

Laboratory Work in Chemistry I

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Aims of the class:

Learning measurement methods for obtaining precise data of basic physico-chemical quantities of substance and studying how the microscopic features of substance affect on the macroscopic properties.

Schedule:

- 11/ 5. Viscosity of ethanol aqueous solution.
- 11/12. Molecular weight measurement of acetic acid by means of freezing point depression of benzene.
- 11/19. Raman spectra of aqueous solutions of phosphorous acid and phosphate salts.
- 12/ 3. Presentation.

Viscosity of ethanol–water mixture

Viscosity is the physical quantity specifying the flowing properties of liquids. Viscosity itself is physically expressed as transportation phenomenon of momentum in flowing liquids. Viscosity is important properties for engineering such that designing chemical plants requires precise information about the viscosity of solutions. Also, dynamic properties are sometimes influenced by the static microscopic structures in solutions. Here, we would like to employ the Ubbelohde type viscometer to determine the viscosity of ethanol aqueous solutions.

Theoretical Background

In flowing liquid, the each small domains have flowing velocity dependent on position x . Such velocity distribution depends on viscosity. Consider two planes 1 and 2 in a liquid under stationary flow, e.g. viscosity distribution are independent of time, flowing at constant velocity $v_0 + v$ and v_0 . Each has the same area A , and the separation between planes l . There exists the force F between the two planes resulting from the shear viscosity. The force F is given by

$$F = \eta \frac{Av}{l}, \tag{1}$$

where the proportional coefficient η is called as viscosity of the liquid. In a liquid of large viscosity, the sheer between planes causes the strong force between two planes which result in small velocity gradient and thus small spacial distribution of velocity. According to the equation (1), viscosity has the dimension of $[MT^{-1}L^{-1}]$, which gives the unit of $[Pa\ s]$ in MKS system, and $[P]$ or $[Poise]$ in cgs system. These units convert as $1\ Pa\ s = 10\ P$.

Consider the flowing down of liquid in the capillary which has cylindrical and concentric velocity distribution under stationary state. Applying the equation (1) to the small planes in liquid vertically flowing down in the capillary, using the cylindrical symmetry of velocity distribution, and integrating from the center to the side of capillary where the velocity is assumed to be zero. The flowing rate u is obtained as

$$u = \frac{\pi (P_1 - P_2)R^4}{8 \eta L}. \tag{2}$$

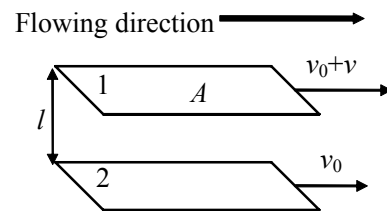


Fig. 1. Forces between two planes in flowing liquids.

Here, P_1 and P_2 are pressures at entrance and exit of capillary, R and L the radius and length of capillary. Thus the P_1 and P_2 are constant, flowing rate u is inversely proportional to the viscosity η . Period t during which a given volume of liquid flows down through the capillary is given by

$$t = \frac{V}{u} = \frac{8}{\pi} \frac{\eta L}{(P_1 - P_2) R^4}, \quad (3)$$

indicating the inversely proportion of t against η .

When the radius and length of capillary are given, absolute value of viscosity is obtained via eq. (3) by determining the flowing rate. In practice, as it is not able to determine these quantities with enough precision, η is obtained as relative value η_r against that of standard substance η_0 (usually water), as follows:

$$\eta_r = \frac{\eta}{\eta_0}. \quad (4)$$

Here, relative viscosity η_r is dimensionless quantity. On the other hand, since the origin of pressure difference in eq. (3) in the actual experiment is gravity working on liquid itself, pressure difference between entrance and exit has to be proportional to sample density. Therefore, relative viscosity is

$$\eta_r = \frac{\rho t}{\rho_0 t_0}, \quad (5)$$

where ρ and ρ_0 are densities of sample and reference liquids, t and t_0 the flowing time of sample and reference liquids measured with the same viscometer.

Experimental Protocol

Preparation of samples

Prepare the solutions of mole fraction x of 0, 10, 12, 15, 17, 20, 22, 25, 27, 30, 35, 40, 50, 60, 80 and 100%. You can prepare them as precise as possible with the following procedure.

