Determination of Molecular Weight by Freezing Point Depression

Freezing point depression is a kind of colligative properties as treated in high school chemistry course. Normally used alcohol or mercury thermometer is not usually precise enough to obtain good data, but more precise one. Beckmann thermometer, which is often used for this purpose, is a kind of mercury thermometer which is extraordinarily precise within rather narrow temperature region. In the present experiment, freezing point depression of benzene solution of acetic acid is measured with the use of Beckmann thermometer. From the data obtained, molecular weight of acetic acid is calculated to discuss dissolving state of acetic acid in benzene.

Theoretical Background

Phase diagram of binary mixture and freezing point depression

Figure 1 shows a schematic drawing of phase diagram of binary mixture between A and B insoluble in crystalline phases. T_A and T_B are temperatures of fusion for pure components A and B, respectively. Two curves, called as liquidus, T_A-E-T_B indicate low temperature limit of homogeneous liquid (shaded region) and two phases coexist below those lines (white region). At the point of E, no liquid is able to exist, *i.e.* whole sample crystallize separately. In the temperature region below E, mixture of two crystalline phases of A and B.

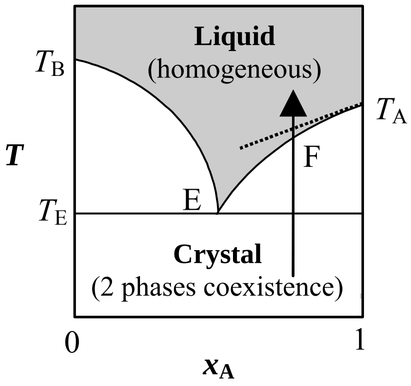

Fig. 1. Phase diagram of binary system with a eutectic point

Now, heating up the crystalline mixture of A and B at concentration rich in A compare with E, *e.g.* indicated by the arrow. At the temperature T_E, the mixture start to fuse, liquid phase of concentration E appears. Further heating causes the increase of liquid along with dissolution of A into liquid. The concentration of liquid changes along the curve E to F. At the temperature of F, at which the arrow crosses with curve E-A, remained crystal A fuses completely getting into homogeneous liquid mixture. For the concentration of E, whole crystalline mixture melts into liquid of the same concentration at point E. Mixture of concentration E is called as eutectic mixture, and fusion temperature T_E, the eutectic point of the system, at which fusion starts at any concentration.

Freezing point depression is regarded as the phenomenon at the infinite dilution limit in the vicinity of T_A for A. The freezing point depression coefficient is the initial slope of liquidus, *i.e.* the slope of dotted line in Fig. 1. Also, the fact that the freezing point depression is a kind of colligative properties indicates that the initial slope of liquidus, denoted by dotted line in Fig. 1, is independent of solute.

Thermodynamics of Freezing Point Depression — Derivation of 'Colligativity' —

Now let's consider a dilute solution consist of solvent A and solute B, indicated as the region near $x_A \approx 1$. As indicated above, solute B is soluble in liquid A and insoluble in crystalline A. Around the freezing point of pure A, you will find two-phase coexistence, between pure crystalline A and liquid solution of B in A, over a finite temperature region.

From the equilibrium condition, chemical potential of A has to be equal between solid and liquid phases.

$$\mu_{\mathrm{A}} = \mu_{\mathrm{A}}^{\mathrm{liq}} + RT \ln x_{\mathrm{A}}, \tag{1}$$

where μ_{A} and $\mu_{\mathrm{A}}^{\mathrm{liq}}$ are chemical potentials of A in solution and pure liquid, x_{A} the mole fraction of A, and R the gas constant. This is equal to the chemical potential $\mu_{\mathrm{A}}^{\mathrm{cr}}$ of crystalline A, that is,

$$\mu_{\mathrm{A}}^{\mathrm{cr}} = \mu_{\mathrm{A}} = \mu_{\mathrm{A}}^{\mathrm{liq}} + RT \ln x_{\mathrm{A}}, \tag{2}$$

since liquid A is insoluble in solid A. This is rewritten as

$$\mu_{\mathrm{A}}^{\mathrm{liq}} - \mu_{\mathrm{A}}^{\mathrm{cr}} = -RT \ln x_{\mathrm{A}} \tag{3}$$

