cated by the accompanying energy effect, the corresponding tetratelluride presumably has a low degree of stability. This is in accord with the observations of Kraus and Chiu referred to above.

To sum up the results of this section, the values obtained for the heats of a number of reactions seem to be reproducible with a fair degree of accuracy. On the whole, they agree fairly well with data in the literature, where such data are available. One advantage of the method is that the heats of formation of compounds of the alkali metals with a number of the more electronegative elements can be measured directly in the calorimeter.

V. Summary

A liquid ammonia calorimeter, in which the heat effect is measured, in the main, by the amount of ammonia vaporized, is described.

The heats of solution of thirteen salts and of metallic sodium have been determined. For the different salts, the heats of solution follow much the same order in ammonia as in water, but, while, in water, the heats of solution are generally negative, in ammonia, the heats of solution are positive in all cases, excepting potassium nitrate. Sodium has a negative heat of solution of about 1400 cal. Silver nitrate and lead bromide have very high heats of solution, 22,400 and 29,800 cal., respectively.

The heat effects accompanying a number of reactions have been determined. From these it has been possible to compute the heats of formation of a number of compounds. In general, the heats of formation so computed are in fairly good agreement with values in the literature. The heat of formation of liquid ammonia as determined from these measurements agrees well with the value computed by Haber. The heats of formation of Na_2S_2, Na_2Te and Na_2Te_2 have been measured for the first time, by direct reaction of S and Te with sodium in liquid ammonia.

PROVIDENCE, R. I. RECEIVED SEPTEMBER 12, 1933

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BROWN UNIVERSITY]

Heats of Solution and Heats of Reaction in Liquid Ammonia. II

BY CHARLES A. KRAUS AND RALPH F. PRESCOTT

In the first article of this series, Kraus and Ridderhof[1] have described a liquid ammonia calorimeter and have presented results of measurements of heats of solution and heats of reaction in liquid ammonia. It seemed worth while to attempt to refine the technique of the method somewhat further in order to increase the precision of the data. We have improved the method of absorbing the ammonia vaporized from the calorimeter so as to keep the pressure rise to a minimum, and have devised an improved thermocouple that accurately follows the temperature of the calorimeter. Some additional heats of solution have been measured.

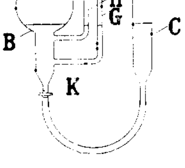

Fig. 1.—Absorption flask.

Apparatus and Procedure

The calorimeter employed was the same as that used by Kraus and Ridderhof and the general arrangement of apparatus and the technique employed were also much the same. We describe here only the modifications that we have introduced.

Instead of determining the amount of ammonia absorbed by increase in weight of the absorption flask, we have found it more convenient and reliable to titrate the solution in the absorption flask. This is particularly true when the amount of ammonia vaporized is small. The absorption flask is outlined in the accompanying figure. The flask A, about two-thirds full of water, is provided with a mercury pool B at the bottom and with a leveling bulb C. The stopcock D connects with the calorimeter system, as shown in the figure of Kraus and Ridderhof, and the stopcock E with a vacuum pump. F is a de Khotinsky seal. After attaching the absorption flask to the system, air in the tubes G and H is replaced by ammonia. In the preliminary adjustments, the stopcock I is kept closed. When the calorimeter is in equilibrium, the stopcock D is opened and the leveling bulb is adjusted so that the ammonia is on the point of passing out under the mercury through the tube H. The stopcock K is then closed and the material whose heat effect is to be measured is dropped into the calorimeter. As the ammonia vaporizes, it passes out under the mercury and is absorbed in water, the maximum rise in pressure amounting to only a few millimeters. The final pressure is adjusted to the original value so that there is no correction for change in the amount of ammonia in the vapor phase. The water introduced into the absorption flask is weighed beforehand and aliquot parts are withdrawn from the flask and titrated to determine the amount of ammonia vaporized.

---

(1) Kraus and Ridderhof, THIS JOURNAL, **56**, 79 (1934).

It is necessary to know accurately the temperature of the calorimeter. Kraus and Ridderhof employed a copper-constantan thermocouple, encased in a thin-walled glass tube. The rate of heat transfer to the thermocouple through a glass tube, however, is too slow to permit of accurately following the temperature of the calorimeter. We have overcome this difficulty by bringing the ends of the thermocouple through a thin-walled platinum tube which, in turn, is sealed into one end of a glass tube. A platinum tube, 1.5 cm. long, having a diameter of 1 mm. and a thickness of 0.05 mm., is sealed into one end of a glass tube 90 cm. long. The ends of a No. 36 enameled copper wire and a No. 36 double silk covered constantan wire were bared and twisted together and introduced into the glass tube in such a position that the junctions extended through the end of the platinum tube. The end of the platinum tube was then collapsed on the junction, the wires extending beyond the platinum tube were cut off and the junctions and platinum tube were soldered with gold. This junction was introduced into the calorimeter in place of the junction described by Kraus and Ridderhof.

