

of the two dimeric forms are easily accounted for in terms of previous work on coördination compounds, the existence of the two isomers of the monomer brings new isomeric distinctions into this domain of chemistry.

The compounds investigated are those in which one europium ion replaces the active hydrogens of three identical diketones and remains in first coördination with the oxygen atoms of the re-

sulting substituents. The following diketones are employed, acetylacetone (pentanedione-1,4), symmetrical methyl acetylacetone (3-methylpentanedione-2,4), and benzoylacetone (1-phenylpentanedione-2,4). A similar compound is formed with salicylaldehyde. The following serve as solvents: benzene, carbon tetrachloride, and chloroform.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF YALE UNIVERSITY]

The Density of Aqueous Solutions of Potassium Hydroxide

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Introduction.—The alkali hydroxides exhibit in many respects a very complex behavior of the greatest interest. To get as clear a picture as possible of their thermodynamic properties in concentrated solutions it is our intention to follow up a previous study¹ of sodium hydroxide with a similar one on potassium hydroxide. With this purpose in mind we will present in this paper some measurements of the density of aqueous solutions of the latter. The "International Critical Tables" (I. C. T.) lists a considerable number of references to such determinations but only one of these seems to give data of higher accuracy at a single temperature. The data referred to are those of Pickering² at 15°.

Experimental Procedure.—A saturated solution of potassium hydroxide dissolves large quantities of potassium carbonate. The elimination of the carbonate down to the last traces by recrystallization requires an elaborate procedure with a considerable danger that other impurities might be picked up since the hydroxide is extremely reactive. Using as material an analytical reagent of unusually high purity the carbonate present in its saturated solution was precipitated with a slight excess of a warm solution of recrystallized barium hydroxide while the potassium hydroxide solution was being stirred by a strong stream of pure nitrogen. The precipitate was allowed to settle and the excess of barium hydroxide remaining in solution was carefully determined and then removed by mixing the required amount of carbon dioxide gas with a large amount of nitrogen and then letting it bubble through the solution. After the solution had cleared up again it was found by analysis to contain only a faint trace of barium. The ratio of barium hydroxide concentration to that of potassium hydroxide was about 1:7000. The error introduced in the density measurements due to the pres-

ence of this trace of barium is for all practical purposes negligible.

The density measurements themselves were carried out in the same manner as previously described for sodium hydroxide and using the same equipment. The corrosive action of potassium hydroxide solutions on the pycnometers was no larger than that of those of sodium hydroxide as found by a recalibration of the pycnometers after the completion of the runs.

Experimental Results.—From the density data the apparent partial molal volume of the hydroxide was first calculated using the values of Smith and Keyes³ for the specific volume of the solvent. These values, summarized in Table I, were then plotted against the square root of the molality. The resulting isothermal curves, shown graphically in Fig. 1, are continuous without any breaks in contrast to the behavior of the corresponding ones for sodium hydroxide solutions. All the curves approach for the lower third of the concentration range used very closely straight lines while their upper portions accurately follow second order equations. Therefore the data in Table I were divided up in two sections which overlapped each other to some extent. The data in the lower range were least squared linearly and those in the higher one to a quadratic equation. The constants acquired were then least squared against the temperature assuming a third order equation. That the procedure outlined is justifiable is shown by Table II which gives a summary of the final equations and constants obtained. The directly observed and the calculated values for the crossing points of the two sets of curves are practically identical. A comparison of our density data and those of Pickering at 15° shows

(1) Akerlof and Kegeles, *THIS JOURNAL*, **61**, 1027 (1939); **62**, 620 (1940).

(2) Pickering, *Phil. Mag.*, [5] **37**, 359 (1894).

(3) Smith and Keyes, *Proc. Am. Acad. Arts Sci.*, **69**, 285 (1934).

