12 ELEVATION OF THE BOILING POINT

The boiling points of a solution and of the pure solvent are determined and used for calculating the molecular weight of a nonvolatile solute.

THEORY. When a nonvolatile solute is dissolved in a solvent, the vapor pressure of the latter is decreased; as a consequence, the boiling point of the solution is higher than that of the pure solvent. The extent of the elevation $\theta$ depends upon the concentration of the solute, and for dilute, ideal solutions it may be shown that

$$T_b - T_0 = \theta = K_b m = \frac{\theta_{1000}}{M_g}$$

where

$$K_b = \frac{RT_b^2}{1000 \lambda_v}$$

and $T_0 = \text{boiling point of pure solvent}$

$T_b = \text{boiling point of solution of molality } m \text{ at same pressure}$

$\lambda_v = \text{enthalpy of vaporization of pure solvent per gram at temperature } T_0$

$K_b = \text{molar boiling-point elevation constant}$

$K_b$ is a constant characteristic of the solvent. Relation (1) permits calculation of the molecular weight of the solute, since it may be transformed into the equivalent form

$$M = \frac{1000K_b \theta}{\theta_{1000}}$$

where $\theta$ is the elevation of the boiling point for a solution containing $g$ g of solute of molecular weight $M$ in $G$ g of solvent of boiling-point elevation constant $K_b$.

It should be noted that even for ideal solutions the foregoing relations are valid only if the solution is also dilute, i.e., if the mole fraction of solute is small.

One of the more interesting applications of this equation is in the study of solutes which can form dimers, trimers, etc. The position of equilibria of the type

$$nA \rightleftharpoons A_{2n}$$

may be strongly dependent on the solvent. Examination of the derivation which leads to Eqs. (1) to (3) will show that if several solute species are present, the value of $M$ (now the number average molecular weight) found by naive application of Eq. (3) is actually the average for the species present; that is,

$$M = \sum_i X_i M_i$$

where $X_i$ is the mole fraction of species $i$ and $M_i$ its molecular weight. Although the position of equilibrium cannot be found with accuracy by this method, it is possible
to characterize systems in which the solute is mainly of a single species by comparing the apparent molecular weight with the known formula weight.

More rigorous thermodynamic equations are required for the analysis of boiling-point elevation data on solutions which deviate markedly from ideal behavior. The effort is rewarded, however, because one gains additional information in such cases, pertaining to the nonideal properties of these solutions. For example, activity coefficients for sodium chloride in aqueous solution have been determined in this way by Smith over the range 60 to 100°C. Thus boiling-point data represent potentially a valuable source of information concerning electrolyte solutions.

For the determination of the boiling temperature of a solution, the thermometer must be in contact with solution rather than with condensed vapor, and the elimination of superheating of the liquid phase is therefore particularly important. Electric heating may be used to reduce the superheating. Often, however, solvent vapor is passed into the solution, where it condenses, and raises the solution to the boiling point. In this way there is no radiation or conduction of heat from a body at a higher temperature, and superheating is eliminated.

**Apparatus.** Boiling-point apparatus of the Cottrell type; Beckmann thermometer or other thermometer graduated to 0.01°; carbon tetrachloride; benzoic acid.

**PROCEDURE.** The elevation of the boiling point of carbon tetrachloride produced by dissolved benzoic acid is to be measured.

A commercially available boiling-point apparatus of the Cottrell type is shown in Fig. 22. A known quantity of solvent is placed in the tube and a Beckmann thermometer (page 475) or other thermometer graduated to 0.01° is inserted. The liquid level must be below the lower end of the glass thermometer. The apparatus is clamped in a vertical position and heated with a small gas flame or, preferably, an electric heater. A hinged vertical shield at the back and sides reduces fluctuations in temperature caused by drafts of air. The purpose of the small inverted funnel, which is raised above the bottom on small projections, is to catch the bubbles of vapor and direct them through the center tube and three vertical spouts. As the bubbles discharge through these outlets, they direct three sprays of liquid and vapor against the thermometer; any superheated solution comes to equilibrium with the vapor by the time it gets to the thermometer bulb.

An inner glass shield, concentric with the outer tube but fastened at the top, improves the efficiency of the pumping system and also serves to shield the thermometer from the cold solvent returning from the condenser. A somewhat more rugged design is one in which the funnel unit is firmly attached by three short pieces of glass rod to the lower end of the inner glass shield.†

† An apparatus of this design is obtainable on special order from the Scientific Glass Apparatus Co., Bloomfield, N.J., as Model 1-2008-1 (modified, Print 577996).
If the liquid does not pump steadily over the thermometer bulb, the rate of heating is changed. The rate should be adjusted so that ebullition takes place primarily within the funnel in order to produce the most efficient pumping action. The rate of heating should be steady and should not be so great as to drive the liquid condensate film too close to the upper end of the condenser, since this may result in loss of solvent and also cause superheating. A metal chimney placed around the burner helps to reduce fluctuations in the rate of heating.

An absolutely constant boiling-point reading cannot be expected, but when equilibrium has been reached, the observed temperature will fluctuate slightly around a mean value and in particular will not show a slow drift, except when there is a corresponding drift in barometric pressure. The thermometer, which must be handled carefully, is tapped gently before a reading is taken. Since the boiling point is sensitive to changes in pressure, the barometer should be read just after the temperature reading is recorded.

