

Boiling point – Composition Diagram of a Binary System (Exp. 8.)

Important concepts

Chemical potential, composition dependence of the chemical potential, conditions of equilibrium in thermodynamic systems, phase rule, phase diagrams of one-component and two-component systems, ideal mixtures, real mixtures, Raoult's law, enthalpy of mixing, entropy of mixing, boiling point diagram, azeotrope, refractive index.

Objective

In this experiment you measure the refractive indexes and the boiling points of different chloroform-acetone mixtures of known composition. You will plot then a refractive index vs. mole fraction diagram (calibration curve) for the determination of the unknown mole fractions of samples taken from the boiling mixtures (both from the liquid phase and the vapor phase). With the help of this curve you will plot the boiling points against the corresponding compositions for the liquidus and vapor curves. From the characteristic features of such curves one can get information about distillation of mixtures and can also decide whether the system forms an azeotrope or not.

Background

According to the phase rule, the number of components (C) and the number of phases (P) in an equilibrium thermodynamic system are connected to the thermodynamic degrees of freedom (F):

$$F = C - P + 2 \quad (1)$$

A two-component system, the components of which are present both in the liquid and the vapor phase in a certain temperature interval, has two degrees of freedom. For instance, at constant external pressure there are two variables, **temperature** and **composition**, which may change without the formation or extinction of a phase.

The composition is usually given by the mole fraction (x_A)

$$x_A = \frac{n_A}{n_A + n_B} \quad (2)$$

where n_A and n_B are the numbers of moles of components A and B.

The volume fraction, φ_A ,

$$\varphi_A = \frac{V_A}{V_A + V_B} \quad (3)$$

can only be applied for ideal mixtures. In all other cases the final volume of the mixture has to be determined. The vapor pressure, p , of a boiling mixture is equal to the external pressure, maintained at a fixed value. The total pressure above a liquid phase can be related to the composition of the mixture according to Raoult's Law:

$$p = p_A + p_B + \dots + p_Z = x_A p_A^* + x_B p_B^* + \dots + x_Z p_Z^* \quad (4)$$

where p_A^*, \dots, p_Z^* mean the vapor pressures of the corresponding components in pure state and p_A, \dots, p_Z are the partial pressures of the same components over the given mixture. For a binary system, when $x_A + x_B = 1$, one can get a linear dependence between the composition of the liquid and the total vapor pressure:

$$p = p_B^* + x_A(p_A^* - p_B^*) \quad (5)$$

When $p_A^* = p_B^*$, there is no difference between the composition of the liquid and its vapor. If $p_A^* > p_B^*$, the relation between the mole fraction of A in the vapor, y_A , and its molar fraction in the liquid phase, x_A , is the same, i.e., $y_A > x_A$, independently of the liquid composition. The partial pressures can be expressed:

$$p_A = y_A p \quad \text{and} \quad p_B = y_B p \quad (6)$$

Combining Eqs. 5 and 6 we get nonlinear dependence between p and y :

$$p = \frac{p_A^* p_B^*}{p_A^* - y_A (p_A^* - p_B^*)} \quad (7)$$

It follows from Eqs. 5 and 7 that even if the molar enthalpy of mixing is zero the total pressure does not depend linearly on the mole fraction of the vapor phase. At constant external pressure the boiling point is a nonlinear function of both x and y (Fig.1.).

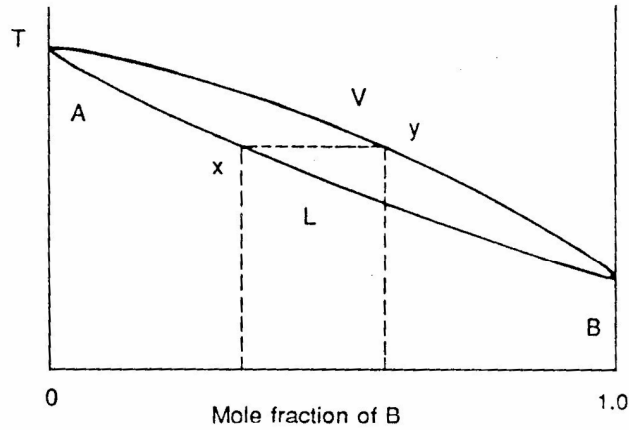


Fig.1.
Boiling point - composition diagram

In some cases i.e., when there is an interaction between the components A and B, a maximum or minimum may occur in the liquidus (L) and vapor (V) curves. This maximum or minimum appears at a definite composition and that mixture is called an **azeotrope** (see Fig.2.). The toluene- CCl_4 mixtures behave approximately ideally and their L and V curves resemble the ones in Fig.1, while the chloroform-acetone system has an azeotrope, similar to Fig. 2.

