tent, errors in the weighings and temperature readings. Of these, the first probably caused the largest errors, since runs in which the vacuum was poor gave very erratic results (runs 9 and 12). Thinner oxide films would not stop the evaporation, but still might slow it down appreciably. However, early in the work it was recognized that this might be the main source of error; accordingly, special care was observed in all the work to reduce this error to a minimum. For results on films of nickel oxide on nickel, see the results on nickel oxide by Johnston and Marshall.[3,10] The temperature control of the furnace was not all that could be desired, and a considerable error might have been caused by temperature variations; however, this source of error was minimized by taking temperature readings at frequent intervals throughout the run. The errors by other causes should be small in relation to these two.

Acknowledgment.—We wish to express our appreciation to the Brush Beryllium Company for the pure beryllium sample, and to Prof. H. G. Heil of the Mendenhall Laboratory of Physics, for the use of the high temperature equipment and for instructions in its use.

Summary

The vapor pressures of metallic beryllium in the range from 1170 to 1340°K. have been determined by the Langmuir method. The results are given in Table I, and a plot of log P *vs*, $1/T$ is given, Fig. 1. Values of ΔH_0^0 have been calculated and found to vary some with temperature, the mean value of ΔH_0^0 being (122,000 ± 2500) cal./mole. The heat of vaporization was also calculated, being 78,800 cal./mole at 1250°K. Possible sources of experimental error are considered, the slowing down of evaporation by thin oxide films probably being the most important. The accommodation coefficient appears to be unity.

COLUMBUS, OHIO RECEIVED NOVEMBER 12, 1943

---

(10) The referee has kindly called our attention to the fact that experiments to settle the oxide film question could be carried out in an apparatus like that described by Blewett, Liebhafsky and Hennelly in *J. Chem. Phys.*, **7**, 478 (1939), for the determination of the vapor pressure and rate of evaporation of barium oxide. He points out that if the rates of evaporation in such an apparatus are proportional to the area of the opening, then oxide films are not retarding the evaporation, provided that the vapor pressure equilibrium is maintained within.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, AGRICULTURAL AND MECHANICAL COLLEGE OF TEXAS]

Temperature Coefficients of Electrical Conductance of Solutions Containing Sodium Chloride, Potassium Chloride or Magnesium Sulfate or Mixtures Thereof

BY RAYMOND W. BREMNER

Introduction

Very little accurate information on the variation of electrical conductance with temperature is available in the literature. In this paper equations for very accurately calculating equivalent conductance as a function of centigrade temperature have been worked out. Temperature coefficients of equivalent conductance have been calculated with five-place accuracy. Temperature coefficients of specific conductance of certain standard potassium chloride solutions and of conductivity water have also been calculated. The variations of the coefficients due to temperature changes, concentration changes and mixing of electrolytes have been determined.

Calculations

Equivalent Conductance as a Function of Temperature.—Equation I was used for representing the equivalent conductances of twenty different solutions as a function of centigrade temperature.

$$\text{Eq. Cond.} = \Lambda = a + bt + ct^2 + dt^3 \qquad \text{(I)}$$

The preparation of solutions and the experimental data have been described previously.[1,2] The ratio of the number of millimoles of sodium chloride to the number of millimoles of magnesium sulfate in a given quantity of each of the four solutions that contain both of these salts is 16.4315. Similarly the ratio of the number of millimoles of sodium chloride to the number of millimoles of potassium chloride in a given quantity of each of the four solutions that contains both of these salts is 47.2916. The most dilute solution of each type is designated as Solution No. 1, while the most concentrated solution is designated as Solution No. 4. Solutions of intermediate concentrations are numbered 2 and 3, respectively.

The constants a, b, c and d of Equation I were evaluated from the experimental data for each solution by the method of least squares. By use of the resulting equations the equivalent conductance was calculated for each solution at 0, 5, 10, 15, 20 and 25°. The average deviation of the calculated from the experimentally determined value was only 0.006%. In no instance was the deviation greater than 0.02%, which is the approximate maximum error in the original data.

In Table I are listed the values of the constants of equation I for each solution. The constant (d), which is the coefficient of the term of highest degree, is in every instance negative. This indicates a point of inflection at a higher temperature

---

[1] Raymond W. Bremner, Thomas G. Thompson and Clinton L. Utterback, THIS JOURNAL, **60**, 2616 (1938).