The second junction was placed in melting ice in a Dewar tube. Experiments showed that the thermoelement followed the temperature of the calorimeter as quickly as readings could be made on the potentiometer. With this couple it was found that, after introducing material into the calorimeter, pressure and temperature equilibrium would be established in from 1.5 to 3 minutes. In general, the temperature rose to a maximum value as quickly as the readings could be made. Thereafter, the temperature fell off to a constant final value in the course of several minutes. The correction for heat transfer between the calorimeter and its surroundings during the course of an experiment was greatly reduced owing to the rapidity with which the measurements were carried out and the small rise in temperature that resulted because of the small pressure rise in the calorimeter.

The constant of the thermoelement was determined by varying the pressure of the liquid in the calorimeter and reading the e. m. f. of the thermoelement. The temperatures at the different pressures were fixed from the vapor pressure curve of ammonia as determined by Cragoe, Meyers and Taylor.[2]

The radiation constant of the calorimeter was redetermined and found to be 0.412, which is in good agreement with the value determined by Kraus and Ridderhof. The amount of heat transfer in the course of an experiment was found by multiplying the radiation constant by the mean temperature rise of the calorimeter above its initial value and by the time.

The following constants were employed in the calculations: heat of vaporization of liquid ammonia, 327.1;[3] specific heat of liquid ammonia, 1.067;[4] heat capacity of calorimeter, 5.58; quantity of ammonia in calorimeter, 20 g., less the ammonia vaporized; radiation constant, 0.41.

For the specific heat of the various salts employed, values were taken from the "International Critical Tables."[5]

Experimental Results

Check determinations were run on the heat of solution of the following salts: silver nitrate, mercuric cyanide, lead iodide, lead nitrate, sodium chlorate and sodium bromide. The procedure, except as indicated above, was the same as that of Kraus and Ridderhof. The method of making the calculations and of applying the corrections were also the same as those of Kraus and Ridderhof and need not be detailed here. The results are tabulated below. The amount of salt used is given in the second column, the ammonia vaporized in the third column, the heat effect due to ammonia vaporized in the fourth column; the net heat effect in the fifth column, the molar heat effect in the sixth column and the mean of the determinations in the last column.

TABLE I

HEATS OF SOLUTION OF SOME SALTS IN LIQUID AMMONIA

Salt	Weight	NH_3 vap.	Heat due to NH_3 vap.	Net heat effect	Molar heat solution	Mean
$AgNO_3$	0.9516	0.3969	139.8	124.2	21,700	21,400
$AgNO_3$	1.0331	.4164	140.6	131.9	21,100	
$Hg(CN)_2$	1.3311	.2747	93.9	+ 73.6	12,900	13,200
$Hg(CN)_2$	1.5987	.2545	86.2	+ 80.9	14,400	
PbI_2	1.3531	.2684	90.6	+ 82.3	28,900	29,100
PbI_2	1.6403	.3348	109.8	+104.0	29,300	
$Pb(NO_3)_2$	1.2233	.3197	106.7	+ 97.1	26,200	26,900
$Pb(NO_3)_2$	1.3234	.3742	122.7	+111.2	27,600	
$NaClO_3$	0.8475	.0719	28.1	+ 16.4	1,970	2,200
$NaClO_3$	.9546	.0902	36.6	+ 23.1	2,480	
NaBr	.9606	.2377	83.6	+ 76.2	7,960	8,000
NaBr	1.3329	.3342	114.5	+107.3	8,030	

Discussion.—In the case of each salt the check determinations are in fair agreement. In general, the deviations from the mean amount to several per cent. In the case of sodium chlorate, the deviations are markedly greater, owing to the fact that the heat of solution of this salt is very low and for the amount of salt employed, the heat effect in the calorimeter (about 20 cal.) was too low to permit of accurate determinations. In all other experiments the net heat effect was above 70 cal. Our values for sodium bromide are lower than those of Kraus and Ridderhof. On the other hand, our value of 21,400 cal. for silver nitrate is in reasonably good agreement with that of Kraus and Ridderhof, 22,700. The order of magnitude of the corrections applied can be seen from the difference between columns 4 and 5.

A striking feature of the results is the high

---

(2) Cragoe, Meyers and Taylor, Bureau of Standards, Scientific Papers, No. 369, issued Apr. 10, 1920.

(3) Osborne and Van Dusen, Bureau of Standards, Scientific Papers, No. 315, issued Dec. 21, 1917; THIS JOURNAL, **40**, 14 (1918).

