TECHNICAL ARTICLES

Improved Thermoelectric Osmometer

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Abstract ☐ The original osmometer described by Goyan and Johnson was improved, resulting in a 10-fold increase in sensitivity and greater convenience in use. A concentration change of 0.001 molal is easily detected in aqueous solutions; however, the instrument may be used without modification for nonaqueous solvents. A new measuring circuit and a new temperature control system are described. The original features for introduction and removal of samples are retained. Solutions contact only glass and platinum. Valuable compounds may be recovered unchanged by evaporation. The instrument may be used in various analytical applications, ranging from the study of complex formation to the determination of concentrations of known solutes. It is useful for the determination of molecular weights and for direct measurement of osmotic properties of solution.

Keyphrases ☐ Osmometer, thermoelectric—improved design ☐ Thermoelectric osmometer, improved—diagram ☐ Temperature control system, osmometer—diagram ☐ Sucrose standard—osmometer calibration

Goyan and Reck (1) used thermocouples to show that the reference junction and sample junction of the conventional thermoelectric osmometer need not occupy the same air chamber. Each may occupy separate cells positioned in a constant-temperature bath so both are subjected to the same minor temperature fluctuations. Goyan and Johnson (2) developed a circuit which permitted the substitution of thermistors for thermocouple junctions in separate chambers saturated with solvent vapor. They showed that the slight heating caused by relatively high battery voltages used to power the bridge did not produce a significant error. A 6-v. battery is now used routinely for this purpose.

Later, the same workers (3) developed a cell or chamber for the sample thermistor that permitted the introduction and removal of sample with fitted medicine droppers without exposing the thermistor to outside air or allowing solvent or sample to contact any material other than platinum and glass. They showed how this instrument could be used with the bridge and reference thermistor previously described for molecular weight determinations in aqueous and nonaqueous solvents. Solvents may be changed by appropriate rinsing without modification of the instrument because of the platinum–glass construction. Johnson et al. (4) used the same equipment to measure isotonicity values and osmotic coefficients of aqueous solutions of several univalent electrolytes.

In concluding this phase of the work, Johnson and Goyan (5) showed that the calibration data for several different solvents related to their latent heats of vaporiza-

tion approximately as predicted for boiling-point elevation. This established the hypothesis that when the sample is in contact with air saturated with solvent vapor, its temperature is elevated sufficiently to compensate for the vapor pressure lowering caused by the solute. Later experiments with better temperature control showed that this elevated temperature is established in minutes and remains essentially unchanged for hours with the same drop of sample solution, refuting the commonly held belief that all instruments of this type operate on the principle of competitive evaporation rather than an approach to an equilibrium temperature. However, the fact that the shape, size, and position of the sample drop is important in work of the highest accuracy indicates that true equilibrium is not fully attained, although it is approached closely enough to prevent significant change in the concentration of the sample solution during the usual period of observation.

When Borazan (6) elected to use this apparatus to study possible complex formation and self-association of compounds of biological interest, he discovered that higher precision was needed and recommended a program of development designed to accomplish this. The essential changes made by Goyan and Borazan (7) are published in outline form, but it remains for this paper to make them clear and to present additional refinements mentioned briefly in the previous paper. All of the essential features of the Goyan–Johnson instrument are retained while achieving improved accuracy and ease of operation.

DISCUSSION

Measuring Circuit—The bridge circuit described by Goyan and Johnson (2) was used by Borazan (6) and Goyan and Borazan (7) in their work, after achieving a 10-fold increase in the sensitivity of the recorder, bringing its sensitivity to 0–1 mv. Measurement shows that, at this higher sensitivity, one small division on the paper used (2.5 mm.) is equivalent to a 0.7-ohm change in resistance of the thermistor at 25°. Random noise may be estimated to be of the order of 0.1 small division under good conditions so that the sensitivity approaches 0.1 ohm. The thermistors used approximate 100 K ohms with 4% temperature coefficient; therefore, the limit of temperature sensitivity is of the order of 2×10^{-5}° or a concentration discrimination of 1×10^{-4} molal, based on the slope of nearly 1000 ohms/molal for sucrose.