Put proper amount of water into weighed 50 ml Erlenmeyer flask (mass m_0) and weigh with the chemical balance (reading of m_1). Obtain the amount of water you put and calculate the amount and mass of ethanol to be added (m_2^{ex})

$$m_2^{\text{ex}} = m_1 + \frac{(m_1 - m_0)}{M_{\text{water}}} \times \frac{x}{1-x} \times M_{\text{ethanol}}. \quad (6)$$

Here, x is mole fraction of ethanol you intend to prepare, M_{water} and M_{ethanol} are the molar masses (or molecular weight) of water and ethanol, respectively. Add ethanol weighing on a balance and try to make to the reading as close to m_2^{ex} as possible. When you make the reading close enough for you

to satisfy, stop at the top of the Erlenmeyer and weigh precisely (m_2).

- You will need about 10 ml of sample solution for the measurement and another ~10 ml of sample for rinsing viscometer when you changed your sample. So you should make at least 30 ml of solutions.
- In this experiment, what is important is not to prepare samples of exact concentration value but to know the precise concentration you made. In this sense, you do not have to make 20.00 mole % for example, but is 21 mole% also fine. However, the one who is good at experiment would try to make 20.0 or 20.00 mole %. This is because he will get more beautiful data and graph, especially for experiments changing concentration finely like this.

Measurement

Put the sample of 5 to 10 ml into well-cleaned (rinsed with sample for a couple of times) Ubbelohde type viscometer and put the three fold legged glass with rubber tubes and fix it vertically in the thermostat controlled at 30 °C. Check that all portion of touch with sample solution locate under the surface and leave as it is for about 15 min in order to equilibrate the temperature of sample with thermostat.

Stop at the by-passing tube with stop cock, pinch the rubber tube at the top of capillary with your fingers to lift up the liquid meniscus above the upper marked line. Remove the stop cock and your fingers from the tube, start running down and start the stopwatch at the time when the meniscus passes through the upper marked line. Stop the stopwatch at the time when the meniscus passes through the lower marked line. Record the time of duration. Repeat this for a couple of times to check the reliability. If the running duration comes long for each time, it might not be enough for temperature equilibration. Repeat the measurements until the time comes almost constant.

- When you lift up the liquid, you would sometimes find a bubble at the bottom of capillary. This may cause the resistance of flow resulting in the error. Try to remove the bubble, by flicking the capillary, before you start measurement.

Start your measurement from distilled water, and then two ethanol solutions with different concentration. When you change your sample, discard the sample, rinse the viscometer with new sample for a couple of time and then put the new sample of about 10 ml. Fix the viscometer at the thermostat and continue the experiments.

Data Analysis

Evaluation of viscosity

Calculate the density ρ of each solution at 30 °C from the table by interpolating linearly the neighboring values. Literature values for density are obtained from the links of Takeda's web site (<http://ostwald.naruto-u.ac.jp/~takeda/takedae.htm>) related to the class. Also obtain the density of water ρ_{water} and viscosity of water η_{water} in the same manner.

- You can get more precise values by interpolating with the 2nd order polynomial function

determined with the least squares method. Do you know any other method of interpolation?

Check it up.

By means of eqs. (4) and (5), viscosity of the sample is obtained from the running duration of water and the sample as follows.

$$\eta = \eta_{\text{water}} \frac{\rho t}{\rho_{\text{water}} t_{\text{water}}}. \quad (7)$$

Presenting results and discussion

Plot the viscosity values against the mole fraction of ethanol. Do not forget to plot your friends' data along as well as yours. Discuss the reason why the viscosity of aqueous ethanol solution shows a maximum at a concentration take the effect of *hydrophobic interaction* between water molecules and ethyl groups into account.

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.

