Exercise 1    DETERMINATION OF MOLAR MASS FROM FREEZING POINT DEPRESSION

Colligative properties

The properties we now consider are the lowering of vapour pressure, the elevation of boiling point, the depression of freezing point, and the osmotic pressure arising from the presence of a solute. In dilute solutions these properties depend only on the number of solute particles present, not their identity. For this reason, they are called **colligative properties**.

We assume that the solute is not volatile, so it does not contribute to the vapour. We also assume that the solute does not dissolve in the solid solvent: that is, the pure solid separates when solution is frozen.

All colligative properties stem from the reduction of the chemical potential of liquid solvent as a result of the presence of solute. For an ideal-dilute solution, the reduction is from \( \mu_A^0 \) for the pure solvent \( A \) to \( \mu_A^0 + RT \ln x_A \), when a solute \( B \) is present (\( \ln x_A \) is negative because \( x_A < 1 \)).

\( x_A \) is molar fraction of solvent \( A \) with solute \( B \). There is no direct influence of the solute on the chemical potential of the solvent vapour and the solid solvent because the solute appears in neither the vapour nor the solid. As can be seen from **Figure 1**, the reduction in chemical potential of the solvent implies that the liquid-vapour equilibrium occurs at a higher temperature (the boiling point raised) and the solid-liquid equilibrium occurs at a lower temperature (the freezing point is lowered).

![Figure 1](image)

**Figure 1** The chemical potential of a solvent in the presence of a solute

*The elevation of boiling point – ebullioscopy*

When a nonvolatile solute is dissolved in a solvent, the vapor pressure of the latter is decrease
\[ \Delta p_A = p_A^0 - p_A \quad [\text{Pa}] \]  

where: 
- \( p_A^0 \) is the vapor pressure of the pure solvent at a particular temperature 
- \( p_A \) is the vapor pressure of the solvent over the solution at the same temperature  

(Figure 2)

**Figure 2** The elevation of the boiling point of a solvent

The extent of the elevation

\[ \Delta T = T_{b'} - T_b \]

depends upon the concentration of the solute, and for dilute, ideal solution it may be shown that:

\[ \Delta T = K_e b_B \quad [\text{K}] \]  

where: \( K_e \) is a constant characteristic of the solvent, called *boiling–point constant* (molal ebullioscopic constant) expressed in units [K kg mol\(^{-1}\)]

\( b_B \) is molal concentration (molality) of the solution

Boiling – point constant \( K_e \):

\[ K_e = \frac{R T_0^2 M_A}{\Delta H_{mv}} \quad [\text{K kg mol}^{-1}] \]  

where:
- \( R \) is universal gas constant
- \( T \) is thermodynamic temperature
- \( \Delta H_{mv} \) is molar heat of vaporization
- \( M_A \) is molar mass of the solvent

For water, \( K_e = 0.51 \text{ K kg mol}^{-1} \)

*Molality* (\( b \)) – it is the number of moles of solute (B) dissolved in solvent (A):

\[ b_B = \frac{m_B}{M_B m_A} \quad [\text{mol kg}^{-1}] \]  

where: \( m_B \) – is mass of solute (B) – unit kg
$M_B$ – is molar mass of solute – unit kg mol\(^{-1}\)

$m_A$ – is mass of solvent – unit kg

**Freezing point depression**

Note, when the partial vapor pressure of the solvent is lowered, the temperature of freezing is also lowered because the vapor-pressure curve of the solvent in the solution intersects the sublimation curve of the solid at a lower temperature (Figure 3). The solid phase, which is assumed to be pure solvent, separates when the temperature is lowered to a point where the partial vapor pressure of the solvent is just infinitesimally greater than the sublimation pressure of the solid.

![Figure 3](image)

**Figure 3** The depression of the freezing point of a solvent

Note, the extent of the freezing point depression is defined as:

\[ \Delta T = T_f - T \]

where $T_f$ is freezing point of a solvent

$T$ is freezing point of the solution ($\Delta T > 0$)

Similarly to above, the extent of the freezing point depression depends on the molal concentration

\[ \Delta T = K_c b_B \]

where $K_c$ is the molal depression constant [K kg mol\(^{-1}\)]

$b_B$ is molal concentration according **Equation 4**

It is also called the cryoscopic constant of a given solvent. The depression of the freezing point is thus **proportional** to the molality of the solute in solution. Cryoscopic constant:

\[ K_c = \frac{RT_0^2 M_A}{\Delta H_{nf}} \] [K kg mol\(^{-1}\)]
where: $\Delta H_{mf}$ is molar heat of vaporization depends only on the properties of the solvent.

