MOLECULAR WEIGHT MEASUREMENT

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Introduction

The importance of molecular weight determinations in estimating the usefulness of polymeric materials has increased the emphasis in recent years on measurements used to calculate this value. The accuracy to which various colligative properties of solutions can now be measured has extended the range of these measurements from small molecules to compounds having molecular weights of hundreds of thousands. Of more importance to this Laboratory, is that increased accuracy also permits molecular weight determinations of new synthetic materials which have molecular weights of less than 1000 but which are only sparingly soluble in most organic solvents.

Ebullioscopy

Boiling point elevation or ebullioscopic measurements give the molecular weight of a compound through the following relationship:

$$\Delta T = \frac{RT_o^2}{L_e} \frac{\bar{V}C}{M}$$

where:

ΔT = boiling point elevation

R = gas constant

T_o = boiling point of solvent

$\bar{V}$ = molar volume of solvent

L_e = molar heat of vaporization

C = concentration of compound in g/ml

M = molecular weight of compound

The 1919 invention of the Cottrell vapor lift pump made it possible to measure the actual boiling point of the solution making this measurement more meaningful. In recent years improvements in the design of ebulliometers to prevent super heating, the use of pressure regulators to avoid errors due to atmospheric pressure changes, and the use of new temperature detectors have greatly increased the accuracy of this measurement.

Using values for a typical solvent, T_o = 353°K, $\bar{V}$ = 96 cc, L_e = 7.3 X 10^3 cal/mole, a concentration of 1 mg/ml of a compound having a molecular weight of 1000 will produce a boiling point change of 3.4 X 10^{-3} °C. While this temperature change is too small to be detected by a Beckmann thermometer, temperature differences of 6 X 10^{-5} °C can be detected using thermistors [1]. Using an 80 junction copper-constantan thermopile, the detection of a temperature difference of 1.5 X 10^{-5} °C in an ebulliometer has been reported [2]. However, the development of commercial instruments for ebullioscopic measurements to this degree of accuracy is lagging.

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Cryoscopy

The freezing point depression equation for molecular weight determination is similar to that given above for ebullioscopy:

$$\Delta T = \frac{RT_o^2}{L_f} \frac{\bar{V}C}{M}$$

where T_o is now the freezing point of the solvent and L_f is the molar heat of fusion of the solvent.

For a typical organic solvent $T_o = 279°K$, $\bar{V} = 89$ cc, $L_f = 2.4 \times 10^3$ cal/mole, so that a concentration of 1 mg/ml of a compound having a molecular weight of 1000 will produce a temperature change of 5.9×10^{-3} °C, which can of course, be detected using thermistors, thermopiles, or liquid filled differential thermometers.

However, there are numerous solvents which have lower heats of fusion and would produce temperature changes more easily detectable, using the same concentration. The investigation and use of these solvents has not been fully exploited. Rast (3) demonstrated the use of camphor as a solvent. Cyclohexanol would produce a change of .078°C, symmetrical difluorotetrachloroethane would produce a temperature difference of .021°C under the above conditions. The limited solubility of many of the new metallo-organic and inorganic polymers in the usual cryoscopic solvents indicates the desirability of determining the cryoscopic constants for other solvents, and developing equipment which may be used over a wide range of melting points.

Vapor Pressure Lowering

The addition of a substance into a solvent lowers the vapor pressure of the solvent. This vapor pressure lowering is measured indirectly in the ebullioscopic and cryoscopic measurements. The direct measurement of vapor pressure depression has not been widely used for molecular weight measurements because of the experimental difficulty in measuring small pressure differences.

The relationship between pressure change and molecular weight is:

$$\Delta p = P_o \, \bar{V}\frac{C}{M}$$

where P_o is the vapor pressure of the solvent and the other symbols are as given above.

At 40°C a concentration of 1 mg/ml of a compound of molecular weight 1000 in a typical organic solvent will give a vapor pressure depression in the order of 1.6×10^{-2} mm of Hg (2.1×10^{-5} atm).

