

Faculty of Chemistry and Chemical Engineering

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# STAGEWISE PROCESSES LABORATORY HANDBOOK

(Collected material)

Maribor, 2017

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CIP – Catalogue record University of Maribor library

66.02/.09(075.8)(076)

KNEZ, Željko Stagewise Processes, Laboratory handbook: (Collected material) / Željko Knez, Mojca Škerget. – Maribor: Faculty of Chemistry and Chemical Engineering, 2000

ISBN 86-435-0361-4

1. Škerget, Mojca COBISS-ID 45348609

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Title of the publication:	STAGEWISE PROCESSES, LABORATORY HANDBOOK		
Type of publication:	Collected material		
Authors:	Full Prof. Dr. Željko Knez, Full Prof. Dr. Mojca Škerget		
Proof-reader:	Dr. Victor Kennedy		
Publisher:	Faculty of Chemistry and Chemical Engineering, Maribor		
Printing:	Printing office of the Technical Faculties		
Copies:	100 copies		
Year of publication:	2000		
First reprint:	2009		

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# **1.THIN FILM EVAPORATION**

## **1.1. THEORETICAL BACKGROUND**

The main parameters that influencee evaporation in a thin film evaporator are the following:

- The temperature of the heating medium,
- The operating pressure in the evaporator and condenser,
- The flow rate of the feed solution,
- The speed of the rotor.

#### 1.1.1. Theoretical thickness of the film

The thickness of the film plays a major role in the evaporation process. It depends on the mass flow of the feed solution, its viscosity and the speed of the rotor. It is important to know the thickness of the film, in order to study the heat transfer in the thin film evaporator.

The theoretical thickness of a falling film is calculated using the Hagen – Poiseuille equation:

$$\delta = \sqrt[3]{\frac{3\eta F}{\rho^2 g \pi d}} \qquad \qquad \text{Eq (1.1)}$$

where:  $\rho$  – density (kg/m<sup>3</sup>),

- F mass flow (kg/s),
- $\pi d$  internal diameter of the evaporator (m),
- $\eta$  dynamic viscosity (Ns/m<sup>2</sup>),
- $\delta$  the thickness of the film entering the evaporator (m).

#### 1.1.2. Retention time of the solution in the evaporator

The retention time is the amount of time the feed solution is exposed to high temperature. The retention time is reduced by mechanically distributing the solution over the heating surface. It

depends on the flow rate of the feed solution through the evaporator, on the film thickness and on the thermal load.

The retention time for the concentrated effluent is higher than that for the distillate, since the solution starts evaporating immediately after entering the evaporator.

#### 1.1.3. Mass balance

The mass balance calculations for a 2-component mixture are carried out considering a differentially small area of the evaporator. A thin film of feed solution flows along the heated wall of the cylinder, and at the point h=Z reaches the evaporation temperature. We assume that the vapours are immediately leaving the surface of the film. At the arbitrary point h+dh, the solution has a flowrate L, and a concentration of the more volatile compound X. Along the dh distance, an amount of vapour dV, with the equilibrium concentration  $Y_E$ , is formed at the film boundary. The remaining flowrate at point h is (L-dV), and the concentration of the more volatile component is smaller by dX. Meanwhile, the flowrate of the vapours V increases along the dh distance by the small amount dV, while the vapour concentration Y is increased by dY.

The mass balance can be written as:

$$L \cdot X = dV \cdot Y_E + (L - dV) \cdot (X - dX)$$
Eq. (1.2)

where: *L* – flowrate of the feed solution;

- *X* concentration of the more volatile compound,
- *dV* the amount of vapour formed at the film boundary along the differentially small distance dh,
- $Y_{\rm E}$  equilibrium concentration of the vapours in dV,
- (L-dV) the resulting flowrate of the solution at point h,
- *dX* the difference in the concentration of the more volatile compound.



**Figure 1.1:** Flow rates and concentration in the differentially small area of a thin film evaporator.

We ignore the second differential term, and we write:

$$dV = L \cdot \frac{dX}{Y_E - X}$$
 Eq. (1.3)

We consider dV = -dL, and we integrate Eq. (1.3) for the boundary conditions h=0 (L=B, X=X\_B) and h=Z (L=F, X=X\_F).

$$\int_{B}^{F} \frac{dL}{L} = \int_{X_{B}}^{X_{F}} \frac{dX}{Y_{E} - X} \qquad \qquad \text{Eq. (1.4)}$$

We introduce the evaporation ratio:

$$m = \frac{B}{F}$$
 Eq. (1.5)

where: B – flowrate of the concentrated effluent (mol/h),

F – flowrate of the feed solution (mol/h).

$$\ln\left[\frac{F}{B}\right] = \ln\left[\frac{1}{m}\right] = \frac{dX}{Y_E - X}$$
 Eq. (1.6)

The integral is solved using the graphical method. We mark the values of the integral  $\int_{X_B}^{X_F} \frac{dX}{Y_E - X}$  as I<sub>F</sub> and I<sub>B</sub>, and we change Eq. (1.4) to:

$$\ln\left[\frac{1}{m}\right] = \int_{X_B}^{X_F} \frac{dX}{Y_E - X} = I_F - I_B \qquad \text{Eq. (1.7)}$$

where:  $I_F$  – the value of the integral at the upper limit, at the concentration of the feed,

 $I_{\text{B}}$  – the value of the integral at the lower limit, at the concentration of the concentrate effluent.

Starting from the mass balance equations, and using the results of the graphical method, we can calculate the concentration Y in the vapour:

$$F = B + D \qquad Eq. (1.8)$$

$$F \cdot X_F = B \cdot X_B + D \cdot X_D \qquad \qquad \text{Eq. (1.9)}$$

The more volatile compound in the vapour:

$$Y_{\rm D} = X_{\rm F} - \frac{{\rm m} \cdot X_{\rm B}}{1-{\rm m}}$$
 Eq. (1.10)

$$D = F \cdot (1 - m)$$
 Eq. (1.11)

From Eq. (1.8) and (1.9), we can determine B and D:

$$D = \frac{F \cdot (X_B - X_F)}{(X_B - X_D)}$$
 Eq. (1.12)

$$B = \frac{F \cdot (X_F - X_D)}{(X_B - X_D)}$$
 Eq. (1.13)

#### 1.1.4. Heat balance

The heat flow, transferred through the wall of the internal cylinder, is used for heating and evaporating the feed solution:

$$dQ = H_i - dV Eq. (1.14)$$

According to Fourier:

$$dQ = U \cdot dA \cdot \Delta T - U \cdot \pi \cdot d_i \cdot d_z \cdot T \qquad \text{Eq. (1.15)}$$

where:  $H_i$  – heat of vaporization,

- di the internal diameter of the evaporator,
- U heat transfer coefficient,
- T the difference between the boiling temperature of the mixture and the temperature of the heating medium.

We consider the average values of U,  $H_i$  and T as constant, and by applying them to Eq. (1.6), (1.12), (1.13) and (1.14), we can calculate the necessary height of the evaporation cylinder:

$$Z = \frac{F \cdot (1-m) \cdot H_i}{\pi \cdot U \cdot d_i \cdot \Delta T}$$
 Eq. (1.16)

Eq. (1.16) is valid if the feed solution (F) is already pre-heated to its boiling point, so that all the heat transferred inside the cylinder is used for evaporation.

The heat transfer coefficient U accounts for the resistance to the flow of heat on the side of the heating medium, in the evaporator wall, and on the side of the evaporation process.

$$\frac{1}{U} = \frac{1}{k_1} + \frac{d}{\lambda} + \frac{1}{k_2}$$
 Eq. (1.17)

where: k1, k2 – heat transfer coefficients on the side of the heating medium and of the evaporation, respectively,

- d thickness of the evaporator wall,
- $\lambda$  thermal conductivity.

U can be calculated using Eq. (1.16) and applying experimental values:

$$U = \frac{F \cdot (1-m) \cdot H_i}{\pi \cdot Z \cdot d_i \cdot \Delta T}$$
 Eq. (1.18)

The heat flow summarizes the heat necessary to bring the solution to the boiling temperature, and the heat necessary for evaporation.

The heat and mass balance:

$$Q = D(h_f - h_n) + F(h - h_v)$$
 Eq. (1.19)

where: Q - heat flow,

D – mass flow of distillate,

F – mass flow of feed solution,

h<sub>v</sub> – enthalpy of the feed solution entering the evaporator,

h<sub>n</sub> – enthalpy of the heating medium,

h<sub>p</sub> – enthalpy of the vapours.

### 1.2. TASK

Use a binary solution of water-ethanol and perform thin film evaporation. Determine the influence of the processing parameters (flowrate and temperature or pressure) on the ethanol concentration in the distillate and concentrated effluent.

### **1.3. TASK IMPLEMENTATION**

The diagram of the apparatus is shown in Fig. 1.2. The main part of the apparatus is represented by the thin film evaporator. The device is supported by a frame, which is fixed on a base plate. The feed solution is introduced in a container, where it can undergo pre-heating. The container has the shape of a Marriott-type bottle (A). The flow of the feed solution is regulated using a needle valve (B), and it is constant, regardless of the level of the feed solution in the container.

The evaporator is made out of chemically resistant glass. The heating surface of the evaporator is 0.016m<sup>2</sup>.

Use the vacuum pump to regulate the pressure inside the evaporator. Because of the vacuum, part of the feed solution will evaporate immediately after entering the evaporator. The distribution ring spreads the remaining solution across the cylinder, while the blades of the rotor ensure uniform film thickness.

The rotor (E) is made of stainless steel, and is supported by Teflon bearings. A magnetic coupling (F) ensures the connection between the rotor and an electromotor (G), which allows control of the rotation speed. The circulating thermostat (H) used for the heating medium is equipped with a contact

and a control thermometer. Paraffin oil is used as the heating medium, since it withstands temperatures of up to 200°C.

The regulating valve for the pressure (K) is connected to a vacuum pump. The part of the solution that does not evaporate is collected in the concentrate container (J). In the lower part of the evaporator, it is possible to add an adapter (O) that will prevent the outflow of the film and will increase the retention time.

The condenser (L) is used for collecting the vapours. It employs water as a cooling medium. It is necessary for the condenser to ensure the fast condensing of the vapours, thus preventing their loss by suction into the vacuum pump. A nozzle located between the condenser and the distillate collector provides the connection to the vacuum pump (N).

#### Execution:

- 1. Prepare 2 L of ethanol solution of a given concentration. Determine the refractive index of the solution, using a refractometer.
- 2. At constant operating temperature and pressure, determine the optimal flow of the feed solution, which can be regulated using the needle valve, and measure the flow using a stop-watch. Perform at least three measurements.
- At constant optimal flow, determine the optimal operating temperature (or pressure). Perform at least 3 measurements.
- 4. For each measurement, use at least 200 mL of the feed solution.
- 5. For each measurement, determine the concentration of ethanol in the distillate and in the concentrate, by measuring the refractive index and reading the concentration values from the calibration curves (see Annexes, Tables A1 and A2, Figure A2).

# 1.4. PRESENTATION OF THE RESULTS IN THE LABORATORY NOTEBOOK

Present the results of the measurements as shown in the table:

		<i>n</i> <sub>D</sub> <sup>20</sup>		w (%)		
T (°C)	P (bar)	Φ <sub>v</sub> (ml/min)	distillate	residue	distillate	residue

For the distillate and the concentrate, represent graphically the following results:  $w(\%) = f(\Phi_v)$ , and w(%) = f(T) or w(%) = f(P)



**Figure 1.2:** Thin film evaporator: A - container in the shape of a Marriott-type bottle, B – needle valve, C – heating coil, D – glass pipe, E – rotor, F – magnetic coupling, G – electromotor, H - circulating thermostat, J – concentrate collector, K – pressure regulating valve, L – condenser, M – distillate collector, N - connection to the vacuum pump, O – adapter

# **2.DIFFERENTIAL DISTILLATION**

### 2.1. THEORETICAL BACKGROUND

The simplest batch distillation method, which is performed in only one stage, is called differential distillation. The apparatus consists of a boiler, heated with steam or oil, a condenser and a distillate collector. During the distillation, the vapours are led away from the boiler and condensed in the condenser. Since the vapours are richer in the more volatile compound, the residue in the boiler becomes richer in the less volatile component. While the vapours are at any given moment in equilibrium with the solution in the boiler, the distillate in the collecting vessel is not in equilibrium with the distillation residue. The target for the distillation of a multicomponent mixture is to obtain a certain amount or a certain composition of the distillate.

Differential distillation has little commercial importance, since it has a low yield, and the resulting products are not sufficiently pure. The method is efficient if there is a large difference between the boiling points of the components in the mixture (high relative volatility). It is used for a small number of mixtures with various initial compositions, and for separations where high purity of the products is not a requirement.

The mass balance can be written as:

$$m_{\rm F} = m_{\rm D} + m_{\rm W}$$
 Eq. (2.1)

and for the more volatile compound:

$$m_F x'_F = m_D x'_D + m_W x'_W$$
 Eq. (2.2)

where m is the mass of the mixture to be distilled (kg), and x' is the mass fraction of the more volatile compound in the feed solution (F), distillate (D) and residue (W).

When distilling the differentially small amount of mixture dm, the distillate will have the equilibrium concentration y', while the concentration in the residue will decrease to x'-dx':

$$m \cdot x' = (m - dm)(x' - dx) + y'dm$$
 Eq. (2.3)

Or:

$$\frac{\mathrm{dm}}{\mathrm{m}} = \frac{\mathrm{dx}'}{\mathrm{y}' - \mathrm{x}'} \qquad \qquad \text{Eq. (2.4)}$$

By integration between the boundary conditions for the liquid mixture at the beginning and at the end of the distillation,  $m_F$  and  $m_W$ , and their corresponding concentrations  $x_F'$  and  $x_W'$ , we obtain:

$$\frac{\ln m_{\rm F}}{m_{\rm w}} = \int_{x'_{\rm w}}^{x'_{\rm F}} \frac{dx'}{y' - x'}$$
 Eq. (2.5)

The integral on the right side of the equation is solved by applying the graphical method. Using the equilibrium data, we calculate the values of the ratio  $\frac{1}{y'-x'}$  for a range of concentrations x' between  $x_{F'}$  and  $x_{W'}$ , and we draw the diagram  $\frac{1}{y'-x'} = f(x')$  (Fig. 2.1). The value of the integral is represented by the area under the curve, calculated between the initial and final concentrations.



