

# **NERNST'S DISTRIBUTION LAW**

**Author:**

dr Małgorzata Jurak

**Editor:**

dr hab. Agnieszka Ewa Wiącek

## Task 22a

# NERNST'S DISTRIBUTION LAW

## I. Aim of the task

The aim of the task is quantitative determination of the distribution of benzoic acid between two immiscible solvents and to provide the partition equation.

## II. Introduction

1. Phases, components, and degrees of freedom.
2. Raoult's and Henry's laws.
3. Vapour pressure (temperature) – composition diagrams.
4. Nernst's distribution law.
5. Process of extraction.

### References:

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2. J. Sangster, „*Octanol-water partition coefficients: fundamentals and physical chemistry*”, John Wiley & Sons, Baffins Lane, Chichester, England, 1997, chapter 1, 1-2.
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## III. Theory

### III. 1. Phases, components, and degrees of freedom

A **phase** is a state of matter that is uniform throughout, not only in chemical composition but also in physical state. Thus we distinguish the solid, liquid, and gas phases of a substance, and its various solid phases (for example black phosphorus and white phosphorus). As a **component** we mean a species present in the system, as the solute and solvent in a binary solution [1].

#### III. 1.1. Definitions

The **number of phases** in a system is denoted  $P$ . A gas, or a gaseous mixture, is a single phase, a crystal is a single phase, and two totally miscible liquids form a single phase. Ice is a single phase ( $P = 1$ ) even though it might be chipped into small fragments. A slurry of ice and water is a two-phase ( $P = 2$ ) system even though it is difficult to map the boundaries between the phases. An alloy of two metals is a two-phase system ( $P = 2$ ) if the metals are immiscible, but a single phase system ( $P = 1$ ) if they are miscible. A **solution** of solid  $A$  in solid  $B$  – a homogeneous mixture of the two components – is uniform on a molecular scale. In a solution, atoms of  $A$  are surrounded by atoms of  $A$  and  $B$ , and any sample cut from the solid, no matter how small, is representative of the composition of the whole. A dispersion is uniform on a macroscopic but not a microscopic scale, for it consists of grains and droplets of one component in a matrix of the other.

The **number of components** in a system  $C$  is the minimum number of **independent** species necessary to define the composition of all the phases present in the system. The definition is easy to apply when the species present in a system do not react, for then we simply count their number. For instance, pure water is a one-component system ( $C = 1$ ) and a mixture of ethanol and water is a two-component system ( $C = 2$ ) [1].

#### III. 1.2. The phase rule

In a single-component system ( $C = 1$ ), the pressure and temperature may be changed independently if only one phase is present ( $P = 1$ ). If we define the **variance**  $F$  of the system as the number of intensive variables that can be changed independently without disturbing the number of phases in equilibrium, then  $F = 2$ . That is, the system is bivariant and has two degrees of freedom. **Gibbs** deduced **the phase rule**, which is a general relation between the variance  $F$ , the number of components  $C$ , and the number of phases at equilibrium  $P$  for a system of any composition [1]:

$$F = C - P + 2 \quad (1)$$

### III. 2. One-component systems

For a one-component system, such as pure water,

$$F = 3 - P \quad (1a)$$

When only one phase is present,  $F = 2$  and both pressure ( $p$ ) and temperature ( $T$ ) can be varied independently. In other words, a single phase is represented by an area on a phase diagram (Fig. 1). When two phases are in equilibrium  $F = 1$ , which implies that pressure is not freely variable if we have set the temperature. That is, the equilibrium of two phases is represented by a line in the phase diagram. Instead of selecting the temperature, we can select the pressure, but having done so the two phases come into equilibrium at a single definite temperature. Therefore, freezing (or any other phase transition) occurs at a definite temperature and at a given pressure. When three phases are in equilibrium  $F = 0$ . This special invariant condition can therefore be established only at a definite temperature and pressure. The equilibrium of three phases is therefore represented by a point, **the triple point**, on the phase diagram. Four phases cannot be in equilibrium in a one-component system because  $F$  cannot be negative. These features are illustrated by the phase diagram for the one-component system shown in Fig. 1 [1].

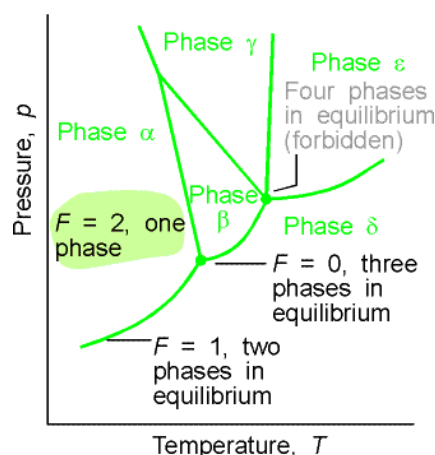


Fig. 1. Typical regions of a one-component phase diagram [1].

