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.

THEORY

For a system of two components (A and B), we have from the phase rule,[1]

$$F = C - P + 2 = 4 - P \tag{1}$$

where C is the number of *components* (minimum number of chemical constituents necessary to define the composition of every phase in the system at equilibrium), P is the number of *phases* (number of physically differentiable parts of the system at equilibrium), and F is the *variance* or number of *degrees of freedom* (number of intensive variables pertaining to the system that can be independently varied at equilibrium without altering the number or kinds of phases present).

When a single phase is present, the pressure p, the temperature T, and the composition X_B (mole fraction of component B) of that phase can be varied independently; thus a single-phase two-component system at equilibrium is defined, except for its size,† by a point in a three-dimensional plot in which the coordinates are the intensive variables p, T, and X_B (see Fig. 1). When two phases, e.g., liquid L and vapor V, are present at equilibrium, there are four variables, but only two of them can be independently varied. Thus, if p and T are specified, X_{BL} and X_{BV} (the mole fractions of B in L and V) are fixed at their *limiting* values (X^0_{BL} and X^0_{BV}) for the respective phases at this p and T. The loci of points $X^0_{BL}\,(p, T)$ and $X^0_{BV}\,(p, T)$ constitute two surfaces, shown in Fig. 1. The shaded region between them may be interpreted as representing the coexistence of two phases L and V *if* in this region X_B is interpreted as a mole fraction of *B for the system as a whole*. Within the two-phase region, X_B is *not* to be regarded as one of the intensive variables constituting the variance (although in a single-phase region it is indeed one of these variables). In a two-phase region the value of X_B determines the relative proportions of the two phases in the system; as X_B varies from X^0_{BL} to X^0_{BV}, the molar proportion x_V of vapor phase varies from zero to unity:

$$x_V = 1 - x_L = \frac{X_B - X^0_{BL}}{X^0_{BV} - X^0_{BL}} \tag{2}$$

Figure 1 is drawn for the special case of two components that form a complete range of *ideal solutions*, i.e., solutions that obey Raoult's law with respect to both components at all compositions. According to this law, the vapor pressure (or partial pressure in the vapor) of a component at a given temperature T_1 is proportional to its mole fraction in the liquid. Thus in Fig. 1 the light dashed lines representing the partial pressures p_A and p_B and the total vapor-pressure line (L, joining p^0_A and p^0_B) are straight lines when plotted against the liquid composition. However, the total vapor pressure as plotted against the *vapor* composition is not linear. The curved line V, joining p^0_A and p^0_B, is convex downward, lying *below* the straight line on the constant-temperature section; its slope has everywhere the same sign as the slope of L.

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†The complete definition of the system would of course include also its shape, description of surfaces, specification of fields, etc.; ordinarily these have negligible effects as far as our present discussion is concerned.

