ing values for the relative partial molal free energy of the solute and solvent as calculated from the equation

$$\overline{F} - \overline{F}_0 = RT \ln a \qquad (11)$$

Theoretical Check of Calculated Values of a_u.—The function, $\left(a_u + \frac{\sqrt{K_1 a_u}}{\gamma_\pm}\right)\frac{1}{m}$, which is obtained from equation 3 and the total phosphate concentration, $m = (H_2PO_4^-) + (H_3PO_4)$, should approach unity as m approaches zero. The values of a_u in Table IV were tested and confirmed by plotting this function against m as shown in Fig. 3. The dislocation of the point at 0.01 molal indicates a slight error in α which is magnified by the very sensitive test.

Acknowledgment.—The assistance of A. D. Jones in many of the calculations and of Winifred M. Blum in the experimental work is acknowledged.

Summary

The vapor pressure (water activity) over orthophosphoric acid in concentrations of 0.16 to 75 molal has been determined at 25°, and the results have been used in the calculation of the activity of the solute and the relative partial molal free energy of both the solute and solvent over the concentration range from 0.01 to 80 molal.

WILSON DAM, ALABAMA RECEIVED MAY 20, 1946

[CONTRIBUTION FROM THE PHYSICAL LABORATORY OF OSLO UNIVERSITY]

Electrolytic Conductivity of NaOH in H_2O and of NaOD in D_2O at 25°. A Vacuum Distilling Apparatus for Deuterium Oxide

BY ENOK HETLAND

In a previous paper[1] measurements were reported for the conductance of dilute aqueous solutions of the strong acids HCl and DCl at 25°. The present communication presents similar measurements on solutions of NaOH and of NaOD.

If accurate conductance measurements of aquous solutions are to be carried out at low concentrations it is necessary to use water of especially high purity. Also, in the case of alkalies, special precautions were taken to avoid contaminations from the carbon dioxide in the air. For this purpose all measurements were carried out in an atmosphere of hydrogen.

Experimental

Distilling Apparatus.—In order to obtain water of of sufficient purity, a vacuum distilling apparatus, only mentioned in the previous paper, will be described here. Figure 1 shows this apparatus which was built of "Jena Geräteglas." It was evacuated using an ordinary water jet pump. The valves V_1, V_2, V_3 and V_4, each containing an iron core, can be opened by solenoids which are not shown in the drawing. The reservoir K_2 is filled from K_1 by lifting the valve V_1. Radiation from two electric heat elements S-S keeps the water in K_2 boiling. The vapor is condensed in K_4, and the conductivity of the distillate can be measured at any time using the electrodes C. After the apparatus had been in use for some time, and if about 1 mg. of citric acid per liter was added to reservoir K_2 and distillation carried out for a half hour or more, the conductivity was usually below 1.10^{-7} ohm^{-1}. From the bulb K_5 the distillate can be led back to K_2 by opening the valve V_3 or out of the system through V_4. The apparatus can also be emptied through the valve V_2 when necessary. The jet pump was operated continuously during the distillation in order to remove the air and assure that the system contained only water vapor. Uninterrupted, steady boiling in K_2 was obtained by using an electrical heating coil W and a bulb K_3. This provided a flow of steam through the tube T. The first trap F_1 was cooled with an ice–salt mixture, the second F_2 with acetone–carbon dioxide to prevent the heavy water from escaping through the pump. After the apparatus had been in use for some time a new bulb was added to the system parallel to K_2 (not shown in the figure). This allowed greater quantities of water to be distilled in the same run and the boiling became more steady.

Conductivity Cells.—Two cells were used, one of transparent quartz for very dilute solutions and one of "Jena Normalglas" (16 III) for more concentrated solutions. The cell constants were respectively 1.6455 and 65.66. Figure 2 shows the latter. The former, described in the previous paper, had a similar construction. In order to secure uniform concentration of the solution and to be able to renew the solution between the electrodes during the measurements, the mounting of the cell allowed it to be tipped about the axis A-A and then brought back into the original position. The tubes T-T (Fig. 2) connected to each other by the tube U made it possible to carry out the measurements in an atmosphere of hydrogen, to avoid contamination by carbon dioxide and other impurities in the air.

