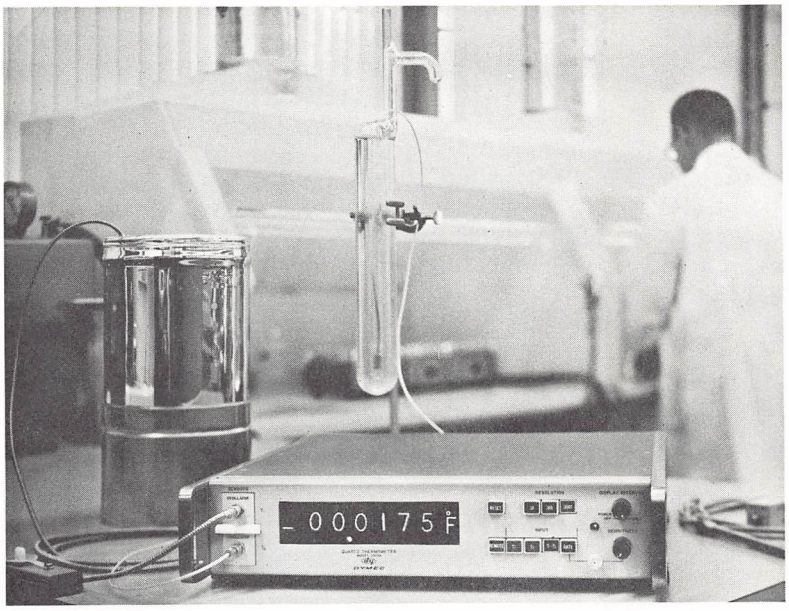
HEWLETT PACKARD hp DYMEC DIVISION

QUARTZ THERMOMETRY

APPLICATION NOTE 78-2 MAY 1966



High resolution and precision of Quartz Thermometer enable it to be used to advantage in wide variety of physical and chemical measurements. In set-up illustrated, Model DY-2801A Quartz Thermometer is measuring difference between ice-point and triple-point of water.

MOLECULAR WEIGHT DETERMINATION WITH THE QUARTZ THERMOMETER

INTRODUCTION

It has been known for many years that the freezing point of a solvent is lowered a predictable amount by the addition of a non-volatile, non-ionizable solute which does not react with the solvent. The boiling point is also elevated by the addition of a solute. This method has been used to measure the molecular weight of such substances as sugar, alcohol, urea, etc. in water solutions, and various hydrocarbons in solution with benzene or napthalene. Alternatively, it has been used to determine the degree of purity of a solvent.

The technique has not been popular in recent years due to the tedious procedures which have had to be employed to measure the temperature accurately. A precision of 10^{-3} degrees Centigrade is desirable, and it is necessary to take a large number of readings to be sure the transient freezing or boiling point can be selected. The best available thermometer has been the platinum resistance bulb. This must be read on a resistance bridge, one point at a time, each point noted by balancing the bridge and, in the case of freezing point determinations, noting the time of each reading. A time-resistance plot must then be drawn to determine the true freezing point, and the resistance value converted to temperature by table look-up or equation.

The Quartz Thermometer with its direct, precise digital readout can be connected to a printer and/or a strip chart recorder, and the complete time-temperature curve drawn automatically without attendance. A precision of better than .001°C can be recorded and read.

It is hoped that this modern thermometry technique will revitalize a very useful analytical method.

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The Measurement Technique

It was shown by Raoult in the late 19th Century that the vapor pressure of a solvent was reduced by the addition of a solute. According to Raoult's law, "The relative lowering of the vapor pressure is equal to the mole fraction of the solute in the solution." The law is exact only for ideal solutions, but the error for dilute solutions is generally less than 3%. An exact measurement of vapor pressure is a tedious affair and cannot easily be done rapidly or automatically. However the vapor pressure reduction also results in a proportional elevation of the solution's boiling point and a depression of the freezing point.

The molality (m) of a solution is defined as the number of moles of solute dissolved in 1000 grams of solvent. The boiling point elevation and freezing point depression are proportional to the molality, and the constant of proportionality depends on the solvent employed. That is:

$$\Delta T_b = K_b m \text{ and}$$

$$\Delta T_f = K_f m$$

Where ΔT_b is the measured elevation of the boiling point and ΔT_f is the measured depression of the freezing point.