### III. 3. Two-component systems

When two components are present in a system,  $C = 2$  and

$$F = 4 - P \quad (1b)$$

For simplicity, we shall keep the pressure constant (at 1 atm., for instance), which uses up one of the degrees of freedom, and write  $F' = 3 - P$  for the remaining variance. One of these remaining degrees of freedom is the temperature, the other is the composition (as expressed by the mole fraction of one component). Hence we should be able to depict the phase equilibria of the system on temperature-composition diagrams, which will be shown in Sec-

tion III. 3.5. Analogically at a constant temperature the pressure-composition diagrams can be obtained (Section III. 3.1) [1].

### III. 3.1. Vapour pressure-composition diagrams

In an ideal solution of **two liquids**, the vapour pressures of the components are related to the composition by the **Raoult's law**:

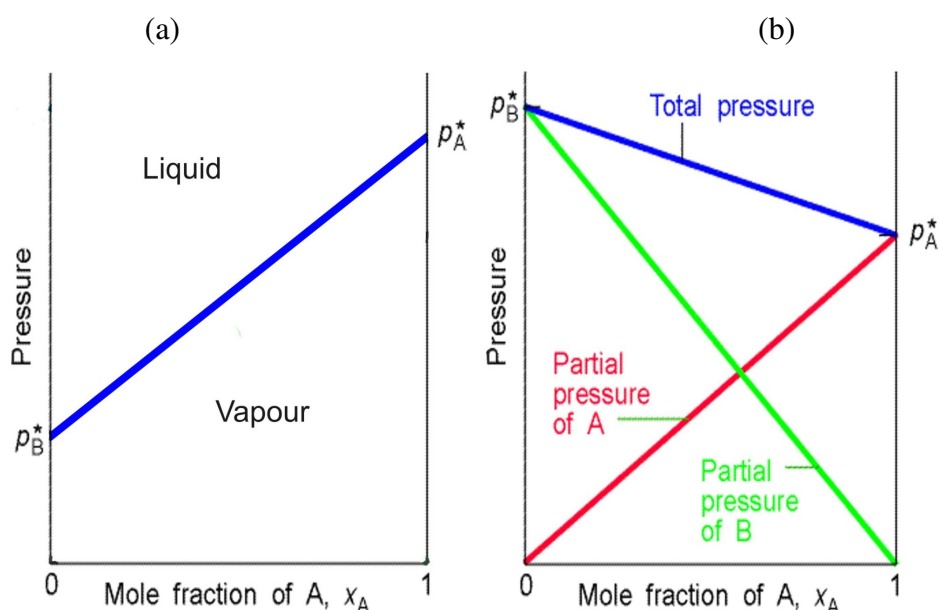
$$p_A = x_A p_A^* \quad p_B = x_B p_B^* \quad (2)$$

where  $p_A$  is the partial pressure of A and  $p_B$  that of B,  $p_A^*$  is the vapour pressure of pure A and  $p_B^*$  that of pure B. When we write equations related to ideal solutions we shall label them with the superscript °.

This law is illustrated in Fig. 2. The total vapour pressure  $p$  of the mixture is therefore:

$$p = p_A + p_B = x_A p_A^* + x_B p_B^* = p_B^* + (p_A^* - p_B^*)x_A \quad (2a)$$

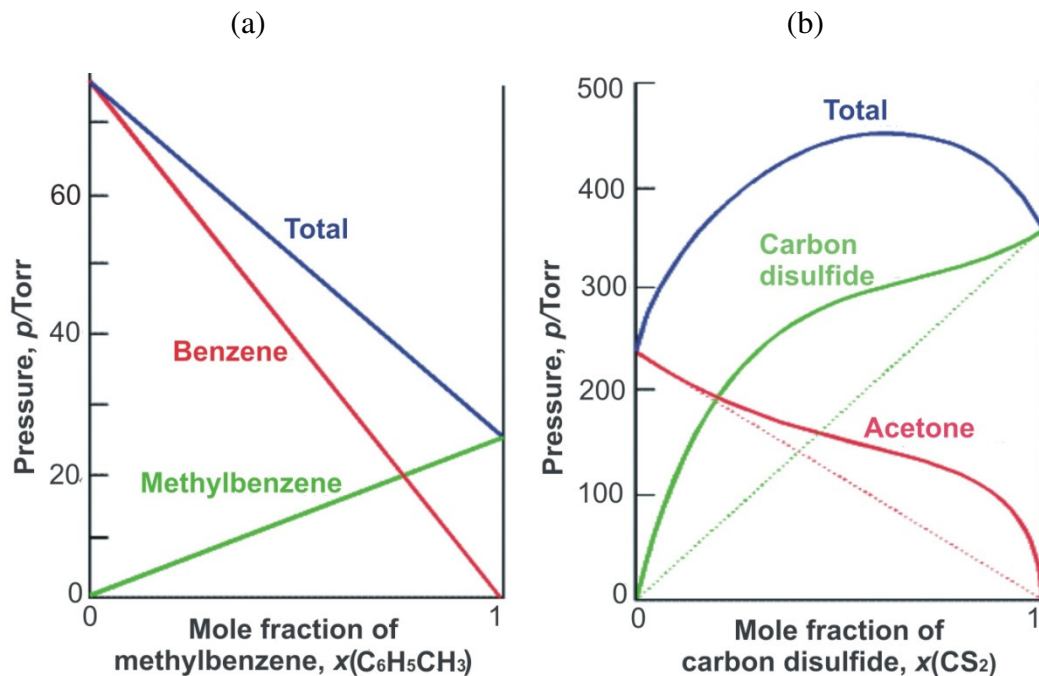
This shows that the total vapour pressure (at a fixed temperature) changes linearly with the composition from  $p_B^*$  to  $p_A^*$  (Fig. 2). All points above the line (where the pressure acting on the system exceeds the vapour pressure) correspond to the liquid being the stable phase. All points below the line correspond to the vapour being stable.



