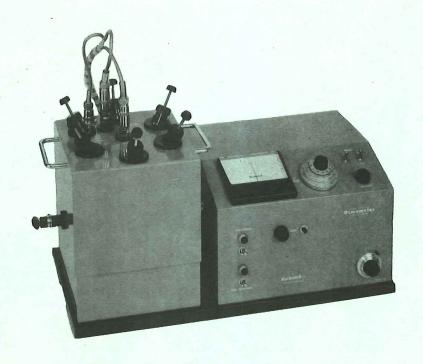
Mechrolab Osmometer*

INSTRUCTION MANUAL



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MODEL 301A OSMOMETER

INSTRUCTION MANUAL

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Figure 1.

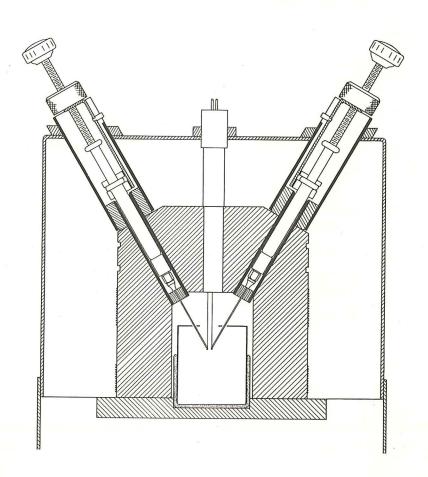


Figure 2.

I. DESCRIPTION

The MECHROLAB Model 301A Osmometer consists of two principal units on a common base. (See Fig. 1). The <u>sample chamber assembly</u> contains the various elements of the Osmometer proper. The <u>control unit</u> houses a Wheatstone bridge, a null indicator, and a heater input control circuit.

The sample chamber assembly comprises the sample chamber with its surrounding thermal block, positioned in and attached to the upper housing by a thick insulating layer of rigid urethane foam. (See Fig. 2). Precise machining provides openings into the sample chamber for the thermistor probe, six syringe assemblies and a viewing path. Another opening permits insertion into the thermal block of interchangeable mercury thermostats, preset to the desired temperature. Low noise connectors on the top of the upper housing join the control unit to the thermistor probe, thermostat, and peripheral electric heating wire through shielded cables.

Two guide pins (not shown in Fig. 2) maintain alignment of the upper assembly and the base assembly. The latter assembly consists of a urethane foam block, bounded by a metal housing, and supporting the sample chamber base plate. A recess in the base plate positions the glass solvent cup and the vapor wick. Raising the upper assembly until it can be removed from the guide pins provides unrestricted access to the sample chamber.

The control unit contains all circuitry required for operation of the instrument. The locations of front panel controls are indicated in Fig. 1. The control unit contains three electrical units: a DC Wheatstone bridge, a fractional-microvolt null detector utilizing a modified Leeds & Northrup amplifier, and a heater control circuit.

Fig. 3 shows the DC Wheatstone bridge circuit. Power is supplied with a mercury cell battery and dropping resistor selected so that about 0.5 volt is applied to the bridge. The ZERO push-button switch disconnects the battery from the bridge but leaves the bridge connected to the null detector. Thus when the needle is centered with this button in, all thermal emfs and other sources of error are compensated. It is important to realize that the ZERO should be checked before each reading of ΔR or re-setting of BALANCE. When the ZERO switch is released, power is restored to the bridge resulting in very slight self-heating (<.001°C.) of the thermistor. Because of this self-heating, the thermistors are slightly unstable for 20 - 30 seconds after the switch is released.

II. UNPACKING AND SETTING UP THE INSTRUMENT

The instrument should be unpacked with care and inspected for any damage that may have occurred in shipping. If damage is suspected, it is advisable to open the container in the presence of the carrier's agent.

Before attempting to set up the Osmometer, please refer to Fig. 1, since the names of the parts indicated thereon are used in the instructions.

A. <u>Sample Chamber</u>.

Open the sample chamber by lifting off the upper assembly. Remove any foreign matter that may have entered in shipment, and clean the metal faces of the upper and base assemblies of the sample chamber to assure good metal to metal contact.

The viewing tube, a short length of black phenolic tubing with internal windows and an angle mirror mounted at one end, will be found in the accessory box. Insert the plain end into the opening in the left-hand side of the upper assembly. NOTE: The tube must be firmly seated to its full depth to prevent drafts which will result in readings which drift.

B. <u>Electrical</u> <u>Connections</u>.

Attach the heater cable to the connector on top of the sample chamber and firmly tighten the collar. Insert the thermostat in the hole next to the heater connection and lock it in place with the set screw in the collar. (A hexagonal key is supplied for this purpose.) Connect the thermostat cable and firmly tighten the collar. Connect the ground wire to a cold water pipe or equally positive ground.

Plug the power cord into an AC line having the voltage and frequency designated for the instrument, and turn on the THERMOSTAT switch. The pilot light will glow until the heater begins to cycle.

C. Thermistor Probe. CAUTION: READ CAREFULLY BEFORE HANDLING PROBE.

The thermistors are small (.043 inch) beads mounted on fine (.004 inch) wire. These wires are in turn welded to heavier stainless steel leads which support the thermistors in the chamber. Because of this construction, which is necessary to thermally isolate the beads, THE PROBE MUST BE HANDLED VERY CAREFULLY.

The probes are shipped in a special, separate container. Two probes are available, one for organic solutions, and one, plainly marked, for aqueous solutions. The thermistor leads of the latter are insulated to prevent shorting by electrolytes. This probe must not be used for organic solvents as they may injure the insulation.

As packed, the thermistor end of the probe is protected by a clear plastic tube. The beads project into this tube about 2 inches, and IT MUST BE REMOVED VERY CAREFULLY to avoid hitting and bending the thermistors, since their position in the chamber is critical to the proper operation of the instrument.

The pin on the side of the probe enters a keyway in the thermal block to prevent turning. To position it properly, point the pin between syringe holes #6 and #1. Hold the probe in a vertical position and carefully lower into hole, paying particular attention that the thin platinum leads are not bent by pressing the beads against the side of the hole. When the probe bottoms and the pin engagement is felt, lock it in place with the set screw in the collar and firmly attach the cable.

