Name ______________________ Section ______________

EXPERIMENT

18 • Molecular Weight Determination by Depression of the Freezing Point

In the preceding experiment you observed the change of vapor pressure of a liquid as a function of temperature. If a nonvolatile solid compound (the solute) is dissolved in a liquid, the vapor pressure of the liquid solvent is lowered. This decrease in the vapor pressure of the solvent results in other easily observable physical changes; the boiling point of the solution is higher than that of the pure solvent and the freezing point is lower.

Many years ago chemists observed that at low solute concentrations the changes in the boiling point, the freezing point, and the vapor pressure of a solution are all proportional to the amount of solute that is dissolved in the solvent. These three properties are collectively known as colligative properties of solutions. The colligative properties of a solution depend only on the number of solute particles present in a given amount of solvent and not on the kind of particles dissolved.

When working with boiling point elevations or freezing point depressions of solutions, it is convenient to express the solute concentration in terms of its molality m defined by the relation:

$$\text{molality of } A = m_A = \frac{\text{no. of moles } A \text{ dissolved}}{\text{no. of kg solvent in the solution}}$$

For this unit of concentration, the boiling point elevation, $T_b - T_b^\circ$ or ΔT_b, and the freezing point depression, $T_f^\circ - T_f$ or ΔT_f, in °C at low concentrations are given by the equations:

$$\Delta T_b = k_b m \qquad \Delta T_f = k_f m \tag{1}$$

where k_b and k_f are characteristic of the solvent used. For water, $k_b = 0.52$ and $k_f = 1.86$. For benzene, $k_b = 2.53$ and $k_f = 5.10$.

One of the main uses of the colligative properties of solutions is in connection with the determination of the molecular weights of unknown substances. If we dissolve a known amount of solute in a given amount of solvent and measure ΔT_b or ΔT_f of the solution produced, and if we know the appropriate k for the solvent, we can find the molality and hence the molecular weight of the solute. In the case of the freezing point depression, the relation would be:

$$\Delta T_f = k_f m = k_f \times \frac{\text{no. moles solute}}{\text{no. kg solvent}} = k_f \times \frac{\dfrac{\text{no. g solute}}{\text{GMW solute}}}{\text{no. kg solvent}} \tag{2}$$

In this experiment you will be asked to estimate the molecular weight of an unknown solute, using this equation. The solvent used will be paradichlorobenzene, which has a convenient melting point and a relatively large value for k_f, 7.10. The freezing points will be obtained by studying the rate at which liquid paradichlorobenzene and some of its solutions containing the unknown cool in air. Temperature-time graphs, called cooling curves, reveal the freezing points very well, since the rate at which a liquid cools is typically quite different from that of a liquid-solid equilibrium mixture.

EXPERIMENTAL PROCEDURE

A. Determination of the Freezing Point of Paradichlorobenzene. From the stockroom obtain a stopper fitted with a sensitive thermometer and a glass stirrer, a large test tube, and a sample of solid unknown. **Remember that the thermometer is both fragile and expensive, so handle it with due care.** Weigh the test tube on a top loading or triple beam balance to 0.01g. Add about 30 g of paradichlorobenzene, PDB, to the test tube and weigh again to the same precision.

Fill your 600 ml beaker almost full of hot water from the faucet. Support the beaker on an iron ring and wire gauze on a ring stand and heat the water with a Bunsen burner. Clamp the test tube to the ring stand and immerse the tube in the water as far as is convenient.

Heat the water to about 70 to 75°C (use your ordinary thermometer to follow the bath temperature), at which point most of the PDB will melt. Insert the stopper-thermometer-stirrer assembly in the test tube, adjusting the level of the thermometer so that the bulb is 1 cm above the bottom of the tube, well down into the melt. When the PDB is at about 65°C, stop heating. Stir, to dissolve any remaining solid PDB. Carefully lower the iron ring and water bath and put the beaker of hot water on the lab bench well away from the test tube. Dry the outside of the test tube with a towel.

