Ostwald coefficient against the reciprocal of the absolute temperature and extrapolated to the critical temperature of the solvent. Several of his curves show a minimum within the experimental range and others may be expected to do so on the basis of their curvature. It seems, therefore, as was pointed out by Kuenen,[13] that solubility minima are a phenomenon that can be deduced from the known behavior of mixtures and that the occurrence of minima is not necessarily dependent on the specific properties of the solvent or solute.

Finally a few words on attempts to calculate the solubility of gases, theoretically, may also be of interest. Van der Waals,[14] using his conception of a simple substance whose equation of state is identical with that of the particular mixture to be treated, attempted to calculate the solubility of nitrogen in water using his equation of state. He obtained a value much too small and attributed this to the association of water and not to the various assumptions needed for the computation. Later on he[15] pointed out that a correction for association would improve the agreement. Horiuti[16] using empirical relations applied van der Waals' idea to the solubilities of gases in organic liquids. For gases above their critical temperatures, he was able to get only the right order of magnitude.

Summary

The solubility of hydrogen in water at 0, 50, 75 and 100° and from 25 to 1000 atmospheres has been determined. The solubility of hydrogen in water shows a minimum within the experimental range similar to that of nitrogen in water.

Existing data seem to show that minima are a general phenomenon that can be deduced from the known behavior of mixtures and not necessarily dependent on specific properties of the solvent or solute.

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[13] Kuenen, *Proc. Roy. Soc. Edinburgh*, **23**, 312 (1900); Kuenen, "Verdampfung und Verflüssigung von Gemischen," Verlag Johann Ambrosius Barth, Leipzig, 1906, p. 82.

[14] Van der Waals-Kohnstamm, "Lehrbuch der Thermodynamik," Verlag Johann Ambrosius Barth, Leipzig, 1912, Vol. II, pp. 132-172.

[15] Van der Waals-Kohnstamm, Ref. 14, pp. 627-629.

[16] J. Horiuti, Ref. 5, pp. 225-252.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BROWN UNIVERSITY]

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

BY CHARLES A. KRAUS AND JOHN A. RIDDERHOF[1]

I. Introduction

Data relating to heats of solution of electrolytes in solvents other than water are almost completely lacking. There are available only several observations of Pickering[2] on the heat of solution of sodium iodide and lithium nitrate in alcohol. Both salts have markedly higher heats of solution in alcohol than in water. It seemed desirable to have data as to the heat of solution of salts in solvents other than water, particularly in solvents of lower dielectric constant. Ammonia seemed a very suitable solvent for this purpose, since many common salts are readily soluble in ammonia, while a good many important substances are soluble in ammonia that are not soluble in water. Numerous reactions, moreover, may be carried on in liquid ammonia which cannot be carried out in water; for example, reactions involving the alkali metals. In the present paper we report the results of a general survey of the field.

II. Apparatus and Method

Method.—Because of its high volatility, it is not possible to make calorimetric measurements with liquid ammonia according to the methods that may be employed in the case of water or other non-volatile liquids. It seemed possible, however, that by determining the ammonia vaporized as a result of the heat effect, the heat effect itself might be determined from the known heat of vaporization of liquid ammonia.

There are, of course, other effects entering, such as a change in the temperature of the calorimeter and its contents. These temperature changes are most conveniently measured by means of a suitable thermocouple. Since the boiling point of liquid ammonia is −33.35°, it was obviously necessary to employ a vacuum-jacketed calorimeter. For this purpose a vacuum-jacketed tube was employed, surrounded by a bath of boiling ammonia. Since the amount of ammonia evaporated gives the principal datum in connection with a determination of the heat effect, it is necessary to establish equilibrium between the liquid and the vapor. For this purpose, a stirrer must be provided which agitates the liquid-vapor

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[1] Du Pont Fellow in Chemistry at Brown University.

[2] Pickering, *J. Chem. Soc.*, **63**, 865 (1888).

surface. The work of Kraus[3] and of Kraus and Zeitfuchs[4] on the vapor pressure depression of solutions in liquid ammonia indicates that equilibrium between the liquid and the vapor phase may be readily established by the stirring method.