Left hand of eq. (3) indicates chemical potential difference between liquid and crystal in pure A. Tailor expansion of chemical potentials around the fusion point of pure A (T=T_{fus}–δT) gives following formulas.

$$\mu_{\mathrm{A}}^{\mathrm{liq}}(T_{\mathrm{fus}} - \delta T) = \mu_{\mathrm{A}}^{\mathrm{liq}}(T_{\mathrm{fus}}) - \left[\frac{\partial \mu_{\mathrm{A}}^{\mathrm{liq}}}{\partial T}\right]_{T=T_{\mathrm{fus}}} \delta T + O(\delta T^2) \tag{4}$$

$$\mu_{\mathrm{A}}^{\mathrm{cr}}(T_{\mathrm{fus}} - \delta T) = \mu_{\mathrm{A}}^{\mathrm{cr}}(T_{\mathrm{fus}}) - \left[\frac{\partial \mu_{\mathrm{A}}^{\mathrm{cr}}}{\partial T}\right]_{T=T_{\mathrm{fus}}} \delta T + O(\delta T^2) \tag{5}$$

Subtracting eq. (5) from eq. (4) neglecting terms of orders higher than δT^2,

$$\begin{aligned}
&\mu_{\mathrm{A}}^{\mathrm{liq}}(T_{\mathrm{fus}} - \delta T) - \mu_{\mathrm{A}}^{\mathrm{cr}}(T_{\mathrm{fus}} - \delta T) \\
&= \left(\mu_{\mathrm{A}}^{\mathrm{liq}}(T_{\mathrm{fus}}) - \left[\frac{\partial \mu_{\mathrm{A}}^{\mathrm{liq}}}{\partial T}\right]_{T=T_{\mathrm{fus}}} \delta T\right) - \left(\mu_{\mathrm{A}}^{\mathrm{cr}}(T_{\mathrm{fus}}) - \left[\frac{\partial \mu_{\mathrm{A}}^{\mathrm{cr}}}{\partial T}\right]_{T=T_{\mathrm{fus}}} \delta T\right) \\
&= \left(\mu_{\mathrm{A}}^{\mathrm{liq}}(T_{\mathrm{fus}}) - \mu_{\mathrm{A}}^{\mathrm{cr}}(T_{\mathrm{fus}})\right) - \left(\left[\frac{\partial \mu_{\mathrm{A}}^{\mathrm{liq}}}{\partial T}\right]_{T=T_{\mathrm{fus}}} - \left[\frac{\partial \mu_{\mathrm{A}}^{\mathrm{cr}}}{\partial T}\right]_{T=T_{\mathrm{fus}}}\right) \delta T .
\end{aligned} \tag{6}$$

The first term gives chemical potential difference between liquid and crystal of pure solvent at melting point (or equilibrium freezing point), which has to be zero according to the equilibrium condition. Since the partial derivatives of chemical potentials in terms of temperature is minus of entropy, the bracket of the second term equals to the entropy difference between liquid and crystal at melting point, that is the entropy of fusion $\Delta_{\mathrm{fus}}S$. On the other hand, when the solution is diluted enough, that is, $x_B = 1 - x_A << 1$, $\ln x_A$ is approximated as $\ln x_A = \ln(1 - x_B) \cong x_B$. Also assuming the degree of freezing point depression is small compared to the fusion point, equilibrium fusion point T is approximated as $T = T_{\mathrm{fus}} - \delta T \cong T_{\mathrm{fus}}$. Equation (3) becomes

$$\Delta_{\mathrm{fus}} S \delta T \cong R T_{\mathrm{fus}} x_{\mathrm{B}} . \tag{7}$$

Finally, the degree of freezing point depression is given by

$$\delta T \cong \frac{R T_{\mathrm{fus}}}{\Delta_{\mathrm{fus}} S} x_{\mathrm{B}} = \frac{R T_{\mathrm{fus}}^2}{\Delta_{\mathrm{fus}} H} x_{\mathrm{B}} . \tag{8}$$