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

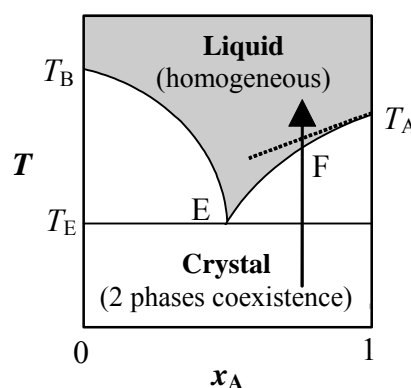


Fig. 1. Phase diagram of binary system with a eutectic point

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.

$$\mu_A = \mu_A^{\text{liq}} + RT \ln x_A, \quad (1)$$

where μ_A and μ_A^{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 μ_A^{cr} of crystalline A, that is,

$$\mu_A^{\text{cr}} = \mu_A = \mu_A^{\text{liq}} + RT \ln x_A, \quad (2)$$

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

$$\mu_A^{\text{liq}} - \mu_A^{\text{cr}} = -RT \ln x_A \quad (3)$$

Left hand of eq. (3) indicates chemical potential difference between liquid and crystal in pure A. Taylor expansion of chemical potentials around the fusion point of pure A ($T=T_{\text{fus}}-\delta T$) gives following formulas.

$$\mu_A^{\text{liq}}(T_{\text{fus}} - \delta T) = \mu_A^{\text{liq}}(T_{\text{fus}}) - \left[\frac{\partial \mu_A^{\text{liq}}}{\partial T} \right]_{T=T_{\text{fus}}} \delta T + O(\delta T^2) \quad (4)$$

$$\mu_A^{\text{cr}}(T_{\text{fus}} - \delta T) = \mu_A^{\text{cr}}(T_{\text{fus}}) - \left[\frac{\partial \mu_A^{\text{cr}}}{\partial T} \right]_{T=T_{\text{fus}}} \delta T + O(\delta T^2) \quad (5)$$

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

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

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 $\Delta_{\text{fus}}S$. On the other hand, when the solution is diluted enough, that is, $x_B = 1 - x_A \ll 1$, $\ln x_A$ 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 $T = T_{\text{fus}} - \delta T \cong T_{\text{fus}}$. Equation (3) becomes

$$\Delta_{\text{fus}}S \delta T \cong RT_{\text{fus}} x_B. \quad (7)$$

Finally, the degree of freezing point depression is given by

$$\delta T \cong \frac{RT_{\text{fus}}}{\Delta_{\text{fus}}S} x_B = \frac{RT_{\text{fus}}^2}{\Delta_{\text{fus}}H} x_B. \quad (8)$$

Here, $\Delta_{\text{fus}}H$ 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 $K = RT_{\text{fus}}^2 / \Delta_{\text{fus}}H$. 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 $x_B \cong m_B M_A / 1000$ with molar mass M_A . Using m_B and molecular weight of B M_B , eq. (8) is expressed as

$$\delta T \cong \left(\frac{M_A}{1000} \frac{RT_{\text{fus}}^2}{\Delta_{\text{fus}}H} \right) m_B = \left(\frac{M_A}{1000} \frac{RT_{\text{fus}}^2}{\Delta_{\text{fus}}H} \right) \frac{m}{M_B}, \quad (9)$$

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

$$\delta T \cong \frac{K_f}{M_B} m. \quad (10)$$

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

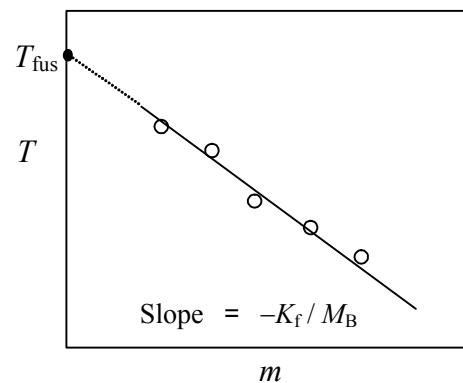


Fig. 2. Experimental determination of molecular weight of solute B by means of freezing point depression.

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	$T_{\text{fus}} / ^\circ\text{C}$	$K_f / \text{K kg mol}^{-1}$
benzene	5.455	5.065
water	0	1.858
sulfuric acid	10.36	6.12
acetic acid	16.635	3.9
cyclohexane	6.2	20.2
<i>t</i> -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 cm³ 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.