Record the temperature of the paradichlorobenzene as it cools in the air. Stir the liquid slowly but continuously to avoid supercooling. Start readings at about 60°C and note the temperature every 30 seconds for eight minutes or until the solution has solidified to the point that you are no longer able to stir it. Near the melting point you will begin to observe crystals of PDB in the liquid, and these will increase in amount as cooling proceeds. Note the temperature at which the first solid PDB appears. In Figure 18.1 we have shown graphically how the temperature of pure PDB will typically vary with time in this experiment.

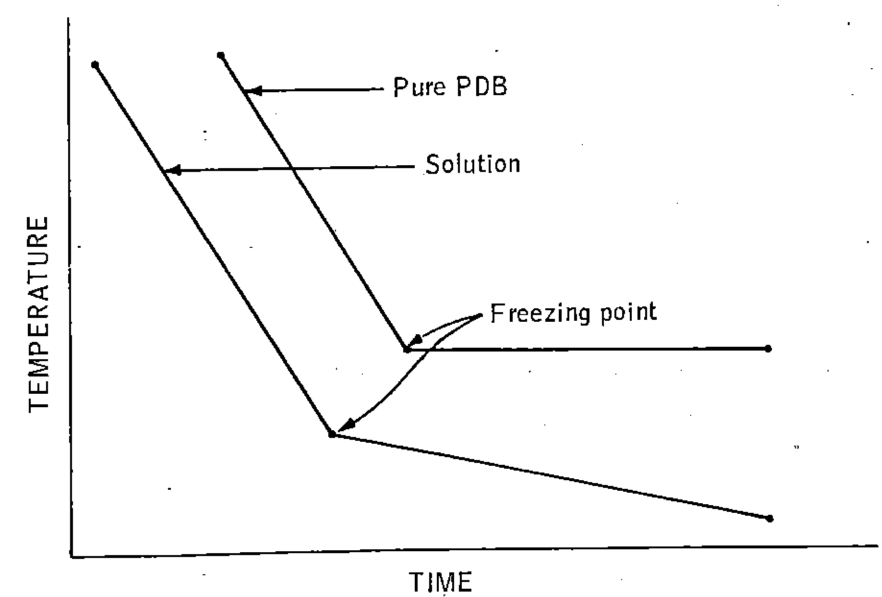


Figure 18.1

B. Determination of the Molecular Weight of an Unknown Compound. Weigh your unknown in its container to 0.01 g. Pour about half of the sample (about 2 g) into your test tube of PDCB and reweigh the container.

Heat the test tube in the water bath until the PDCB is again melted and the solid unknown is dissolved. When the melt has reached about 65 °C, remove the bath, dry the test tube, and let it cool as before. Start readings at about 60 °C and continue to take readings, with stirring, for eight minutes.

The dependence of temperature on time with the solution will be similar to that observed for pure PDCB, except that the first crystals will appear at a lower temperature, and the temperature of the solid-solution system will gradually fall as cooling proceeds. There may be some supercooling, as evidenced by a rise in temperature shortly after the first appearance of PDCB crystals. In this case, the freezing point of the solution is best taken as the temperature at which the two lines on the temperature-time graph intersect (Figure 18.1).

Add the rest of your unknown (about 2 grams) to the PDCB solution and again weigh the container. Melt the PDCB as before, heating it to about 65 °C before removing the water bath.

