250-mL Erlenmeyer flasks; 10-mL graduated cylinder; three 250-mL beakers; burette clamp and stand; large rubber bulb for pipetting; wash bottle.

Constant-temperature bath set at 25°C; bath clamps for holding 500-mL Erlenmeyer flasks; pure CCl_4; acetone for rinsing; large carboy for waste liquids. Solutions: 0.08 *M* solution of I_2 in CCl_4 (300 mL); 0.04 *M* I_2 in CCl_4 (250 mL); 0.02 *M* I_2 in CCl_4 (100 mL); 0.15 *M* KI solution (800 mL); 0.03 *M* KI solution (400 mL); 0.1 *M* $Na_2S_2O_3$ solution (500 mL); 0.01 *M* $Na_2S_2O_3$ solution (100 mL); approximately 0.1 *M* KI solution (500 mL); Thyodene or 0.2 percent soluble starch solution, containing a trace of HgI_2 as preservative (50 mL). See the *warning* given above about the storage and handling of CCl_4.

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VIII Phase Behavior

Experiments 3

EXPERIMENTS

13. Vapor Pressure of a Pure Liquid
14. Binary Liquid–Vapor Phase Diagram
15. Ordering in Nematic Liquid Crystals
16. Liquid–Vapor Coexistence Curve and the Critical Point

EXPERIMENT 13

Vapor Pressure of a Pure Liquid

When a pure liquid is placed in an evacuated bulb, molecules will leave the liquid phase and enter the gas phase until the pressure of the vapor in the bulb reaches a definite value, which is determined by the nature of the liquid and its temperature. This pressure is called the vapor pressure of the liquid at a given temperature. The equilibrium vapor pressure is independent of the quantity of liquid and vapor present, as long as both phases exist in equilibrium with each other at the specified temperature. As the temperature is increased, the vapor pressure also increases up to the critical point, at which the two-phase system becomes a homogeneous, one-phase fluid.

If the pressure above the liquid is maintained at a fixed value (say by having the bulb containing the liquid open to the atmosphere), then the liquid may be heated up to a temperature at which the vapor pressure is equal to the external pressure. At this point vaporization will occur by the formation of bubbles in the interior of the liquid as well as at the surface; this is the boiling point of the liquid at the specified external pressure. Clearly the temperature of the boiling point is a function of the external pressure; in fact, about a given *T, p* point, the variation of the boiling point with external pressure is the inverse of the variation of the vapor pressure with temperature.

In this experiment the variation of vapor pressure with temperature will be measured and used to determine the molar heat of vaporization.

We are concerned here with the equilibrium between a pure liquid and its vapor:

$$X(l) = X(g) \qquad (p, T) \tag{1}$$

It can be shown thermodynamically[1] that a definite relationship exists between the values of p and T at equilibrium, as given by

$$\frac{dp}{dT} = \frac{\Delta S}{\Delta V} \tag{2}$$

In Eq. (2) dp and dT refer to infinitesimal changes in p and T for an equilibrium system composed of a pure substance with both phases always present; ΔS and ΔV refer to the change in S and V when one phase transforms to the other at constant p and T. Since the change in state (1) is isothermal and ΔG is zero, ΔS may be replaced by $\Delta H/T$. The result is

$$\frac{dp}{dT} = \frac{\Delta H}{T\Delta V} \tag{3}$$

Equation (2) or (3) is known as the *Clapeyron equation*. It is an exact expression that may be applied to phase equilibria of all kinds, although it has been presented here in terms of the one-component liquid–vapor case. Since the heat of vaporization ΔH_v is positive and ΔV is positive for vaporization, it is seen immediately that the vapor pressure must increase with increasing temperature.

For the case of vapor–liquid equilibria in the range of vapor pressures less than 1 atm, one may assume that the molar volume of the liquid $\tilde{V}_l$ is negligible in comparison with that of the gas $\tilde{V}_g$, so that $\Delta\tilde{V} = \tilde{V}_g$. This assumption is very good in the low-pressure region, since $\tilde{V}_l$ is usually only a few tenths of a percent of $\tilde{V}_g$. Thus we obtain

$$\frac{dp}{dT} = \frac{\Delta\tilde{H}_v}{T\tilde{V}_g} \tag{4}$$

Since $d \ln p = dp/p$ and $d(1/T) = -dT/T^2$, we can rewrite Eq. (4) in the form

