0.315 at 3130 Å., 0.38 at 2654 Å. and 0.41 at 2537 Å.

A technique using a commercial mercury vapor arc and a quartz monochromator was employed. As a cross-check on the apparatus quantum yield measurements were made on the decomposition of the uranium oxalate actinometer with results in good agreement with the standard results of Leighton and Forbes.

To overcome the difficulty of low intensities at the slit of the monochromator, a special optical procedure for measuring the small amounts of iodine produced was devised.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BROWN UNIVERSITY]

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

BY CHARLES A. KRAUS AND FREDERIC C. SCHMIDT

In the earlier papers of this series,[1] a liquid ammonia calorimeter was described and results of measurements of heats of solution and heats of reaction were presented. In the present paper, we present further results by the same method in which both the apparatus and the procedure have been improved.

I. Experimental Details

To save space, only the changes in apparatus and procedure over those of the earlier papers will be described. These consist essentially of the following.

(1) The substance whose heat of solution or reaction was to be measured was sealed in a fragile, glass bulb which was crushed under the liquid when thermal equilibrium was established in the calorimeter.

(2) The spring, from which the stirrer was suspended, was fitted closely into the surrounding tube so as to provide sufficient friction to damp out the natural vibrations of the stirrer system.

(3) In the case of substances that dissolve with absorption of heat, ammonia was introduced into the calorimeter through a needle valve at such a rate as to maintain the temperature of the calorimeter as nearly constant as possible. An ammonium nitrate solution of ammonia, in a weighed bulb, served as source of ammonia. Several hundred cc. of ammonia vapor were withdrawn from the bulb into a chamber over mercury, the pressure being suitably adjusted by means of a leveling bulb, and the ammonia was allowed to pass into the calorimeter through the needle valve. Ammonia remaining in the chamber on completion of the experiment was reabsorbed in the ammonium nitrate tube, which was then weighed back.

(4) In order to prevent oscillations of pressure due to the pumping action of the glass-encased armature of the stirrer system, a by-pass was provided for the ammonia vapor between the two ends of the armature.

Temperatures were read by means of a copper–constantan thermocouple (0.0385 m. v./deg.) similar to that of Kraus and Prescott. Temperature readings were taken at intervals of one-half minute from the moment of breaking the bulb until temperature equilibrium was reëstablished.

In the case of processes accompanied by the evolution of heat, the pressures were maintained constant according to the method described by Kraus and Prescott. The pressures were read on a mercury manometer by means of a cathetometer.

It is essential to remove liquid adhering to the walls of the calorimeter above the liquid surface, particularly in the case of endothermic processes. This was accomplished by attaching a 100-cc. flask to the system and allowing ammonia vapor to expand into this flask, thus reducing the pressure momentarily. The weight of ammonia in the calorimeter was corrected for the ammonia withdrawn in this process. The amount of ammonia vaporized was determined by titrating the solution in the absorption flask. All measurements were at the boiling point of ammonia, −33°.

Constants and Corrections.—The calorimeter constant was determined experimentally and found to be 7.73 cal./deg. at 25°. Allowing for the change of the specific heat of silica and glass, due to temperature, this reduces to 6.73 cal./deg. at the boiling point of liquid ammonia. Uncertainties in this value do not affect the precision of the results since the temperature changes involved are small. The radiation constant of the calorimeter was determined and found to be 0.481 cal./deg./min., which value agrees with that obtained by Kraus and Ridderhof for the same calorimeter. The pressure equivalent of the calorimeter was found to be 0.00608 g./cm. of mercury. This is the amount of ammonia required to change the pressure in the apparatus one cm. under conditions of use. The amount of ammonia employed in the calorimeter was 26.57 g., which was corrected for ammonia vaporized or condensed during a measurement.

The following constants of ammonia were employed: specific heat,[2] 1.067 cal./deg.; heat of vaporization,[3] 327.1 cal./g.

The time–temperature curves were plotted in all cases and the mean radiation temperature was obtained by dividing the area under the curve by the time.

II. Results

The data for solutions of sodium, potassium and acetamide are given in Table I, of lithium, sodium

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[1] Kraus and Ridderhof, THIS JOURNAL, **56**, 79 (1934); Kraus and Prescott, *ibid.*, **56**, 86 (1934).

