Summary

Both nitric oxide and propylene inhibit the *n*-butane decomposition. The inhibition reaches a limit as the inhibitor concentration increases. It fades out as the reaction proceeds, the rate eventually becoming nearly equal to that of the normal decomposition. This phenomenon is attributed to the reversible formation of an intermediate.

These results are compared with the normal reaction and the inference drawn that there are two chain processes involved with only one type of carriers or one mechanism concerned with the reversible inhibitor reaction.

The Density of Aqueous Solutions of Sodium Hydroxide

BY GÖSTA ÅKERLÖF AND GERSON KEGELES

Introduction

As a preliminary to an extensive study of the thermodynamics of sodium hydroxide at very high concentrations, the density of its pure aqueous solutions was determined over a temperature range of 0 to 70° and the concentration range of 1 to 26 molal. The corresponding data given in Volume III of "International Critical Tables" are only in fair agreement with ours and differences frequently were found even in the third decimal place. A mathematical analysis of the former had shown, however, that they without much doubt do contain large errors. Although practically hidden by the manner of interpolating the original data, they show nevertheless distinct indications of a break occurring at relatively high concentrations in the isothermal curves for the apparent partial molal volume of the hydroxide. This break, which at 0° appears at a hydroxide concentration of about 10 molal and with rising temperature slowly shifts toward still higher concentrations, seems according to our measurements to be fairly sharp, and the curve on either side of the break follows at all temperatures nearly precisely a square root linear law. Similar breaks have been noticed previously by Scott in the case of the lithium halides, and earlier by Masson[1] for several other strong electrolytes.

Experimental Procedure.—Sodium hydroxide is extremely reactive, deliquescent in the solid phase and absorbs quantitatively any free carbon dioxide present. It is therefore difficult to prepare and preserve in a highly pure form. Since large quantities were needed, the preparation from pure sodium metal was excluded. The material used was an analytical reagent of unusually high purity and no attempts at further purification, except the

removal of carbonate present were considered necessary. A saturated solution of the hydroxide in air-free conductivity water was made up in an old soft glass bottle previously used for similar purposes over a number of years. The precipitate that appeared was allowed to settle during a period of about three weeks after which time the solution had become perfectly clear without the least trace of suspended matter visible. The careful study of Freeth[2] of the system sodium carbonate–sodium hydroxide–water at various temperatures does not allow an exact calculation of the concentration of the two electrolytes when they are both present as coexistent solid phases but apparently at ordinary temperatures the ratio between carbonate and hydroxide concentrations at this point is approximately 0.001 or lower. The change of the apparent partial molal volume of sodium carbonate in the presence of large amounts of the hydroxide cannot be obtained and thus any calculation of the error caused by the presence of the former electrolyte would only be approximate in nature. However, using the "I. C. T." density data for pure aqueous solutions of sodium carbonate which at 30° give as its apparent partial molal volume the equation

$$\varphi_{30} = -4.163 + 10.849 \sqrt{m}$$

where *m* is the molality and assuming that no changes occur due to the presence of the hydroxide, it is found that for all practical purposes the error introduced is negligible or at least appreciably smaller than that caused by analytical errors in the determination of the hydroxide concentration.

All solutions used for the density measurements were made up to approximately the desired concentration in quantities of about 300 g. using boiled conductivity water and old, alkali-etched soft glass bottles provided with ground-in stoppers. The finished solutions were analyzed in triplicate by adding to weighed samples a slight excess of hydrochloric acid above the amount needed for neutralizing the hydroxide, evaporating to dryness and igniting lightly until constant weight had been obtained. As a rule the different analyses of a given solution agreed to better than one part in 5000. The analytical weights used were standardized with a high degree of precision and all the appropriate vacuum corrections were carefully observed. The calculation of the hydroxide concentra-

(1) Scott, *J. Phys. Chem.*, **39**, 1031 (1935); Masson, *Phil. Mag.*, [7] **8**, 218 (1929).

(2) Freeth, *Trans. Roy. Soc. London*, Series **A**, 223 (1922).