$$\frac{d\ln p}{d(1/T)} = -\frac{\Delta\tilde{H}_v}{R}\frac{RT}{p\tilde{V}_g} = -\frac{\Delta\tilde{H}_v}{RZ} \tag{5}$$

where we have introduced the *compressibility factor* Z for the vapor:

$$Z = \frac{p\tilde{V}_g}{RT} \tag{6}$$

Equation (5) is a convenient form of the Clapeyron equation. We can see that, *if* the vapor were a perfect gas ($Z \equiv 1$) and $\Delta\tilde{H}_v$ were independent of temperature, then a plot of $\ln p$ versus $1/T$ would be a straight line, the slope of which would determine $\Delta\tilde{H}_v$. Indeed, for many liquids, $\ln p$ is almost a linear function of $1/T$, which implies at least that $\Delta\tilde{H}_v/Z$ is almost constant.

Let us now consider the question of gas imperfections, i.e., the behavior of Z as a function of temperature for the saturated vapor. It is difficult to carry out p–V–T measurements on gases close to condensation and such data are scarce, but data are available for water[2] and theoretical extrapolations[3] have been made for the vapor of "normal" liquids based on data obtained at higher temperatures. Figure 1 shows the variation of the compressibility factor Z for a saturated vapor as a function of temperature in the

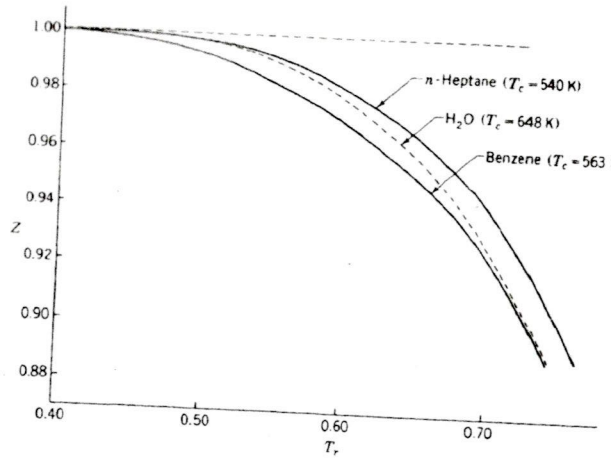

FIGURE 1
The compressibility factor Z of saturated vapor as a function of reduced temperature T_r for water, benzene, and n-heptane.

case of water and two normal liquids, benzene and n-heptane. For the temperature axis, a "reduced" temperature T_r is used; $T_r = T/T_c$, where T_c is the critical temperature. This has the effect of almost superimposing the curves of many different substances; indeed, by the law of corresponding states, such curves would be exactly superimposed. In general it is clear that Z decreases as the temperature increases. Water, owing to its high critical temperature, is a reasonably ideal gas even at 100°C, where Z equals 0.986. But n-heptane at its 1-atm boiling point of 98°C has a value of Z equal to 0.95 and is relatively nonideal. For many substances, sizable gas imperfections are present even at pressures below 1 atm.

Next we must consider the variation of $\Delta\tilde{H}_v$ with temperature. For a change in state such as Eq. (1),

$$\Delta H_{T_2} = \Delta H_{T_1} + \int_{T_1}^{T_2} \Delta C_p \, dT + \int_{p_1}^{p_2} \left(\frac{\partial \Delta H}{\partial p}\right)_T dp \tag{7}$$

Since $(\partial H_g/\partial p)_T$ is zero for a perfect gas and very small for most real gases and $(\partial H_l/\partial p)_T$ is always very small for liquids, it is possible to neglect the final term and approximate Eq. (7) by

$$\Delta H_{T_2} \simeq \Delta H_{T_1} + \overline{\Delta C_p}(T_2 - T_1) \tag{8}$$

where $\overline{\Delta C_p}$ is the average value over the temperature interval. For $\Delta\tilde{H}_v$ to be independent of temperature, the average value of ΔC_p must be very close to zero, which is generally not true. Heat capacities for water, benzene, and n-heptane are given in Table 1 as typical examples.[4,5] For n-heptane, the specific heat of both gas and liquid changes rapidly with temperature; use of average values will give only an order-of-magnitude result. In general the value of $\Delta\tilde{H}_v$ will decrease as the temperature increases.