Here, $\Delta_{\mathrm{fus}}H$ is molar enthalpy of fusion (minus of latent heat of fusion). Equation (8) indicates that degree of freezing point depression δT is proportional to the mole fraction of solute at the limit of infinite dilution, and its proportionality coefficient $K = R T_{\mathrm{fus}}^2 / \Delta_{\mathrm{fus}} H$. It should be noted that the *freezing point depression constant K is determined by only the properties of pure solvent A*. This is why we consider the freezing point depression is one of colligative properties. In dilute solutions, mole fraction x_B is approximately proportional to molality m_B such as $x_{\mathrm{B}} \cong m_{\mathrm{B}} M_{\mathrm{A}} / 1000$ with molar mass M_A. Using m_B and molecular weight of B M_B, eq. (8) is expressed as

$$\delta T \cong \left(\frac{M_{\mathrm{A}}}{1000} \frac{R T_{\mathrm{fus}}^2}{\Delta_{\mathrm{fus}} H} \right) m_{\mathrm{B}} = \left(\frac{M_{\mathrm{A}}}{1000} \frac{R T_{\mathrm{fus}}^2}{\Delta_{\mathrm{fus}} H} \right) \frac{m}{M_{\mathrm{B}}} , \tag{9}$$

where m is the mass of solute B dissolved in 1 kg of solvent A. Defining K_f as $K_{\mathrm{f}} = M_{\mathrm{A}} R T_{\mathrm{fus}}^2 / (1000 \Delta_{\mathrm{fus}} H)$, degree of freezing point depression is given by

$$\delta T \cong \frac{K_{\mathrm{f}}}{M_{\mathrm{B}}} m . \tag{10}$$

K_f called as *molar freezing point depression constant* is a constant dependent on solvent.

Using a solvent whose K_f value is known, measurement of freezing point of solution as a function of concentration gives molecular weight of solute B from eq. (10). Figure 2 shows the schematic representation of analysis for this. The plot of experimental values of freezing point gives a straight line with negative slope $-K_f / M_B$, and cross section of

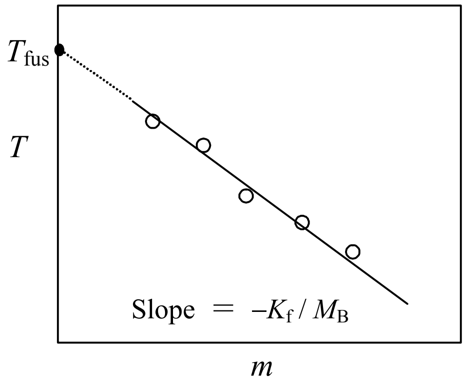

Fig. 2. Experimental determination of molecular weight of solute B by means of freezing point depression.

the line against m = 0 gives the fusion of pure solvent A. Molar freezing point depression constants of some typical solvents are listed in Table 1.

Table 1 Molal freezing point depression of several solvents.

Solvent	T_{fus} / °C	K_{f} / K kg mol^{-1}
benzene	5.455	5.065
water	0	1.858
sulfric acid	10.36	6.12
acetic acid	16.635	3.9
cyclohexane	6.2	20.2
t-butyl alcohol	25.1	8.37

Usage of Beckmann Thermometer

Beckmann thermometer is a mercury thermometer in order to measure the temperature with high resolution in very narrow temperature region of about 6 °C. To change the accessible temperature region, the amount of mercury is possible to adjust by upper mercury storage. Before starting the measurement, volume of mercury should be adjusted to the volume suitable for the objective temperature region. Accordingly, the scale drawn on the thermometer is merely the relative value, not the absolute one. Exactly speaking, the scale should be converted by measuring the temperature of a body simultaneously with standard thermometer far more reliable than Beckmann thermometer (CALIBRATION of Thermometer). The accuracy and precision of Beckmann thermometer depends on those of thermometer used for the calibration.

The method to adjust the amount of mercury of Beckmann thermometer is as follows:

1. Move the mercury in the upper storage to the top of measuring part.
2. Put the lower storage into the water at high temperature enough to connect the top of mercury to the one at upper storage.
3. Put the lower storage into the water at the temperature a few degrees higher than the objective temperature region and leave it for a while to reach the temperature equilibrium.
4. Direct the thermometer upside down rapidly to disconnect the mercury at the top of measuring part. When the mercury is not able to disconnect, shake up and down for a few times carefully.
5. Redirect the thermometer to normal paying attention to move the upper mercury to curved portion.