TABLE I

OBSERVED VALUES FOR THE APPARENT PARTIAL MOLAL VOLUME OF SODIUM HYDROXIDE

m	$\sqrt{m}$	0°	10°	20°	30°	40°	50°	60°	70°
1.0089	1.0044	−5.205	−3.328	−2.278	−1.620	−1.054	−0.734	−0.656	−0.631
1.9779	1.4064	−3.302	−1.742	−0.892	−0.225	0.238	0.499	0.587	0.576
2.9716	1.7238	−1.455	−0.148	0.570	1.050	1.415	1.644	1.713	1.694
3.9807	1.9952	0.214	1.127	1.731	2.149	2.466	2.655	2.724	2.686
5.9724	2.4439	2.565	3.227	3.669	3.981	4.221	4.358	4.413	4.396
7.9733	2.8237	4.395	4.887	5.233	5.491	5.747	5.800	5.823	5.835
10.199	3.1935	6.305	6.390	6.674	6.904	7.073	7.175	7.221	7.216
11.968	3.4595	7.084	7.434	7.701	7.895	8.045	8.141	8.188	8.197
14.048	3.7481	8.152	8.481	8.732	8.923	9.064	9.157	9.207	9.222
16.232	4.0289	9.121	9.472	9.685	9.866	10.002	10.090	10.122	10.158
18.242	4.2711	9.927	10.253	10.457	10.626	10.755	10.841	10.892	10.914
20.022	4.4746	10.551	10.879	11.071	11.218	11.339	11.427	11.475	11.496
21.860	4.6755	11.127	11.423	11.620	11.760	11.875	11.962	12.000	12.035
24.033	4.9026	11.724	12.004	12.190	12.323	12.434	12.517	12.568	12.594
25.740	5.0735	12.133	12.412	12.577	12.705	12.813	12.893	12.945	12.973

tion was carried out employing the international atomic weights of 1937.

The pycnometers used were identical with those previously used by Åkerlöf and Teare.[3] The change of the pycnometer volume with temperature was determined experimentally using the data of Smith and Keyes[4] for the specific volume of water. The volume change observed was found to agree closely with the value calculated from the known expansion coefficient of Pyrex glass, which also gives a measure of the high precision attained in our density measurements. The volume change of the pycnometers due to corrosion by the hydroxide solutions was surprisingly small and the loss in weight was observed to decrease with continued use. After the measurements were completed a re-calibration of the pycnometers gave an average volume increase of 0.0134 cc. or about 0.01% of the total volume. As a comparison an error of 0.00001 in the density of a one molal hydroxide solution corresponds to an error of 0.001 cc. in φ. On the other hand, an error of 1 part in 5000 for the hydroxide concentration gives an error of 0.012 cc. in φ or nearly the same as the maximum error that could be caused by the corrosion of the pycnometers.

The measuring temperature was determined with a solid stem mercury thermometer calibrated for total immersion against a platinum resistance thermometer certified by the Bureau of Standards. The temperature of the thermostat was maintained and regulated with an accuracy of 0.02°.

Experimental Results.—From the density data obtained the apparent partial molal volume φ of the hydroxide was first calculated using the values of Smith and Keyes for the specific volume of the solvent. These values, summarized in Table I, were then plotted against the square root of the molality of the solutions. As already indicated, the resulting isothermal curves, shown graphically in Fig. 1, are best represented by a series of straight lines which all

(3) Åkerlöf and Teare, THIS JOURNAL, **60**, 1226 (1938).

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

have a break, which slowly shifts toward higher concentrations with increasing temperature. The data on either side of the breaks were least squared separately. The constants of the equations thus obtained were then also least squared according to third order equations in the following way. The least squared φ^0 values were re-introduced in the original normal equations, a new set of k values calculated and after that the latter were

TABLE II

LEAST SQUARED EQUATIONS AND CONSTANTS FOR THE CALCULATION OF THE APPARENT PARTIAL MOLAL VOLUME OF SODIUM HYDROXIDE

(A) For concentrations below the break

$\varphi_1^0 = -10.580 + 0.2863t - 0.00470t^2 + 0.0000266t^3$

$k_1 = 5.3342 - 0.08788t + 0.001603t^2 - 0.00000994t^3$

(B) For concentrations above the break

$\varphi_2^0 = -3.798 + 0.1030t - 0.001312t^2 + 0.000008563t^3$

$k_2 = 3.181 - 0.0155t + 0.000201t^2 - 0.00000145t^3$

(C) Comparison between constants derived from "I. C. T." data and values computed from above equations (A)