We then determine the mass of the distillation residue by applying the equation:

$$m_W = m_F \cdot e^{-A} \qquad \qquad \text{Eq. (2.6)}$$

### 2.2. TASK

Knowing the mass and concentration of the feed solution, determine the amount of distillate that needs to be produced in order to obtain the required concentration of the more volatile compound. The feed solution is composed of a mixture of methanol and water.

### 2.3. TASK IMPLEMENTATION

Starting from the given input data and from the equilibrium data for the methanol-water mixture, determine the amount of distillate that needs to be produced in order to obtain the required concentration of the more volatile compound. Use experimental measurements to verify the calculated values. The apparatus is shown in Fig. 2.2. Before starting the experiment, turn on the thermostat used for heating the oil, which is employed as a heating medium in the double-jacketed boiler. Pour the binary solution of known mass and composition into the distillation boiler. During the experiment, follow the temperature in the boiler and the temperature of the vapours. Collect the necessary amount of distillate, then turn off the thermostat and wait for the distillation residue in the boiler to cool down below its boiling point. Determine the concentration of methanol in the distillate and residue by measuring the refractive index (see Annex). Weigh the amounts of distillate and residue, and determine the losses that occurred during the distillation process.



Figure 2.2: Apparatus for differential distillation.

#### Calculation:

Assume the concentration of the distillation residue  $x_{w'}$ , and calculate the area under the curve  $\frac{1}{y'-x'} = f(x')$ . Using Eq. (2.6), calculate the amount of distillation residue  $m_w$ . Next, calculate the amount of distillate, first using Eq. (2.1), and again using Eq. (2.2). Repeat the steps above with other values of  $x_{w'}$  until the amount of distillate calculated with the two equations is the same.

# 2.4. PRESENTATION OF THE RESULTS IN THE LABORATORY NOTEBOOK

Use the following table to show the calculation steps for the amount of distillate that needs to be collected:

xw	Α	m <sub>w</sub> (2.6)	m <sub>D</sub> (2.1)	m <sub>D</sub> (2.2)

Compare the calculated and experimental results.

# **3.RECTIFICATION**

# 3.1. THEORETICAL BACKGROUND

The distillation process where part of the condensed vapours is returned as reflux in the distillation apparatus is called rectification. When the vapours and the reflux come in contact in the rectification column, both mass and heat transfer take place. The high volatile compound evaporates from the reflux, while the low volatile compound condenses from the vapours. This leads to an increase in the concentration of the more volatile compound in the vapours, and of the less volatile compound in the reflux.

Contact between the reflux and the vapours takes place in the rectification column. The vapours enter in the lower part of the column and rise, while the reflux is introduced in the upper part. In the column, the vapours are at boiling temperature, and the reflux is at condensation temperature. Towards the top of the column, the concentration of the more volatile compound increases in both phases, while the temperature decreases.

#### 3.1.1. Rectification apparatus

The diagram of the continuous rectification apparatus is shown in Fig. 3.1. The feed solution (F) is introduced in the middle section of the column. The solution flows down towards the reboiler, where it is evaporated. The liquid part is removed as residue, while the vapours rise through the column, come into contact with the counterflow reflux, and leave the column at the top. The vapours pass through the condenser, part of the condensate is recirculated as reflux ( $L_0$ ), and part is collected as distillate (D).

The section of the rectification column above the feed plate is called the rectifying section, while the lower section, including the feed plate, is called the stripping section. If we were to introduce the feed solution directly into the reboiler, we would obtain the desired purity of the more volatile compound in the distillate, but not of the less volatile compound in the residue; and the other way around when introducing the solution at the top of the column.



Figure 3.1: The continuous rectification apparatus.

#### 3.1.2. Mass balance

#### a) The mass balance of the entire rectification column:

$$F = W + D \qquad Eq. (3.1)$$

and for the more volatile compound:

$$F \cdot x_F = W \cdot x_W + D \cdot x_D$$
 Eq. (3.2)

If we know D and the initial and final concentrations, we can determine W from Eq. (3.1) and (3.2):

$$W = D \cdot \frac{x_D - X_F}{x_F - x_B}$$
 Eq. (3.3)

b) The mass balance for the upper (rectifying) section of the column

$$V = L + D \qquad Eq. (3.4)$$



Figure 3.2: Diagram of the upper section of the rectification column.

If the temperature of the reflux flowing in at the top of the column is not lower than the condensation temperature, then  $L = L_0$  and the reflux ratio R is:

$$R = \frac{L}{D}$$
 Eq. (3.5)

#### c) The mass balance for the lower (stripping) section of the column

The flow of the vapours or/and of the reflux is affected in the lower section of the column by the input of the feed solution. The change in the flow of reflux in the stripping section of the column caused by every mol/h of feed solution is marked with e:

$$e = \frac{L' - L}{F}$$
 Eq. (3.6)

$$W = L' - V'$$
 Eq. (3.7)

$$V' = V - (1 - e)F$$
 Eq. (3.8)



Figure 3.3: Diagram of the lower section of the rectification column.

The value of e is obtained from the mass and heat balance of the feed plate f. If we consider  $z(h_{f}-h_{F})$  the energy necessary to heat up 1 mol of feed solution to its boiling point, and  $z(H_{f}-h_{f})$  the condensation heat for 1 mol of vapours, e can be calculated applying the Eq.:

$$e = \frac{H_f - h_F}{H_f - h_f}$$
 Eq. (3.9)

If the feed solution is introduced in the column at its boiling temperature, then  $h_F = h_f$ , e = 1 and V' = V. If we introduce saturated vapours into the column, then  $h_F = H_f$ , e = 0 and L' = L.

# 3.1.3. Determining the theoretical number of plates with the McCabe-Thiele graphical method

This method for determining the theoretical number of plates assumes that the equilibrium between vapours and reflux is achieved on every plate. The practical number of plates is higher than the theoretical one, since, during real-life rectification processes, the system approaches equilibrium, but does not reach it.

Starting from the mass balance for the upper section of the column, we can determine the **equation** of the upper operating line:

$$y_{n+1} = \frac{L}{L+D} x_n + \frac{D}{L+D} x_D$$
 Eq. (3.10)

Or:

$$y_{n+1} = \frac{R}{R+1} x_n + \frac{x_D}{R+1}$$
 Eq. (3.11)

The line intersects the diagonal of the diagram x - y in the point  $x = y = x_D$ .

Starting from the mass balance for the lower section of the column, we can determine the **equation** of the lower operating line:

$$y_{m} = \frac{L'}{L'-W} x_{m-1} - \frac{W}{L'-W} x_{W}$$
 Eq. (3.12)

where:

$$\mathbf{L}' = \mathbf{L} + \mathbf{e} \cdot \mathbf{F} \qquad \qquad \mathbf{Eq.} (3.13)$$

The line intersects the diagonal of the diagram x - y at the point  $x = y = x_w$ .

If we calculate the intersection of the upper and lower operating lines, and we consider the mass balance for the entire column, we can obtain **the equation for the e-line**:

$$y = \frac{e}{e^{-1}}x - \frac{x_F}{e^{-1}}$$
 Eq. (3.14)

The e-line shows the intersection points of all upper and lower operating lines corresponding to different reflux ratios R, and it intersects the diagonal of the diagram y = f(x) at the point  $x = y = x_F$ .

You can determine the theoretical number of plates using the McCabe-Thiele method by following the steps below (Fig. 3.4):

- a) Draw the equilibrium diagram y = f(x) (see the data in the Annex, table A2).
- b) On the horizontal axis, mark the points  $x_W$ ,  $x_F$  and  $x_D$ .
- c) From the ( $x_F$ ,  $x_F$ ) point on the diagonal, draw the e-line with the slope  $\frac{e}{e-1}$ , for the corresponding enthalpy of the feed solution.
- d) Draw the upper operating line from the (x<sub>D</sub>, x<sub>D</sub>) point on the diagonal; the line intersects the vertical axis at the point  $y = \frac{x_D}{R+1}$ .
- e) Draw the lower operating line by connecting the (x<sub>w</sub>, x<sub>w</sub>) point on the diagonal with the point of intersection between the upper operating line and the e-line.
- f) Using the equilibrium curve and the operating lines, determine graphically the theoretical number of plates nt. Starting from the (x<sub>D</sub>, x<sub>D</sub>) point on the diagonal, draw steps between the operating lines and the equilibrium curve. The number of steps represents the number of plates. The step that intersects the e-line, and has one corner on the upper and one on the lower operating line, represents the feed plate. The step that crosses the vertical line in x<sub>w</sub> represents the reboiler.



**Figure 3.4:** Equilibrium diagram and determination of the theoretical number of plates using the McCabe-Thiele method.

#### 3.1.4. Reflux ratio

When decreasing the reflux ratio and maintaining the same values for all other parameters, the slope of the upper operating line is decreasing, while the theoretical number of plates increases. The extreme situation is represented by the minimum reflux ratio, which requires an infinite number of plates. If the equilibrium curve is uniformly convex, the upper operating line will have the lowest possible slope when it intersects the lower operating line and the e-line exactly on the equilibrium curve. In this case, the minimum reflux ratio is:

$$R_{\min} = \frac{x_D - y'}{x_D - x'}$$
 Eq. (3.15)

where x' and y' represent the coordinates of the point where the e-line intersects the equilibrium curve.

By increasing the reflux ratio, the slope of the upper operating line increases, and the theoretical number of plates decreases. The extreme situation is represented by the infinite reflux ratio, where

the slope of the line is 1, the number of plates is at the minimum, and the capacity of the column is 0, since no distillate is produced.

Therefore, by decreasing the reflux ratio and maintaining the requirements regarding the purity of the products, the height of the column will increase; while an increase in the reflux ratio with the same product requirements will lead to an increase in the width of the column. The practical reflux ratio is thus chosen between the minimum and maximum values, and it is usually 1.2 to 2 times higher than the minimum value.

#### 3.1.5. Pseudo-equilibrium curve

In practice, equilibrium is not attained on the plates of the rectification column. The cause is the very short contact time between the vapours and the reflux, or deficient contact between phases. Based on this, the efficiency on the plate for the liquid or the vapour phase is defined as:

$$E_V = \frac{y_n - y_{n+1}}{y_n^* - y_{n+1}}$$
 Eq. (3.16)

$$E_{L} = \frac{x_{n-1} - x_{n}}{x_{n-1} - x_{n}^{*}}$$
 Eq. (3.17)

where y\* and x\* represent the equilibrium concentrations on the plate.

The efficiency on the plate can be further applied to determine the efficiency of the column. For this purpose, we use the pseudo-equilibrium curve to draw the x - y diagram for the graphical determination of the number of plates (Fig. 3.5). The pseudo-equilibrium curve has the following equation:

$$y'_{r} = y + E_{r}(y_{r} - y)$$
 Eq. (3.18)

where: y<sub>r</sub> - the equilibrium composition in the phase for a given x,

y – the operating composition in the vapour phase for a given x,

yr' – the pseudo-equilibrium coordinate,

 $E_r$  – efficiency on the plate.



Figure 3.5: Pseudo-equilibrium curve.

#### 3.1.6. The average efficiency of the column

The efficiency of a rectification column with plates is calculated as:

$$E = \frac{n_t}{n_p}$$
 Eq. (3.19)

where: n<sub>t</sub> – the theoretical number of plates,

n<sub>p</sub> – the practical number of plates.

#### 3.1.7. Heat balance

The enthalpy of a binary mixture is calculated as:

$$H = x_1 H_1 M_1 + x_2 H_2 M_2$$
 Eq. (3.20)

The enthalpy values are read from the table (Annex – tables A3 and A5) for the corresponding phase and temperature.

The heat that has to be removed in the condenser is:

$$q_c = D\left(\frac{L}{D} + 1\right)(H_1 - h_D) = D(R + 1)(H_1 - h_D)$$
 Eq. (3.21)

The heat that has to be provided in the reboiler is:

$$q_r = Dh_D + Wh_W + q_c - Fh_f \qquad Eq. (3.22)$$

The heater delivers the energy:

$$P = U \cdot I \qquad \qquad Eq. (3.23)$$

The heat loss is:

$$q_{izg} = P - q_r \qquad \qquad \text{Eq. (3.24)}$$

The heating efficiency is:

$$\eta = \frac{q_r}{p} \qquad \qquad \text{Eq. (3.25)}$$

### 3.2. TASK

Applying a given reflux ratio, perform the rectification of a mixture of water-methanol with a starting methanol concentration of 30 %. Based on the equilibrium data and experimental measurements, determine graphically the theoretical number of plates for the rectification column. Repeat the process using the pseudo-equilibrium curve.

Determine the average efficiency of the column and the minimum reflux ratio.

Present the mass and energy balance for the rectification process.

### 3.3. TASK IMPLEMENTATION

#### 3.3.1. Apparatus

The column for continuous rectification is presented in Fig. 3.6, and was provided by NGW – Normschliff Gerätebau Wertheim.

#### The component parts of the column:

- Three sections, each containing 5 bell plates,
- Three feed plates,
- Reboiler with two electric heaters,
- Electric heater for the feed solution, connected to the feed plate,
- Flowmeter, for adjusting and controlling the in-flow of the feed solution,

- Regulating valve for the reflux ratio,
- Regulating valve for total shutdown in case the flow of cooling water is interrupted,
- Regulating valve for controlling the constant level of liquid in the reboiler and an appropriate flow of the residue solution,
- Three devices with thermostat and sensors, replacing contact thermometers. They are used to ensure the constant temperature of the feed solution and to initiate total shutdown in case of overheating in the reboiler and condenser.
- Temperature sensors and transducers for digital recording.
- "DEST STAR III" device, that controls the entire operation of the rectification column, and is directly or indirectly connected to all other devices.