In the case of water, for example,

$$\Delta T_b = 0.513 \times \text{molality}$$

$$\Delta T_f = 1.86 \times \text{molality}$$

Since molality $m = \dfrac{W_2}{MW_1} \times 1000$

where W_2 is the weight of solute,

W_1 is the weight of solvent, and

M is the molecular weight

the molecular weight can be expressed as:

$$M = K_b \frac{1000 W_2}{\Delta T_b W_1} = K_f \frac{1000 W_2}{\Delta T_f W_1}$$

In order to apply this it is necessary to know the value of K_b or K_f. This can be determined experimentally for a solution containing a solute of known molecular weight, or the standard handbook values for common solvents can be used.

TABLE 1 MOLAL ELEVATION CONSTANTS

SOLVENT	K_b	SOLVENT	K_b
Water	0.513	Benzene	2.63
Methanol	0.83	Acetic Acid	3.14
Ethanol	1.20	Chloroform	3.85
Acetone	1.72	Carbon Tetrachloride	

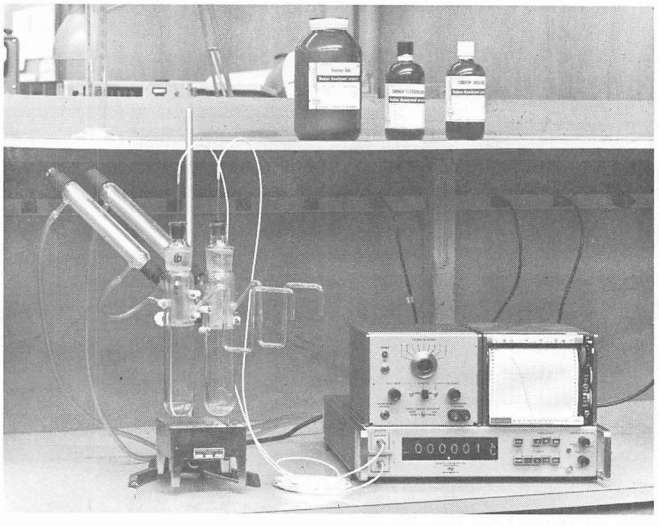
TABLE 2 MOLAL DEPRESSION CONSTANTS

SOLVENT	K_f	SOLVENT	K_f
Water	1.86	Napthalene	7.0
Acetic Acid	3.90	Bromoform	14.3
Benzene	5.12	Cyclohexane	20.2
Nitrobenzene	6.90	Camphor	40.0

Practical Considerations

Both the boiling point elevation and freezing point depression can be measured with modern thermometry techniques. The boiling point determination is simpler in that boiling can be sustained and readings taken and averaged over a period of time. Boiling points, however, are very sensitive to pressure. Thus, barometric pressure and other pressure variations in the boiler can significantly influence the reading.

The irregular agitation of boiling also creates variations in reading that increase the error band. Fairly accurate results can be obtained by using the Washburn-Cottrell apparatus (Figure 1) which holds the quartz thermometer above the surface of the liquid and the boiling solution is made to pump itself continuously over the thermometer bulb. This covers the bulb with a thin layer of boiling solution, and thus the temperature recorded should be close to the true boiling point. Two such apparatus can be used simultaneously, one with pure solvent, the other with the test solution. As both solutions boil, the quartz thermometer differential can then be read and recorded as the boiling point elevation. In this way the effect of barometric pressure is eliminated.



Washburn-Cottrell Apparatus for Measuring Elevation of Boiling Point. Instruments at right are DY-2801A Quartz Thermometer, hp 581A Digital-Analog Converter, and Moseley 680A Strip Chart Recorder.