TABLE I
OBSERVED VALUES FOR THE APPARENT PARTIAL MOLAL VOLUME OF POTASSIUM HYDROXIDE

<i>m</i>	0°	10°	20°	30°	40°	50°	60°	70°
0.5815	3.40	5.22	6.49	7.32	7.79	7.95	7.82	7.36
1.689	6.049	7.432	8.398	9.051	9.408	9.602	9.764	10.011
3.003	8.372	9.412	10.143	10.627	10.946	11.138	11.131	11.029
3.204	8.657	9.755	10.364	10.832	11.121	11.295	11.310	11.208
3.644	9.209	10.122	10.772	11.208	11.493	11.657	11.624	11.584
4.414	10.225	11.034	11.596	11.979	12.233	12.375	12.370	12.276
4.495	10.313	11.108	11.666	12.046	12.286	12.420	12.419	12.328
5.187	10.978	11.691	12.206	12.556	12.765	12.890	12.879	12.820
5.246	11.100	11.800	12.318	12.656	12.874	13.005	13.003	12.932
5.639	11.495	12.164	12.639	12.966	13.173	13.289	13.283	13.190
5.689	11.532	12.197	12.670	12.997	13.204	13.325	13.334	13.265
6.093	11.920	12.552	13.002	13.309	13.503	13.606	13.608	13.540
6.208	12.011	12.632	13.077	13.377	13.571	13.687	13.689	13.621
6.577	12.315	12.898	13.324	13.615	13.802	13.901	13.910	13.853
7.037	12.648	13.200	13.606	13.882	14.063	14.164	14.154	14.107
7.324	12.882	13.418	13.812	14.083	14.258	14.354	14.362	14.306
7.532	13.019	13.551	13.938	14.210	14.377	14.476	14.474	14.432
7.907	13.247	13.759	14.138	14.395	14.561	14.657	14.656	14.621
8.615	13.741	14.223	14.574	14.816	14.977	15.068	15.071	15.035
8.971	13.936	14.402	14.746	14.984	15.139	15.228	15.234	15.205
9.551	14.295	14.740	15.079	15.305	15.448	15.543	15.554	15.530
9.989	14.515	14.947	15.370	15.493	15.633	15.724	15.736	15.708
10.228	14.624	15.055	15.369	15.586	15.729	15.810	15.829	15.803
10.945	15.008	15.413	15.719	15.927	16.062	16.147	16.161	16.147
11.539	15.309	15.692	15.986	16.192	16.325	16.411	16.431	16.418
11.984	15.502	15.887	16.170	16.370	16.501	16.587	16.606	16.594
12.987	15.869	16.234	16.501	16.689	16.820	16.896	16.922	16.903
14.012	16.283	16.627	16.882	17.064	17.189	17.269	17.295	17.287
14.987	16.628	16.957	17.201	17.377	17.499	17.575	17.605	17.601
15.988	16.968	17.267	17.501	17.670	17.789	17.866	17.899	17.894
17.074	17.276	17.576	17.802	17.964	18.081	18.158	18.193	18.198

TABLE II
LEAST SQUARE EQUATIONS AND CONSTANTS FOR THE CALCULATION OF THE APPARENT PARTIAL MOLAL VOLUME OF POTASSIUM HYDROXIDE

(A) Equations for concentrations up to m_{12} : $\varphi = \varphi^0 + k_1 \sqrt{m}$
 $\varphi^0 = -0.5018 + 0.27747t - 0.0043513t^2 + 0.000022066t^3$
 $k_1 = 5.0720 - 0.085726t + 0.0014002t^2 - 0.0000074634t^3$

(B) Equations for concentrations above m_{12} :
 $\varphi = \varphi^0 + k_2 \sqrt{m} + b_2 m$
 $\varphi^0 = -2.5869 + 0.27856t - 0.0049582t^2 + 0.000027789t^3$
 $k_2 = 7.4462 - 0.11874t + 0.0023154t^2 - 0.000014093t^3$
 $b_2 = -0.6405 + 0.014580t - 0.0002992t^2 + 0.0000019214t^3$