[2] Raymond W. Bremner, Thomas G. Thompson and C. L. Utterback, *ibid.*, **61**, 1219 (1939).

in each conductance *vs.* temperature curve, which is an essential requirement for an equation that satisfactorily represents electrical conductance as a function of temperature. The second degree equations $\Lambda = a + bt + ct^2$ and $\Lambda = \Lambda_0 (1 + at + bt^2)$ were found to be inadequate for making the calculations. The deviations of the calculated from the experimental values ranged up to 0.1% or more when they were used.

TABLE I

CONSTANTS FOR THE EQUATION $\Lambda = a + bt + ct^2 + dt^3$

Solution	Grams of solute in 1000 g. of water		$a \times 10^4$	$b \times 10^4$	$c \times 10$	$d \times 10^4$
	Sodium Chloride Solutions					
1	NaCl	5.6183_6	57326_9	$17669._9$	98.08_1	-0.348_1
2	NaCl	11.3002_0	54944_1	$16719._7$	92.31_5	$-\ .329_2$
3	NaCl	19.9443_9	52738_6	$15822._3$	88.05_8	$-\ .319_1$
4	NaCl	27.2615_9	51355_7	$15338._6$	80.87_4	$-\ .227_7$
	Potassium Chloride Solutions					
1	KCl	0.15069_9	79601_6	$23802._6$	125.65_4	$-\ .727_0$
2	KCl	0.30144_2	78764_0	$23472._6$	123.69_5	$-\ .690_3$
3	KCl	0.53788_2	77909_7	$23225._7$	118.65_5	$-\ .641_3$
4	KCl	0.71622_2	77443_7	$23027._0$	119.22_4	$-\ .631_5$
	Magnesium Sulfate Solutions					
1	$MgSO_4$	0.70416_6	45266_0	$14624._2$	87.68_6	$-\ .645_7$
2	$MgSO_4$	1.4162_9	40171_7	$12922._4$	75.58_3	$-\ .632_1$
3	$MgSO_4$	2.4996_9	36145_7	$11664._6$	60.41_2	$-\ .453_6$
4	$MgSO_4$	3.4167_8	34105_3	$10905._1$	64.45_8	$-\ .660_4$
	Mixed Solutions of Sodium Chloride and Potassium Chloride					
1	NaCl	5.6183_6				
	+ KCl	0.15152_2	57582_0	$17686._1$	97.93_0	$-\ .378_7$
2	NaCl	11.3002_0				
	+ KCl	0.30475_6	55165_3	$16695._6$	97.24_0	$-\ .470_0$
3	NaCl	19.9443_9				
	+KCl	0.53788_2	52913_1	$15896._9$	85.32_8	$-\ .278_8$
4	NaCl	27.2615_9				
	+ KCl	0.73522_0	51573_9	$15320._1$	85.14_0	$-\ .347_0$
	Mixed Solutions of Sodium Chloride and Magnesium Sulfate					
1	NaCl	5.6183_6				
	+ $MgSO_4$	0.70416_6	54853_2	$16883._9$	97.26_6	$-\ .398_5$
2	NaCl	11.3002_0				
	+ $MgSO_4$	1.4162_9	52080_2	$15835._2$	95.81_0	$-\ .517_9$
3	NaCl	19.9443_9				
	+ $MgSO_4$	2.4996_9	49534_0	$14940._6$	84.32_5	$-\ .341_8$
4	NaCl	27.2615_9				
	+ $MgSO_4$	3.4167_8	48002_4	$14331._2$	83.20_9	$-\ .390_9$

For these reasons Equation I is recommended for use in calculating equivalent conductance as a function of centigrade temperature.

Temperature coefficients of equivalent conductance were calculated by use of Equation II and the constants are listed in Table I.

$$\text{Temp. coef. of eq. cond.} = \frac{d\Lambda}{\Lambda dt} = \frac{b + 2ct + 3dt^2}{\Lambda} \quad \text{(II)}$$

They were calculated with five-place accuracy for each of the 20 different solutions at 0, 5, 10, 15, 20 and 25°, and are listed in Part 1 of Table II.