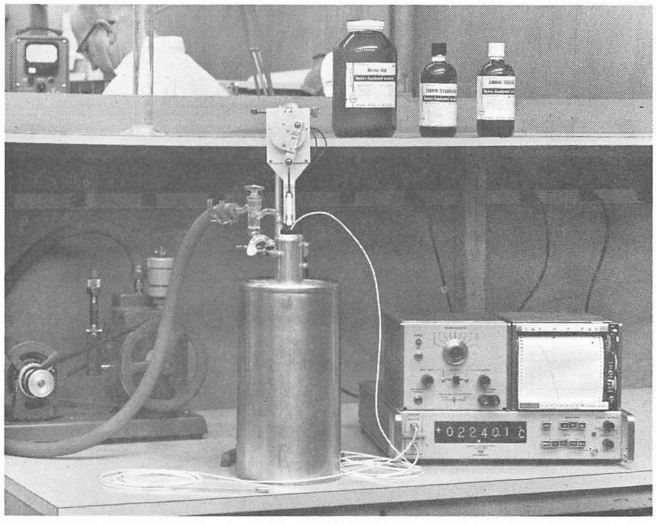
FIGURE 1

This freezing point method, it should be noted, is useful only if the solid which separates on freezing is pure solvent, e.g. pure ice. Sometimes a solid solution separates which contains both solute and solvent; the freezing point method is not applicable to this situation. Nor is it applicable to solutes that ionize, such as the electrolytes NaCl or H_2SO_4. Since the vapor pressure reduction is essentially dependent on the number of particles

present in the solution, ionized solutions yield greater pressure reductions, e.g. NaCl produces almost twice the freezing point depression expected from its molecular weight. This is due to ionization producing almost two particles per molecule. Since the ionic disassociation is never complete, the molal constant is seldom multiplied by an exact whole number.

Practical System for Measuring Freezing Point Depression

The apparatus illustrated in Figure 2 is a convenient system for using the freezing point depression method. It is essentially the same equipment described in ASTM Designation D1015-55 entitled "Measurement of Freezing Points of High Purity Compounds for Evaluation of Purity".



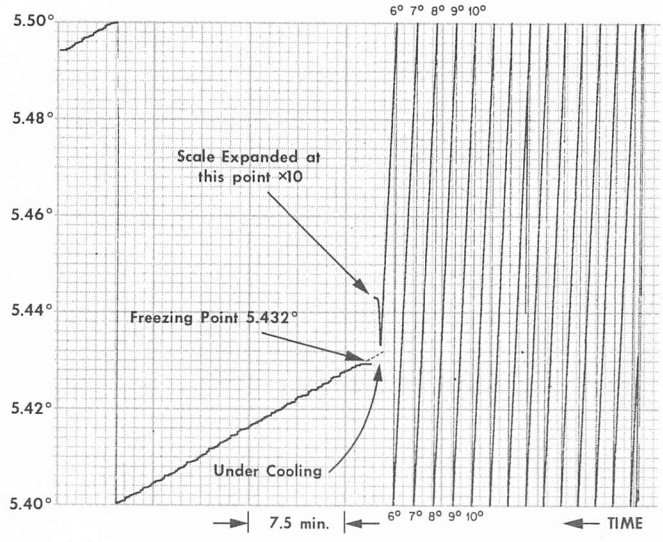
Apparatus for Measuring Depression of Freezing Point. Electronic instrumentation consists of DY-2801A Quartz Thermometer with a digital-to-analog converter and strip chart recorder.

FIGURE 2

It consists of a small dewar whose jacket is not sealed, but is connected instead to a vacuum pump. The dewar is suspended in a freezing solution which, for water and benzene solvents, consists of an alcohol bath into which dry ice (solid CO_2) has been dropped. The temperature approaches -78°C and is sufficiently below the freezing point of the solution so that a constant cooling rate can be achieved. Cooling is controlled by the degree of evacuation of the dewar jacket. In order to insure an equithermal condition, the solution is stirred by a reciprocating stirrer driven by a small motor. A rate of 120 rpm is sufficient. The temperature sensing probe, a type DY-2850D, is inserted through a rubber cork which is also notched to clear the stirrer rod. The system is filled at room temperature, the vacuum pump and stirrer started and the large dewar containing the refrigerant brought up to immerse the small dewar as deeply as possible.

