1.a. Determination of molar mass and dimerization constant of benzoic acid

Molar mass of some substances determined by cryoscopic method may deviate from the tabulated molar mass, even though the solution behaves ideally. Deviation can be caused by dissociation, association, and by others effects that change the number of moles of constituent entities in the solution. For example, benzoic acid in the benzene solution partially dimerizes:

$$2A \xleftrightarrow{K_d} A_2 \tag{1.1.}$$

In this case, the cryoscopic method can be used to determine both the molar mass *M* and the thermodynamic dimerization constant K_d, which can be defined by

$$K_d = \frac{a_d}{(a_1)^2} = \frac{m_d/m_*}{\left(m_1/m_*\right)^2} = \frac{n_d \cdot m_* \cdot m_R}{(n_1)^2} \tag{1.2.}$$

where symbols a_1 (a_d) and m_1 (m_d) are activity and molarity of the solute in the form of monomer (respectively dimer), m_* is a standard molarity whose value is *1 mol kg^{-1}* . n_1 and n_d are molar amounts of monomer and dimer in the solution, m_R is the weight of the solvent (i.e. benzene).

Thus, the difference between the freezing-point point of the benzoic acid solution and benzene is:

$$\Delta T = K_f \cdot \frac{(n_1+n_d)}{m_R} \tag{1.3.}$$

where K_f is the cryoscopic constant of benzene (**xxxxxx Table I.).**

TASK: Determine molar mass and dimerization constant of benzoic acid in freezing benzene. Measure the freezing-point depressions for at least three solutions at concentrations.

LABORATORY AIDS AND CHEMICALS: Apparatus for cryoscopy (see **xxxxx Fig. 2**), digital thermometer, burette for measuring volumes of volatile liquids *(25 cm^3)*, analytical balance, *3* small weighting bottle *(25 cm3)*, spoon, benzene, naphthalene, ice, stopwatch.

INSTRUCTIONS: Determine the benzene cooling curve (**XXXXFIG.3**) as instructed in the introductory chapter. Apply *20 cm^3* of pure benzene. Weight benzene liquid in small weighting bottle (need for 4 significant digits). Repeat this curve measurement three times using new benzene liquid.

Weigh about (*0,2±0,02) g* (4 significant digits) of benzoic acid in small weighting bottle and add it in the cryoscopic tube with benzene liquid. Dissolve the benzoic acid and determine the freezing-point of the solution twice.

In the same way, measure the freezing-point temperature of the other solutions at solute concentrations corresponding to the total additions of (*0.2, 0.4, 0.6, ...) g* of benzoic acid in *20 cm^3* benzene.

DATA ANALYSIS: METHOD 1 (SOLVING TWO EQUATIONS OF TWO UNKNOWNS):

We compile the equation of the matter conservation law for the benzoic acid in the solution:

$$\frac{m_B}{M_B} = n_1 + 2 \cdot n_d \tag{1.4.}$$

where m_B is weight of benzoic acid and M_B is tabular molar mass of benzoic acid in monomer form.

Equations (1.3.) and (1.4.) we can write as follow:

$$\Delta T \cdot \frac{m_R}{K_K} = n_1 + n_d \tag{1.5.}$$

$$\frac{m_B}{M_B} = n_1 + 2 \cdot n_d \tag{1.6.}$$

These two equations involve experimental data ΔT, m_B, m_B , and two unknowns n_1 and n_d. Unknowns n_1 and n_d can be obtained and the result values can be inserted into expression (1.2.), which give the dimerization constant of the benzoic acid K_d in benzene solution.

Use the results obtained with various benzoic acid concentration to determine the confidence interval of the dimerization constant K_d.

METHOD 2 (THE NON-LINEAR LEAST SQUARE METHOD):

The molar amounts of the dimer n_d can be obtained from eqn (1.2.) and inserted in eqn (1.3.) and eqn (1.4.). Thus, we obtain

$$\Delta T = K_K \cdot \frac{n_1 + K_d (n_1)^2 / (m_* \cdot m_R)}{m_R} \tag{1.7.}$$

and

$$\frac{m_B}{M_B} = n_1 + 2 \cdot K_d \cdot (n_1)^2 / (m_* \cdot m_R) \tag{1.8.}$$

The eqn (1.8.) is quadratic equation with respect to n_1, which can be rewritten in quadratic formula:

$$\frac{2 \cdot K_d}{(m_* \cdot m_R)} \cdot (n_1)^2 + n_1 - \frac{m_B}{M_B} = 0 \tag{1.9.}$$

the value of unknown n_1 can be obtained as a positive root:

$$n_1 = \frac{-1 + \sqrt{1 + 8 \cdot K_d m_B / (M_B m_* \cdot m_R)}}{4 K_d / (m_* \cdot m_R)} \tag{1.10.}$$

This equation can be inserted in eqn (1.7.) and we obtain model function $\Delta T = f(m_B)$ (the complete function is not listed here for its large size). ΔT can be treated as dependent value y, m_B as independent value x. m_* and m_R are constants. The model function have two parameters K_d and M_B , which can be optimized as a best match of model function on experimental data set $[x, y]$ (i.e. $[m_B, \Delta T]$) using least square method. The data analysis can be done by MS-EXCEL using "Solver" tool for example. The parameters K_d and M_B can be obtained if the experimental error was low. The more experimental cooling curves we obtain, the better. Otherwise, we use tabulated value of molar mass M_B for data analysis. Thus the dimerization constant should be obtained with better accuracy.

✍ **REPORT:** Systematic deviation of the digital thermometer, tabulated molar mass of benzoic acid M_B. **Table 1:** for each experiment: weight of benzene m_R as used, weight of benzoic acid m_B, experimental benzene/solution freezing point temperature *T*, mean benzene freezing-point temperature T_0 or solution freezing-point temperature T_f. **Table 2:** for each solution experiment: weight of benzene m_R in solution, weight of benzoic acid m_B, freezing-point depression ΔT, apparent molar mass of benzoic acid in benzene calculated by means eqn (xxxxxx1.3). **Common graph 1:** cooling curves of pure benzene liquids and benzoic acid solutions.

UNDER THE METHOD I: **TABLE 3**: for each solution experiment: unknowns n_1 and n_d, dimerization constant K_d, coincidence interval of K_d. **Graph 2:** symbols of the experimental dependence ΔT on m_B.

UNDER THE METHOD II: **TABLE 3**: for each solution experiment: weight of benzoic acid m_B, experimental freezing-point depression ΔT, freezing-point depression given by model function after parameter optimization, least squares of the difference between experimental and theoretical freezing-points, sum of least squares, parameters M_B and K_d. **Graph 2:** symbols of experimental values $[x, y]$ and curve of model function $\Delta T = f(m_B)$ after optimisation.

Graph 3: the same as Graph 2 but add two limiting lines. First line for $K_d = 0$ (i.e no dimerization). The second line for $K_d = \infty$ (i.e dimer only in solution). Use union of eqns xxxx (1.1) and (1.2), suppose $m = m_B$.