = x_A p_A^o$$

Pairs perfect solution can be considered as ideal gas, and in this case it should be applicable law Dalton. Consequently, the total vapor pressure (p) of the two-part solution is the sum of the partial pressures of each component of a pair:  $p = p_A + p_B$ . It follows that the

$$p = x_A \cdot p_A^o + x_B \cdot p_B^o$$

The total vapor pressure two-part of the solution and the partial pressure of a couple more volatile component increases with the increase of molar shares more volatile component in solution. At the same time, the partial pressure of the steam is less volatile component of the solution decreases.

The relative decrease of solvent vapour pressure above the solution does not depend on the nature of the solute, and is determined only by the number of particles in solution. These solutions are called colligative. These properties are also raising the boiling point and freezing point temperature of solution osmotic pressure.

Has been found to lower the freezing temperature of diluted solution is proportional to the concentration of dissolved substances. In 1883, the chemist F.m. Raul found that lowering the freezing temperature, caused by the different dissolved substances taken in identical quantities of the same molart for the given solvent.

For diluted solutions in pressure of steam proportional to the concentration, and increasing the boiling point and freezing temperature of diluted solutions in proportion to their concentration. In this case (unlike in law Raul) concentration of customary to molality. Thus

$$\Delta T_{\text{boiling}} = E \cdot m$$

$$\Delta T_{\text{crystallization}} = K \cdot m$$

The proportionality coefficients are called respectively ebullioscopic and cryoscopic constants. They do not depend on the nature of the solute.

Lowering the freezing temperature and the boiling point of the solution compared to solvent:

$$\Delta T_{\text{melt}} = \frac{RT_{\text{melt}}^2 X_2}{\Delta H_{\text{melt}}} = \frac{RT_{\text{melt}}^2 M_1 m_2}{\Delta H_{\text{melt}}} = K m_2,$$

$$\Delta T_{\text{boil}} = \frac{RT_{\text{evap}}^2 X_2}{\Delta H_{\text{evap}}} = \frac{RT_{\text{evap}}^2 M_1 m_2}{\Delta H_{\text{evap}}} = E m_2,$$

where  $m_2$  is molality of the solution, and  $K$  is cryoscopic constant,  $E$  is ebullioscopic constant of the solvent,  $X_2$  is mole fraction of solute.  $\Delta H_{\text{melt}}$  and  $\Delta H_{\text{evap}}$  are enthalpies of melting and evaporation of the solvent,  $T_{\text{melt}}$  and  $T_{\text{boil}}$  are melting and boiling temperatures of solvent,  $M_1$  - the molar mass of the solvent,  $R$  - universal gas constant.

Thus, these characteristics of the equation contains only the solvent.

Since  $\Delta T_{\text{boil.}}$  and  $\Delta T_{\text{cryst.}}$  vary proportionally gram molecules and each gram molecule contains the same number of molecules (6,024.1023 ), these characteristics of the solution depends only on the number of solute particles .

From here the second law Raul: raising the boiling point and freezing point temperature of solutions are proportional to the number of particles, dissolved substances and do not depend on its nature.

Relationship between increasing the boiling point and low temperature crystallization can show through the image. It contains the four curves depicting the Gibbs energy of the temperature dependency of four phases — solid, liquid and gaseous solvents and solution. Point and is responsible to, the point of crystallization solvent, points (b) and (d) respectively, and boiling the solution crystallization. In each of these points in accordance with the general criteria of balance is respected equality of Gibbs energies of the coexisting phases.

Methods and ebullioscopic are in fact the cryoscopic result from Raul.

For diluted solutions in pressure of steam proportional to the concentration, and increasing the boiling point temperature of crystallization and diluted solutions proportionally to the concentration

For diluted solutions in pressure of steam proportional to the concentration, and increasing the boiling point temperature of crystallization and diluted solutions proportionally to the concentration

$$\Delta T_{\text{boil.}} = E \cdot m$$

$$\Delta T_{\text{cryst.}} = K \cdot m$$

The proportionality coefficients are called respectively ebullioscopic and cryoscopic constants.

Ebullioscopic (e) and some constants to cryoscopic solvent (deg/mol)

<b>Solvent</b>	<b>K, °C</b>	<b>E, °C</b>
Water	1,85	0,52

Benzene	5,07	2,57
Phenol	7,27	3,60
Acetic acid	3,9	3,07
Ethyl alcohol	-	1,04
Chloroform	4,9	3,80
Carbon tetrachloride	29,9	5,30

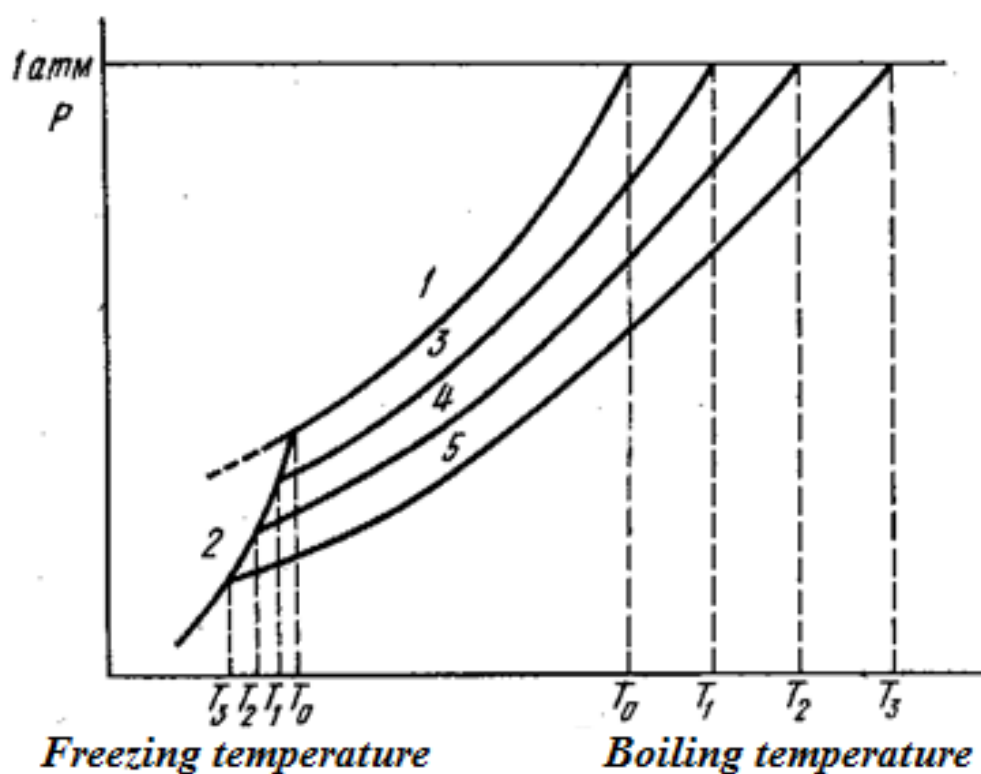


Fig. 2. Image based on vapor pressure with temperature.

1-curve for a pure liquid solvent; 2-curve for a pure solid solvent; 3, 4, 5 is the vapor pressure of the solvent over solutions with increasing concentration of non-volatile substances.

If the solution is made up of two volatile components, you can divide it into components by distillation. The essence of the process in the simplest case



(law Raoult observed for both components throughout the range of concentrations) is displayed in Figure 3.3.