D. Syringes.

Assemble the syringes by inserting the plungers through the coil springs with the larger ends of the springs against the flange of the barrel, and attaching the needles. Install the syringes in the holders by backing the knurled feed screws out of the way of the plungers and inserting the syringes in the spring clips with the flange of the syringe barrel in the slot provided. NOTE: Syringes are most easily removed if held parallel to the axis of the holder and pulled directly out of the clip.

Insert the syringe assemblies in the holes #1 to 6 with the withdrawn pins pointing away from the probe. Turn the NULL DETECTOR switch on and rotate the mirror on the tube so that the thermistor beads inside the chamber are visible from normal working position in front of the instrument. Very carefully, lower the #6 syringe while watching the thermistor beads in the mirror. The syringe should bottom in the guide tube assembly with the end of its needle directly above the sample bead (the one near the center of the viewing circle). The gap between the end of the needle and the bead should be sufficiently small (0.010") to allow liquids to easily bridge the gap. The needle should not deflect the bead although it may actually touch the surface without hindering operation. Syringes #1 - 4 should be checked in similar manner against the sample bead; and then #5, against the reference bead.

The instrument may now be placed in operation.

III. PRINCIPLE OF OPERATION

For the detailed theory of the "thermoelectric" type of Osmometer, the reader is referred to the listed bibliography, particularly the paper by Brady, et al. It should suffice here to briefly state the operating principle, which is that of vapor pressure lowering. A solution of any given solvent, will always have a lower vapor pressure than the pure solvent. In the Model 30lA, a drop of solution and a drop of solvent are suspended, side by side, in a closed chamber saturated with solvent vapor. Because of the difference in vapor pressure of the two drops, a differential mass transfer will occur between the two drops and the solvent vapor phase resulting in greater condensation on (or lower evaporation from) the solution drop than from the solvent drop. This transfer will cause a temperature difference between the two drops (because of the heat of vaporization) which is proportional to the vapor pressure lowering, and hence proportional to the solute concentration.

Since this temperature shift is a colligative effect, dependent solely upon the number of dissolved molecules and independent of their chemical characteristics, the instrument may be calibrated with a concentration series of a known solute. Unknowns in the same solvent may then be read directly from the calibration curve. In general, one should work with dilute solutions.

Concentrations between 0.005 and 0.1 molar are optimal, since at higher concentrations, condensation may cause concentration shifts and at lower concentrations reproducibility is reduced. A 0.01 M solution of a solute in benzene, for example, will result in a temperature difference of about 0.016°C . between the drops. Since the Model 301A is designed to read to \pm 0.0001 $^{\circ}\text{C}$. or better, good precision can be maintained at these levels.

Sensitivity will vary somewhat with the solvent, being dependent primarily upon heat of vaporization. Benzene, toluene, and carbon tetrachloride are excellent solvents for the Model 301A. If a choice of solvents exists, the one with the lowest heat of vaporization will usually show the greatest sensitivity.

Since the operation depends upon the solution drop retaining a constant concentration, the instrument is limited to solutes with low vapor pressures. In general, the ratio of vapor pressure of solvent to that of solute should be comparable to the percent accuracy desired. Thus, if working with benzene at a temperature where the vapor pressure is 100 mm., the solute vapor pressure should be below 1 mm. for 1% accuracy, below 5 mm. for 5% accuracy. The limit on a solute vapor pressure is thus a function of solvent vapor pressure and operating temperature.

IV. SETTING UP A RUN

A. Thermal Equilibrium.

If the block is at room temperature, three to four hours are required for it to reach thermal equilibrium. The heater circuits are designed to be left on continually, if desired, to avoid this delay. If the chamber is opened briefly, for example, to remove liquid from the cup, about 30 - 45 minutes will be required for stabilization. If only syringes are exchanged or refilled, no waiting at all is necessary. Equilibration can always be checked by reading T, as described below.

B. Sample Chamber. To prepare the sample chamber:

- 1. Place a clean paper towel just to the left of the thermal chamber.
- 2. Remove the upper chamber assembly, and place upright on the paper towel.
- 3. Rinse the solvent cup, using the solvent to be employed in operation.
- 4. Install a vapor wick in the cup. The large piece is rolled to form a cylinder against the inside of the solvent cup. A slight overlap of the outer wick is not harmful. The smaller die-cut piece is rolled into a cylinder, inserted about half-way into the flat circular piece and the combination placed inside the outer wick against the bottom of the jar, so that the U-shaped cuts in the inner wick line up with the holes in the outer wick. It is important that the inner wick be vertical. If it is tipped, it may strike the thermistor beads when the upper chamber is lowered into place.
- 5. Fill the cup with solvent at least to the level of the U-shaped cuts in the inner wick. Failure to keep the solvent level at least this high will result in instability in operation. It is also important that the solvent in the cup be of the same grade as that used to make up the samples being run. (Because of the sensitivity of the instrument to impurities, it may be necessary to use solvent from the same bottle for both purposes when one wishes extreme reproducibility.)
- 6. Place the cup in the chamber base recess, against the rear wall of the recess to avoid possible interference between the inner wick and the reference bead; align the vapor wick openings with the viewing tubes, and replace the upper assembly, taking care that the guide pins properly engage matching holes in the thermal block and that the meeting surfaces of the base and block are entirely clean and smooth.
- 7. Check cable connections and turn on THERMOSTAT switch.

C. Syringes.

All syringes should be rinsed very thoroughly with the solvent to be used, since very slight contamination of the samples will vitiate results. With very dilute samples, the syringe should be rinsed with sample solution and emptied before the sample is loaded. Since only about 4 drops are required for a measurement, very little sample is required; 0.1 ml. will allow several replicate measurements.

The syringes for guide tubes #5 and #6 should be filled with solvent. Samples for #1 through 4 should be arranged in order of increasing concentration to minimize possibility of cross-contamination errors.

Now insert syringes into thermal block, keeping pins pointed away from probe. Observing the thermistors in the viewing mirror, lower holder #5 by rotating the knurled collar fully clockwise. The needle end should appear directly above the reference (rear) thermistor. Turn the feed screw knob clockwise until the bead has been rinsed with at least 3 drops, then deposit one drop of solvent on the bead. (A useful method to gage drop size is to approximately double the size of the dry thermistor bead.) Raise the #5 syringe by rotating counterclockwise until the pin points away from the probe. Repeat the above with the #6 syringe, approximately matching the size of the drops. (Drop size has no effect on readings except in extreme differences such as may be possible with a solvent with a very high surface tension.)