The Calorimeter.—The calorimeter employed is outlined in the figure. The calorimeter proper was a vacuum-jacketed quartz tube A having an internal diameter of 2.8 cm. At the top, the neck of the quartz tube was provided with a ground joint into which fitted the Pyrex glass top B, which carried an addition tube C, the stirrer system D, the thermocouple E and a tube F connecting the interior of the calorimeter with the remainder of the apparatus. The calorimeter proper was surrounded by a bath of boiling ammonia contained in a Dewar tube.

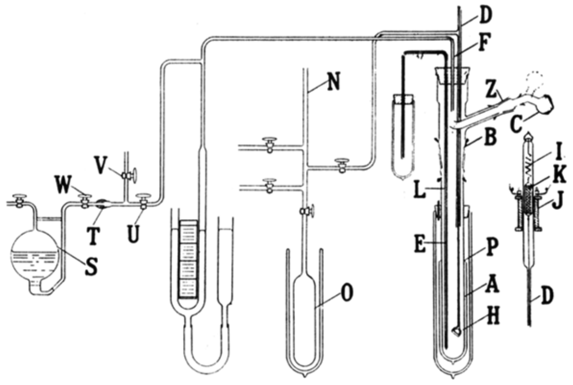

Fig. 1.—Liquid ammonia calorimeter and assembly.

The stirrer consisted of a glass shoe H suspended by a stiff wire from the spiral I (shown at the right). It was actuated by means of an external solenoid J acting on an iron core K (encased in glass). The rate of motion of the stirrer was controlled by means of a mechanical contact device and the displacement of the stirrer could be varied by changing the position of the solenoid.

The temperature of the liquid in the calorimeter was determined by means of a copper–constantan thermocouple. The junction was carried through a glass tube L which at one end was drawn down to a capillary into which the junction fitted.

Liquid ammonia was dried by means of sodium in a stock cylinder which was connected to the apparatus at N. The ammonia was condensed in the calibrated measuring tube O, which had a capacity of 20 g., at −33.4°. From the measuring cell, the ammonia was evaporated and condensed in the calorimeter. For this purpose, ordinary ammonia was introduced into the Dewar flask surrounding the calorimeter to a point above the Dewar seal P. When condensation was complete, the level of ammonia in the bath was lowered below the seal P.

Materials whose heats of solution or reaction were to be measured, were introduced into the addition bulb C. From this bulb they could be dropped into the calorimeter by turning the tube around its axis through 180°. In the case of ammonoscopic substances, the substances were sealed in a glass bulb at one end of a stout glass tube. The glass tube passed through a steel tube in which it was movable through a rubber slipjoint. The glass bulb fitted into an expansion at one end of the steel tube. This expansion was serrated and ground sharp. By pulling on the glass stem the bulb was broken off by the steel teeth. The whole was mounted in a rubber stopper which fitted into the ground joint Z in place of the addition bulb C.

Ordinarily, the process of solution in liquid ammonia is accompanied by evolution of heat, which leads to evaporation of ammonia. In this case, the procedure was to stir the original ammonia until pressure and temperature equilibrium was reached. Then the substance, whose heat of solution was to be measured, was dropped into the calorimeter and as ammonia was evolved it was absorbed in water in the flask S. This flask was joined to the system at T by means of a de Khotinsky seal. The flask was filled about two-thirds full of water and was provided at the bottom with a shallow pool of mercury that served as a trap. The connecting tube between the flask and stopcock U was exhausted through stopcock V and filled with ammonia. As soon as ammonia began to vaporize in the calorimeter, stopcock W of the absorption flask was opened, allowing the ammonia to pass through the mercury into the water where it was absorbed. The process was continued until the pressure became constant at its original value. In this way, no corrections had to be made for change in the amount of ammonia in the vapor phase.