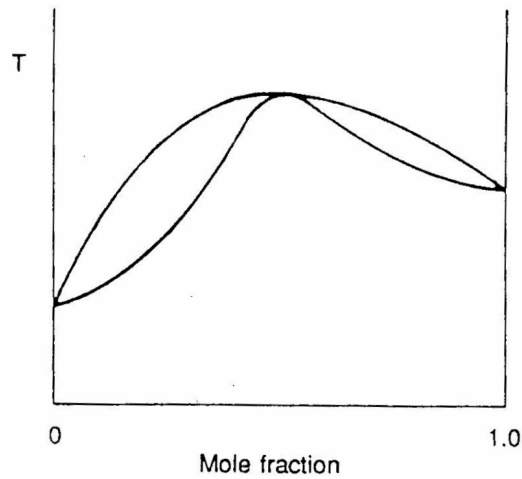


Fig.2.
A boiling point - composition diagram for a mixture having a maximum boiling point azeotrope.

Apparatus

1. A three-necked flask provided with a thermometer, a condenser, and a liquid sampler (Fig.3).
2. An Abbe refractometer (the description is given in the Supplement).

Procedure

1. Prepare a series of chloroform-acetone mixtures in a 25 cm³ volumetric flask with the volume ratio given in the following table. It is easy to prepare the mixtures measuring the exact volumes of both components by the provided burettes. Determine (measure) the mass of both components in the volumetric flask. Mix the solutions well by vigorously shaking the volumetric flasks. When the mixtures are homogeneous you can proceed to the next step.

sample	1.	2.	3.	4.	5.
chloroform (cm ³)	0	7	15	19	25
acetone (cm ³)	25	18	10	6	0

2. In order to construct the calibration curve you should measure the refractive index of your mixtures just prepared. Switch on the light source of the Abbe refractometer. Open the prism (rotate the illuminating prism downward and away from you). Introduce a couple of drops of your sample with an eyedropper onto the horizontally positioned illuminating prism and close it tight to the refracting prism. A thin liquid layer will be formed between the two prisms. Rotate the prism until the boundary between the dark and light fields appears in the field of view. If necessary, adjust the mirror to obtain the best illumination possible. By the aid of the Amici prism eliminate the color fringe and sharpen the boundary. Set the light/dark boundary exactly to the intersection of the cross hairs in the field of view. Read the value of refractive index with an accuracy of ± 0.0005 . Make measurements with the pure components of your mixtures. Report the temperature of the measurements too.

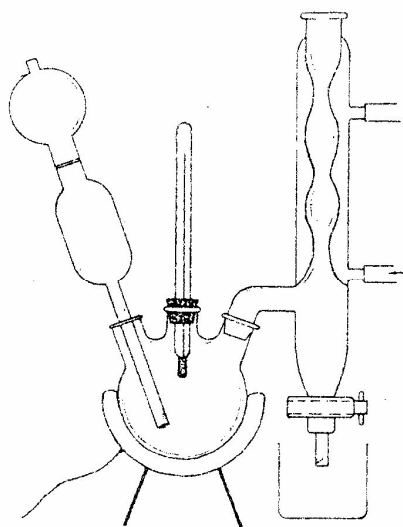


Fig.3.
Distillation apparatus for the determination of the boiling point of a liquid

3. Fill the whole liquid into a three necked flask, supply it with a condenser, thermometer, and liquid sampler. Set the bulb of the thermometer at the neck level of the condenser. Apply gentle heating of the heating mantle and boil the mixture. Be careful, and avoid the overheating of the

liquid. Note that it takes at least 10 minutes to establish the equilibrium temperature after the mixtures started boiling. Observe and record the equilibrium temperature of the boiling mixture carefully. Take a sample from the vapor by turning down the condenser and collecting a few drops into a vial. Take a sample from the liquid sampler. Close each vial carefully by a stopper. Having done this you must pour the rest of the measured mixture, into a waste collector. Repeat step 3 for the whole series of mixtures and for both pure solvents. When you have a two necked flask only, after collecting the vapor sample you must change the thermometer for the liquid sampler to take the liquid sample.

4. In order to construct your liquidus and vapor curves, measure the refractive index for all vapor and liquid samples (see step 2.).