[2] Osborne and Van Dusen, Bureau of Standards, Scientific Papers, No. 313, issued Dec. 13, 1917; THIS JOURNAL, **40**, 1 (1918)

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

bromide, ice, urea and phthalimide in Table II, and for solutions of sodium in the presence of potassium bromide and of potassium in the presence of sodium bromide in Table III. In Table IV, are given data for the following reactions:

(1) $\underline{(CH_3)_3SnBr} + NH_3\,(liq.) + am = (CH_3)_3SnBr \cdot NH_3 \cdot am - 15{,}100$

(2) $\underline{(CH_3)_3SnBr \cdot NH_3} + am = (CH_3)_3SnBr \cdot am - 6{,}980$

(3) $(CH_3)_3SnBr \cdot NH_3 \cdot am + \underline{Na} = \underline{(CH_3)_3Sn} + NaBr \cdot am - 30{,}470$

(4) $(CH_3)_3SnBr \cdot NH_3 \cdot am + \underline{2Na} = (CH_3)_3SnNa \cdot am + NaBr \cdot am - 34{,}300$

III. Discussion

As may be seen from the tables giving the heats of solution for sodium, lithium and water the measured values are reproducible within about 1%. The reproducibility is better in the case of exothermic than of endothermic processes, the reason being that the rate of condensation of ammonia is limited by the area of the condensing surface and rate of stirring. The form of the time–temperature curves varies with the nature of the substance. Owing to the low rate of con-

TABLE I

ENDOTHERMIC PROCESSES

Subs.	Wt., g.	NH$_3$ cond., g.	Δt soln.	Δp soln.	Rad. temp. diff.	Time, min.	Obs. heat effect	Molar heat effect
Sodium	0.4204	0.0763	0.00	−0.26	−0.22	4	−25.90	−1416
Sodium	.3865	.0695	+ .02	.40	.20	4	−23.19	−1380
Sodium	.5994	.1069	.00	.20	.22	7	−36.10	−1385
Sodium	.7530	.1365	.00	.44	.21	4	−45.92	−1403
Sodium	.9653	.1684	.00	.60	.23	8	−52.16	−1362
Sodium	1.2031	.2123	.00	.64	.12	6	−71.06	−1358
Potassium	0.1170	.00	.00	.00	.01	1.5	0.00	0.0
Potassium	1.3960	.00	.00	.26	.01	1.5	− .51	− 14.0
Acetamide	0.6139	.00	.00	.18	.00	1	− .36	− 30

TABLE II

EXOTHERMIC PROCESSES

Subs.	Wt., g.	NH$_3$ vap., g.	Δt soln.	Rad. temp. diff.	Time, min.	Obs. heat effect	Molar heat effect
Lithium	0.1054	0.3674	+0.02	+0.01	5	120.9	7961
Lithium	.1047	.3703	.00	.00	2	121.1	8029
Lithium	.1020	.3620	.00	.00	1	118.4	8057
Lithium	.0720	.2385	.14	.10	2	82.95	7996
Sodium bromide	.3992	.1068	.08	.00	3	37.74	9730
Sodium bromide	.7477	.1714	.29	.20	3	66.52	9160
Sodium bromide	.7787	.1925	.18	.06	5	69.43	9180
Sodium bromide	1.1296	.2703	.18	.06	2	94.73	8630
Sodium bromide	1.5229	.3305	.24	.40	7	117.87	7960
Sodium bromide	1.8321	.3779	.36	.09	1	136.13	7640
Ice	0.3430	.0714	.29	.18	4	33.85	1776
Ice	.3831	.0796	.34	.00	4	37.96	1784
Ice	.4215	.0959	.30	.15	3	42.11	1798
Ice	.8075	.1667	.69	.42	8	80.35	1790
Urea	.7177	.0454	.10	.00	2	18.79	1590
Phthalimide	.5055	.0412	.06	.00	3	15.70	4560

TABLE III

HEATS OF SOLUTION OF SODIUM AND POTASSIUM IN THE PRESENCE OF POTASSIUM BROMIDE AND SODIUM BROMIDE, RESPECTIVELY

Na	0.3791	K	0.2379
KBr, 5% excess	1.9610	NaBr, 5% excess	.6573
NH$_3$ cond.	0.0696	Δp soln.	+ .28
Δt soln.	+ .05		+ .02
Rad. temp. diff.	− .35		− .00
Time, minutes	4		3
Net heat effect	− 22.21		+ 1.27
Atomic heat effect	−1346		+204

TABLE IV

ENERGIES OF REACTION

No.	1	2	3	4
(CH$_3$)$_3$SnBr·NH$_3$	1.3208[a]	0.4811	3.9302	2.7810
Na	....	....	0.3468	0.4908
NH$_3$ vap.	0.2369	0.0371	1.3886	1.0901
Δt soln.	.11	.03	0.13	0.29
Rad. temp. diff.	.21	.05	.26	.25
Time, minutes	5	2	6	4
Net heat effect	81.85	12.83	459.4	366.9
Energy of reaction	−15,100	−6,980	−30,470	−34,300

