Identification of Substances by Physical Properties

EXPERIMENT 2

OBJECTIVE

To become acquainted with procedures used in evaluating physical properties and the use of these properties in identifying substances.

APPARATUS AND CHEMICALS

balance
250-mL beaker
burner and hose
dropper
50-mL Erlenmeyer flask
10-mL graduated cylinder
large test tubes (2)
small test tubes (6)
test-tube rack
spatula
10-mL pipet
5-mL pipet
tubing with right-angle bend
ring stand and ring
utility clamp
wire gauze
thermometer
no. 3 two-hole stopper with one of the holes slit to the side or a buret clamp
two-hole stopper
stirring rod
small rubber bands (or small sections of $\frac{1}{4}$-in. rubber tubing)
20 mL cyclohexane
boiling chips
15 mL ethyl alcohol
1 g naphthalene
5 mL toluene
two unknowns (one liquid, one solid)
capillary tubes (5)
50-mL beakers (2)
small watch glass
soap solution

DISCUSSION

Properties are those characteristics of a substance that enable us to identify it and to distinguish it from other substances. Direct identification of some substances can readily be made by simply examining them. For example, we see color, size, shape, and texture, and we can smell odors and discern a variety of tastes. Thus, copper can be distinguished from other metals on the basis of its color.

Physical properties are those properties that can be observed without altering the composition of the substance. Whereas it is difficult to assign definitive values to such properties as taste, color, and odor, other physical properties, such as melting point, boiling point, solubility, density, viscosity, and refractive index, can be expressed quantitively. For example, the melting point of copper is 1087°C, and its density is 8.96 g/cm^3. As you probably realize, a specific combination of properties is unique to a given substance, thus making it possible to identify most substances just by careful determination of several properties. This is so important that large books have been compiled listing characteristic properties of most known substances. Many scientists, most notably several German scientists during the latter part of the nineteenth century and earlier part of the twentieth, spent their entire lives gathering data of this sort. Two of the most complete references of this type that are readily available today are The Chemical Rubber Company's *Handbook of Chemistry and Physics* and N. A. Lange's *Handbook of Chemistry*.

In this experiment you will use the following properties to identify a substance whose identity is unknown to you: solubility, density, melting point, and boiling point. The *solubility* of a substance in a solvent at a specified temperature is the maximum weight of that substance that dissolves in a given volume (usually 100 mL or 1000 mL) of a solvent. It is tabulated in handbooks in terms of grams per 100 mL of solvent; the solvent is usually water.

In the preceding experiment you learned that the density of a substance is defined as the mass per unit volume:

$$d = \frac{m}{V}$$

Melting or freezing points correspond to the temperature at which the liquid and solid states of a substance are in equilibrium. These terms refer to the same temperature but differ slightly in their meaning. The *freezing point* is the equilibrium temperature when approached from the liquid phase, that is, when solid begins to appear in the liquid. The *melting point* is the equilibrium temperature when approached from the solid phase, that is, when liquid begins to appear in the solid.

A liquid is said to boil when bubbles of vapor form within it, rise rapidly to the surface, and burst. Any liquid in contact with the atmosphere will boil when its vapor pressure is equal to atmospheric pressure—that is, the liquid and gaseous states of a substance are in equilibrium. Boiling points of liquids depend upon atmospheric pressure. A liquid will boil at a higher temperature at a higher pressure or at a lower temperature at a lower pressure. The temperature at which a liquid boils at 760 mm Hg is called the *normal* boiling point. To account for these pressure effects on boiling points, people have studied and tabulated data for boiling point versus pressure for a large number of compounds. From these data, nomographs have been constructed. A *nomograph* is a set of scales for connected variables (see Figure 2.5 for an example); these scales are so placed that a straight line connecting the known values on some scales will provide the unknown value at the straight line's intersection with other scales. A nomograph allows you to find the correction necessary to convert the normal boiling point of a substance to its boiling point at any pressure of interest.

PROCEDURE

A. Solubility

CAUTION: *Cyclohexane is highly flammable and must be kept away from open flames*. Qualitatively determine the solubility of naphthalene (mothballs) in three solvents: water, cyclohexane, and ethyl alcohol. Determine the solubility by adding a few crystals of napthalene to 2 to 3 mL (it is not necessary to measure either the solute weight or solvent volume) of each of these three solvents in separate, clean, *dry* test tubes. Make an attempt to keep the amount of napthalene and solvent the same in each case. Place a cork in each test tube and shake briefly. Cloudiness indicates insolubility. Record your conclusions on the report sheet using the abbreviations s (soluble), sp (sparingly soluble), and i (insoluble). Into each of three more clean, *dry* test tubes place 2 or 3 mL of these same solvents and add 4 or 5 drops of toluene in place of naphthalene. Record your observations. The formation of two layers indicates immiscibility (lack of solubility). Now repeat these experiments using each of the three solvents (water, cyclohexane, and ethyl alcohol) with your solid and liquid unknowns and record your observations.