Only metallic sodium dissolved with marked absorption of heat. In this case, the pressure of the system fell as a result of the process of solution and a portion of the ammonia in the vapor phase was condensed in the calorimeter. The amount of ammonia per centimeter of pressure in the apparatus was determined under working conditions by allowing ammonia to enter the apparatus to produce a given pressure change, and determining the amount. The ammonia used for this purpose was absorbed in ammonium nitrate which was contained in a small bulb. This was weighed before and after a determination, thus giving the amount of ammonia in the calorimeter and its connections.

Procedure.—The material whose heat effect was to be measured, was introduced into the addition bulb C and the calorimeter and its connecting tubes were thoroughly exhausted and flushed out with ammonia vapor. The calorimeter was surrounded with a bath of boiling ammonia to a point well above the top of the Dewar seal of the calorimeter. Ammonia vapor was allowed to enter the calorimeter until the pressure was just below one atmosphere. Twenty grams of liquid ammonia was condensed in the measuring tube O and the absorption flask was weighed and attached to the system at T. The ammonia in the measuring tube was now condensed in the calorimeter, after which the Dewar tube surrounding the calorimeter was lowered until the level of the surrounding ammonia was below the Dewar seal P of the calorimeter. The stirrer was set in motion, the temperature of the thermocouple was read and the pressure was noted. Observations were continued until pressure and temperature remained constant over a period of ten minutes. The substance was then dropped into the calorimeter from the addition tube and the stopcock W to the absorption flask was opened. The temperature was read at intervals until

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(3) Kraus, THIS JOURNAL, **30**, 1197 (1908).

(4) Kraus and Zeitfuchs, *ibid.*, **44**, 1249 (1922).

the pressure returned to its original value. The absorption flask was now detached and weighed, which, together with the temperature change indicated by the thermocouple, provided the necessary data for calculating the heat of solution.

Corrections and Constants.—The total heat effect accompanying solution or reaction was distributed among a number of different effects. These were (1) temperature change of the solvent; (2) temperature change of the substance introduced; (3) temperature change of the calorimeter, thermocouple and stirrer; (4) heat flow out of or into the calorimeter; (5) heat absorbed by the ammonia vaporized.

(1) The heat effect due to change in temperature of the calorimeter liquid was determined from the known temperature change and the specific heat of liquid ammonia. The value 1.067, determined by Osborne and Van Dusen[5] was adopted for −33.35°, the boiling point of liquid ammonia. In all experiments, 20 g. of solvent was employed and the weight of solvent evaporated was subtracted from 20 to give the amount of liquid remaining in the calorimeter.

(2) The heat effect due to the substance introduced into the calorimeter was calculated from the known weight of substance, its specific heat (taken from "International Critical Tables")[6] and the observed temperature change. The temperature of the addition bulb was always noted prior to adding the material to the calorimeter. In the case of ammonoscopic substances, which were sealed in glass bulbs, heat was also introduced due to cooling the glass from room temperature to the calorimeter temperature. The weight of glass was determined after each experiment and a correction was made for the heat introduced, using 0.20 for the specific heat of glass.

(3) The heat capacity of the calorimeter is due to the material of the thermocouple tube, the stirrer and the quartz of the calorimeter tube. The weight of glass in the stirrer and thermocouple tube could be closely estimated but that of the calorimeter walls could not be closely estimated. Accordingly, this constant was determined by introducing a volume of water equal to that of 20 g. of ammonia and the temperature change due to a measured input of electrical energy was measured. This gave the values: 5.83, 5.54; mean, 5.68 cal./deg.