In measurement, the solvent drop on the front bead is rinsed off with 3 - 4 drops of sample, then the sample drop is hung in place. In most circumstances, it is not necessary to renew the reference solvent drop (#5 syringe) except when a new series is started. In cases where a slightly volatile solute or an "impure" solvent (such as denatured ethanol) is used, it may be preferable to renew the reference solvent drop with each sample drop.

NOTE: Capillarity between the barrel and plunger of a syringe and solvent evaporation will, over a period of time, produce solute incrustations around the top of the barrel. It is advisable, for this reason, to remove and rinse syringes immediately following completion of a sample series.

V. OPERATION

A. <u>Temperature Stability Check</u>.

- 1. Thermostat should be on at least 3 hours before temperature is checked, longer if ambient temperature is unusually low.

 NOTE: This instrument is built with special Helipot potentiometers wound with manganin alloy wire. This wire was selected because of its very low temperature coefficient and thermal emp property. However, the manganin alloy does slowly develop a thin oxide layer which can give rise to additional resistance and appears as meter noise when the "T" control is rotated. If this occurs, spin the control 5 or 6 times rapidly by hand. The wiper will remove the very thin oxide layer and the noise will disappear.
- 2. Null detector should be on for at least 30 minutes prior to measurements.
- 3. Turn BRIDGE ON-OFF switch to ON position.
- 4. Turn $\triangle T$ -T switch to T position.
- 5. Hold ZERO button in and center needle on meter with ZERO control; then release button.
- 6. Rotate T potentiometer knob until needle is near center of scale. If needle drifts slowly to the right, the temperature is not equilibrated. When well equilibrated, the needle drift in the T position should be less than 8 small divisions per 30 minutes.
- B. <u>Measurement Procedure</u>. (Should only be started after temperature has stabilized.)
 - 1. Setting Balance.
 - a. Set ΔT -T switch to ΔT position.
 - b. Set ΔT decade resistance dials to zero.
 - c. Be sure both beads have solvent drops in place.
 - d. Hold ZERO button in and center needle with ZERO control; then release button.
 - e. Center needle with BALANCE control.
 - f. Rebalance at 1 minute intervals until stable (3 5 minutes).
 - g. Repeat with another drop from #6 to be sure of good reference zero.

2. Sample Measurement.*

- a. Lower #1 syringe, rinse bead, and deposit drop. It is best to rinse with 6 8 drops. If sample volume is very limited, 2 3 drops may be used if each rinsing drop is allowed to hang for a few seconds to get mixing of the two liquids.
- b. Start stopwatch.
- c. Shortly after 1 minute has elapsed, check zero and readjust if necessary. (This should be done before any ΔR decade adjustment or BALANCE adjustment. Keep in mind that the thermistor beads need to "reheat" after the ZERO button is released, so one must allow about 30 seconds for the meter needle to stabilize after this check.)
- d. Center needle with ΔR decade dials and take reading at 2 minutes. (If working with a new solvent, one should take readings at 2, 3, 4, and 5 minutes to select a fixed reading time. In general, the shortest time at which the reading is sufficiently stable to be read should be used. Thus, if at 2 minutes, the ΔR value is slowly drifting but the drift is slow enough to allow a valid reading, it will be found that this reading will repeat 2 minutes after a fresh drop of the same sample is applied. With the vast majority of solvent, 2 minutes is quite adequate.)
- e. For greatest accuracy, one may wish to take duplicate or triplicate readings on the sample before proceeding to syringe #2.
- f. Read other syringes in similar fashion. It is preferable that sample syringes preheat in their guide holes for a few minutes before reading. However, if high work output is required, some solvents will permit the omission of this prewarming, but comparative measurements by the two methods should be made to avoid the possible introduction of a systematic error.

*See Para. E for Sample Measurement with Micro-Syringe.

g. On completion of each sample series, rinse the sample thermistor with solvent and recheck the zero point.

The meter needle should reproduce the initial indication within ± 0.5 mm. If the final sample in the series was of a high concentration, 8 to 10 drops of solvent may be required for adequate rinsing. As was pointed out with the sample, better rinsing will be obtained if every other solvent drop is allowed to hang for a few seconds to permit any solute on the glass surface of the bead to diffuse out into the solvent.

If the meter needle reads out of tolerance on the (-) side, the sample thermistor should be rinsed again. If the indication is excessive in the (+) direction, the solvent drop on the reference thermistor may be contaminated and should be rinsed off and replaced.

C. Summary of Operating Procedure.

- 1. Place solvent on both beads.
- 2. Wait 2 minutes.
- 3. Press ZERO button, center needle with ZERO knob.
- 4. Wait 1/2 minute.
- 5. Center needle with BALANCE knob.
- 6. Rinse sample bead with sample and leave drop in place.
- 7. Wait 1-1/4 minutes.
- 8. Check ZERO, adjust if necessary.
- 9. Center needle with Dekastat, read ΔR at 2 minutes after sample drop was applied.

D. Changing Solvents.

It is important, when changing from one solvent to another, that all residue of the first solvent be completely removed from the thermal chamber. Even slight traces of the old solvent will result in instability in the instrument, usually showing itself in balance drift and/or instability in readings on a new sample material. It is, therefore, strongly recommended that the following steps be taken:

- 1. After all runs with the solvent have been completed, remove all syringes from the guide tubes.
- 2. Remove the thermal chamber from the base, and place it on its side on the bench-top adjacent to the main unit. The thermostat should be left on so that the block remains above room temperature.
- 3. Mount a small fan on the bench-top so that the air stream is directed into the thermal chamber, and allow this air stream to play into the main aperture for at least five minutes. A small hair dryer is very satisfactory for this purpose; however, if such a device is used, one must be careful to keep the heater element turned off as it may raise the air temperature so high as to injure the thermistors on the probe assembly.
- 4. After the old solvent jar has been removed, direct the air stream on the base plate for a few minutes.
- 5. As a final precaution, the air stream from the blower should be directed down each of the syringe guide tubes, in turn, to remove any solvent which may have dripped into these cavities.
- 6. A dry, clean solvent cup should now be prepared with a new wick assembly, and the new solvent introduced into this to the appropriate level (to the bottom of the notches in the inner wick).
- 7. Following these operations, the thermal chamber can be returned to its original position, and after equilibration, the instrument is ready to use again.
- 8. In particularly difficult cases, it may be necessary to remove the syringe guide assemblies for better transfer of air through the block apertures. This, however, is a rather extreme measure, and this type of disassembly is rarely necessary.