DATA AND CALCUALTIONS:

A. Molecular Weight Determination by Freezing Point Depression.

Mass of the test tube ________________ g

Mass of test tube plus about 30 g of PDCB (solvent) ________________ g

Mass of Sample I (solute) ________________ g

Mass of Sample II (solute) ________________ g

B. Calculation of Molecular Weight

	Solution I	Solution II
Mass of unknown used (total amount in solution)	________ g	________ g
Mass of paradichlorobenzene (PDCB) used	________ g	________ g
Freezing point of pure PDCB	________ °C	________ °C
Freezing point of solution	________ °C	________ °C
Freezing point depression	________ °C	________ °C
Total molal concentration of unknown solution (from equation 2)(k_f = 7.10 °C/m)	________ m	________ m
Molecular Mass of unknown (See ASA #1b)	________ g/mol	________ g/mol

Average Molecular Mass ________________ g/mol

Unknown Compound Formula ________________ = ________________ g/mol

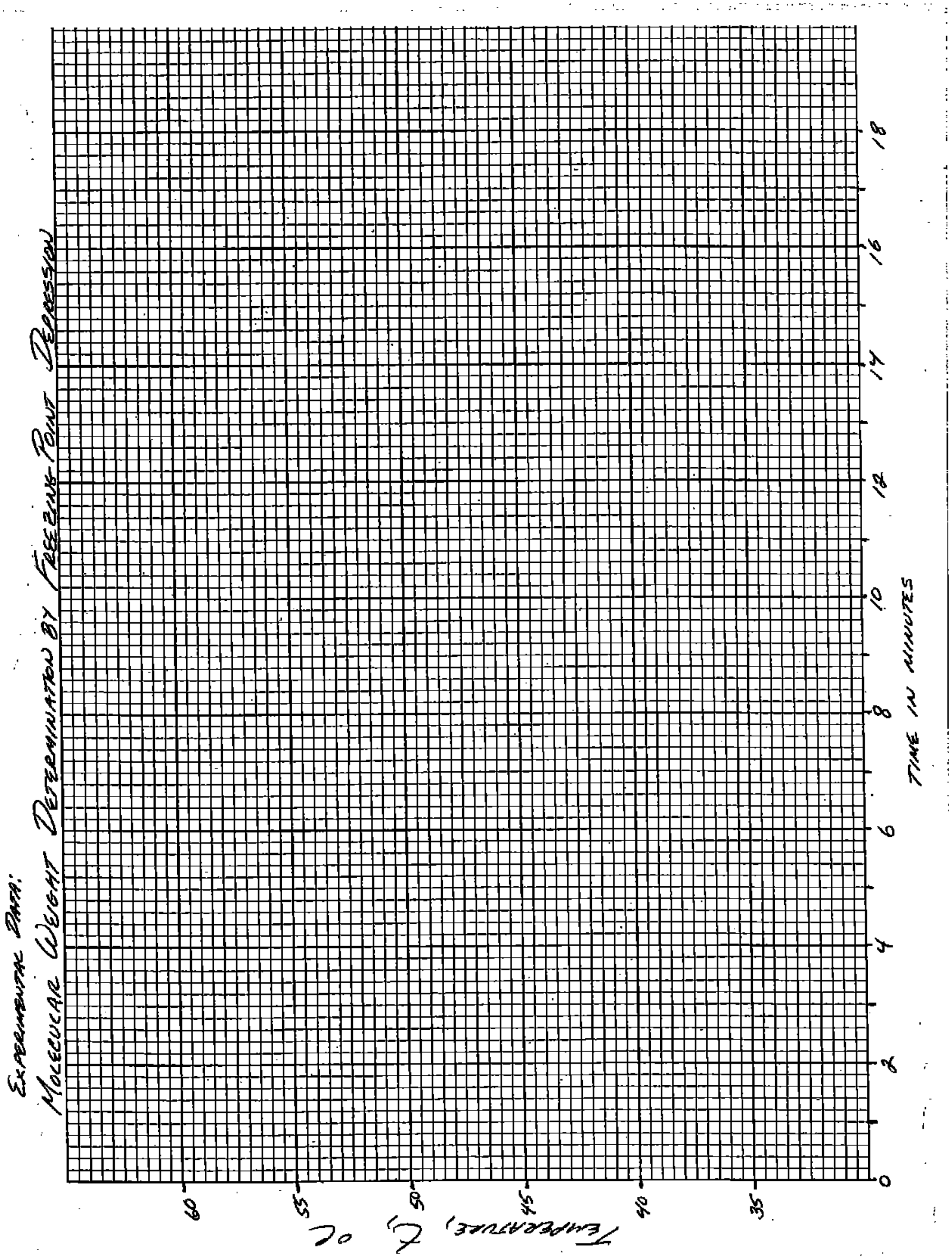
% Error ________________

C. Time Temperature Readings

Time (min)	Pure PDCB	Solution I	Solution II	Time (min)	Pure PDCB	Solution I	Solution II
0				4.5			
0.5				5.0			
1.0				5.5			
1.5				6.0			
2.0				6.5			
2.5				7.0			
3.0				7.5			
3.5				8.0			
4.0				8.5			

Estimation of Freezing Point