Figure 3.6. Pilot rectification column for continuous operation.

#### Technical data

• Height of the colu	mn:	approx. 4.25 m,
• Number of plates:		15,
• Internal diameter	of the column:	50 mm,
• Type:		column with bell plates,
• Weight of the colu	ımn:	approx. 33 kg,
• Voltage supply:		220/380 V,
• Maximum operati	ng temperature:	200°C,
• Pressure inside th	e column:	from atmospheric to 133 mbar,
• Amount of liquid i	n the column, without vapour:	250 mL,
• Amount of liquid i	n the reboiler:	approx. 2000 mL,
• Maximum vapour	flow:	7.5 L/h,
Maximum efficien	cy on the plate:	80 %.

The column, the reboiler and the condenser are made of glass. The column is adiabatically isolated with a vacuum jacket coated with silver, while the other components, such as the reboiler and the connection to the feed plate, are not thermally isolated. The plates are provided with openings for samplers and temperature sensors.

#### 3.3.2. Execution:

#### Operation of the pilot installation:

- Prepare the necessary amount of feed solution and place it in the feed container. The amount of feed solution should allow the operation for at least 3-4 h, as a longer time is required to adjust the process parameters and allow the installation to achieve steady state.
- 2. Fill the reboiler with approx. 2 L of solution.
- 3. Start the LR I device, used for controlling the flow of cooling water, and start the flow of cooling water in the cooling system.
- 4. Start the "DEST STAR III" device and the connected VA measuring device (LM I). Set the desired heating power and temperature in the reboiler.
- 5. Start all remaining devices and measuring instruments, and observe the increase of temperature in the reboiler and on the plates.
- 6. Check the valve of the container for residue solution: it should be closed.

- 7. When the vapours in the column reach the feed plate (see the temperature on the plates), set the desired temperature for the feed solution and the heating power. The heating power should be the minimum possible, to ensure easier adjustment of the temperature to a constant value.
- When the vapours in the column reach the condenser and the feed solution has the desired temperature, open the valve of the feed solution, and use the flowmeter to set the chosen flow. The flow of the feed solution should be continuously observed, to prevent possible interruptions.
- 9. On the "DEST STAR III" device, set the chosen value of the reflux ratio, and change the operating state of the column from closed (total reflux) to normal or inverse operation (as required to reach the desired value of the reflux ratio).
- 10. Immediately open the valve of the container for residue solution (being careful not to empty the reboiler!!!). Adjust the level of liquid in the reboiler by using the NR II regulator, provided with a control light. When the light is on, the valve is open, and it turns off when the valve closes.
- 11. Observe and record the temperature variations on the plates, in the reboiler and in the condenser, until they reach their constant values. This signifies that the column has reached its steady state at the given process parameters.
- 12. Measure the flow of the feed solution and of the distillate.
- 13. Collect samples from the distillate, the residue and, as a control, from the feed solution. Measure the refractive index and determine their composition.
- 14. In order to stop the experiment, stop the heating of the feed solution and its flow into the column.
- 15. On the "DEST STAR III" device, change the operating state of the column to "closed", and stop heating the reboiler.
- 16. When the temperature on the plates and in the boiler is low enough, close the valve of the container for residue solution.
- 17. Turn off the "DEST STAR III" device, and all remaining devices and measuring instruments.
- 18. Stop the flow of cooling wate, r and turn off its regulating device.

#### **Calculations**

- 1. Calculate the mole fraction composition of the feed solution, distillate and residue.
- 2. Present the flow of feed solution and distillate as mol/L:

$$F\left(\frac{mol}{h}\right) = \frac{\rho_F(\frac{g}{L}) \cdot F(\frac{L}{h})}{\overline{M}_F(\frac{g}{mol})} \qquad \qquad \text{where:} \qquad \qquad \overline{M}_F = x_1 M_1 + x_2 M_2$$

The density of the methanol-water mixture at various compositions and temperatures can be found in Annex – Table A6.

- Present the mass balance for the entire column (consider the experimental values for the flow of distillate D and concentrations x<sub>D</sub>, x<sub>W</sub> and x<sub>F</sub>, and calculate W and F). Present also the mass balance for the upper and lower sections of the column.
- 4. Determine the theoretical number of plates using the McCabe-Thiele graphical method. The equilibrium data for the methanol-water binary system are given in the Annex Table A2.
- 5. Estimate the minimum reflux ratio.
- 6. Draw the pseudo-equilibrium curve and use the graphical method to determine the number of plates.
- 7. Calculate the average efficiency of the column (consider both the ideal number of plates and the number of plates determined with the pseudo-equilibrium curve).
- 8. Present the heat balance for the rectification process.

# 3.4. PRESENTATION OF THE RESULTS IN THE LABORATORY NOTEBOOK

Use the table below to record the values of the temperature in the reboiler, feed plate and condenser.

reboiler	feed solution	condenser

Use the table below for the calculation of the pseudo-equilibrium data

Х	<b>y</b> r	У	, <b>y</b> r

Present the graphical determination of the theoretical number of plates.

# **4.SOLID-LIQUID EXTRACTION**

### 4.1. THEORETICAL BACKGROUND

One can separate the various components of a solid mixture by extraction with an appropriate solvent.

Extraction is used mainly to obtain oil from fruits and seeds, or to separate aromas, spices and pharmaceutically active compounds from plants and fruit. One can use volatile organic solvents, and in some cases also water. According to the EU directive (88/344/EEC), the following solvents can be used without restriction in extraction processes: water, propane, butane, butyl acetate, ethyl acetate, ethanol, carbon dioxide, acetone and N<sub>2</sub>O. All other solvents are either prohibited, or have very clear limitations regarding their use (not to be used in the food, cosmetics or pharmaceutical industries).

The process depends on the amount and distribution of the soluble component in the material, the nature of the solid material and the size of the particles (grit). If the soluble component is uniformly distributed throughout the solid particle, first the compound on the particle surface will dissolve. Then the soluble compound must diffuse from the inside of the particle towards the surface, and through the liquid film into the bulk of the solvent. If the material has a cellular structure, the extraction rate will be lower, since the cell walls will present additional resistance.

If the rate of the process is controlled by the diffusion of the soluble compound through the porous material, the grit should be as low as possible, to decrease the diffusion path. If the rate of the process is controlled by the diffusion of the component from the solid surface into the bulk of the solvent, it will not be influenced by the small grain size; however, it will be increased by intensive fluid mixing.

When choosing the equipment for the extraction process, we have to consider the following four factors that influence the extraction rate:

- The size of the particles influences the extraction rate in several ways. The smaller the size, the greater the interface between the solid and liquid phases, thus favouring the mass transfer. Also, the diffusion path for the soluble compound towards the surface of the particle is smaller. On the other hand, too small particles are difficult to separate from the liquid solution, and they can aggregate into larger solids that will hinder the flow of the liquid. Generally, one should avoid very small particles. It is desirable to have a narrow distribution of particle size, so that all particles require almost the same extraction time.
- *Solvent.* The selection of the solvent is very important. One should choose a selective solvent with low viscosity. During the extraction process, the concentration of solute in the solvent increases,

while the extraction rate goes down because of the lower concentration gradient and, partially, because of the increased viscosity of the solution.

• *Mixing.* Mixing is important, since it favours the mass transfer from the surface of the material to the bulk of the solvent. Also, it prevents the sedimentation of the particles.

If the aggregated solid material forms a permeable layer, we extract it by using percolation, that is by the flow of solvent through the layer. If the layer is or becomes impermeable or almost impermeable, we perform the extraction by dispersing the material in the solvent and, at the end, by solid-liquid separation. Both methods are used on an industrial scale in continuous or batch regimes.

Extraction from the solid material can be performed in batches, semi-continuous (when the solid material is stationary, while the liquid flows through the permeable layer) or continuous (when the solid and liquid phases are moving in counterflow or parallel flow.

During single-stage batch extraction, the entire process (the extraction using the solvent and the separation of the solution from the solid material) takes place in only one step. This process is little used on an industrial scale, because of its low efficiency and the relatively diluted solutions generated during the extraction.

During the multi-stage, parallel flow extraction (Fig. 4.1), the solvent and the solid material are first mixed at the first stage. After extraction during the first stage, the solid material is transferred to the second stage, where fresh solvent is added. The solution is collected after each stage. The process is repeated in all subsequent stages. The solutions obtained during the process are quite diluted, but the yield of extraction is higher than that of a single-stage batch process.



Figure 4.1: Continuous, multi-stage, parallel flow extraction. → solid phase (L) ⇒ solvent (V)

During multi-stage, counterflow extraction (Fig. 4.2), the solvent and the sold material flow in opposite directions. The yield of this extraction process is high, since the extracted material in the final stage comes into contact with fresh solvent, while the concentrated extract solution leaves the system after coming in contact with the fresh solid material.





#### 4.1.1. Determining the theoretical number of stages for counterflow extraction

In extraction systems, equilibrium is reached when the soluble compound from the solid material is totally soluble in the solvent, and the solution bound to the solid material has the same concentration as the bulk of the solution. Assuming that equilibrium is reached at every stage of the extraction procedure, we can define the process of counterflow extraction if the following 6 parameters are known:

- a) the concentration of the soluble compound in the material that comes into contact with the fresh solvent in the last stage of extraction,
- b) the necessary amount of solvent. This can be calculated using the mass balance, and by determining the concentration of the final extract solution.
- c) the composition of the solid material used for extraction.
- d) the flow of solid material in the system. This can be calculated using the mass balance, and knowing the targeted amount of final product (solid residue or soluble compound),
- e) the amount of solution bound to the solid substrate, which leaves each stage together with the solid material,
- f) the number of stages of the extraction process, which allows the determination of the product composition. The alternative is the determination of the number of required extraction stages in order to obtain product with a specific composition.

If equilibrium is reached, the concentration of the solution leaving the stage together with the solid material is the same with the concentration of the extract solution from the corresponding stage. During solid-liquid extraction, the equilibrium is seldom reached, because of the short contact time between the solid material and the solvent, and of the slow mass transfer. For this reason, when designing extraction equipment for a specific process, one should determine the real number of extraction stages, which is calculated knowing the efficiency of the equipment and the ideal number of extraction stages. In order to determine the ideal number of extraction stages, one can use the

McCabe-Thiele graphical method, or the numerical method. If the equilibrium and operating data are represented by straight lines, the Kremser equation can be applied.

We consider: L – the amount of solid material,

V – the amount of liquid,

x – the mass fraction of the compound of interest in the solid phase,

y - the mass fraction of the compound of interest in the liquid phase.

Mass balance:

$$V_{n+1} + L_0 = L_n + V_1$$
 Eq. (4.1)

$$y_{n+1}V_{n+1} + x_0L_0 = x_nL_n + y_1V_1$$
 Eq. (4.2)

The equilibrium line can be generally expressed as:

$$y^* = m \cdot x^* + B$$
 Eq. (4.3)

By combining Eq. (4.2) and (4.3), we obtain:

$$y_{n+1} = \frac{L_n}{V_{n+1}} \cdot \frac{y_n - B}{m} + \frac{y_1 V_1 - x_0 L_0}{V_{n+1}}$$
 Eq. (4.4)

Here we consider that when exiting stage n, the solution bound to the solid has the same concentration as the extract solution,  $y_n$ . If, in any extraction stage, the amount of solvent bound to the solid is constant and independent of the composition of the extract solution, then the same amount of solvent exits together with the solid in all stages. Also, the same amount of solvent leaves all stages as the extract solution.

To simplify, we mark with a all flows and concentrations on the side of the input of solid material, and with b all flows and concentrations on the side of the fresh solvent. We define the extraction factor:

$$\frac{L}{V \cdot m} = \varepsilon \qquad \qquad \text{Eq. (4.5)}$$

$$y_{n+1} = \varepsilon(y_n - B) + y_a - \varepsilon \cdot m \cdot x_a$$
 Eq. (4.6)

$$y_{n+1} = \varepsilon \cdot y_n - \varepsilon (m \cdot x_a + B) + y_a \qquad \qquad \text{Eq. (4.7)}$$

and:

$$y_{n+1} = \varepsilon \cdot y_n - \varepsilon \cdot y_a^* + y_a$$
 Eq.(4.8)

We can calculate the composition of the liquid phase at each extraction stage:

n=1: 
$$y_2 = \varepsilon \cdot y_1 - \varepsilon \cdot y_a^* + y_a = y_a(1 + \varepsilon) - \varepsilon \cdot y_a^*$$
 Eq. (4.9)

n=2: 
$$y_3 = \varepsilon \cdot y_2 - \varepsilon \cdot y_a^* + y_a = y_a(1 + \varepsilon + \varepsilon^2) - y_a^*(\varepsilon + \varepsilon^2)$$
 Eq. (4.10)

n=n: 
$$y_{n+1} = y_a(1 + \varepsilon + \varepsilon^2 + \dots + \varepsilon^n) = y_a^*(\varepsilon + \varepsilon^2 + \dots + \varepsilon^n)$$
 Eq. (4.11)

The terms in the brackets represent the sum of a geometric series, which can be determined with the equation:

$$S_n = \frac{a_1(1-r^n)}{(1-r)}$$
 Eq. (4.12)

where:  $S_n$  – the sum of n terms in the series,

 $a_1$  – the first term in the series,

r - the constant ratio between two consecutive terms.

Then:

$$y_{n+1} = y_b = y_a \frac{1 - \varepsilon^{n+1}}{1 - \varepsilon} - y_a^* \frac{\varepsilon(1 - \varepsilon^n)}{1 - \varepsilon}$$
 Eq. (4.13)

The graphical representation of the extraction process is shown in Fig. 4.3. The extraction factor is:

$$\epsilon = rac{y_b - y_a}{y_b^* - y_a^*}$$
 Eq. (4.14)


Figure 4.3: The extraction process.