Bridge.—The direct reading bridge was essentially the same as that described by Jones and Josephs.[2] It was, however, not shielded. Shielding of several parts of it was found to have negligible effect. The errors in the bridge readings were far below 0.1% except for the lowest resistances in which case it might reach this value. Precision dial resistance boxes 0.1 to 100,000 ohms were used. Between 100,000 and 1,000,000 ohms, however, a precision binding post box was used. The bridge was connected to a vacuum tube oscillator with a frequency of 1800 cycles per second, and a high resistance telephone without amplifier was used as detector.

Procedure.—At the start of a run the cell was cleaned with water from the vacuum distilling apparatus, two of which were constructed, one for heavy and one for ordinary water. The cell was then dried by evacuating with a water jet pump, filled with pure hydrogen gas to atmospheric pressure, closed with short rubber tubings and Hofmann pinchcocks, weighed and connected to the distilling apparatus by the rubber tubing G_3 in a manner

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[1] O. E. Frivold, O. Hassel and E. Hetland, *Avhandl. Norske Videnskaps-Akad. Oslo, I. Mat.-Naturv. Klasse*, No. 9 (1942).

[2] Jones and Josephs, THIS JOURNAL, **50**, 1049 (1928).

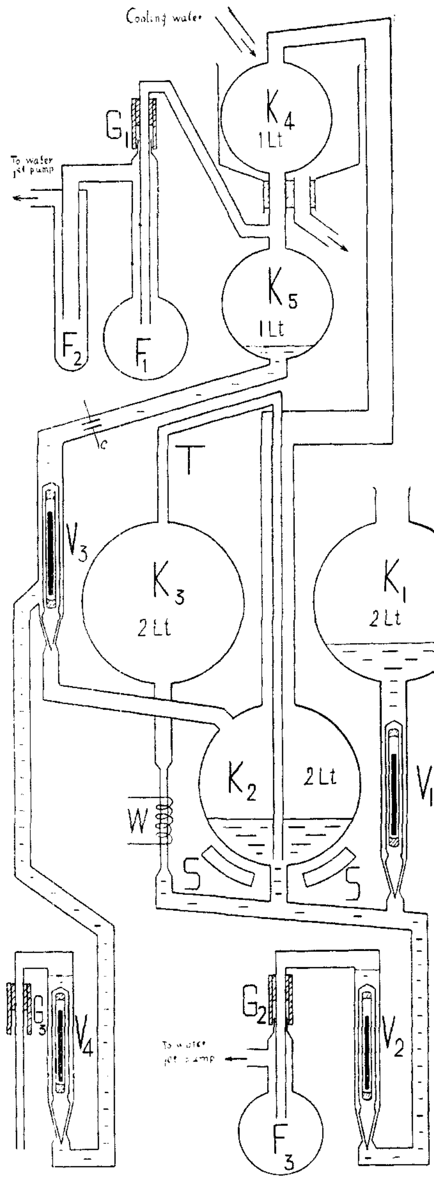

Fig. 1.

similar to that of the trap F_3, Fig. 1. Evacuating through the opening C, Fig. 2, now allowed the cell to be partially filled with conductivity water (250–300 cc.) by opening the valve V_4, Fig. 1.

The cell was refilled with hydrogen gas and removed as the gas current was still running to prevent the entrance of air. The cell was closed with the same rubber tubings as before, weighed for the second time, and the quantity of water was thus determined.

The cell was then placed in an oil thermostat at 25 ± 0.01°, and the resistance of the pure solvent was measured.

Solutions of progressively increasing concentrations were made up in the cell by adding successive increments of stock solutions of known strength from weight burets, passing a counter-current of hydrogen through the upper part of the cell, indicated by the arrows, Fig. 2. Immediately after a portion of the stock solution had been added, the cell was closed by the rubber tubings and pinchcocks.

Preparation of Solutions.—The solution of NaOH or NaOD was prepared from metallic sodium which was dropped into H_2O or D_2O in an atmosphere of hydrogen and the concentration was determined by weight titration with HCl or DCl of known strength, using traces of phenolphthalein as indicator. The meaning of the symbols used in the calculations are

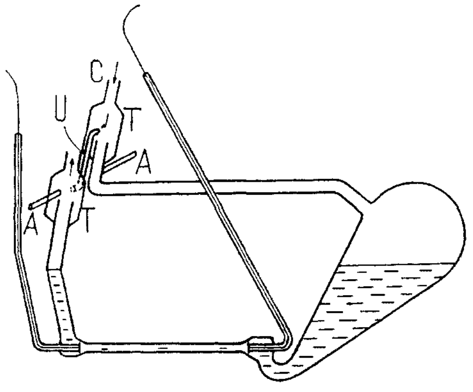

Fig. 2.