Temp., °C.	Values of φ_1^0		Values of k_1	
	Å. and K.	"I. C. T."	Å. and K.	"I. C. T."
0	−10.580	−10.86	5.3342	5.55
10	8.160	9.09	4.6058	4.81
20	6.520	7.64	4.1383	4.37
30	5.500	6.51	3.8721	4.09
40	4.941	5.67	3.7475	3.94
50	4.682	5.15	3.7049	3.86
60	4.565	4.95	3.6847	3.86
70	4.428	5.06	3.6272	3.91

(D) Intersection $\sqrt{m_x}$ of φ curves derived from equations (A) and (B)

Temp., °C.	0	10	20	30
$\sqrt{m_x}$	3.150	3.375	3.609	3.787

Temp., °C.	40	50	60	70
$\sqrt{m_x}$	3.875	3.910	3.979	4.162

least squared. A summary of the equations and constants arrived at as a final result is given in Table II. As shown in the lower right-hand corner of Fig. 1, the use of these constants gives the temperature dependence of the concentration at the break in the isothermal straight lines for φ a somewhat irregular appearance. An indirect comparison between our density measurements and the "I. C. T." data for from 0 to 10 molal hydroxide concentrations was obtained by calculating the values of φ^0 and k from the latter at corresponding temperatures. The result is included in Table II.

The differences between the two sets of values partially balance each other out and actually they do not on the whole give any larger discrepancies in density, although individual points may be found where differences appear even in the third decimal place. A direct comparison with the "I. C. T." density table is given in Table III, representing a summary of the corresponding densities as calculated using the constants from Table II. The densities of the hydroxide solutions were computed employing the equation

$$d = \frac{1000}{mw/1000 + V}$$

where w is the weight and V the apparent volume of water per 1000 g. of solution. The actual partial molal volume of the hydroxide may be calculated from the apparent values according to the equation

$$\bar{v}_2 = \varphi^0 + 3/2k\sqrt{m}$$

The partial molal volume of the solvent may be obtained from the values of $\bar{v}_2$ from the equation

