are given in Table I. They are slightly lower than those of the integrant ternary systems.

No new compound occurs in the quaternary system.

A correction of the lowest formation temperature of the α-calcium chloride tetrahydrate in the ternary system potassium chloride–calcium chloride–water must be made! In the ternary system mentioned the new determinations gave 43.0°.

The Quinary Aqueous System Ca^{2+}, Sr^{2+}, K^+, Na^+, Cl^-.—This system shows no features worthy of special note. The general observation can be made that sodium chloride is only very slightly soluble in solutions saturated with respect of the other three chlorides within the temperature area in question. Results from three determinations in saturated solutions are given in Table II.

TABLE II

THE QUINARY SYSTEM $SrCl_2$–$CaCl_2$–KCl–NaCl–H_2O SOLUTIONS SATURATED AT THE TEMPERATURES

Temp., °C.	Solution $SrCl_2$	$CaCl_2$	KCl	NaCl	Solid phase
18.0	0.5	39.6	2.7	0.3	f + h + k
36.5	1.0	50.2	6.7	0.3	b + d + h + k
100.0	2.5	57.2	3.0	1.0	e + g + h + k

No new compound occurs in the quinary system mentioned.

VAPOR PRESSURES OF AQUEOUS POTASSIUM CHLORIDE SOLUTIONS AT 25° BY MEANS OF A NEW TYPE OF DIFFERENTIAL MANOMETER

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A new type of differential manometer is described, which utilizes a flexible brass bellows and a Statham Strain Gage. The manometer may be made sensitive to a differential pressure of 10^{-6} mm. of mercury. This instrument was used as a null point indicator in comparing the temperatures of equal vapor pressure of potassium chloride solutions and pure water. The results indicate that high precision is possible, with temperature measurement and control the limiting factors.

Introduction

The investigation reported here was concerned with developing an extremely sensitive method for determining when the pressures on opposite sides of a barrier are equal, so that the lowering of the vapor pressure of a solvent by the addition of a non-volatile solute may be determined by measuring the difference in temperature required to establish equal vapor pressures over the solution and the pure solvent. It was felt that such a method might be useful in dealing with solutes whose high molecular weights limit the applicability of other vapor pressure methods. For this purpose, a differential manometer was constructed in which a pressure difference of 10^{-6} mm. of mercury would cause a deflection of about 0.5 mm. on the galvanometer scale. This sensitivity was far greater than could be used for our purposes in view of the limitations in temperature measurement. The sensitivity was therefore reduced by the substitution of a Statham model G-1-4.5-225 Strain Gage for the more sensitive model G-1-1.5-315, and by shunting the galvanometer.

The development of the Isopiestic Method[3,4] has made the vapor pressures of potassium chloride solutions at 25° of particular importance as a standard of reference for other solutions. Since the various indirect means of determining the vapor pressure lowering as a function of concentration lead to important differences in the result, it was felt that a direct determination would be of value in itself, as well as providing information as to the precision of the apparatus.

Experimental

Materials.—The potassium chloride was of the highest commercially obtainable purity, and before use was recrystallized three times from conductance water and dried at 500° for 48 hours. The water used for recrystallization as well as in making up the solutions for study had a specific conductance of not more than 1.05×10^{-6} ohm^{-1} cm.$^{-1}$

Apparatus.—The null point manometer consisted of a very flexible brass bellows about four inches deep and two inches in diameter, to the closed end of which was attached the feeler arm of a Statham Strain Gage, model G-1-4.5-225. The strain gage is a Wheatstone bridge in which the resistance wires making up the arms of the bridge undergo changes in tension with motion of the feeler arm. This unit was soldered inside a heavy brass can in such a way that two chambers were formed, one on either side of the bellows. These chambers were connected through Pyrex tubes to a system of stopcocks, and through these to a vacuum pump and to two specially designed Pyrex vessels, one of which held a sample of pure water and the other the potassium chloride solution under investigation. The vessels were two inches in diameter and one inch deep and were each equipped with a Pyrex-sealed bar magnet and a ground glass ball joint for attachment to the manometer system.