For the present case, measuring the temperature around fusion of benzene (5.533 °C), adjust the temperature at 7 or 8 °C. Calibration of thermometer for the absolute value is usually done by any of followings:

1. Measure the temperature of the same body simultaneously with well-calibrated another thermometer.
2. Put the lower mercury storage into some well-purified substance that shows first order phase transition (such as fusion) in the same temperature region, and calibrate in the cooling direction at the equilibrium transition temperature.

The latter method is not possible to calibrate the precision of scale interval but is only absolute temperature. In the present temperature region, since the deviation of scale interval is very small, we adopt the calibration at freezing point of benzene.

Experimental Protocol

Preparation of samples

Weigh the weighing bottle, and put 0.60, 0.90, 1.20, 1.50 and 1.80 g of acetic acid into each bottle. Add small amount of benzene, dissolve acetic acid completely, and pour the solution into an Erlenmeyer flask weighed ahead. Wash the bottle with benzene for several times, and put the benzene into the flask. Weighing the flask on a chemical balance, add the benzene until total mass of solution is about 50 g. Weigh the mass of flask stopping at the top to determine the mass of solution. You can adjust the total mass depending on the mass of acetic acid to keep the separation of concentration being constant although not necessarily.

- When you weigh the mass of volatile liquid precisely, you should use a container with a cap to avoid vaporization.
- You can open the top when you adjust the amount or adding liquid, but it is necessary to stop at the top when you read.
- In the present measurement, as the concentration can be determined in 3 digits only, you do not have to correct buoyancy error.

Measurement

Combining two glass tubes to set up double tube, put 30 – 40 cm^3 of sample solution into inner tube and setup the Beckmann thermometer. Check that the lower mercury storage is completely sunk in the solution. The interstitial air relaxes the radical temperature change, and lessens the temperature distribution in sample solution. Put the double tube into ice bath and fix it with clump. Check the level of ice is high enough to cover the level of solution. Figure 3 shows the schematic drawing of the system.

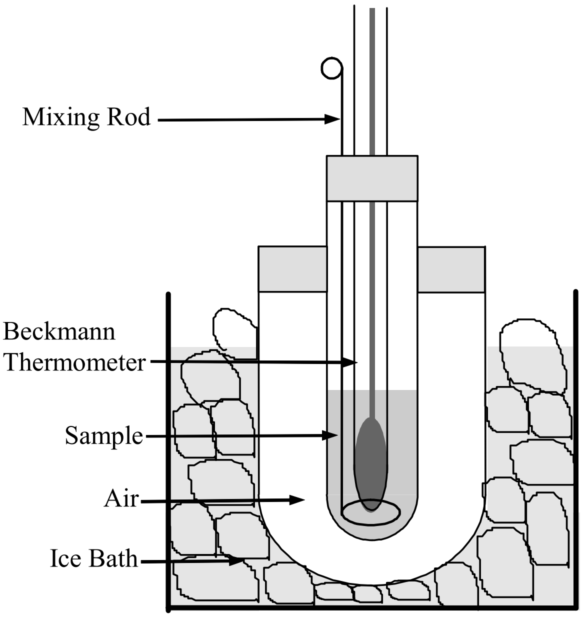

Fig. 3. Experimental set-up for measuring freezing point.

Moving the mixing rod up and down, homogenize the solution temperature and read the Beckmann thermometer. Record the readings every 15 − 30 s as you read. Note that the reading increases with the temperature going down.

Figure 4 shows the time dependence of typical measurement schematically. The temperature decreases down below the freezing point (B in Fig. 4). Even cooled down below the freezing point, sample still in liquid phase for a while (B to C), which is known as supercooling phenomenon. Crystallization suddenly happens at C, and the temperature of sample rises rapidly (C to D). Then the sample temperature starts lowering at D and keeps lowering gradually (E). After that, there exists a plateau at eutectic temperature (F). As soon as the crystallization completed, the temperature starts going down again (G).