$$\frac{1000\bar{v}_1}{M} + m\bar{v}_2 = \frac{1000\bar{v}_1^0}{M} + m\varphi$$

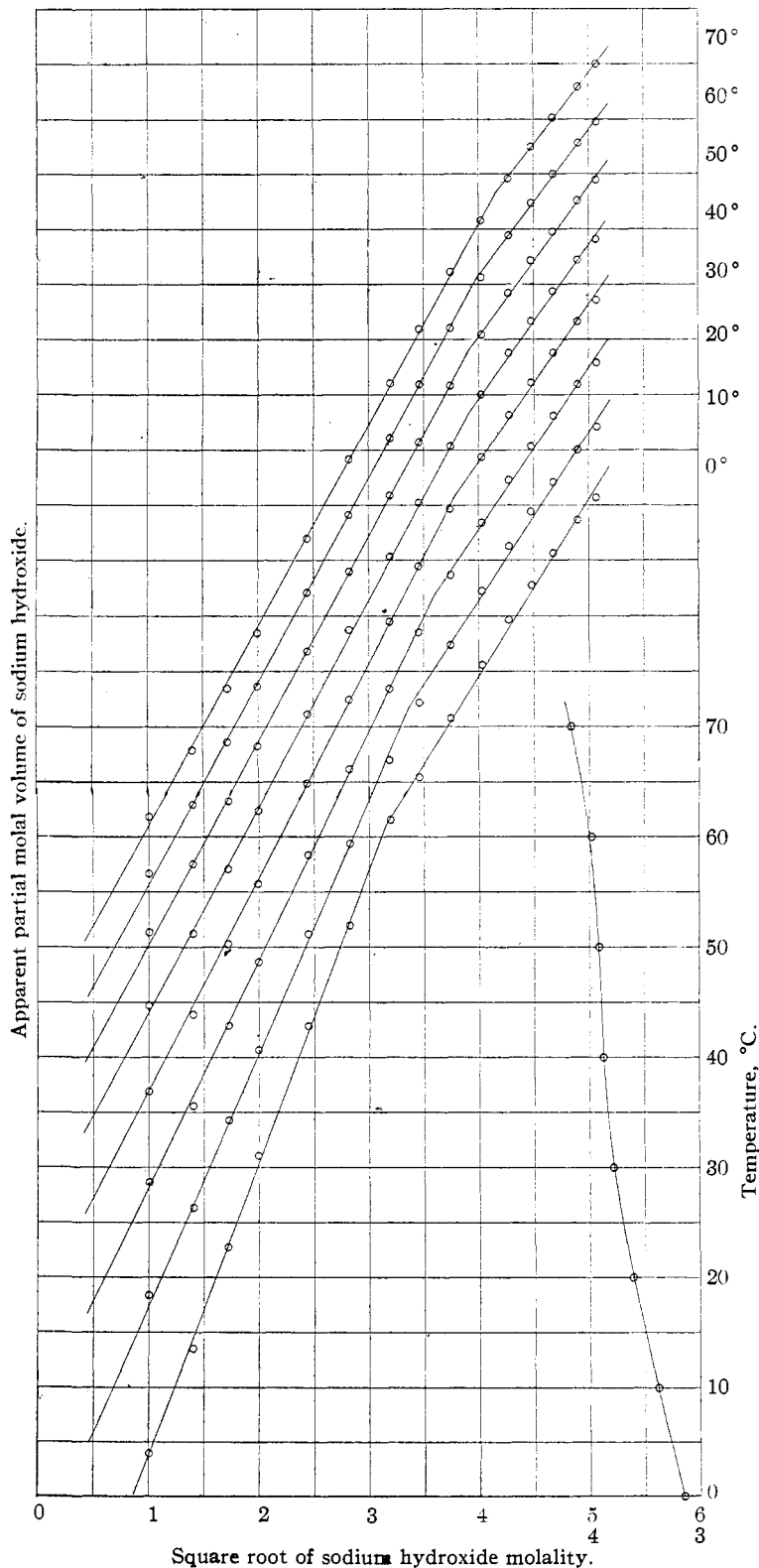where M is the molecular weight of water. Rearranging and intro-

Fig. 1.—0 to 70° isotherms for apparent partial molal volume of sodium hydroxide in pure aqueous solutions plotted against square root of molality. Ordinates shifted successively for the different curves by 1 cc. each.