For water $K_C = 1.86 \, \text{K} \, \text{kg mol}^{-1}$. For justification for $K_e$ and $K_C$ (Equations 3 and 6) see [1, 2].

The lowering of the freezing point constitutes one of the simplest and most accurate means of determining the apparent molecular weight of a solute. It is of practical value and is important in theoretical studies of solution behavior.

**Task**

Cryoscopic determination of molar mass of unknown non-dissociating substance (non-electrolyte), in aqueous solution.

**Equipments**

Apparatus for cryoscopic measurements as it is shown in Figure 4: Beckman's thermometer (B, Figure 5), test tube with thick walls (S), mixer (M), vessel containing cooling mixture (K); magnifying glass, 3 pieces of weighing bottle, 20 cm$^3$ pipette, beaker, laboratory thermometer, stopwatch.

**Procedure**

**Step 1 Preparation of cryoscopic test tube**

- Using analytical balances weigh 3 portions of unknown substance in a clean and dry weighing bottles, each sample with 0.5 grams of approximate weight – write the mass of bottle+sample into Table 1.
- Clean the cryoscopic test tube using distilled water and dry it with filter paper.
- Using a pipette or automatic burette add 20 cm³ of distilled water with known temperature \( t \) (record measured temperature into the Table 2).
- After insertion of the mixer, place the adjusted Beckman's thermometer (B) so, that it's whole reservoir, containing mercury is immersed to the solution and it is not touching inner walls of the test tube.
- Insert the prepared cryoscopic test tube into the cooling mixture. The surface of the cooling bath should be set 2-3 cm above the solvent’s level.

**Step II  Measurements with pure solvent**
- Record the initial temperature of the liquid inside the cryoscopic test tube when it drops to 5 degrees.
- Start the stop watch and record the temperature every 5 seconds. Because the Bekman’s thermometer displays relative temperature and the thermometer's scale is given in degrees (which numerically equals to 1 Kelvin), the temperature depression will be given in Kelvins.
- The temperature will decrease until the solid phase starts to precipitate from the solution which is indicated with sharply increasing temperature.
- Curve of undercooling looks as it is shown in Figure 4. As a freezing point \( (T_0) \) will be regarded that temperature, which represents the highest value on flat part on the mentioned curve (point A in Figure 6). Record this temperature to the Table 2.

![Figure 4](image)

**Figure 4** Cryoscopic curves (dependence temperature vs time) for pure liguid (curve a) and aqueous solution (b)

**Step III  Measurements with aqueous solution of unknown sample**
- After the last repetition of the measurement with pure solvent heat up the test tube again, so the Beckman's thermometer could be gently removed from the liquid.
- Add the first portion of weighed sample into the solvent and mix it. After the sample dissolution
the Beckman’s thermometer should be restored back to its original place in the test tube and the previous procedure should be repeated as it was described for pure solvent (see again step II).

- The maximum temperature, measured after undercooling, will be considered again as the freezing point of the solution \( T_i \).
- Repeat the measurement for 3 different concentrations given with gradually added portions of weighed unknown sample.
- Record the determined freezing points of these solutions to the Table 3.
- The total mass of added sample is given as sum of the masses of all previous additions. Each temperature determination for the given concentration must be repeated 2 times and the results should be averaged.

**Step IV Completion the measurements**

- When the measurements are finished discharge the solution from the apparatus.
- The kryoscopic test tube, thermometer and mixer should be carefully cleaned and dried up.
- Finally weight the masses of empty weighing bottles and record the results to the Table 1.

Table 1 Weighing the samples

<table>
<thead>
<tr>
<th>Sample No:</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>weighing bottle+sample (g)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>empty weighing bottle (g)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>mass of the sample ( m_B ) (g)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2 Solvent data

\( t = \ldots \ldots \ \degree C \)

<table>
<thead>
<tr>
<th>Solvent</th>
<th>( K_K ) K kg mol(^{-1} )</th>
<th>( m_A ) g</th>
<th>( T ) ( ^\circ Bk )</th>
<th>( T_{01} ) ( ^\circ Bk )</th>
<th>( T_{02} ) ( ^\circ Bk )</th>
<th>( T_{03} ) ( ^\circ Bk )</th>
</tr>
</thead>
<tbody>
<tr>
<td>water</td>
<td>1.859</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\( T_0 \) average freezing point \( ^\circ Bk \)