Although there is no need to change the bridge circuit, the modified circuit shown in Fig. 1 offers the advantage of requiring only one decade resistance box. This circuit can be switched so that the box may be substituted for either thermistor when it is desired to follow both temperatures. Another switching mode allows the box to be connected in series with either thermistor. This is an advantage when experimenting with different thermistors because it avoids
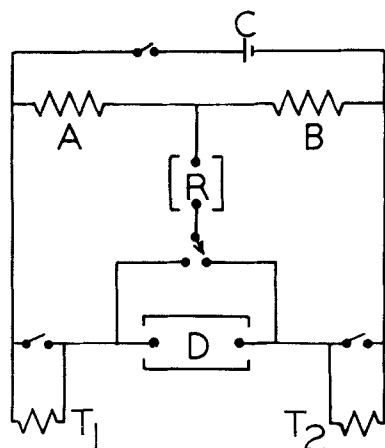
Figure 1—*Measuring bridge. Key: A and B, ratio arm box, 10K ohms each; C, battery (6 v. normally used); D, General Radio Decade Resistance Box Type 7433G. Ser. 543, 7 dials; T_1 and T_2, thermistors (Victory Engineering 51 A 1); and R, Leeds and Northrup Speedomax Recorder Type G with regulated power supply (part No. 099012) and range card (part No. 650999), 0–1- and 0–10-mv. range.*

the need to select the one with slightly lower resistance for use with the sample, as was required before. No attempt was made to calibrate the decade boxes used in either circuit or the resistors used in the ratio arm box. For this reason, minor differences in the slopes of calibration curves may be expected when comparing results from two different bridges and when using the new bridge with interchanged components. This is of little importance because all results in ohms are related to the calibration data obtained for the thermistors and bridge circuit in current use.

Sample Compartment—Figure 2 shows how the sample may be delivered to the platinum spiral surrounding the measuring thermistor. The sample passes through the capillary and continues down the glass body of the thermistor where it is held by capillary action to the loosely fitting spiral of platinum wire (F of Fig. 2 made from 0.33 mm. wire). The spiral is fastened firmly at one point by a second much finer piece of platinum wire. The most important improvement over the earlier design (3) is the short length of glass rod (H of Fig. 2) sealed onto the lower portion of the platinum spiral. This serves to draw away larger drops into the retrieval area so that the spiral and thermistor expose a nearly uniform sample each time the sample is changed.

Another innovation is the air vent (C of Fig. 2). It has always been possible to lift the thermistor holder (B of Fig. 2) for the purpose of renewing the solvent on the platinum gauze fitted against the inner surface of the chamber. When this is done without the vent, a liquid seal often develops, causing unwanted changes in pressure within the chamber.

All of the advantages of the sample compartment described by Goyan and Johnson (3) are retained. Less than 1 ml. of solution is sufficient for rinsing and establishing a new concentration, although the usual practice is to rinse and fill several times with 0.5-ml. portions. After each filling, most of the excess is removed from the bottom of the cell by means of a medicine dropper with a tip ground to fit the top of the waste tube. It is easy to save the waste solution without contamination when the solute is worth reclaiming by evaporation.

Best results are obtained when the sample compartment is cleaned from time to time with a suitable cleaning solution so that the inner glass surfaces wet easily. Other obvious precautions associated with precise analytical work are important.

Water Bath—Figure 3 shows a schematic diagram of the water bath built around a 4-l., wide-mouthed, vacuum flask. A brass cylinder fitted around the outside of the mouth of the flask provides a secure anchor for a brass top insulated on the underside with about 2 cm. of plastic foam. This heavy brass cover is provided with four large holes to accommodate the corks used to mount the cells. The stirring shaft passes through a bearing attached to the cover, which also provides a hole for the thermometer. The retaining cylinder extends 1 cm. above the brass cover. This extension serves to hold an inverted cover made of plastic foam and designed to protect the cells from air currents. This cover is split so the front

half is easily removed when changing samples. The brass cover also serves as a firm foundation for attaching aluminum rods to support the cover when it is desired to remove the vacuum flask for cleaning or adjusting the attached frame holding the cells in a vertical position. Uniform stirring is an essential part of the water bath.

Temperature Control—Goyan and Borazan (7) mentioned the occasional use of a servo system to control temperature but were forced to resort to manual control. Either system requires an adequate air bath. The constant-temperature air bath has served well for several years and consists of a chamber 63 cm. deep, 65 cm. wide, and 120 cm. high. It is constructed with double walls packed with insulation on a table 75 cm. high. Access to the interior is provided in front by a sliding double-pane glass window 44 cm. wide. The window slides up and down and closes against a board 41 cm. high inserted in the lower part of the window frame. This arrangement enables the operator to open the window a crack at the level of the top of the water bath. Cloth draped on the lower part of the sliding window further discourages the entrance of outside air while changing samples.