M = Weight of pure solvent in the cell
m = Weight of standard solution added
C = Cell constant
R = The measured resistance in ohms
p' = Concentration of the standard solution
p = $\Sigma p'm/(M + \Sigma m)$ Final concentration of the solution g. of NaOH (NaOD)/g. of soln.
s = Specific gravity of the solution
A = Molecular weight of NaOH or NaOD
η = ps/A, $1000\eta = \gamma$ concentration in g. equivalents/liter
κ = Specific conductivity = C/R
Λ = κ/η, equivalent conductivity

Results

The results are given in Table I for water and in Table II for deuterium oxide and plotted graphically in Fig. 3. The slopes of the tangents at infinite dilution, shown on the figure, are calculated using Onsager's equation.[3] The values used for the dielectric constants of water and deuterium oxide at 25° are $D_{H_2O} = 78.55$ and $D_{D_2O} = 78.25$. The viscosity values used in the calculations are $\eta_{H_2O,\,25°} = 0.008949$ and $\eta_{D_2O,\,25°} = 0.01103$. The conductance of the pure water used for the most dilute solutions did not exceed 1.5×10^{-7} ohms^{-1} and therefore no solvent correction is made.[4] The values Λ_0 were found by the method of Shedlovsky.[4]

For concentrations above 0.02 N the results show good agreement as compared with those by Goworecka[5] for sodium hydroxide in water. In very dilute solutions, however, the deviation is considerable. Points marked by crosses refer to Goworeckas' measurements, Fig. 3. Using the limiting conductance for the sodium ion in water or deuterium oxide given by MacInnes and

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[3] T. Shedlovsky, THIS JOURNAL, **54**, 1405 (1932).

[4] If acid impurities are present some fast OH^- ions will be replaced by slower anions, so that the correction should be added and if salt or alkaline impurities are present, since there will be no ion interaction, the correction should be subtracted. The dissociation for the pure water will be suppressed and no correction for this should be made.

[5] J. Goworecka u. M. Hlasko, Landolt–Börnstein, Physikalisch-chemische Tabellen, E IIIc, p. 2050.