The theoretical number of extraction stages can be calculated applying the equation:

$$N = \frac{\log\left(\frac{y_b - y_b^*}{y_a - y_a^*}\right)}{\log\left(\frac{y_b - y_a}{y_b^* - y_a^*}\right)}$$
Eq. (4.15)

Eq. (4.15) cannot be used to design the entire extraction battery, when the concentration of the solution bound to the solid material is not the same with the equilibrium concentration. In this case, the mass balance of the first stage is determined separately, and Eq. (4.16) is used to calculate the N-1 number of stages.

$$N - 1 = \frac{\log\left(\frac{y_{b} - y_{b}^{*}}{y_{a} - y_{a}^{*}}\right)}{\log\left(\frac{y_{b} - y_{a}}{y_{b}^{*} - y_{a}^{*}}\right)}$$
 Eq. (4.16)

The real number of extraction stages is then determined by dividing the ideal number of stages with the average efficiency of the extraction battery, which depends on the contact time between the solid material and the solution, and on the diffusion rate of solute through the solid material and into the solution.

### 4.1.2. Isolation of hypericin from St. John's wort (Hypericum perforatum)

The medicinal properties of St. John's wort have been known for a very long time in all European countries, and it was used as an analgesic and antidepressant, as well as for treating liver disease and pneumonia. The plant is again popular today, mainly due to its antiviral properties, conferred by one of its compounds – hypericin. It is supposed that hypericin can be also used against HIV.

St. John's wort (Fig. 4.4) belongs to the HYPERICUM genus. The species is called HYPERICUM PERFORATUM. It is found in forest clearings, at woodland edges and in grassy fields in the countries of Western Europe, the Balkan peninsula, Russia, Ukraine, India, Iran and North Africa. It contains numerous pharmaceutically active compounds, and it is used in the treatment of various diseases and medical conditions. It contains bitter substances, tannins, volatile oils, carbohydrates, proteins, resins, pectin, myristic acid, hyperin, hypericin, hyperforin and other compounds.



Figure 4.4: St. John's wort.

#### HYPERICIN

Hypericin is an aromatic, polycyclic dione (Fig. 4.5). Its molecular formula is  $C_{30}H_{16}O_8$ , and it has a molar mass of 504.43 g/mol. It has an asymmetric structure, with one half of the molecule being hydrophilic, and the other half hydrophobic.



Figure 4.5: Hypericin.

Hypericin is a violet, crystalline compound, with a melting temperature of approx. 320°C. It is soluble in polar solvents, and insoluble in nonpolar solvents. It is partially soluble in water when the pH is lower than 4 or higher than 8. With most organic solvents, hypericin forms a red solution, which becomes green in basic medium. In water, it forms a violet dispersion. The more polar the solvent, the more intense the red colour of the solution, and thus the higher the absorbance. If hydrogen bonds are formed, the colour changes towards blue. The absorbance spectrum of hypericin in neutral organic solvents displays two absorbance bands in the visible spectrum: 500-600 nm and 485-425 nm. In methanol, the maximum absorbance is recorded at: 588, 545, 509, 471, 384, 328 and 282 nm.

Hypericin belongs to the class of hydroxyquinones, which are characterized by photodynamic behaviour. It is known for all compounds with photodynamic behaviour that they inactivate tumour cells and virus infected cells.

Hypericin is photosensitive, since it decomposes under the influence of light. At the same time, hypericin is a photosensitizing compound, and when ingested, can cause the skin to become sensitive to light, to get inflamed or to show even more serious symptoms.

### 4.2. TASK

Isolate hypericin from St. John's wort by means of two methods: using the Soxhlet apparatus, and by batch extraction with a cold solvent. Calculate the yield of extraction for each method. Determine the amount of hypericin in the extract solutions by spectrophotometric analysis. Perform a qualitative analysis of the extracts using thin layer chromatography.

Starting from the experimental results, determine the ideal number of stages necessary during counterflow extraction.

### 4.3. TASK IMPLEMENTATION

### 4.3.1. Extraction

### 1. Extraction using the Soxhlet apparatus

The Soxhlet apparatus – Fig. 4.6 (named after the German chemist F. Soxhlet, 1884-1926) is a laboratory device that uses volatile organic solvents for the extraction of compounds from solid materials. The elements of the apparatus are as follows: the distillation flask, the reflux condenser, and the Soxhlet extractor. The extraction with the Soxhlet apparatus works on the principle of reflux of the cooled solvent.

<u>Procedure</u>: Grind the St. John's wort plant material. Place the powder (approx. 1.5 g) in a thimble made out of filter paper. Carefully position the thimble in the Soxhlet extractor. Pour acetone (150 mL) in the distillation flask, and add a few boiling stones. Before starting to heat the solvent, check that the apparatus is tightly closed and the cooling water is running. When the operating temperature is reached, the solvent starts circulating. Proceed with the extraction, maintaining the temperature of the water bath constant at approx. 75°C, until colour is no longer observed in the circulating solvent. When the solvent is colourless, stop the heating source, and allow the system to cool down. Transfer the extract solution into a round-bottom flask of known weight. Remove the solvent from the extract solution by rotoevaporation. Determine the mass of the extract, and calculate the yield of the extraction. Use this data to calculate the content of hypericin in the starting solid material.

### 2. Batch extraction with cold solvent

Place 1.5 g of ground St. John's wort plant material into the flask. Add 130 mL of acetone, and perform the extraction under constant stirring, using a magnetic mixer. The extraction time should be the same as for the Soxhlet apparatus. When extraction is finished, filter the solid material. As in the case of the

extraction with the Soxhlet apparatus, transfer the extract solution into a round-bottom flask of known weight. Remove the solvent from the extract solution by rotoevaporation. Determine the mass of the extract, and calculate the yield of the extraction.

To determine the mass of solution bound to the inert material, transfer the filtered solid material to a glass plate, and dry until the weight is constant. Use the mass difference between the wet and dry residue to determine the mass of adsorbed solvent on the inert material.

For diluted solutions, the amount of solvent bound to the solid material is constant and does not depend on the concentration of the extract solution. To determine the relation between the mass of solution bound to the inert material and the concentration of the extract solution, perform batch extraction for 30 minutes, followed by filtration for 30 minutes. Use the concentrated solution to perform extraction 2 more times, using fresh solid material.

Use spectrophotometry and thin layer chromatography to analyse the extracts obtained by the two methods.

The advantage of extraction with the Soxhlet apparatus consists in the fact that the material comes repeatedly in contact with fresh solvent, and that the temperature in the Soxhlet extractor is lower than the temperature in the distillation flask, where the solvent is boiling and evaporating. The latter is important when extracting thermally sensitive substances. There is also an economic advantage, since the process does not require a step for separating the extract solution from the solid residue.



Figure 4.6: Diagram of the Soxhlet apparatus.

# **4.3.2.** Using spectrophotometry to determine the concentration of hypericin in the extract (by DAC – Deutsche Arzneimittel Codex)

### Preparing the solution for spectrophotometric measurements

Use methanol to dissolve the extract in a 25 mL volumetric flask. Filter the obtained solution. Collect 5 mL of the filtered solution, and dilute it further with methanol in a 25 mL volumetric flask. For the resulting solution, determine the absorbance at 590 nm, using pure methanol as a control sample. The amount of hypericin in the sample is calculated with the following equation:

amount of hypericin in the sample (%) =  $\frac{A \cdot 125}{Z \cdot 870}$ 

where: specific absorbance for hypericin  $E^{1\%,1cm} = 870$  (by DAC)

A = measured absorbance

Z = the mass of plant material, in g

### 4.3.3. Thin layer chromatography (TLC)

The setting is shown in Fig. 4.8. It comprises the beaker and the chromatography plate, for which we decide the size function of the amount of sample. The plate is made of aluminium, covered with a thin layer of silicate.

When analysing hypericin, the following methods and reagents are used:

Mobile phase: a mixture of solvents; toluene, ethyl formate and formic acid with the ratio 5:4:1.

<u>Derivatization reagent</u>: 1% methanol solution of diphenylboricacid b-aminoethyl ester, and 5% ethanol solution of PEG 4000.

Sample preparation: use methanol to dissolve the extract in a 25 mL volumetric flask.

<u>Procedure</u>: prepare a chromatography plate with the dimensions 12 x 5 cm. Draw a pencil line, approx. 1 cm from the bottom edge. Carefully apply the samples to the line, using a capillary tube (Fig. 4.7). Pour the solvent into the beaker, and positon the plate, taking care that the edges don't touch the glass walls. The solvent will travel upwards on the plate. When the solvent front is about 1 cm below the upper edge of the plate, remove the plate from the beaker, dry the chromatogram, and then spray with the derivatization reagent. An array of spots, characteristic for distinct compounds, will be immediately visible on the chromatogram. Next, observe the chromatogram under UV light, where the red colour of hypericin is more visible. The distribution constant is calculated using the equation:

$$R_f = \frac{\text{path of a sample}}{\text{path of a mobile phase}}$$

An example of a chromatogram where hypericin appears as a red spot is shown in Fig. 4.9.



Figure 4.7: Chromatography plate, with applied sample.



Figure 4.8: Setting for thin layer chromatography.

### 4.3.4. Calculation

Calculate the initial concentration of hypericin in the material as:

 $x_{vs} = \frac{m_{prod}}{m_{prod} + m_{inert.mater.}}$ 

For the mass value of hypericin, use the experimental mass of the extract, even though it also contains other compounds.

Express the mass of the solution bound to the solid, m(a), as kg of solution / kg of inert material. Assume that the remaining concentration of hypericin in the material after extraction is m(os) = 0.1 kg hypericin / 100 kg of inert material.

Then: 
$$y_b^* = \frac{m(os)}{m(a)+m(os)}$$

The concentration of hypericin in the fresh solvent is:  $y_b = 0$ 

The concentration of hypericin in the extract solution is:  $y_{iz} = \frac{m_{oil}}{m_{oil}+m_{solvent}}$ 

Calculate  $y_a$  from the mass balance for hypericin over the entire system.

The amount of hypericin leaving together with the solvent after the 1<sup>st</sup> stage:

 $(V - 100 \cdot m(a)) \cdot y_{iz}$  kg hypericin / 100 kg of inert material

After the last stage: 0.1 kg hypericin / 100 kg of inert material

The amount of hypericin entering together with the fresh material in the 1<sup>st</sup> stage:

Therefore, the mass balance for the entire system is:

$$0.1 + (V - 100 \cdot m(a)) \cdot y_{iz} = \frac{x_{vs} \cdot m_{material} \cdot 100}{m_{inert.mater.}}$$

y<sub>a</sub> is then calculated using the mass balance for hypericin over the 1<sup>st</sup> stage:

$$V \cdot y_a^* = \frac{x_{vs} \cdot m_{material} \cdot 100}{m_{inert.mater.}} + m_a$$
$$y_a = \frac{m_a}{V}$$

and:

where  $m_a$  is the mass of hypericin in the extract solution entering the 1<sup>st</sup> stage. Next, calculate the number of stages, by applying Eq. (4.16).



Figure 4.9: TLC chromatogram for a sample containing hypericin.

# 4.4. PRESENTATION OF THE RESULTS IN THE LABORATORY NOTEBOOK

Use the table below to present the results of the extraction experiments:

	Mass of solid material (g)	Volume of solvent (mL)	Time (min)	Т (°С)	Extraction yield (%)	Content of hypericin (%)	R <sub>f</sub>
Extraction with the Soxhlet apparatus							
Batch extraction							

Attach the TLC chromatogram and explain.

Use the table below to present the results of the experiment for determining the mass of the solution bound to the inert material:

	Mass of solid material	= Ma	ss of solvent =
	Extraction time (min)	Concentration in the extract (kg/m <sup>3</sup> )	Mass of solution bound to the material (kg/kg inert material)
1 <sup>st</sup> STAGE			
2 <sup>nd</sup> STAGE			
3 <sup>rd</sup> STAGE			

## **5.ABSORPTION**

### 5.1. THEORETICAL BACKGROUND

The liquid absorption of one or more components from a gas mixture is a process based on the interface mass transfer. Mass transfer, that is the movement of particles, can take place in two ways:

- by diffusion, which is a consequence of the movement of molecules caused by a concentration gradient, and
- by convection, which is connected with the turbulent flow of liquid at the phase boundary.

The absorption process is best described using the film theory proposed by Whitman. According to this theory, in the bulk of both phases the mass transfer occurs by convection, and the concentration gradients are negligible, except for the region near the phase boundary. On both sides of the phase boundary, there exists a thin film of fluid (boundary layer), where the mass transfer occurs through diffusion. According to Fick's 1<sup>st</sup> law, the diffusive flux is proportional to the concentration gradient and to the interface area through which the mass transfer takes place. The direction of the mass transfer through the interface does not depend on the concentration gradient, but on the equilibrium values. Therefore, the mass transfer can occur from the phase with smaller concentration towards the phase with higher concentration, if this would satisfy the equilibrium.

Figure 5.1 shows the distribution of concentrations for component A, during transfer from the gas phase, through the interface, and into the liquid. According to the theory mentioned above, the concentrations at the phase boundary are in equilibrium, and both boundary layers display resistance to mass transfer.

The mass flux of component A is given by the Eq.:

$$W_A = k_G A(p_A - p_{A,i}) = k_L A(c_{A,i} - c_A)$$
 Eq. (5.1)

where  $p_A$  is the partial pressure in the bulk of gas,  $c_A$  is the concentration in the bulk of liquid, and  $c_{A,i}$  and  $p_{A,i}$  are the concentrations at the phase boundary, where we assume equilibrium is reached.



Figure 5.1: Distribution of concentrations for component A, during mass transfer from gas to liquid.

Figure 5.2 shows the concentrations of component A in both phases. The points in the diagram represent:

- Point D(c<sub>A</sub>, p<sub>A</sub>) the concentration values in the bulk of gas and liquid,
- Point A(c\*<sub>A</sub>, p<sub>A</sub>) the concentration in the liquid, c\*<sub>A</sub>, in equilibrium with the p<sub>A</sub> value from the gas,
- Point B(c<sub>A,i</sub>, p<sub>A,i</sub>) the concentration in the liquid, c<sub>A,i</sub>, in equilibrium with the p<sub>A,i</sub> value from the gas,
- Point F(c<sub>A</sub>, p\*<sub>A</sub>) the partial pressure in the gas phase, p\*<sub>A</sub>, in equilibrium with the c<sub>A</sub> value from the liquid.