After the boiling point of the pure solvent has been determined, the liquid is allowed to cool. The condenser is then removed, and a weighed quantity of benzoic acid sufficient to produce a 2 to 3 percent solution is added. To prevent loss, the benzoic acid is made up into a pellet in a pellet machine or is placed in a short glass tube and rammed tight with a central rod acting as a plunger. Alternatively, if it is feasible to do so, the pellets may be dropped in through the condenser. The steady boiling point of the solution is then determined in the manner previously described. Additional determinations are made by adding more pellets.

When possible, a second series of measurements should be made, starting again with pure solvent and covering the same general range of concentrations as before. In this way, a valuable check is obtained on reproducibility.

Serious error can result from failure to wait for equilibrium to be attained. Other experimental errors may be caused by fluctuations in atmospheric pressure or by appreciable holdup of solvent in the condenser or escape of solvent vapor. The first difficulty may be met by making corrections for pressure changes, by employing a manostat to maintain a constant pressure, or by using two sets of apparatus at the same time, one for solvent and one for solution. Errors from loss or holdup of solvent are tolerable in student work provided reasonable care is taken to minimize these effects. For work of highest accuracy, one may use an apparatus† in which provision has been made for withdrawing a sample of the liquid just after the temperature measurement has been made. The molality is then found by weighing this sample, evaporating the solvent, and then weighing the residue.

CALCULATIONS. The molecular weight is calculated by means of Eq. (3), from

† The Washburn and Read modification of the Cottrell boiling-point apparatus is available from several commercial sources.
the values for $K_b$ shown in Table 1, corrected by use of the pressure coefficient
given in the last column, unless the correction is negligible.

The necessary correction to $\theta$ required by a difference in the barometric
pressures at the times the boiling points of the solvent and solution were recorded
may be made by use of Eq. (1) of Experiment 7. For this purpose, it is assumed
that $dp/dT$ may be set equal to $\Delta p/\Delta T$. The value of $\Delta H_{\text{m}}$ or $\lambda_v$ may be taken from
tables.

The calculated apparent molecular-weight values are graphed against molality
and compared with the formula weight. Any discrepancies among these values
should be discussed in the light of the estimated experimental error.

Practical applications. Many materials cannot be vaporized for direct determinations of the
vapor density without decomposition. In such cases the material is dissolved in a suitable solvent,
and the elevation of the boiling point furnishes a rapid and convenient method for determining
the molecular weight. Molecular weights of some substances in solution, however, may be differ-
ent from the values found from vapor-density measurements.

Suggestions for further work. A more elaborate and accurate method may be used in which
a thermocouple gives directly the difference in boiling point between the solvent and solution in
two different vessels. This method has been described by Mair. 7

The molecular weight of benzoic acid in a polar solvent such as ethanol may be determined,
and the result compared with that obtained with the nonpolar solvent.

Caution is required when an inflammable solvent is used.

A complete treatment of the experimental determination of the boiling point of solutions is
given by Swietoslawski and Anderson. 8

References
1. H. S. Harned and B. B. Owen, “Physical Chemistry of Electrolyte Solutions,” 3d ed., Rein-
13 ACTIVITIES FROM FREEZING-POINT DEPRESSION DATA

The freezing point of a solution is lower than that of the pure solvent. Freezing-point depression data are of considerable value in the thermodynamic study of solutions. In particular, activity coefficients of both solvent and solute can be determined as a function of concentration to a high degree of accuracy.

THEORY. The activity $a_1$ of solvent† in a solution at temperature $T$ is defined by

$$\bar{C}_1 = \bar{C}_1^f + RT \ln a_1$$  \hspace{1cm} (1)

where $\bar{C}_1^f$ is partial molar Gibbs free energy of solvent in solution at temperature $T$

$\bar{C}_1^f$ is molar Gibbs free energy of pure liquid solvent at temperature $T$

For a solution at the temperature $T_0$ of freezing of the pure solvent, Eq. (1) is equivalent to

$$\bar{C}_1 = \bar{C}_1^f + RT_0 \ln a_1$$  \hspace{1cm} (2)

where $\bar{C}_1^f$ is the molar free energy of pure crystalline solvent at temperature $T_0$, because at $T_0$ the equilibrium condition

$$\bar{C}_1 = \bar{C}_1^f$$  \hspace{1cm} (3)

is satisfied. Therefore $a_1$ for a solution at temperature $T_0$ can be calculated from

$$R \ln a_1 = \left( \frac{\bar{C}_1^f}{T_0} - \frac{\bar{C}_1^f}{T_0} \right) = \frac{\Delta \bar{C}_1}{T_0}$$  \hspace{1cm} (4)

Here, and throughout this discussion, the increment symbol $\Delta$ will refer to a change in a function of state for solvent in going from the pure crystalline solid to a solution at the same temperature $T$; for example, for water solvent,

$$\text{H}_2\text{O}(\text{c, pure}) \rightarrow \text{H}_2\text{O}(\text{liquid solution})$$

$$\left( \frac{\bar{C}_1}{T} \right)$$  \hspace{1cm} (5)

$\uparrow$ Solvent properties are designated throughout by subscript 1 and solute properties by subscript 2.