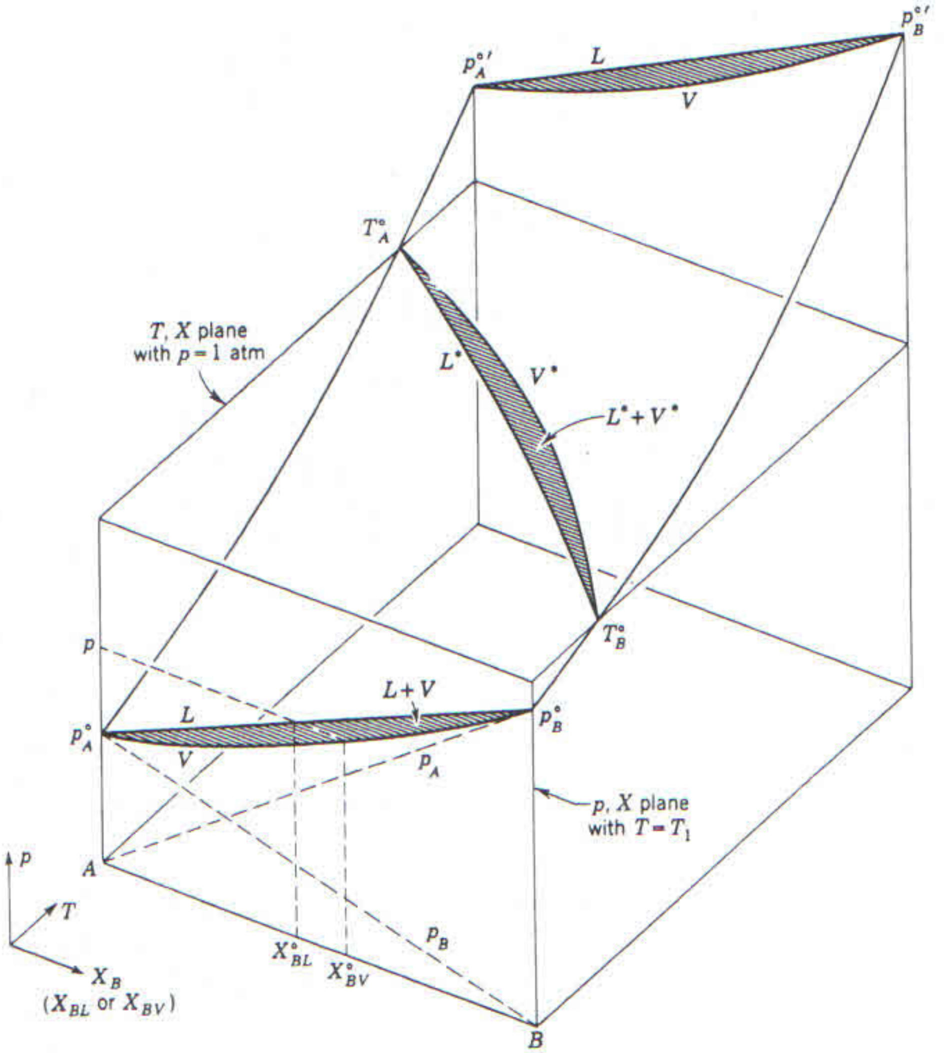

FIGURE 1
Schematic three-dimensional vapor–liquid equilibrium diagram for a two-component system obeying Raoult's law.

The vapor pressures p_A^0 and p_B^0 of the pure liquids increase with temperature (in accord with the Clapeyron equation) as indicated by the curves joining p_A^0 with $p_A^{\prime 0}$ and p_B^0 with $p_B^{\prime 0}$. At a constant pressure, say 1 atm, the boiling points of the pure liquids are indicated as T_A^0 and T_B^0. The boiling point of the solution, as a function of X_{BL} or X_{BV}, is represented by the curve L^* or V^* joining these two points. Neither curve is in general a straight line. If Raoult's law is obeyed, both are convex upward in temperature, the vapor curve lying above the liquid curve in temperature and being the more convex.

In most binary liquid–vapor systems, Raoult's law is a good approximation for a component only when its mole fraction is close to unity. Large deviations from this law are commonplace for the dilute component or for both components when the mole fraction of neither is close to unity. If at a given temperature the vapor pressure of a solution is higher than that predicted by Raoult's law, the system is said to show a *positive deviation* from that law. For such a system, the boiling-point curve L^* at constant pressure is usually convex downward in temperature. If at a given temperature the vapor pressure of the solution is lower than that predicted by Raoult's law, the system is said to show a *negative deviation*; in this case the curve L^* is more convex upward. These deviations from Raoult's law are often ascribed to differences between "heterogeneous" molecular attractions (A – – – B) and "homogeneous" attractions (*A* – – – *A* and *B* – – – *B*). Thus the existence of a positive desvio ⊕

