

ART. V.—ON THE RELATIVE BULK OF AQUEOUS SOLUTIONS OF CERTAIN HYDROXIDES AND THEIR CONSTITUENT WATER. By PROF. J. G. MACGREGOR, D. SC., *Dalhousie College, Halifax, N. S.*—(Plate I).

(Read 10th February, 1890.)

Thomsen,* in the course of his thermo-chemical work, found on determining the specific gravities of solutions of sodium hydroxide in water, of known composition, that in the case of dilute solutions of this substance, the volume of a solution was less than the volume of the water which had been used in its preparation. This seems to me so important a result that I have thought it desirable to check it by the aid of other available observations, and to determine whether or not it applies also to other hydroxides. The only other observations of the specific gravities of solutions of hydroxides to which I have access, and indeed of which I know, are those of Kohlrausch;† and although they do not include all the hydroxides, they enable us to verify Thomsen's observations, and to make the desired determination in the case of three others.

For this purpose I have calculated, with the aid of the data furnished by both the above observers, the volume of unit mass of the various solutions examined by them, and the volume which the solvent water contained in unit mass would occupy if its temperature were the same as that of the solution. The difference of these quantities gives at once the amount by which the volume of unit mass of the solution is less or greater than that of the solvent water employed in its preparation. There is one difficulty in making the necessary calculations from Thomsen's data, viz., that he does not say to what standard his specific

* Thermo-chemische Untersuchungen, Bd. I, p. 47, (1882.)

† Wiedemann's *Annalen*, Bd. VI (1879), p. 21.

gravities are referred. But on repeating some of his own calculations I found their results to be consistent only with the supposition that his standard was water at the temperature at which the specific gravities of his solutions were determined.

In all my calculations I have taken for the atomic weights of the elements the values given by Clarke,* and for the densities of water at different temperatures, the values given by Volkmann,† as quoted in both cases by Landolt and Börnstein.‡

SODIUM HYDROXIDE.—NaOH.

Thomsen's data give the following table. The temperature of the solutions examined by him was about 18° C. The headings of the various columns will sufficiently explain their contents, except in the case of the last, which to avoid circumlocution is headed expansion. Expansion here means the excess of the volume of one gramme of a solution over the volume which at the same temperature and in the free state, the solvent water in one gramme of the solution would have. Possibly I should state also that by "Percentage of a substance in solution," I mean the mass of the substance contained in 100 units of mass of the solution.

Percentage of NaOH in solution.	Density at 18° C. (grms. per cu. cm.)	Volume of 1 grm. of solution at 18° C. (cu. cm.)	Volume at 18° C. of solvent water in 1 grm. of solution. (cu. cm.)	Expansion. (cu. cm.)
1.1001	1.0111	0.9891	0.9903	—0.0012
2.1762	1.0232	0.9773	0.9795	—0.0022
4.2597	1.0472	0.9549	0.9587	—0.0038
6.9035	1.0768	0.9287	0.9322	—0.0035
12.9154	1.1435	0.8745	0.8720	+0.0025
22.8762	1.2559	0.7962	0.7723	+0.0239

The fifth column exhibits Thomsen's result that for dilute solutions of this hydroxide, the expansion is negative; *i. e.*, the

* Constants of Nature, V., Smithsonian Institution, Washington, 1882.

† Wiedemann's Annalen, Bd. XIV (1881), p. 260.

‡ Physikalisch-Chemische Tabellen, Berlin, 1883.

volume of the solution is less than the volume of the water used in preparing it. If we treat the data of the above table graphically, plotting expansion against percentage composition, we find that the contraction has its greatest value, about 0.0041 cu. cm., for a solution containing about 5.35 per cent. of the hydroxide, and that for all solutions containing less than 10.5 per cent. of the hydroxide the expansion is negative.

The following table is based on Kohlrausch's observations, which were made at a temperature of 15° C.:

Percentage of NaOH in solution.	Density at 15° (grms. per cu. cm.)	Volume of 1 gm. of solution at 15° C. (cu. cm.)	Volume at 15° C. of solvent water in 1 gm. of solution (cu. cm.)	Expansion (cu. cm.)
4.87	1.0552	0.9477	0.9521	-0.0044
10.80	1.1222	0.8911	0.8927	-0.0016
19.66	1.2224	0.8181	0.8041	+0.0140
29.67	1.3337	0.7498	0.7039	+0.0459
42.72	1.4685	0.6810	0.5733	+0.1077

Kohlrausch's observations, therefore, substantiate Thomsen's result qualitatively, though the expansions calculated from them differ from those calculated from Thomsen's to a greater extent, probably, than is accounted for by the difference in the temperatures of their solutions. The relation between expansion and percentage composition, according to Kohlrausch, both for this substance and for those considered below, is shown in Plate I. The curve gives, as the maximum contraction, 0.0045 cu. cm., and as the solution exhibiting this contraction one containing about 6 per cent. of the hydroxide, and it gives about 12.3 per cent. as the limit of concentration within which the expansion is negative.