Processing the results

1. Using Table 2 calculate the average temperature \( T_0 \) from the columns \( T_{01} \), \( T_{02} \), \( T_{03} \).
2. Using Table 3 calculate step by step \( T_i \) and \( \Delta T_i \) as difference between the average freezing point of pure solvent \( T_0 \) and the solutions \( T_i \) according to Equation 7:

\[
\Delta T_i = T_0 - T_i
\]  \( (7) \)
Table 3  Solution data

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Mass of the sample $m_{Bi}$ (g)</th>
<th>Freezing points of samples ($^\circ$Bk)</th>
<th>$T_i$ ($^\circ$Bk)</th>
<th>$\Delta T_i$ (K)</th>
<th>$M_{Bi}$ (g mol$^{-1}$)</th>
<th>Ratio $m_B/\Delta T_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>individual</td>
<td>total</td>
<td>$T_{i1}$</td>
<td>$T_{i2}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3 Calculate the molar mass of unknown substance as follows

3A Direct calculation from a formula:

$$M_{Bi} = \frac{K_K m_{Bi}}{\Delta T_i m_A}$$  \hspace{1cm} (8)

where: $m_{Bi}$ – is the total mass of the unknown sample in grams

$m_A$ – is the mass of the solvent in grams calculated from volume density data

(Table 4)

Calculate the average value of molar mass ($\overline{M_B}$), Equation 9:

$$\overline{M_B} = \frac{\sum_{i=1}^{N}M_{Bi}}{N}$$  \hspace{1cm} (9)

where: $N$ is the number of measurements

Calculate the appropriate standard deviation ($s$) using Equation 10:

$$s = \sqrt{\frac{\sum_{i=1}^{N}(M_{Bi} - M_{Table})^2}{N - 1}}$$  \hspace{1cm} (10)

Table 4  Density of water at various temperatures

<table>
<thead>
<tr>
<th>Temperature ($^\circ$C)</th>
<th>Density (kg m$^{-3}$)</th>
<th>Temperature ($^\circ$C)</th>
<th>Density (kg m$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>999.129</td>
<td>21</td>
<td>998.022</td>
</tr>
<tr>
<td>16</td>
<td>998.972</td>
<td>22</td>
<td>997.801</td>
</tr>
<tr>
<td>17</td>
<td>998.804</td>
<td>23</td>
<td>997.569</td>
</tr>
<tr>
<td>18</td>
<td>998.625</td>
<td>24</td>
<td>997.327</td>
</tr>
<tr>
<td>19</td>
<td>998.435</td>
<td>25</td>
<td>997.075</td>
</tr>
<tr>
<td>20</td>
<td>998.234</td>
<td>26</td>
<td>996.823</td>
</tr>
</tbody>
</table>

3B Calculation of the limit value

In case of solutions which differ from the ideal it is necessary to make an extrapolation to zero weight. The unknown molar mass should be calculated from Equation 11 (below).

Process the dependence [$y=f(x)$]:

\[ y = f(x) \]

\[ M_B = \text{...} \]
\[
\frac{m_{Bi}}{\Delta T_{Ki}} = f(m_{Bi})
\]

using the least square method (MS Excel). The intercept of the linear function represents the requested limit value in Equation 11:

\[
\lim_{m_{Bi} \to 0} \frac{m_{Bi}}{\Delta T_{Ki}}
\]

Finally, the molar mass is than determined using the Equation 11:

\[
M_{Bi} = \left[ \frac{K_K}{m_A} \right] \lim_{m_{Bi} \to 0} \frac{m_{Bi}}{\Delta T_{Ki}}
\]

In this treatment, we will express the experimental error of the molar mass in %, so called relative error, where the table value of molar mass represents the reference (100%) data:

\[
\delta(\%) = \left| \frac{M_{Bi} - M_{Table}^B}{M_{Table}^B} \right| \times 100\%
\]

where: \( M_{Bi} \) is value of molar mass calculated from Equation 11

\( M_{Table}^B \) is molar mass of substance from Chemical Table

**Report**

*Include in your report the following points:*

- Theoretical principles of the molar mass determination using cryoscopy.
- Brief description of the used device and procedure.
- Tables of measured data.
- Calculations of molar mass (procedures A and B), standard deviation, relative error.
- Diagrams:
  - Times dependence of temperature for measurement of pure solvent and solution of unknown substance (first solution)
  - Dependence \( \frac{m_{Bi}}{\Delta T} = f(m_{Bi}) \) for determination of \( m_{Bi} \to 0 \)
- Discussion and conclusions.

**Literature:**