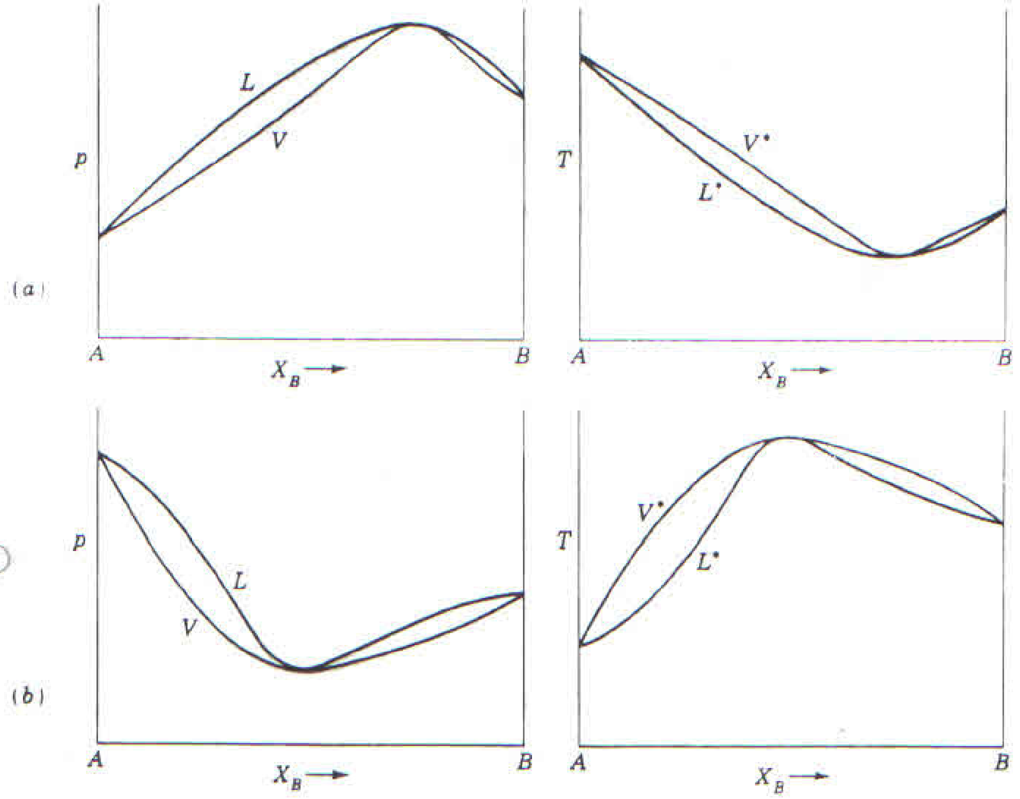

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FIGURE 2
Schematic vapor-pressure and boiling-point diagrams for systems showing (*a*) a strong positive deviation and (*b*) a strong negative deviation from Raoult's law.

deviation implies that homogeneous attractions are stronger than heterogeneous attractions, and a negative deviation implies the reverse. This interpretation is consistent with the fact that positive deviations are usually associated with positive heats of mixing and volume expansions on mixing, while negative deviations are usually associated with negative heats and volume contractions.

In many cases the deviations are large enough to result in maxima or minima in the vapor-pressure and boiling-point curves, as shown in Fig. 2. Systems for which the boiling-point curves have a maximum include acetone–chloroform and hydrogen chloride–water; systems with a minimum include methanol–chloroform, water–ethanol, and benzene–ethanol. At a maximum or a minimum, the compositions of the liquid and of the vapor are the same; accordingly, there is a *point of tangency* of the curves L and V and of the curves L^* and V^* at the maximum or minimum. At every value of X_B, the slope of V (or V^*) has the same sign as the slope of L (or L^*); one is zero where and only where the other is zero, at the point of tangency. (A common error in curves of this kind, found even in some textbooks, is to draw a cusp—a point of discontinuity of slope—in one or both curves at the point of tangency; both curves are in fact smooth and have continuous derivatives.)

If the homogeneous attractions are very much stronger than the heterogeneous ones, phase separation may occur in the liquid; i.e., there is a limited mutual solubility of the two liquid components over certain pressure and temperature ranges. If the pressures and temperatures at which two liquid phases coexist include those at which equilibrium also exists with the vapor phase, a boiling-point diagram of a type similar to that shown in Fig. 15-1 is found. (That figure is a *melting-point* diagram, showing two solid phases in equilibrium with a liquid phase, but the principles are the same. It will be noted that boundaries of fields show discontinuities in slope at points representing the coexistence of three phases.)