Two small water-baths were insulated with glass wool and placed inside a larger copper container, which in turn was placed in a larger constant temperature water-bath, whose temperature was controlled with a cooling coil and an on-off Thyratron heating circuit. One of the small baths contained the vessel with the potassium chloride solution. A stirrer with a bar magnet at the lower end of the shaft was mounted over the vessel, and coupled with the magnet inside the vessel to stir the solution. A thermistor was mounted as close as possible to the outside wall of the vessel. This bath was allowed to reach a steady state at or close to 25°. The second small bath contained the vessel with the pure water, and was nearly the same as the solution bath, except that it had a small cooling coil and a phase-shifting Thyratron circuit for temperature control. The phase-shifting Thyratron operated from the unbalance of the

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(3) D. A. Sinclair, THIS JOURNAL, **37**, 495 (1933).

(4) R. A. Robinson and D. A. Sinclair, *J. Am. Chem. Soc.*, **56**, 1830 (1934).

strain gage bridge through a galvanometer and photocell. The manometer was housed in an air-bath which was insulated and immersed in the large water-bath. An insulated protective cover was built over the large water-bath, and the air space above the water was kept warmer than the water, to prevent condensation in the glass lines and stopcocks which were located in this air space. The manometer had a small steady heat supplied to it for the same reason.

The temperature of the solution was determined with a platinum resistance thermometer of the calorimetric type which had been calibrated in terms of a National Bureau of Standards certified platinum resistance thermometer. The temperature difference between the solution and the pure water for the condition of equal vapor pressures was measured by a Wheatstone bridge consisting of two thermistors, a fixed resistance and an approximately equal fixed resistance with a higher resistance variable shunt which was adjusted to balance the bridge. The thermistors were Western Electric model 14-B which had been aged for 30 days at 150°. The thermistors were calibrated separately against the platinum resistance thermometer, about 25 points being taken for each in the range from 23 to 26°. The ratio of the resistances of the two thermistors when at the same temperature was determined as a function of temperature. The results of these three series of calibrations were combined in an equation relating the reading of the variable shunt to the temperature difference measured by the thermistors. The fixed resistances of the Wheatstone bridge were calibrated in terms of National Bureau of Standards certified standard resistors. Great care was taken to eliminate thermals in the bridge circuit.

Procedure.—Prior to making an observation of the vapor pressure lowering, a solution of potassium chloride and a sample of conductance water were placed in the two vessels, leaving an air space above the liquids. The vessels were then placed in their respective thermostats, connected to the stopcock system, and degassed. The degassing was a time-consuming operation since it had to be accomplished stepwise to avoid bumping or undue loss of solvent from the solution.

The manometer was evacuated, flushed out with vapor from one vessel, and this process repeated several times. The ultimate test for complete degassing lay in the instantaneous response of the manometer to very small temperature differences between solvent and solution. The temperature of the solvent was then adjusted so that its vapor pressure was less than that of the solution, which was kept as close as possible to 25°. The solvent vapor was allowed to enter both chambers of the manometer to establish the zero point of the instrument, then the two chambers were isolated and the solution vapor was allowed to enter one while the solvent vapor remained in the other. Both vapors, of course, were in contact with their respective liquids. The inequality of the two vapor pressures caused a motion of the bellows which was picked up by the strain gage, whose degree of unbalance was indicated by the galvanometer. The galvanometer mirror reflected a beam of light to the phototube of the phase-shifting Thyratron heater, which allowed ever decreasing amounts of heat to flow into the solvent-bath until the vapor pressure of the solvent just equalled that of the solution. At this point the temperature of the solution was measured, and also the temperature difference between solvent and solution. The average of five observations was taken as a run. The zero point of the manometer was then rechecked, and the connections of solvent and solution to the manometer were reversed for the next run. From six to eight runs were taken for each concentration of solution. The temperature of the solvent-bath was constant within 0.0005° during each run.

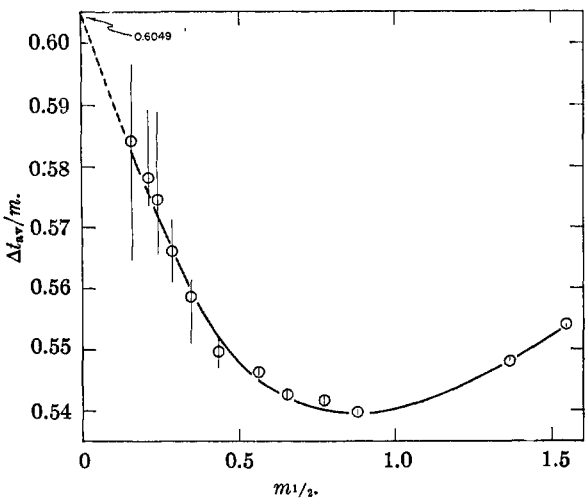

Fig. 1.—Plot of molal vapor pressure lowering *vs.* (molality)$^{1/2}$.

