sociation pressure data of $Na_2SO_4 \cdot 10H_2O$. It has been very accurately measured by a number of observers and the value 19.19 cm. Hg = 0.02525 atm. is probably accurate to 0.1%. Thus for hydration

$$\Delta F = 10RT \ln P \text{ dissoc.}$$

$$\Delta F_{298.15°K.} = -21,795 \text{ cal. mole}^{-1}$$

The heat of hydration may be obtained from the heat of solution data including the value -560 cal. mole^{-1} for Na_2SO_4 to infinite dilution obtained by Pitzer and Coulter.[4] Their value is supported by the more recent work of Coughlin,[9] who made solution measurements at 30°. Coughlin's result calculated to 25° is -541 ± 35 cal. mole^{-1} in satisfactory agreement with the result of Pitzer and Coulter.

The heat of vaporization of water[10] is taken as 10,520 cal. mole^{-1} when the ideal gas is the final state. The entropy of water[11] in the ideal gas state is available from spectroscopic data. $S_{298.16} = 45.106$ cal. deg.$^{-1}$ mole^{-1} on the scale 0°C. = 273.16°K. When this is corrected to the new scale, 0°C. = 273.15°K., $S_{298.15°K.} = 45.104$ cal. deg.$^{-1}$ mole^{-1}.

The above values give for the entropy of hydration

$$Na_2SO_4(s) + 10H_2O(g) = Na_2SO_4 \cdot 10H_2O(s)$$
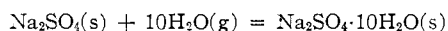
$$\Delta S = \frac{\Delta H - \Delta F}{T} = \frac{-124,749 + 21,795}{298.15}$$

$$= -345.31 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$S \text{ deca.} = S \text{ anh.} + 10S_{H2O(g)} - 345.31$$

$$= 35.73 + 451.04 - 345.31$$

$$= 141.46$$

The $\int_0^T C_p \, d \ln T$ given above for $Na_2SO_4 \cdot 10H_2O$ was found to be 139.95 cal. deg.$^{-1}$ mole^{-1}. The discrepancy indicates that $Na_2SO_4 \cdot 10H_2O$ retains $141.46 - 139.95 = 1.51$ cal. deg.$^{-1}$ mole^{-1} of residual entropy. This confirms the result obtained by Pitzer and Coulter.[4] Pitzer and Coulter used earlier values of the entropy and heat of vaporization of water. Correction of their results by

(9) J. P. Coughlin, This Journal, 77, 868 (1955).

(10) M. N. Papadopoulos and W. F. Giauque, ibid., 77, 2740 (1955).

(11) "Selected Values of Chemical Thermodynanic Properties," National Bureau of Standards Circular No. 500, issued 1952.

means of the values used here yields a discrepancy of 1.54 cal. deg.$^{-1}$ mole^{-1}. However, as noted above, their values of the heat of hydration and entropy vary by substantial amounts from the ones determined here. The agreement results partly from inherent cancellation of some of the errors due to maldistribution of water in their samples and partly due to chance cancellation within about their estimated 0.3 cal. deg.$^{-1}$ mole^{-1} error on their value of $\int_0^T C_p \, d \ln T$. Pitzer and Coulter placed their data books at our disposal and it was of interest to check some preliminary data obtained near the eutectic region shortly after the sample had been placed in the calorimeter. This showed a heat absorption of 127 cal. mole^{-1} at the eutectic. After standing for 17 days the heat absorption at the eutectic had decreased to 23.5 cal. mole^{-1} showing that water was reaching the anhydrous portion and converting it to the decahydrate. This contributes evidence in line with the earlier statement above to the effect that the samples used in the heat of solution measurements of P. and C. may have had some incomplete adjustment of the water content. Additional evidence may be noted from the fact that the heat capacities of P. and C. above the eutectic temperature are considerably higher than the present results due to a heat of solution effect. Our experience with other hydrates leads us to conclude that this particular hydrate system can distribute water at a much greater rate than is possible in most other cases many of which might require years. Within the limits of accuracy the disorder effect of 1.51 cal. deg.$^{-1}$ mole^{-1} is equivalent to $R \ln 2 = 1.38$ cal. deg.$^{-1}$ mole^{-1} which could result from one water molecule with a double choice of position or a grouping with multiple choice of orientation. It seems highly probable that most of the water molecules are held in definitely ordered arrangement by the attracting ions. In general the orienting forces between ions and water molecules are so great that in nearly all cases order will be produced at the temperatures where the hydrates are formed from solution. Cases where two or more positions of nearly equal energy exist, leading to the persistence of disorder to temperatures so low that an ordering mechanism cannot operate, are likely to occur very rarely.