The temperature of the air bath is maintained by means of a special Melabs proportional temperature controller modified to use thermistors as transducers. The bath also contains the cooling coil of a Kelvinator (model 4D2CR) designed as a portable cooler. The refrigeration unit is operated so that the cooling coil is coated with ice and maintained in a plastic bucket secured in the upper part of the bath. The bucket is equipped with a drain to the outside and can be raised and lowered with respect to the coil so as to expose more or less cold surface. A 10-cm. Muffin fan was recently installed to replace the old fan. Either one keeps the air stirred sufficiently so that the cooling unit compensates for heat generated
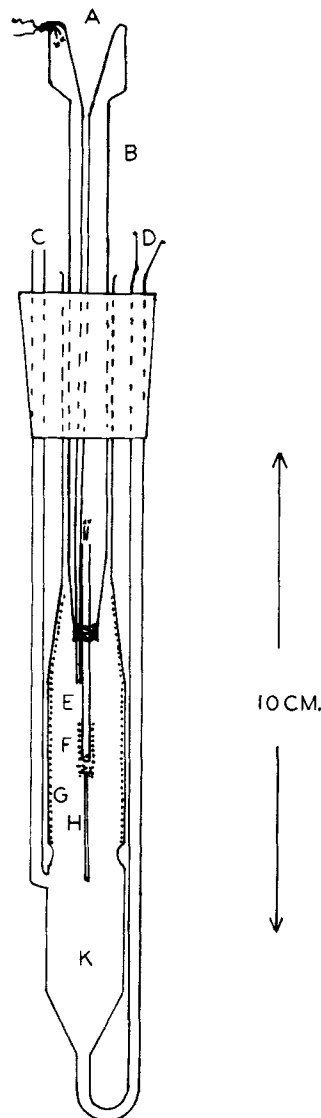
Figure 2—*Sample compartment. Key: A, ground-glass socket for fitted dropper; B, inner tube holding thermistor and capillary; C, air vent; D, ground-glass socket for withdrawing samples after rinsing; E, thermistor (Victory Engineering 51 A1) and tip of capillary sealed at the bottom of tube B with dental amalgam; F, platinum coil for holding sample; G, platinum gauze on inner surface for holding solvent; H, glass rod; and K, lower compartment for collecting rinse.*
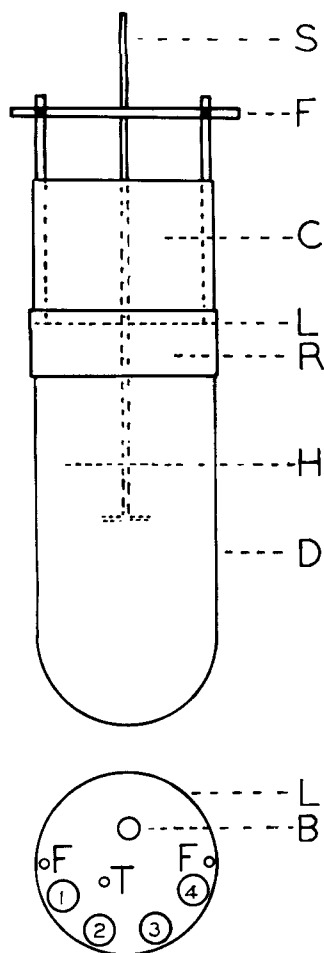
Figure 3—*Water bath (in regulated air bath). Key: S, stirrer rotated by a 300 r.p.m. 2.0 in-oz. Haydon general duty synchronous motor; F, part of standard frame; C, cover made of plastic foam; L, brass cover; R, felt-covered brass cylinder soldered to cover; H, metal cell holder attached to cover; B, bearing for stirrer; T, thermometer; and holes 1–4, location of thermistors, etc., mounted in corks.*

Table I—Standardization with Aqueous Solutions of Sucrose

Molal Concentration	ΔR (ohms), av. of 3	ΔR Calculated from Slope	Difference, ohms	Molal Concentration Calculated
0.01	9.6	9.3	0.3	0.0103
0.02	18.5	18.6	0.1	0.0199
0.03	27.5	27.8	0.3	0.0296
0.05	46.1	46.4	0.3	0.0497
0.1	92.7	92.8	0.1	0.0999
0.2	185.6	185.6	0.0	0.2000

was no need to change the solvent in the reference compartment since its only function was to follow slight variations in the temperature of the water bath. Later it was found that the reference thermistor worked about as well without the platinum when the tip of the thermistor was submerged about 1 cm. below the surface of water contained in the same tube. Care was taken to avoid keeping the amalgam seal under water. In all cases the reference tube is mounted in one of the holes of the cover (Fig. 3) and extends well under the surface of the water. Theoretically, it would seem that the reference thermistor should be arranged in a tube as nearly the equivalent of the sample tube as possible to follow temperature changes at the same rate. However, with the new servo control, this consideration has little practical importance.