[a] $(CH_3)_3SnBr$.

densation, a considerable temperature decrease (0.36°) occurs in the case of sodium (Fig. 1a). In the case of potassium, there was a slight transient temperature decrease, as is shown in Fig. 1b, but without a resultant temperature change. The momentary temperature change was due to the process of breaking the bulb, as is shown in Fig. 1c, in which case an empty bulb was crushed. In the case of lithium (Fig. 1d), there was an initial drop in temperature followed by a rise as the process of solution continued and ammonia was evolved at atmospheric pressure. The initial drop in temperature is difficult to account for. The process of solution of lithium is evidently slower and more regular than that of ordinary substances which are added in a finely divided condition. In the latter case, there is a sudden rise in temperature, followed by a gradual drop to the final value. This is illustrated in Curve I of Fig. 2 for trimethyltin bromide monoammine. A considerable initial temperature change occurs in the case of reactions, as, for example, that between trimethyltin bromide monoammine and sodium, shown in Curve II, Fig. 2 Here the initial temperature change amounted to 0.87°. It will be noted that in nearly all cases the process of solution or reaction is completed at the end of from two to five minutes.

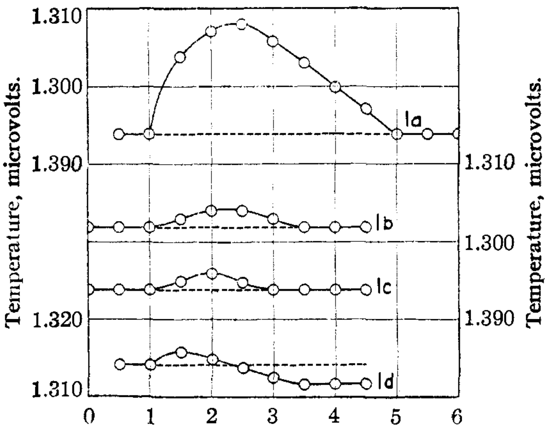

Fig. 1.—Time-temperature curves for: (a) sodium, (b) potassium, (c) empty bulb, (d) lithium.

The greatest contribution to the measured heat effect is due to ammonia condensed or vaporized; other effects appear only as minor corrections. The effects due to radiation and to pressure change can be computed quite accurately. The correction due to temperature change of the calorimeter introduces the greatest uncertainty, for an error of 0.01° introduces an error of 0.35 cal. This error is thus the greater the lower the heat effect actually measured. In some cases the difficulty can be overcome by working at higher concentration, but, if the heat effect of the process is a function of concentration, the precision can be increased only by increasing the precision of the temperature measurements.

The heat of solution of sodium in liquid ammonia, like its solubility in the same solvent, is exceptional with respect to that of lithium and potassium. In the alkali metal salts, however, the heat effects progress regularly from lithium to potassium. The rather marked heat effect in the case of phthalimide is probably due to the fact that this compound forms an ammonium salt in liquid ammonia as is indicated by its high conductance.[4] Urea also forms a compound with ammonia whose dissociation pressure is 88.9 cm. at 0°.[5]

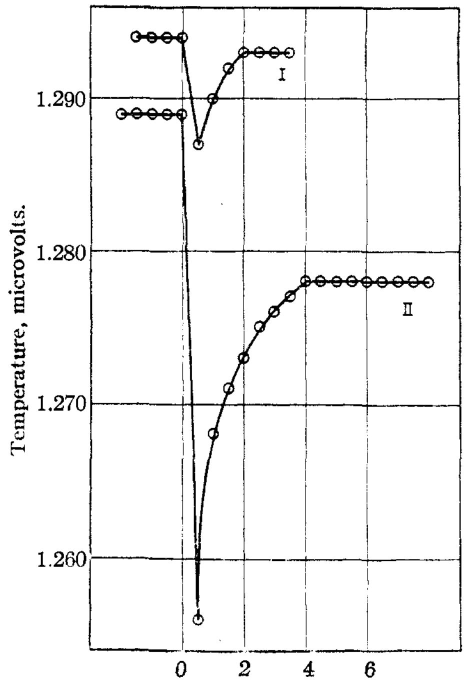

Fig. 2.—Time-temperature curves: I, solution of $(CH_3)_3SnBr\cdot NH_3$; II, reaction of $(CH_3)_3SnBr\cdot NH_3$ with 2Na.