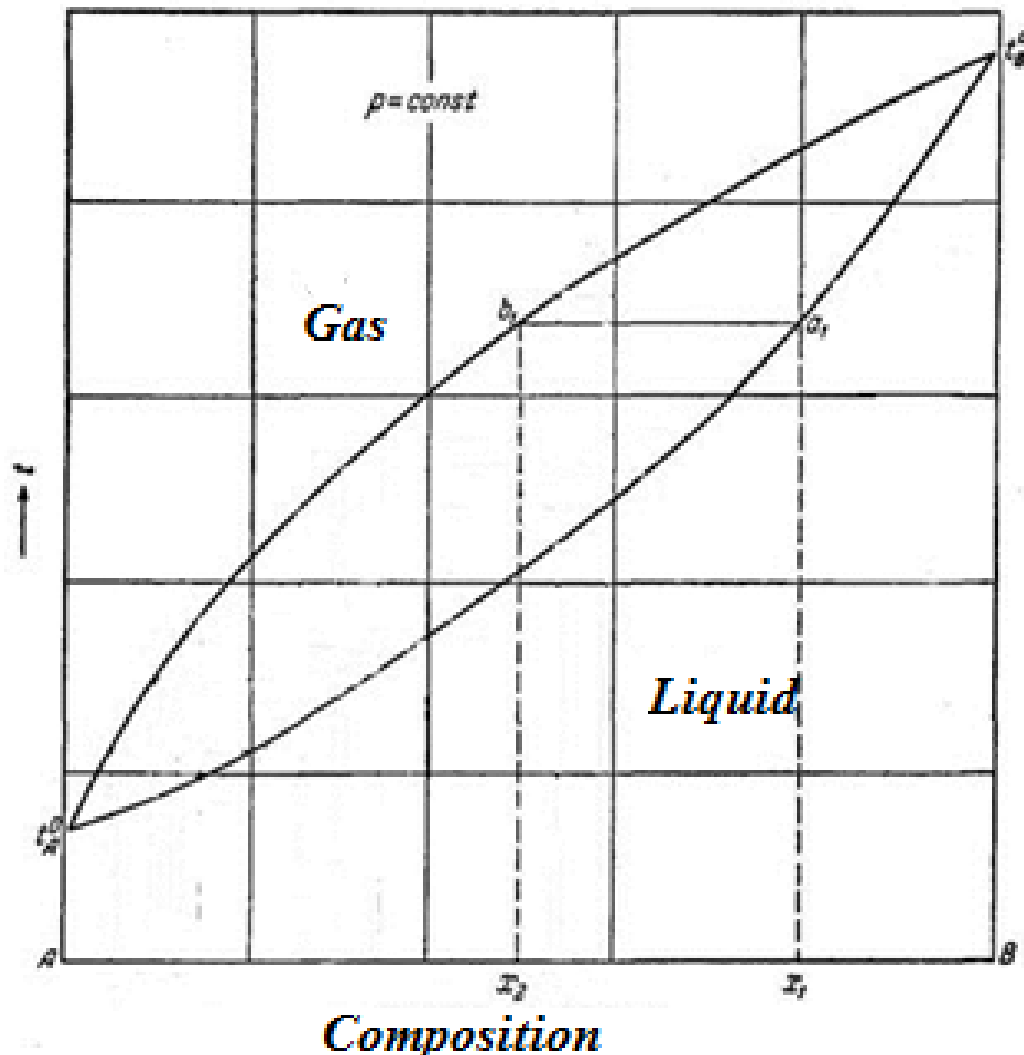


Fig. 3. the dependence of the boiling point of liquid solution from the composition of the fluid (N) and the couple have.

When heated to boiling point (A1) mortar composition N1 first couple will have the corresponding point b1, that is U1. The resulting condensation will be enriched by the more volatile component, and the remaining solution will be enriched with the less volatile component.

With successive steps from point 1 to point with the index at index 3 and on the left we get almost pure low-volatile and condensed fractions steam enriched with volatile component.

Repeating the procedure with condensate in steam, you can share the solution to clean the components.

In real systems, there are often variations of Raul, and charts are the boiling temperature Maxima and minima. They correspond to the case where the steam and fluids is the same; mix boiling water at a constant temperature, are called azeotropic.

The most famous azeotrope-ethanol-water boils at 78, 17 Celsius degrees, contains 96% ethanol, while pure ethanol (100%) boils at 78 degrees. The mixture cannot be separated by distillation, and to obtain 100% ANHYDROUS alcohol use other methods. Properties of solutions are collegiate properties, i.e. properties that depend on the concentration of particles in solution. Study of the properties of solutions of different substances has revealed that for the majority of the solutions are observed deviations from law r. Raul.

For example, if dissolved 0.1 mol of sodium chloride in 1000 g of water freezing temperature of solution was not 0,186°, 0,318°, that is, approximately in 2 times more theory.

Imagine that in the solution entered N molecules of solute that can dissolve the ions, and the degree of dissociation of the solute  $\alpha$ . Whereas the number of molecules dissolved ions will be  $N \alpha$  and  $\alpha \cdot N$  ions formed r. nondecomposed number of molecules will be  $N - N \alpha$  or  $N \alpha (1 - \alpha)$ .

The total number of particles in a solution of electrolyte will be the sum of the number of ions and molecules:

$$N_{\text{elect.}} = N\alpha p + N(1 - \alpha) = N(\alpha p + (1 - \alpha)) = N(\alpha(p - 1) + 1)$$

If dissociation occurred (the electrolyte), then the number of particles in a solution imposed would remain unchanged, N

The ratio of the number of particles of solute in a solution of electrolyte to the number of particles of solute dissociation is not

$$I = \frac{N_{elect.}}{N_{nonelect.}} = \frac{N(\alpha(p-1) + 1)}{N} = \alpha(p-1) + 1$$

The same amount is relevant variables describing the colligative properties solutions, measured for electrolytes, the values calculated for nonelectrolytes.

This amount Vant-Goff called isotonic coefficient is the ratio of the observed values to the calculated value.

$$i = \frac{\Delta P_{elect}}{\Delta P_{nonelect}} = \frac{P_{osm.elect}}{P_{osm..nonelect}} = \frac{\Delta t_{boil.elect}}{\Delta t_{boil.nonelect}} = \frac{\Delta t_{cryosc.elect}}{\Delta t_{cryosc.nonelect}}$$

Thus, the value of the colligative property for the electrolyte solutions (i) times more than for the corresponding quantity of dissolved non-electrolyte.

So, solutions that do not permeate the dissociation occurs ions are called solutions of nonelectrolytes. The system is characterized by the absence of ions in solution and does not have the Ionic conductivity.

Solutions in which the dissolved substance breaks down into ions are called solutions of electrolytes. Solutions of electrolytes are ion conductors.

## 6. The osmotic pressure of solutions.

If erythrocytes (red blood cells) put in clean water, they swell, become round and finally burst. This is due to the fact that the water penetrates through the wall of the cells, while dissolved in intracellular fluid substances (hemoglobin and other proteins) can not penetrate through the walls of the cell; in view of the fact that the system is at equilibrium between the two fluids (water vapour pressure for equality), water and penetrates into cells. If the cell walls are sufficiently strong, the balance would come at a time when the hydrostatic pressure inside the cell has reached a certain value at which the vapour pressure of the solution would be equal to the saturated vapor pressure of pure water outside the cells.

This equilibrium hydrostatic pressure is called the osmotic pressure of a solution.

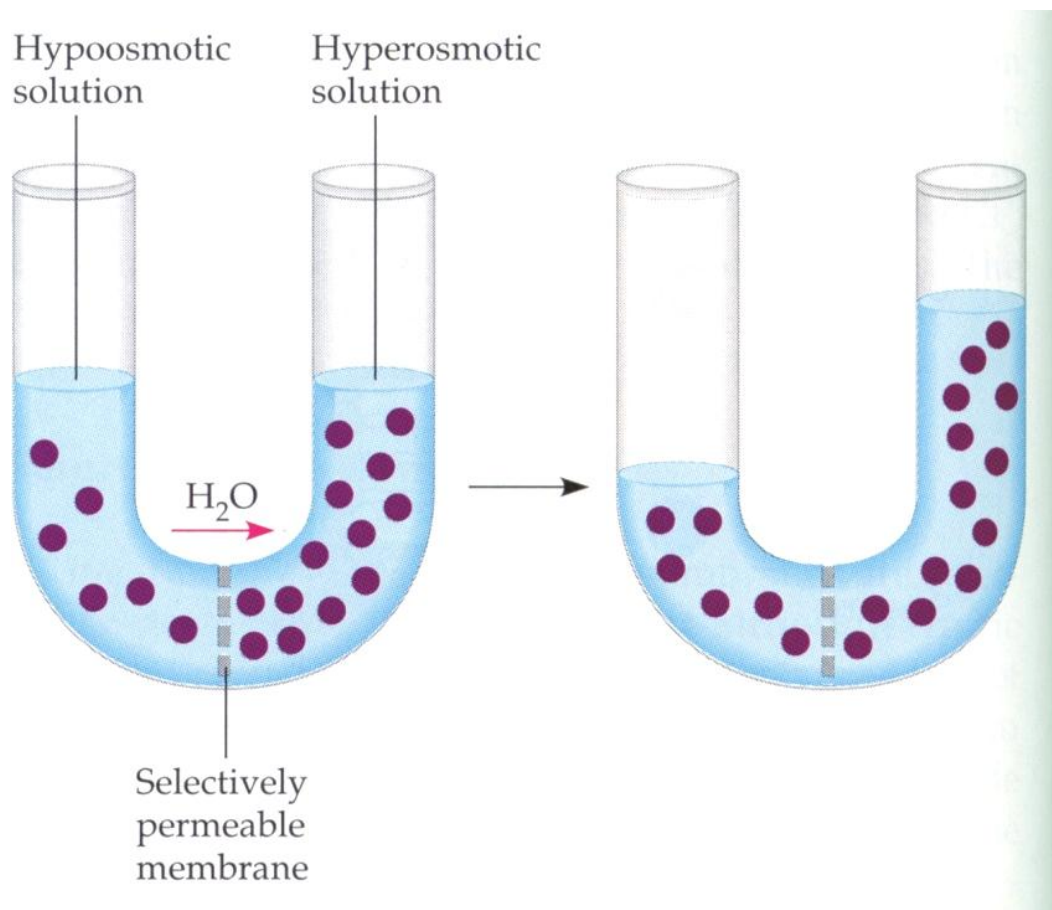


Fig. 4. Process of osmosis

Consider a closed cylinder, divided into two parts, piston, which is a semi-permeable barrier, let alone solvent. At the bottom of the solvent, and is placed at the top is the solution. Due to differences in concentrations of solvent on either side of the wall, he spontaneously (in accordance with the principle of Le Chatelier's principle) comes across a semi-permeable barrier in solution, diluting it. Primary driving force of diffusion of solvent in a solution is the free energy difference between the pure solvent and the solvent in a solution. Dilution solution by solvent diffusion spontaneous volume solution increases and the piston moves from position I to position II.