B. Density

Determine the densities of your two unknowns in the following manner.

The Density of a Solid Weigh about 1.5 g of your solid unknown to the nearest 0.001 g and record the weight. Using a pipet or a wash bottle, half fill a *clean, dry* 10-mL graduated cylinder with a solvent in which your unknown is *insoluble*. Be *careful* not to get the liquid on the inside walls, because you do not want your solid to adhere to the cylinder walls when you add it in a subsequent step. Read and record this volume to the nearest 0.1 mL. Add the weighed solid to the liquid in the cylinder, being careful not to lose any of the material in the transfer process and ensuring that all of the solid is beneath the surface of the liquid. Carefully tapping the sides of the cylinder with your fingers will help settle the material to the bottom. Do not be concerned about a few crystals that do not settle, but if a large quantity of the solid resists settling, add one or two drops of a soap solution and continue tapping the cylinder with your fingers. Now read the new volume to the nearest 0.1 mL. The difference in these two volumes is the volume of your solid (see Figure 2.1). Calculate the density of your solid unknown.

You may recall that by measuring the density of metals in this way Archimedes proved to the king that the charlatan alchemists had in fact not transmuted lead into gold. He did this after observing that he weighed less in the bathtub than he did normally by an amount equal to the weight of the fluid displaced. According to legend, upon making his discovery Archimedes

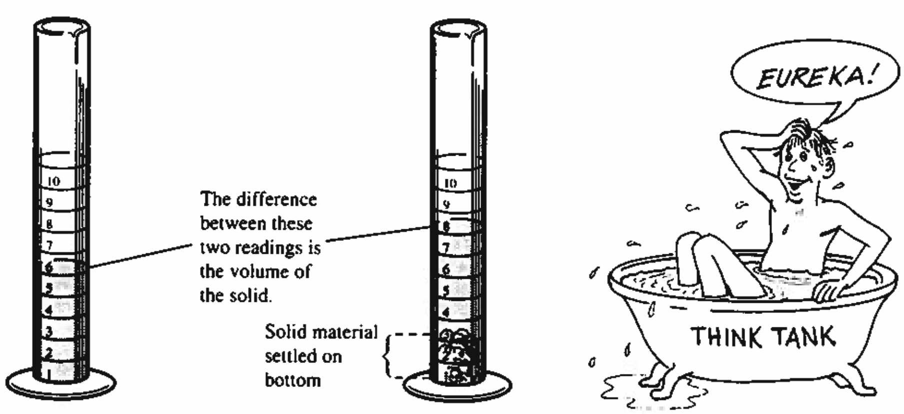

Figure 2.1

emerged from his bath and ran naked through the streets shouting *Eureka!* (I have found it).

The Density of a Liquid Weigh a clean, *dry* 50-mL Erlenmeyer flask to the nearest 0.0001 g. Obtain at least 15 mL of the unknown liquid in a clean, *dry* test tube. Using a 10-mL pipet, pipet exactly 10 mL of the unknown liquid into the 50 mL Erlenmeyer flask and quickly weigh the flask containing the 10 mL of unknown to the nearest 0.0001 g. Using the calibration value for your pipet (from Experiment 1) and the weight of this volume of unknown, calculate its density. Record your results and show how (with units) you performed your calculations. (SAVE THE LIQUID FOR YOUR BOILING-POINT DETERMINATION.)

C. Melting Point (for Solid Unknown)

Obtain a capillary tube and a small rubber band. Seal one end of the capillary tube by carefully heating the end in the edge of the flame of a Bunsen burner until the end *completely* closes. Rotating the tube during heating will help you to avoid burning yourself (see Figure 2.2).

Pulverize a small portion of your solid-unknown sample with the end of a test tube on a clean watch glass; partially fill the capillary with your unknown by gently tapping the pulverized sample with the open end of the capillary to force some of the sample inside. Drop the capillary into a glass tube about 38 to 50 cm in length, with the sealed end down to pack the sample into the bottom of the capillary tube. Repeat this procedure until the sample column is roughly 5 mm in height. Now set up a melting-point apparatus as illustrated in Figure 2.3.