Operation—Solutions are prepared and stored in small bottles in the air bath along with a sample of the pure solvent. A medicine dropper, with its tip ground to fit the top of the capillary (A of Fig. 2), is used to transfer about 0.5 ml. of solvent or solution to the

by motors in the air bath as well as for heat coming in from outside. The air temperature inside the bath is adjusted so as to require a minimum of help from the servo system or from manual control of current flowing through the heater in the water bath. At present the air is maintained at 25.1° and the bath at 25.00°. In spite of the apparently tight cover, there is sufficient evaporation of water from the water bath to compensate for stirring and a very small amount of heating current (about 1 v. a.c. across a 17-ohm heater). The heating current varies and is controlled by a servo system or manually, based upon the resistance of a thermistor *versus* a decade resistance box. Even when the control systems are in perfect order, any large change in temperature of the water bath must be made manually by using hot and cold water. The servo system is not designed to handle large amounts of heating current.

Figure 4 is a diagram of the servo system used to control the temperature of the water bath. A separate bridge circuit balances a decade box against a thermistor maintained in the water of the bath. Any off-balance signal of this bridge is amplified and presented to a typical recording potentiometer circuit. However, instead of a mechanical link to a recording device, the servo motor is geared to a variable resistor which controls the current going through the heater. The mechanical link to the servo motor uses a large gear attached to both resistors through a clutch mechanism that allows the servo motor to continue after the resistors have reached their limit. The large gear is meshed with the output of the servo motor. When operating normally, this circuit holds the temperature within 1 × 10⁻⁴°, with changes of this magnitude occurring slowly enough that the reference thermistor compensates for these small changes.
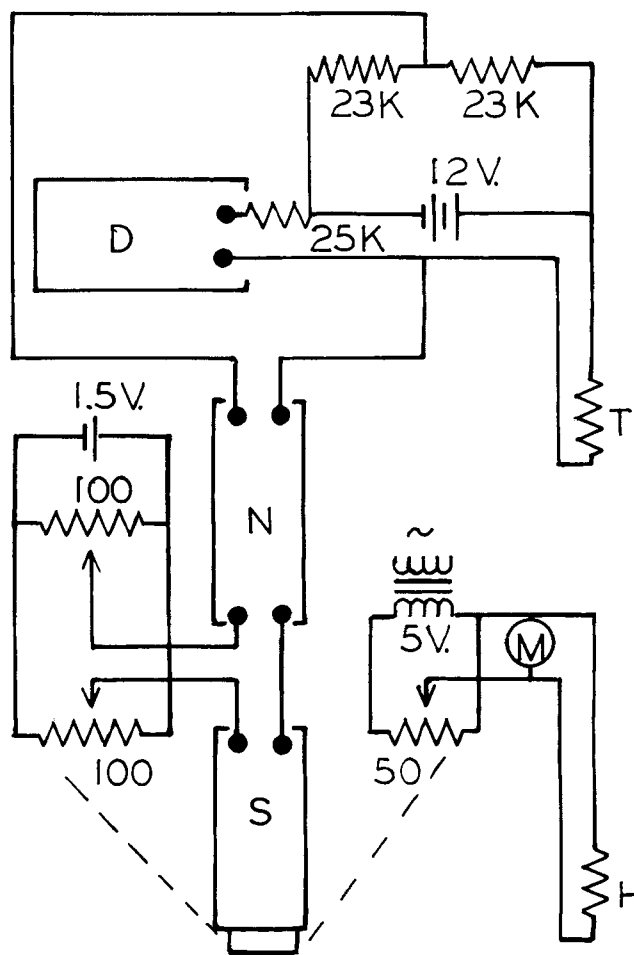
Reference Thermistors—The reference thermistor used in previous studies (2–5) nearly matched the one used for the sample. The resistance of the sample thermistor plus a selected value on the decade resistance box equaled the resistance of the reference thermistor and balanced the bridge. A drop of solvent was placed on a platinum loop in contact with the reference and the whole kept in a tube with fitted platinum gauze on the inner surface also wet with solvent. It soon became apparent that when changing solvents, there