The phenomenon of selective diffusion of a certain class of particles in a solution through the semi-permeable wall is called osmosis. A force of sufficient magnitude to osmosis, related to one surface of the semi-permeable membrane is called the osmotic pressure. Vant-Goff has shown that osmotic

pressure in non-electrolyte solution is proportional to the molar concentration of dissolved substances:

$$p = cRT,$$

where  $c = n/V$  is the molar concentration, mol/l. Expression in form similar to equation Clausius-Mendeleev for ideal gases, but those equations describe different processes. Who is risking the osmotic pressure in solution at the penetration of the additional quantity of solvent through a semipermeable barrier. This pressure is the force that prevents the further alignment of concentrations.

The formal analogy is allowed Guys-Goff (1887) to formulate the law of osmotic pressure: osmotic pressure is the pressure that produced the dissolved substance, if it is in the form of an ideal gas occupies the same amount, that is, at the same temperature.

Like Mendeleev-Clapeyron equation, equation Vant-Goff to determine the molecular mass of the substance. So hemoglobin is 6000 and the molecule is a dimer ( $m = 12000$ ).

Many biological processes (turgor and plasmolysis, hemolysis) linked to osmosis in cells due to the presence of so-called biological membranes. In medical practice are applied:

a) isotonic solutions (the osmotic pressure of their equal osmotic pressure of blood plasma). The normal osmotic pressure of blood plasma is  $7 \cdot 10^6 - 8 \cdot 10^6$  Pa;

b) hypotonic (the osmotic pressure of hypertonic solution greater osmotic pressure of blood plasma);

in) hypertonic (the osmotic pressure of hypertonic solution greater osmotic pressure of blood plasma).

Isotonic solutions do not cause changes in cells, so they are widely used in medical practice to recover the blood volume and blood pressure, as well as in dehydration of the body for example in case of Burns, severe vomiting use 0.9% sodium chloride aqueous solution or 5% glucose solution.

Define plasmolysis, hemolysis and turgescence is given to you in accordance with Ukrainian-Latin-English medical dictionary, explanatory Lviv-1995 year:

Plasmolysis is the detachment of cytoplasm of sheath cells in hypertonic solution;

Hemolysis is destruction (dissolution) of red cells in the hypertonic solution;

Turgor-the State of tension, tension and elasticity of the tissue, which varies according to its physiological state.

All of these laws are infinitely diluted perfect solutions. Apply them to real solutions is limited to the greater, the higher the concentration of the solution.

## QUESTIONS FOR SELF-TRAINING

1. Definitions and concepts: what is called a solution, solubility, solvent.
2. The theory of education solutions (physical, chemical, modern).
3. Factors influencing solubility.
4. Classifying solutions.
5. Composition of solutions. Concentration of solutions. Ways of expressing concentration of solution.
6. Raul Law. What are the properties of solutions are called colligative?
7. That is called the saturated vapor pressure? How it changes over the solution increases the concentration of non-volatile non-electrolyte?
8. What is the semipermeable membrane? Give examples of semi-permeable membranes.
9. Give the definition of osmosis and osmotic pressure. What are the methods of determining the osmotic pressure?
10. Whether two aqueous solutions isotonic nonvolatile nonelectrolytes if temperature and molar concentrations of solutions are the same? The answer motivating.
11. Whether two aqueous solutions isotonic nonvolatile nonelectrolytes ( $M_1 > M_2$ ), if the temperature of the solution and mass fraction of these substances in the solutions are the same? If, in your opinion, nonisotonic solutions, which is the first or second is the osmotic pressure is higher? Why?
12. How will change in time, the osmotic pressure of oxidized solution of sucrose at  $80^\circ \text{C}$ ? The answer motivating.
13. Describe the behavior of erythrocytes in the  $37^\circ \text{C}$  in aqueous solutions of the following compounds: a) of fructose,  $\omega = 2\%$ , density of  $1,010 \text{ g/ml}$ ;  
b) sodium sulphate,  $\omega = 16\%$ ,  $1.151 \text{ density g/ml}$ ,  $\alpha = 1$ ; in the urea) =  $0.3 \text{ mol/l}$ .

14. Diffusion in solution. Factors affecting rate of diffusion. Fick's Law. The role of diffusion in the process of moving substances in biological systems.
15. The essence of osmosis. Osmotic pressure of diluted solutions of nonelectrolytes. The Law Vant-Hoff. Hypo-, hyper-and isotonic solutions. Measurement of osmotic pressure.
16. Deviation of electrolyte solutions from the law Guys-Hoff. Isotonic coefficient and its relation with the degree of dissociation of electrolyte. The concept of the osmotic concentration of the solutions.
17. The osmotic pressure of solutions of biopolymers. Osmotic pressure of plasma and blood serum and its biological role.
18. The role of osmosis and osmotic pressure in biological systems. Isoosmotic organisms. The formation of edema. Plasmolysis, hemolysis. Medical application of hyper-and isotonic solutions.
19. Not generating calculation, specify which of the three solutions with the same mass-barium chloride, magnesium chloride, calcium chloride, has a minimum and maximum temperature of freezing. The answer motivating.



## TASKS

1. A 0.750 L aqueous solution contains 90.0 g of ethanol,  $\text{C}_2\text{H}_5\text{OH}$ . Calculate the molar concentration of the solution in  $\text{mol}\cdot\text{L}^{-1}$ .
2. What mass of NaCl are dissolved in 152 mL of a solution if the concentration of the solution is 0.364 M?
3. What mass of dextrose,  $\text{C}_6\text{H}_{12}\text{O}_6$  is dissolved in 325 mL of 0.258 M solution?
4. A mass of 98 g of sulfuric acid,  $\text{H}_2\text{SO}_4$ , is dissolved in water to prepare a 0.500 M solution. What is the volume of the solution?
5. A solution of sodium carbonate,  $\text{Na}_2\text{CO}_3$ , contains 53.0 g of solute in 215 mL of solution. What is its molarity?
6. What is the molarity of a solution of  $\text{HNO}_3$  that contains 12.6 g of solute in 5.00 L of solution?
7. What mass of copper(II) nitrate,  $\text{Cu}(\text{NO}_3)_2$ , is present in 50.00 mL of a  $4.55 \times 10^{-3}$  M aqueous solution?

## THE STANDARD ANSWERS

### Exercise #1

0.750 L aqueous solution contains 90.0 g of ethanol, C<sub>2</sub>H<sub>5</sub>OH. Calculate the molar concentration of the solution in mol·L<sup>-1</sup>.

Solution:

1. The question asks for concentration, which means finding molarity, or:  $\frac{\text{mole}}{\text{L}}$

2. To convert mass of ethanol to moles, we need to find the molar mass of C<sub>2</sub>H<sub>5</sub>OH using the periodic table. Molar mass is 46.1 g·mol<sup>-1</sup>

3. Molarity also requires volume; the question tells us we have 0.750 L.

Put this information together to solve the problem, arranging the information to end up with the desired unit:

$$\frac{\text{mol}}{\text{L}} = 90.0 \text{ g} \times \frac{1 \text{ mol}}{46.1 \text{ g}} \times \frac{1}{0.750 \text{ L}} = \frac{2.60 \text{ mol}}{\text{L}} \text{ or } 2.60\text{M}$$

Our final answer: [C<sub>2</sub>H<sub>5</sub>OH ] = 2.60M

### Exercise #2

What mass of NaCl are dissolved in 152 mL of a solution if the concentration of the solution is 0.364 M?