Since both $\Delta\tilde{H}_v$ and Z decrease with increasing temperature, it is possible to see why $\Delta\tilde{H}_v/Z$ might be almost constant, yielding a nearly linear plot of $\ln p$ versus $1/T$.

TABLE 1

Compound	Temp. Range, °C	Average values, J K^{-1} mol^{-1} $\bar{C}_p(g)$	$\bar{C}_p(l)$	$\Delta\bar{C}_p$
Water	25–100	33.5	75	−41.5
Benzene	25–80	92	146	−54
n-Heptane	25–100	~197	~243	−46

METHODS

There are several experimental methods of measuring the vapor pressure as a function of temperature.[5] In the *gas-saturation method,* a known volume of an inert gas is bubbled slowly through the liquid, which is kept at a constant temperature in a thermostat. The vapor pressure is calculated from a determination of the amount of vapor contained in the outcoming gas or from the loss in weight of the liquid. A common *static method* makes use of an *isoteniscope,* a bulb with a short U tube attached. The liquid is placed in the bulb, and some liquid is placed in the U tube. When the liquid is boiled under reduced pressure, all air is swept out of the bulb. The isoteniscope is then placed in a thermostat. At a given temperature the external pressure is adjusted so that both arms of the U tube are at the same height. At this setting, the external pressure, which is equal to the pressure of the vapor in the isoteniscope, is measured with a pressure gauge. A common *dynamic method* is one in which the variation of the boiling point with external applied pressure is measured. The total pressure above the liquid can be varied and maintained at a given value by use of a large-volume ballast bulb; this pressure is then measured with a pressure gauge. The liquid to be studied is heated until boiling occurs, and the temperature of the refluxing vapor is measured in order to avoid any effects of superheating. The experimental procedure for both the isoteniscope method and a boiling-point method is given below.

EXPERIMENTAL

1 BOILING-POINT METHOD

The apparatus should be assembled as shown in Fig. 2. Use pressure tubing to connect the condenser and the pressure gauge to the ballast bulb. Fill the flask about one-third full with the liquid to be studied. A few carborundum boiling chips should be added to reduce "bumping." If a mercury thermometer is used, be sure that the thermometer scale is visible over a range of at least 50°C below the boiling point at 1 atm. Also, make sure that the thermometer bulb (or any other thermometer sensor) is positioned carefully so that the temperature of coexisting vapor and liquid is measured. Heating should be accomplished with an electrical heating mantle. Turn on the circulating water to the condenser before heating the liquid, and turn it off at the end of the experiment.

To make a reading, adjust the heating so as to attain steady boiling of the liquid, but avoid heating too strongly. When conditions appear to be steady (i.e., when pressure gauge and thermometer readings appear to be as constant as they can be maintained), record p and T values as nearly simultaneously as possible. The thermometer should be read to the nearest 0.1°C, and vapor should be condensing on and dripping from the thermometer to ensure that the equilibrium temperature is obtained. In reading the pressure gauge, estimate the pressure to the nearest 0.1 Torr. Record the ambient air temperature at the manometer several times during the run.

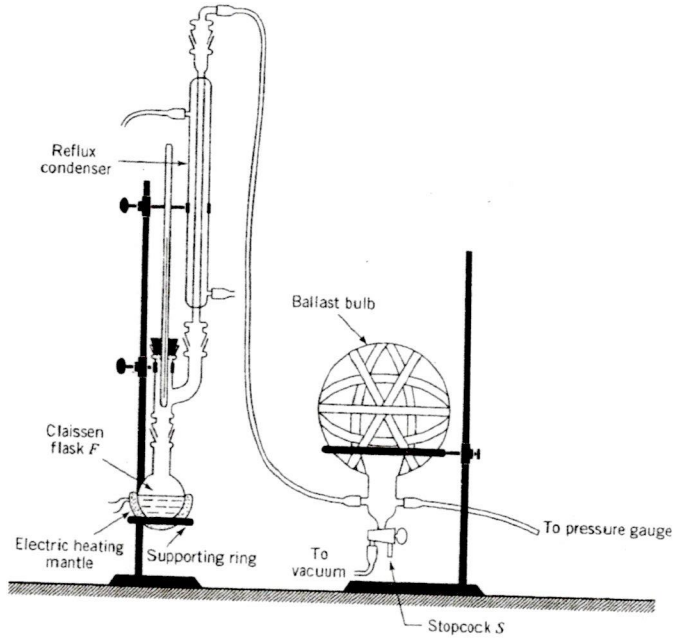

FIGURE 2
Boiling-point apparatus. The mercury thermometer can be replaced by a resistance thermometer or other direct-reading thermometric device.

