

TABLE III
THE RELATIVE PARTIAL MOLAL HEAT CONTENT AND HEAT CAPACITY CONSTANTS OF EQUATION (6)

m	$\bar{L}_2(0)$	α	β	$(\bar{C}_p - \bar{C}_{p0})_{25}$	$(C_p - C_{p0})_{25}^0$	$(C_p - C_{p0})_{25}^{12}$
0.05	20	2.6	0.015	3.3	3.5	4.8
.1	—	10	4.4	.020	5.4	6.8
.2	—	105	7.8	.025	9.0	9.6
.5	—	330	14.4	.038	16.2	15.3
1	—	640	20.5	.046	22.7	15.6
1.5	—	917	25.2	.053	26.5
2	—	1160	30.9	.059	33.8
2.5	—	1435	37.0	.064	40.2
3	—	1625	41.2	.071	44.7

Robinson at 25° is somewhat lower than ours. At $m^{1/2}$ equal to 0.9, their value at 20° agrees with ours but their result at 25° is lower. We have also indicated by the dotted line the results of Rossini's¹³ computations at 18°. The agreement with our results is within the estimated error of the two series.

Values of the relative partial specific heat derived from the electromotive force data are compiled in the fifth column of Table III. The values obtained by Gulbransen and Robinson at the lower concentrations and those obtained by Rossini at the higher concentrations are given in the last two columns. Excellent agreement with Rossini's results is obtained from 0.2 to 2 M and with Gulbransen and Robinson's from 0.05 to 0.2 M . At 0.5 and 1 M Gulbransen and Robin-

(12) Rossini, *Bur. Standards J. Research*, **7**, 47 (1931).

(13) Rossini, *ibid.*, **6**, 791 (1931).

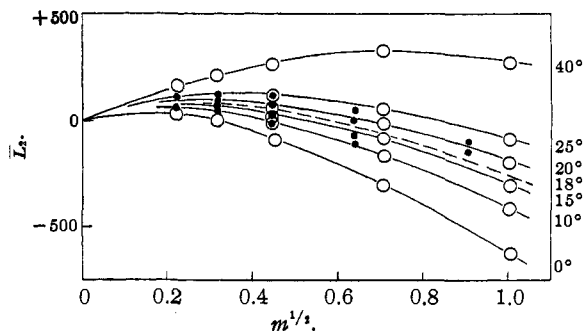


Fig. 1.— \bar{L}_2 versus $m^{1/2}$: ○, 60 cal.; ●, 20 cal.

son's values are lower than either of the other series of data. At the higher concentrations, 2 to 3 M , our results are higher than Rossini's. This indicates that our values of \bar{L}_2 spread too rapidly from 2 M to the higher concentrations since the calorimetric determination of $\bar{C}_p - \bar{C}_{p0}$ should be accurate in the concentrated solutions.

Summary

1. The thermodynamics of aqueous sodium chloride solutions derived from electromotive force measurements has been reconsidered.

2. The results have been considered in their relation to other electromotive force measurements, vapor pressure, freezing point, heat of dilution and specific heat measurements. Good coordination between the results derived from all these sources is obtained.

NEW HAVEN, CONN.

RECEIVED JULY 30, 1938

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

The Boiling Point Elevation. I. Apparatus for the Study of Aqueous Solutions with Non-Volatile Solutes

BY RODNEY P. SMITH

In recent years considerable progress has been made in the development of the physical chemistry of ionized solutes, through a comprehensive program of experimental research on the thermodynamic properties of solutions, carried out by a large number of investigators. Many different types of measurement have been used, each method giving the same fundamental thermodynamic quantities, within certain limits of the more important variables involved, namely, the concentration, the temperature, the dielectric constant, and the pressure.¹ It is of considerable im-

(1) For a general review of the subject see Harned, *J. Franklin Inst.*, **225**, 623 (1938).

portance to extend the measurements over as wide a range of the variables as is practical. Extensive data are already available for a number of solutions of widely varying concentration and dielectric constant in the temperature range 0 to 50°, while very little work is available in the temperature range 60 to 100°. As a part of this general program we have undertaken a systematic study of the properties of solutions in the latter temperature range, by measuring the boiling point rise. These results combined with the material already available from measurements of the freezing point lowering, electromotive force, and vapor pressure lowering will yield a knowledge of the

thermodynamics of ionized solutes over the considerably extended temperature range 0 to 100°.