Specific Conductance as a Function of Temperature.—Equation III has been used previously to calculate the specific conductances of 0.01 demal and 0.1 demal potassium chloride solutions in the temperature range 0 to 25°[3]

$$\text{Sp. cond.} = L = a + bt + ct^2 + dt^3 \quad \text{(III)}$$

TABLE II

PART 1—TEMPERATURE COEFFICIENTS OF EQUIVALENT CONDUCTANCE

Coef. × 10^6 = $(d\Lambda/\Lambda dt) \times 10^6$

Solution	0°	5°	10°	15°	20°	25°
	Sodium Chloride Solutions					
1	3082_3	2804_8	2571_3	2371_6	2198_6	2047_0
2	3043_1	2773_2	2545_3	2349_9	2180_2	2031_2
3	3000_1	2740_3	2519_5	2329_2	2163_4	2017_2
4	2986_7	2723_6	2502_6	2314_0	2150_8	2008_0
	Potassium Chloride Solutions					
1	2990_2	2723_6	2495_3	2297_3	2123_5	1969_6
2	2980_1	2715_6	2489_5	2293_0	2120_8	1968_3
3	2981_1	2712_8	2484_5	2287_6	2115_4	1963_4
4	2973_4	2708_4	2482_5	2287_2	2116_3	1965_2
	Magnesium Sulfate Solutions					
1	3230_7	2927_2	2666_1	2439_0	2239_4	2062_4
2	3216_8	2911_7	2648_3	2418_5	2216_0	2035_9
3	3227_1	2904_5	2633_3	2401_3	2200_1	2023_4
4	3197_5	2896_0	2631_4	2397_6	2189_4	2002_6
	Mixed Solutions of Sodium Chloride and Potassium Chloride					
1	3071_5	2795_6	2562_8	2363_3	2190_1	2037_9
2	3026_5	2765_9	2541_6	2346_3	2174_6	2022_1
3	3004_4	2739_3	2516_0	2324_7	2158_8	2013_3
4	2970_5	2716_1	2498_7	2310_3	2145_4	1999_6
	Mixed Solutions of Sodium Chloride and Magnesium Sulfate					
1	3078_0	2805_9	2574_6	2375_3	2201_5	2048_4
2	3040_6	2781_7	2556_8	2359_5	2185_0	2029_5
3	3016_2	2754_4	2531_2	2338_3	2169_7	2020_9
4	2985_5	2733_2	2515_3	2325_1	2157_4	2008_5

PART 2—TEMPERATURE COEFFICIENTS OF SPECIFIC CONDUCTANCE

Coef. × 10^6 = $(dL/Ldt) \times 10^6$

°C.	0	5	10	15	18	20	25
KCl 0.01D	2979_2	2703_6	2470_4	2270_1	2162_7	2095_7	1942_1
KCl 0.1D	2918_5	2653_9	2427_2	2230_4	2124_1	2057_5	1904_1
Conductivity water	43_{500}	36_{200}	31_{800}	29_{000}	28_{000}	27_{400}	26_{300}

When applied to the conductivity water used the constants obtained for specific conductance × 10^6 are $a = 0.49_5$, $b = 0.021_8$, $c = -0.00000_2$ and $d = 0.000003_9$. Since the conductance of the water used was only a small correction factor, it was less accurately determined.

By use of Equation IV temperature coefficients of specific conductance were calculated; those of 0.01 demal and 0.1 demal standard potassium chloride solutions with five-place accuracy, and those of the conductivity water with three place accuracy. They are listed in Part 2 of Table II.

$$\text{Temp. coef. of sp. cond.} = \frac{dL}{Ldt} = \frac{b + 2ct + 3dt^2}{L} \quad \text{(IV)}$$

Discussion of Results

Effects of Concentration.—As illustrated by Part 1 of Table II the temperature coefficients of equivalent conductance decrease with increasing concentration in every instance. This is probably because the coefficients for water are higher, as shown in Part 2 of Table II. The data on standard potassium chloride solutions substantiate this observation.

The effect of temperature on this decrease depends upon the particular salt or mixture of salts

---

[3] Raymond W. Bremner and Thomas G. Thompson, THIS JOURNAL, **59**, 2372 (1937).

involved. The decrease is most rapid at 0° and progressively becomes slower up to 25°, for all the solutions containing a high proportion of monovalent ions. Solutions containing only magnesium sulfate and water exhibit the reverse behavior. The decrease is slowest for the most dilute solutions (potassium chloride only) and progressively becomes more rapid to those of higher concentration (sodium chloride). These effects are best observed by plotting coefficients against concentrations.