Liquid–vapor phase diagrams, and boiling-point diagrams in particular, are of importance in connection with *distillation*, which usually has as its object the partial or complete

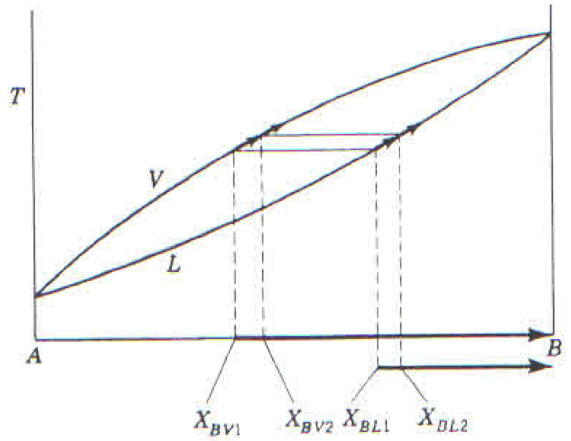

FIGURE 3
Variation of liquid and vapor compositions during distillation of a system with small positive deviations from Raoult's law.

separation of a liquid solution into its components. Distillation consists basically of boiling the solution and condensing the vapor into a separate receiver. A simple "one-plate" distillation of a binary system having no maximum or minimum in its boiling-point curve can be understood by reference to Fig. 3. Let the mole fraction of B in the initial solution be represented by X_{BL1}. When this is boiled and a small portion of the vapor is condensed, a drop of distillate is obtained, with mole fraction X_{BV1}. Since this is richer in A than is the residue in the flask, the residue becomes slightly richer in B, as represented by X_{BL2}. The next drop of distillate X_{BV2} is richer in B than was the first drop. If the distillation is continued until all the residue has boiled away, the last drop to condense will be virtually pure B. To obtain a substantially complete separation of the solution into pure A and B by distillations of this kind, it is necessary to separate the distillate into portions by changing the receiver during the distillation, then subsequently to distill the separate portions in the same way, and so on, a very large number of successive distillations being required. The same result can be achieved in a single distillation by use of a fractionating column containing a large number of "plates"; discussion of the operation of such a column is beyond the scope of this book. If there is a maximum in the boiling-point curve (Fig. 2*b*), the compositions of vapor and residue do not approach pure A or pure B but rather the composition corresponding to the maximum. A mixture with this composition will distill without change in composition and is known as a *constant-boiling mixture* or *azeotrope*. These terms are also applied to a mixture with a minimum boiling point. Azeotropes are important in chemical technology. Occasionally they are useful (as in constant-boiling aqueous hydrochloric acid, used as an analytical standard); often they are nuisances (as in the case of the azeotrope of 95 percent ethanol with 5 percent water, the existence of which prevents preparation of absolute ethanol by direct distillation of dilute solutions of ethanol in water). Extensive lists of azeotropes have been compiled.[2]

METHOD

A boiling-point curve can be constructed from data obtained in actual distillations in an ordinary "one-plate" distilling apparatus. Small samples of the distillate are taken directly from the condenser, after which small samples of the residue are withdrawn with a pipette. The samples of distillate and residue are analyzed, and their compositions are plotted on a boiling-point diagram against the temperatures at which they were taken. In the case of the distillate, the temperature to be plotted for each sample should be an average of the initial and final values during the taking of the sample. In the case of the residue,

TABLE 1 Logarithm of refractive index for cyclohexanone–tetrachloroethane mixtures

	W%		W%		W%
Log n_D^{20}	$C_6H_{10}O$	Log n_D^{20}	$C_6H_{10}O$	Log n_D^{20}	$C_6H_{10}O$
0.17441	0	0.16864	40	0.16360	80
0.17298	10	0.16719	50	0.16256	90
0.17155	20	0.16582	60	0.16158	100
0.17010	30	0.16473	70		

the temperature to be plotted should be that recorded at the point where the distillation is stopped to take the sample of residue.