E. Sample Measurement with Micro Syringe.

- 1. Syringes are filled, placed in special syringe holders, and inserted in usual fashion. Standard syringes and holders are used in #5 and #6 positions.
- 2. Allow usual prewarm period.
- 3. Balance as described above.
- 4. Lower #6 syringe to lowest position. Discharge enough solvent to bridge any gap between end of needle and thermistor bead. Then turn feed screw knob counterclockwise, allowing syringe plunger to rise slightly and suck off the solvent surrounding the sample bead. The purpose of this technique is to avoid dilution of the sample and thus minimize the amount of sample required for rinsing.
- 5. Rinse sample bead with two drops and leave third drop in position. With most solvents, the total volume required will be 12 14 microliters.
- 6. Read $\triangle R$ as described above.

VI. CALIBRATION AND CALCULATIONS

A. Calibration Curve.

The instrument must be calibrated with a known solute for each solvent to be used. Benzil is a good reference for most organic solvents; dextrose, or NaCl, for water. Solutions should be made to cover the range expected in samples. Normally six values from 0.01M to 0.1M give a good curve. Users in the polymer field will probably wish to calibrate over an approximate range of 0.005 to 0.025 molar, since with such sample material concentration dependence must always be considered.

The data may be plotted in several ways. For most convenience, ΔR vs. C permits the concentration of an unknown to be read directly from a graph, entering with ΔR . For greater accuracy, plot $\Delta T/C$ vs. ΔR . One can then easily read the molar constant and calculate the molecular weight to 1% or better.

The shape and slope of the above curves will depend upon the solvent. $\triangle R$ vs. C is usually straight or a very slightly decreasing slope. $\triangle R/C$ vs. $\triangle R$ may be straight or with a pronounced decreasing negative slope. For representative graphs, see Figures 3 and 4.

The user may wish to plot data in molar, molal, or mole fraction terms, depending upon his particular problem. For a detailed discussion of related calculations, please refer to "Number-Average Molecular Weights", by Bonnar, et al, Interscience Publishers, N. Y., 1959.

B. Sources of Error.

The Model 301A Vapor Pressure Osmometer operates by "counting heads" of the solute particles, whether they are molecules, ions, dimers, or any other form. In some cases, therefore, the apparent number average molecular weight may be seriously in error.

1. Association.

With organic solutes, the most likely source of trouble is association due to hydrogen bonding. Likely suspects are molecules with OH, NH, NH $_2$, and COOH groups. If these are dissolved in a nonpolar solvent such as benzene, CCl $_4$, cyclohexane, etc., association may occur. This leads to fewer "particles", thus giving apparent molecular weights which are too high.

The way to solve this problem in most cases is to use a polar solvent which can prevent the association. Such solvents as alcohols, ethers, ketones, acids, and amides such as dimethyl formamide minimize this problem.

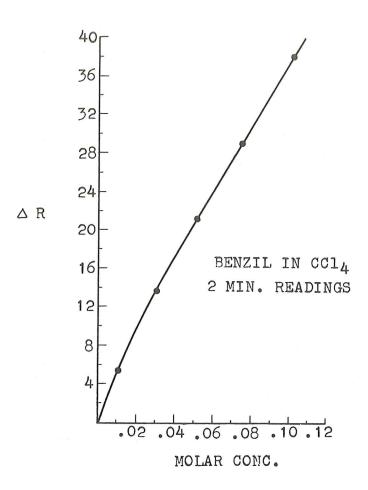


Figure 3. Calibration Curve for Carbon Tetrachloride (AR vs. C)

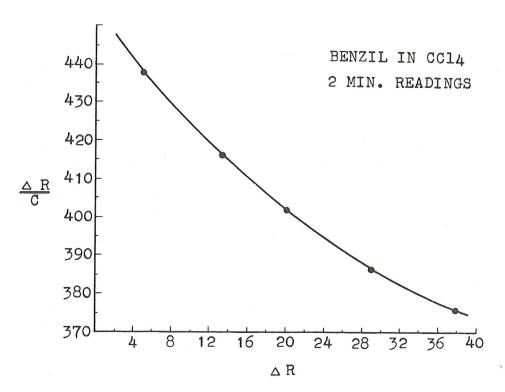


Figure 4. Calibration Curve for Carbon Tetrachloride ($\triangle R/C$ vs. $\triangle R$)

2. Concentration Dependence.

Polymer molecules have a strong tendency to show concentration dependence in molecular weight measurements and a concentration series should always be run on such samples. If nothing is known of the molecular weight range, initial concentrations of 0.5, 1.0, 1.5 percent by weight are a logical choice. With such materials, the technique of calculating results can be very important. An excellent recent book on this subject is "Number-Average Molecular Weights" by Bonnar, Dimbat, and Stross, Interscience Publishers. The authors cover methods of calculating results in considerable detail.

3. Dissociation.

Data from number-average methods applied to aqueous solutions must always be used with consideration for dissociation effects. Hence, if at all possible, organic solvents should be used, dioxane or ethanol being suitable for many water-soluble compounds. These solvents minimize the dissociation problems while retaining the generally high sensitivity of organic solutions. (Because of its heat of vaporization, water has only about one-sixth the sensitivity of benzene at 37°C.)

If the sample material dissolves only in water, one may be able to correct for dissociation by plotting apparent molecular weight against a concentration series, but this is not always meaningful. Compounds forming zwitterions, such as amino acids, may be measured accurately in water provided only relatively low concentrations (below about 0.1 molar) are used.

4. Use of Errors.

One of the great assets of the Vapor Pressure Osmometer is that it works with virtually any solvent. Thus, if measuring an unknown material, runs in two or three different solvents chosen appropriately is advisable, since the trend in the apparent molecular weight may indicate the chemical character of the material under investigation. If working with compounds which dissociate in water, apparent molecular weights are a direct function of activity coefficients and hence the Osmometer may be the source of valuable thermodynamic data.