Table III

Density of Sodium Hydroxide Solutions

Wt. %	NaOH, m	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	0.5101	1.02376	1.02242	1.02022	1.01726	1.01360	1.00929	1.00434	0.99876
4	1.0415	1.04708	1.04489	1.04207	1.03868	1.03473	1.03021	1.02511	1.01939
6	1.5955	1.07019	1.06726	1.06390	1.06010	1.05587	1.05116	1.04592	1.04006
8	2.1736	1.09321	1.08963	1.08577	1.08161	1.07711	1.07221	1.06682	1.06085
10	2.7774	1.11614	1.11120	1.10773	1.10324	1.09849	1.09340	1.08787	1.08179
12	3.4087	1.13900	1.13445	1.12979	1.12499	1.12000	1.11472	1.10906	1.10289
14	4.0693	1.16173	1.15686	1.15192	1.14686	1.14164	1.13618	1.13040	1.12416
16	4.7613	1.18433	1.17925	1.17409	1.16882	1.16340	1.15774	1.15185	1.14555
18	5.4871	1.20661	1.20155	1.19628	1.19084	1.18523	1.17942	1.17340	1.16706
20	6.2492	1.22863	1.22371	1.21844	1.21288	1.20711	1.20114	1.19501	1.18866
22	7.0504	1.25023	1.24567	1.24049	1.23488	1.22898	1.22286	1.21662	1.21029
24	7.8938	1.27133	1.26731	1.26237	1.25679	1.25078	1.24452	1.23820	1.23189
26	8.7827	1.29180	1.28855	1.28402	1.27852	1.27244	1.26606	1.25965	1.25342
28	9.7210	1.31150	1.30929	1.30530	1.30000	1.29389	1.28740	1.28093	1.27479
30	10.7129	1.33383	1.32940	1.32612	1.32112	1.31503	1.30845	1.30192	1.29592
32	11.7632	1.35683	1.34996	1.34637	1.34177	1.33576	1.32910	1.32253	1.31672
34	12.8772	1.37958	1.37243	1.36590	1.36182	1.35595	1.34924	1.34267	1.33705
36	14.0607	1.40198	1.39654	1.38748	1.38050	1.37547	1.36873	1.36216	1.35682
38	15.3207	1.42388	1.41629	1.40906	1.40198	1.39485	1.38753	1.38089	1.37587
40	16.6646	1.44515	1.43744	1.43215	1.42298	1.41585	1.40853	1.40078	1.39403
42	18.1012	1.46561	1.45783	1.45047	1.44334	1.43625	1.43117	1.42138	1.41318
44	19.6404	1.48505	1.47732	1.46998	1.46292	1.45591	1.44881	1.44132	1.43336
46	21.2936	1.50330	1.49568	1.48847	1.48153	1.47465	1.46772	1.46070	1.45284
48	23.0740	1.52008	1.51272	1.50569	1.49893	1.49226	1.48559	1.47864	1.47137
50	24.9969	1.53811	1.52814	1.52142	1.51495	1.50855	1.50219	1.49561	1.48882
52	27.0799	1.54827	1.54174	1.53541	1.52931	1.52326	1.51727	1.51116	1.50492

ducing the expressions for $\bar{v}_2$ and φ, this equation gives

$$\bar{v}_1 = 18.016 \,(v_s - k m^{3/2}/2000)$$

where v_s is the specific volume of the solvent. Tables IV and V summarize the values calculated for $\bar{v}_1$ and $\bar{v}_2$ from 1 to 16 molal hydroxide solutions.

Discussion

In contrast with the density measurements of Åkerlöf and Teare for aqueous solutions of hydrochloric acid, which gave very low k values, those presented in this paper for sodium hydroxide have given unusually high k values. A study of the density data for concentrated aqueous solutions of other strong acids and bases seems to show, however, that this may represent a general rule; acids have low and bases high k values. Thus nitric acid at concentrations below 8.5 molal and a temperature of 20° appears to have a k value of 1.05 while potassium hydroxide below 9.2 molal and at 15° has a k value of 4.02. Above the concentrations given nitric acid has for solutions up to approximately 26 molal a considerably higher k value (1.88) than the one given for the lower concentration range, but in the case of potassium hydroxide a reversal in behavior appears

and the k value decreases to 2.42. In comparison the k values for all the alkali halides with the exception of the lithium salts at extremely high concentrations come at a given temperature close together and fairly near the theoretical value. This would seem to give the conclusion that the deviations of the k values of strong acids and bases from the theoretically predicted one should be ascribed to the hydrogen and hydroxyl ions of these electrolytes. No other electrolyte with as low a k value as that for hydrochloric acid has been found but there are, however, several other electrolytes besides the alkali hydroxides which have very high k values although in most cases the comparison is highly dependent upon the temperature at which it is made. It should be emphasized that the above discussion is founded upon data for concentrated solutions only and does not take into consideration that in very dilute solutions the k values may closely approach the theoretical ones.

The break occurring in the curves for the partial molal volume of sodium hydroxide or any other electrolyte must be due to some structural change in the solution whatever this change may be. As indicated above the occurrence of such