Effects of Temperature.—The temperature coefficients of equivalent conductance considered decrease by about 1.5 to 2.0% of their values for each degree increase in temperature. The fact that they decrease is consistent with measurements showing coefficients to be negative at much higher temperatures. This decrease is most rapid for water and becomes less rapid the more concentrated the solution, except for solutions containing only magnesium sulfate and water. This difference and also the one mentioned in the preceding paragraph are likely due to the fact that magnesium sulfate is a different type of electrolyte in that it yields divalent ions.

Effects of Adding a Second Salt.—The addition of a salt that forms solutions with temperature coefficients higher or lower than those of sodium chloride solutions to the latter, produces solutions with coefficients of intermediate value. The magnitude of the intermediate value depends upon the concentration, and the temperature, even though the mole ratios are kept constant. The effect of adding a salt is either in opposition to or in addition to the effect of increasing the concentration, depending upon whether the coefficients of solutions of the added salt are higher or lower, respectively, than those of solutions containing only sodium chloride and water. For example, the addition of magnesium sulfate to sodium chloride solutions increases the temperature coefficients of the latter. Thus, two opposing factors are in operation, the effect of adding a salt with a larger temperature coefficient outweighing the effect of increasing the concentration.

When temperature coefficient is considered as a function of concentration, there is a pronounced maximum in the temperature coefficient at concentration no. 3 for magnesium sulfate solutions at 0°. Slight maxima occur also at the same concentration for this salt at 25° and for potassium chloride solutions at 0°. These maxima are reflected in the corresponding sodium chloride solutions to which the salts mentioned have been added. The maxima, particularly for the magnesium sulfate solutions at 0°, are larger than could be attributed to experimental errors, and as yet we can offer no explanation for them. It is a noteworthy fact that they occur mainly at 0°.

Summary

1. An equation is recommended for calculating the equivalent conductances of solutions as a function of centigrade temperature. The maximum deviation of the calculated from the experimental equivalent conductance was 0.02%, and the average deviation was only 0.006%.

2. By use of the differentiated form of the equation the temperature coefficients of equivalent conductance of twenty different solutions have been calculated with five-place accuracy at 0, 5, 10, 15, 20 and 25°. Also temperature coefficients of specific conductance have been calculated at 0, 5, 10, 15, 18, 20 and 25° for the conductivity water used and for 0.01 demal and 0.1 demal standard potassium chloride solutions.

3. Variations of temperature coefficients of electrical conductance of the salt solutions, due to concentration changes, temperature changes and the addition of a second salt have been determined.

COLLEGE STATION, TEXAS RECEIVED AUGUST 31, 1943

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Osmotic Pressures for Mixed Solvents[1]

BY FREDERICK T. WALL

During recent years osmotic pressure measurements have assumed increased importance as a means of determining molecular weights of high polymeric substances.[2a,b] Although the theory of osmotic pressures for simple systems has been well formulated, little attention has been devoted to the theoretical aspects of osmotic pressures for systems with mixed solvents. Since G. Gee[2] has carried out measurements under such conditions, it appears desirable to consider thermodynamically the significance of osmotic pressures for mixed solvents and to find out just what it is that one measures experimentally.

For an ordinary solution consisting of a solvent (A) and a solute (S), the osmotic pressure is a definite thermodynamic property of the solution. It is defined simply as the excess pressure which must be applied to the solution to increase the partial pressure of the solvent up to the vapor pressure of the pure solvent at the same tempera-

---

(1) Original manuscript received July 12, 1943.

(2) (a) G. V. Schulz, *Z. physik. Chem.*, **176**, 317 (1936); R. M. Fuoss and D. J. Mead, *J. Phys. Chem.*, **47**, 59 (1943); P. J. Flory, THIS JOURNAL, **65**, 372 (1943). See also H. Mark, "Physical Chemistry of High Polymeric Systems," Interscience Publishers, New York, N. Y., 1940, p. 228, for a general discussion. (b) G. Gee *Trans. Faraday Soc.*, **36**, 1171 (1940)