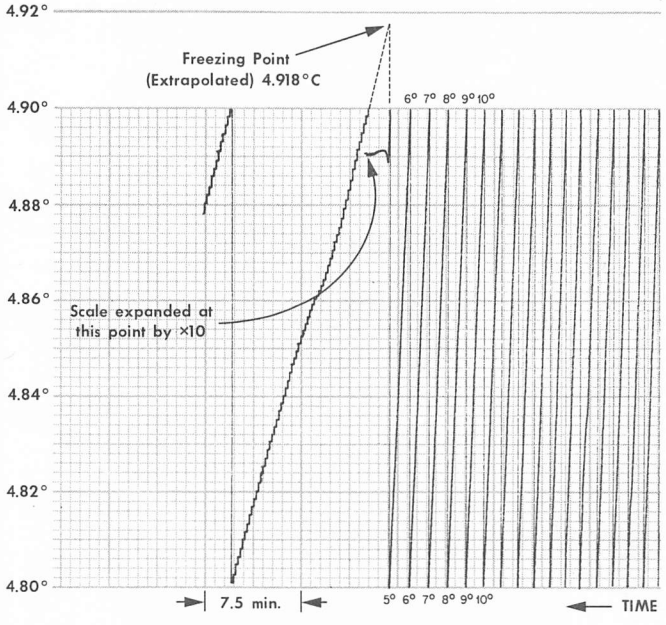
The DY-2850D Probe is connected to a DY-2801A Quartz Thermometer. This in turn can be connected to an hp 562A Printer and a Moseley 680 Strip Chart Recorder, or to an hp 580A Digital-Analog Converter and a 680A Strip Chart Recorder.

Typical strip chart recordings are shown in Figures 3, 4 and 5. The freezing point depression of the 0.1 molal solution in Figure 4 is computed as 5.432° - 4.918° = 0.514°. This agrees closely with the constant given for benzene in Table 2. Figure 5 shows the perfectly flat freezing plateau achievable with a pure solvent, such as distilled water.



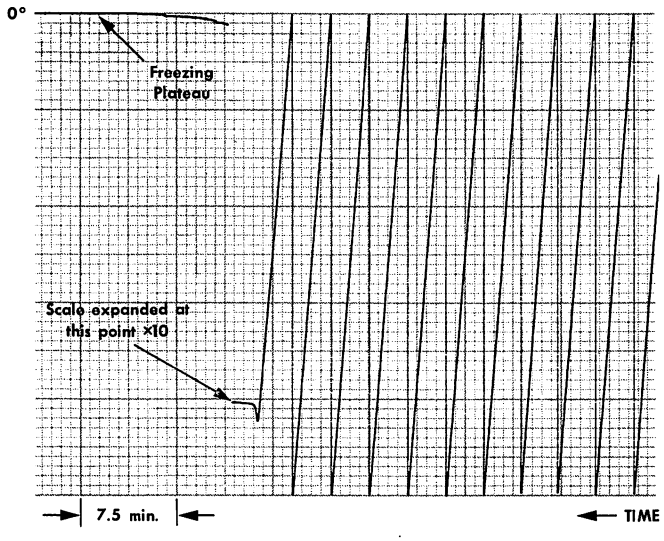
FREEZING CURVE OF REAGENT GRADE BENZENE (.005% H_2O)

FIGURE 3



FREEZING POINT OF 0.1m SOLUTION OF CARBON TETRACHLORIDE (CCl_4) IN BENZENE (C_6H_6)

FIGURE 4



FREEZING RECORD FOR PURE WATER

FIGURE 5

A cooling rate between 0.5° and 1°C per minute appears to be adequate for most purposes. The system is set to provide a recorder span of 1°C until the freezing point is reached and then switched to a span of 0.1°C for the rest of the recording.

In this way the graphic record can be read to .002°C and values as precise as .0001°C can be noted on the chart or printed on paper tape.

The system once started can be left unattended as all data is automatically recorded and plotted. It can be shut down about an hour after the start and flushed out for another run.

Solvents such as napthalene which melt above room temperature (approximately 80°C) are handled without refrigeration. They are melted in a test tube placed in an air jacket. This consists of a beaker and cover plate containing a hole to support the tube and molten solution. This is stirred and measured as described above. It is necessary, of course, to remelt the solution in order to free the thermometer and stirrer.

References

1. Elements of Physical Chemistry, Samuel Glasstone, D. Van Nostrand Co., New York
2. ASTM Designation D1015-55: Standard method of Test for Measurement of Freezing Points of High Purity Compounds.
3. Handbook of Chemistry and Physics, 35th Edition, Chemical Rubber Publ. Co., pages 2116-2118.