**Fig. 2.** The dependence of the total vapour pressure of a binary mixture on the mole fraction of A in the liquid when the Raoult's law is obeyed (a). The total vapour pressure and the two partial vapour pressures of an ideal binary mixture are proportional to the mole fractions of the components (b) [1].

Some mixtures obey the Raoult's law very well, especially when the components are chemically similar (Fig. 3a). The mixtures that obey the law throughout the composition range from pure A to pure B are called **ideal solutions**. Some solutions depart significantly

from the Raoult's law (Fig. 3b). Nevertheless, even in these cases the law is obeyed increasingly closely for the component in excess (the solvent) as it approaches purity. This means that the law is a good approximation for the solvent so long as the solution is dilute [1].



**Fig. 3.** Variation of the total vapour pressure of a binary mixture with mole fraction of A in the liquid. Two similar liquids, in this case benzene and methylbenzene (toluene), behave almost ideally, and the variation of their vapour pressures with composition resembles that for an ideal solution (a). Strong deviations from ideality are shown by dissimilar liquids (in this case carbon disulfide and acetone (propanone)) (b) [1].

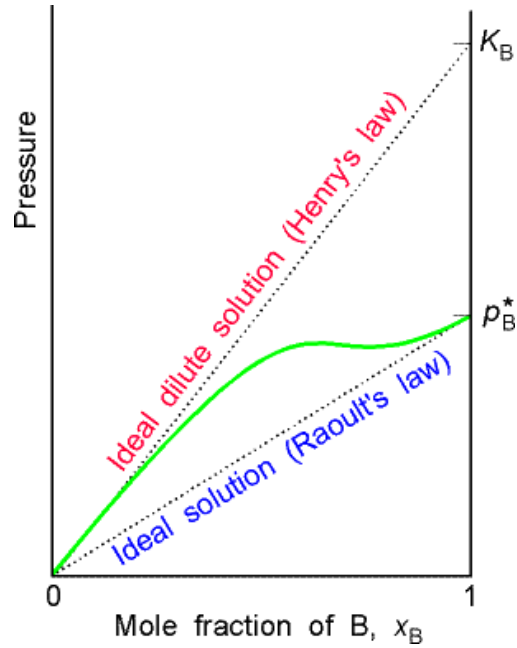
### III. 3.2. Ideal dilute solutions

In ideal solutions the solute, as well as the solvent, obey the Raoult's law. However, in real solutions at low concentrations, although the vapour pressure of the solute is proportional to its mole fraction, the slope is not equal to the vapour pressure of the pure substance (Fig. 4). This linear but different dependence was discovered by Henry, and is now called the **Henry's law**. We express it quantitatively by writing:

$$p_B = x_B K_B \quad (3)$$

where  $x_B$  is the mole fraction of the solute and  $K_B$  is a constant (with the dimensions of pressure) chosen so that the plot of the vapour pressure of B against its mole fraction is tangent to the experimental curve at  $x_B = 0$  (Fig. 4). The mixtures obeying the Henry's law are ideal in a different sense from those obeying the Raoult's law and are called **ideal dilute solutions**. We shall also label **equations with <sup>0</sup>** when they have been derived from the Henry's

law. Over the range of compositions where the solvent obeys the Raoult’s law, the solute obeys the Henry’s law [1].



**Fig. 4.** When a component (the solvent) is nearly pure, it has a vapour pressure that is proportional to the mole fraction with a slope  $p_B^*$  (Raoult's law). When it is the minor component (the solute), its vapour pressure is still proportional to the mole fraction, but the constant of proportionality is now  $K_B$  (Henry's law) [1].

### III. 3.3. The composition of the vapour

The compositions of liquid and vapour in equilibrium are not necessarily the same. Common sense suggests that vapour should be richer in a more volatile component [1]. This can be explained as follows. The partial pressures of the components are given by Eq. 2. It follows from the Dalton’s law that the mole fraction in the gas,  $y_A$  and  $y_B$ , are:

$$y_A = \frac{p_A}{p} \quad y_B = \frac{p_B}{p} \quad (3a)$$

The partial pressures and the total pressure may be expressed in terms of the mole fractions in the liquid using Eq. 2 which gives:

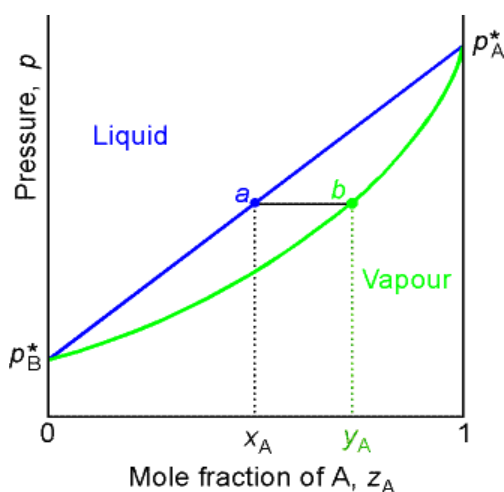
$$y_A = \frac{x_A p_A^*}{p_B^* + (p_A^* - p_B^*)x_A} \quad y_B = 1 - y_A \quad (3b)$$

This equation shows how the total vapour pressure depends on the composition of the liquid. Since we can relate the composition of the liquid to the composition of the vapour through Eq. 2, we can now also relate the vapour pressure to the composition of the vapour itself using the Dalton’s law. This leads to:

$$p = \frac{p_A^* p_B^*}{p_A^* + (p_B^* - p_A^*) y_A} \quad (4)$$

### III. 3.4. The interpretation of the diagrams

We can use a diagram to discuss the phase equilibria of the mixture. However, if we are interested in distillation, both the vapour and the liquid compositions are of equal interest. It is then sensible to combine both diagrams into one. This is done in Fig. 5, where the composition axis is labelled  $z_A$ , the overall mole fraction of A in the system. On and above the upper line, only liquid is present and then  $z_A = x_A$ ; on and below the lower line only vapour is present, and then  $z_A = y_A$ . If a point lies between the lines, we know at once that both phases are present in equilibrium [1].

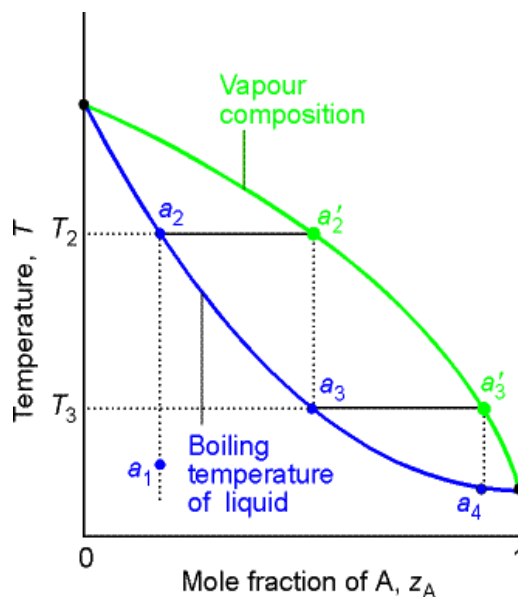


**Fig. 5.** The dependence of the total vapour pressure of an ideal solution on the mole fraction of A in the entire system [1].

### III. 3.5. Temperature-composition diagrams

Reducing the pressure at constant temperature is one way of doing distillation, but it is more common to distil at constant pressure by increasing temperature. To discuss distillation in this way we need a temperature-composition diagram in which the boundaries show the composition of the phases that are at equilibrium at various temperatures (and a given pressure, typically 1 atm.). An example is shown in Fig. 6. Note that the liquid phase region now lies in the lower part of the diagram. A vertical line in the diagram represents a system with the same composition at different temperatures and is called an **isopleth** ('equal abundance') [1].





**Fig. 6.** The temperature-composition diagram corresponding to an ideal mixture with  $A$  more volatile than  $B$  [1].

Successive boiling and condensation of a liquid originally of the composition of  $a_1$  lead to a condensate that is pure  $A$ . This is the process of **fractional distillation**. Let's consider what happens when a liquid of composition  $a$  is heated. Initially its state is  $a_1$ . It boils when the temperature reaches  $T_2$ . Then the liquid has composition  $a_2$  and the vapour (which is present only as trace) has composition  $a_2'$ . The vapour is richer in the more volatile component  $A$ , as common sense leads us to expect. From the location of  $a_2'$  we can state the vapour composition at the boiling point, and from the location of the tie line joining  $a_2$  and  $a_2'$  we can read off the boiling temperature of the original liquid mixture.

In a simple distillation, the vapour is withdrawn and condensed. If the vapour in this example is drawn off and completely condensed, then the first drop gives a liquid of composition  $a_3$ , which is richer in the more volatile component than the original liquid. In fractional distillation, the boiling and condensation cycle is repeated successively. We can follow the changes that occur by seeing what happens when the condensate of composition  $a_3$  is reheated. The phase diagram shows that this mixture boils at  $T_3$  and yields a vapour of composition  $a_3'$  which is even richer in the more volatile component. That vapour is drawn off, and the first drop condenses to a liquid of composition  $a_4$ . The cycle can then be repeated until in due course almost pure  $A$  is obtained [1].

### III. 4. One-phase three-component systems

Let's consider a system consisting of two immiscible liquids (solvents) and a solid substance (solute) dissolved in both solvents.