Figure 4—*Servo system. Key: D, Heathkit Decade Resistor model DR-1 (to 1 ohm); N, Leeds and Northrup D.C. Null Detector Cat. 9834; S, Honeywell Brown Electronic continuous balance amplifier and servo motor; M, a.c. milliampmeter converted to a voltmeter; T, thermistor (Victory Engineering 51 A1); and H, heater (approx. 17 ohms).*

capillary and to pass slowly down the thermistor and over the platinum coil (F of Fig. 2). The first portion of this sample serves to rinse the coil, and the last portion is automatically retained by capillary action as the next sample. Before replacing the front half of the cover (C of Fig. 3), all of the fluid accumulated at the bottom of the tube is withdrawn with a different medicine dropper fitted to the waste tube (D of Fig. 2). The waste fluid is collected so far below the working sample that its complete removal is not a matter of concern, although a large accumulation should be avoided.

Within 5 min. after the sample is placed on the coil, the resistance box may be adjusted to approximately its final reading. Any line on the recorder, preferably near zero, may be selected as a null position for the purpose of this initial adjustment. When the recorder shows a vertical line (10–30 min., depending upon solvent and concentration), the resistance box may be changed so as to bring the pen exactly to the selected null position. The new resistance value thus established is recorded for the sample. Exactly the same results are obtained by calculation based on the pen displacement from the null position compared to the displacement caused by changing the decade box by 10 ohms.

Several samples of the same solution are read in this way to test the adequacy of the rinsing when highest accuracy is sought. The second and third measurements, and often the first, agree within 0.4 ohm or better, and undisturbed samples tend to retain their established position within 0.1 ohm. The average values may be plotted directly against concentration, but it is more convenient to obtain ΔR values by subtracting the average for the pure solvent from the resistance reading for each sample (or vice versa if box and reference are in series). These ΔR values may be treated as colligative properties of the various solutions studied (3–5).

Calibration—Sucrose is chosen as a standard substance when working with aqueous solutions. Although not an ideal substance up to 0.2, molal the osmotic coefficients given by Robinson and Stokes (8) may be used to make slight corrections. Table I shows the results obtained using all of the new equipment described. The first column gives the molal concentration, and the second column shows the corresponding ΔR values calculated directly from the measurements, with the exception that for 0.1 molal the tabulated value shows the effect of dividing by 1.008 and the 0.2 molal reading is divided by 1.017 according to the values given by Robinson and Stokes (8) for osmotic coefficients, ϕ, represented in this case by the equation, $\phi = \Delta R_m / \Delta R_i$. The subscripts m and i represent measured and ideal, respectively. The more dilute sucrose solutions studied may be assumed to be ideal without correction.

When ΔR values for an ideal solute are plotted against molal concentration, a straight line results within the limit of concentration studied. In this case, the points fall on the line so closely that a simple plot on a small scale fails to show error. When the data given in the first two columns of Table I are treated by the method of least squares, a slope of 928 ohms molal^{-1} is found. Without including the origin as an experimental point, the intercept is found to be 0.08 ohm. A further test of precision is displayed in the third and fourth columns where, for each solution, a ΔR value is calculated by multiplying concentration by the slope of the line. The difference between the calculated and experimental values is shown in column four. Since, with corrections, sucrose is an ideal substance, any difference between molal and osmolal concentration may be attributed to experimental error. The osmolal concentration for each solution is calculated by dividing the ΔR value by the slope to obtain the values shown in the last column. The average error is 2×10^{-4} molal in concentration units or 0.2 ohm for ΔR.

Nonaqueous Solvents—Earlier work (5) showed that the calibration slopes for nonaqueous solvents are much steeper, as would be

predicted from the lower latent heat of vaporization. While this factor alone may be expected to improve accuracy when converting ΔR values to osmolal concentration, the lower heat of vaporization and larger size of the molecules require a longer time to approach equilibrium. It is assumed that solvent molecules must diffuse through the air space and condense on the sample to elevate the temperature to nearly equilibrium value. Since this source of heat in calories per minute is less than with water, it takes longer to read each sample. As a result, the work with nonaqueous solvents is more difficult, especially if manual temperature control is required continuously. With the servo system described, this problem is eliminated, with the result that the recorder draws out smooth curves ending in vertical lines. Another difficulty is encountered with some nonaqueous systems. The solvent is essentially held in place by capillary action. Careful inspection of the cell from time to time is desirable to avoid attempting to work when the platinum gauze is not holding a sufficient amount of solvent. The gauze should be adjusted to press tightly against the glass.

CONCLUSIONS

The new features described have greatly improved the use of the instrument, both from the standpoint of accuracy and of ease of operation without diminishing any of the original advantages.

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