Solution:

1. The question asks for mass, so we want to calculate grams
2. We are given the concentration. I suggest you rewrite the concentration as shown to the right, to better see how the units will cancel out.
3. Because the question involves mass, we will need to know the molar mass of NaCl

Using a periodic table we find the molar mass of NaCl to be 58.5 g·mol<sup>-1</sup>

4. The question gives us the volume in mL. Our unit of concentration uses L, so we will convert 152 mL into 0.152 L.

Put this information together to solve the problem, arranging the information to end up with the desired unit:

$$\text{g} = \frac{58.5 \text{ g}}{\text{mol}} \times \frac{0.364 \text{ mol}}{\text{L}} \times 0.152 \text{ L} = 3.24 \text{ g}$$

Answer: 3.24 g of NaCl will be required.

### Exercise #3

What mass of dextrose,  $\text{C}_6\text{H}_{12}\text{O}_6$  is dissolved in 325 mL of 0.258 M solution?

Solution:

1. The question asks for mass, so we want to calculate grams
2. We are given the concentration (0.258 M). I suggest you rewrite the concentration as shown to the right, to better see how the units will cancel out.

3. Because the question involves mass, we will need to know the molar mass of  $\text{C}_6\text{H}_{12}\text{O}_6$

Using a periodic table we find the molar mass of  $\text{C}_6\text{H}_{12}\text{O}_6$  to be  $180.1 \text{ g}\cdot\text{mol}^{-1}$

4. The question gives us the volume in mL. Our unit of concentration uses L, so we will convert 325 mL into 0.325 L.

Put this information together to solve the problem, arranging the information to end up with the desired unit:

$$\text{g} = \frac{180.1 \text{ g}}{\text{mol}} \times \frac{0.258 \text{ mol}}{\text{L}} \times 0.325 \text{ L} = 15.1 \text{ g}$$

Answer: 15.1 g of dextrose will be required.

### Exercise #4

A mass of 98 g of sulfuric acid,  $\text{H}_2\text{SO}_4$ , is dissolved in water to prepare a 0.500 M solution. What is the volume of the solution?

Solution:

1. The question asks for volume, so we want to calculate litres, L (or mL)

2. The concentration of the  $\frac{0.500 \text{ mol}}{\text{L}}$  solution is:

3. Because the question involves mass, we will need to know the molar mass of  $\text{H}_2\text{SO}_4$

Using a periodic table we find the molar mass of  $\text{H}_2\text{SO}_4$  to be  $98.1 \text{ g}\cdot\text{mol}^{-1}$

Put this information together to solve the problem, arranging the information to end up with the desired unit:

$$\text{L} = \frac{1 \text{ L}}{0.500 \text{ mol}} \times \frac{1 \text{ mol}}{98.1 \text{ g}} \times 98.0 \text{ g} = 2.00 \text{ L}$$

Answer: The volume of the solution will be 2.00 L.

#### Exercise #5

A solution of sodium carbonate,  $\text{Na}_2\text{CO}_3$ , contains 53.0 g of solute in 215 mL of solution. What is its molarity?

Solution:

1. The question asks for molarity:  $\frac{\text{mole}}{\text{L}}$

2. To convert mass of ethanol to moles, we need to find the molar mass of  $\text{Na}_2\text{CO}_3$  using the periodic table. The molar mass of  $\text{Na}_2\text{CO}_3$  is  $106.0 \text{ g}\cdot\text{mol}^{-1}$

3. Molarity also requires volume; the question tells us we have 215 mL, or 0.215 L.

Put this information together to solve the problem, arranging the information to end up with the desired unit:

$$\frac{\text{mol}}{\text{L}} = 53.0 \text{ g} \times \frac{1 \text{ mol}}{106.0 \text{ g}} \times \frac{1}{0.215 \text{ L}} = \frac{2.33 \text{ mol}}{\text{L}}$$

Our final answer:  $[\text{Na}_2\text{CO}_3] = 2.33 \text{ M}$

#### Exercise #6

What is the molarity of a solution of  $\text{HNO}_3$  that contains 12.6 g of solute in 5.00 L of solution?

Solution:

1. The question asks for molarity:  $\frac{\text{mole}}{\text{L}}$
2. To convert mass of ethanol to moles, we need to find the molar mass of  $\text{HNO}_3$  using the periodic table. Molar mass is  $64.0 \text{ g}\cdot\text{mol}^{-1}$
3. Molarity also requires volume, L; the question tells us we have 5.00 L.

Put this information together to solve the problem, arranging the information to end up with the desired unit:

$$\frac{\text{mol}}{\text{L}} = 12.6 \text{ g} \times \frac{1 \text{ mol}}{64.0 \text{ g}} \times \frac{1}{5.00 \text{ L}} = \frac{0.0393 \text{ mol}}{\text{L}}$$

Final answer:  $[\text{HNO}_3] = 3.93 \times 10^{-2} \text{ M}$

#### Exercise #7

What mass of copper(II) nitrate,  $\text{Cu}(\text{NO}_3)_2$ , is present in 50.00 mL of a  $4.55 \times 10^{-3} \text{ M}$  aqueous solution?

Solution:

1. The question asks for mass, so we need to calculate grams
2. We are given the concentration:  $\frac{4.55 \times 10^{-3} \text{ mol}}{\text{L}}$
3. Because the question involves mass, we will need to know the molar mass of  $\text{Cu}(\text{NO}_3)_2$

Using a periodic table we find the molar mass of  $\text{Cu}(\text{NO}_3)_2$  to be  $187.6 \text{ g}\cdot\text{mol}^{-1}$

4. The question gives us the volume in mL. Our unit of concentration uses L, so we will convert 50.00 mL into 0.05000 L.

Put this information together to solve the problem, arranging the information to end up with the desired unit:

$$\text{g} = \frac{187.6 \text{ g}}{\text{mol}} \times \frac{4.55 \times 10^{-3} \text{ mol}}{\text{L}} \times 0.0500 \text{ L} = 4.27 \times 10^{-2} \text{ g}$$

Final answer:  $4.27 \times 10^{-2} \text{ g}$  of copper(II) nitrate are present.

#### Exercise #8

Distinguish between solute, solvent and solution.

*The solvent is the major component in solution. The solute is the minor component in solution. A solution is a homogeneous mixture that contains two or more substances.*

Exercise #9

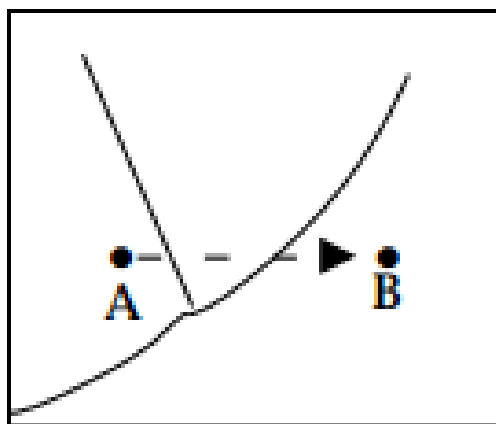
What are the units of molarity and molality.

*Molarity =  $M = \text{moles solute} / \text{liter solution}$*

*Molality =  $m = \text{moles solute} / \text{kg solvent}$*

Exercise #10

The phase diagram for water is shown below. Label the axis and the regions where water is a gas, a liquid and a solid. Indicate where the triple point is located and define the triple point.



a) What do the solid lines in the phase diagram represent? What phase changes occur in going from point A to point B?

The solid lines show the phase changes:  
solid liquid  
liquid gas  
solid gas

*In a phase change, the two phases are in equilibrium. In going from point A to point B, the phase changes that occur are solid to liquid to gas.*

b) Is the triple point for water, above or below 1 atm pressure?

*The triple point for water is below 1 atm pressure.*

c) According to the phase diagram above, starting at point A, what phase change occurs if the pressure is increased and the temperature remains constant?

*Starting at point A, if the pressure is increased while temperature remains constant indicates that the solid will undergo a phase change to a liquid. On the phase diagram draw a vertical line upward starting at point A.*

d) If NaCl is added to water, the vapor pressure of the resulting solution is reduced relative to that of pure water. Draw the vapor pressure curve of the solution on the phase diagram and show the effect on the boiling point and the freezing point.