Analysis of Solutions.—The potassium chloride solution was removed from its vessel with a special transfer tube designed to prevent change in concentration by solvent loss. The solution was first analyzed by titration with silver nitrate solution using dichlorofluorescein as the indicator. The final analysis was made with a Rayleigh Interferometer, using as a comparison standard a solution made up by direct weighing to correspond as closely as possible to the approximate concentration as determined by the titration. All weighings were made with weights recently calibrated against National Bureau of Standards certified weights, and were corrected to vacuum. The accuracy of the interferometric method is about ±4 parts per million.

Results and Discussion

The experimental results are given in Table I, and in more detail in Table II. The temperature of the solution bath is t_1, and that of the solvent bath is $t_1 - \Delta t$. The osmotic coefficient ϕ, which is defined by equation 2 below, has been calculated from the observations by methods I and II, as described in the next paragraph, and is tabulated as ϕ, method I and method II. Figure 1 is a plot of $\Delta t/m$ *versus* $m^{1/2}$, with vertical lines used to mark the limits for extreme values of Δt as listed for each point in Table II. The point for zero concentration was obtained from equation 3 below and the relation

$$(\Delta t/m)_{m=0} = (2/55.5062)(dT/d \ln P)_{25°} = 0.6049 \quad (1)$$

TABLE I

Series	t_1 (av.)	Δt (av.)	m[a]	$m^{1/2}$	ϕ Method I	ϕ Method II
1	25.042	0.0147	0.02515	0.1586	0.9588	0.9659
2	25.001	.0257	.04445	.2108	.9472	.9558
3	25.003	.0323	.05621	.2371	.9402	.9500
4	25.000	.0454	.08020	.2832	.9280	.9359
5	25.000	.0676	.1210	.3479	.9150	.9237
6	25.000	.1045	.1901	.4360	.9015	.9091
7	25.005	.1738	.3180	.5639	.8978	.9040
8	25.011	.2309	.4254	.6522	.8924	.8980
9	25.001	.3265	.6025	.7762	.8924	.8969
10	25.001	.4179	.7741	.8798	.8903	.8938
11	25.001	1.0211	1.8631	1.3650	.9096	.9095
12	25.001	1.3176	2.3783	1.5422	.9205	.9204

[a] m is the number of moles of KCl/kg. H_2O.

The conformity to a smooth curve extrapolating to the theoretical limit indicates a precision of better than 0.0005° for all points. Table II shows no systematic trend in Δt for runs taken with pure solvent vapor inside or outside the bellows. This indicates a precision of about 0.0001 mm. of mercury in reaching zero pressure differential.

The reduction of the measured temperature differences to the corresponding lowering of the vapor pressure of water required a precise vapor pressure–temperature relationship for water in the

TABLE II

DEVIATIONS OF INDIVIDUAL RUNS FROM AVERAGES IN TABLE I

(The numbers 3 and −68 for series 1, run A, for example, mean that for this particular observation the value of Δt was 3×10^{-4} degrees greater, and the value of t_1 was 68×10^{-3} degrees less than the averages for Series 1 listed in Table I. Other entries have corresponding meanings.)

Series Runs	1	2	3	4	5	6	7	8	9	10	11	12
A	3	0	−1	0	2	3	2	−1	1	0	1	1
	−68	0	−1	0	−2	0	−5	−11	−1	0	0	−1
B	0	5	−1	0	3	1	1	−3	−4	4	−2	−4
	−25	1	0	0	−1	0	−5	15	1	0	0	1
C	−3	−2	−4	3	−9	−3	−2	1	−3	6	−5	−9
	22	3	1	0	1	2	−5	20	2	1	−1	−1
D	−5	1	2	−3	0	−2	−2	1	4	−1	7	5
	100	6	2	1	1	0	14	23	−2	2	0	0
E	−1	−1	−5	−4	−2	5	−1	−1	2	−4	7	3
	112	−7	4	0	1	0	7	−11	0	−1	0	−1
F	2	1	8	0	3	−5	−1	−1	−3	−3	−1	5
	−72	−3	10	2	0	−1	−5	−9	0	−1	−1	0
G	2	−2	−1	3				2			−4	−3
	−70	0	−9	−1				−11			0	1
H			1	4				3				
			−7	−1				−12				