The heat of solution of sodium bromide changes markedly with concentration, indicating that, as the concentration changes, interactions are occurring in the solution. The results are shown graphically in Fig. 3. The heat of solution

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[4] Franklin and Kraus, THIS JOURNAL, 27, 191 (1905).

[5] E. W. Johnson, Thesis, Clark University, 1922.

extrapolates to 10,350 calories (for $c = 0$) and the heat of dilution between $c = 1.0$ and $c = 0$ amounts to 5600 calories. It is to be expected that many other salts will show marked heats of dilution in liquid ammonia solution.

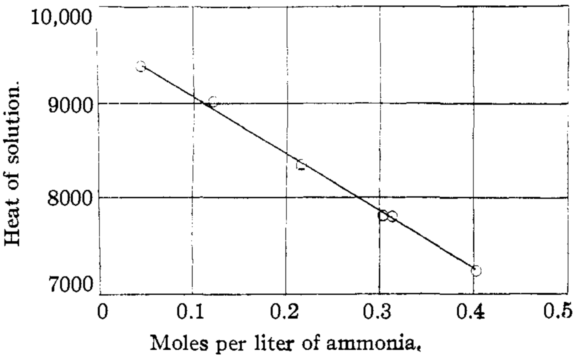

Fig. 3.—Heat of solution of sodium bromide as a function of concentration.

The negative heat of solution of sodium in the presence of potassium bromide seems to be slightly lower than that in pure ammonia, while the heat of solution of potassium in the presence of sodium bromide seems to be distinctly positive by several hundred calories. We may conclude that the heats of solution of sodium and potassium in the presence of salts differ slightly from those of the same metals in the pure solvent.

According to Kraus and Ridderhof, the heat of solution of potassium bromide in liquid ammonia is 2900 calories and according to the present measurements the heat of solution of sodium bromide at the concentration of the Na--KBr solution above, is 9280 calories. Combining these effects with the measured effects accompanying the solution of the metals in the presence of the respective salts, we obtain the energy of the following reaction

$$NaBr + K = KBr + Na - 7930$$

According to the literature ("I. C. T."), the difference between the heats of formation of sodium and potassium bromides is 7700 calories, with which our present result is in reasonably good agreement.

According to our present measurements, the heat of solution of sodium bromide in ammonia at the concentration of reaction (3) is 8100 calories. Introducing this value and the value for the heat of solution of trimethyltin bromide from equation (1) in equation (3), we obtain the energy of the reaction

$$(CH_3)_3SnBr + Na = NaBr + (CH_3)_3Sn - 37{,}470 \text{ cal.}$$

Introducing the heat of formation of sodium bromide (−86,300 cal.), we have

$$(CH_3)_3Sn + Br \text{ (liq.)} = (CH_3)_3SnBr - 48{,}860 \text{ cal.}$$

The heat of formation of trimethyltin bromide from free trimethyltin and bromine is rather high, indicating a relatively stable compound. For comparison, the heat of formation of thallous bromide is 41,000 cal.; that of stannic bromide is 91,800 cal./mole, or 23,200 cal./atom of bromine, and that of stannous bromide 61,400 cal./mole, or 37,000 cal./atom of bromine. It is evident that when three of the valences of the tin atom are satisfied by methyl groups, the energy effect accompanying the combination of the remaining valence with bromine is high.

From equations (3) and (4), we have

$$(CH_3)_3Sn + Na + am = (CH_3)_3SnNa{\cdot}am - 3830$$

The low value of the energy effect accompanying this reaction indicates that the electron of the trimethyltin ion is not firmly held. The energy value above relates to the formation of sodium trimethylstannide in solution. This cannot differ greatly from the energy change accompanying the formation of this compound in the free state, for the heat of solution of the compound, if negative, could hardly be large, while a positive heat of solution would lead to a smaller energy effect for the formation of the compound in the free state. The low energy of reduction of the trimethyltin anion accords with the chemical properties of this and other similar ions and accounts for their reactivity toward negative elements and compounds of such elements.

Summary

Improvements in the construction and in the technique of manipulation of the liquid ammonia calorimeter are described.

Heats of solution are reported for a number of substances, in some cases over a range of concentration. Sodium bromide has a marked heat of dilution.

Energies of reduction are reported for trimethyltin bromide to trimethyltin and to sodium trimethylstannide. From these are calculated the energies of bromination of trimethyltin and reduction of trimethyltin to the corresponding negative ion.

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