Place the rubber band about 5 cm above the bulb on the thermometer and out of the liquid. Carefully insert the capillary tube under the rubber band with the closed end at the bottom. Place the thermometer with attached capillary into the beaker of water so that the sample is covered by water, the thermometer does not touch the bottom of the beaker, and the open end of the capillary tube is above the surface of the water. Heat the water slowly while gently agitating the water with a stirring rod. Observe the sample in the capillary tube

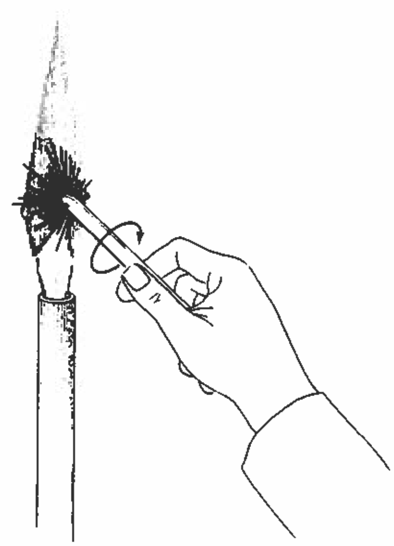

Figure 2.2 Sealing one end of a capillary tube.

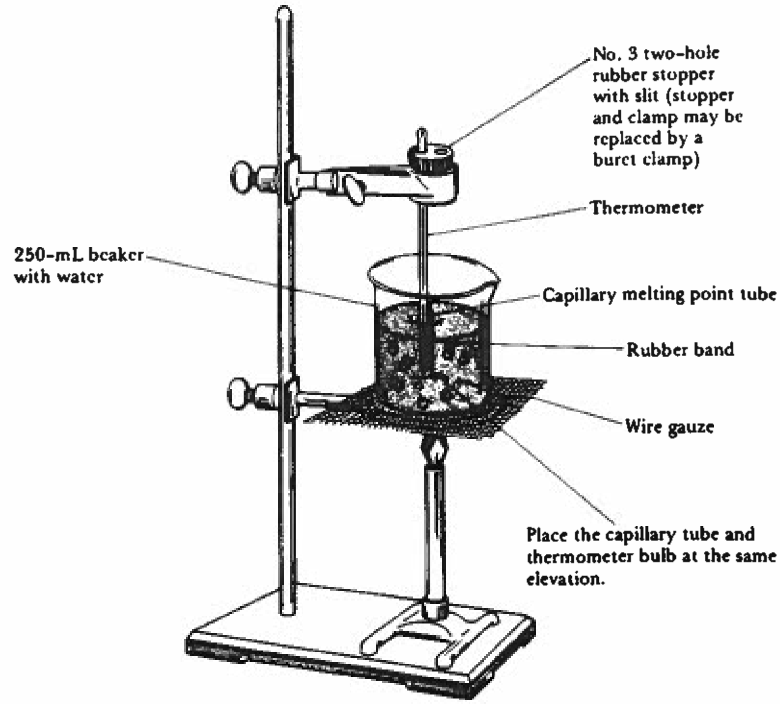

Figure 2.3 Apparatus for melting-point determination.

while you are doing this. At the moment that the solid melts, record the temperature. Also record the melting-point range, which is the temperature range between the temperature at which the sample begins to melt and the temperature at which all of the sample has melted. Using your thermometer-calibration curve (from Experiment 1), correct these temperatures to the true temperatures and record the melting point and melting-point range. These temperatures may differ by only 1°C or less.

D. Boiling Point (for Liquid Unknown)

Determine the boiling point of your liquid unknown (use some of the same material you used to determine the density) by adding about 3 mL to a clean, dry test tube. Fit the test tube with a two-hole rubber stopper that has one slit; insert your thermometer into the hole with the slit and one of your right-angle-bend glass tubes into the other hole, as shown in Figure 2.4. Add one or two small boiling chips to the test tube to ensure even boiling of your sample. Position the thermometer so that it is about 1 cm above the surface of the unknown liquid. Clamp the test tube in the ring stand and connect to the right-angle-bend tubing a length of rubber tubing that reaches to the sink. Assemble your apparatus as shown in Figure 2.4. (CAUTION: *Be certain that there are no constrictions in the rubber tubing. Your sample is flammable. Keep it away from open flames.*)

Heat the water gradually and watch for changes in temperature. The temperature will become constant at the boiling point of the liquid. Record the observed boiling point. Correct the observed boiling point to the true boiling point at room atmospheric pressure using your thermometer-calibration curve. The normal boiling point (b.p. at 1 atm = 760 mm Hg) can now be calculated (see Example 2.1, below) using the nomograph provided in Figure 2.5. Your boiling-point correction should not be more than +5°C.