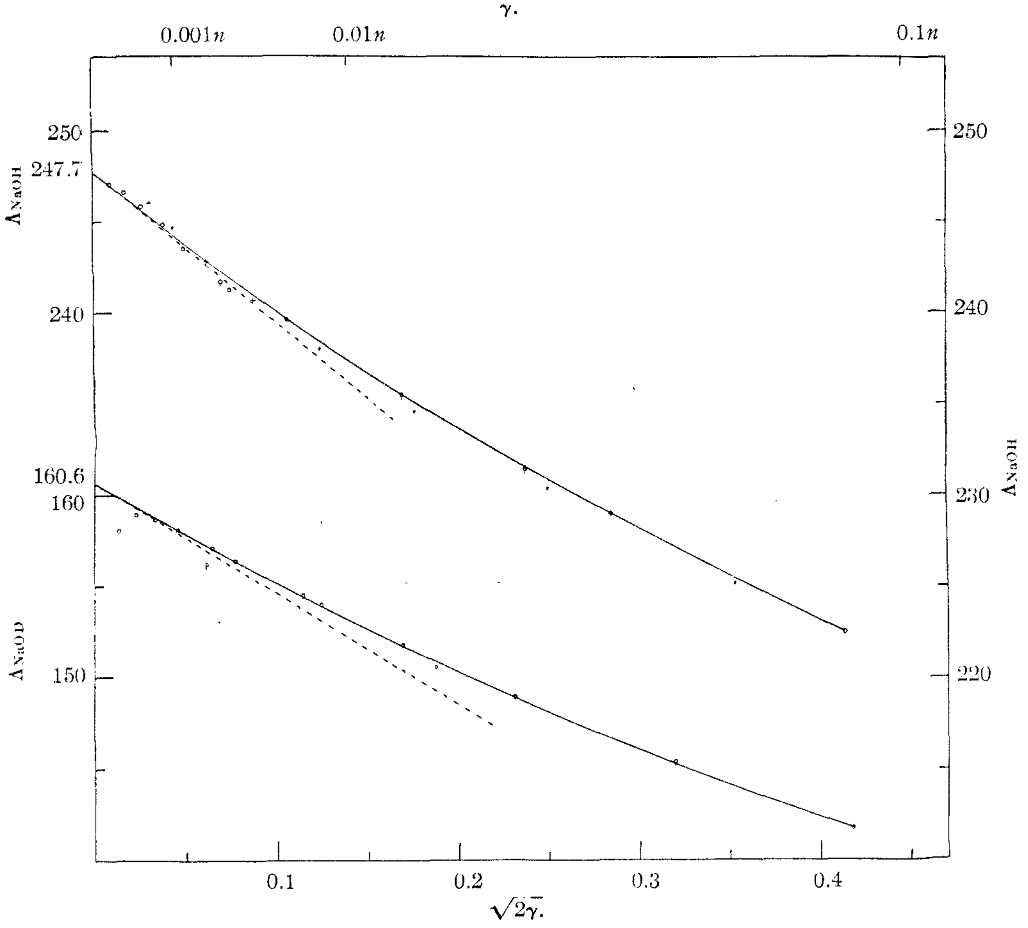

Fig. 3.

TABLE I

NaOH IN H_2O, $\Lambda_0 = 247.7$

s	$p \times 10^6$	$\gamma \times 10^4$	$\kappa \times 10^6$	Λ
Series 1. $C = 1.6455$				
0.9971	0	0	0.15	...
.9971	1.5785	0.3933	9.71	246.9
.9971	5.7950	1.4440	35.61	246.6
.9971	14.142	3.524	86.61	245.8
.9971	29.265	7.292	178.49	244.8
.9971	50.768	12.650	308.20	243.6
.9972	111.30	27.736	669.45	241.4
.9973	224.58	55.971	1341.0	239.6
Series 2. $C = 65.66$				
0.9971	0	0	1.6	...
.9972	97.985	24.418	589.7	241.5
.9978	578.52	144.25	3398.5	235.6
.9984	1137.9	283.91	6571.9	231.5
.9989	1632.8	407.59	9338	229.1
1.0009	3430.9	858.15	19094	222.5

Longsworth[6] the following values are found at infinite dilution

$$OH^- = 197.6 \text{ (in } H_2O)$$
$$OD^- = 119.0 \text{ (in } D_2O)$$

TABLE II

NaOD IN D_2O (99.55% D_2O). $\Lambda_0 = 160.6$

s	$p \times 10^6$	$\gamma \times 10^4$	$\kappa \times 10^6$	Λ
Series 1. $C = 1.6455$				
1.1040	0	0	0.14	...
1.1040	3.370	0.90705	14.33	158.0
1.1040	9.589	2.5809	41.02	158.9
1.1040	20.737	5.5815	88.59	158.7
1.1040	39.98	10.7610	170.11	158.1
1.1041	77.96	20.985	329.76	157.1
1.1041	111.68	30.062	470.28	156.4
1.1042	289.86	78.031	1201.53	154.0
1.1047	656.90	176.92	2663.91	150.6
Series 2. $C = 65.66$				
1.1040	0	0	(0)	...
1.1040	70.003	18.842	294.3	156.2
1.1042	243.00	65.417	1010.6	154.5
1.1046	537.88	144.85	2198.1	151.8
1.1052	994.00	267.83	3990.2	149.0
1.1062	1903.7	513.41	7463.9	145.4
1.1077	3226.2	871.26	12353.0	141.8

Although the present measurements were carried out in the same way as those for HCl and DCl, the errors are, however, somewhat higher, prob-

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[6] D. A. MacInnes, *J. Franklin Institute*, **225**, 680 (1938). L. G. Longsworth and D. A. MacInnes, THIS JOURNAL, **59**, 1666 (1937).

ably about 0.2%. The main difficulty is in estimating the concentration by titration with relatively small quantities of solutions. I wish to express my gratitude to Det videnskapelige forskningsfond and to Universitetets jubileumsfond for grants enabling me to carry out these investigations and toward Norsk Hydro-Elektrisk Kvælstofaktieselskab for placing heavy water at my disposal. I also wish to thank Docent Dr. Frivold and Professor Dr. Hassel for helpful suggestions and for constant interest throughout the progress of this research.

Summary

A vacuum distilling apparatus for deuterium oxide, and a conductivity cell are described. The construction of the cell allowed measurements to be carried out in an atmosphere of hydrogen.

Conductance measurements at 25° are reported on solutions of NaOH in H_2O, and of NaOD in D_2O.

The limiting values of the ion conductances of OH^- and of OD^- in ordinary and in heavy water respectively have been computed.