At constant temperature, equilibrium between the two condensed phases is bivariant. Temperature and concentration of the solute in one solvent layer determine explicitly concentration of this solute in the second layer regardless of the solute phase. However, the solute

cannot increase the mutual solubility of both liquids. If gas is the solute, its concentrations  $c_1$  and  $c_2$ , according to the Henry's law, are proportional to pressure  $p$ :

$$\begin{aligned}c_1 &= \alpha_1 \cdot p_1 \\c_2 &= \alpha_2 \cdot p_2\end{aligned}\quad (5)$$

At equilibrium:

$$\frac{c_1}{c_2} = \frac{\alpha_1}{\alpha_2} = \text{const}\quad (6)$$

where:  $\alpha_1$  and  $\alpha_2$  – the Bunsen's absorption coefficients.

At equilibrium the concentrations ratio of gas  $c_1/c_2$  is constant and independent of pressure. It depends on temperature.

### III. 5. Nernst's distribution law

#### III. 5.1. The partition coefficient

Many organic liquids are more or less immiscible with each other or with water at ordinary temperatures and pressures. In 1881 Nernst enunciated the rules for partitioning of a solute between two immiscible solvents. If a third substance is added to a system of two immiscible liquids, the added component will tend to distribute itself between the two solvents until, at equilibrium, the ratio of the activities of the distributed substance will attain a certain value (Eq. 7). For a solute distributed between two immiscible solvents 1 and 2, the ratio came to be called the partition or distribution ratio (or constant or coefficient). Its relative insensitivity to variations in temperature and concentration led to the use of the terms '**distribution law**' or '**partition law**' [2-4].

$$K = \frac{a_1}{a_2}\quad (7)$$

where:  $K$  is the distribution constant,  $a_1$  and  $a_2$  are the activities of the solute in particular liquids.

The law holds only for the systems which are ideal and for which the solute is in the same molecular state in both solvents at a constant temperature. If single molecular species of a solute were being considered as partitioned between two solvents, the partitioning could be treated as classical thermodynamics as in the equilibrium process where the activity coefficients remain relatively constant [4].

#### III. 5.2. Deviations

Many organic compounds deviate considerably from their ideal behaviour in water and various solvents. Under these conditions the distribution law equation (7) is modified accordingly. The deviations in the simple distribution law are due to the following factors [4]:

– dissociation in one phase

If the solute undergoes dissociation in lower aqueous phase (layer 2, Fig. 7) and  $\alpha$  is its degree of dissociation, activity of undissociated molecules will be  $(1 - \alpha_2) \cdot a_2$ . When  $a_2$  is the activity in that phase the partition ratio becomes:

$$\frac{a_1}{(1 - \alpha_2) \cdot a_2} = K \tag{8}$$

– association in the second phase

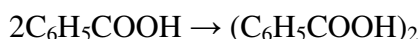
It is possible that the same solute which dissociates in the aqueous layer, associates in the organic layer. Thus, if a substance is associated in organic solution, then this fact is taken into account in formulating the distribution law. Then the equilibrium may be represented as follows:

$$K = \frac{\sqrt[n]{a_1}}{(1 - \alpha_2) \cdot a_2} \tag{9}$$

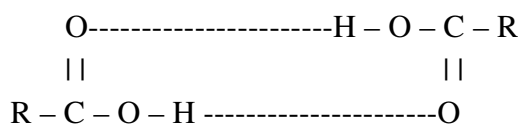
where:  $a_1$  – the activity of solute in the hydrocarbon phase,  $a_2$  – the activity of solute in the aqueous phase.

– dimerization of the solute takes place in one of the layers

For example, in the distribution of benzoic acid between hydrocarbon and aqueous phase, it was found that the dimerization process takes place in the organic layer.



Due to hydrogen bonding the carboxylic acids and some other classes of polar molecules tend to form double molecules.



This effect becomes marked when the carboxylic acid is dissolved in a solvent with a low dielectric constant such as benzene. This is because the hydrogen bond is due to electrostatic attraction and the force between two charges at a given separation in a medium of dielectric constant  $D$  is inversely proportional to  $D$ . If a carboxylic acid is distributed between a solvent such as benzene in which dimerization is found to occur and another solvent such as water in which dimerization is unlikely to take place, deviations from the linear distribution law will occur.

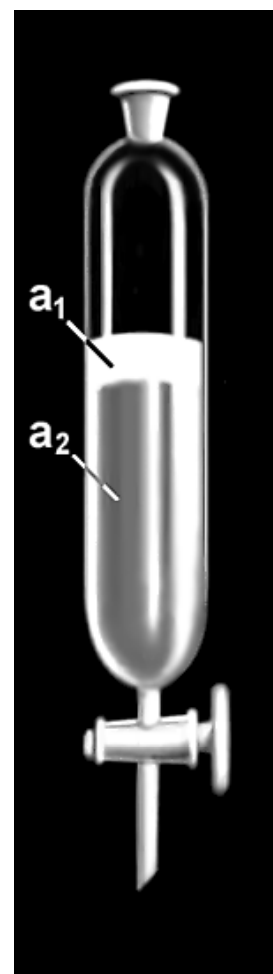


Fig. 7. The cylindrical separatory funnel [5].

Principal assumptions involved are that the acid forms an ideal solute in water and that both monomer and dimer species of the acid are ideal solutes in the organic phase.  $\alpha$  is the degree of dissociation and its value used in equation (8) is obtained from the known value of dissociation constant  $K_a$  [4].