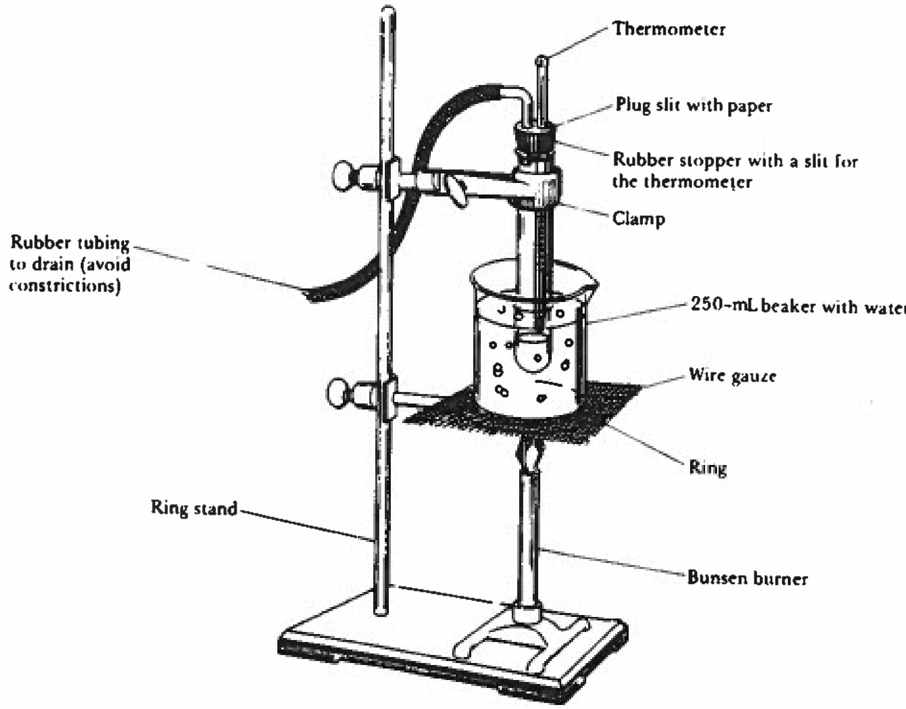

Figure 2.4 Apparatus for boiling-point determination.

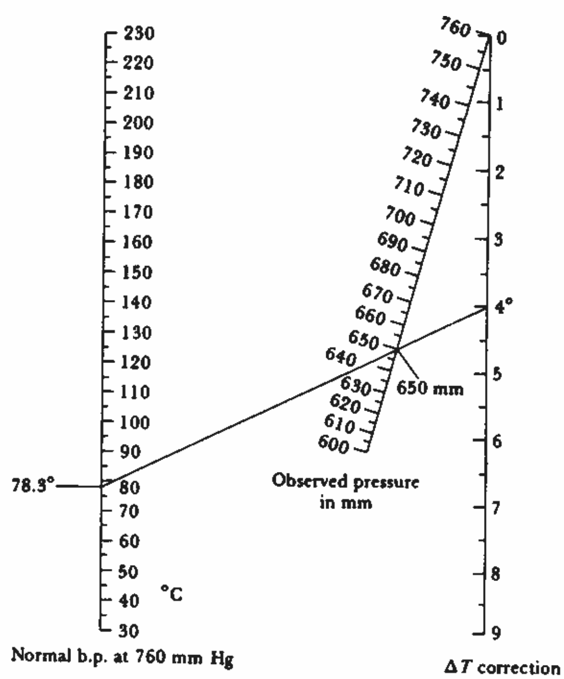

Figure 2.5 Nomograph for boiling point correction to 760 mm Hg.

EXAMPLE 2.1

What will be the boiling point of ethanol at 650 mm Hg when its normal boiling point at 760 mm Hg is known to be 78.3°C.

