COLLIGATIVE PROPERTIES

Purpose

The purpose of this experiment is to investigate colligative properties of solutions and how they can be used to determine molecular weight of solute.

Discussion

From the Clausius-Clapeyron equation,

$$\ln \frac{P_2}{P_1} = \frac{\Delta H \left(T_2 - T_1\right)}{R T_2 T_1} \qquad (1)$$

the vapor pressure of a solution of a non-volatile solute may be compared to that of the pure solvent. It can be shown that the boiling point elevation is

$$\Delta T_b = \frac{R T_0^2 M_1}{\Delta H_V} m \qquad (2)$$

where T_0 is the boiling point of the solvent, M_1 is molecular weight of solvent, ΔH_V is heat of vaporization of solvent, and *m* is the molal concentration. This equation is valid for ideal solutions and for small temperature changes.

The equation may be rewritten as

$$\Delta T_b = K_b m \qquad (3)$$

where K_b is the molal boiling point constant. Since the molal concentration is

$$m = \frac{W_2 / M_2}{W_1} \qquad (4)$$

where,
$W_2 = \text{mass of solute in grams}$,
$M_2 = \text{molecular weight of the solute}$,
$W_1 = \text{mass of solvent in grams}$

Combining both equations the molecular weight of the solute is

$$M_2 = \frac{K_b W_2}{\Delta T_b W_1} \qquad (5)$$

Analogous equations may be derived for freezing point depression.

$$\Delta T_f = K_f m \qquad (6)$$

$$M_2 = \frac{K_f W_2}{\Delta T_f W_1} \qquad (7)$$

Values of K_b and K_f are best determined experimentally, but may be determined from equation 2, as presented in the following table:

Solvent	B.P. (°C)	K_b (°C / molal)	M.P. (°C)	K_f (°C / molal)
Water	100.0°	0.52	0.0°	1.86
Benzene	80.2°	2.53	5.50°	5.12
Carbon Tetrachloride	76.6°	5.03		
Camphor			178.0°	37.7
Cyclohexane			6.6°	20.4

Equipment and Chemicals

Boiling Point:

Cottrell boiling point apparatus, Beckman thermometer, micro-burner, solvent (CC14), naphthalene, other solute ("unknown", diphenyl, benzoic acid, salicylic acid, *p*-nitrotoluene.

Melting Point:

Beckman freezing point apparatus, Beckman thermometer, cyclohexane, naphthalene, other solute ("unknown", such as p-dichlorobenzene, biphenyl, p-bromochlorobenzene).

Directions

Boiling Point:

1. Pipet 75 *ml* CCl_4, <u>with a bulb</u>, into the apparatus.

2. Insert Beckman thermometer. Note: this is a special thermometer with a six degree range. Each division is 0.01°. The mercury in the reservoir may be varied to coincide with the desired temperature. Thus, absolute temperatures are not measured, only temperature changes. A hand lens may be used to facilitate reading the thermometer.

3. .Boil solvent gently and determine boiling point. The thermometer bulb must be in contact with the boiling solution, not the condensing vapor which is pure solvent. Take several readings, which should agree with ± 0.003°.

4. Add an amount of naphthalene which will give a 1-2° temperature change. Measure the boiling point as before. (Use pellet press to facilitate sample handling.)

5. Add another quantity of naphthalene and again determine the boiling point.

6. From the data determine two values of K_b and the average K_b. (Use a rearranged equation 5.)
7. Pour solution into waste solvent bottle, not the drain.

8. Repeat steps 1 - 5 with an "unknown" instead of naphthalene.

9. Determine average molecular weight of "unknown". Use equation 5.

Directions

Melting Point

1. Pipet 20 *ml* (to nearest 0.01 *ml*) cyclohexane into apparatus.

2. Place tube in larger test tube (air jacket) which is submerged in ice bath. Freezing point of cyclohexane is measured with Beckmann thermometer to nearest 0.002° on a cooling cycle. Melt and repeat.

3. Dissolve about 0.03 g (measured to ± 0.0001 g) naphthalene. To determine melting point, the solution is frozen to a slurry, the test tube is placed in the air jacket, and the solution is allowed to warm to several degrees above the melting point. Record the temperature at 30 second intervals. Plot temperature vs. time. The melting point is the intersection of the two straight-line portions of the curve. Repeat until melting points differ by no more than 5%.