neighborhood of 25°. In method I, the values for the vapor pressure of water were taken from the "International Critical Tables."[5] To aid in smooth interpolation, an equation was derived which reproduced exactly the thirteen table entries from 24 to 25.2°. P^0 was interpolated to the value of t_1 for each run, and P to the value of $t_1 - \Delta t$. The osmotic coefficient was then calculated from the relation

$$\phi = -(55.5062/2m) \ln P/P^0 \qquad (2)$$

No correction was made for the very small change in P/P^0 with temperature over the 0.04° range by which t_1 departed from 25°. In method II it was assumed that the vapor pressure of water in the range from 15 to 25° could be expressed by the following equation[6]

$$P_{mm} = e^{[a - b/T + c/T^{3/4}]} \qquad (3)$$

Differentiating and using the Clapeyron equation, we obtain

$$dP/dT = \frac{[b - (3/4)cT^{1/4}]}{T^2} e^{[a - b/T + c/T^{3/4}]}$$

$$= \Delta H_v/T(V_g - V_l) \qquad (4)$$

Using the precisely known values of ΔH_v and $(V_g - V_l)$ from the tabulation of Osborne, Stimson and Ginnings[7] it was found that equation 4 reproduced exactly the five values of $\Delta H_v/T(V_g - V_l)$ for temperatures of 15, 20, 25, 30 and 35° when a = 14.779367, b = 10,794.0544, c = 1764.4607 and $T = t + 273.1600$. Therefore equation 3 with these same constants should reproduce the vapor pressure of water from 15 to 25°. It was found that the vapor pressures calculated from equation 3 for temperatures of 15, 20, 25, 30 and 35° were higher than the corresponding values for reference 7 by 0.013, 0.013, 0.012, 0.012 and 0.011 mm., respectively, and were higher than those of reference 5 by 0.007, 0.006, 0.005, 0.004 and 0.003 mm., respectively. Substituting values of T_1 and $T_1 - \Delta t$ into equation 3 gave values of ln P/P^0 from which the ϕ values listed in Table I under method II were obtained. An Antoine equation was assumed using method II and while it fitted the five values of $\Delta H_v/T(V_g - V_l)$ exactly, it produced calculated pressures less than reference 5 by 0.025,

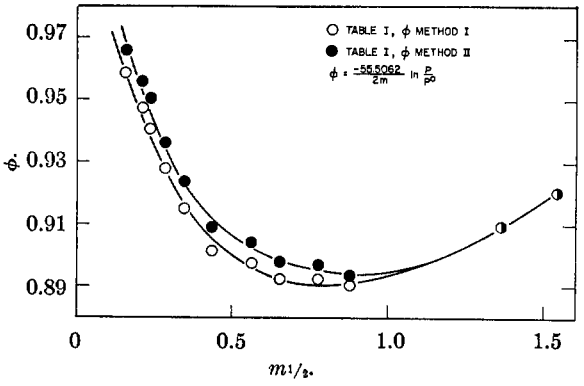

Fig. 2.—Osmotic coefficient *vs.* (molality)$^{1/2}$.

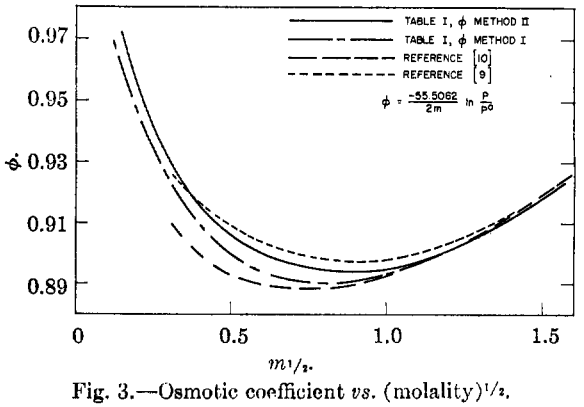

Fig. 3.—Osmotic coefficient *vs.* (molality)$^{1/2}$.

(5) "International Critical Tables," Vol. III, McGraw-Hill Book Co., Inc., New York, N. Y., 1928, pp. 211–212.

(6) A paper in preparation by O. L. I. Brown will present the evidence supporting this new type of equation.

(7) N. S. Osborne, H. F. Stimson and D. C. Ginnings, *J. Research Natl. Bur. Standards*, **23**, 261 (1939).

0.026, 0.026, 0.038 and 0.029 mm., respectively, and was therefore considered less accurate than equation 3.