(C) Values of the constants at round temperatures

Temp., °C.	φ^0	k_1	φ^0	k_2	b_2
0	-0.5018	5.0720	-2.5869	7.4462	-0.6405
10	+1.8598	4.3473	-0.2693	6.4762	-0.5227
20	3.4836	3.8578	+1.2233	5.8848	-0.4532
30	4.5019	3.5589	2.0578	5.5873	-0.4205
40	5.0471	3.4056	2.4009	5.4992	-0.4134
50	5.2517	3.3532	2.4192	5.5360	-0.4194
60	5.2479	3.3570	2.2796	5.6131	-0.4279
70	5.1683	3.3722	2.1487	5.6459	-0.4271

(D) Values of m_{12} at round temperatures: $\sqrt{m_{12}} = 2.276 + 0.00386t$

Temp. °C.	0°	10°	20°	30°	40°	50°	60°	70°
$\sqrt{m_{12}}$ obsd.	2.276	2.315	2.353	2.392	2.430	2.469	2.508	2.546
$\sqrt{m_{12}}$ calcd.	2.269	2.309	2.353	2.412	2.428	2.469	2.522	2.539

The calculated values for m_{12} are extremely sensitive to very slight variations of the constants used, since the

curves for φ above and below m_{12} meet without a definite break. The agreement between observed and calculated values must therefore be considered as excellent.

an excellent agreement. Table III gives calculated values of the density of potassium hydroxide solutions at round weight per cent. concentrations and temperatures. These values should have an accuracy of about 2 in the fifth decimal place.

Discussion.—It has some thermodynamic interest to calculate the φ^0 value for water as an electrolyte. We may do this according to the following scheme: $\varphi_{HX}^0 + \varphi_{KOH}^0 - \varphi_{KX}^0 = \varphi_{HOH}^0$, where HX is a strong electrolyte, by assuming (1) additivity of ionic volumes at infinite dilution and (2) that our values for k_1 are valid for very dilute solutions. The second assumption introduces a small, unknown error but it must be made since in the case of these solutions accurate values for k_1 cannot be obtained by direct measurements. However, the values found for k_1 of both potassium hydroxide and let us say hydrochloric acid from data for concentrated solutions