It is preferable to define the partition coefficient as referring to the same molecular species in both solvents, as Nernst did. This provision is now part of the definition of the true partition coefficient. Even if the distributed substance does not associate or dissociate in the solvents, in general there will be a concentration dependence of the partition coefficient as defined by Eq. 7. This is due to the fact that, as concentration is increased, the solute passes from the dilute solution region to the concentrated solution region, i.e., beyond the region where the Henry's law holds. Outside the dilute solution region, solute-solute interactions become progressively more important and cannot be neglected [2].

In the case of dilute solutions activity can be replaced by concentration. Then, the partition law gives:

$$K = \frac{\sqrt[n]{c_1}}{(1 - \alpha_2) \cdot c_2} \quad (10)$$

where:  $c_1$  – the concentration of solute in the hydrocarbon phase,  $c_2$  – the concentration of solute in the aqueous phase.

#### – combination with one solvent

If the distributed substance combines with one phase, forming solvates, and is normal in the other phase, the molecular state in the two phases is not identical.

#### – reactions in both phases

When partition of solute is made in two solvents and reaction takes place in both phases, then in general the equilibrium constant cannot be derived.

#### – hydrogen bonding

Hydrogen bonding is an important factor to consider in studying the energy requirements in the phase transfer. This factor determines the character of both the solute and the organic solvent phase.

#### – dispersion forces

Other intramolecular forces which must be considered in the partitioning process are dispersion forces. These forces involved in complex formation in solution cancel out when a solute molecule leaves one phase and enters a new one.

### – pH of an acid

The partition coefficient also depends upon pH of an acid. Solutes which are ionized and completely dissociated in the aqueous phase are related with electrical conductivity. Solutes in the organic solvents which have relatively high dielectric constant could be considered to be 90 % dissociated into single ions [4].

## III. 6. Applications of the distribution law

The partition measurements are found to have great importance in the field of chemistry and industry [3,4].

### – process of extraction

It is an important application that organic compounds are extracted with immiscible solvents. The compounds which are more soluble in organic solvents than in water can be removed from aqueous solutions by shaking with another immiscible organic liquid. In extraction from water, the greater the distribution coefficient in favour of an organic solvent, the more rapidly the substance can be extracted from the aqueous phase. The distribution coefficient can be easily increased artificially by making the substance less soluble in the aqueous phase. This can be done by adding a substance which depresses the electrolytic dissociation of the compound being extracted.

While washing precipitates, impurity is distributed between water and the precipitate, and it would be more effective to use small quantities of water and repeat the process a number of times. This also shows that the smaller the portion of the extracting liquid and the larger the number of extractions, more complete is the extraction for a definite volume of the extracting liquid.

Optimization of separation processes to produce the purest possible product at the highest yield and lowest possible cost, and under the most favorable environmental conditions, requires detailed knowledge about the solute reactions in the aqueous and organic phases.

Solvent extraction is used in nuclear reprocessing, ore processing, extraction of metals from their oxides, production of fine organic compounds, processing of perfumes, production of vegetable oils and biodiesel, and other industries.

### – complex ion formation, hydrolysis of salts and association or dissociation

### – measurement of dissolution and partitioning rate of drugs

It is widely accepted that the dissolution rate of any drug given in a solid form can have marked influence up to the amount effectively absorbed. Since drug absorption is also affected by its effective partition coefficient, it is desirable to measure these properties simultaneously. This becomes more important in view of the observation that some surfactants are capable of increasing the rate of partitioning.

In the past decade far more partition coefficients have been determined in connection with biological structure-activity relationship studies. A large number of these studies have been carried out and showed the usefulness of the octanol-water parameter to predict the binding of solutes to serum albumin and to purified enzymes [3,4].

## IV. Experimental

### A. Devices and materials

#### 1. Equipment:

- measuring flask – 25 cm<sup>3</sup> – 4 u,
- measuring flask – 50 cm<sup>3</sup> – 1 u,
- separatory funnel – 250 cm<sup>3</sup> – 4 u,
- digital burette – 1 u,
- conical flask – 200 cm<sup>3</sup> – 4 u,
- beaker – 100 cm<sup>3</sup> – 4 u,
- graduated pipette: 10, 25, 50 cm<sup>3</sup> – 3 u,
- weighing bottle – 1 u,
- funnel – 1 u,
- apparatus for shaking – 1 u,
- stand for the separatory funnel – 1 u.

#### 2. Materials:

- toluene,
- benzoic acid,
- distilled water,
- NaOH solution – 0.01 M,
- phenolphthalein solution.

### B. Use of devices

#### 1. Operation of digital burette (Fig. 8) for titration:

- turn the burette on when you have prepared solutions for titration,
- unscrew the **red cap** at the tip of burette,
- turn the burette display on with the black button on the left side in the **On/Off** position (zero will appear on the screen),
- press the black button on the right to the **Fill** position (arrow under the zeros on the display set under the first two zeros) and turn the titrate wheel up on the right side of electronic head casing to fill the burette (burette moves to the top). Under the plastic part of the burette, you can see the metal teeth and behind them the transparent container with the liquid for titration. If you see a large air bubble at the top of the container, turn the titrate wheel down with fast movement to remove liquid from the container. Repeat this operation until you get rid of the air (small bubbles can stay inside),
- it is not allowed to turn the titrate wheel up if the black button is not in the **Fill** position!