For analysis of the samples, a physical method is often preferable to chemical methods. Chemical analysis usually is appropriate only when a simple titration of each sample is involved, as in the case of the system HCl–H_2O. If a physical property is chosen as the basis for an analytical method, it should be one that changes significantly and smoothly over the entire composition range to be studied. The refractive index is one property that can be used for the cyclohexanone–tetrachloroethane system. The values of n_D^{20} are 1.4507 for cyclohexanone and 1.4942 for 1,1′,2,2′-tetrachloroethane, and log n_D^{20} is almost a linear function of the weight percent of cyclohexanone. Thus one can interpolate linearly between the values listed in Table 1, and then convert weight percentages into mole fractions.

Another property that could also be used is the density, which varies in a nonlinear way between 0.9478 g/mL for cyclohexanone and 1.600 g/mL for tetrachloroethane at 20°C. In this case, a calibration curve should be constructed from known solutions or provided by the instructor. The density of each distillation sample can be measured by pipetting 1 mL into a small, previously weighed vial and then weighing again (to the nearest 0.1 mg).

Warning: These solutions will decompose slowly at room temperature (~1 day) and more rapidly during distillation at high temperatures. Impure solutions become yellowish, which can interfere with the refractive index measurements. Use well-purified starting materials and do not prolong the distillations unnecessarily. It should also be noted that many chlorinated hydrocarbons, including tetrachloroethane, are toxic chemicals. *Chronic* exposure to tetrachloroethane can cause liver damage. The toxic oral dose is high (~0.5 g per kilogram of body weight, or 27 g for someone weighing 120 lb), but smaller doses can cause short-term medical problems.[3] **Do not pipette by mouth.** The vapor is irritating to eyes and mucous membranes, and the toxic level is 4.5 g m^{-3}. **Do not inhale the vapor while taking samples.**

EXPERIMENTAL

A simple distilling apparatus that can be used for this experiment is shown in Fig. 4. The thermometer bulb should be about level with the side arm to the condenser so that the temperature of coexisting vapor and liquid is measured. Except when samples of distillate are being taken for analysis, an adequate receiving flask should be placed at the lower end of the condenser.

Before beginning the distillations, prepare twenty 5-mL vials for taking samples and label with the designations 1*L*, 1*V*, 2*L*, . . . , 10*V* (*L* = *liquid* residue; *V* = condensed *vapor* or distillate). Take samples of about 2 mL in size. Turn on the circulating water to the condenser before heating the liquid, and turn it off at the end of the experiment.

When the distillation is proceeding at a normal (not excessive) rate at about the desired temperature, quickly replace the receiver with a vial and read the thermometer.