On the graph paper provided, plot your temperature vs. time readings for pure paradichlorobenzene (PDCB) and each run of the two solutions. To avoid overlapping graphs, add four minutes to all observed times in making the graph for the cooling curve for pure PDCB. Add three minutes to all times for solution I and add two minutes to all times for solution II. The freezing point of the liquid may, in each case, be taken to be the point of intersection of the approximately straight line portions of the cooling curve.



ADVANCE STUDY ASSIGNMENT: Determination of Molecular Weight by Freezing Point Depression

1. A student determines the freezing point of a solution of 1.96 g of naphthalene in 25.64 g of paradichlorobenzene. He obtains the following temperature-time readings.

Time (min)	0	1/2	1	1 1/2	2	2 1/2
Temperature (°C)	59.7	58.0	56.5	54.8	53.4	52.1

Time (min)	3	3 1/2	4	4 1/2	5	5 1/2
Temperature (°C)	50.9	49.5	48.4	48.6	48.7	48.6

Time (min)	6	6 1/2	7	7 1/2	8
Temperature (°C)	48.5	48.4	48.3	48.2	48.1

(a) Plot these data on the graph paper provided. Estimate the freezing point of the solution to ±0.1°C by determining the intersection of the straight line portions of the cooling curves.

______________°C

(b) Taking k_f for paradichlorobenzene to be 7.10, calculate the molecular weight of the solid. Assume 53.0°C to be the freezing point of pure paradichlorobenzene.