An electronic differential micromanometer capable of measuring these small pressure differences was developed for Materials Central by the Arthur D. Little Company. This instrument uses a "microphone condenser" principle similar to that used in non-dispersion infrared analyzers. The pressure sensor contains an aluminized "Mylar" film diaphragm which separates the vapor above the solvent from that above the solution. This diaphragm is one plate of a condenser. The other plate is a fixed electrode mounted

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a short distance from the diaphragm. This condenser is part of the tuning circuit of a self excited oscillator. The spacing between the electrodes which is determined by the pressure difference in the system causes a change in frequency in the circuit measured by a frequency counter.

A sensitivity of better than 50 cycles/micron is readily achieved. The frequency can be measured to ± 1 cycle/sec. The instrument is calibrated using an inclined oil manometer or using dilute solutions of compounds with known molecular weights. Vapor pressure depressions of 2×10^{-5} mm can be measured.

The cells containing the solvent and solution and the pressure sensor are immersed in an oil bath usually maintained at 40°C though other temperatures can be used if more favorable for the system being studied.

It is necessary to degas the system completely before making measurements. This is accomplished by freezing and pumping the system to a pressure of about a tenth of a micron, several times.

Figure 1 shows the cabinet containing the oscillator and frequency counter, the pressure sensor, and a cell which contains the solvent and four solutions of varying concentration with valves for isolation of the various solutions.

Figure 2 is a typical calibration curve. The sensitivity calculated from this curve is 56 cycles/micron.

Although considerable time is needed to make a measurement, the instrument is capable of good accuracy.

Within the last year or so an instrument which measures vapor pressure lowering in-directly at temperatures other than the boiling or freezing point of the solvent has become commercially available. The "vapor pressure osmometer" measures the temperature change caused by solvent vapor condensing on a thermistor containing a drop of a solution. Measurements can be made quickly and an accuracy of 1 percent for molecular weights up to 5000 is claimed. This instrument has been described by Hill (4) and Baldes (5) and by Neumayer (6).

Isopiestic measurements in which the solvent and solution are allowed to come to equi-librium in a closed system, and volume change used to calculate the vapor pressure difference will give the molecular weight. However, long periods of time are usually required to attain equilibrium.

Osmometry

The relationship between osmotic pressure and molecular weight is:

$$\pi = RT\frac{C}{M}$$

where π = osmotic pressure and the other symbols are as above. At a temperature of 300°K (R in gm.cm.), a concentration of 1 mg/ml of a compound of M = 1000 will produce an osmotic pressure of 25.4 gm/cm^2 (2.5 $\times$ 10^{-2} atm). This is by far the largest change in a measured value for the techniques discussed. Osmotic pressure changes are there-fore more amenable to high molecular weight measurements. The retentiveness of the

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osmotic membrane determines the minimum molecular weight which can be measured. Although 15,000 is about the lower limit for commercial gel cellophane membranes, recent experiments with other films indicate much smaller molecules can be retained.

We have used the Stabin modification of the Zimm-Myerson osmometer which is a high speed static type. A comparison between this instrument and its earlier modification indicates that the time required to reach equilibrium is only 1/6th of that required with the earlier instrument.

In the discussion of various techniques, ideal solutions were assumed. Corrections for nonideality are normally needed, the simplest of which is extrapolation to infinite dilution. For osmotic measurements:

$$\left(\frac{\pi}{C}\right)_0 = \frac{RT}{M}$$

is usually used for calculations.

Other techniques for measuring molecular weights include end group analysis either by titration or quantitative light absorption analysis, x-ray analysis for crystalline polymers, light scattering, intrinsic viscosity and an ultracentrifuging. The latter three are usually applied only to very high polymers and do not give results directly comparable with the number average obtained from colligative properties.