Figure 5.2: Concentration of component A in the gas phase and the liquid phase.

For low concentrations, the equilibrium is given by Henry's law:

$$p_{A} = He \cdot c_{A} \qquad \qquad Eq. (5.2)$$

where He is Henry's constant.

For determining the values of  $k_L$  and  $k_G$ , it would be necessary to measure the concentration at the interface, which can only be done in special circumstances. To simplify the calculations, the overall mass transfer coefficients  $K_G$  and  $K_L$  are introduced:

$$W_A = k_G A(p_A - p_A^*) = k_L A(c_A^* - c_A)$$
 Eq. (5.3)

When combining Eq. (5.1) - (5.3), one can obtain the formula for the mass flux of component A through the interface:

$$W_{A} = \left[\frac{1}{k_{L}} + \frac{1}{Hek_{G}}\right]^{-1} A(c_{A}^{*} - c_{A}) = K_{L}A(c_{A}^{*} - c_{A})$$
 Eq. (5.4)

The overall mass transfer coefficient  $K_L$  is a diffusion rate constant that relates the mass transfer rate, mass transfer area, and concentration difference as the driving force.

$$\frac{1}{K_{\rm L}} = \frac{1}{k_{\rm L}} + \frac{1}{k_{\rm G}{\rm He}}$$
 Eq. (5.5)

Eq. (5.5) shows that the inverse value of the overall mass transfer coefficient is the sum of the inverse values of the mass transfer coefficients on both sides of the interface, that is the sum of the resistances to mass transfer displayed by the boundary layers on both sides of the interface.

The value of Henry's constant is high in the case of poorly soluble gases (CO<sub>2</sub> in water). In this case, if  $k_G$  and  $k_L$  are of the same order of magnitude, then  $K_L \approx k_L$ , and the resistance to mass transfer is concentrated in the liquid boundary layer.

When dimensioning the absorption column, it is very important to know the value of the mass transfer coefficient. Also, it is necessary to determine the optimum flow on the unit surface for both phases involved. Here, the flow of gas is limited by the flooding point, while, for economic reasons, the flow of liquid cannot be too low. Therefore, when dimensioning the absorption column, it is necessary to also determine the influence of the flow of gas and liquid on the mass transfer coefficient. Moreover, one should also consider the influence of temperature, pressure and diffusivity.

Empirical correlations for mass transfer in a wide variety of systems are available in the literature.



Figure 5.3: Device for studying mass transfer during absorption from gas into liquid.

Using a similar apparatus as shown in Fig. 5.3, Stephens and Morris (1951) determined the following empirical correlation:

$$\frac{k_{\rm L}L_0}{D_{\rm A}} = 2.42 {\rm Re}^{0.7} {\rm Sc}^{0.5}$$
 Eq. (5.6)

Eq. (5.7)

where the Reynolds number is:  $\mathrm{Re}=rac{4\Gamma}{
ho \mathrm{D}_{\mathrm{A}}}$ 

and the Schmidt number is: 
$$Sc = \frac{\eta}{\rho D_A}$$
 Eq. (5.8)

In the equations above: D<sub>A</sub> – diffusivity of compound A in liquid,

$$\Gamma$$
 – mass flow per mean perimeter of the discs,  $\Gamma = \frac{\Phi_m}{L_0} = \frac{\Phi_{\nu}\rho}{L_0}$ 

 $\mathsf{L}_0$  – mean perimeter of the discs:  $L_0=2(d_0+1)$ 

The absorption of gases into liquids requires intensive contact between phases, and therefore columns with plates or packed columns are used for the process. During absorption, the mass flux passes through the interface with area A, which has to be accurately determined when studying the mass transfer.

The assembly shown in Fig. 5.3 ensures that the liquid is uniformly distributed over the entire available surface. Therefore, one can assume that area A is the same as the geometrical surface.

In the present case, the concentration difference  $(c^*_A - c_A)$  changes with the height of the column. However, the average concentration difference stays the same:

$$\Delta c_{A,ln} = \frac{(c_A^* - c_A)_1 - (c_A^* - c_A)_2}{\ln \frac{(c_A^* - c_A)_1}{(c_A^* - c_A)_2}}$$
 Eq. (5.9)

We use pure component A as gas, and we can assume that its concentration in the bulk gas phase remains constant along the column. At the same time, on account of the mass transfer, its concentration in the liquid phase increases from the inflow (point 1) towards the outflow (point 2) of liquid.

For the steady state, one can use the following equation to describe the mass balance for the gas component A in the liquid phase, at the outflow from the column:

$$W_{A} = \Phi_{v}[(c_{A})_{2} - (c_{A})_{1}] = K_{L}A\Delta c_{A,ln}$$
 Eq. (5.10)

Using this equation and the experimental data, one can calculate the mass transfer coefficient KL.

### 5.2. TASK

Using the absorption column for mass transfer from gas to liquid, determine the dependence of the mass transfer coefficient  $K_L$  on the flowrate of liquid. Use the system pure  $CO_2$  – water. Compare the experimental data with the values obtained by applying the correlation proposed by Stephens and Morris.

### 5.3. TASK IMPLEMENTATION

The device for studying the absorption of gases into liquids is shown in Fig. 5.3.

The component parts of the device are as follows:

- glass tube open at both ends,
- support wire with discs,
- upper constant level vessels,
- screw valve,
- lower constant level vessel,
- flowmeters for water and CO<sub>2</sub>,
- thermometer for water.

### Procedure:

- 1. Set the flowrate of  $CO_2$  at approx. 200 L/h.
- Start and set the flow of water, ensuring a constant level of liquid in the upper vessel. Using the screw valve, set the desired flowrate of water in the column, and use the flowmeter to determine the value of the flowrate.
- 3. Follow the change of the concentration of CO<sub>2</sub> in the outflow of water. A constant value for the concentration indicates that the column is operating at steady state (at a constant temperature).
- Use the CO<sub>2</sub> concentration measured during steady-state operation to determine the mass transfer coefficient. Compare the experimental value with the one calculated by applying the equation proposed by Stephens and Morris.
- 5. Perform at least 5 measurements using different flowrates of water.

### Determining the concentration of CO<sub>2</sub> in water:

In a conical flask, place 25 mL 0.1 M NaOH solution, add 5 mL masking agent (K-Na-tartrate, Nacitrate), and 50 mL of the sample (outflow water). For adding the sample, use a pipette, and make sure that the sample is discharged below the surface of the mixture in the flask. Add phenolphthalein as an indicator. Titrate immediately with 0.1 M HCl solution, until the pink colour of the mixture disappears. Repeat the procedure for a blind sample (inflow water). The reaction in the flask:

$$2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O_3$$

The excess NaOH is then titrated with acid, and the concentration of CO<sub>2</sub> in water can be calculated:

$$m(gCO_2/L) = \frac{(A - B)E_{CO_2}\frac{1000}{V}0.1}{1000}$$

where:  $E_{CO2} = 44 \text{ g/eqv}$ 

V – mL of sample

A – mL of 0.1 M HCl solution used for the blind sample

B – mL of 0.1 M HCl solution used for the sample

# 5.4. PRESENTATION OF THE RESULTS IN THE LABORATORY NOTEBOOK

Use the table below to present the experimental and calculated data:

Φ <sub>ν</sub> (mL/s)	с <sub>А2</sub> (g/L)	Sc	Re	Δc <sub>A,In</sub> (g/L)	K <sub>L,calc</sub> (m/s)	K <sub>L,exp</sub> (m/s)

Compare the experimental and calculated values of the mass transfer coefficient by drawing the diagrams  $K_L = f(Re)$  and  $K_L = f(\Phi_V)$ .

# 6.DRYING

### 6.1. THEORETICAL BACKGROUND

### 6.1.1. Drying solid materials

Drying is used to remove a volatile liquid from a solid material by evaporation or boiling.

When drying by evaporation, the temperature of the wet material is lower than the boiling temperature of water, and vaporization is the consequence of the difference between the vapour pressure for water inside the material and the partial pressure of water in the gas surrounding the wet material. The vapours are removed by the flow of gas, which is also used to provide evaporation heat to the system.

Drying by boiling, when the temperature of the wet material is higher than the boiling temperature of water, is the consequence of the pressure difference between the water vapour inside the material and the surrounding gas. The vapour need not be removed by a flow of gas, and the necessary evaporation heat is provided by conduction through the heated surface on which the wet material is dispersed, or by radiation from the walls of the dryer, which can be heated with steam, hot liquids or gases, or with electric heaters.

When in contact with air of a certain temperature and humidity, the moisture content in the solid material is at equilibrium, or it tends towards equilibrium by absorbing or releasing liquid.

The moisture in the solid material can be

- Unbound; in this case the equilibrium vapour pressure is the same as the vapour pressure of water at the given temperature. The unbound moisture is found at the surface of the solid material and in large capillaries. The materials that contain only unbound moisture are nonhygroscopic. They can be totally dried under a flow of air that is not saturated with moisture.
- *Bound*; in this case the equilibrium vapour pressure is lower than the vapour pressure of water at the given temperature. The bound moisture is found in the capillaries, adsorbed to the surface or in the cells of fibres, or in various physico-chemical combinations with the solid material. The materials that contain bound moisture are called hygroscopic. They can only be dried to an equilibrium content of moisture, which depends on the temperature and humidity of the surrounding air, and on the nature of the material.

The difference between the moisture content in the solid material and the content corresponding to equilibrium under certain conditions is called **free moisture**. When drying a solid material in air with relative humidity A (Fig. 6.1), one can only remove the free moisture (X-X\*) corresponding to the conditions in the air.



Figure 6.1: Moisture content for a solid material.

Based on the methods of providing the heat necessary for drying, devices are classified into convection, conduction and radiation dryers. In practice, bulk or continuous dryers are used. When choosing and designing a dryer, one should consider the following factors:

- properties of the material: toxicity, abrasion potential and flammability,
- characteristics of the drying process: initial moisture content reported to the equilibrium content under different conditions, the type of moisture (bound or unbound), limitations of the drying temperature, and the necessary drying time,
- *requirements for the dry product*: purity, final moisture content, physical form and the size distribution of the dry product,

• *loss of product during drying* (as dust or vapour); if solvent is present, one should also consider the loss of solvent.

### 6.1.2. Basics of psychrometry

The humidity of the air is given by the amount of water vapour (in kg) present in 1 kg of dry air:

$$H = \frac{18 \cdot p_A}{29 \cdot (P - p_A)}$$
 Eq. (6.1)

where: 18 – molar mass of water,

29 - molar mass of air,

p<sub>A</sub> – partial pressure of water vapour,

P – atmospheric pressure.

Saturated humid air is the air in equilibrium with liquid water at a given temperature and pressure.

**Psychrometry** is the science concerned with the properties of gas-vapour mixtures. The properties of humid air are described by psychrometric curves (Annex – Figure A3). The lines corresponding to adiabatic cooling, or adiabatic saturation, show how the unsaturated humid air cools down and how its humidity increases in contact with water at the temperature of adiabatic saturation. Originally, the lines are not straight or parallel; therefore, the diagram is distorted along perpendicular coordinates, to create straight and parallel lines which facilitate interpolation. Each line corresponds to a specific temperature of the adiabatic saturation, and the data on the horizontal axis represent the values of their intersection with the curve for 100% saturation.

The **wet-bulb temperature** is a non-equilibrium temperature, corresponding to a small amount of water in a constant flow of air, under adiabatic conditions. In this case the amount of water is smaller than the mass of air; therefore, the properties of the air are very little affected by the evaporation of water.

For a mixture of air and water vapour, one can reliably use the psychrometric curves to determine the wet-bulb temperature corresponding to air of a certain humidity and temperature. The method is shown in Fig. 6.2.



Drying

Figure 6.2: Using psychrometric curves to determine the wet-bulb temperature.

Find the intersection between the vertical line in  $T_{M1}$  and the curve for 100% saturation. Draw a parallel to the curve for adiabatic saturation starting from this intersection point and finishing at  $T_{S1}$ . Read the corresponding values  $H_{S1} = H_{S2}$ . Draw a parallel to the curve for adiabatic saturation starting from the point ( $T_{S2}$ ,  $H_{S2}$ ) and finishing on the 100% saturation curve. Here, read the values of  $T_{M2}$  and  $H_{M2}$ .

### 6.1.3. Drying rate

It is important to know the drying rate under different conditions, since sometimes one should avoid the maximum drying rate if it would cause undesirable effects on the material (shrinking, surface hardening, etc.).

Fig. 6.3 shows the general curve for the drying rate. Section A'A of the curve marks the non-steady state operating conditions, that is the beginning of the drying process, when the wet surface of the material is heated or cooled to the wet-bulb temperature. The full line in Fig. 6.3 describes the steady-state operation.



Figure 6.3: Drying rate for a solid material.

#### a) Constant rate period

Segment AB in Fig. 6.3 marks the constant drying rate period, when the moisture evaporates from the saturated surface. In this part of the drying process, the drying rate does not depend on the moisture content in the material, but only on the resistance to mass transfer in the thin film of air through which the moisture diffuses from the wet surface to the bulk of the gas.

The moisture content in the solid is given by the Eq.:

$$X = \frac{m - m_0}{m_0}$$
 Eq. (6.2)

The equilibrium moisture content in the solid is:

$$X^* = \frac{m^* - m_0}{m_0}$$
 Eq. (6.3)

where: m - weight of the wet material,

m<sub>0</sub> – weight of the dry material.

m\* - weight of the material with the equilibrium moisture content.

The mass flow in the region of the constant drying rate:

$$n_{A} = \frac{\left(\frac{dX}{dt}\right)_{const}}{A} \cdot m_{0}$$
 Eq. (6.4)

The flow of water vapours through the film of air is given as:

$$n_{A} = k_{g}(p_{Ai} - p_{A})$$
 (kg/ms<sup>2</sup>) Eq. (6.5)

where: k<sub>g</sub> – mass transfer coefficient (s/m),

 $p_{Ai}$  – vapour pressure for water at the wet-bulb temperature (atm),

 $p_A$  – partial pressure of water vapour in the bulk of air (atm),

A – surface area of the material  $(m^2)$ ,

$$\left(\frac{dX}{dt}\right)_{const}$$
 – constant drying rate.