*Students should draw the phase diagram with the solid lines for pure water and the dashed lines to represent the solution as shown in Figure 1, Pg. 240. In your lecture draw this diagram on the board to show boiling point elevation,  $T_b$ , and freezing point depression,  $T_f$ .*

#### Exercise #11

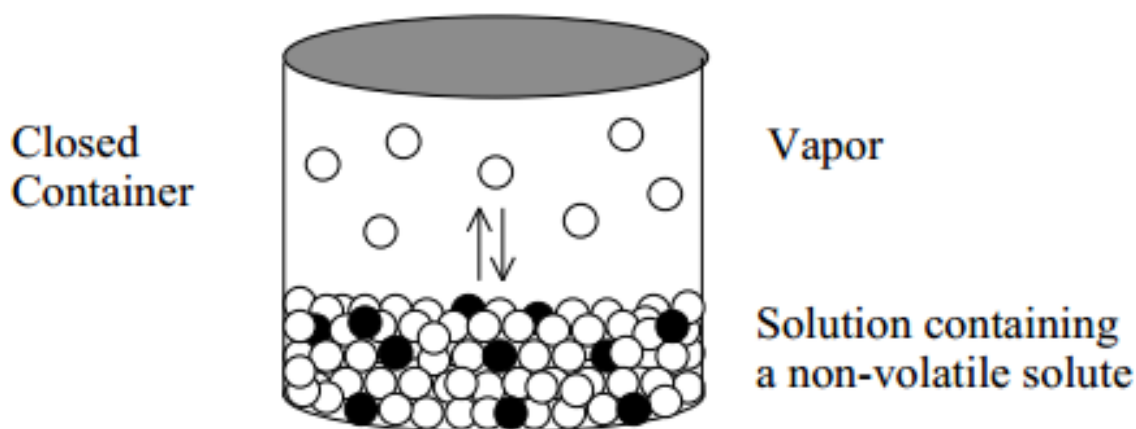
What is a non-volatile solute? What is a volatile solute?

*A non-volatile solute remains in solution, it does not produce a vapor above the solution.*

*A volatile solute implies that it does produce a vapor above the solution.*

#### Exercise #12

Why is the vapor pressure of a solution containing a non-volatile solute lower than the pure solvent? If the solution consists of a solvent and a volatile solute, would anything be different in the drawing? Discuss any differences.



*In a phase transition from liquid to gas, molecules escape from the surface of the liquid phase into the gas phase. The solute reduces the surface area from*

*which solvent molecule can escape, decreasing the vapor pressure. If the solute were volatile, some solute molecules would be present in the gas phase. That is, some of the molecules diagramed solid black in the figure would be present as gas molecules above the solution.*

#### Exercise #13

If  $\Delta T_f = -iK_f m$  and  $\Delta T_b = iK_b m$ , then  $i$  is used to remind you to determine the total number of dissolved particles in solution. What is  $i$  for each of the following?

- |                               |               |                   |
|-------------------------------|---------------|-------------------|
| a) glucose ( $C_6H_{12}O_6$ ) | b) $Na_2SO_4$ | c) $(NH_4)_3PO_4$ |
| $i = 1$                       | $i = 3$       | $i = 4$           |

#### Exercise #14

If a 1.0 m solution of glucose ( $C_6H_{12}O_6$ ),  $Na_2SO_4$  and  $(NH_4)_3PO_4$ , is made, which one will have the lowest vapor pressure, highest boiling point and lowest freezing point?

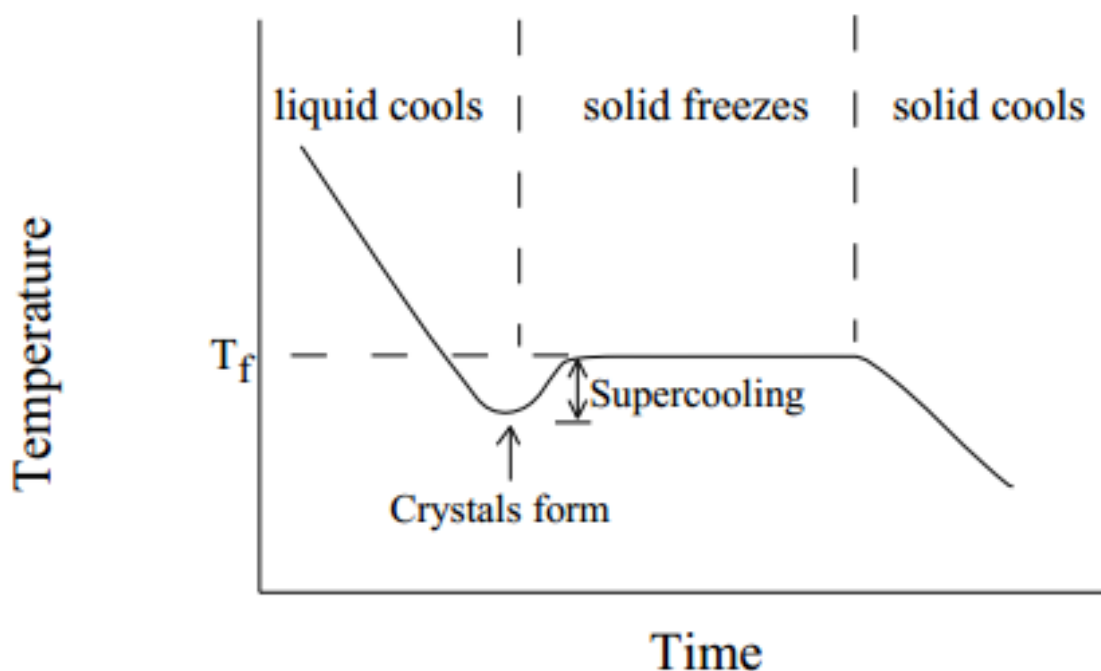
*1.0 m  $(NH_4)_3PO_4$  will have the lowest vapor pressure, the highest boiling point and the lowest freezing point.*

#### Exercise #15

In part 1 of this experiment you will determine the freezing point of benzophenone. Benzophenone is a solid at room temperature and is completely dissolved at 50°C. By letting the liquid cool and measuring the temperature as a function of time, the freezing point,  $T_f$ , of benzophenone is



obtained.



For pure benzophenone the temperature drops only a few degrees. Crystals form and the temperature goes back up and then remains constant. The dip in the curve is due to supercooling. What is supercooling?

*Supercooling is defined as the phenomenon in which a liquid is temporarily cooled below its freezing point without freezing. Stirring or imperfections in the glassware will generally minimize supercooling.*

*Analogy: In a sudden hail-storm, supercooled water droplets in the air can turn into ice due to dust in the air. Similarly superheating water is often observed when heating water in the microwave. A slight disturbance in the water can cause the water to violently boil over and out of the container. This can be very dangerous causing serious burns.*

#### Exercise #16

In part 2 of this experiment cyclohexanone is added to the benzophenone. You will be able to smell the cyclohexanone.

a) Does this indicate that cyclohexanone is a non-volatile or volatile solute?

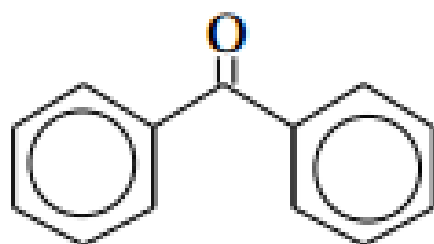
*Cyclohexanone is a volatile solute.*

b) Would the freezing point depression be different for a volatile than for a non-volatile solute? Explain how it would be different.

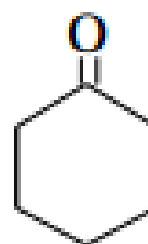
*A non-volatile solute in a solution will produce a larger freezing point depression (greater  $T_f$ ) than a volatile solute in a solution.*

#### Exercise #17

Consider the structures for benzophenone and cyclohexanone shown as



**benzophenone**



**cyclohexanone**

follows.

*Students have been introduced to steric numbers (SN) and hybridization in lecture.*

*SN = Number of Effective Electron Pairs around a given atom in a molecule*

*SN = # of atoms bonded to a given atom plus the # of lone pairs on that atom.*

<i>SN</i>	<i>Hybridization</i>	<i>Electron Arrangement</i>
2	<i>sp</i>	<i>Linear</i>
3	<i>sp<sup>2</sup></i>	<i>Trigonal planar</i>
4	<i>sp<sup>3</sup></i>	<i>Tetrahedral</i>
5	<i>dsp<sup>3</sup></i>	<i>Trigonal bipyramid</i>

*If an atom is  $sp^2$  hybridized the geometry is trigonal planar so the atoms attached to this atom will be in the same plane. In lecture we looked at ethylene,  $C_2H_4$ , and benzene,  $C_6H_6$ . All the carbons in both of these molecules are  $sp^2$  hybridized so all the atoms in each molecule are in the same plane. This will help to answer the following questions.*

a) Are all the atoms in the same plane in the benzophenone?