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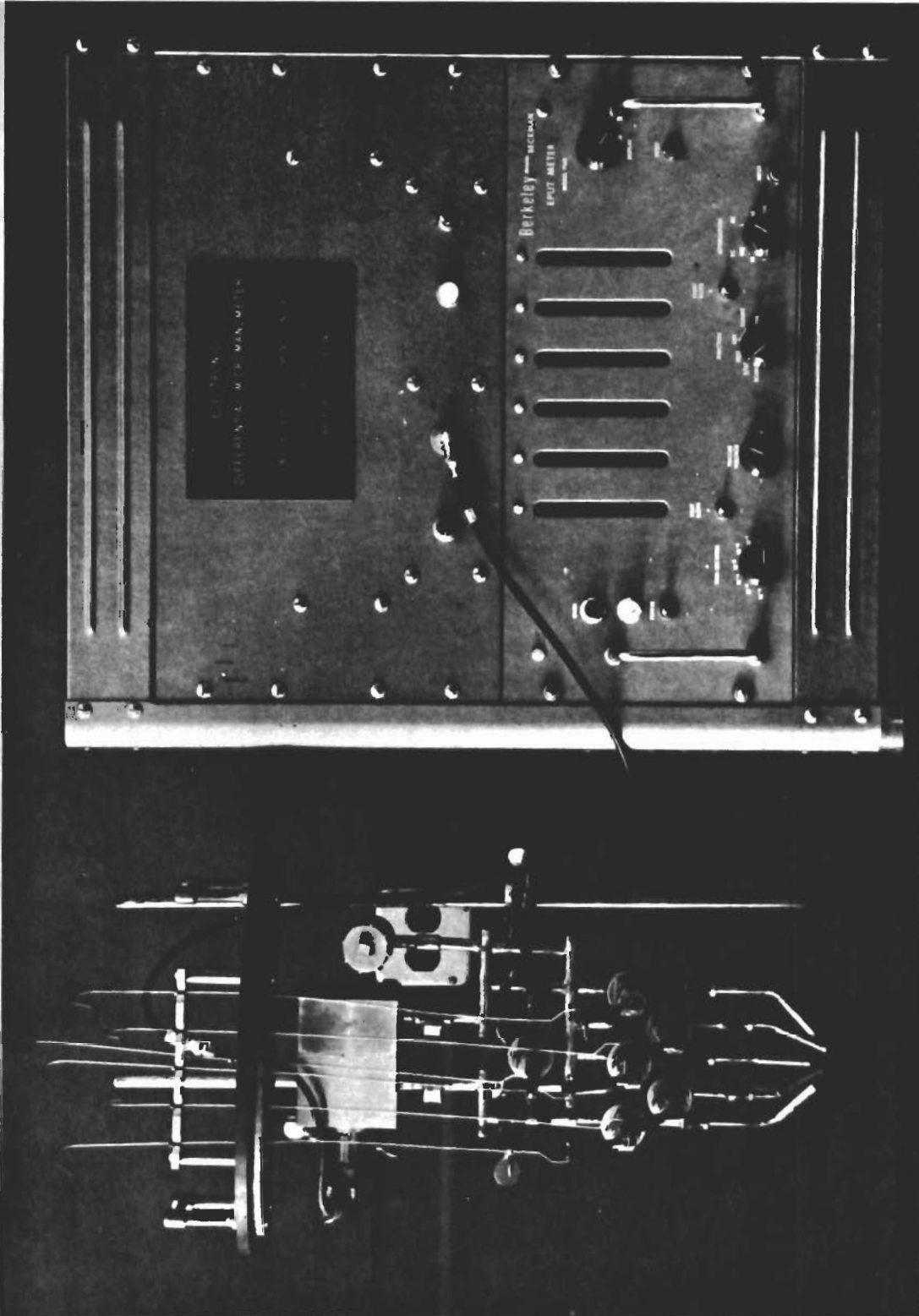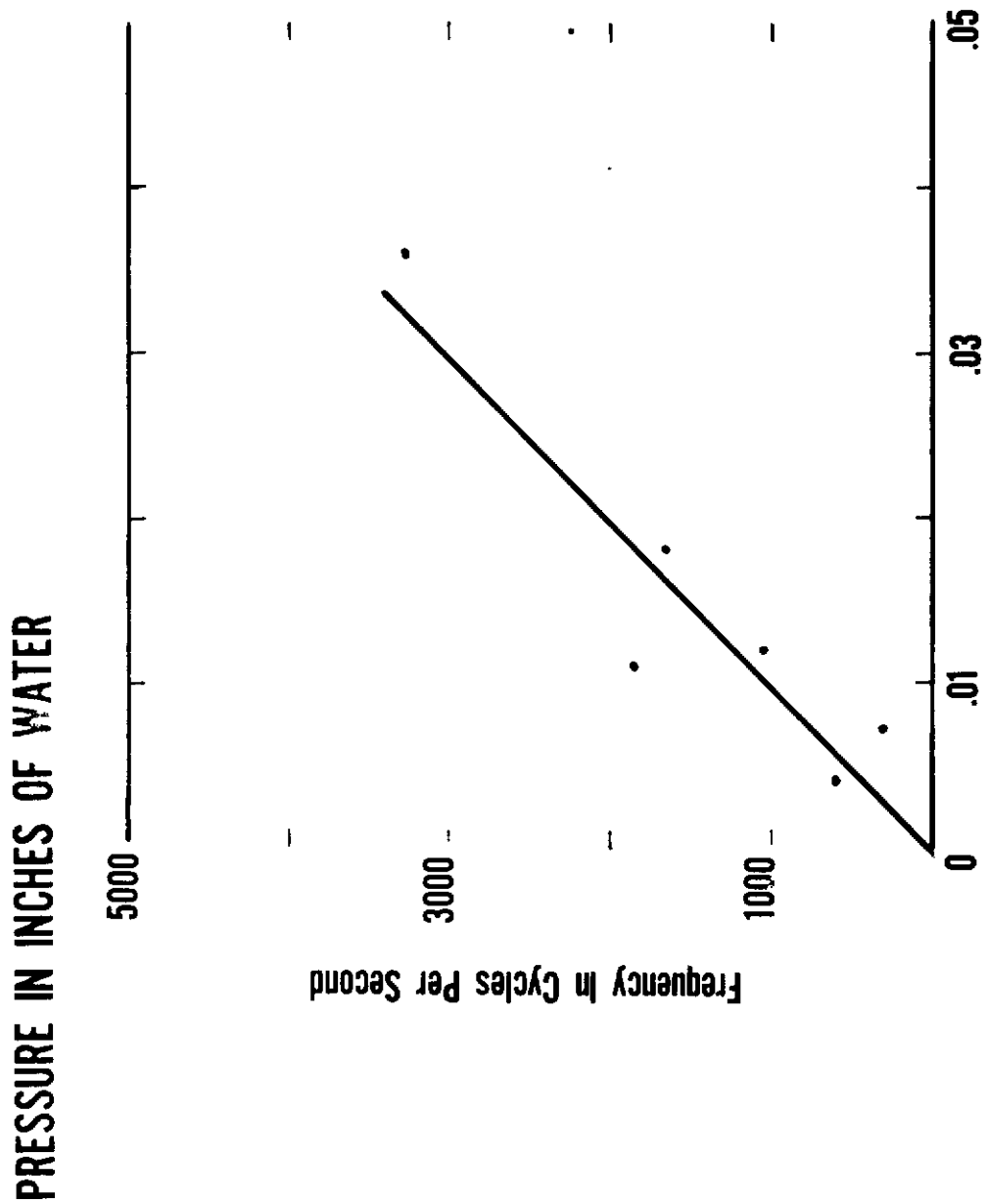EXTERIOR OF ELECTRONIC CABINET & ASSEMBLY

Figure 1.

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Figure 2.

PRESSURE IN INCHES OF WATER

Frequency In Cycles Per Second

5000

3000

1000

0   .01   .03   .05