(4) Osborne and Van Dusen, Bureau of Standards, Scientific Papers, No. 313, issued Dec. 13, 1917; *ibid.*, **40**, 1 (1918).

(5) "International Critical Tables," McGraw-Hill Book Co., Inc., New York, 1929, Vol. V, p. 100.

values obtained for the heat of solution of silver nitrate, mercuric cyanide, lead bromide and lead nitrate. These are all salts of metals that have a marked tendency to form stable complexes with ammonia. The heat effects in the case of the lead salts are particularly high. The value of 29,100 for lead iodide is close to that found by Kraus and Ridderhof for lead bromide, 29,600 cal.

Summary

Some improvements to the liquid ammonia calorimeter of Kraus and Ridderhof are described.

The heats of solution of silver nitrate, mercuric cyanide, lead iodide, lead nitrate, sodium chlorate and sodium bromide have been determined.

PROVIDENCE, R. I. RECEIVED SEPTEMBER 16, 1933

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Heat Capacity and Entropy of Potassium Chlorate from 13 to 300°K. The Entropy of Chlorate Ion

BY WENDELL M. LATIMER, PHILIP W. SCHUTZ AND J. F. G. HICKS, JR.

This determination of the entropy of potassium chlorate completes the data on the entropy of the halogenate[1] ions.

Material.—Potassium chlorate of C. P. quality was recrystallized from distilled water three times and dried at 110° for sixty-five hours. The sample showed only very slight traces of chloride with acid silver nitrate. We are indebted to Dr. J. E. Ahlberg for the preparation of the sample. Specific heat measurements were made on a sample weighing 118.867 g. *in vacuo* (0.9699 mole).

TABLE I

HEAT CAPACITY OF POTASSIUM CHLORATE

MOLECULAR WEIGHT OF $KClO_3$ = 122.55

T, °K.	Molal C_p	T, °K.	Molal C_p
13.95	0.44	122.64	16.53
15.84	0.77	128.23	16.81
18.48	1.28	133.94	17.13
22.35	2.01	139.75	17.43
24.66	2.62	145.79	17.75
27.79	3.53	151.83	18.07
32.60	4.67	157.89	18.37
37.31	5.84	164.00	18.65
41.16	6.80	169.83	18.89
44.78	7.65	175.89	19.20
48.92	8.52	181.35	19.40
53.30	9.41	182.23	19.46
58.11	10.28	189.02	19.89
63.23	11.13	196.71	20.18
67.91	11.82	204.38	20.51
72.60	12.40	212.30	20.79
74.04	12.59	220.76	21.12
79.07	13.15	229.13	21.47
84.51	13.77	236.81	21.84
89.52	14.23	245.50	22.04
94.86	14.68	254.21	22.57
100.26	15.06	262.95	22.84
105.92	15.49	272.28	23.33
111.69	15.90	283.85	23.39
117.17	16.22	293.35	23.84

Measurements.—The molal heat capacity values fall on a smooth curve and are presented in Table I and graphically as a function of log T in Fig. 1. The heating intervals employed in various temperature regions are as follows: below 30°K., about 3° per run; 30 to 200°K., about 5° per run and above 200°K., about 8° per run.

Entropy of Potassium Chlorate.—The entropy of $KClO_3$ was obtained by graphical integration of the equation $S^\circ_{298.1} = \int_0^{298.1} C_p \, d \ln T$ from a larger scale plot of the curve shown in Fig. 1. The curve was extrapolated graphically to 10°K. and by means of the T^3 law below that. A summary of the entropy calculation is given in Table II.

TABLE II

0—10°K.	T^3 extrapolation	0.054 E. U.
10—298.1°K.	Graphical	34.116 E. U.
S° at 298.1° of $KClO_3$ =		34.17 E. U.

The relative accuracy of 34.17 E. U. is estimated at ±0.05 per cent.

Heat and Free Energy of Solution.—Stackelberg[2] gives 10,500 cal. for ΔH° at 16° for the reaction

$$KClO_3(s) = (K^+ + ClO_3^-) \text{ (hypothetical one molal)}$$

Correcting this figure to 25° gives $\Delta H^\circ_{298.1}$ = 10,120 cal.

---

(1) (a) $Ba(BrO_3)_2 \cdot H_2O$, Greensfelder and Latimer, THIS JOURNAL, **50,** 3286 (1928); (b) $AgIO_3$, G. and L., *ibid.*, **53,** 3813 (1931); (c) $KBrO_3$ and KIO_3, Ahlberg and Latimer, *ibid.*, to be published.

(2) Stackelberg, *Z. physik. Chem.*, **26,** 540 (1898).