C. Precision, Accuracy, and Sensitivity.

1. Precision.

The null detector in the Model 30lA permits the measurement of resistance changes to the nearest 0.0l ohms. Reproducibility of repetitive readings is better than 1% except at very low

readings (less than about 3 ohms). Ten repetitive measurements on a dilute solution of sucrose yielded a mean value of 1.30 ohms, and a standard deviation of .015 ohms. However, consideration of a typical production instrument, including noise, drop size, and other minor effects, indicate repeatibility at the few ohms signal level of about ± .03 ohms. At higher signal levels (above 10 ohms) drift effects become larger than electrical noise, but repeatibility should always be better than 1% of reading.

2. Accuracy.

Table I shows some preliminary runs on several types of samples. These are results of measurements made while evaluating engineering aspects of the Osmometer and represent accuracies attainable by relatively unskilled personnel.

<u>TABLE I</u>
REPRESENTATIVE DETERMINATIONS

I Benzene calibrated with benzil.

<u>Sample</u>	Formula Wt.	Det.Mol.Wt.	Error
Anthracene	178.2	177.0	0.7%
Biphenyl	154.2	152.7	1.2%
Sucrose Octoacetate	679.	686.	1.0%
Triphenylmethane	244.3	252.	3.3%

II Water calibrated with dextrose.

Sample	Formula Wt.	Det.Mol.Wt.	Error
Raffinose	594.5	586	1.3%
Hydroxyproline	131.1	132	0.7%
Phenylalanine	165.2	167	1.1%

Accuracy on higher molecular weight samples is difficult to evaluate and awaits comparative tests now underway. Known samples in the 10,000 to 20,000 range are difficult to obtain, so estimates must be made on extrapolated values. At least three major industrial polymer laboratories have worked extensively with samples in the 10 - 12,000 molecular weight range, and all report accuracies of 4 - 5%. Comparisons were by ebulliometry, viscosity, and end group analysis.

3. Sensitivity.

For an organic solvent such as benzene, at the standard operating temperature of 37°C. , the Osmometer shows a bridge

imbalance of 350 to 400 ohms per mole of solute. (The exact figure depends on solvent, thermistor resistance, and temperature.) Thus a 0.01 molar solution can be read to about 1%. To specify sensitivity in terms of molecular weight, one must select some acceptable weight concentration level. By comparison with ebulliometry, 5% might be chosen. A simple calculation shows that one should be able to read to molecular weight of 5000 to 1% precision on a 5% weight concentration.

Similar extrapolations show that a 5% concentration of 20,000 molecular weight in benzene should produce a bridge imbalance of one ohm, certainly readable to \pm 5%, but concentration dependence of such materials probably will yield accuracies of only \pm 10%.

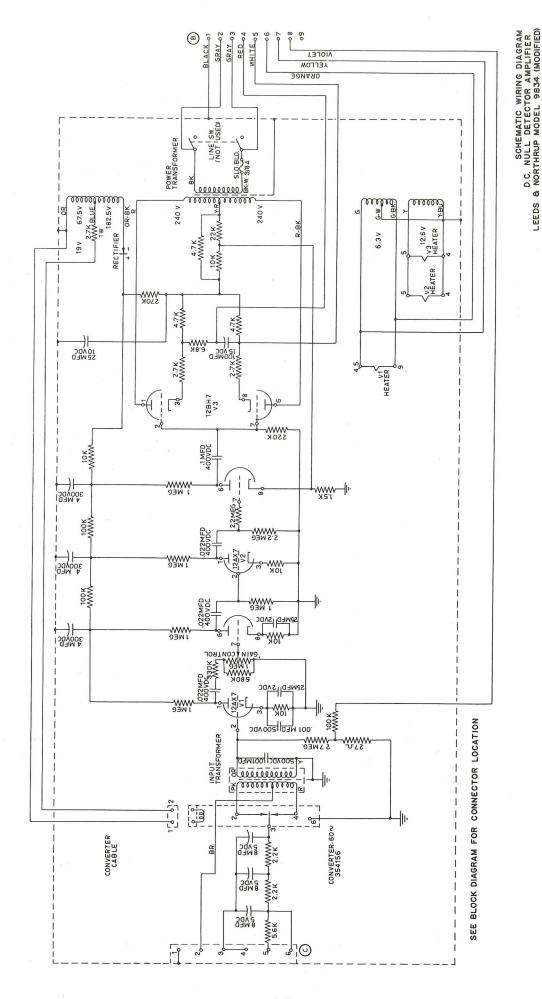
In aqueous solutions, sensitivity is considerably lower, due primarily to the high heat of vaporization of water. The molar constant is about 55 ohms per mole. Consequently, the extrapolated figures would be 1% precision to molecular weights of 700, and 5% precision to 3500. Fortunately, physiological solutions are relatively concentrated. Plasma, for example, corresponds to about 0.14 molar concentration, and being largely dissociated, gives bridge imbalances of the order of 14 to 16 ohms.

SUMMARY

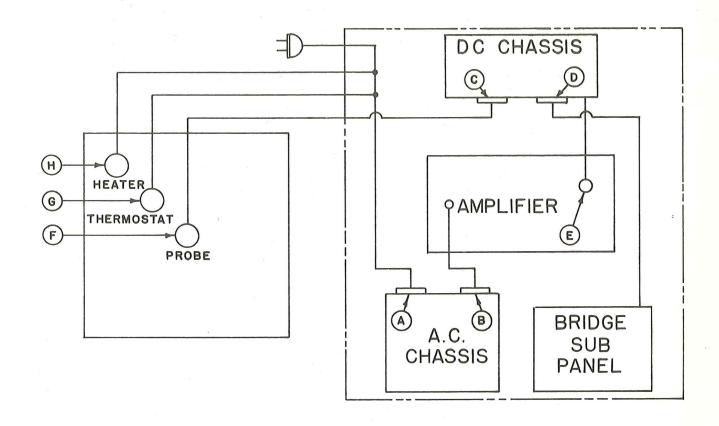
It is regretted that more specific information and data cannot be given on higher molecular weight measurements. We are presently undertaking such a program and a high proportion of our early customers are active also in this field. We will make additional reports as soon as the information is available.