The above observations enable us also to determine the values of the expansion when the above solutions are prepared by adding sodium monoxide (Na_2O) to water, if we assume that the oxide, when added to water, combines with a portion of the water to form the hydroxide.

According to Thomsen.

Percentage of Na ₂ O in solution.	Density at 18°C. (grms. per cu. cm.)	Volume of 1 gm. of solution at 18°C. (cu. cm.)	Volume at 18°C. of solvent water in 1 gm. of solution. (cu. cm.)	Expansion. (cu. cm.)
0.8528	1.0111	0.9891	0.9928	—0.0037
1.6871	1.0232	0.9773	0.9844	—0.0071
3.3023	1.0472	0.9549	0.9683	—0.0134
5.3519	1.0768	0.9287	0.9477	—0.0190
10.0126	1.1435	0.8745	0.9011	—0.0266
17.7346	1.2559	0.7962	0.8237	—0.0275

According to Kohlrausch.

Percentage of Na ₂ O in solution.	Density at 18°C. (grms. per cu. cm.)	Volume of 1 gm. of solution at 18°C. (cu. cm.)	Volume at 18°C. of solvent water in 1 gm. of solution. (cu. cm.)	Expansion. (cu. cm.)
3.7754	1.0552	0.9477	0.9631	—0.0154
8.3726	1.1222	0.8911	0.9170	—0.0259
15.2413	1.2224	0.8181	0.8483	—0.0302
23.0015	1.3337	0.7498	0.7706	—0.0208
33.1184	1.4685	0.6810	0.6694	+0.0116

As might be expected, the values of the expansion are (algebraically) much smaller than in the case of the solution of the hydroxide. The results of the last table are shown graphically in Plate I. The curve shows that the maximum contraction in this case is 0.0306 cu. cm., and is exhibited by a solution containing about 14 per cent. of the oxide, and that the expansion is negative for all solutions containing less than 29.6 per cent.

POTASSIUM HYDROXIDE,—KOH.

The following table is calculated from Thomsen's data :

Percentage of KOH in solution.	Density at 18° C. (grms. per cu. cm.)	Volume of 1 gm. of solut'n. at 18° C. (cu. cm.)	Volume at 18° of solvent water in 1 gm. of solution. (cu. cm.)	Expansion. (cu. cm.)
1.5344	1.0130	0.9871	0.9860	+0.0011
3.0224	1.0270	0.9737	0.9711	+0.0026
5.8674	1.0536	0.9491	0.9426	+0.0065
9.4109	1.0872	0.9198	0.9071	+0.0127

Kohlrausch's observations give the following results :

Percentage of KOH in solution.	Density at 15° C. (grms. per cu. cm.)	Volume of 1 gm. of solut'n. at 15° C. (cu. cm.)	Volume at 15° of solvent water in 1 gm. of solution. (cu. cm.)	Expansion. (cu. cm.)
4.19	1.0381	0.9633	0.9589	+0.0044
8.42	1.0778	0.9278	0.9166	+0.0112
16.78	1.1587	0.8630	0.8329	+0.0301
25.11	1.2430	0.8045	0.7495	+0.0550
33.33	1.3302	0.7518	0.6673	+0.0845
41.7	1.427	0.7008	0.5835	+0.1173

Kohlrausch's observations, therefore, substantiate Thomsen's result, that solutions of Potassium Hydroxide have in all cases volumes which are greater than the volumes of the water used in preparing them. Though the weakest solution examined was one containing 1.5 per cent. of the hydroxide, the trend of the KOH curve in Plate I, by which the relation between the expansion and the concentration of Kohlrausch's solutions is exhibited, and with which a similar curve based on Thomsen's results almost exactly coincides, shews that for solutions still weaker than the weakest examined, the expansion is probably positive.

The following tables give the values of the expansion when the above solutions are formed by adding Potassium monoxide (K_2O) to water :

According to Thomsen.

Percentage of K_2O in solution.	Density at 18° (grms. per cu. cm.)	Volume of 1 gm. of solut'n at $18^\circ C.$ (cu. cm.)	Volume at $18^\circ C.$ of solvent water in 1 gm. of solution. (cu. cm.)	Expansion, (cu. cm.)
1.2882	1.0130	0.9871	0.9884	—0.0013
2.5375	1.0270	0.9737	0.9759	—0.0022
4.9261	1.0536	0.9491	0.9520	—0.0029
7.9011	1.0872	0.9198	0.9222	—0.0024

According to Kohlrausch.