*In benzophenone, all the carbons are  $sp^2$  hybridized and therefore all the atoms in benzophenone are in the same plane.*

b) Are all the atoms in the same plane in the cyclohexanone?

*All the carbon atoms in cyclohexanone are  $sp^3$  hybridized.  $sp^3$  corresponds to a tetrahedral geometry. Thus, the atoms in cyclohexanone are not in the same plane.*

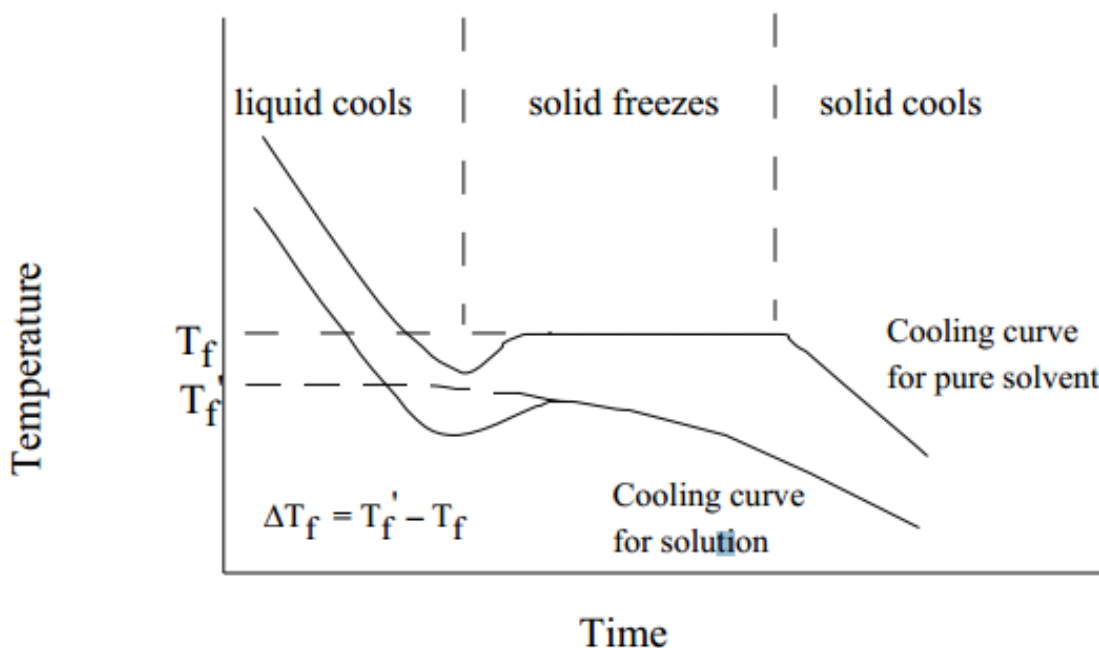
d) Explain why benzophenone is a solid at room temperature and why cyclohexanone is a liquid at room temperature.

*The surface area of contact is greater for a planar molecule like benzophenone than for a non-planar molecule like cyclohexanone.*

*Greater surface area  $\Rightarrow$  greater LDF  $\Rightarrow$  higher melting and higher boiling point.*

Exercise #18

The cooling curves for a pure solvent and a solution are shown in the figure below. It shows how the freezing point of a solution must be determined by extrapolation of the cooling curve. Extrapolation is necessary because unlike the pure solvent, as the solution freezes, the freezing point drops continuously. Why doesn't the solution reach a constant temperature like the pure solvent?



The solvent (benzophenone) freezes at a higher temperature than the solute (cyclohexanone). As the solvent freezes, the concentration of the cyclohexanone in solution increases. Thus,  $T_f$  continues to increase – causing the freezing point to drop continuously. Clearly, supercooling produces an ambiguity in the freezing point and should be minimized. Stirring the solution helps to minimize supercooling. Please make sure you understand this and how to extrapolate the data to obtain  $T_f$  for the solution. They must extrapolate the data as shown in the figure above: follow the upward trend of the cooling curve slightly beyond the point where crystallization was first observed, then the line is horizontal and continues to be horizontal until it intersects with the y-axis, to obtain  $T_f$ .

## EXPERIMENTSL PART

### Freezing Point Depression

The freezing points of solutions are all lower than that of the pure solvent. The freezing point depression is directly proportional to the *molality* of the solute.

$$\Delta T_f = T_f(\text{solvent}) - T_f(\text{solution}) = K_f \times m$$

Where:  $\Delta T_f$  is the freezing point depression,  $T_f(\text{solution})$  is the freezing point of the solution,  $T_f(\text{solvent})$  is the freezing point of the solvent,  $K_f$  is the freezing point depression constant,  $m$  is the molality.

### Introduction

Nonelectrolytes are substances with no ions, only molecules. Strong electrolytes, on the other hand, are composed mostly of ionic compounds, and essentially all soluble ionic compounds form electrolytes. Therefore, if we can establish that the substance that we are working with is uniform and is not ionic, it is safe to assume that we are working with a nonelectrolyte, and we may attempt to solve this problem using our formulas. This will most likely be the case for all problems you encounter related to freezing point depression and boiling point elevation in this course, but it is a good idea to keep an eye out for ions. It is worth mentioning that these equations work for both volatile and nonvolatile solutions. This means that for the sake of determining freezing point depression or boiling point elevation, the vapor pressure does not effect the change in temperature. Also remember that a pure solvent is a solution that has had nothing extra added to it or dissolved in it. We will be comparing the properties of that pure solvent with its new properties when added to a solution.

Adding solutes to an ideal solution results in a positive  $\Delta S$ , an increase in entropy. Because of this, the newly altered solution's chemical and physical properties will also change. The properties that undergo changes due to the addition of solutes to a solvent are known as **colligative properties**. These properties are dependent on the amount of solutes added, not on their identity.

Two examples of colligative properties are boiling point and freezing point: due to the addition of solutes, the boiling point tends to increase and freezing point tends to decrease.

The freezing point and boiling point of a pure solvent can be changed when added to a solution. When this occurs, the freezing point of the pure solvent may become lower, and the boiling point may become higher. The extent to which these changes occur can be found using the formulas:

$$\Delta T_f = -K_f \times m$$

$$\Delta T_b = K_b \times m$$

where  $m$  is the solute molality, and the  $K$  values are proportionality constants.

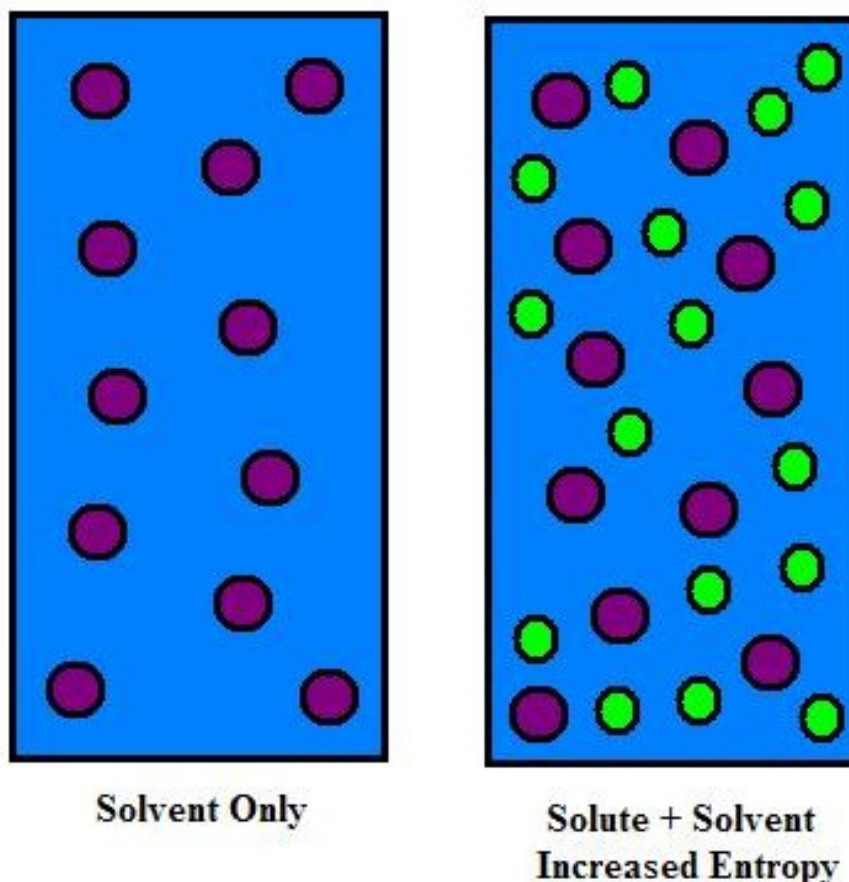
If solving for the proportionality constant is not the ultimate goal of the problem, these values will most likely be given. Some common values for  $K_f$  and  $K_b$ , respectively, are:

- Water: 1.86, .512
- Acetic acid: 3.90, 3.07
- Benzene: 5.12, 2.53
- Phenol: 7.27, 3.56

Molality is defined as the number of moles of solute per kilogram **solvent**. Be careful not to use the mass of the entire solution. Often, the problem will give you the change in temperature and the proportionality constant, and you must find the molality first in order to get your final answer.