In a preliminary investigation² an apparatus was described for the determination of the boiling point elevation at 100°, with a reproducibility of 0.0015°. While this is a fair accuracy for the determination of the boiling point elevation, the nature of the functions involved in the calculation of the thermodynamic properties is such that an accuracy of the order of 0.0001° is necessary, in the dilute range of concentration, to obtain results comparable in precision to those obtained by other methods at lower temperatures. From the point of view of the general study, a single determination at 100° is of far less value than measurements over a temperature range. Therefore, it

tensive improvements in design and technique of operation have made it possible to obtain results consistent to $\pm 0.0002^\circ$.

One must always keep in mind the fact that the reproducibility may not represent the limits of absolute accuracy. A study of the extensive data on the boiling point elevations of various types of solutions indicates that the determination of the equilibrium temperature and concentration presents a difficult problem, even under normal conditions. The absolute accuracy of the results obtained with this apparatus can only be estimated by a comparison of the derived thermodynamic quantities with those determined by other methods.

Apparatus

A front and side view of the boiling point apparatus is shown in Fig. 1(a) and Fig. 1(b), respectively. A 1-liter flask A is filled with solution to a point about one-half inch (1.3 cm.) above the hemisphere at the end of tube E. The solution is brought to boiling by a gas flame impinging directly on the glass. Steam passes through the tube B, the capillary C, the tube D, into the two 1-liter flasks containing the tubes R and P. Due to the capillary C a slight steam pressure, controlled by the rate of heating, is developed in the flask A. This pressure forces solution up the pump tube E and forces steam through a pinhole F, Fig. 1(b), into E. Thus a mixture of liquid and vapor is forced up through E and flows over R. The solution flowing from R passes through M, into G and back to flask A. The steam which passes through the capillary C is somewhat too warm due to the pressure required to operate the pump. Partial condensation in D allows this steam to come to equilibrium with water at the pressure of the measurement. The steam is condensed by the condensers I and K, and the condensate returns to flask A. The flasks containing the tubes R and P are protected from air drafts by an insulite box and cotton packing. The case S of a 26-junction thermel fits into the tubes R and P. The space between these tubes and the thermel case is filled with mercury to a point about two inches (5 cm.) above the junctions. The center portion of the thermel is heated to within 1° of the temperature of the cold junctions, or *reference temperature*, by a metal steam coil. The thermel then registers the boiling point of the solution relative to the condensation temperature of steam. To ensure regular boiling, small coils of stainless steel wire were placed in the bottom of flask A. Even with this precaution, solutions of concentrations greater than 2 M have a tendency to bump at pressures of 150 to 250 mm. In future experiments we intend to supplement the steel coils with an electric heater made of a thin glass capillary filled with mercury.

The pressure in the apparatus is maintained at any desired value between 150 and 760 mm. by a large pressure reservoir connected to the boiling point apparatus at the top of condenser K, and through stopcocks to a vacuum pump and the atmosphere. For subsequent calculations the reference temperature is more important than the corre-