Moving the mixing rod up and down, homogenize the solution temperature and read the Beckmann thermometer. Record the readings

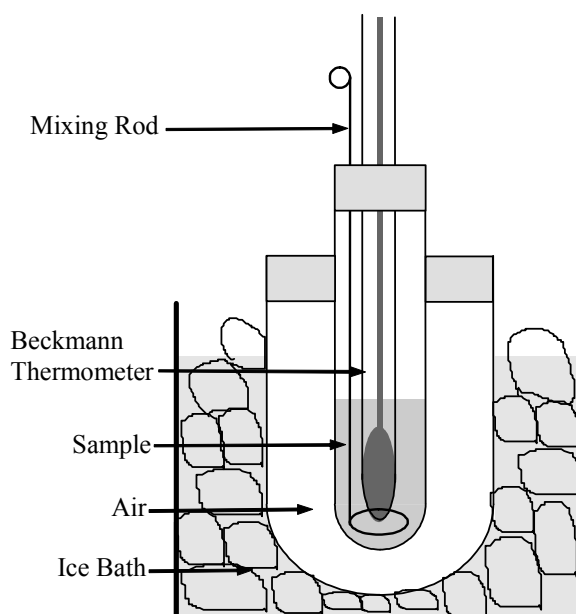


Fig. 3. Experimental set-up for measuring freezing point.

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.

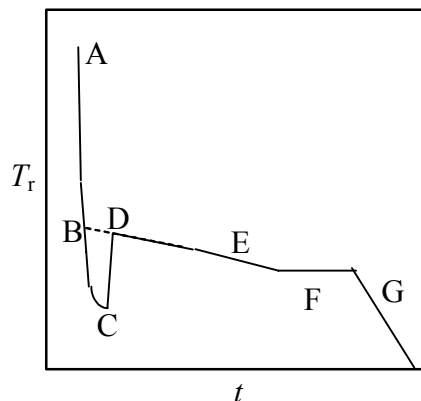


Fig. 4. Schematic drawing of time dependence of sample temperature.

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).

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 $\theta / ^\circ\text{C} = 5.455 + \Theta_B - \Theta$, 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.

Raman Spectra of Phosphorous Acid and Alkali Phosphate Aqueous Solutions

Raman spectroscopic method is an inelastic light scattering spectroscopy applicable to detect molecular and lattice vibrations. Although Raman effect which Raman spectroscopy is based on discovered in 1920's, the study about this phenomenon was not carried out actively at first. Since 1970's, however, when the laser technique was established, it was widely applied to various field of physics, chemistry and biology. In this theme, we measure the Raman spectra of aqueous solutions of phosphorous acid and phosphate salts. A basic qualitative and quantitative technique is suggested to check the contents of chemical species in solutions.

Theoretical Background

Raman Effect and Raman Spectroscopy

Once light is thrown to a substance, a part of light is absorbed or scattered. The scattered light comes out with different direction from that of the incident. A typical geometry of measurement is to detect the light directed at the angle 90° with incident. In some cases, the angle is taken as 180° , which is called as *back scattering geometry*. The most general data acquisition is to detect the scattered light as a function of scattering direction.

We consider the situation that light with frequency ν_0 is thrown to the sample, which is called as *excitation light*. Most of the light is scattered with the same frequency as that of incidence. This is called as Rayleigh scattering, which is the origin of blue color of sky. When the polarizability of the sample is oscillating with frequency ν , the scattered light includes components of frequency changed for ν from ν_0 . This phenomenon is called as Raman effect. In

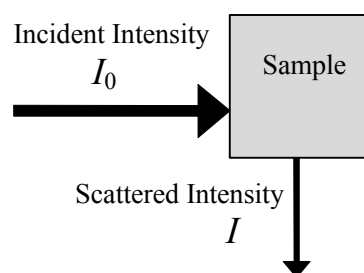


Fig. 1. Geometrical configuration for Raman spectroscopy.