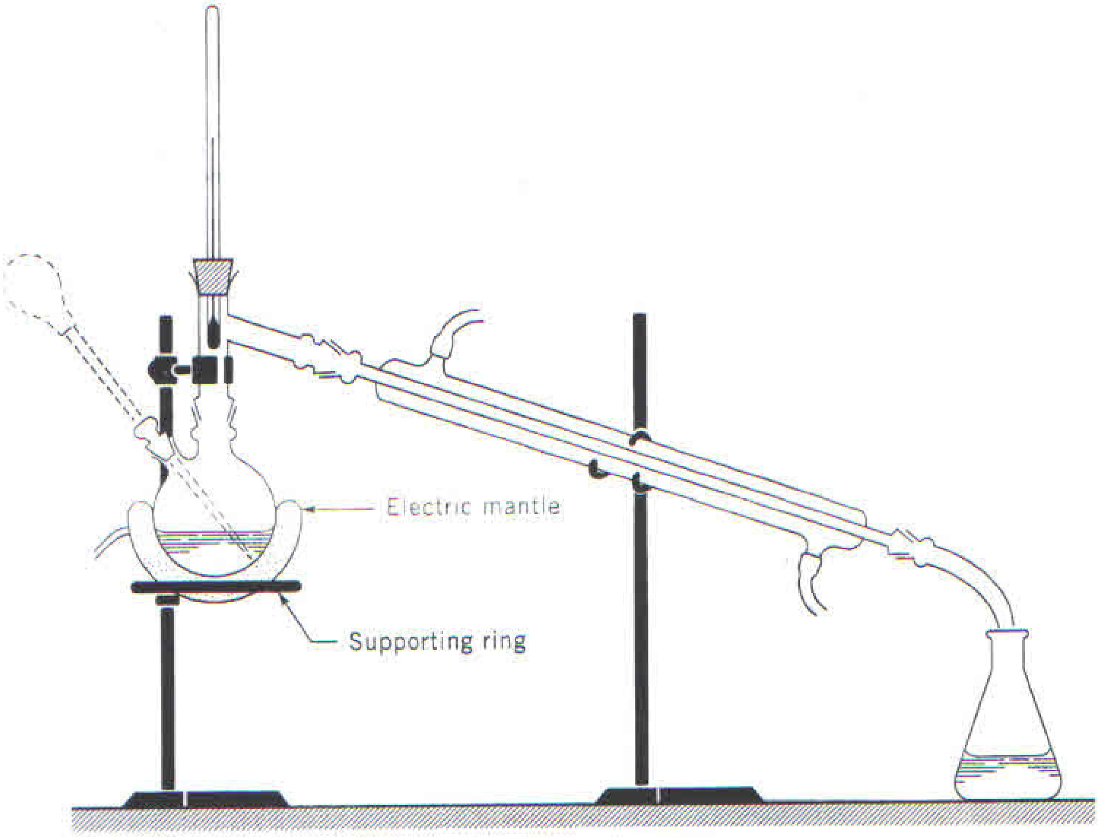

FIGURE 4
Distillation apparatus. The mercury thermometer can be replaced by a resistance thermometer or other direct-reading thermometric device.

After about 2 mL has been collected, read the thermometer again, replace the receiver, and seal the vial tightly. Turn off and lower the heating mantle to halt the distillation. When the temperature just begins to fall, record another thermometer reading. After the flask has cooled about 15°C, remove the glass plug on the side arm of the flask and insert a 2-mL pipette equipped with a rubber bulb. Fill the pipette, discharge it into the appropriate vial, and stopper the vial.

The following procedure is recommended for economical use of materials in carrying out this experiment. The paragraph numbers correspond to sample numbers. A graduated cylinder is adequate for measuring liquids. The temperatures recommended are those appropriate for 760 Torr; at ambient pressure differing markedly from this value, the temperatures should be adjusted accordingly. For example at Denver (altitude 1609 m) the average atmospheric pressure is 836 mbar = 627 Torr. Since the enthalpies of vaporization of cyclohexane and tetrachloroethane are both near 40 kJ mol^{-1}, this pressure change will reduce the boiling points of the pure materials by ~7°C compared with the values at 760 Torr. Comparable changes are expected for the azeotrope and for intermediate compositions.

1. Pure tetrachloroethane: Introduce 125 mL (~200 g) of 1,1′,2,2′-tetrachloroethane into the flask. Distill enough to give a constant temperature (should be near 146°C at 760 Torr). Collect samples ($1V$ and $1L$) for analysis.
2. 149°C (tetrachloroethane-rich side of azeotrope): Cool the distilling flask, and return the excess distillate of paragraph 1 to the flask. Add 38 mL (~36 g) of cyclohexanone. Begin distillation. When the temperature reaches 149°C, collect about 2 mL of distillate ($2V$) and 2 mL of residue ($2L$).
3. 151°C: Resume the distillation. Distill until the temperature reaches 151°C (this may take some time) and collect samples ($3V$, $3L$).