Graphs, results, data to be reported

1. The data for boiling points, the refractive indexes for the calibration curve and the boiling mixtures (vapor phase and liquid phase samples, as well).
2. The mole fraction of the chloroform in the calibrating mixtures. The mole fraction data should be calculated from the mass measurements.
3. The refractive index vs. mole fraction of chloroform (calibration curve). The calibration curve is not a straight line. Fit a parabola ($n = a x^2 + b x + c$) to the calibration points. From the calibration curve, read down the mole fraction composition of the vapor phase and liquid phase samples.
4. Construct the liquidus and vapor curves. Prepare a graph showing the boiling point of the mixtures as the function of the mole fraction of chloroform in the vapor phase (vapor curve) *and* as the function of the mole fraction of chloroform in the liquid phase (liquidus curve).

Data for molar fraction calculation

Molar mass of chloroform:	119,38 g mol ⁻¹
Density of chloroform:	1,479 g/cm ³
Molar mass of acetone:	58,08 g mol ⁻¹
Density of acetone:	0,793 g/cm ³

Supplement

Operating the Abbe refractometer

The refractive index for a liquid or isotropic solid is the ratio of phase velocity of light in vacuum to that in the medium. For a phase boundary it can be defined as a ratio of the sine of the angle φ_v , that a ray of light makes with a normal to the surface in vacuum to the of the corresponding angle φ_m in the medium:

$$n = \frac{c_v}{c_m} = \frac{\sin \varphi_v}{\sin \varphi_m}$$

The Abbe refractometer operates on the concept of critical angle $\varphi_{crit.}$. In this case $\varphi_v = 90^\circ$ and so

$$n = \frac{1}{\sin \varphi_{crit}}$$

A thin layer of liquid is placed on the rectangle prism with refractive index n_g and $n_g > n_s$, where n_s is the refractive index of our sample. If we follow different angles of incidence (Fig.4.), from the normal to the glancing incidence, i , we find that the angle of refraction increases. At the glancing incidence we obtain the critical angle of refraction, which is the last angle that lets light through in the prism. Any higher angle of refraction will provide a dark field. The whole prism surface is illuminated with glancing incident light and a telescope collects all the refracted rays with the same φ into one line in the focal plane. Thus a sharp boundary is seen in the telescope between the dark field and the bright illuminated field by a **monochromatic** light source. If white light is used as a

source the critical boundary is sharpened by the use of compensator (two Amici prisms) and the refractive index obtained is that for the sodium D light (Fig.5.).

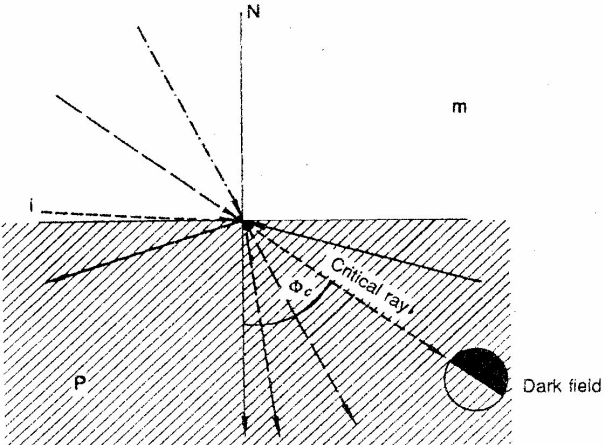


Fig.4. Critical angle of refraction.

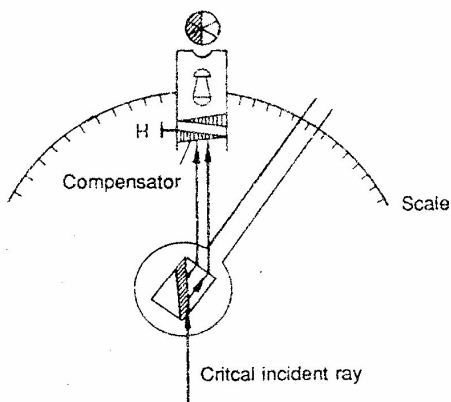


Fig.5. Schematic diagram of an Abbé refractometer.

Sample questions and answers for the minimum level tests (MLT).

MLT is devoted for practicing and preparing to labs at home, and its topical list covers the problems we discuss at the beginning of the lab.

MLT Q.and A:

Q1. The definition of mole fraction, calculation of mole fraction from volume, density and molar mass data.