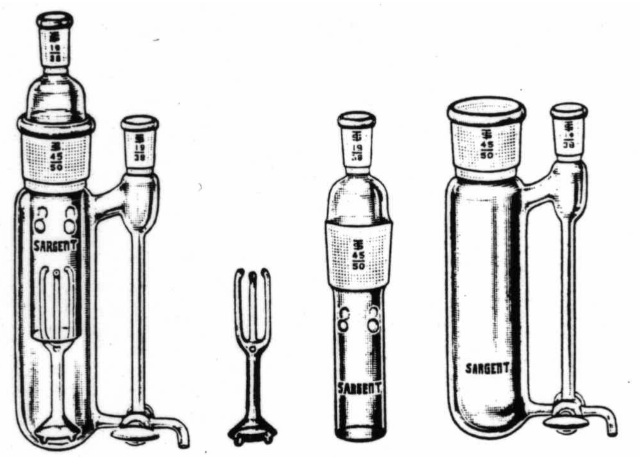
4. Add another quantity of naphthalene and again determine melting point.

5. From the data determine K_f.

6. Pour solution into waste solvent bottle, **<u>not</u>** the sink.

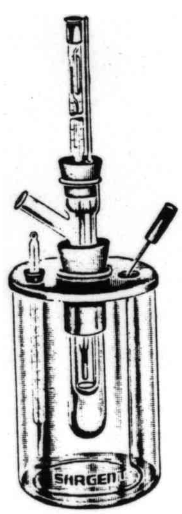
7. Repeat steps 1 - 4 with an "unknown" instead of naphthalene.

8. Determine molecular weight of "unknown".



Molecular Weight Apparatus-Boiling Point, Cottrell-Choppin, T. Grindings, PYREX Brand Glass.

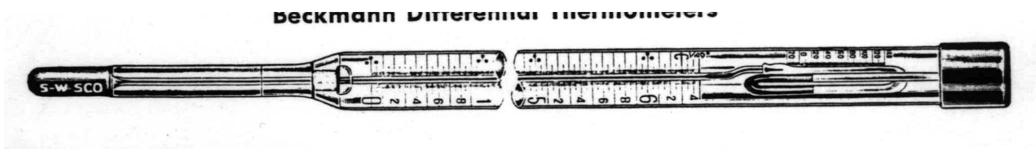
Basic Cottrell design, but of heavy construction with separate pump, reducing fragility and a three way stopcock permitting the withdrawal of samples from boiling tube or condenser or the return of condensate to the vessel. For technique, refer to “Journal of Chemical Education,” 24, 491 (1947). For thermometer with T grinding, see S-62004. For condenser, see S-22530-B. T grindings, outer part, No. 19/38 are provided to receive thermometer and condenser. The inner and outer elements are joined by a T grinding No. 45/50. Overall height, 310 *mm*: overall width, 115 *mm*.



Molecular Weight Apparatus- Freezing Point, Beckmann

Improved form, intended for use of sample pellets prepared in presses. Consists of a freezing point tube, 190 *mm* by 25 *mm*, with a side tubulature for the introduction of pellets, tub being supported by a rubber stopper in an air jacket tube 150 x 37 *mm* which rests in a corresponding hole in a nickel plated brass cover fitted to a glass freezing job, S-43725-D.

The freezing point tube is equipped with stopper through which are inserted a Beckmann thermometer and a chromel wire stirrer, the latter operating through a small piece of glass tubing inserted in the stopper. The internal stirrer is finished in a ring form agitating end which moves vertically within the freezing point tube and is so adjusted as to clear the Beckmann thermometer bulb when located in the center of the tube.



Thermometer-Beckmann Differential, Upward Scale

For accurate measurements of very small temperature differentials such as those encountered in boiling point determinations and calorimeter measurements. The range covers approximately 5°C graduated in 1/100 subdivisions. Has a mercury reservoir with auxiliary scale providing a rough indication of the amount of mercury to be trapped in the reservoir to provide the desired operating range. A dropping trap is included. This instrument can be used only for determining temperature differences.

Thermometer-Beckmann Differential, Downward Scale

Similar to the 14-5905 Thermometer, but for measurement of small differentials in freezing point and molecular weight determinations, and with scale reading downward. Subdivided to 1/100°.