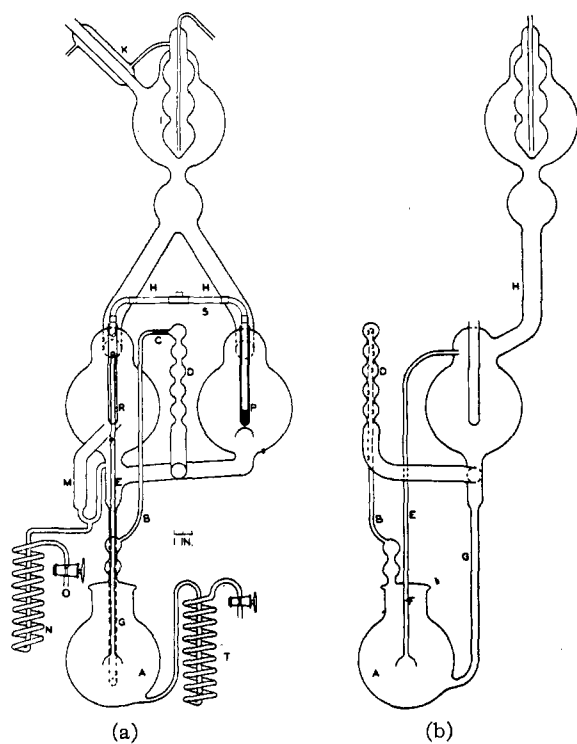


Fig. 1.—Boiling point apparatus.

seemed worth while not only to attempt to improve the accuracy of the measurement but also to design the apparatus to allow determinations at reduced pressure. A considerable amount of time has been devoted to the construction and testing of various modifications of the apparatus, and to improvement of the construction and calibration of the thermels. In the present apparatus the fundamental principle of operation is the same as that of Saxton and Smith.² However, ex-

(2) Saxton and Smith, *THIS JOURNAL*, **54**, 2626 (1932).

sponding pressure. This temperature is determined to 0.01° by a single-junction thermel, enclosed in a rigid glass case, and extending from tube P to an ice-bath. Since the reference temperature is determined simultaneously with the boiling point rise, small changes in pressure will not cause an error in the final result. A momentary difference in pressure of 0.003 mm. between the space containing the tubes R and P will cause a variation in the observed elevation of 0.0001° . With a liquid and a vapor moving through the apparatus true pressure equilibrium is impossible; however, in the present apparatus an attempt has been made to reduce the pressure effects by increasing the volume of the vapor space, providing better contact between the space containing the hot and cold junctions of the 26-junction thermel, and increasing the area of the condensing surface.

With any vapor lift pump the boiling point at the lower end of the pump will be higher than at the upper end by an amount which depends upon the pressure required to operate the pump and the rate of change of the vapor pressure of the liquid with the temperature. With the apparatus described the pressure required to operate the pump is fixed within narrow limits by the design of the apparatus, and has a value of 13.7 mm. of mercury. Thus the boiling point of pure water in flask A will be higher than its boiling point at R by approximately 2.0, 1.4, 0.95, 0.69, and 0.50° at reference temperature of 60, 70, 80, 90, and 100° , respectively. A determination of the temperature difference between R and P gave values, reproducible to ± 0.00005 , of 0.00092, 0.00068, 0.00042, and 0.00010° at reference temperature of 60, 70, 80, and 90° , R being warmer than P. Within the accuracy of the determination the difference at a reference temperature of 100° was zero. This indicates that at the lower pressures the temperature of R is higher than the condensation temperature of steam by 0.05% of the temperature gradient along the pump. A second apparatus, identical with the first except for the flask containing tube P, and connected to the pressure system near the top of condenser K, makes it possible to measure the temperature of the liquid pumped over R relative to water similarly pumped in the second apparatus, or relative to the condensation temperature of steam in the first apparatus. In the former case, with water in each apparatus, the temperature difference was 0.0005° at all pressures, the tube R being warmer than the corresponding tube in the second apparatus. Considering the temperature differences observed with pure water as constants of the apparatus, measurement of the boiling point elevation of a 0.5 and a 1.0 *M* sodium chloride solution by both procedures and with reference temperatures ranging from 60 to 100° , gave results differing by not more than 0.0003° in any case. Since this difference is of the order of the reproducibility of the determinations, we may assume that either method gives the elevation of the boiling point, provided the proper precautions are considered.