Heat flux:

$$q = \dot{n}_A \cdot \Delta h_{vap}$$
 (J/hm<sup>2</sup>) Eq. (6.6)

where:  $\Delta h_{evp}$  – the change in evaporation enthalpy ( $\Delta h_{evp} = h_{vap} - h_{liq}$ )

Heat transfer coefficient:

$$h = \frac{q}{T_{S2} - T_{M2}}$$
 (J/hm<sup>2</sup>K) Eq. (6.7)

where: T<sub>S2</sub> - final dry-bulb temperature,

 $T_{M2}$  – final wet-bulb temperature.

#### b) First falling-rate period

The moisture content at point B in Fig. 6.3, which marks the end of the constant drying rate period, is defined as the critical moisture content. At this point, the surface of the solid material is no longer saturated with moisture, and dry areas appear. The wet surface A is smaller, and the drying rate decreases linearly with the average moisture content in the material. Point C marks the conditions at which all the water has evaporated from the surface of the material. In this part of the process, the drying rate is determined partly by the resistance to mass transfer in the thin film of air, and partly by

the resistance in the layer of dry solid material through which the moisture has to diffuse in order to reach the surface.

#### c) Second falling-rate period

Between points C and D in Fig 6.3, the drying rate is independent of the outside conditions, decreases almost linearly with the average moisture content in the material, and is 0 when the equilibrium moisture content is reached. The DC line has a slope different from BC, and the drying rate is almost entirely determined by the resistance to mass transfer in the layer of dry material, which is always thicker, since the remaining water is found deeper inside the material.

The constant of the dryer is given by the following Eq.:

$$K = \frac{\left(\frac{dx}{dt}\right)_{const}}{(X-X^*)_{cr}}$$
 Eq. (6.8)

where  $(X-X^*)_{cr}$  represents the free moisture content in the critical point.

According to a second definition:

$$K' = {n_A \over H_{M2} - H_{S2}}$$
 Eq. (6.9)

where:  $H_{S2}$  – moisture at temperature  $T_{S2}$ 

 $H_{M2}$  – moisture at temperature  $T_{M2}$ 

### 6.2. TASK

Use the device shown below to dry a body with known surface area. Determine the equilibrium moisture content, the constant drying rate, and the free moisture in the critical point. Calculate the mass and heat transfer coefficients, and the constant of the dryer.

### 6.3. TASK IMPLEMENTATION

The *device* used for drying is shown in Fig. 6.4. It is composed of a 1350 mm long tube with a diameter of 160 mm. In front, it is provided with a window which allows the observation of the solid material being dried. The sample is placed on a hook, which is connected with a balance. The air is heated using

an electric heater. The dryer is equipped with two thermometers: a dry-bulb one, which measures the temperature in the bulk of air inside the dryer, and a wet-bulb one, which measures the temperature at the phase boundary.



Figure 6.4: Dryer for solid materials.

#### Procedure:

- 1. Measure the dimensions of the sample and calculate its surface area.
- 2. Measure the mass of the dry sample.
- 3. Soak the sample in distilled water for 2 to 3 hours.
- 4. Start the ventilator and use the hatch to set the flow of air.
- 5. Start the air heater, set the desired temperature, and wait for 10 minutes until the device is operating at steady state. Read the dry-bulb and wet-bulb temperatures ( $T_{S1}$ ,  $T_{M1}$ ).
- 6. Remove the sample from the water, and use a paper towel to remove excess water from the surface. Introduce the sample into the dryer, and place it on the hook connected to the balance.
- 7. Start the stopwatch, and write down the mass of the sample at moment 0. For correct weight measurements, stop the ventilator during weighing, read the value displayed by the balance, then re-start the flow of air by turning on the ventilator.
- Measure the weight of the sample every 30 s for the first 5 minutes of drying, then every minute for the next 10 minutes of drying, and finally every 5 minutes for the last 15 minutes of the process (total drying time: 30 mins).
- 9. Read the final dry-bulb and wet-bulb temperatures ( $T_{S2}$ ,  $T_{M2}$ ).

# 6.4. PRESENTATION OF THE RESULTS IN THE LABORATORY NOTEBOOK

Use the table below to record the values of the measurements:

t(min)	M(g)	х	X-X*	$\frac{\Delta X}{\Delta t}$
0				
0.5				
1				
5				
6				
15				
20				
30				

Draw the diagram m = f(t) and determine  $m^*$  by extrapolating the curve to 60 mins.

Draw the diagram  $\frac{\Delta X}{\Delta t} = f(X - X^*)$  and determine the free moisture content at the critical point  $(X - X^*)_{cr}$ .

Calculate the mass and heat transfer coefficients, and show the results in the following table:

_	SAMPLE	SAMPLE
X*		
(dX/dt) <sub>const</sub> (min <sup>-1</sup> )		
(X-X*) <sub>cr</sub>		
$\dot{n}_A$ (kg/m <sup>2</sup> s)		
kg (s/m)		
q (W/m²)		
h (W/m²K)		
K (min <sup>-1</sup> )		
K* (kg/m <sup>2</sup> s)		

# **ANNEX**

# Physicochemical properties of substances

# REFRACTOMETRY

When passing through an optical medium, light changes its direction. The phase velocity of the light wave is modified, and this phenomenon is called refraction. When passing the boundary between a medium with lower optical density and a medium with higher optical density, light changes its propagation direction. The refractive index is calculated using the ratio between the angles of incidence and refraction, reported to the perpendicular on the interface (See Fig.). It has been demonstrated that the ratio between the sinus of the incidence angle ( $\alpha$ ) and the sinus of the refraction angle ( $\beta$ ) is proportional to the ratio between the values of the light velocity in the two mediums. The refractive index n is given by the Eq.:

$$\frac{\sin\alpha}{\sin\beta} = \frac{v_1}{v_2} = n$$

The refractive index is a physical parameter that changes with temperature, wavelength and solution concentration. Therefore, when the temperature and wavelength are constant, a refractometer can be used to measure the refractive index of a certain solution, and the concentration of the solution is determined by reading the value from the calibration curve.



Compounds				
Α	В	Mass%	$n_{D}^{20}$	
Methanol	Water	0.00	1.333	
		5.00	1.3341	
		10.00	1.3354	
		15.00	1.3368	
		20.00	1.3382	
		30.00	1.3408	
		40.00	1.3426	
		48.00	1.343	
		60.00	1.3426	
		68.00	1.3414	
		80.00	1.3384	
		84.00	1.3372	
		88.00	1.3357	
		90.00	1.3348	
		93.00	1.3331	
		97.00	1.3312	
		100.00	1.3291	
Ethanol	Water	0.50	1.3333	
		1.00	1.3336	
		10.00	1.3395	
		20.00	1.3469	
		30.00	1.3535	
		40.00	1.3583	
		50.00	1.3616	
		60.00	1.3638	
		70.00	1.3652	
		80.00	1.3658	
		90.00	1.3650	
		98.00	1.3630	
		100.00	1.3614	

**Table A1:** The relation between the refractive index and composition at T = 20°C.



**Figure A1:** Composition of the methanol-water solution (mass %), as a function of the refractive index.



**Figure A2:** Composition of the ethanol-water solution (mass %), as a function of the refractive index.

	Table A2: Eq	uilibrium da	ıta for binaı	ry systems at	atmospheric	pressure.
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Compou	ınds	Temperature	Mole fr	action A	Pressure
Α	В	(°C)	Liquid	Vapour	(kPa)
Ethanol	Water	95.5	0.0190	0.1700	101.3
		89.0	0.0721	0.3891	
		86.7	0.0966	0.4375	
		85.3	0.1238	0.4704	
		84.1	0.1661	0.5089	
		82.7	0.2337	0.5445	
		82.3	0.2608	0.5580	
		81.5	0.3273	0.5826	
		80.7	0.3965	0.6122	
		79.8	0.5079	0.6564	
		79.7	0.5198	0.6599	
		79.3	0.5732	0.9841	
		78.74	0.6763	0.7385	
		78.41	0.7472	0.7815	
		78.15	0.8943	0.8943	
Methanol	Water	100	0.000	0.000	101.3
		96.4	0.020	0.134	
		93.5	0.040	0.230	
		91.2	0.060	0.304	
		89.3	0.080	0.365	
		87.7	0.100	0.418	
		84.4	0.150	0.517	
		81.7	0.200	0.579	
		78.0	0.300	0.665	
		75.3	0.400	0.729	
		73.1	0.500	0.779	
		71.2	0.600	0.825	
		69.3	0.700	0.870	
		67.5	0.800	0.915	
		66.0	0.900	0.958	
		35.0	0.950	0.979	
		64.0	1.000	1.000	

Temp.	Pressure	Volume (m³/kg)		Enthalpy (kJ/kg)		Viscosity Ns/m <sup>2</sup>	
(К)	(bar)	Liquid	Vapour	Liquid	Vapour	Liquid	Vapour
		×10 <sup>3</sup>				×10 <sup>6</sup>	×10 <sup>6</sup>
273.25	0.00611	1.000	206.30	0	2502	1750	8.02
275	0.00697	1.000	181.70	7.8	2505	1632	8.09
280	0.0099	1.000	130.40	28.8	2514	1422	8.29
285	0.01387	1.000	99.40	49.8	2523	1225	8.49
290	0.01917	1.001	69.70	70.7	2532	1080	8.69
295	0.02617	1.002	51.94	91.6	2540	959	8.99
300	0.03531	1.003	39.13	112.3	2550	833	9.09
305	0.04712	1.005	27.90	133.4	2559	769	9.29
310	0.06211	1.007	22.93	154.3	2565	695	9.49
315	0.08132	1.009	17.82	175.2	2577	631	9.69
320	0.1053	1.011	13.95	196.1	2586	577	9.89
325	0.1351	1.013	11.06	217	2595	528	10.09
330	0.1719	1.016	8.82	237.9	2604	489	10.29
335	0.2167	1.018	7.09	258.8	2613	453	10.43
340	0.2713	1.021	5.74	279.8	2622	420	10.69
345	0.3372	1.024	4.683	300.7	2630	389	10.89
350	0.4163	1.027	3.846	321.7	2639	363	11.09
355	0.51	1.030	3.180	342.7	2647	343	11.29
360	0.6209	1.034	2.645	363.7	2655	324	11.49
365	0.7314	1.035	2.212	384.7	2663	306	11.69
370	0.904	1.041	1.861	405.8	2671	289	11.89
373.15	1.0133	1.044	1.679	419.1	2676	279	12.02
375	1.0815	1.045	1.574	426.8	2679	274	12.09
380	1.2869	1.049	1.337	448	2687	260	12.29
385	1.5233	1.063	1.142	469.2	2694	249	12.49
390	1.794	1.066	0.980	490.4	2702	237	12.69
400	2.455	1.067	0.731	532.9	2716	217	13.05
410	3.302	1.077	0.553	575.6	2729	200	13.42
420	4.37	1.088	0.425	618.6	2742	185	13.79
430	5.699	1.100	0.331	661.8	2753	173	14.14
440	7.333	1.110	0.261	705.3	2764	162	14.30
450	9.319	1.123	0.206	749.2	2773	152	14.55
460	11.71	1.137	0.167	793.5	2782	143	15.19
470	14.55	1.520	0.136	838.2	2789	136	15.34
480	17.9	1.167	0.111	883.4	2795	129	15.55
490	21.83	1.184	0.0922	929.1	2799	124	16.23
500	26.4	1.203	0.0766	975.6	2801	119	16.59

**Table A3:** Physicochemical properties of saturated vapours.



**Figure A3:** *Psychrometric curves for the air-water system at atmospheric pressure.* 



**Figure A4:** Solubility of CO<sub>2</sub> in water, as a function of temperature and pressure.
T(°C)	0	10	20	30	40	50	60
Solubility (g/L)	3 346	2 318	1 688	1 257	0 973	0 761	0 576

**Table A4:** Solubility of  $CO_2$  in water at air pressure 1 atm.

7. K	P. bar	rj. m <sup>3</sup> kg	r <sub>ø</sub> . m <sup>s</sup> . kg	hj. kJ kg	h <sub>e</sub> . kj kg	sj. kj (kg·K)	s <sub>e</sub> . kJ (kg·K)	cop. kJ ikg-Ki
175.4	1 887 -6	1.1053	241200	314.3	1624.3	2.766	10 233	2.177
180	39096	1.111 -3	119600	324.4	1629.9	2 522	10.075	2.181
190	1.6935	1.124 - 3	29690	346.1	1642.2	2.940	9.761	2.190
200	6.2745	1.1373	S278	367.8	1654.5	3 051	9.465	2.201
210	2.035 4	1.150 - 3	2680	389.9	1666.9	3.169	9.240	2.215
220	5.8814	1.1633	970.7	412.5	1679.2	3.264	9.022	2.281
230	1.539 3	1.1763	385.3	435 6	1691 9	3.366	6.529	2.251
240	3.6873	1 1 1 1 1 9 3	168.7	-459.1	17013	3.467	8.655	2.275
250	8.1893	1.203 3	· 79.02	483.0	1716.6	3.664	8.499	2.303
260	1.7002	1.216 3	39.49	507.1	1728.9	3 659	6.355	2.337
270	3.3272	1.230 - 3	20.93	531.5	17407	3 751	8.230	2.375
280	6.208 2	1.2443	11.62	556.1	1752.1	3 \$40	8.112	2.420
290	0.1094	1.259 - 3	6.775	581.0	1763.2	3.928	5.005	2.471
300	0.1860	1.2743	4.095	606.2	1773.5	-4.013	7.904	2.528
310	0.3043	1.290 3	2.566	631.7	1783.1	4 097	7.511	2.59
320	0.4817	1.306 3	1.661	657.5	1791 9	4.179	7.723	2.67
330	0.7395	1.323 3	1.103	683.6	1799 \$	4.259	1.040	215
337.5	1.0012	1.337 3	0.5110	703.4	1504 5	-1.310	7.551	2.81
340	1.1044	1.3425	0.7533	710.1	1506.5	4.335	7.562	2.83
350	1.6082	1.361 3	0.5256	736.9	1512.4	4.415	7.455	2.91
360	2.288	1 381 - 3	0.3752	764.3	1817.4	4.492	7.417	3.01
370	3.188	1403-3	0.2723	792.5	1821 6	4.569	7.350	3.11
380	4.357	1.4263	0.2015	\$20.2	1825.1	4.643	7.257	3.22
390	5.845	1.4523	0.1512	856.4	1825.1	4.736	1.44	3.34
400	7.703	1.4803	0.1135	855 5	1830.7	4.517	1.1.2	3.48
410	10.00	1.5103	0.0893	917.7	1832.8	4.888	7.120	3.63
420	12.83	1.5433	0.0635	947.7	1534.0	4.959	7.069	3.80
430	16.26	1.591 - 3	0.0542	962 2	1834.1	5.039	7.020	4.05
440	20.40	1.6243	0.0425	1022.7	1832.4	5.130	6.971	4.33
450	25.30	1.6743	0.0333	1069.2	1828.4	5.233	6.920	4.68
460	31.08	1.7333	0.0263	1120.6	1820.5	5.344	6.566	5.06
470	37 80	1.8063	0 0202	1175.8	1907.5	5.460	6.504	5.29
480	45.61	1.6963	0.0156	1233.4	1785.6	5.578	6.725	5.54
490	54.66	2.0213	0.0115	1292.5	1751.4	5.696	6.633	5.11
500	65.17	2.214 - 3	0.0094	1353.7	1704.3	5.816	6.516	6.1
510	77.43	2.69 - 3	0.0059	1437.6	1649.4	5.975	6.391	,
512.7	81 03	354-3	0.0036	1532	1532	6.170	6.170	-20