Percentage of K_2O in solution.	Density at 15° (grms. per cu. cm.)	Volume of 1 gm. of solut'n. at 15° (cu. cm.)	Volume at 15° of solvent water in 1 gm. of solution. (cu. cm.)	Expansion, (cu. cm.)
3.5178	1.0381	0.9633	0.9656	—0.0023
7.0692	1.0778	0.9278	0.9301	—0.0023
14.0879	1.1587	0.8630	0.8598	+0.0032
21.0815	1.2430	0.8045	0.7899	+0.0146
27.9828	1.3302	0.7518	0.7208	+0.0310
35.0099	1.147	0.7008	0.6504	+0.0504

Both sets of experiments agree in showing that on adding Potassium oxide to water in sufficiently small proportions, solutions are formed smaller in bulk than their constituent water.

The expansion-concentration curve given by Kohlrausch's experiments (Plate 1) makes the greatest contraction in the case of solutions of this oxide, have the value 0.0024 cu. cm., and gives as the solution exhibiting this contraction one containing about 5.6 per cent. of the oxide, while the limit of concentration within which the expansion is negative is about 11.2 per cent.

LITHIUM HYDROXIDE.—LiOH.

The following table is based on Kohlrausch's observations of the densities of solutions of Lithium hydroxide at a temperature of 18° C.

Percentage of Li O H. in solution.	Density at 18° (grms. per cu. cm.)	Volume of 1 gm. of solut'n. at 18° (cu. cm.)	Volume at 18° of solvent water in 1 gm. of solution. (cu. cm.)	Expansion. (cu. cm.)
1.25	1.0132	0.9888	0.9869	—0.0019
2.50	1.0276	0.9763	0.9731	—0.0032
4.99	1.0546	0.9513	0.9482	—0.0031
7.71	1.083	0.9241	0.9233	—0.0008

Thus for dilute solutions of Lithium hydroxide also the expansions are negative. The LiOH curve of Plate I shows that the solution exhibiting the greatest contraction is one containing about 3.6 per cent. of the hydroxide, that the amount of its contraction is 0.0036 cu. cm., and that the limit of concentration within which contraction occurs is 8.2 per cent.

From the same data the following table has been calculated giving the expansion on adding Lithium Oxide (Li₂O) to water

Percentage of Li ₂ O in solution.	Density at 18° (grms. per cu. cm.)	Volume of 1 gm. of solut'n. at 18° (cu. cm.)	Volume at 18° of solvent water in 1 gm. of solution. (cu. cm.)	Expansion. (cu. cm.)
0.7816	1.0132	0.9869	0.9935	—0.0066
1.5633	1.0276	0.9731	0.9856	—0.0125
3.1203	1.0546	0.9482	0.9701	—0.0219
4.8211	1.083	0.9233	0.9530	—0.0297

As might be expected the contraction is much greater in the case of solutions of the oxide than in that of solutions of the hydroxide. The experiments are not sufficient to determine the

maximum contraction, the solution which exhibits it, or the limit of concentration within which contraction occurs.

AMMONIUM HYDROXIDE,— NH_4OH .

As Ammonium is closely related in the properties of its compounds to the metals of the alkalies, it may be well to give a table similar to the above, for solutions of its hydroxide, though as the densities of these solutions are less than unity it is obvious that their expansions must be positive. The table is based on experiments by Thomsen.

Percentage of NH_4OH in solution.	Density at 18° (grms. per cu. cm.)	Volume of 1 gm. of solut'n. at 18° (cu. cm.)	Volume at 18° of solvent water in 1 gm. of solution (cu. cm.)	Expansion (cu. cm.)
1.9103	0.9954	1.0046	0.9822	+0.0224
3.7491	0.9914	1.0087	0.9638	+0.0349
6.0961	0.9865	1.0137	0.9403	+0.0734

The NH_4OH curve of Plate I. shews the results of this table graphically. It is much steeper than the others; and, if the observations are exact, has a point of contrary flexure. If we regard the experiments as not sufficiently exact to establish the contrary flexure, the curve must be regarded as practically a straight line.

BARIUM HYDROXIDE,— $\text{Ba O}_2\text{H}_2$.

