

# Molecular Weight Determination in Aqueous and Nonaqueous Solvents I. Instrumentation

By FRANK M. GOYAN and RICHARD D. JOHNSON

The apparatus previously used by Goyan and Johnson to study colligative properties has been improved. Provisions have been made for introducing and removing the sample without disturbing the closed system, and techniques have been developed for using aqueous and nonaqueous solvents interchangeably with the same equipment. The results presented show improvement in rapidity of operation and reliability. Circuitry is basically the same but has been somewhat improved.

THE THERMOELECTRIC METHOD for measuring colligative properties of solutes is becoming increasingly popular for the routine determination of molecular weights (1-3). Modern instrumentation favors the use of thermistors instead of thermocouples for these measurements. Recent studies by the authors (4) suggested a new development in this field which permits the addition of sample solutions without direct observation and without opening the equilibrium chamber. Provision is also made for withdrawing old samples, and the instrument is designed so that only glass and platinum come in contact with solvents or solutions.

The results show that the new instrument makes possible more rapid and accurate determinations than previously. Water and organic solvents may be used with a minimum of difficulty in changing from one solvent to another.

## EXPERIMENTAL

The circuitry and method of measurement used were described under *Phase II* in the previous paper (4). A 6-v. battery was used throughout to power the bridge, and the switches were always arranged in order to utilize the reference thermistor. The only significant improvement in the circuitry was the substitution of a proportional temperature control device<sup>1</sup> for the on-off control previously described; it was modified in order to use a thermistor probe which was inserted in the Dewar flask used as a water bath. All measurements were made at 25.00°. Commercially available chemicals of reagent or equivalent quality were used without purification; ratio-arm settings were 10,000 ohms.

The essential new feature of the instrument is shown in Fig. 1. It consists of two parts—the thermistor holder and the equilibrium chamber. The thermistor holder is one piece of glass made by sealing a tapered capillary tube to the upper part of the outer tube of the holder with a ring seal. This capillary is prepared before the sealing operation so that the tip is small enough to fit alongside the thermistor in the narrow lower part of the holder. The upper part of the capillary where the ring seal is made is a shaped part of the tube from which the capillary was drawn; the shaping is accomplished with a carbon rod sharpened in a pencil sharpener before blowing the bulb needed for the seal. The

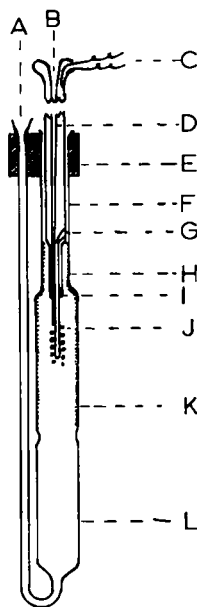


Fig. 1.—Thermistor chamber and holder. Key: A = ground-glass socket to receive ground-glass tip of medicine dropper used for removing waste liquid; B = same for adding sample through inner capillary; C = electric leads from thermistor; D = inner capillary, terminating in tip just above coils on thermistor; E = stopper for holding chamber in water bath; F = narrow portion of chamber; G = wide portion of thermistor holder selected to fit part F; H = platinum gauze for holding solvent and supporting thermistor holder; I = narrow portion of thermistor holder showing dental amalgam seal of thermistor and capillary in holder; J = platinum wire (0.013 in. in diam.) coiled in an open spiral from the tip of the filling capillary to beyond the tip of the thermistor; K = platinum gauze for holding solvent by capillary action; L = lower part of chamber for isolating waste from gauze. The figure is drawn to approximate scale. The overall length to the top of the stopper is 18 cm.

tapered tip of a special medicine dropper is ground into this socket after the glass blowing is finished. The thermistor is inserted from the bottom after threading its insulated leads through the outer tube and the upper opening. An open spiral of platinum wire (0.013 in. in diameter) is wound around the lower part of the thermistor and allowed to extend slightly below the end; the tip of the capillary is arranged to deliver liquid along the side of the thermistor just above the platinum spiral where it is drawn into the spiral by capillary action. The spiral and capillary are self-cleaning either with solvent or by rinsing with the next solution to be used. A 5-ml. sample is adequate for several determinations; 0.5 ml. would be sufficient if the spiral were first washed with solvent, dried, and

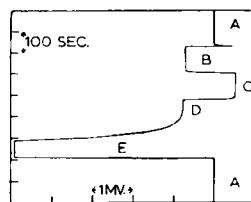


Fig. 2.—Tracing of a typical recording. Key: A = switch open; B = final equilibrium; C = displacement produced by changing the decade resistance box by 100 ohms; D = first indication of equilibrium; E = start.

Received June 3, 1963, from the School of Pharmacy, University of California Medical Center, San Francisco. Accepted for publication July 19, 1963.

The authors gratefully acknowledge the support from the Academic Research Funds, University of California, San Francisco, and Grant 5-TL-GM-728-01 from the National Institutes of Health, U. S. Public Health Service, Bethesda, Md.

Presented to the Scientific Section, A. Ph. A., Miami Beach meeting, May 1963.