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Vapor Pressure and Heat of Vaporization of Some Simple Molten Electrolytes

By H. Bloom, J. O'M. Bockris, N. E. Richards and R. G. Taylor

The vapor pressures of the molten electrolytes NaBr, AgCl, AgBr, $ZnCl_2$, $ZnBr_2$, $CdBr_2$, CdI_2 and $PbBr_2$ have been measured over a pressure range of 2 to 600 mm. by a boiling point method. Heat and entropy of vaporization, and normal boiling point have been calculated for each electrolyte.

Introduction

Investigation of vapor pressure of molten electrolytes is beset with considerable experimental difficulty which has led to the publication of numerous, widely varying results for many individual substances. Kelley[1] has coördinated and assessed the best available information on vapor

(1) K. K. Kelley, U. S. Bureau of Mines Bulletin No. 383, 1935.

pressure at high temperature. Brewer[2] has tabulated and compared such results and the thermodynamic quantities derived from them. The importance of vaporization data to the investigation of the structure of molten electrolytes is considerable. Normal boiling points of the different molten electrolytes obtained from the vapor pressure equations, are related to the degree of ionic character of the substances.[3] For mixtures of molten electrolytes the activity of each component of the mixture can be calculated from its partial vapor pressure. Variation of vapor pressure with temperature gives heat of vaporization from which entropy of vaporization is obtained. The purpose of the present investigation was to determine accurate values of vapor pressure and derived information for eight molten salts for which determinations by earlier investigators were either fragmentary, in mutual disagreement, or carried out by a method of doubtful accuracy without confirmation by other investigators.

Of the methods available, non-absolute methods were rejected owing to the necessity of knowing the molecular weight of the vapor. Recent papers by Brewer,[4] and Miller and Kusch,[5] have demonstrated conclusively that many electrolyte vapors are partially polymerized, e.g., NaCl exists to a large extent as a dimer in the gas phase; hence methods depending on the knowledge of molecular weight of the vapor are best avoided. Of the absolute methods available, many investigators, e.g., Maier,[6] Horiba and Baba,[7] and others, have used modifications of the static method. In all such determinations, the direct balance of the vapor pressure by a reference manometric liquid is subject to errors due to slight traces of volatile impurity in the sample. The most reliable absolute method is probably the boiling point method as described by Barton and Bloom[8] since no assumption as to the molecular weight of the vapor is made therein that it is relatively unaffected by small quantities of volatile impurity. In this method special care is taken to avoid superheating, which is the main possible source of error.

Experimental

Materials.—The salts used were of analytical reagent purity. PbBr₂, AgCl and AgBr were prepared by standard precipitation methods. All salts were dehydrated by careful heating in an oven and were melted *in vacuo* to remove the last traces of water.

Apparatus.—The boiling point determination apparatus was similar to that described by Barton and Bloom.[8] The melt was heated in a Vycor glass tube in an electric furnace. Pressure was reduced by means of a mechanical pump and was controlled within ±0.05 mm. by means of a "Precision" manostat. Pressure in the apparatus was measured by a mercury manometer which was read to ±0.05 mm. by a cathetometer. Super-heating of the melt was prevented by the slow passage of nitrogen bubbles through a porcelain capillary tube immersed in the melt (cf. Barton and Bloom) and temperature was measured by means of

(2) L. Brewer, "National Nuclear Energy Series," IV-19b, McGraw-Hill Book Co., New York, N. Y., 1950, p. 193.

(3) N. V. Sidgwick, "The Electronic Theory of Valency," Oxford Univ. Press, London, 1927.

(4) L. Brewer and J. S. Kane, J. Phys. Chem., 59, 105 (1955).

(5) R. C. Miller and P. Kusch, J. Chem. Phys., 25, 865 (1956).

(6) C. G. Maier, Technical Paper 360, Bureau of Mines, 1929.

(7) S. Horiba and H. Baba, Bull. Soc. Chem. Japan, 3, 11 (1928).

(8) J. L. Barton and H. Bloom, J. Phys. Chem., 60, 1413 (1956).

13% Rh–Pt vs. Pt. thermocouples and a Leeds and Northrup type K potentiometer. The junction of the thermocouple was located just above the surface of the melt.

The positioning of the thermocouple was of utmost importance. If the junction is immersed below the surface of the melt, the pressure due to the column of liquid above it adds to the applied pressure causing an error when this applied pressure is low. With pressures of the order of 2 mm., this error is important and can be avoided by the positioning of the thermocouple junction just above the surface of the melt. Direct gain of heat from the furnace walls by radiation was shown to be unimportant as the thermocouple registered a constant temperature at the boiling point in spite of a 20–50° increase of temperature of the furnace walls.