To change the pressure in the system between measurements, first remove the heating mantle. After a short time, admit some air or remove some air by opening stopcock S for a few seconds. Be especially careful in removing air from the ballast bulb to avoid strong bumping of the hot liquid. Check the pressure. Repeat as often as necessary to attain the desired pressure, and then restore the heating mantle to its position under the flask.

Take readings at approximately the following pressures:

Pressure descending:	760, 600, 450, 350, 260, 200, 160, 130, 100, 80 Torr
Pressure ascending:	90, 110, 140, 180, 230, 300, 400, 520, 670 Torr

2 ISOTENISCOPE METHOD

In this technique much of the equipment shown in Fig. 2 is used, but the distilling flask and reflux condenser are replaced by an isoteniscope mounted in a glass thermostat as shown in Fig. 3. The water in the bath should be stirred vigorously (or circulated) to ensure thermal equilibrium. Place the liquid to be studied in the isoteniscope so that the bulb is about two-thirds full and there is no liquid in the U tube. Then place the isoteniscope in the thermostat (which should be at room temperature) and connect it to the ballast bulb and pressure gauge (which are assembled and connected as in Fig. 2).

Sweep the air out of the bulb by **cautiously** and slowly reducing the pressure in the ballast bulb until the liquid boils very gently. Continue pumping for about 4 min, but be careful to avoid evaporating too much of the liquid. Then tilt the isoteniscope so that some liquid from the bulb is transferred into the U tube. Carefully admit air to the ballast bulb through stopcock S until the levels of the liquid to both arms of the U tube are the same.

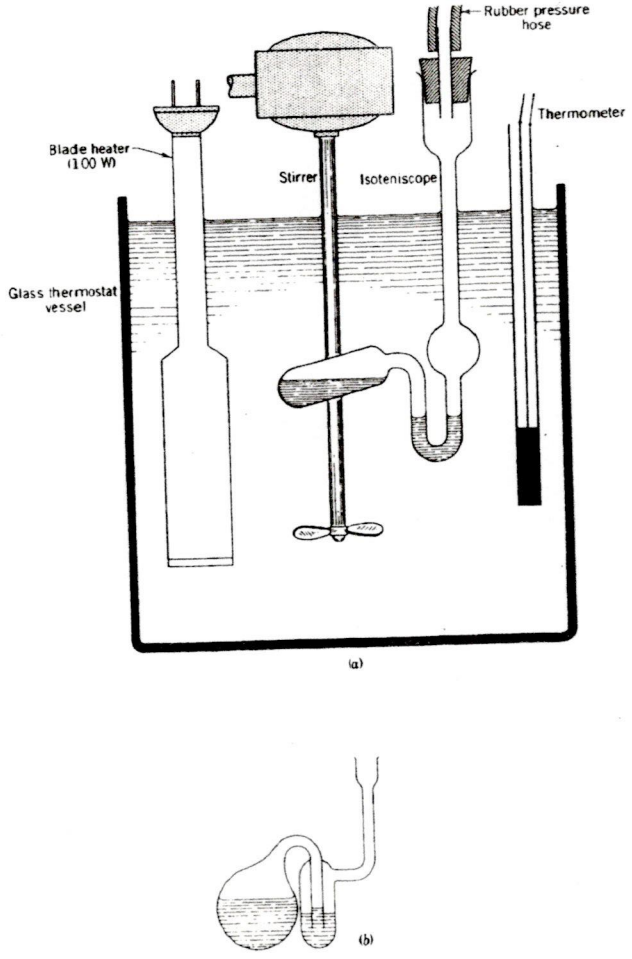

FIGURE 3
Isoteniscope. (*a*) Schematic diagram of the apparatus, which must be connected to the ballast bulb and manometer shown in Fig. 2. A temperature controller is also needed, or a commercial circulating-type temperature control bath can be used. (*b*) An alternate design for the isoteniscope. (An even more elaborate type of isoteniscope is described by Arm, Daeniker, and Schaller.[7])

Read and record the temperature and the pressure. To establish that all the air has been removed from the isoteniscope, **cautiously** reduce the pressure in the ballast bulb until a few bubbles are observed passing through the U-tube liquid. Then determine the equilibrium pressure reading. Repeat the above procedure, if necessary, until successive vapor-pressure readings are in good agreement.