The solute, in order for it to exert any change on colligative properties, must fulfill two conditions. First, it must not contribute in the vapor pressure of the solution and second, it must remain suspended in the solution even during phase changes. Because the solvent is no longer pure with the addition of solutes, we can say that the **chemical potential** of the solvent is lower. Chemical potential is the molar Gibb's energy that one mole of solvent is able to contribute to a mixture. The higher the chemical potential of a solvent is, the

more it is able to drive the reaction forward. Consequently, solvents with higher chemical potentials will also have higher vapor pressures.



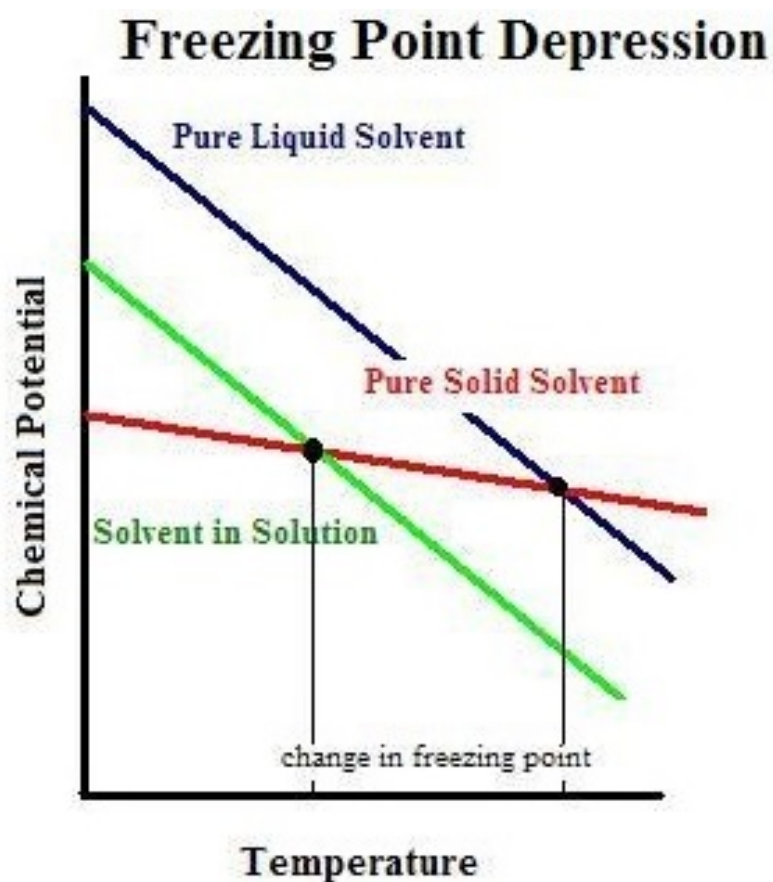
Boiling point is reached when the chemical potential of the pure solvent, a liquid, reaches that of the chemical potential of pure vapor. Because of the decrease of the chemical potential of mixed solvents and solutes, we observe this intersection at higher temperatures. In other words, the boiling point of the impure solvent will be at a higher temperature than that of the pure liquid solvent. Thus, **boiling point elevation** occurs with a temperature increase that is quantified using

$$\Delta T_b = K_b b_B$$

Where:

- $K_b$  is known as the *ebullioscopic constant* and
- $b_B$  is the molality of the solute.

Freezing point is reached when the chemical potential of the pure liquid solvent reaches that of the pure solid solvent. Again, since we are dealing with mixtures with decreased chemical potential, we expect the freezing point to change. Unlike the boiling point, the chemical potential of the impure solvent requires a colder temperature for it to reach the chemical potential of the solid pure solvent. Therefore, we observe a **freezing point depression**. We measure the change in the freezing point temperature using  $\Delta T_f = K_f b_B$  where  $K_f$  is known as the cryoscopic constant and  $b_B$  is again the molality of the solute.



*Laboratory work:* The determination of molecular weight of dissolved substance by cryoscopic method

*Work is performed in Cryoscope.*

1. The temperature is measured with an electronic thermometer.
2. Fill the glass of cryoscope with cooling mixture of ice and NaCl.
3. Measure 25 ml of distilled water and put into the working tube.
4. Put the thermometer into tube and then both into cooling mixture.



5. Watch the thermometer while stirring the liquid stirrer to avoid hypothermia.

6. Mark temperature loss of the first crystals of the pure solvent. Repeat this operation three times and take the average value of the crystallization temperature. Temperature measurement precision is 0,1°C.

7. Take a sample of the test substance (0.5 g).

8. Remove the tube with crystallized solvent from the cooling mixture.

9. Melt the crystals of solvent by heating the tube by hand.

10. Put the test substance into solvent, mix it thoroughly until it is completely dissolved.

11. Determine the freezing point of the solution, recording three times the temperature when crystals fall from solution.

12. Find the freezing point depression of a solution comparing to the pure solvent.

$$\Delta t = t_1 - t_0$$

Calculate the molecular weight of the sample using following formula:

$$M = \frac{K \cdot g \cdot 1000}{g_0 \cdot \Delta t},$$

where  $K$ - water cryoscopic constant (1,86);

$g$ - sample of the test substance;

$g_0$ - sample of water;

$\Delta t$  - freezing point depression of a solution.

## TESTS

How velocity of diffusion depends on the temperature and viscosity?

- a) \*Increases with growth of temperature and decrease of viscosity;
- b) Increases with a temperature decrease and growth of viscosity.
- c) Increases with a temperature and viscosity decrease;

The aqueous solutions of saccharose,  $\text{CaCl}_2$ ,  $\text{NaCl}$ ,  $\text{Al}_2(\text{SO}_4)_3$  and  $\text{K}_3[\text{Fe}(\text{CN})_6]$  with identical molarity were prepared. What from the listed solutions boils at greatest temperature?

- a) \*Solution of  $\text{Al}_2(\text{SO}_4)_3$ ;
- b) Solution of  $\text{K}_3[\text{Fe}(\text{CN})_6]$ ;
- c) Solution of saccharose;
- d) Solution of  $\text{CaCl}_2$ ;
- e) Solution of  $\text{NaCl}$ .

What ratio connects a cryoscopic constant to melting heat of resolvent?

- a) \*Vant-Hoff;
- b) Arrhenius;
- c) Henry.

What equation the diffusion expresses by?

- a) \*By Fick equation;
- b) By Einstein's equation;
- c) By Raoul equation.

On what the diffusion coefficient depends?

- a) \*From radius of particles;
- b) From a gradient of concentration;
- c) From time;

d) From the charge of particles.

To what concentration the temperature decrease is proportional at a freezing of solutions?

- a) \*Molal concentration;
- b) Molar fraction;
- c) Mass fraction;
- d) Molar concentration.

How the freezing temperature of solution depends on its concentration?

- a) \*Decreases with growth of concentration;
- b) Does not depend of;
- c) Increases with growth of concentration.

How the saturation pressure is changed at increase of concentration of solution?

- a) \*Decreases
- b) Increases
- c) Is not changed

What law expresses dependence of saturation pressure on concentration of solution?

- a) \*Raoult law;
- b) Henry law;
- c) Vant-Hoff law;
- d) Mendelejev-Clapeyrons law.

How the concentration in an equation of a Raoult law expresses?

- a) \*Molar fraction;
- b) Molar concentration;
- c) Mass fraction;

d) Molal concentration

The aqueous solutions NaCl,  $\text{Al}_2(\text{SO}_4)_3$ , KI, urea and hexamethylenetetramine of identical molal concentration were prepared. What from the listed solutions crystallizes at lowest temperature?

- a) \*Solution of  $\text{Al}_2(\text{SO}_4)_3$
- b) Solution of NaCl;
- c) Solution of KI;
- d) Solution of urea;
- e) Solution of hexamethylenetetramine.

How far the boiling point for 5 % solution of glucose will be increased?