Figure 2 presents our calculated values of ϕ from the above two methods, and Fig. 3 shows a comparison of these with the "best values" of Robinson, quoted by Harned and Owen[8] and with direct measurements by Lovelace, Frazer and Sease as recalculated to 25° from 20° by Robinson and Sinclair.[9] The present authors calculated the values of ϕ from the smoothed values of $\Delta P/P^0m$, the molal vapor pressure lowering, tabulated by Robinson and Sinclair.

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(8) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 2nd Edition, Reinhold Publ. Corp., New York, N. Y., 1950.

(9) R. A. Robinson and D. A. Sinclair, *J. Am. Chem. Soc.*, **56**, 1830 (1934).

BINDING ENERGIES OF GASEOUS DIATOMIC HYDRIDES AND HALIDES OF GROUP II AND GROUP III METALS[1]

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The available data relating to binding energies of gaseous diatomic hydrides and halides of Group II (Be, Mg, Ca, Sr and Ba) and Group III (B, Al, Ga, In and Tl) metals have been correlated on the basis of an ionic model similar to that used previously for the alkali halides and hydrides. Experimental values for the binding energies are calculated through thermochemical cycles. In the cases studied the binding energies calculated on the basis of pure ionic attraction (e^2/r) and neglecting repulsion and polarization effects compared well with the experimental values with an average deviation of ±12 kcal./mole. The use of estimated polarizabilities in a series of refined calculations gave values for the binding energies about the same as those given by e^2/r. This correlation has been used for critically evaluating the experimental data on molecules and for determining a series of gaseous cationic radii.

There are available in the literature spectroscopic data for nearly all of the diatomic gaseous hydrides and halides of the Group II (Be, Mg, Ca, Sr and Ba) and Group III (B, Al, Ga, In and Tl) metals. In addition a number of the halides have been studied by electron diffraction and microwave spectroscopy. In this work an attempt is made to correlate the experimental observations with a satisfactory model for these gaseous molecules.

The gaseous alkali metal halides and hydrides have been treated successfully on the basis of an ionic model by Brewer and Mastick,[2] Rittner,[3] and Klemperer and Margrave.[4] These compounds are definitely ionic and consist of metals and non-metals having electronegativity differences ranging from about 3.2 for CsF to about 1.3 for LiH. Binding in the alkali halides may be fairly well described by using only e^2/r for the ionic binding energy since detailed calculations taking into account polarization and repulsion effects show that they almost exactly counterbalance each other. In the alkali hydrides, however, these two effects make quite different contributions and must be considered separately to get proper values for ionic binding energies. The success of the ionic model in these cases indicates its possible application to Group II and III metal halides and hydrides.

The idea lying behind use of the ionic model for molecules of this type may be most easily understood by considering that in a molecule for which the difference between the ionization potential of the metal and the electron affinity of the non-metal is small, the ground state potential energy curve will be primarily determined by coulombic attraction of the ions. Herzberg[5] and others have considered this problem in detail and suggested rules for deciding when ionic character will be most important and when atomic character will predominate. One such rule is

$$R = r_s/r_e = [14.43/(I - E)]/r_e \geq 1.5$$

where r_s is the internuclear distance at which electrostatic attraction between ions has just compensated for the energy $(I - E)$, r_e is the observed internuclear equilibrium distance, $(I - E)$ is the difference in ionization potential and electron affinity as previously defined, and 14.43 is the constant necessary when $(I - E)$ is expressed in electron volts and r_e is expressed in Å. Herzberg states that in the range $R = 1.5$–2 the decision between ionic and atomic molecules is often difficult, but for $R >$ 2, a molecule usually shows ionic character in its ground state.

Values of R have been calculated for all the molecules involved and range from near 1.0 for some of the alkaline earth hydrides to nearly 4.0 for some Group III halides. Thus, a relatively wide range of R values is being considered, some actually outside the range suggested by Herzberg for ionic molecules.

In order to make a comparison of experimental and calculated ionic binding energies, one may use

(1) Presented before the Physical and Inorganic Division of the American Chemical Society in Chicago, September, 1953.

(2) L. Brewer and D. F. Mastick, *J. Am. Chem. Soc.*, **73**, 2045 1951).

(3) E. S. Rittner, *J. Chem. Phys.*, **19**, 1030 (1951).

(4) W. A. Klemperer and J. L. Margrave, *ibid.*, **20**, 527 (1952).

(5) G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Co., Inc., New York, N. Y., 1950.