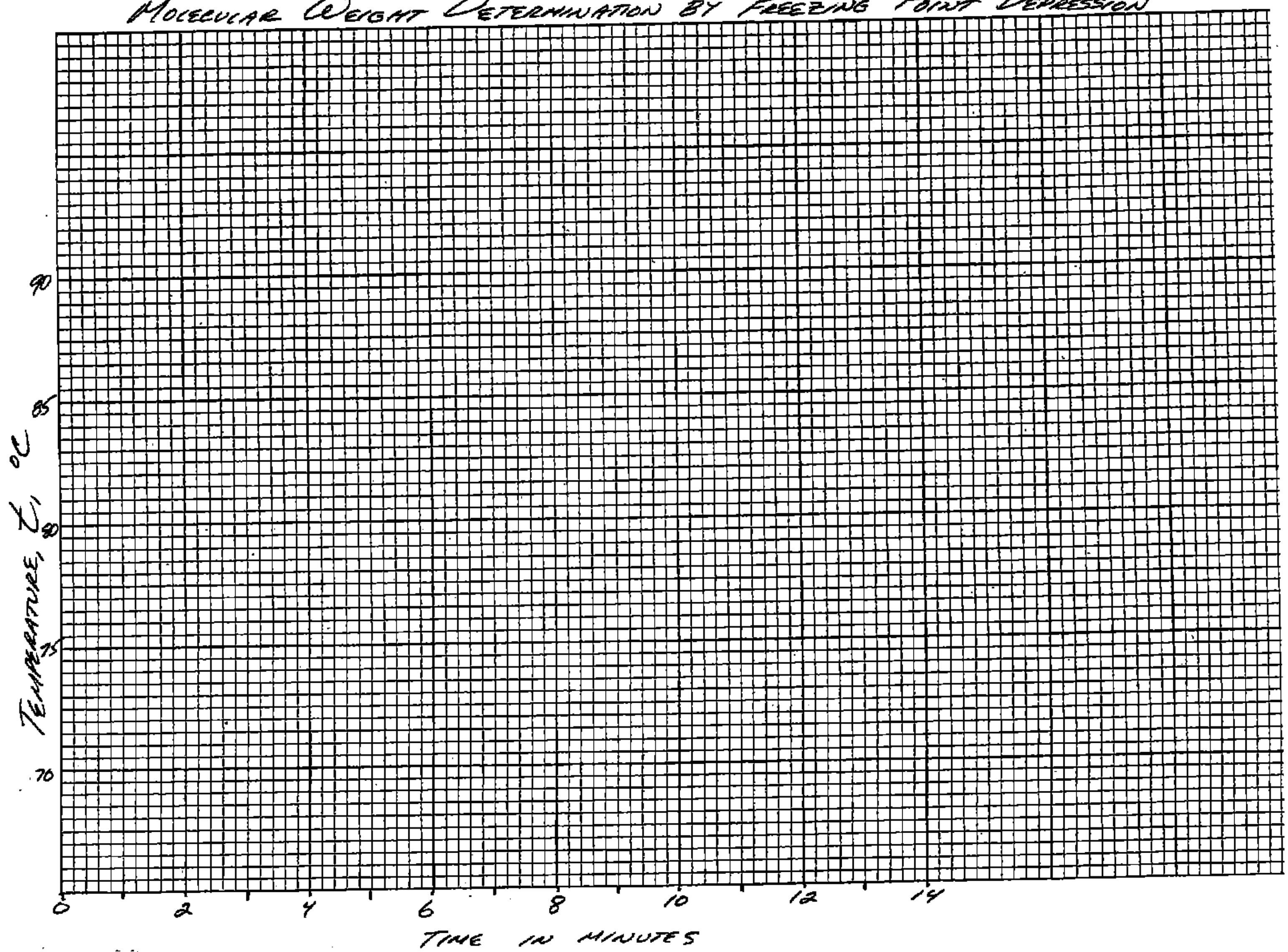
REWRITTEN FORM OF EQ (2):

$$GMW = \frac{(g\ \text{SOLUTE})(k_f)}{(\Delta T_f)(\text{Kg SOLVENT})}$$

NOTE: k_f HAS UNITS OF °C/m OR $\frac{(°C)(\text{Kg SOLVENT})}{(\text{MOLE SOLUTE})}$

ADVANCED STUDY ASSIGNMENT:

MOLECULAR WEIGHT DETERMINATION BY FREEZING POINT DEPRESSION



2. Precise freezing point determinations show that Equation 2 is really valid only for dilute solutions and that at high concentrations, the molecular weights obtained are appreciably in error. By calculating apparent molecular weights at various concentrations by Equation 2 and extrapolating those values to zero concentration, one can obtain the best value possible for the molecular weight of a given solute.

Sucrose solutions in water, in very precise experiments, are found to have the following freezing points:

$m = \frac{|\Delta T_f|}{k_f}$ $MW = \frac{(g\ sucrose/kg\ H_2O)}{m}$

g sucrose/kg H_2O	T_f, °C	m(effective)	MW (apparent)
100	−0.56	______	______
200	−1.15	______	______
400	−2.42	______	______
600	−4.05	______	______

Given that k_f for water is 1.86, use Equation 2 to calculate the effective molality m and the apparent molecular weight of sucrose in each solution. Make a graph of MW apparent vs. g sucrose present, and extrapolate the line to g sucrose equals zero to find the best value of the molecular weight of sucrose. (We will not use this procedure in the experiment you perform, since experimental errors are too high. Under such conditions, averaged results are probably best.)

APPARENT MW VS. g SUCROSE IN SOLUTION
(THE EFFECT OF CONCENTRATION ON COLLIGATIVE PROPERTIES)