TABLE IV
PARTIAL MOLAL VOLUME OF SOLUTE IN SODIUM HYDROXIDE SOLUTIONS

m	$\sqrt{m}$	0°	10°	20°	30°	40°	50°	60°	70°
1	1.0000	−2.579	−1.251	−0.313	+0.308	+0.680	+0.875	+0.962	+1.013
2	1.4142	+0.735	+1.610	+2.259	2.714	3.009	3.177	3.251	3.266
3	1.7321	3.279	3.807	4.232	4.560	4.796	4.944	5.008	4.996
4	2.0000	5.423	5.657	5.895	6.116	6.302	6.433	6.489	6.454
5	2.2361	7.312	7.289	7.360	7.488	7.629	7.745	7.794	7.738
6	2.4495	9.019	8.763	8.685	8.727	8.828	8.931	8.974	8.899
7	2.6458	10.590	10.119	9.904	9.867	9.932	10.022	10.058	9.967
8	2.8284	12.051	11.381	11.037	10.928	10.958	11.036	11.068	10.961
9	3.0000	13.424	12.566	12.102	11.924	11.923	11.990	12.016	11.894
10	3.1623	11.290	13.687	13.110	12.867	12.835	12.892	12.913	12.777
11	3.3166	12.027	14.753	14.068	13.763	13.702	13.750	13.766	13.617
12	3.4641	12.730	12.930	14.983	14.620	14.532	14.569	14.581	14.419
13	3.6056	13.406	13.576	15.862	15.442	15.327	15.356	15.363	15.189
14	3.7417	14.055	14.197	14.305	14.380	16.092	16.112	16.116	15.930
15	3.8730	14.681	14.797	14.884	14.943	16.830	16.842	16.841	16.644
16	4.0000	15.287	15.377	15.444	15.488	15.508	15.503	15.473	17.335

TABLE V
PARTIAL MOLAL VOLUME OF SOLVENT IN SODIUM HYDROXIDE SOLUTIONS

m	0°	10°	20°	30°	40°	50°	60°	70°
1	17.971	17.984	18.015	18.061	18.123	18.202	18.289	18.390
2	17.883	17.907	17.947	17.997	18.062	18.141	18.228	18.331
3	17.769	17.809	17.858	17.915	17.982	18.062	18.150	18.253
4	17.635	17.693	17.754	17.817	17.887	17.968	18.056	18.162
5	17.482	17.561	17.635	17.706	17.780	17.862	17.951	18.058
6	17.313	17.415	17.504	17.583	17.661	17.745	17.834	17.943
7	17.129	17.257	17.362	17.450	17.532	17.617	17.707	17.818
8	16.932	17.086	17.209	17.307	17.393	17.480	17.571	17.684
9	16.722	16.905	17.046	17.154	17.246	17.334	17.426	17.541
10	17.113	16.713	16.873	16.993	17.090	17.180	17.272	17.390
11	16.974	16.511	16.692	16.824	16.925	17.017	17.111	17.231
12	16.828	16.885	16.503	16.646	16.754	16.848	16.942	17.065
13	16.676	16.740	16.305	16.461	16.575	16.671	16.766	16.892
14	16.518	16.588	16.665	16.748	16.389	16.487	16.583	16.711
15	16.354	16.432	16.514	16.601	16.196	16.296	16.394	16.525
16	16.185	16.270	16.357	16.449	16.549	16.663	16.788	16.332

breaks appears by no means to be unusual provided it is possible to extend the density measurements to sufficiently high concentrations. Scott has ventured the idea that these breaks are due to packing changes of ions and solvent molecules but no inferences were drawn as to how this was brought about. Changes in the solvent envelope for the immediate neighborhood of the ions of let us say from four to three water molecules or the breaking up of a more or less definite tetrahedral structure rather than complete hydration, which always has been the traditional approach to similar problems, might possibly serve as a working hypothesis. It would eliminate the possibility of breaks occurring at lower concentrations and at the same time allow a considerable range for their appearance in concentrated solutions. The occurrence of more than one break

as reported by Scott in the case of aqueous solutions of the lithium halides would still be difficult to understand. It may, however, be mentioned that in several other cases studied by us, using data in the literature, none showed the slightest trace of a second break at any concentration. Thus the density data for nitric acid at 20° do not show any indications of a break in the curve for φ at concentrations above the one at 8.5 molal, although it was followed up to 94 weight per cent. solutions. In the case of complete dissociation of the hydroxide our idea naturally fails.