While the apparatus corrections could probably be made smaller by decreasing the height to which the liquid is raised above the solution level of flask A, or by providing some kind of an expansion chamber at the upper end of the pump, there can be no assurance that such changes would increase the accuracy of the determination. Since the momentary fluctuations in the observed boiling point

elevations were somewhat smaller in the measurement relative to the condensation temperature of steam, this method was used in all subsequent determinations.

For an aqueous solution of a uni-univalent electrolyte the rise in the boiling point is roughly proportional to the concentration of the solution; therefore the determination of the equilibrium concentration is equally as important as the determination of the equilibrium temperature. Since there is a decrease in temperature and pressure along the tube E, one would expect the solution concentration to be greater at R than at flask A.³ With the present apparatus samples of the solution in flask A, or of the solution flowing from R, may be obtained through the coils T and N, respectively. In either case, a beaker of ice water is placed around the coil, sufficient solution is slowly withdrawn into an evacuated flask to thoroughly rinse out the coil, the flask is replaced by an evacuated bottle and the solution for analysis slowly withdrawn. Analyses of samples taken simultaneously from the two points show that for a 1 *M* sodium chloride solution the liquid flowing from R is more concentrated than the solution in flask A by 0.31, 0.25, 0.18, 0.11, and 0.04% at reference temperatures of 60, 70, 80, 90, and 100° . For sodium chloride solutions of lower concentrations this difference is nearly proportional to the concentration. It is of interest to note that these values are in close agreement with concentration changes estimated from the loss of solvent required to reduce the temperature of a 1 *M* sodium chloride solution from its boiling point at flask A to its boiling point at R. If one assumes that the heat capacity and the heat of vaporization are those of pure water, the calculated concentration changes at the corresponding reference temperatures are 0.34, 0.32, 0.16, 0.11, and 0.09%. Triplicate silver chloride determinations were made on all samples. The weights used were calibrated against a similar set which had a Bureau of Standards certificate. All weighings were corrected to vacuum. The accuracy of the determination of the solution concentrations was $\pm 0.02\%$. In subsequent tables the concentrations recorded are those of the solution flowing from the thermel tube R.

All e. m. f. measurements were made with a Leeds-Northrup 100,000 μ v. range White potentiometer in conjunction with a Leeds-Northrup type HS galvanometer. All instruments were shielded. Two thermostated standard cells were used, one as a working standard, the other for calibration purposes only. The e. m. f. of the latter was determined by comparison with a set of six standard saturated Eppley cells.

Thermels

All thermels were made of no. 30 double silk covered constantan wire and no. 36 enamel covered copper wire. The 26-junction thermel consisted of two 13-junction thermels which could be connected in series or in opposition. The junctions were insulated with wire enamel, baked rapidly at about 250° and the wires were enclosed in a rigid case. The end portions of this case were made of thin glass tubing, the center portions and the bends of seamless copper tubing and copper elbows. The junctions were imbedded in anthracene. The insulation resistance, measured with a "megger," was between 500 megohms and infinity.

(3) W. Swietoslowski, "Ebulliometry," Chemical Publishing Co. of N. Y., New York, N. Y., 1937.

A 13-junction thermel of similar construction, except that the entire case was glass, was calibrated with one set of junctions in melting ice at 0° and the other set at each of ten different temperatures between 40 and 130°. The temperature of the hot junctions was determined within 0.01° with a platinum resistance thermometer that had been calibrated by the Bureau of Standards; the resistance was measured with a Leeds and Northrup Mueller-type bridge. The calibration was performed in duplicate, first with one set of junctions in ice and then with the hot and cold junctions reversed. The agreement between the two sets of results was within the experimental error and indicated a satisfactory homogeneity of the thermel. The 26-junction thermel was calibrated against the 13-junction thermel by a direct differential method.⁴ The single-junction thermel used in the measurement of the reference temperature of the boiling point elevations was calibrated by a method similar to that described for the 13-junction thermel.