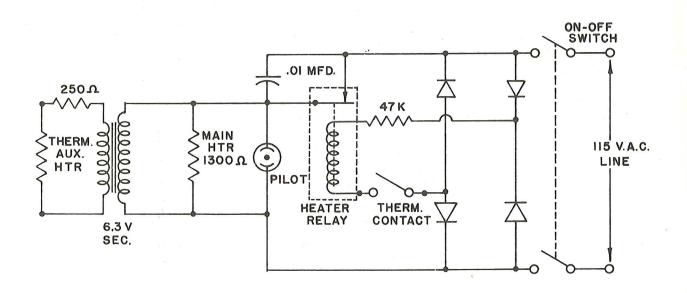
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BLOCK DIAGRAM & CONNECTOR LOCATION

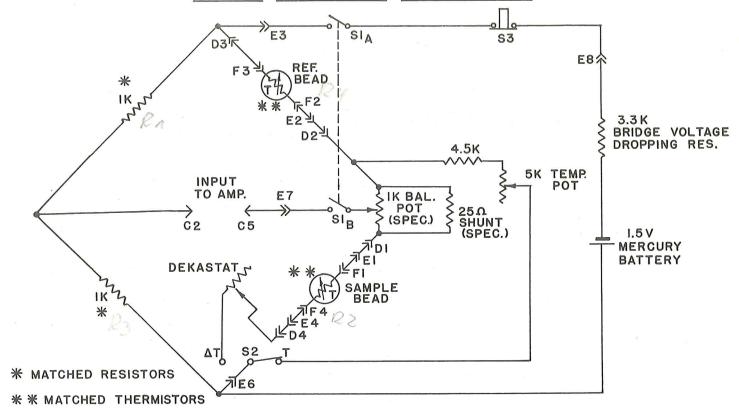




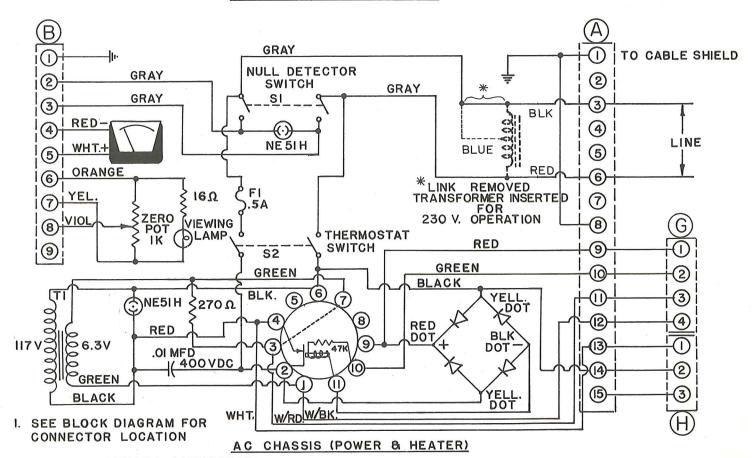
SIMPLIFIED HEATER CONTROL CIRCUIT

Figure 6.

MODEL 301A VAPOR PRESSURE OSMOMETER



THERMISTOR BRIDGE CIRCUIT



- 2. LETTERS DENOTE CONNECTORS
- 3. NUMBERS DENOTE PINS

PRICE LIST

Part No.	Description	<u>List Price</u>
301-0000	<u>VAPOR PRESSURE OSMOMETER</u> , <u>Model 301A</u> , complete with 37°C. probe (either aqueous or non-aqueous), 6 syringes and holders, and 37°C. thermostat	\$ 2390.00
301-1300	Non-Aqueous Probe*	140.00
301-1310	Aqueous Probe*	140.00
301-1400	Thermostat*	45.00
2 × 301-1620	Ultramicro Syringe	20.00
301-1610	Ultramicro Syringe Holder	5.50
301-1601	VPO Needle, specially fitted & cut (2 per box)-	3.80
301-1101	VPO Syringe, with matched barrel and piston	3.80
301-1350	Dummy Probe (for service check-out)	11.90
301-1220	Syringe Guide Assembly	9.80
301-1200	Syringe Holder Assembly	5.50
301-1500	Viewing Tube Assembly	22.50
301-1503	Mirror	3 . 75
301-1701	Solvent Cup	3.75
+301-1702	Vapor Wicks (10 per pkg.)	2.00
301-3110	Holder Relay Socket Assembly	6.85
EB-1001	Battery	1.25
EF-1101	Fuse	.50
EI-2101	Light (GE 47)	.35
EI-1102	Pilot Light (NE51N)	.70
EK-1102	Relay	11.45
EV-1903	Tube	3.00
301-3400	A.C. Chassis (Price quoted on request)	,
301-3300	D.C. Chassis (Price quoted on request)	
301-1217	Syringe Spring	. 25

*Probe and thermostat must be ordered together for any temperature other than 37°C. , with an upper limit of 65°C. Above prices apply to 25° , 37° , 50° and 65°C. Prices for other temperatures will be quoted upon request.

Prices are f.o.b. factory, Mountain View, California, and include domestic packing only. Minimum order - \$10.00.

Prices are subject to change without notice at any time.

OPERATION CHECK LIST #1

This is the Vapor Pressure Osmometer Operation Check List #1. This sheet should be used as follows:

- A) Use as an operational check sheet before commencing operation until checking each item becomes habit.
- B) Use as a preliminary check list prior to going to the Service Check List #2.
- 1. Visually insure there is no foreign matter (oil, solvent, dust) between the upper thermal chanber and base plate.
- 2. Ascertain that the solvent level in the cup is correct, per Instruction Manual.
- 3. All syringes should be in place.
- 4. Viewing tubes should be firmly seated in the thermal block. The phenolic tube should seat into a counter bore in the aluminum block, and be held firmly by the light press fit.
- 5. Make certain chamber has been cleaned (per Page 12 of Instruction Manual), and saturated with new solvent if there has been a switch to a different solvent.
- 6. Check that the instrument is not located in a position where it is subject to strong air drafts or ambient temperature changes (heat or cooling ducts, strong sunlight, etc.).
- 7. Has the heater circuit been left on overnight or at least for four hours prior to obtaining readings?

SERVICE & TROUBLE-SHOOTING CHECK LIST

Service on the MECHROLAB Vapor Pressure Osmometer consists of the following procedure. It has been our experience with this instrument that, because of its rugged construction and reliable design, a high percentage of problems are solved by Steps III or IV. However, for repair of any sub-assemblies, we insist they be returned to the factory under Step V, thus assuring you an instrument that meets factory specifications.

Step I	Review item-by-item Check List #1, Operation
	Check List.
Step II	Review item-by-item Check List #2, Service
	Check List.
Step III	Telephone MECHROLAB, INC., Mountain View, California
	collect (area code 415, 967-5796), identifying the
	call as a "service call."
Step IV	If necessary, we will schedule a service visit from
	our local Regional Manager or traveling factory
	representative.
Step V	The repair or exchange of instrument components.