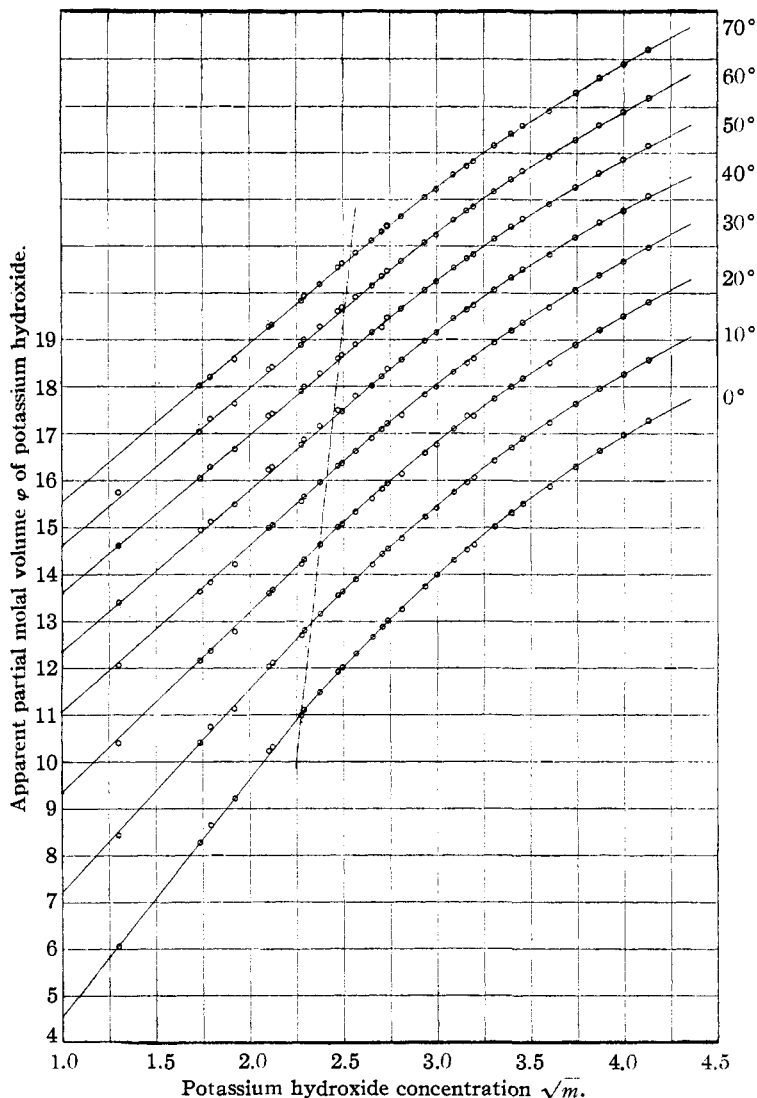


Fig. 1.—Least squared curves and observed points for the apparent partial molal volume of potassium hydroxide in pure aqueous solutions. Dotted line indicates the border between the ranges of linear and quadratic curves. Ordinates shifted successively for the different curves to avoid confusion.

are very far from the limiting value demanded by theory. It would therefore somewhat strengthen the plausibility of our second assumption or limit the validity of the theory to extremely dilute solutions if the values obtained for ϕ_{HOH}^0 from one set of measurements would agree with those computed from another set.

Table IV gives the values of two sets of data for ϕ_{HOH}^0 from 0 to 70° as obtained from the measurements presented in this paper for potassium hydroxide, those of Akerlof and Kegeles for sodium hydroxide, of Akerlof and Teare⁴

for hydrochloric acid and the density tables in Volume III of "I. C. T." for solutions of potassium and sodium chloride. The agreement between the two sets of values for ϕ_{HOH}^0 is remarkably good and the small differences are probably well within the experimental errors. A similar calculation of ϕ_{HOH}^0 using the "I. C. T." density tables for solutions of potassium and sodium nitrate and nitric acid gave practically the identical result. The large negative values of ϕ_{HOH}^0 indicate that the small amount of ionized water present in pure water may have a comparatively very large effect on its structure.

(4) Akerlof and Teare, *THIS JOURNAL*, **60**, 1226 (1938).

TABLE III

DENSITY OF POTASSIUM HYDROXIDE SOLUTIONS									
Wt. %	KOH, <i>m</i>	0°	10°	20°	30°	40°	50°	60°	70°
0	0.0000	0.99982	0.99948	0.99800	0.99553	0.99219	0.98809	0.98330	0.97789
2	.3637	1.01927	1.01822	1.01623	1.01341	1.00985	1.00562	1.00076	.99529
4	.7427	1.03849	1.03681	1.03437	1.03124	1.02749	1.02315	1.01822	1.01269
6	1.1377	1.05773	1.05548	1.05262	1.04922	1.04528	1.04083	1.03583	1.03026
8	1.5499	1.07706	1.07429	1.07106	1.06739	1.06329	1.05872	1.05366	1.04804
10	1.9804	1.09650	1.09327	1.08970	1.08579	1.08153	1.07686	1.07174	1.06607
12	2.4305	1.11607	1.11243	1.10855	1.10443	1.10002	1.09526	1.09008	1.08437
14	2.9016	1.13576	1.13177	1.12763	1.12332	1.11877	1.11392	1.10868	1.10293
16	3.3951	1.15557	1.15130	1.14694	1.14245	1.13779	1.13285	1.12756	1.12176
18	3.9126	1.17546	1.17098	1.16645	1.16183	1.15706	1.15205	1.14670	1.14087
20	4.4560	1.19542	1.19082	1.18617	1.18145	1.17659	1.17151	1.16610	1.16024
22	5.0273	1.21532	1.21069	1.20600	1.20122	1.19630	1.19116	1.18570	1.17981
24	5.6287	1.23575	1.23094	1.22614	1.22132	1.21635	1.21115	1.20565	1.19973
26	6.2625	1.25642	1.25145	1.24650	1.24154	1.23651	1.23128	1.22576	1.21982
28	6.9316	1.27730	1.27219	1.26712	1.26204	1.25691	1.25159	1.24602	1.24006
30	7.6389	1.29840	1.29318	1.28799	1.28280	1.27758	1.27217	1.26653	1.26054
32	8.3878	1.31973	1.31442	1.30913	1.30384	1.29852	1.29302	1.28733	1.28129
34	9.1821	1.34132	1.33591	1.33053	1.32514	1.31974	1.31416	1.30840	1.30232
36	10.0260	1.36314	1.35766	1.35219	1.34672	1.34124	1.33558	1.32976	1.32364
38	10.9244	1.38524	1.37969	1.37413	1.36857	1.36303	1.35729	1.35141	1.34524
40	11.8826	1.40765	1.40199	1.39634	1.39071	1.38510	1.37930	1.37335	1.36713
42	12.9070	1.43037	1.42459	1.41884	1.41313	1.40747	1.40160	1.39560	1.38932
44	14.0046	1.45347	1.44751	1.44164	1.43585	1.43015	1.42422	1.41817	1.41182
46	15.1834	1.47700	1.47079	1.46477	1.45889	1.45315	1.44718	1.44108	1.43465
48	16.4529	1.50097	1.49442	1.48820	1.48222	1.47645	1.47045	1.46431	1.45779
50	17.8240	1.52565	1.51861	1.51211	1.50600	1.50022	1.49419	1.48802	1.48139