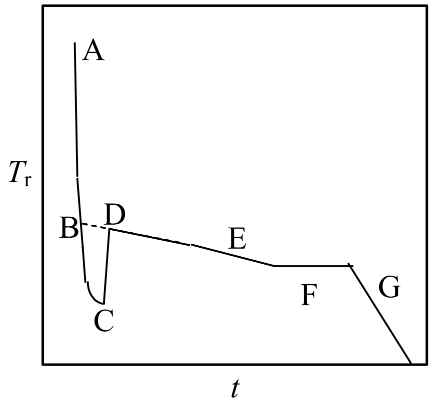

Fig. 4. Schematic drawing of time dependence of sample temperature.

Between A and C, read the temperature as frequent as possible, *e.g.* 10 to 15 sec. After the crystallization started (at C) and the temperature goes up rapidly (at D), the reading interval can be stretched to 30 to 60 sec. It is easier to make pairs to share the jobs; one read the temperature, the other measure the time, record the value and plot the graph of reading against time. You don't have to keep on measuring until the Plato (F) and/or temperature lowering (G) are observed. Taking the data for 7 − 10 min in D to E region would be enough in order to extrapolate properly as broken line shown in Fig. 4 (D to B). Measure for benzene at first, and then acetic acid solution.

Data Analysis

Calibration of Beckmann thermometer

For the calibration of scale of the Beckmann thermometer, cooling curve of benzene is used. As shown in Fig. 4, extrapolate the line D–E, and get the crossing with A–C curve. This process gives hypothetical equilibrium point B (which never detected by any experiments in principle) that appears infinitesimal amount of crystal. The temperature of this point is defined as the melting point of pure benzene 5.455 °C. The relation between actual temperature θ and the reading of Beckmann thermometer Θ is given by $\theta/{}^\circ\mathrm{C} = 5.455 + \Theta_\mathrm{B} - \Theta$, where Θ_B is the reading of Beckmann thermometer at B for pure benzene.

- If each pair carries out the experiment independently, this process is not always necessary. This is because molecular weight of solute depends only on the freezing temperature difference between pure solvent and solution as seen in Eq. (10) and accuracy of data is not significant at all for the precision of molecular weight. It is important, however, to share the data with each other, because same measurement is required to calibrate.

- Calibration process is significant to determine some physical quantity precisely. You would experience via this experiment that any kinds of scale are defined artificially in practice.
- The absolute temperature scale (or thermodynamic temperature scale more exactly) is defined as using Carnot cycle with ideal gas working medium, such that the origin of the scale as the temperature at which the efficiency of Carnot cycle becomes 0. This indicates the only thermometer measurable of the absolute temperature is *ideal gas thermometer*. Unfortunately, however, since the ideal gas doesn't exist on earth, absolute temperature is never possible to measure in principle. Defining the other point of temperature, normal ice point is used in reality, you can define the interval of temperature scale K. The ice point at normal pressure (0 °C) is defined as 273.15. With this definition, the scale interval is almost identical to that of Celsius temperature scale. This is the *Kelvin* temperature expressing the absolute temperature used with unit K.

  Experimentally used unit of K is defined as ITS90 (International Temperature Scale 1990) defined in 1990. ITS90 defines how the thermometer should be corrected using freezing points of standard substances. This indicates the interval of temperature scale is not perfectly uniform, depending on temperature regions. So this scale is completely different definition from that of absolute temperature and should be distinguished in principle, but gives very close value in practice (the deviation is within ±10 mK). So it is normally no problem to regard ITS90 as absolute temperature.

Evaluation of Molecular Weight of Acetic Acid

Draw the graph showing temperature vs. time, and get the reading of Beckmann thermometer of B point for every sample solution. Convert the reading to Celsius temperature scale using calibration function. Plot the values of freezing point as a function of molality, obtain the slope of the plot assuming linear relationship. You can obtain the molecular weight from the slope as denoted in Fig. 2. To evaluate the slope of the plot, apply linear least squares method. If the graph is systematically curved, you can use the 2nd order regression function and extrapolate to the infinite dilution and evaluate using the initial slope at $m = 0$.

Compare the molecular weight you get with that calculated from atomic weights. Discuss the difference from the viewpoint of microscopic structure state of acetic acid in benzene.