UNIVERSITETET I
OSLO, NORWAY

RECEIVED JULY 19, 1946

[CONTRIBUTION FROM THE CHEMICAL ENGINEERING DEPARTMENT, JOHNS HOPKINS UNIVERSITY]

Adsorption of Hydrogen and Nitrogen on Chromium Oxide Gel

BY P. H. EMMETT[1] AND MARTIN CINES[1a]

A number of years ago the late J. Howard[2] contributed one of the clearest indications that the activated adsorption of hydrogen on chromium-oxide gel was really a surface adsorption and not an activated diffusion of hydrogen into the particles of gel to form a solid solution. He found that the activated adsorption of 75 cc. of hydrogen on 37.5 g. of gel caused a decrease of about 50% in the physical adsorption of hydrogen at −78° and a 40% decrease in the physical adsorption of nitrogen at 0°. However, at the time his experiments were performed there was no good means available for judging the surface area and the size of the pores in the gel. His results could only be interpreted reasonably by assuming that much of the adsorbing surface was located in pores so small that they could be completely blocked by a layer of hydrogen held tightly by activated adsorption. Since very few examples have come to light of the inhibiting effect of activated adsorption on physical adsorption and, since a method is now available[3,4,5] for measuring the surface area and judging something as to the pore size,[6] it seemed worthwhile to repeat his results on a similar sample of chromium oxide gel.

Experimental Procedure

A sample of chromium oxide gel was prepared by the method used by Howard and originally described by Lazier and Vaughen.[7] To a liter of 0.04 *M* chromic nitrate was added slightly more than a liter of 0.12 *M* ammonium hydroxide. The excess ammonium hydroxide was required to help form flocs. The precipitate was washed by decantation ten times with the original volume of water. The gel was then filtered, and dried at 150°; 2.33 g. was taken as a sample.

The adsorption and surface area measurements were made in a standard adsorption apparatus that has already been described.[8] The dead space in the adsorption bulb was calibrated in the usual way with pure helium at the temperature of each run. Dried tank hydrogen and prepurified tank nitrogen were used as the adsorbates.

Results and Discussion

The nitrogen adsorption isotherm for the sample of gel as measured at −195° is shown in Fig. 1. The B.E.T.[4] plot indicates an area of 310 sq. meters per gram. The nitrogen monolayer on the 2.33-g. sample contained 165 cc. of nitrogen (S.T.P.). The isotherm is the normal S-shaped

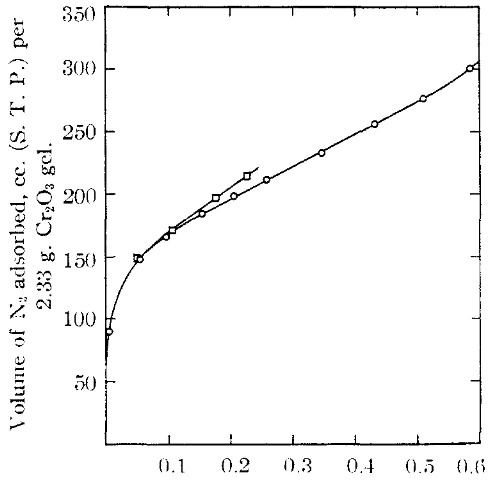

Fig. 1.—Influence of chemisorbed hydrogen on the physical adsorption of N_2 at −195° on chromic oxide gel: ○, N_2 adsorption before hydrogen chemisorption; □, N_2 adsorption at −195° after chemisorption of 8.3 cc. of hydrogen at 150°.

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[1] Present Address: Mellon Institute of Industrial Research, Pittsburgh, Pa.

[1a] Present Address: Phillips Petroleum Company, Borger, Texas.

[2] Howard, *Trans. Faraday Soc.*, **30**, 278 (1934).

[3] Emmett and Brunauer, THIS JOURNAL, **59**, 1553 (1937).

[4] Brunauer, Emmett and Teller, *ibid.*, **60**, 309 (1938).

[5] Emmett, *Ind. Eng. Chem.*, **37**, 639 (1945).

[6] Ries, Van Nordstrand, Johnson and Bauermeister, THIS JOURNAL, **67**, 1242 (1945).

[7] Lazier and Vaughen, *ibid.*, **54**, 3080 (1932).

[8] Emmett, "Am. Soc. Testing Materials, Symposium on New Methods for Particle Size Determination," 1941, p. 95.