TABLE IV

CALCULATED VALUES FOR THE PARTIAL MOLAL VOLUME OF WATER AS AN ELECTROLYTE

Temp., °C.	\bar{v}^0_{KCl}	\bar{v}^0_{KOH}	\bar{v}^0_{NaCl}	\bar{v}^0_{NaOH}	\bar{v}^0_{HCl}	$\bar{v}^0_{HOH(K)}$	$\bar{v}^0_{HOH(Na)}$
0	23.05	-0.50	12.57	-10.58	16.40	-7.15	-6.75
10	24.78	+1.86	14.45	-8.16	17.16	-5.76	-5.45
20	26.07	3.48	15.98	-6.52	17.75	-4.84	-4.75
30	26.92	4.50	16.97	-5.50	18.16	-4.26	-4.31
40	27.53	5.05	17.62	-4.94	18.39	-4.09	-4.17
50	27.87	5.25	17.97	-4.68	18.43	-4.19	-4.22
60	27.92	5.25	18.16	-4.57	18.30	-4.37	-4.43
70	27.85	5.17	18.20	-4.43	17.98	-4.70	-4.61
80	27.66	..	18.16

Summary

The density of aqueous solutions of potassium hydroxide has been measured over a concentration range of from 0.5 to 17 molal in the temperature range 0 to 70°. The partial molal volume of the hydroxide as calculated from these measurements gives when plotted against the square root of the concentration continuous curves without any breaks. The lower portion of the curves approaches closely a straight line, the upper one a quadratic. The values of the apparent partial molal volume of the hydroxide for the separate portions may be calculated using the following equations:

(A) For potassium hydroxide concentrations belonging to the straight line section

$$\bar{v}_1^0 = -0.502 + 0.2775t - 0.004351t^2 + 0.00002207t^3$$

$$k_1 = 5.072 - 0.08573t + 0.001400t^2 - 0.000007463t^3$$

(B) For potassium hydroxide concentrations belonging to the quadratic section

$$\bar{v}_2^0 = -2.587 + 0.2786t - 0.004958t^2 + 0.00002779t^3$$

$$k_2 = 7.446 - 0.1187t + 0.002315t^2 - 0.00001409t^3$$

$$b_2 = -0.6405 + 0.01458t - 0.0002992t^2 + 0.000001921t^3$$

where t is the temperature in °C. A density table similar to those in "I. C. T." was computed using these equations.

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