4. 154°C: Resume the distillation. When the temperature reaches 154°C, collect samples (4*V*, 4 *L*).
5. 157°C: Cool the flask somewhat, and add 35 mL of tetrachloroethane and 25 mL of cyclohexanone. Resume the distillation. When the temperatures reaches approximately 157°C, collect samples (5*V*, 5*L*).
6. Azeotrope: Cool the flask somewhat and add 36 mL of tetrachloroethane and 54 mL of cyclohexanone. Resume the distillation until the boiling point ceases to change significantly, and take samples (6*V*, 6*L*). (If the boiling point does not become sufficiently constant, analyze the remaining residue, and make up 100 mL of solution to the composition found. Distill to constant temperature and take samples.)
7. Pure cyclohexanone: Introduce 105 mL of cyclohexanone into the clean flask and determine the boiling point as in paragraph 1. (The temperature should be near 155°C at 760 Torr). Collect samples (7*V* and 7*L*).
8. 156.5°C (cyclohexanone-rich side of azeotrope): Cool the distilling flask, return the excess distillate of paragraph 7, and add 20 mL of tetrachloroethane. Resume the distillation, and take samples (8*V*, 8*L*) at about 156.5°C.
9. 157°C: Cool the flask somewhat, and add 50 mL cyclohexanone and 17 mL tetrachloroethane. Resume the distillation and collect samples (9*V*, 9*L*) at about 157°C.
10. Azeotrope: Resume the distillation, continue to constant boiling temperature, and take samples (10*V*, 10*L*).

The indexes of refraction should be measured and recorded as soon as possible (the samples decompose on standing). The refractometer and the procedure for its use are described in Chapter XX. (If the experiment is being done by several teams using the same refractometer, it is wise to take samples to the refractometer as soon as six or eight samples are ready, or fewer if the instrument happens to be free.) If careful attention is given to the proper technique of using the refractometer, it should be possible to take readings at the rate of one sample per minute.

At the end of the experiment, all cyclohexanone–tetrachloroethane mixtures should be poured into a designated waste vessel.

At some time during the laboratory period, the barometer should be read. The ambient temperature should be recorded for the purpose of making thermometer stem corrections if these are necessary; see pp. 605–6.

CALCULATION

Determine the weight-percent compositions by interpolation in Table 1 and then convert the weight percentages to mole fractions. Plot the temperatures (after making any necessary stem corrections; see Chapter XVIII) against the mole fractions. Draw one smooth curve through the distillate points *V* and another through the residue points *L*. Label all fields of the diagram to indicate what phases are present. Report the azeotropic composition and temperature, together with the atmospheric pressure (i.e., the properly corrected barometer reading).

SAFETY ISSUES

Tetrachloroethane has a known toxicity, as described in the warning in the Method section. Do not pipette this or any other chemical by mouth, and avoid inhaling the vapor while withdrawing samples. Dispose of waste chemicals as instructed.

APPARATUS

Distilling flask; mercury thermometer, graduated to 0.1°C or a digital resistance thermometer with a resolution of ±0.1°C; one-hole stopper for thermometer to fit flask and allow adjustment in thermometer position; straight-tube condenser; two lengths of rubber hose for condenser cooling water; distilling adapter to fit flask and condenser; two clamps and clamp holders; two ring stands; one iron ring; electrical heating mantle (or steam bath); 20 small vials; 100-mL graduated cylinder; two wide-mouth 250-mL flasks; 2-mL pipette; pipetting bulb; two 500-mL glass-stoppered Erlenmeyer flasks.

Refractometer, thermostated at 25°C; sodium-vapor lamp (optional); eye droppers; *clean* cotton wool; acetone wash bottles; pure 1,1′,2,2′-tetrachloroethane (300 mL) and pure cyclohexanone (350 mL); acetone for rinsing; large bottle for disposal of waste solutions.

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EXPERIMENT 15

Binary Solid–Liquid Phase Diagram

In this experiment we are concerned with the heterogeneous equilibrium between solid and liquid phases in a two-component system. From the many systems[1-3] that are suitable for study, the system naphthalene–diphenylamine has been selected for this experiment because of the simplicity of its phase diagram and the convenience of its temperature range.

THEORY

The principles underlying this experiment are identical with those discussed in Exp. 14. For our discussion here we can merely replace L (liquid) in that experiment by S (solid) and V (vapor) by L (liquid). Solid–liquid equilibria differ from liquid–vapor equilibria in being essentially independent of pressure changes of the order of a few atmospheres. This is a consequence of the Clapeyron equation, Eq. (13-3), owing to the small molar volume change associated with fusion. Accordingly, we shall be concerned only with temperature–composition diagrams at 1 atm pressure.