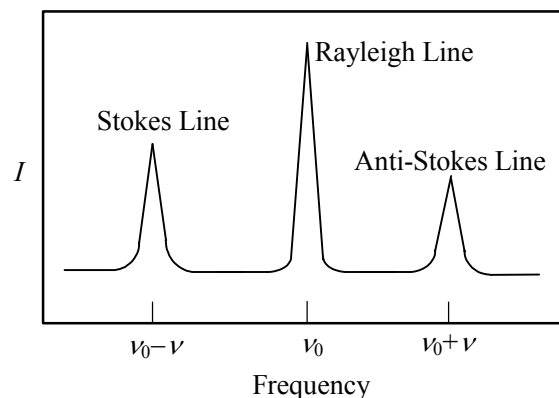


Fig. 2. Schematic Raman spectrum from a sample with intrinsic frequency ν .

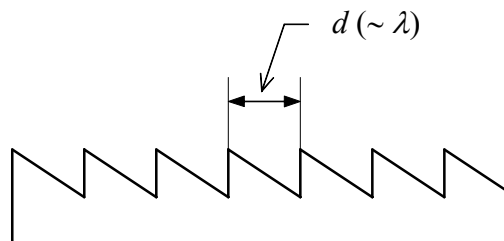


Fig. 3. Conceptual draw of the surface of grating. λ : wave length of excitation light.

Fig. 2, an intensity distribution of scattered light is shown schematically. Not only Rayleigh Line due to the component of Rayleigh scattering, but also two kinds of components due to Raman effect are observed.

The Raman components of frequency $\nu_0 - \nu$ and $\nu_0 + \nu$ are called as Stokes and anti-Stokes lines, respectively. The change in frequency indicates the change in energy of photon indicating *inelastic* scattering. Stokes component is the photon scattered by the molecule excited from ground to the first excited state in vibration and vice versa. Stokes component is usually more intense than anti-Stokes component because population of molecules in the ground state, the origin of Stokes component, is higher than that in the excited state, the origin of anti-Stokes. In low frequency region (below about 100 cm^{-1}), because the population changes with temperature, the intensities of Stokes and anti-Stokes components change simultaneously.

In the instrument at our university, scattered light is monochromated by grating, a device worked with high density parallel lines on the surface of mirror, functioning as a diffraction lattice. The magnified shape at the surface is drawn in Fig. 3 schematically. The light incident on the grating surface refracted to specific direction satisfying the Bragg's condition. By rotating the grating, monochromated light is introduced into the detector selectively.

Intensity of scattered light monochromated by grating is measured by *photoelectron multiplier* with photon counter. Photoelectron multiplier amplifies weak light as follows.

1. A photon come into the glass bulb ionizes the remained gas.
2. The ionized atoms are accelerated by high voltage to hit the cathode to produce multiple electrons.
3. Released electrons are accelerated by high voltage to hit the next cathode.
4. Repeating the above processes for several times, released electrons enormously increased to give a detectable current pulse.

Current pulse produced by photoelectron multiplier is counted by pulse counter. The count observed in a given period is proportional to the number of photon come into the glass bulb in the period, which is exactly regarded as intensity of light.

Molecular Vibration and Raman Spectroscopy

A multiatomic molecules consist of N atoms has 3 translational, 3 rotational and $3N-6$ vibrational (for linear molecules, 3 rotational and $3N-5$ vibrational) modes. Each molecular vibrational mode is properly considered as a harmonic oscillator, treated by quantum mechanically.

Consider an oscillator consist of 2 atoms with masses m_1 and m_2 , assuming one dimensional harmonic potential as the interatomic interaction:

$$V = \frac{1}{2} kx^2, \quad (1)$$

where x , k and V are the coordinate along bond, force constant and interatomic potential. Schrödinger equation for one dimensional harmonic oscillator,

$$\left(-\frac{\hbar^2}{8\pi^2\mu} \frac{d^2}{dx^2} + \frac{1}{2}kx^2 \right) \Psi_n = E_n \Psi_n . \quad (2)$$