The suggestion made here is somewhat analogous to the result of a number of recent studies of the X-ray diffraction of water by Stewart, Amaldi, Meyer, Katzoff, Morgan and Warren.[5]

(5) Stewart, Phys. Rev., 37, 9 (1931); Amaldi, Physik. Z., 32, 914 (1931); Meyer, Ann. Physik, 5, 701 (1930); Katzoff, J. Chem. Phys., 2, 841 (1934); Morgan and Warren, ibid., 6, 666 (1938).

As shown already by the pioneer theoretical work of Bernal and Fowler,[6] these studies seem to indicate that independently of the temperature the water molecules tend to bond themselves tetrahedrally to four neighboring molecules although according to Morgan and Warren the intensity distribution curves cannot be interpreted uniquely in terms of an exact number of neighbors at definite distances.

Summary

The density of aqueous solutions of sodium hydroxide has been measured over a concentration range of from 1 to 26 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 a straight line up to a defi-

nite point at which a break occurs which shifts toward higher concentrations with increasing temperature. The values of the apparent partial molal volume of the hydroxide and the slope of the curves on either side may be calculated from the following equations:

(A) For sodium hydroxide concentrations below the break

$$\varphi_1^0 = -10.580 + 0.2863t - 0.00470t^2 + 0.0000266t^3$$
$$k_1 = 5.3342 - 0.08788t + 0.001603t^2 - 0.00000994t^3$$

(B) For sodium hydroxide concentrations above the break

$$\varphi_2^0 = -3.798 + 0.1030t - 0.001312t^2 + 0.000008563t^3$$
$$k_2 = 3.181 - 0.0155t + 0.000201t^2 - 0.00000145t^3$$

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

(6) Bernal and Fowler, *J. Chem. Phys.*, 1, 515 (1933).
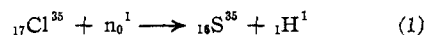

Exchange Reactions with Radiosulfur

BY HERVEY H. VOGE[1]

Radioactive isotopes are peculiarly suitable for indicators or "labels" in chemical reactions, and the technique of their use is usually simpler than that for concentrated, stable, mass isotopes, because an electroscope or Geiger counter can be used for analysis instead of a mass spectrograph or elaborate density measurements. Furthermore, radioactive specimens of common elements are now quite easy to obtain. Radiosulfur, though it emits beta rays of low penetrating power, is attractive because of the long half-life, eighty days. Experiments with radiosulfur were made for the purpose of investigating certain phases of the chemistry of sulfur. A number of exchange reactions of inorganic sulfur compounds were studied; a few of these already have been reported briefly.[2]

Production of Radiosulfur

Radiosulfur was first reported by Andersen,[3] who produced it by neutron bombardment of carbon tetrachloride. The supposed reaction is

$$_{17}Cl^{35} + n_0^1 \longrightarrow {}_{16}S^{35} + {}_1H^1 \qquad (1)$$

A small amount of inactive sulfur was added as a carrier, and after evaporation of the carbon tetrachloride the active sulfur remained concentrated in the residue. Much stronger samples of radiosulfur than those used by Andersen were obtained by leaving a liter bottle of carbon tetrachloride near the California cyclotron when it was producing fast neutrons. It may be questioned whether all the radiosulfur produced in reaction (1) exists as free sulfur and remains in the residue. When first formed, the sulfur atom has a large recoil energy, amounting to about one hundred volts, and is undoubtedly removed from the original carbon tetrachloride molecule, but its further history is uncertain. Probable end-products are S, $SCCl_3$, SCl_2, $CSCl_4$, and SCl_4. Of these only sulfur would remain in the residue upon distillation. The others are for the most part hydrolyzable in alkali to sulfide or sulfite, and to test for their presence a carbon tetrachloride distillate was shaken with concentrated sodium hydroxide solution and sodium hypobromite for about twenty-four hours. To the acidified aqueous phase was added a small amount of sodium sulfate, and then barium sulfate was precipitated. The sulfur activity of the barium sulfate from the

(1) Now at Shell Development Co., Emeryville, Calif.
(2) H. H. Voge and W. F. Libby, THIS JOURNAL, 59, 2474 (193).
(3) E. B. Andersen, *Z. physik. Chem.*, B32, 237 (1936).