The temperature of the melt was first held below the boiling point at a controlled pressure and the furnace allowed to heat at a controlled uniform rate. The boiling point was then indicated by the constant temperature attained by the thermocouple above the melt in spite of the continued steady rise in temperature of the furnace, as indicated by a second thermocouple situated between the boiling tube and the furnace wall. Determinations were carried out at about 15 different pressures from about 2 to 600 mm. for each salt, the temperature ranges being given in Table I. Measurements were repeated on other samples of the same salt.

Results and Discussion

Vapor pressure equations calculated by the method of least squares are given in Table I. These equations enable pressure at any desired absolute temperature T, to be calculated to ±0.1 mm.

TABLE I
VAPOR PRESSURE EQUATIONS[a]
Maximum probable error in $P = \pm 0.1$ mm.)

Salt	Log₁₀ P mm. at T°K.	Temp. range, °C.
NaBr	8.9567– 9,686.7/T	870–1130
AgCl	8.5974–10,385.6/T	1028–1260
AgBr	8.7141–10,366.9/T	967–1224
ZnCl₂	9.5286– 6,612.8/T	470– 690
ZnBr₂	9.5473– 6,192.9/T	428– 650
CdBr₂	8.2523– 6,011.3/T	568– 725
CdI₂	8.8120– 6,012.4/T	500– 655
PbBr₂	8.8467– 6,953.6/T	563– 860

[a] Actual numerical values are available in four reports given to the office of Ordnance Research under Contract DA 436/036/ORD/765 during the year 1956.

From these equations, normal boiling points at 760 mm. pressure are calculated. They are presented in Table II. Heat and entropy of vaporization are given in Table III.

TABLE II
BOILING POINTS IN °K. (MAXIMUM PROBABLE ERROR IN PARENTHESES)

NaBr, 1594 (±5); AgCl, 1818 (±5); AgBr, 1778 (±5); ZnCl₂, 995 (±1); ZnBr₂, 929 (±1); CdBr₂, 1120 (±3); CdI₂, 1014 (±2); PbBr₂, 1166 (±3)

TABLE III
HEAT AND ENTROPY OF VAPORIZATION

Salt	ΔH_{vap} kg. cal. mole⁻¹	ΔS_{vap} e.u. at normal b.p.
NaBr	44.3 ± 0.6	27.8 ± 0.4
AgCl	47.5 ± .5	26.1 ± .3
AgBr	47.4 ± .5	26.7 ± .3
ZnCl₂	30.2 ± .1	30.4 ± .1
ZnBr₂	28.3 ± .1	30.5 ± .1
CdBr₂	27.5 ± .2	24.6 ± .2
CdI₂	27.5 ± .2	27.1 ± .2
PbBr₂	31.8 ± .2	27.3 ± .2

Heat of vaporization ΔH_{vap}, was constant over the range of temperature investigated. Entropy of vaporization ΔS_{vap}, is given at the normal boiling point.

Accuracy.—It can be shown[9] that the controlled nitrogen leak into the melt (rate 0.14 cm.[3] sec.$^{-1}$) has a negligible effect (approx. 10^{-5} mm.) on the equilibrium between pressure of vapor above the melt and pressure of nitrogen in the rest of the apparatus. Another possible error,[10] that due to difference of temperature between the surface of the melt (max. 1260°) and the manometer at room temperature, is only of the order of 3×10^{-5} mm. The only significant errors therefore, since superheating has been eliminated, and the effect of radiation is negligible, are due to the limit of temperature measurement, ($\pm 0.1°$), and of pressure measurement (± 0.05 mm.)

NaBr.—Investigations by Ruff and Mugdan[11] and by Von Wartenburg and Albrecht[12] using different modifications of the boiling point method, are in fair agreement but neither method effectively overcomes the problem of super-heating and must be regarded as approximate. Comparison of the present results with those of earlier workers is consistent with the fact that superheating has been avoided in the work here reported. The present results give boiling points of 1370° (cf. 1393° from the previous investigators) at 0.1 atm. and 1594° (cf. 1665° by previous investigators) at 1 atm.

AgCl.—The results of Maier[6] are in marked disagreement with those of Von Wartenburg and Bosse.[13] Kelley accepts Von Wartenburg and Bosse's boiling point method in preference to Maier's static method, but places no great reliance on his results. For the normal boiling point, 1818° is reported here, compared with Von Wartenburg's value of 1837°.

AgBr.—Jellinek and Rudat[14] obtained only a few experimental points for this compound but these are not included in Kelley's paper.