- a) \* $T_b = E \cdot 5 \cdot 1000 / 95 \cdot M_b \cdot \text{C}_6\text{H}_{12}\text{O}_6$
- b)  $T_b = E \cdot 5 \%$
- c)  $T_b = I \cdot E \cdot 5 \%$
- d)  $T_b = I \cdot 5 \cdot 1000 / 95 \cdot M \cdot b \text{ C}_6\text{H}_{12}\text{O}_6$
- e)  $T_b = I \cdot E \cdot 5 \cdot 1000 / 95 \cdot M_b \cdot \text{C}_6\text{H}_{12}\text{O}_6$

How far the freezing temperature for 3 % solution of KJ will be decreased?

- a) \* $T_f = i k \cdot 3 \cdot 1000 / 97 \cdot M_b \text{KJ}$
- b)  $T_f = k \cdot 3 \% \text{KJ}$
- c)  $T_f = i k \cdot 3 \% \text{KJ}$
- d)  $T_f = k \cdot 3 \cdot 1000 / 97 \cdot M_b \text{KJ}$

What is level of molarities  $\text{Na}_2\text{SO}_4$  and  $\text{MgSO}_4$  in isoosmotic solutions?

- a) \*For  $\text{MgSO}_4$  it is higher;
- b) For  $\text{Na}_2\text{SO}_4$  it is higher;
- c) They are identical.

How the molecular concentration is determined by a cryoscopic method?

- a)  $M = K \cdot a \cdot 1000 / dT_c \cdot b$
- b)  $M = K \cdot a \cdot 100 / (dT_c - b)$
- c)  $M = dT_c \cdot a \cdot 1000 / k \cdot b$
- d)  $M = dT_c \cdot b \cdot k / a \cdot 1000$

The increase of concentration of solution initiates:

- a) \*Increase of temperature of boiling and decrease of temperature of freezing;
- b) Decrease of temperature of boiling and increase of temperature of freezing;
- c) Increase of temperature of boiling and increase of temperature of freezing;
- d) Decrease of both boiling and freezing temperatures.

What equation is mathematical expression of a Raoult law?

- a)  $N_2 = (P_0 - P) / P_0$
- b)  $P = (P_1 - P) / N_2$
- c)  $N_2 = P / (P_0 + P)$
- d)  $N_2 = (P + P) / P$

How the isotonic coefficient of Vant-Hoff is determined?

- a)  $i = 1 + a(v - 1)$
- b)  $i = (v - 1) / (1 + a)$
- c)  $i = (1 - a) / (v + 1)$
- d)  $i = (1 + a) / (v - 1)$

What is a hypertonic solution?

- a) \*Solution having the greater osmotic pressure in comparison to the standard;
- b) Solution having identical osmotic pressure in comparison to the standard.

- c) Solution having smaller osmotic pressure in comparison to the standard.

How to determine the osmotic pressure under the law of Vant-Hoff?

- a)  $*p=n/V*RT$
- b)  $p=nRT/V$
- c)  $p=V/n*RT$
- d)  $p=V*RT/n$

On what equation the speed of diffusion through cell-like membranes is determined?

- a)  $*dm/dt = -PS (C_1 - C_2)$
- b)  $dT = -PS (C_1 - C_2) * dm$
- c)  $dm/dt$
- d)  $C_1/C_2 = -PS * (dM/dT)$
- e)  $PS = -dM/dT = (C_2 - C_1)$

How to determine the speed of diffusion on a Fick's law?

- a)  $*dm/dt = -DS * dC/dx$
- b)  $DS = -dm/dt * dC/dX$
- c)  $dC/dX = -DS * dm/dt$
- d)  $dX = dC/DS - dm/dt$

What colligative property of solutions is determined by?

- a) \*By amount of particles of solute.
- b) By the nature of solvent.
- c) By the nature of solvent.
- d) By amount of solvent.

At manufacturing some liquid medicinal forms it is necessary to take into account the value of osmotic pressure. What from listed 0,1 M solutions: glucose, saccharose,  $\text{AlCl}_3$ ,  $\text{KNO}_3$ ,  $\text{CaCl}_2$ , has a greatest osmotic pressure?

- a) \*0,1 M solution of  $\text{AlCl}_3$
- b) 0,1 M solution of  $\text{CaCl}_2$
- c) 0,1 M solution of glucose
- d) 0,1 M solution of saccharose
- e) 0,1 M solution of  $\text{KNO}_3$

During an osmosis:

- a) \*Resolvents from solution with smaller concentration moves to solution with the greater concentration;
- b) Resolvents in solutions moves simultaneous from one solution to another;
- c) Resolvents in solutions with the greater intensity moves to solution with smaller concentration.

Does velocity of diffusion depends on the temperature and viscosity?

- a) \*Yes]
- b) NO

The aqueous solutions of saccharose,  $\text{CaCl}_2$ ,  $\text{NaCl}$ ,  $\text{Al}_2(\text{SO}_4)_3$  and  $\text{K}_3[\text{Fe}(\text{CN})_6]$  with identical molarity were prepared. What from the listed solutions boils at greatest temperature?

- a) \*Solution of  $\text{Al}_2(\text{SO}_4)_3$ ;
- b) Solution of  $\text{K}_3[\text{Fe}(\text{CN})_6]$ ;
- c) Solution of  $\text{CaCl}_2$ ;
- d) Solution of  $\text{NaCl}$ .

What process is expresses by Fick equation?

- a) \*Diffusion;

- b) Osmosis;
- c) Crystallization.

What law connects cryoscopic constant with melting heat of solvent?

- d) \*Vant-Hoff;
- e) Arrhenius;
- f) Henry.

To what concentration the temperature increase is proportional at a boiling of solutions?

- e) \*Molal concentration;
- f) Molar fraction;
- g) Mass fraction;
- h) Molar concentration.

The decrease of concentration of solution initiates:

- a) Increase of temperature of boiling and decrease of temperature of freezing;
- b) \*Decrease of temperature of boiling and increase of temperature of freezing;
- c) Increase of temperature of boiling and increase of temperature of freezing;
- d) Decrease of both boiling and freezing temperatures.

How the saturation pressure is changed at decrease of concentration of solution?

- a) Decreases
- b) \*Increases
- c) Is not changed

How the boiling temperature of solution depends on its concentration?



- d) Decreases with growth of concentration;
- e) Does not depend of;
- f) \*Increases with growth of concentration.

The aqueous solutions  $\text{Al}_2(\text{SO}_4)_3$ , urea and hexamethylenetetramine of identical molal concentration were prepared. What from the listed solutions crystallizes at lowest temperature?

- f) \*Solution of  $\text{Al}_2(\text{SO}_4)_3$
- g) Solution of urea;
- h) Solution of hexamethylenetetramine.

How far the boiling point for 3 % solution of glucose will be increased?

- f)  $T_b = E \cdot 3 \cdot 1000 / 95 \cdot M_b \cdot \text{C}_6\text{H}_{12}\text{O}_6$
- g)  $T_b = E \cdot 3 \%$
- h)  $T_b = I \cdot E \cdot 3 \%$
- i)  $T_b = I \cdot 5 \cdot 1000 / 95 \cdot M \cdot b \cdot \text{C}_6\text{H}_{12}\text{O}_6$
- j)  $T_b = I \cdot E \cdot 5 \cdot 1000 / 95 \cdot M_b \cdot \text{C}_6\text{H}_{12}\text{O}_6$

How far the freezing temperature for 5 % solution of KJ will be decreased?

- e)  $T_f = i \cdot k \cdot 5 \cdot 1000 / 97 \cdot M_b \cdot \text{KJ}$
- f)  $T_f = k \cdot 5 \cdot \text{KJ}$
- g)  $T_f = i \cdot k \cdot 3 \cdot \text{KJ}$
- h)  $T_f = k \cdot 3 \cdot 1000 / 97 \cdot M_b \cdot \text{KJ}$

What is a hypotonic solution?

- d) Solution having the greater osmotic pressure in comparison to the standard;
- e) Solution having identical osmotic pressure in comparison to the standard.
- f) \*Solution having smaller osmotic pressure in comparison to the standard.

What is a isotonic solution?

- a) Solution having the greater osmotic pressure in comparison to the standard;
- b) \*Solution having identical osmotic pressure in comparison to the standard.
- c) Solution having smaller osmotic pressure in comparison to the standard.

During diffusion:

- d) Resolvents from solution with smaller concentration moves to solution with the greater concentration;
- e) Resolvents in solutions moves simultaneous from one solution to another;
- f) \*Resolvents in solutions with the greater intensity moves to solution with smaller concentration.

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