Example of Reproducibility

As a typical example of the observed deviations, the measurements obtained with a 0.3 *M* sodium chloride solution are given in Table I. Each value of the boiling point elevation θ is the average of three sets of observations, each set consisting of 10 consecutive readings taken at quarter minute intervals. A small correction has been applied to the observed values of θ to make them correspond to a concentration of exactly 0.3 *M* and to the even reference temperature *t*; $\Delta\theta$ is the difference in θ for two independent determinations; columns A, B, and C give the deviation, to one hundred thousandth of a degree, of the average

(4) See Burlew and Smith, *THIS JOURNAL*, **61**, in press (1939), for a description of the technique of calibration of a thermel by a direct differential method.

<i>t</i>	θ	$\Delta\theta \times 10^5$	A	B	C	D	E
60	0.21570		+ 2	+1	-3	+25	-22
60	.21634	64	+ 7	-7	0	+47	-32
70	.23115		+ 1	-5	-4	+27	-20
70	.23109	6	-13	+8	+6	+33	-41
80	.24703		- 4	+8	-4	+16	-27
80	.24695	8	- 6	+1	+4	+33	-22
90	.26359		+ 4	+4	-8	+38	-32
90	.26362	3	+ 4	+2	-6	+16	-20
100	.37443		+ 3	-1	-2	+20	-31
100	.37478	35	+ 3	+5	-8	+32	-32

of each of the three sets of 10 readings from the mean of the thirty readings; columns D and E give the maximum positive and negative deviation, to one hundred thousandth of a degree, of the individual observations from the mean of the thirty. The value of $\Delta\theta$ represents the combined errors of the temperature and the concentration determinations. A consideration of these results together with those obtained at other concentrations shows no systematic relation between the magnitude of the deviations and the reference temperature.

Summary

1. An apparatus for measuring the boiling point elevation of aqueous solutions at pressures of 150 to 760 mm. is described.

2. The reproducibility of the boiling point elevations was found to be $\pm 0.0002^\circ$. A typical example of the observed deviations is given.

NEW HAVEN, CONN.

RECEIVED JULY 29, 1938

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

The Boiling Point Elevation. II. Sodium Chloride 0.05 to 1.0 *M* and 60 to 100°

BY RODNEY P. SMITH

The thermodynamic properties of aqueous sodium chloride solutions have been determined accurately in the temperature range 0 to 40°.¹⁻³ To extend the knowledge of these properties to higher temperatures we have determined the boiling point elevation of these solutions in the temperature range 60 to 100°. The evaluation of the activity coefficient of one salt in this temperature range may also be used as a basis for the determination of the activity coefficient of other salts in the same temperature range, by the iso-

piestic vapor pressure method of Robinson and Sinclair.⁴

Results and Calculations

If the boiling point of the solvent under a certain pressure *p* is T_0 and that of the solution under the pressure *p* is $T_0 + \theta$, and if the molal heat of vaporization of the solvent under the same pressure is expressed as a function of θ by the equation⁵

$$\Delta H = \Delta H_0 - b\theta - c\theta^2 - d\theta^3 \quad (1)$$

(4) Robinson and Sinclair, *ibid.*, **56**, 1830 (1934).

(5) The constants of equation (1) were evaluated from the data given by Keyes and Keenan, "Thermodynamic Properties of Steam," John Wiley and Sons, Inc., New York, N. Y., 1936, and Osborne, Stimson and Fiock, *Bur. Standards J. Research*, **5**, 411 (1930).

(1) Harned and Cook, *THIS JOURNAL*, **61**, 495 (1939).

(2) Brown and MacInnes, *ibid.*, **57**, 1356 (1935).

(3) Scatchard, *ibid.*, **55**, 4355 (1933).