ZnCl₂.—Investigations by Jellinek and Koop,[15] Maier,[6] Tarasenkov and Skulkova,[16] and Tarasenkov and Babaeva[17] are in marked disagreement. Although Maier claims only "technical accuracy" for his method, Kelley accepts his results as being the best of those available regardless of their considerable experimental scatter. Results reported here differ somewhat from the approximate values of Maier.

ZnBr₂.—The only available values, obtained by Desai,[18] indicate large errors due to superheating, e.g., the normal boiling point is 929° according to the present measurements compared with 975° by Desai.

CdBr₂.—Greiner and Jellinek[19] carried out vapor pressure determinations at one temperature only. Weber[20] used an inaccurate boiling point method. The present vapor pressure results are slightly higher than those of Greiner and Jellinek at his temperature of measurement.

CdI₂.—Kelley quotes the results of Schmidt and Walter[21] whose data over their small temperature range are approximate only. The present data lead, at different pressures, to boiling points which are 30 to 55° lower than those of Schmidt and Walter.[21]

PbBr₂.—Determinations by Greiner and Jellinek[19] are in poor agreement with those of Von Wartenburg and Bosse.[13] Volmer[22] also measured the vapor pressures in the range near the melting point. Our results agree well with the mean weighted values calculated from the previous investigators by Kelley in the temperature range around 1000° but deviate considerably toward the normal boiling point.

Derived Information. Boiling Point.—From Table II it can be seen that AgCl is more ionic than AgBr; $CdBr_2 > CdI_2$; and $ZnCl_2 > ZnBr_2$. This agrees with Biltz and Klemm,[23] Mulcahy and Heymann[24] and others who arrived at similar conclusions from a study of electrical conductance.

Entropy of Vaporization.—Lennard-Jones and Devonshire,[25] Mayer,[26] and Eyring and Hirschfelder[27] have shown that Trouton's rule can be derived from well founded equations of state for liquids. For the present group of molten salts, the entropy of vaporization varies between 24.6 and 30.5 e.u.

Although this range is higher than for normal unassociated room temperature liquids, these values do not necessarily indicate association in the molten electrolyte. Molten KCl and NaCl, commonly regarded as ionic liquids, have entropies of vaporization of 22.9 and 23.4 e.u., respectively.[8] The relatively high values of the entropy of vaporization for molten salts have been explained by Eyring and Hirschfelder[27] on the basis of their high boiling points and small molar volumes. These melts may therefore be regarded as normal, unassociated liquids.

Philadelphia, Penna.

(9) Strong, "Procedures in Experimental Physics," Prentice Hall Book Co., New York, N. Y., 1951, p. 99.

(10) Knudsen, "The Kinetic Theory of Gases," John Wiley and Sons, Inc., New York, N. Y., 1950, p. 37.

(11) O. Ruff and S. Mugdan, Z. anorg. Chem., 117, 147 (1921).

(12) H. Von Wartenburg and P. Albrecht, Z. Elektrochem., 27, 162 (1921).

(13) H. Von Wartenburg and O. Bosse, ibid., 28, 384 (1922).

(14) K. Jellinek and A. Rudat, Z. physik. Chem., A143, 55 (1929).

(15) K. Jellinek and R. Koop, ibid., A145, 305 (1929).

(16) D. N. Tarasenkov and G. V. Skulkova, J. Gen. Chem., U.S.S.R., 7, 1721 (1937).

(17) D. N. Tarasenkov and A. V. Babaeva, ibid., 6, 311 (1936).

(18) M. S. Desai, Proc. Nat. Acad. Sci. India, 2, 119 (1933).

(19) B. Greiner and K. Jellinek, Z. physik. Chem., A165, 97 (1933).

(20) O. H. Weber, Z. anorg. Chem., 21, 305 (1899).

(21) G. C. Schmidt and R. Walter, Ann. Physik, 72, 565 (1923).

(22) F. Volmer, Phys. Z., 30, 590 (1929).

(23) W. Biltz and W. Klemm, Z. anorg. Chem., 152, 267 (1926).

(24) M. F. R. Mulcahy and E. Heymann, J. Phys. Chem., 47, 485 (1943).

(25) J. E. Lennard-Jones and A. F. Devonshire, Proc. Roy. Soc (London), 165A, 1 (1938).

(26) J. E. Mayer, J. Chem. Phys., 5, 67 (1937); J. E. Mayer and P. G. Ackermann, ibid., 5, 74 (1937).

(27) H. Eyring and J. O. Hirschfelder, J. Phys. Chem., 41, 249 (1937).