- if during the above steps any digits appear on the display you can reset the burette by pressing with the button on the left in the **Clear** position (zero will appear on the display),
- press the black button on the right side in the **Titr.** position (arrow under the last two zeroes) – the burette is ready to titrate,
- titrate the particular samples by turning the black titrate wheel down on the right side of burette,
- during titration you get the volume of liquid in  $\text{cm}^3$  on display,
- after the end of titration of each sample, press the **Clear** button (to zero the display) then you can titrate the next sample. A completely filled burette contains  $25 \text{ cm}^3$  of liquid – during the titration its upper part decreases (you can see how much titrant is left),
- if necessary, the burette may be refilled at any time during titration by pressing the button on the right side in the **Fill** position (by turning the titrate wheel up),
- after making all titrations leave the button on the right side in the **Fill** position and turn the burette off by pressing the black button on the left in the **On/Off** position,
- turn the **red cap** off at the tip of burette,
- if during the usage of burette you feel strong resistance, it is forbidden to turn on using force, you should ask for help the demonstrator.



Fig. 8. The digital burette.

### C. Methods

Prepare a stock solution containing approximately 2.50 g of benzoic acid in toluene using the measuring flask of  $50 \text{ cm}^3$  volume; write the acid weight to three decimal places. Prepare the four working solutions taking 3.8, 7.5, 15 and  $20 \text{ cm}^3$  of the stock solution to the flasks of  $25 \text{ cm}^3$  volume and filling to the mark with toluene. Pour the obtained working solutions to the separatory funnels containing  $50 \text{ cm}^3$  of water and carry them from the stand to the handles (holders) of apparatus for shaking at the locked position of the crank (cotter pin in the hole). Close the jaws gently tightening the screws of the particular holders. Before shaking check the safety elements of stoppers in the separatory funnels.

Shake the separatory funnel content for 15 min making the rhythmic 180-degree turns with the crank. After each half turn a short pause of about 0.5 s should be. Then the lighter liquid, which after rotating the separator is on the bottom, squeezes through the aqueous layer to provide good mixing. Another rotation should be performed only when the lighter liquid is



above the aqueous layer. Smooth turns of the crank do not meet the conditions for good mixing and distribution of the substance. After the expiry of the time (15 min) put the separatory funnels in stand and leave those until the layers separate and the liquid solutions clarify.

When the aqueous layer (lower layer) is already quite clear, then remove the stoppers and carefully drain the lower layer into a beaker or conical flask. Only well stratified aqueous phase should be drained, the toluene (upper) layer remains in the separatory funnel.

From each aqueous solution pipette two volumes of 10 cm<sup>3</sup> and titrate the dissolved therein benzoic acid with 0.01 M NaOH solution using phenolphthalein as an indicator.

The average value of titration results allows calculating the concentration of benzoic acid in water. Knowing the total amount of acid in the separatory funnel and the volume of water and toluene one can calculate the concentration of acid in the aqueous phase.

The results of measurements should be included in Table 1.

**Table 1.** The results of titration of benzoic acid with 0.01 M NaOH solution.

Separatory funnel No.	Volume of NaOH in cm <sup>3</sup>		
	Sample 1	Sample 2	Average
1			
2			
3			
4			

#### D. Results and conclusions

The aim of the task is:

- calculation of the distribution constant  $K$  for each measurement.
- determination of the molecular state of benzoic acid in the phases of the system studied.
- determination of  $K$  and  $n$  values by means of the graphical method and expression of mathematical equation describing the partition of benzoic acid between toluene and water. All the data needed for the calculations and drawing the graph should be listed in Tables 1 and 2.

The sequence of calculations:

1. Calculate the amount of benzoic acid in the working solutions (the number of moles in 25 cm<sup>3</sup>).
2. Calculate the number of moles of benzoic acid in the aqueous phase after extraction having the aqueous phase volume of 50 cm<sup>3</sup>.
3. Calculate the number of moles of benzoic acid in 25 cm<sup>3</sup> of the organic phase (in toluene); the difference between its amount in the working solution and in 50 cm<sup>3</sup> of the aqueous phase.

4. Calculate the molar concentration of benzoic acid in the organic ( $c_1$ ) and aqueous ( $c_2$ ) phases.
5. Calculate the partition constant  $K = c_1/c_2$  for each sample.
6. Calculate the degree of dissociation of benzoic acid in the aqueous phase ( $\alpha_2$ ).
7. Plot the relationship:  $\log [c_2(1-\alpha_2)] = f(\log(c_1))$  and determine the parameters of the obtained straight line ( $K$  and  $n$ ).

Put the obtained results in Table 2.