**Table A5:** Physicochemical properties of methanol.

<sup>°</sup>Interpolated from Zubarev, Prusakov, and Sergeyeva, Thermophysical Properties of Methanol—A Handbook, Standartov, Moscow, 1973 (in Russian). v = specific volume, m<sup>3</sup> kg, h = specific enthalpy, kJ kg; s = specific entropy, kJ kg·K);  $c_p =$  specific heat at constant pressure, kJ (kg·K). The notation 1.687. –6 signifies 1.867 × 10<sup>-6</sup>

%	0°C.	10°C.	15.56°C.	20°C.	15°C. 1	ev.	0°C.	10°C.	15.56°C	20°C.	15°C. 1	5	0°C. 1	10°C.	15.56°C. 1	800 1	1797-
Q	0.9999	0.9997	0.9990	0.9982	0.99913.	35	0.9534	0.9484	0 9456	0.9433	0.94570	70	0.8869	0.8794	0.8748	0.8715	0.87507
1	.9981	.9980	.9973	. 990)	997274	30	.9520	.9469	.9440	.9416	.94404	71	.8847	.8770	. 8726	.8690	. 87 27 1
45	.9946	9945	9938	.9931	.99370	38	.9490	.9417	9405	.9381	940671	2	.0529	.8/4/	.8702	.8665	.87033
4	.9930	.9929	.9921	.9914	.99198	39	.9475	.9420	.9387	.9363	.93894	74	.8778	.8699	.6070	.0091	.80/92
		0015															
2	.9914	.9912	.9904	. 9890	.99029	40	.9459	.9403	.9369	.9345	.93720	75	.8754	.8676	.8629	.8592	.86300
7	9884	.9881	.9872	. 9863	98701	42	9427	.9370	.9333	.9309	.93365	77	.8705	10051	.8604	.8567	.86051
8	.9870	.9865	.9857	.9847	98547	43	.9411	.9352	.9315	.9290	.93185	78	.8680	.8602	.8554	8518	45555
2	.98%	.9849	.9841	.9831	.98394	44	.9395	.9334	.9297	.9272	.93001	79	.8657	.8577	.8529	.8494	.85300
10	.9842	.9834	.9826	9815	96241	45	.9377	.9316	9279	9252	07815	an	8634	8551	8503	\$440	920.00
1	.9829	.9820	.9811	.9799	.98093	46	.9360	.9298	.9261	.9234	92627	81	.8610	.8527	.8478	8446	84704
12	.9816	.9805	.97%	.9784	.97945	47	.9342	. 9279	.9242	.9214	.92436	82	.8585	.8501	.8452	.8420	.84536
13	. 9804	.9/91	.9781	.9768	.97602	48	.9324	.9260	9223	.9196	.92242	83	.8560	.8475	.8426	.8394	.84274
9.4				. 90 .94	.77000	47	.,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,	.7410		.7170	. 9.0040	101	.000	. 8999	.590	. 6066	.84009
15	.9780	.9764	.9752	.9740	.97518	50	.9287	.9221	.9185	.9156	.91852	85	.8510	.8422	.8374	.8340	.83742
16	.9769	.9751	.9738	.9725	.97377	51	.9269	.9202	.9166	.9135	.91653	86	.8483	.8394	.8347	.8314	.83475
1A	9747	9726	9769	9/10	97006	52	9730	9162	9176	9114	.91421	80	.0400	. 6367	.8320	.8286	.83207
19	.9736	.9713	.9695	.9681	.96955	ŝá	.9211	.9142	.9106	.9073	.91044	89	.8400	.8314	8267	8730	87667
-	6435	0360	l Aria							1		1					-61656
21	9714	9687	9666	. 9000	. 90014	22	9177	9101	9000		.90839	90	.8374	. 8287	.8239	.8202	.82396
22	9702	.9673	1 . 9652	. 9636	.96533	57	.9151	9080	.9045	. 9010	.90421	92	8320	8234	8185	A110.	81840
23	.9690	. 9660	.9638	.9622	.96392	58	.9131	.9060	.9024	. 8968	.90210	1 93	.8293	6208	.8157	.8118	81568
24	.9678	.9646	.9624	.9607	.96251	59	.9111	.9039	.9002	8968	. 89996	94	.8266	. 8180	.8129	. 8090	.81285
ъ	.9666	.9632	.9609	.9592	.96108	60	.9090	.9018	.8980	8946	89781	95	8740	1 8157	8101	8063	60000
26	.9654	.9618	.9595	.9576	.95963	61	.9068	.8998	.8958	. 8924	.89563	96	.8212	.8124	8073	8034	80713
IJ	.9642	.9604	.9580	.9562	.95817	62	.9046	.8977	.8936	. 8902	.89341	97	.8186	, 80%	.8045	8005	.80428
29	9616	9575	0550	.9540	95518	1 60	9007	.8933	.8913	. 88/9	.8911/	90	0218.	. 8068	.8016	7976	.80143
						ິ						7"	.0130	.0040	10704	. 7740	.17039
30	.9604	.9560	1 .9535	.9515	.95366	65	.8980	.8911	. 8867	.8534	.88662	2100	.8102	.8009	:7959	.7917	.79577
31 37	9576	9521	. 95/21	1 .9499	95054	00 67	0958 801c	6866	.6544	.8511	.88433	N.	1				
33	.9563	9516	. 9489	1,9466	.94896	68	8913	. 8842	8797	8763	87971	1		1		1	1
Й	9549	9500	9473	1 .9450	94734	69	. 8891	8818	8771	1 8738	87735	ł.	1				l

**Table A6:** Density of the aqueous solution of methanol, as a function of composition and<br/>temperature (density as g/cm³, composition as mass %).

<sup>•</sup> It should be noted that the values for 100 per cent do not agree with some data available elsewhere, e.g., "American Institute of Physics Handbook," McGraw-Hill, New York, 1957. Also, see Atack, "Handbook of Chemical Data," Reinhold, New York, 1957.