Once the air is removed and a good pressure reading at room temperature is obtained, heat the thermostat bath to a new temperature about 5°C above room temperature. Keep the liquid levels in the U tube approximately equal at all times. When the bath temperature is steady at its new value, adjust the pressure in the ballast bulb until the levels in the U tube are equal and record both temperature and pressure.

Take readings at approximately 5°C intervals until the bath is at about 75°C, and then take readings at decreasing temperatures that are between the values obtained on heating. The thermometer shown in Fig. 3 can be a thermocouple or a digital resistance thermometer and must have a resolution of ±0.1°C or better.

CALCULATIONS

Correct all pressure readings to absolute values in Torr if calibration corrections are needed.

Convert all Celsius temperature readings to absolute temperatures T and plot ln p versus $1/T$. If there is no systematic curvature, draw the best straight line through the points. If there is noticeable curvature, draw a smooth curve through the points and also draw a straight line tangent to the curve at about the midpoint. Determine the slope of the straight line or tangent. From Eq. (5) it follows that this slope is $-\Delta\widetilde{H}_v/RZ$.

In addition to this graphical analysis, carry out a least-squares fit to your p-versus-T data. If visual inspection of your ln p-versus-$1/T$ plot does not indicate any systematic curvature, make a direct linear fit of ln p as a function of $1/T$. If systematic curvature is observed, make a least-squares fit of ln p with the empirical power-series form $a + b/T + c/T^2$. Then differentiate the resulting expression to obtain $\Delta\widetilde{H}_v/RZ$.

Report both the graphical and the least-squares values of $\Delta\widetilde{H}_v/Z$. Estimate the value of Z for the saturated vapor at the appropriate temperature from Fig. 1 and calculate $\Delta\widetilde{H}_v$ in J mol^{-1}. Report the value of the heat of vaporization and the vapor pressure for the liquid at the applicable temperature (corresponding to the midpoint of the range studied).

DISCUSSION

Using Fig. 1 and Eq. (8), estimate the variation in $\Delta\widetilde{H}_v/Z$ expected over the range of temperatures studied. Indicate clearly whether $\Delta\widetilde{H}_v/Z$ should increase or decrease with increasing temperature. Does your ln p-versus-$1/T$ plot show a curvature of correct sign?

Evaluate a quantitative uncertainty in your value of $\Delta\widetilde{H}_v/Z$ by the method of "limiting slopes" and compare this with the standard deviation obtained from the least-squares fit to your data. Comment on this uncertainty in relation to the variation with temperature calculated above. Discuss possible sources of systematic errors.

If water or some other compound with a simple molecular structure has been studied, it is possible to combine the entropy of vaporization, $\Delta\widetilde{S}_v = \Delta\widetilde{H}_v/T$, with the third-law calorimetric entropy of the liquid to obtain a thermodynamic value for the entropy of the vapor. The statistical mechanical value of $\widetilde{S}_g$ can be calculated using the known molar mass and the spectroscopic parameters for the rotation and vibration of the gas-phase molecule. A comparison of $\widetilde{S}_g$ (thermodynamic) with $\widetilde{S}_g$ (spectroscopic) provides a test of the validity of the third law of thermodynamics. The case of H_2O is particularly interesting, since ice has a nonzero residual entropy at 0 K due to frozen-in disorder in the proton positions.[8]

The pertinent thermodynamic data needed to carry out the calculation of $\widetilde{S}_g$(thermodynamic) for water vapor are as follows: $\widetilde{S}_l$(1 bar, 298.15 K) = 66.69 J K^{-1} mol^{-1}, which is the calorimetric value obtained by assuming (erroneously) that the third law is valid for ice;[9] $\widetilde{C}_p(l)$, which is essentially independent of temperature over the range 298–355 K, has the average value 75.36 J K^{-1} mol^{-1}.[5] You may neglect the effect of pressure on the value of the molar entropy of the liquid, an approximation that has very little effect on the calculated thermodynamic value of $\widetilde{S}_g(p_m, T_m)$ for $H_2O(g)$ at the vapor pressure

p_m associated with the temperature T_m at which $\Delta\tilde{H}_v$ has been determined. To facilitate comparison with the ideal gas statistical entropy discussed below, one can also make the simplifying assumption that corrections for the nonideality of water vapor at p_m, T_m have negligible effect on the value of $\tilde{S}_g(p_m, T_m)$.