**Table 2.** The results of calculations.

Number of grams of benzoic acid in the separatory funnel	Average volume of NaOH in $\text{cm}^3$	$c_2$ $\text{mol/dm}^3$	$c_1$ $\text{mol/dm}^3$	$\log [c_2(1-\alpha_2)]$	$\log (c_1)$
1					
2					
3					
4					

### Example of calculation

DATA : (fictitious)

The acid weight (mass): 2.5 g. The results from the subsequent titration are: 6.1; 9.1; 13.6; 16  $\text{cm}^3$ , respectively. Studying the distribution of benzoic acid between water and toluene at  $T = 298 \text{ K}$  the following results can be obtained:

$$\begin{array}{ll} \text{aqueous layer,} & c_2 = 0.0061, 0.00910, 0.01360, 0.0160 \text{ mol/dm}^3 \\ \text{toluene layer,} & c_1 = 0.0500, 0.10463, 0.21845, 0.2955 \text{ mol/dm}^3 \end{array}$$

Replacing activity by concentration, it is possible to calculate from equation (7) the value of partition constant  $K$  and obtain:  $K = 8.2020, 11.4975, 16.0628, 18.4716$ . As can be seen the concentration ratio  $c_1/c_2$  is not constant. This proves the different molecular state of benzoic acid in both phases. In this case, use the general equation (10). Knowing that benzoic acid undergoes the electrolytic dissociation in water, it is expected to associate in the toluene layer. Taking logarithm of equation (10) the following expressions were obtained:

$$-\log K = \log [c_2(1-\alpha_2)] - \frac{1}{n} \log (c_1)$$

Hence

$$-\log K + \frac{1}{n} \log (c_1) = \log [c_2(1-\alpha_2)] \quad (11)$$

Taking logarithm of equation (10) gave a linear relationship between:

$$\log(c_1) \quad \text{and} \quad \log[c_2(1-\alpha_2)] \quad (12)$$

The value of  $\alpha_2$  was calculated from the equation:  $\alpha_2 = \sqrt{\frac{K_d}{c_2}}$

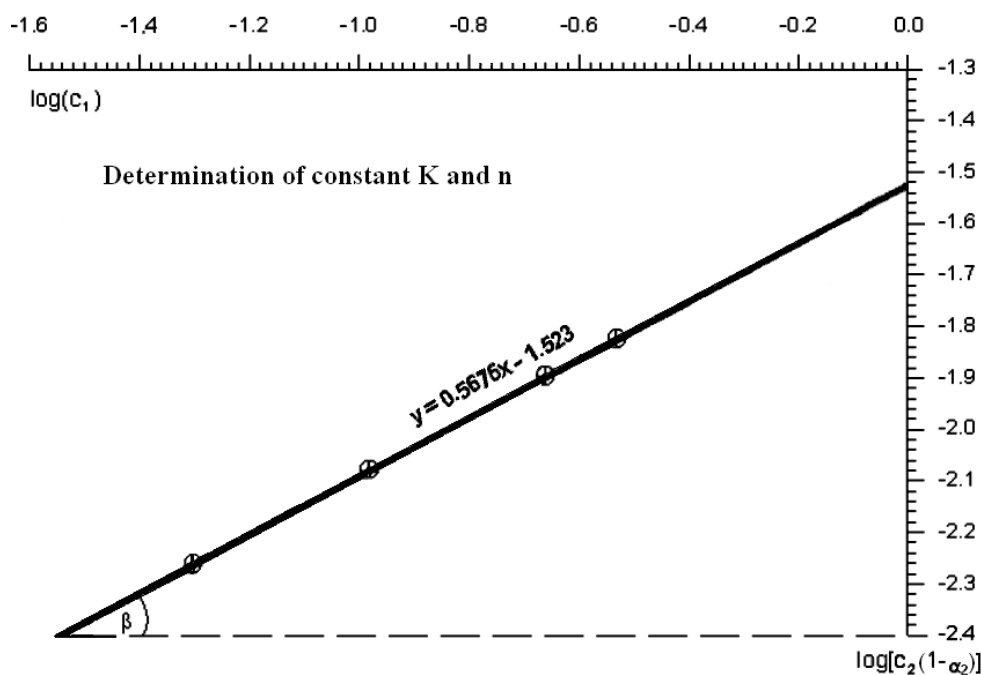
The dissociation constant of benzoic acid:  $K_d = 6.46 \cdot 10^{-5}$

The molecular mass:  $M = 122.123 \text{ g}$

The value of  $n$  was calculated from the slope of the straight line:

$$n = 1/\text{tg}(\beta) = 1.74$$

The value of  $-\log(K)$  was read from the intersection of the straight line with the axis:  $-\log(K) = -1.523$ , hence:  $K = 10^{1.523} = 33.3426$ .



**Fig. 9.** Graph of the relationship  $\log [c_2(1-\alpha_2)] = f(\log(c_1))$  [5].

After completing the task pour the aqueous solutions after titration into the sink, and **the toluene phase to the bottle labelled as slops (swill)**, placed in the fume hood. Rinse the conical flasks with water. Then, pour a few  $\text{cm}^3$  of acetone to one of the separatory funnels, rinse it, and pour acetone into the subsequent separatory funnels and repeat the procedure. After rinsing pour acetone into a bottle of swill. With a small portion of acetone, rinse the pipettes used for sucking the benzoic acid solutions.