<sup>1</sup> Electron-O-Therm Sr., model 148, Technical Equipment Co., Walnut Creek, Calif.

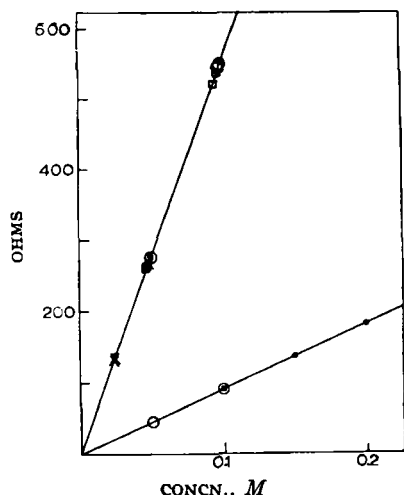


Fig. 3.—Calibration chart. The steeper line represents readings with benzene. Key: ● = benzil and sucrose; ○ = diphenyl and dextrose; X = anthracene; □ = naphthalene.

allowed to come to temperature equilibrium in the chamber.

The equilibrium chamber is made with an enlarged portion to provide free fall of drops from the thermistor. A smaller upper portion is just large enough to accept the thermistor holder. In making this chamber, platinum gauze (three wires per millimeter) is fitted to the inside of the upper part of the large tube before sealing the lower end; it is held in place by a constriction made after the gauze is inserted. The gauze lining the lower part of the smaller tube is inserted after the glass blowing is finished and serves to check the downward slipping of the thermistor holder at a point which places the tip of the thermistor near the geometrical center of the larger cylinder of gauze.

In use, a sample is drawn into the special medicine dropper which fits the upper ground-glass attachment to the capillary. The sample is forced through the capillary and excess allowed to drop to the bottom of the equilibrium chamber. The excess can be withdrawn through the small tube (Fig. 1) which also terminates with a ground-glass connection to a different medicine dropper used to withdraw liquid that accumulates in the bottom of the chamber. While these operations are performed, all parts of the apparatus below the stopper are in the Dewar flask covered with water. Inspection of this operation is seldom necessary.

#### RESULTS

Figure 2 shows the results obtained in a typical case. Millivolt readings are converted to ohm readings by the method described earlier (4). Equilibrium is attained in 400 seconds and in half that time significant readings can be taken.

TABLE I.—RELATIVE RESISTANCES OF THE THERMISTOR<sup>a</sup>

Substance	Concn., <i>M</i>	Ohms
Benzil (in benzene)	0.100	554
	0.050	277
	0.025	138
Naphthalene (in benzene)	0.100	538, 523
	0.050	265, 262
Anthracene (in benzene)	0.050	270, 270
	0.025	137, 135
Diphenyl (in benzene)	0.100	550, 546
	0.050	277, 277
Sucrose (in water)	0.200	184
	0.150	138
	0.100	92
Dextrose (in water)	0.100	92
	0.050	46

<sup>a</sup> Readings subtracted from solvent readings.

TABLE II.—RESULTS OF MOLECULAR WEIGHT CALCULATIONS<sup>a</sup>

Substance	<i>M</i> Concn. (graph)	Mol. wt. (calcd.)	% Error
Naphthalene, mol. wt. = 128.2	0.0975	131.2	2.3
	0.0950	134.5	4.9
	0.0481	133.0	3.7
	0.0475	134.5	4.9
Anthracene, mol. wt. = 178.2	0.0488	182.0	2.1
	0.0488	182.0	2.1
	0.0248	179.0	0.4
	0.0245	182.0	2.1
Diphenyl, mol. wt. = 154.2	0.0994	155.2	0.6
	0.0988	156.0	1.2
	0.0500	154.2	0.0
	0.0500	154.2	0.0
Dextrose, mol. wt. = 180.2	0.1000	180.2	0.0
	0.0500	180.2	0.0

<sup>a</sup> Solvents given in Table I.

Figure 3 and Table I show the results obtained with two different solvents—water and benzene. Table II shows these results converted to molecular weights; the required calibration was established with benzil in benzene and sucrose in water. In Table II, the column headed—*Concn. (graph)* represents the molar concentration of the reference material corresponding to the reading obtained. In Table I, *Concn. M* refers to the nominal molar concentration of each solution weighed out on the basis of the theoretical molecular weight. The calculated molecular weight shown in Table II is simply weight per liter (known from weight and volume) divided by moles per liter read from the calibration chart.

#### REFERENCES

- (1) Wilson, A., Bini, L., and Hofstader, R., *Anal. Chem.*, 33, 135(1961).
- (2) Tomlinson, C., *Mikrochim. Acta*, 3, 30(1961).
- (3) Pasternak, R., Brady, P., and Ehrmantraut, H., "An Instrument for the Fast and Precise Determination of Molecular Weights," Mechrolab, Inc., Mountain View, Calif., 1961.
- (4) Goyan, F. M., and Johnson, R. D., *THIS JOURNAL*, 52, 390(1963).