Here $\mu = m_1 m_2 / (m_1 + m_2)$ is the reduced mass. Left hand of equation (2) is the differential operator to the function Ψ_n and the right hand the constant E_n multiplied to the same function Ψ_n . This is called as eigenvalue equation, which has plural solutions indexed by integer n . Solution Ψ_n is called as *eigenfunction* for *eigenvalue* E_n . The significance of Schrödinger equation is that the eigenvalue E_n obtained as solution corresponds to the energy of the system, for which E_n and Ψ_n are called as energy eigenvalue and wave function, respectively. The energy eigenvalue E_n obtained from Eq. (2) is the energy of harmonic oscillator. The energy eigenvalue for (2) is obtained as

$$E_n = h\nu \left(n + \frac{1}{2} \right) \quad (n = 0, 1, 2, \dots) . \quad (3)$$

The non-negative integer n is called as vibrational quantum number, and because of the integer n , states of discrete energies are allowed only. The other character of energy eigenvalue of harmonic oscillator is that the energy level separation is constant $h\nu$ for any two adjacent states. In general, the real oscillator has energy level splitting decreases in higher excitation states.

Selection Rule and Raman Active Modes

Even when vibrational modes of vibrating at frequency of ν exist, you do not always observe the Raman scattering from the modes at ν . For it depends on the probabilities of light absorption and scattering if the mode is observed or not. Qualitatively, probabilities of absorption and scattering of light are defined by two factors; i.e. transition moment and symmetry of corresponding normal modes.

Transition probability from the n^{th} state to m^{th} is proportional to transition moment $I_{n,m}$:

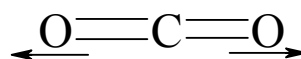
$$I_{n,m} = \int \Psi_n(\mathbf{r}) \mathbf{r} \Psi_m(\mathbf{r}) d\mathbf{r} . \quad (4)$$

Integration is carried out all over the space coordinate \mathbf{r} defined. For harmonic oscillators, $I_{n,m}$ is nonzero only when $m = n \pm 1$. This indicates that the transition between adjacent states ($\Delta n = \pm 1$) are the only allowed transition but not others. This is the selection rule for vibrational spectra. Transition mode with finite value of $I_{n,m}$ is referred as *allowed* transition, and the one with zero value as *forbidden* transition. This selection rule is hold for both infrared and Raman spectra.

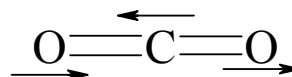
- In an actual molecule, this selection rule is not exactly hold. This is because the molecular vibration slightly deviates from harmonic oscillation. Anharmonicity causes the incompleteness of symmetry in wave function. Therefore, transitions with $\Delta n = +2$ or more

(multiple vibration) are observed though very weak.

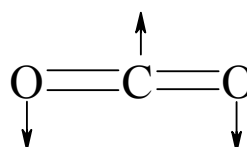
On the other hand, even though both IR and Raman spectra are vibrational spectroscopy, they do not always provide identical information. The difference is because of the different modes of detection of radiation, *i.e.* absorption and scattering of radiation for IR and Raman spectroscopes, respectively. IR absorption phenomenon is observed only for the vibrational mode with change in dipole moment of molecule, whereas Raman scattering for the one with change in molecular polarizability. This difference is clear for linear molecules. For example, a carbon dioxide (CO_2) molecule has 4 vibrational modes; *i.e.* symmetric (ν_1 ; 1340 cm^{-1}) and Antisymmetric (ν_2 ; 2349 cm^{-1}) stretching and two fold degenerated bending (667 cm^{-1}) modes. The ones by which molecular dipole moment changes are ν_2 and bending modes, which are IR active, and the one by which the molecular polarizability changes is ν_1 only, which is Raman active.



Symmetric stretching (Raman active; 1340 cm^{-1})



Antisymmetric stretching (IR active; 2349 cm^{-1})



Bending (IR active; 667 cm^{-1})

- For linear molecules, IR active mode is Raman inactive, and vice versa. This exclusiveness in IR and Raman activity is held for linear molecules only. In general molecule, most of modes are active in both methods.
- The IR activity of molecular vibration is closely related to the greenhouse effect which became famous for the relation with environmental problem. As N_2 and O_2 molecules, which are the principal component of atmosphere, has just one vibrational mode of IR inactive, IR radiation is not absorbed but transmitted through these molecules. On the other hand, molecules which has IR active modes like CO_2 , absorbs IR radiation, which should be released to space, to store the energy inside the atmosphere. This is the mechanism of greenhouse effect of CO_2 . There are, of course, various kinds of molecules which has the IR active modes. In general, molecules with no IR active modes are just homonuclear-diatomic and monatomic molecules only. However, the most components of atmospheric gas are such ones and most significant origin of greenhouse effect is provided by CO_2 molecules, which exist with highest concentration in the air among greenhouse gases. This is why the reduction of CO_2 release becomes the global issue.