SERVICE CHECK LIST #2

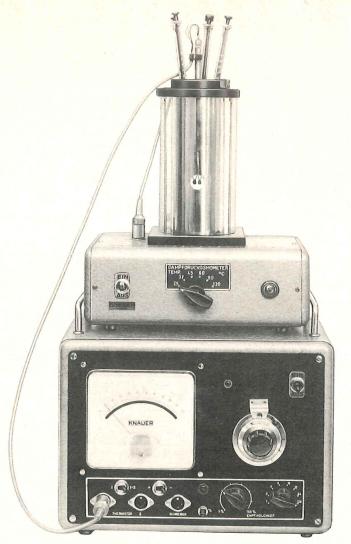
Perf	Form all tests, except 8d, with solvent on both beads.
1.	What is the model number?
2.	What is the serial number?
3.	What is the purchase date?
4.	The probe has serial number,
	calibration temperature,
	reference bead resistance in ohms
	(printed on its decal).
5.	What is the temperature set-point printed on the
	thermostat decal?

6.	COL	the ΔT -T switch to T position and adjust T atrol for balance near the center of the meterale.
	a.	The T potentiometer dial reading (0.00) multiplied by the potentiometer resistance (either 2500 ohms or 5000 ohms) plus the value of the series resistance (4500 ohms) should approximate the resistance printed on the probe, when at the specified temperature.
	b.	What is the T drift in millimeters on the meter over a 10-minute period?
	C.	What is the heater cycle in seconds? On Off
7.		t is your particular problem? (reproducibility, ft, etc.)
8.	a.	What solvent are you using?
	b.	How long has it been since you have used a different solvent?
	С.	Are readings reproducible on pure solvent?
	d.	Are readings reproducible on samples?(If "no," list samples and some data below)
	e.	What is the difference in readings between small, medium, and large sized drops on the reference bead? (small) (medium) (large)
9.	a.	Will null meter balance with zero adjust? (DUMMY PROBE)
	b.	With Zero button depressed, zero adjust should give same deflection to either side of the null zero.
	С.	Set dekastat to 00.00 (switch at ΔT), and balance null indicator using balance control. Can you achieve a null balance?
	d.	Turn balance control full counter-clockwise (switch at ΔT) and balance null indicator with dekastat. Record this dekastat reading.
		(The difference between the dekastat reading and 25 ohms is the differential

10.		drift or meter fluctuation when using my probe?			-
11.	a.	Gain: Using balance knob (switch at ΔT , dekastat at 00.00), set null meter at a minus 1.0 cm. Then set dekastat at 01.00 ohms. Record null meter reading.			
		(For proper gain control, null meter shall read zero on 301, and +1.0 on 301A).			
	b.	You should be using a Mallory ZM-9 battery	(yes)	(no)	***************************************
	C.	Can you check the battery voltage? Use pins 3 and 4 on the probe connector, with switch at ΔT . If so, record voltage. (It should be .5 volts).			
12.	to	ter resistance. Can you use an ohmmeter check the following? 3 connector plug rear of thermal block assembly.			
	a.	Pins 1 to 2 - 1300 ohms			-
	b.	Pins 1 to 3 - open circuit			
	C.	Pins 2 to 3 - open circuit			
13.	to	be resistance. Can you use an ohmmeter check the following? 4 connector plug probe.			
	a. *	Pins 1 to 4 - About 6,000 ohms at 37°C (or about 10,000 ohms at ambient).	3 - 1 1 - 1 2	***************************************	
	b.	Pins 2 to 3			

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KNAUER

BESTIMMUNG VON

MOLEKULARGEWICHTEN DURCH MODERNES DAMPFDRUCK-OSMOMETER

BEI MESSTEMPERATUREN VON 25°, 37°, 45°, 60°, 90° und 120°C

bis zu 20 000 zuverlässig und genau in 2—5 Minuten

	Preise ab Berlin DM
Komplettes Dampfdruck-Osmometer, betriebsfertig bestehend aus:	5 650.—
Elektronischem Universal-Temperatur-Meßgerät für Temperatur-Einzel- und Differenzmessungen, Auflösungsvermögen 2/10 000°C und	
Dampfdruck-Osmometer-Zusatzgerät für Meßtemperaturen von 25°, 37°, 45°, 60°, 90°, 120°C, mit 1 Meßsonde	
Zubehör zum Arbeiten unter Inertgas	58.—
Ersatzteile	
Meßsonde mit 2 abgeglichenen Thermistoren für organische Lösungsmittel — gewünschte Arbeitstemperatur bitte angeben: 25 und 37°C, 37 und 45°C, 45 und 60°C, 60 und 90°C, 90 und 120°C	150.—
Meßsonde für wässrige Lösungen 12 Nadeln mit Federn	150.—
Spritze mit austauschbarem Glaskolben (Bestellung von 3 Ersatzspritzen empfehlenswert) Spritze mit austauschbarem Teflonkolben	6 12
10 Dampfdochte	3.—
Zusatzgerät zur Halbmikro-Kryoskopie, betriebsfertig bestehend aus:	895.—
Thermoelektrischem Kühlgerät (Peltier-Effekt) und Meßkopf mit Temperaturfühler und Mikrorührer. Reproduzierbarkeit des Gefrierpunktes von Wasser und Benzol 2/1000°C bei einem Probevolumen von 0,15 ml bzw. 0,3 ml.	
Ersatz-Meßkopf mit Thermistorfühler und Rührmotor	120.—
Meßgefäß zur Kryoskopie für 0,15 ml oder 0,3 ml	5

DR.-ING. HERBERT KNAUER

WISSENSCHAFTLICHER GERÄTEBAU 1 BERLIN 33 · DAVOSER STRASSE 2B · RUF 89 82 21

DAMPFDRUCK-OSMOMETER

Anwendungen in der Chemie

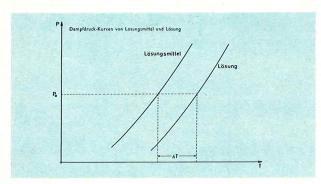
Bestimmung von Molekulargewichten bis 20000 aller Stoffe, die in einem geeigneten Lösungsmittel zwischen 25° und 120°C genügend löslich sind, wie z.B. Polyolefine, Polyamide, Silikone, Wachse, Fette. Bestimmung von Dissoziation und Assoziation sowie von Aktivitätskoeffizienten.