A1. The molar mass of a two component system, A and B can be given as,

$$x_A = \frac{n_A}{n_A + n_B} \text{ where } n_A \text{ is the number of moles for component A, and it can be also defined}$$

as: $n_A = m_A/M_A$. The mass of component A is obtained from the density ρ_A and the volume V_A added to the mixture by

$$m_A = V_A \cdot \rho_A.$$

By combining equations given above we get

$$x_A = \frac{\frac{V_A \rho_A}{M_A}}{\frac{V_A \rho_A}{M_A} + \frac{V_B \rho_B}{M_B}} = \frac{1}{1 + \frac{M_A V_B \rho_B}{M_B V_A \rho_A}}$$

Q2. Boiling point.

A2. The temperature at which the vapor pressure of boiling liquid is identical to the external pressure is called boiling point at that temperature.

Q3. Raoult's law.

A3. Raoult's law refers to ideal liquid mixtures. The enthalpy of mixing is zero for ideal liquid mixtures. The total pressure p at constant temperature is a function of molar fractions in the liquid and vapour pressure of pure components at that temperature. For a binary mixture:

$$p = x_A p_A^* + x_B p_B^*$$

Q4. Azotropic composition.

A4. On a boiling point composition diagram for non-ideal mixtures extremum (minimum or maximum) can be observed. At azeotropic composition the liquid and vapor compositions are identical. The liquid pair having azeotropic composition can not be separated by simple distillation process.

Q5. From figure given below, find

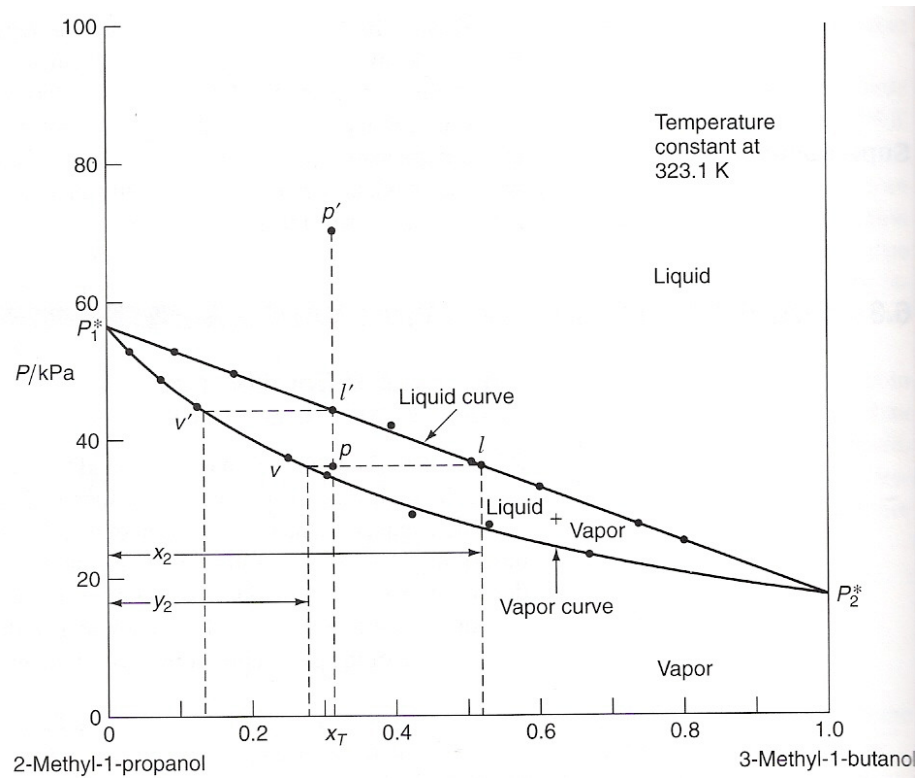
- whether 2-methyl-1-propanol (component A) and 3-methyl-1-butanol (component B) form ideal mixture or not,
- which of them is the more volatile component,
- which of them has higher boiling point,
- which of them has greater molar fraction in vapor phase.

A5a. Component A and B do form ideal mixture that is indicated the straight line of vapor pressure vs. liquid composition. The system obeys Raoult's law.

A5b. Component A is the more volatile component. In its pure state it shows higher vapor pressure than that of component B.

A5c. Component B, the less volatile component has higher boiling point. Its vapor pressure reaches external pressure, e.g. 1 bar, at higher temperature than component A.

A5d. Horizontal lines like $V - l$ or $V' - l'$ are constant pressure lines. Their intersections are vapor and liquid compositions belonging to phase equilibria, so that can be compared. All the horizontal lines between vapor pressures of pure components show that component A has higher molar fraction in vapor phase than liquid phase.



Q6. Could you give the equation for the straight line in figure of vapor pressure vs. composition diagram?

A6. Answer it for yourself!