Experimental Protocol

Preparation of materials

Prepare the sample solutions as shown in Table 1. Use well-boiled water for the solvent to remove CO₂ gas dissolved in the distilled water. Put the samples into 10 ml sample tubes and close with caps tightly to avoid evaporation of solvent.

Measurement of Raman Spectra

Set up the spectrometer according to the manual. Turn on power source, flow the cooling water, start the spectrometer and laser source, and then turn the computer on and start the measurement program. Laser source and photoelectron multiplier needs to wait for about 1 hour for stabilization.

Set the sample tube at the stand in the sample chamber. Adjust the sample as close to detector lens as possible and the position of mirror

of incident laser light. Set the measurement conditions using the **Config** mode of measurement program. Typical set suitable for the present measurements are summarized in Table 2. Remain as it was the values of the items not included in Table 2.

- Never change other items because changing some of them may cause trouble.

Enter **Meas** mode, press **From** key to move the wave number of spectrometer to set value for **From** in **Config** mode. After the movement of diffraction mirror finished, press **Start** key to start measurement. In the present condition, since measurement is carried out at 1500 points at gate time of 1 second, it takes at least 25 min (= 1500 s). Including the movement of mirror, it takes 35 – 40 min. After finished the measurement, save the data to go ahead the next. Repeat the above processes for every sample.

Table 1. Samples to be prepared

Sample 1	0.25 mol dm ⁻³ NaClO ₄	0.5 mol dm ⁻³ H ₃ PO ₄
Sample 2		0.5 mol dm ⁻³ NaH ₂ PO ₄
Sample 3		0.5 mol dm ⁻³ Na ₂ HPO ₄
Sample 4		0.5 mol dm ⁻³ Na ₃ PO ₄
Sample 5	0.25 mol dm ⁻³ NaNO ₃	0.5 mol dm ⁻³ H ₃ PO ₄
Sample 6		0.5 mol dm ⁻³ NaH ₂ PO ₄
Sample 7		0.5 mol dm ⁻³ Na ₂ HPO ₄
Sample 8		0.5 mol dm ⁻³ Na ₃ PO ₄
Sample 9	0.25mol dm ⁻³ NaClO ₄ + 0.25mol dm ⁻³ NaNO ₃	
Sample 10	distilled water	

Table 2. Measurement conditions

Item	Value
From	4000 (cm ⁻¹)
To	1000 (cm ⁻¹)
Cycle	1
Scan Increment	2 (cm ⁻¹)
Delay	1 (sec)
Date	Date of measurement
Experimentalist	Name of experimentalist

Data Analysis

Drawing Raman spectra

Draw the graph of Raman scattering intensity against Raman shift (frequency shift) in cm^{-1} . Since the counting number of photon counter, which is the vertical axis of Raman spectra, depends on the fluctuation of laser power, sample position, direction of sample cell and so on, the absolute value has little significance. Spectrum you got here is output in different unit. This is why the graph of Raman spectra is shown in arbitrary unit (a.u. or A.U.) for each measurement. To compare the spectra of different measurement, you have to reduce the spectra in any way. In the present experiment, you have doped the sodium perchlorate or sodium nitrate at 0.25 mol dm^{-3} . The peak originated from these species can be used for the normalization. Comparison of peak intensity of samples which include perchlorate and nitrate ion requires normalization with the peak intensity using the peak areas for both ions are included simultaneously.

Interpretation of Raman spectra

Comparing the spectrum of water with that of each solution, assign the vibrational band from water molecule. Also, assign the band from phosphate ions to each vibrational mode. Refer to the literature table of the group vibrational frequency on assignment.