The experimental data needed to calculate the statistical entropy $\tilde{S}_g$ are the rotational temperatures $\Theta_r = hcB/k$ and the vibrational temperatures $\Theta_v = h\nu/k = hc\tilde{\nu}/k$, where $B\,(= h/8\pi^2 Ic)$ and $\tilde{\nu}$ are frequencies in wavenumber units (cm^{-1}), and c is the speed of light in cm s^{-1}. Since the nonlinear H_2O molecule is an asymmetric top, the three principal moments of inertia are all different. The three rotational temperatures are $\Theta_A = 40.1$ K, $\Theta_B = 20.9$ K, and $\Theta_C = 13.4$ K.[10] There are three nondegenerate normal modes of vibration (one bend, one symmetric stretch, and one antisymmetric stretch), and the vibrational temperatures are $\Theta_{v1} = 2290$ K, $\Theta_{v2} = 5160$ K, and $\Theta_{v3} = 5360$ K.[10] The statistical-mechanical entropy of an ideal gas of *nonlinear* molecules is a sum of a translational contribution (the so-called Sackur-Tetrode term), a rotational contribution for three degrees of rotational freedom, and a vibrational contribution for $3N - 6$ vibrational degrees of freedom, where N is the number of atoms in the molecule. These three contributions are given by[10]

$$\tilde{S}(\text{trans}) = R[1.5 \ln M + 2.5 \ln T - \ln p - 1.15171] \tag{9}$$

where M is the molar mass in grams and p is the pressure in bar,

$$\tilde{S}(\text{rot}) = R\left[1.5 + \ln \frac{\pi^{1/2} T^{3/2}}{\sigma(\Theta_A \Theta_B \Theta_C)^{1/2}}\right] \tag{10}$$

where σ is the symmetry number[1,10] ($\sigma = 2$ for the case of H_2O), and

$$\tilde{S}(\text{vib}) = R\left\{\sum_i \left[\frac{\Theta_{vi}}{T} \frac{1}{(e^{\Theta_{vi}/T} - 1)} - \ln(1 - e^{\Theta_{vi}/T})\right]\right\} \tag{11}$$

with $i = 1$ to 3 in the case of H_2O.

Calculate a statistical/spectroscopic value of $\tilde{S}_g(p_m, T_m)$, compare this with your thermodynamic value, and report the discrepancy. For most substances, these two $\tilde{S}_g$ values agree and the third law is valid for the solid as T approaches 0 K. However, you should find that $\tilde{S}_g$(spectroscopic) $>$ $\tilde{S}_g$(thermodynamic) for H_2O, which means that ice does not have the perfect order at 0 K required by the third law. The explanation for this in terms of the disorder in the proton configurations in ice was first given by Pauling[11] and is well described by Davidson.[8]

SAFETY ISSUES

Method 1—The ballast bulb must be taped to prevent flying glass in the unlikely event of breakage. As always, safety glasses must be worn in the laboratory.

Method 2—None.

APPARATUS

Ballast bulb (5 L); pressure gauge; three long pieces of heavy-wall rubber pressure tubing. If the boiling-point method is used: distillation flask; appropriate thermometer to cover the desired range, with one-hole rubber stopper to allow adjustment of thermometer position; reflux condenser; electrical heating mantle; two long pieces of rubber tubing for circulating water through condenser; two condenser clamps and clamp holders; ring stand; iron ring (and clamp holder if necessary).

If an isoteniscope is used: a glass thermostat (e.g., large battery jar) with mechanical stirrer, electrical blade heater, and temperature controller (alternatively a commercial water bath circulator/heater); thermometer; isoteniscope.

Liquid, such as water, *n*-heptane, cyclohexane, or 2-butanone.

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EXPERIMENT 14

Binary Liquid–Vapor Phase Diagram

This experiment is concerned with the heterogeneous equilibrium between two phases in a system of two components. The particular system to be studied is cyclohexanone–tetrachloroethane at 1 atm pressure. This system exhibits a strong negative deviation from Raoult's law, resulting in the existence of a maximum boiling point.