Anwendung in der Medizin und Botanik

Für medizinische Anwendung kann bei der physiologisch richtigen Temperatur von 37°C der osmotische Druck von Serum, Urin und sonstigen biologischen Lösungen mit einem Probevolumen von 0,02 ml bestimmt werden. In der Botanik wird der osmotische Druck von Pflanzensäften bei natürlichen Bedingungen, d.h. bei 25°C, bestimmt. Ferner können Saugspannungen gemessen werden.

Wirkungsweise

In einer sehr konstant temperierten Meßzelle stellt sich der Sättigungsdampfdruck Po über dem Lösungsmittel ein. In der Meßzelle befinden sich 2 Thermistorperlen als Temperaturfühler. An beide Thermistorperlen wird mit je einer Spritze ein Tropfen Lösungsmittelt gebracht. Beide Thermistoren mit den Lösungsmitteltropfen nehmen die Meßzellentemperatur an. Das Temperatur-Meßgerät, das die Temperaturunterschiede zwischen beiden Thermistoren mißt, wird auf Null-Ausschlag eingestellt. Wird ein Lösungsmitteltropfen durch einen Lösungstropfen ersetzt (hierfür stehen 4 weitere Spritzen zur Verfügung), so stellt sich ein \triangle T zwischen beiden Tropfen ein. Der Lösungstropfen weist gegenüber dem Lösungsmittel einen geringeren Dampfdruck auf. Aus dem Dampfraum kondensiert an der Oberfläche des Tropfens so viel Lösungsmittel, daß sich durch die Kondensationswärme \triangle T einstellt.



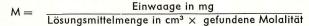
Da die Temperaturdifferenz beider Tropfen von deren Dampfdruck-Differenz und diese nur von der Zahl der gelösten Moleküle abhängt, können auf diese Weise Konzentrationen bestimmt werden. Das Temperatur-Meßgerät zeigt die Temperaturdifferenz direkt an. Das Auflösungsvermögen des Temperatur-Meßgerätes ist 0,0002 °C.

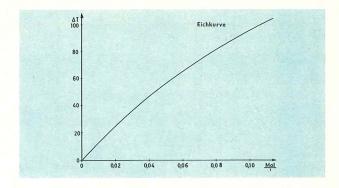
Das Temperaturgleichgewicht stellt sich in organischen Lösungsmitteln in ca. 2 Minuten ein. Das Verfahren ermöglicht es, in weitem Umfang alle gängigen Lösungsmittel wie z. B. Benzol, Toluol, Chloroform, Bromoform, Tetrachlorkohlenstoff, Cyclohexan, Tetrahydrofuran, Aceton, Mesithylen, m-Xylol, o-Dichlorbenzol, zu verwenden. Mit den einstellbaren Temperaturen für die Meßzelle von 25°, 37°, 45°, 60° 90 und 120°C ist es möglich, sich der Löslichkeit der Substanz und dem Lösungsmittel anzupassen.

Eine Lösungsmenge von 0,1 ml reicht aus, um eine Molekulargewichtsbestimmung durchzuführen.

Die sich einstellende Temperaturdifferenz für eine bestimmte Konzentration hängt vom Lösungsmittel und vom Temperaturfühler ab. Das Dampfdruck-Osmometer muß daher für jedes Lösungsmittel einmal mit Lösungen bekannter Konzentrationen geeicht werden.

Diese Eichung ist für das betreffende Lösungsmittel nur einmal durchzuführen und bleibt dann konstant. Bei der Messung einer Lösung stellt sich ein bestimmtes $\varDelta T$ ein. Aus der Eichkurve kann nun die Konzentration abgelesen und das Molekulargewicht wie folgt berechnet werden:





Vergleich mit anderen Meßmethoden

Im Gegensatz zur Kryoskopie und Ebullioskopie sind die Messungen mit dem Dampfdruck-Osmometer in einem weiten Temperaturbereich zwischen Gefrierpunkt und Siedepunkt des Lösungsmittels möglich. Die Kryoskopie findet neben der Molekulargewichtsbestimmung häufig Anwendung in der Untersuchung der Reinheit von Lösungsmitteln wie Benzol, Xylol, Toluol etc.

Das Dampfdruck-Osmometer benötigt im Gegensatz zur Kryoskopie und Ebullioskopie sehr viel geringere Lösungsmengen, d. h. < 0,1 ml. Das Dampfdruck-Osmometer ist in der Regel in organischen Lösungsmitteln den genannten Meßmethoden an Genauigkeit und Reproduzierbarkeit überlegen.

Molekulargewichtsbestimmungen durch Dampfdruck-Osmometer:

Substanz	theoret. Molgew.	gef. Molgew.	% Fehler
Atropin	289,4	291	+0,5%
Acetanilid	135,2	137	+1,2%
Azobenzol	182,2	185	+1,8%
In Benzol, mit Be	enzil geeicht		
Acetanilid	135,2	134	-1%
Azobenzol	182,2	180	-1,5%
Naphthalin	128,2	129	+0,8%

Besondere Vorteile unseres Meßsystems

- Das Dampfdruck-Osmometer ist durch die einstellbaren Meßtemperaturen von 25°, 37°, 45°, 60°, 90° und 120°C sehr universell zu verwenden.
- Mit einer Thermistorsonde können Messungen bei zwei Temperaturen durchgeführt werden: 25 und 37°C, 37 und 45°C, 45 und 60°C, 60 und 90°C, 90 und 120°C.
- Das elektronische Universal-Temperatur-Meßgerät ist für alle im Labor vorkommenden thermometrischen und kalorischen Messungen zusätzlich einsetzbar, z.B. auch für Molekulargewichtsbestimmungen durch Ebullioskopie und Kryoskopie.
- Das Temperatur-Meßgerät sowie die Temperaturregelung des Dampfdruck-Osmometers arbeiten volltransistorisiert und sind daher besonders betriebssicher.

Literaturhinweise

- A. V. Hill, "A Thermal Method of Measuring the Vapour Pressure of an Aqueous Solution." Proceed. Royal Soc. London, A 127, 9 (1930).
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- 3. A. Wilson, L. Bini, R. Hofstader, "Thermistor Micromethod for Molecular Weight", Analytical Chemistry 33, 135 (1961).
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