Solution: The answer is easily found by consulting the nomograph in Figure 2.5. A straight line drawn from 78.3°C on the left scale of normal boiling points through 650 mm Hg on the pressure scale intersects the temperature correction scale at 4°C. Therefore,

$$\text{Normal b.p.} - \text{correction} = \text{observed b.p.}$$

$$78.3°C - 4.0°C = 74.3°C$$

Similar calculations could be done for the compounds in Table 2.1 at any pressure listed on the nomograph in Figure 2.5. In this experiment you will observe a boiling point at a pressure other than at 760 mm Hg, and you wish to know its normal boiling point. In order to estimate its normal boiling point, assume that your observed boiling point is 57.0°C and the observed pressure is 650 mm Hg. Use your observed boiling point of 57.0°C as if it were the normal boiling point and find the correction

Table 2.1 Physical Properties of Pure Substances

Substance	Density (g/mL)	Melting point (°C)	Boiling point (°C)	Solubility[a] in Water	Cyclohexane	Alcohol
Acetanilide	1.22	114	304	sp	sp	s
Acetone	0.79	−95	56	s	s	s
Benzophenone	1.15	48	306	i	s	s
Bromoform	2.89	8	150	i	s	s
2,3-Butanedione	0.98	−2.4	88	s	s	s
t-Butyl alcohol	0.79	25	83	s	s	s
Cadmium nitrate · $4H_2O$	2.46	59	132	s	i	s
Chloroform[b]	1.49	−63.5	61	i	s	s
Cyclohexane	0.78	6.5	81.4	i	s	s
p-Dibromobenzene	1.83	86.9	219	i	s	s
p-Dicholorobenze	1.46	53	174	i	s	s
m-Dinitrobenzene	1.58	90	291	i	s	s
Diphenyl	0.99	70	255	i	s	s
Diphenylamine	1.16	53	302	i	s	s
Diphenylmethane	1.00	27	265	i	s	s
Ether, ethyl propyl	1.37	−79	64	s	s	s
Hexane	0.66	−94	69	i	s	s
Isopropyl alcohol	0.79	−98	83	s	s	s
Lauric acid	0.88	43	225	i	s	s
Magnesium nitrate · $6H_2O$	1.63	89	330[c]	s	i	s
Methyl alcohol	0.79	−98	65	s	sp	s
Methylene chloride[b]	1.34	−97	40.1	i	s	s
Naphthalene	1.15	80	218	i	s	sp
α-Naphthol	1.22	94	288	i	i	s
Phenyl benzoate	1.23	71	314	i	s	s
Propionaldehyde	0.81	−81	48.8	s	i	s
Sodium acetate · $3H_2O$	1.45	58	123	s	i	sp
Stearic acid	0.85	70	291	i	s	sp
Thymol	0.97	52	232	sp	s	s
Toluene	0.87	−95	111	i	s	s
p-Toluidine	0.97	45	200	sp	s	s
Zinc chloride	2.91	283	732	s	i	s

[a] s = soluble; sp = sparingly soluble; i = insoluble.
[b] Toxic. Most organic compounds used in the lab are toxic.
[c] Boils with decomposition.

for a pressure of 650 mm Hg. Using the nomograph, you can see that the correction is 3.8°C. You would then add this correction to your observed boiling point to obtain an approximate normal boiling point:

$$57°C + 3.8°C = 60.8°C, \text{ or } 61°C$$

By consulting Table 2.1, you can find the compound that best fits your data; in this example, the data are for chloroform.

E. Unknown Identification

Your unknowns are substances contained in Table 2.1. Compare the properties that you have determined for your unknowns with those in the table. Identify your unknowns and record your results.

REVIEW QUESTIONS

Before beginning this experiment in the laboratory, you should be able to answer the following questions:

1. List five physical properties.
2. A 8.792-mL sample of an unknown weighed 10.12 g. What is the density of the unknown?
3. Are the substances methylene chloride and diphenyl solids or liquids at room temperature?
4. Could you determine the density of benzophenone using water? Why or why not?
5. What would be the boiling point of hexane at 670 mm Hg?
6. Why do we calibrate thermometers and pipets?
7. Is bromoform miscible with water? with cyclohexane?
8. When water and toluene are mixed, two layers form. Is the bottom layer water or toluene? (See Table 2.1.)
9. What solvent would you use to determine the density of zinc chloride?
10. The density of a solid with a melting point of 52 to 54°C was determined to be 1.45 ± 0.02 g/mL. What is the solid?
11. The density of a liquid whose boiling point is 63–65°C was determined to be 1.36 ± 0.05 g/mL. What is the liquid?
12. Which has the greater volume, 10 g of chloroform or 10 g of acetone? What is the volume of each?