$ \begin{array}{c c c c c c c c c c c c c c c c c c c $				No. of Concession, name							
0         4.579         4.613         4.547         4.621         4.750         4.785         4.820         4.855         4.890         5.235         5.765         5.605         5.645         5.225         5.765         5.605         5.645         5.225         5.765         5.807         5.725         5.766         5.807         5.848         5.835         5.935         5.035         5.645         6.010         6.144         6.187         6.230         6.274         6.318         6.335         6.408         6.435         6.486         6.437         6.589         6.635         6.648         6.775         6.822         6.809         6.917         6.965           7         7.513         7.565         7.617         7.668         7.711         7.657         7.822         7.930         7.360         7.411         7.462           9         8.609         8.668         8.727         8.786         8.845         8.905         9.025         9.046         9.779         9.783         9.779         9.783         9.748         9.521         9.7649         9.774         9.779           11         9.971         9.977         9.775         9.783         9.748         9.525         9.649         9.	t, °C.	0.0	01	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
1         4.923         5.321         5.327         5.437         5.447         5.447         5.446         5.525         5.565         5.665         5.647         5.448         5.889         5.931         5.973         6.015         6.043         6.448         6.488         5.889         5.931         5.973         6.015         6.043         6.448         6.483         6.448         5.687         5.667         6.013         6.016         6.443         6.453         6.408         6.453         6.408         6.453         6.408         6.453         6.408         6.453         6.408         6.444         6.517         6.622         7.320         7.340         7.411         7.469           7         7.13         7.565         7.617         7.669         7.223         7.332         8.384         8.521         8.385         8.905         8.373         8.494         8.551           9         8.609         8.668         8.727         8.768         8.451         8.9521         9.663         9.025         9.086         9.147           11         9.209         9.21         9.335         9.345         9.042         10.051         10.241         10.311         10.831         10.849 <td< td=""><td>0</td><td>4.579</td><td>4.613</td><td>4.647</td><td>4.68</td><td>4.715</td><td>4.750</td><td>4.785</td><td>4.820</td><td>4.855</td><td>4.890</td></td<>	0	4.579	4.613	4.647	4.68	4.715	4.750	4.785	4.820	4.855	4.890
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	2	9.920 5 794	5.332	5.370	5.408	5.447	5.486	5.525	5.101	5.219	5.256
4         6.101         6.144         6.187         6.230         6.274         6.318         6.363         6.408         6.433         6.336         6.441         7.339         7.340         7.342         7.339         7.340         7.342         7.339         7.340         7.342         7.339         7.340         7.342         7.339         7.340         7.342         7.339         7.340         7.342         7.339         7.340         7.342         7.343         7.342         7.343         7.342         7.343         7.342         7.343         7.343         7.343         7.343         7.343         7.343         7.3	3	5.685	5.725	5.766	5.807	5.848	5.889	5.931	5.973	6.015	6.058
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	4.	6.101	6.144	6.187	6.230	6.274	6.318	6.363	6.408	6.453	6.498
b         7.013         7.032         7.11         7.163         7.203         7.213         7.203         7.213 <th7.213< th="">         7.203         7.213</th7.213<>	5	6.543	6.589	6.635	6.681	6.728	6.775	6.822	6.869	6.917	6.965
8         8.045         8.100         8.155         8.211         8.257         8.322         8.380         8.437         8.444         8.551           9         8.609         8.668         8.727         8.786         8.8451         8.905         8.665         9.025         9.086         9.147           10         9.209         9.21         9.333         9.335         9.448         9.521         9.585         9.649         9.714         9.779           11         9.844         9.910         9.976         10.042         10.079         10.781         10.321         10.380         10.449           12         10.518         10.588         10.658         10.728         10.791         10.741         11.031         11.335         11.379         11.451         11.528         11.604         11.651         11.583           12         10.518         10.528         10.781         13.327         13.411         10.321         10.344         11.433         11.528         11.6041         1.6331         1.537           14         1301         14.522         14.716         13.609         13.898         13.977         15.092         15.188         15.284         15.380	7	7 513	7 565	7.617	7.669	7.722	7.775	7 828	7 882	7 036	7.462
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	8	8.045	8.100	8.155	8.211	8.267	8.323	8.380	8.437	8.494	8.551
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	9	8.609	8.668	8.727	8.786	8.845	8.905	8.965	9.025	9.086	9.147
$      \begin{array}{c} 10 & 9.209 & 9.2 & 1 \\ 9.384 & 9.910 & 9.976 & 10.042 & 10.109 & 10.76 & 10.244 & 10.312 & 10.380 & 10.449 \\ 10.518 & 10.588 & 10.588 & 10.728 & 10.799 & 10.870 & 10.941 & 11.031 & 11.085 & 11.158 \\ 11.1305 & 11.237 & 11.453 & 11.528 & 11.604 & 11.680 & 11.756 & 11.833 & 11.910 \\ 14 & 11.987 & 12.065 & 12.144 & 12.223 & 12.302 & 12.382 & 12.462 & 12.543 & 12.624 & 12.706 \\ 15 & 12.788 & 12.870 & 12.953 & 13.037 & 13.121 & 13.205 & 13.290 & 13.375 & 13.461 & 13.547 \\ 16 & 13.634 & 13.721 & 13.809 & 13.898 & 13.987 & 14.076 & 14.166 & 14.256 & 14.347 & 14.530 \\ 17 & 14.530 & 14.622 & 14.715 & 14.809 & 14.907 & 15.092 & 15.188 & 15.284 & 15.380 \\ 18 & 15.477 & 15.575 & 15.673 & 15.772 & 15.871 & 15.971 & 16.071 & 16.171 & 16.272 & 16.374 \\ 19 & 16.477 & 16.581 & 16.685 & 16.789 & 16.894 & 16.999 & 17.105 & 17.212 & 17.319 & 17.427 \\ 20 & 17.535 & 17.644 & 17.753 & 17.863 & 17.974 & 18.085 & 18.197 & 18.309 & 18.422 & 18.536 \\ 11 & 18.650 & 18.765 & 18.880 & 18.996 & 19.113 & 19.231 & 19.349 & 19.468 & 19.587 & 19.707 \\ 22 & 19.827 & 19.948 & 20.070 & 20.193 & 20.316 & 20.440 & 20.565 & 20.690 & 20.815 & 20.941 \\ 21 & 22.377 & 22.512 & 22.648 & 22.785 & 22.922 & 23.060 & 23.198 & 23.337 & 23.476 & 23.616 \\ 25 & 23.756 & 23.897 & 24.039 & 24.182 & 24.326 & 24.471 & 24.617 & 26.774 & 24.912 & 24.326 \\ 27 & 25.799 & 25.399 & 25.60 & 25.81 & 22.954 & 27.117 & 26.271 & 26.426 & 25.582 \\ 27 & 25.799 & 25.397 & 27.055 & 27.214 & 27.374 & 27.353 & 27.696 & 27.858 & 28.021 & 28.185 \\ 28 & 28.349 & 28.514 & 28.680 & 28.847 & 29.015 & 29.184 & 29.354 & 29.525 & 29.697 & 29.870 \\ 29 & 30.043 & 30.217 & 30.327 & 30.247 & 32.543 & 30.923 & 31.102 & 31.1281 & 31.461 & 31.642 \\ 30 & 31.824 & 32.007 & 32.191 & 32.376 & 32.561 & 32.747 & 32.934 & 33.122 & 33.112 & 33.123 \\ 31 & 35.693 & 33.883 & 34.082 & 34.276 & 34.471 & 34.579 & 46.050 & 46.325 & 26.677 & 29.578 & 25.566 & 15.880 & 13.75 & 13.642 \\ 35 & 42.175 & 42.409 & 42.644 & 42.880 & 43.117 & 43.355 & 43.864 & 35.064 & 35.778 & 35.783 \\ 31 & 35.843 & 35.64 & 53.9$	t,° C.	0.0	0.1	0.2	0.3	04	0.5	0.6	0.7	0.8	0.9
11         9.844         9.910         9.976         10.042         10.176         10.244         10.312         10.380         10.478           12         10.518         10.588         10.658         10.728         10.799         10.870         10.941         11.081         11.085         11.158           13         11.231         11.305         11.379         11.453         11.528         11.604         11.680         11.756         11.833         11.910           14         11.987         12.263         12.271         13.809         13.987         14.166         14.168         14.347         14.333           14         14.530         14.622         14.715         14.809         14.907         15.092         15.188         15.284         15.380           18         15.477         15.575         15.673         15.772         15.871         15.977         16.071         16.171         16.2722         16.374           19         16.477         16.581         16.685         16.789         16.894         16.999         17.105         17.212         17.319         17.427           20         17.535         17.644         17.753         17.863         17.974         18.8	10	9.209	9.Z 1	9.333	9.395	9.458	9.521	9.585	9.649	9.714	9.779
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		9.844	9.910	9.976	10.042	10.109	10.176	10.244	10.312	10.380	10.449
11       11.397       12.005       12.144       12.222       12.302       12.302       12.462       12.543       12.624       12.706         15       12.788       12.870       12.953       13.037       13.121       13.205       13.275       13.461       13.547         16       13.634       13.771       13.809       13.898       13.997       14.005       14.166       14.256       14.434       14.438         17       14.530       14.622       14.715       14.809       14.907       15.092       15.188       15.284       15.380         18       15.477       15.575       15.673       15.772       15.871       15.977       16.834       16.894       16.894       16.999       17.105       17.212       17.319       17.427         20       17.535       17.644       17.753       17.863       17.974       18.805       18.197       18.309       18.422       18.221       18.524         18.227       18.301       18.301       19.349       14.451       19.567       19.707       10.2243       21.977       22.110       22.432       23.977       22.110       22.432       23.977       22.102       23.060       23.198       23.337 <td>13</td> <td>11.731</td> <td>11.305</td> <td>11 379</td> <td>11.453</td> <td>11 578</td> <td>11.604</td> <td>10.941</td> <td>11.013</td> <td>11.065</td> <td>11.158</td>	13	11.731	11.305	11 379	11.453	11 578	11.604	10.941	11.013	11.065	11.158
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	14	11.987	12.065	12.144	12.223	12.302	12.382	12.462	12.543	12.624	12.706
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$		1									12-200
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	16	12/00	12.8/0	12.953	13.03/	13.121	13.205	13.290	13.375	13.461	13.547
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	17	14 530	14 622	14 715	13.090	12.90/	14 007	15 002	14.220	14.34/	14.450
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	18	15.477	15.575	15.673	15.772	15.871	15.971	16.071	16.171	16.272	16.374
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	19	16.477	16.581	16.685	16.789	16.894	16.999	17.105	17.212	17319	17.427
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	20	17.535	17.644	17.753	17.863	17.974	18.085	18.197	18.309	18.422	18.536
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	21	18.650	18.765	18.880	18.996	19.113	19.231	19.349	19.468	19.587	19.707
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	22	19.84	21 106	20.0/0	20.193	20.316	20.440	20.505	20.690	20.815	20.941
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	24	22.377	22.512	22.648	22.785	22.922	23.060	23.198	23.337	23.476	23.616
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	25	23 756	23 897	24 030	74 187	74 376	24 471	24 617	24 764	24 012	25 060
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	26	25.209	25.359	25.509	25.660	25.812	25.964	26.117	26.271	26.426	26.582
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	27	26.739	26.897	27.055	27.214	27.374	27.535	27.6%	27.858	28.021	28.185
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	28	28.349	28.514	28.680	28.847	29.015	29.184	29.354	29.525	29.697	29.870
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	29	50.045	50.217	50.592	50.500	50.745	30.923	51.102	31.281	31.401	31.642
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	30	31.824	32.007	32.191	32.376	32.561	32.747	32.934	33.122	33 312	33.503
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	32	35 663	35 865	36 (68)	24.270	36 477	34.00/	34.804	35.062	35.261	35.462
34       39.898       40.121       40.344       40.569       40.796       41.023       41.251       41.480       41.710       41.942         35       42.175       42.409       42.644       42.880       43.117       43.355       43.595       43.836       44.078       44.320         36       44.563       44.503       44.504       45.301       45.549       45.799       46.050       46.302       46.556       46.811         37       47.067       47.324       47.582       47.841       48.102       48.364       48.627       48.391       49.157       49.424         38       49.692       49.961       50.231       50.502       50.774       51.048       51.323       51.600       51.879       52.160         39       52.442       52.725       53.009       53.294       53.580       53.867       54.156       54.446       54.737       55.030         40       55.324       55.61       55.91       56.21       56.51       56.81       57.11       57.41       57.72       58.03         41       58.34       58.65       58.96       59.27       59.58       59.90       60.22       60.54       60.86       61.18       <	33	37 729	37.942	38.155	38.369	33.584	38.801	39.018	39.237	39.457	39.677
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	34	39.898	40.121	40.344	40.569	40.7%	41.023	41.251	41.480	41.710	41.942
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	35	42.175	42.409	42.644	12.880	13.117	43.355	43.595	43.836	44.078	<b>H.32</b> 0
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	36	44.563	44.808	45.054	5.3014	15.549	45.799	<b>16.050</b>	46. <b>30</b> 2	46.556	6.811
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	38	49 692	47.524	47.002 50.73	50 502	10.102 50 774	48.304	1 272	18.391	49.157	19.424
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	39	52.442	52.725	53.009	53.294	53.580	53.867	4.156	54.446	54.737	5.030
41       58.34       58.65       58.96       59.27       59.58       59.90       60.22       60.54       60.86       61.18         42       61.50       61.82       62.14       62.47       62.80       63.13       63.46       63.79       64.12       64.46         43       64.80       65.14       65.82       66.16       66.51       66.86       67.21       67.56       67.91         44       68.26       68.61       68.97       69.33       69.69       70.05       70.41       70.77       71.14       71.51         45       71.88       72.25       72.62       72.99       73.36       73.74       74.12       74.50       74.88       75.26         46       75.65       76.04       76.43       76.82       77.21       77.60       78.00       78.40       78.80       79.20         47       79.60       80.00       80.41       80.82       81.23       81.64       82.05       82.46       82.87       83.29         48       83.71       84.13       84.56       84.99       85.42       85.85       86.28       86.71       87.14       87.58         49       88.02       88.46	40	55.324	55.61	55.91	6.21 5	6.51	56.81 5	7.11	57.41	57.77	8.03
42       61.50       61.82       62.14       62.47       62.80       63.13       63.46       63.79       64.12       64.46         43       64.80       65.14       65.82       66.16       66.51       66.86       67.21       67.56       67.91         44       68.26       68.61       68.97       69.33       69.69       70.05       70.41       70.77       71.14       71.51         45       71.88       72.25       72.62       72.99       73.36       73.74       74.12       74.50       74.88       75.26         46       75.65       76.04       76.43       76.82       77.21       77.60       78.00       78.40       78.80       79.20         47       79.60       80.00       80.41       80.82       81.23       81.64       82.05       82.46       82.87       83.29         48       83.71       84.13       84.56       84.99       85.42       85.85       86.28       86.71       87.14       87.58         49       88.02       88.46       88.90       89.34       89.79       90.24       90.69       91.14       91.59       92.05	41	58.34	58.65	58.96	9.27 5	9.58	59.90 6	0.22	0.54	50.86	51.18
43       64.80       65.14       65.48       65.82       66.61       66.51       66.86       67.21       67.56       67.91         44       68.26       68.61       68.97       69.33       69.69       70.05       70.41       70.77       71.14       71.51         45       71.88       72.25       72.62       72.99       73.36       73.74       74.12       74.50       74.88       75.26         46       75.65       76.04       76.43       76.82       77.21       77.60       78.00       78.40       78.80       79.20         47       79.60       80.00       80.41       80.82       81.23       81.64       82.05       82.46       82.87       83.29         48       83.71       84.13       84.56       84.99       85.42       85.85       86.28       86.71       87.14       87.58         49       88.02       88.46       88.90       89.34       89.79       90.24       90.69       91.14       91.59       92.05	42	61.50	61.82	62.14	2.47 6	2.80	53.13 6	3.46	3.79	54.12	4.46
45       71.88       72.25       72.62       72.99       73.36       73.74       74.12       74.50       74.88       75.26         46       75.65       76.04       76.43       76.82       77.21       77.60       78.00       78.40       78.80       79.20         47       79.60       80.00       80.41       80.82       81.23       81.64       82.05       82.46       82.87       83.29         48       83.71       84.13       84.56       84.99       85.42       85.85       86.28       86.71       87.14       87.58         49       88.02       88.46       88.90       89.34       89.79       90.24       90.69       91.14       91.59       92.05	42	68 26	68.61	69.40 0	0 32 6	0.16		0.86	7.21	57.56	7.91
45       171.88       172.25       172.62       172.99       173.36       173.74       174.12       174.50       174.88       175.26         46       175.65       176.04       164.3       168.22       177.21       177.60       18.00       184.40       180.82       19.20         47       179.60       80.00       80.41       80.82       81.23       81.64       82.05       82.46       82.87       83.29         48       83.71       84.13       84.56       84.99       85.42       85.85       86.28       86.71       87.14       87.58         49       88.02       88.46       88.90       89.34       89.79       90.24       90.69       91.14       91.59       92.05						7.07		0.71	0.11	1.17	121
47         79.60         80.00         80.41         80.82         81.23         81.64         82.05         82.46         82.87         83.29           48         83.71         84.13         84.56         84.99         85.42         85.85         86.28         86.71         87.14         87.58           49         88.02         88.46         88.90         89.34         89.79         90.24         90.69         91.14         91.59         92.05	45	71.88	72.25	72.62 7	2.99 7	3.36	3.74 7	4.12 7	4.50 7	4.88 7	5.26
48         83.71         84.13         84.56         84.99         85.42         85.85         86.28         86.71         87.14         87.58           49         88.02         88.46         88.90         89.34         89.79         90.24         90.69         91.14         91.59         92.05	47	79.60	80.00	10.72 / R0 41 R	0.02 /	1.2	1.00 7	0.00 7	0.40 7	0.00 7	9.20
49 88.02 88.46 88.90 89.34 89.79 90.24 90.69 91.14 91.59 92.05	48	83.71	34.13	34.56 8	4.99 8	5.42	35.85	6.28	6.71 8	7.14 8	7.58
	49	88.02 li	38.46	38.90 8	9.34 8	9.79	0.24 9	0.69 9	1.14 9	1.59 9	2.05

**Table A7:** Vapour pressure of water (as mm Hg), as a function of temperature.

nan -Daaraa	54 WARMON (1995)									-10 - 2 million
<i>t</i> , °C.	0	1	2	3	4	5	6	7	8	9
50	92.51	97.20	102.09	107.20	112.51	118 04	123 80	120 82	136 08	142.60
60	149.38	156.43	163.77	171 38	170 31	187 54	106 00	204 06	214 17	272 72
20	233.7	243.9	254.6	265 7	277 2	280 1	201 4	314 1	277 2	2110
80	355.1	369.7	384.9	400.6	416.8	433.6	450.9	468.7	487.1	506.1
00	For me									-
90	20.16	527.76	529.77	531.78	533.80	535.82	537.86	539.90	541.95	544.00
91	240.05	548.11	550,18	552.26	554.35	556.44	558.53	560.64	562.75	564.87
92	200.99	569.12	571.26	573.40	575.55	577.71	579.87	582.04	584 22	586.41
93	268.60	590.80	593.00	595.21	597.43	599.66	601.89	604.13	606 38	608 64
94	610.90	613.17	615.44	617.72	620.01	622.31	624.61	626.92	629.24	631.57
95	633 00	636 74	638 50	40.01	(12.00)					
66	657 62	660 02	667 45	664 00	043.30	645.67	648.05	650.43	652.82	655.22
07	682 07	684 55	697 04	690 54	00/31	669.75	672.20	674.66	677.12	679.69
02	707 27	700 92	712 40	714 00	092.05	694.57	697.10	699.63	702.17	704.71
00	722 24	725 89	720 52	741 10	(17.56	120 15	722.75	725.36	727.98	730.61
100	740 00	762 72	746 46	741.10	743.85	740.52	/49.20	751.89	754.58	757.29
100	707 57	700.27	702 10	700.19	770.93	113.68	776.44	779.22	782.00	784.78
101	101.51	190.31	193.18	190.00	/98.82	801.66	804.50	807.35	810.211	813.08

 Table A7: Vapour pressure of water (as mm Hg), as a function of temperature.

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