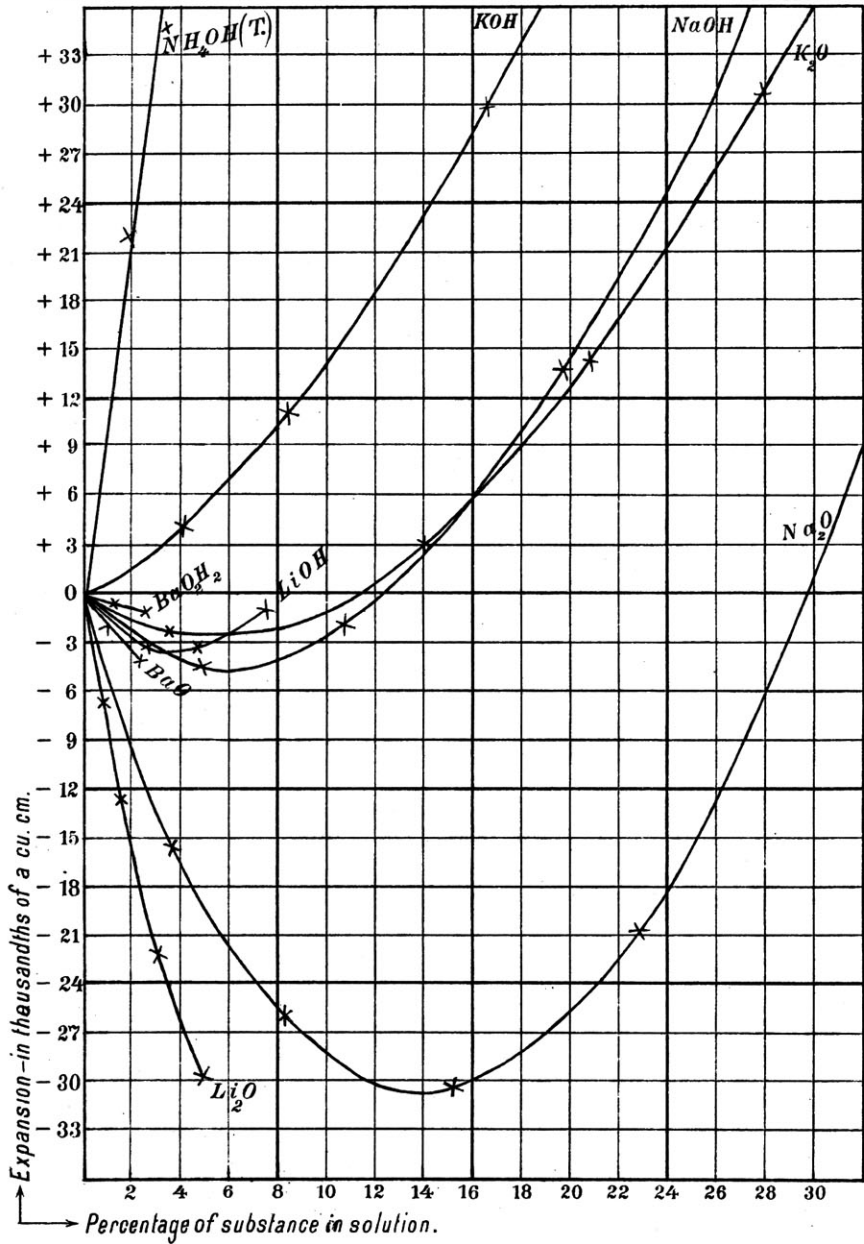
For Barium Hydroxide, Kohlrausch has published two determinations which serve as the basis of the following table:—

Percentage of $\text{Ba O}_2\text{H}_2$ in solution.	Density at 18° (grms. per cu. cm.)	Volume of 1 gm. of solut'n. at 18° (cu. cm.)	Volume at 18° of solvent water in 1 gm. of solution (cu. cm.)	Expansion (cu. cm.)
1.33	1.0128	0.9873	0.9880	—0.0007
2.67	1.0271	0.9736	0.9746	—0.0010

For dilute solutions of Barium Hydroxide, therefore, the expansions are negative. But the available data are not sufficient to shew fully how the contraction varies with the concentration.

The following table shews the values of the expansions on dissolving Barium oxide in water :—

Percentage of Ba O in solution.	Density at 18° (grms. per cu. cm.)	Volume of 1 grm. of solut'n. at 18° (cu. cm.)	Volume at 18° of solvent water in 1 grm. of solution. (cu. cm.)	Expansion. (cu. cm.)
1.1900	1.0128	0.9873	0.9894	—0.0021
2.3890	1.0271	0.9736	0.9774	—0.0038



Illustrating Prof. MacGregor's Paper on Solutions of Hydroxides.