(4) Since the reactions carried out were in most cases accompanied by evolution of heat, the mean temperature was higher than the equilibrium temperature and heat flowed from the calorimeter to the surrounding bath. The measured heat effects were therefore too low. Accordingly, the radiation constant of the calorimeter was determined. Twenty grams of liquid ammonia was distilled into the calorimeter and stirred until thermal equilibrium was reached as indicated by the temperature. The temperature of the liquid was then raised 2° by condensing a small quantity of ammonia in the calorimeter at a pressure of about 15 cm. above that of the atmosphere. The temperature was read at five-minute intervals as the liquid cooled. From the known heat capacity of the calorimeter and its rate of cooling, the radiation constant of the calorimeter was found. The change of temperature of the calorimeter in a five minute interval for a temperature difference of 1° was found to be 0.0774°, or 0.01548° per minute. Multiplying this by the heat capacity of the liquid and calorimeter (27.02), the heat transfer between calorimeter and the surroundings was found to be 0.418 cal./deg./min. In carrying out a measurement, the temperature was observed at intervals of a few minutes. These temperatures were averaged as functions of the time to give the mean radiation temperature difference.

Check runs carried out with the calorimeter on the heat effect due to cooling of potassium sulfate from room temperature gave 57.1 and 103.1 calories of total heat effect against 55.4 and 101.5 calories calculated from the known temperature change of the potassium sulfate. The measured heat effects were, respectively, 3.0 and 1.6% above those calculated.

The thermocouple was calibrated at the boiling point of water and the freezing point of carbon tetrachloride, the second junction being placed in melting ice. A deviation curve was constructed and it was found that the couple differed little from the copper-constantan curve given by Adams.[7] The section of the curve between −31 and −35° was constructed on an enlarged scale from which the temperatures corresponding to observed e. m. f.'s were read off.

The ammonia equivalent of the vapor phase was determined as already described. It was found that 0.00578 g. of ammonia caused a pressure change of one centimeter.

In general, the heat absorbed by the vaporized ammonia was the major heat effect and other effects appeared only as correction terms so that small uncertainties in these corrections had no great influence on the final result. Naturally, the greater the heat effect, the smaller was the influence of the correction terms. For the heat of vaporization, the value 327.1 cal./g. due to Osborne and Van Dusen[8] has been adopted.

The values of the various constants employed in the calculations were as follows: heat of vaporization, 327.1 cal./g.; specific heat, 1.067 cal./deg.; calorimeter constant (21.54 + 5.68), 27.02 cal./deg.; radiation constant, 0.418 cal./deg./min.; ammonia equivalent to a pressure of 1 cm., 0.00578 g./cm.

III. Heats of Solution

Below are tabulated heats of solution for a variety of salts. A sufficiently high precision cannot be claimed for these data to warrant giving the original data necessary for calculating the final values. The weights given are those actually introduced into the calorimeter. Concentrations can be calculated by subtracting from 20, the weight of ammonia vaporized (col. 3). The heat effect is given in col. 4. Illustrative examples, below, will give some idea of the magnitude of the several effects entering into the calculations.

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

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

(7) Adams, THIS JOURNAL, **36**, 65 (1914).

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

TABLE I

HEATS OF SOLUTION IN LIQUID AMMONIA

Subst.	Weight	NH_3 vaporized	Net heat effect	Molar heat of soln.	Heat of soln. in H_2O
$NaNO_3$	0.727	0.1061	30.94	3,600	−5000
NaBr	1.867	.5369	171.6	9,500	− 190
NaI	1.258	.3520	147.1	17,500	+1400
KNO_3	0.872	.0199	− 3.53	− 400	−8460
KBr	1.021	.1344	24.52	2,900	−5070
KI	1.420	.1538	50.18	5,900	−5110
NH_4Cl	0.471	.1821	56.27	6,400	−3900
NH_4NO_3	.685	.2007	55.92	5,700	−6330
NH_4Br	.835	.2210	68.73	8,100	−4440
NH_4I	1.174	.2842	89.17	11,000	−3560
$LiNO_3$	0.585	.2937	91.87	10,800	+ 430
$AgNO_3$	1.459	.6115	192.12	22,400	−8800
AgI	2.007	.1811	56.87	6,700	....
Na	0.830	.0000	52.34	− 1,450[a]	....

[a] The mean value of eleven measurements for sodium, ranging from 0.536 to 1.617 g., was 1415 cal./mole.

Discussion

A couple of examples will serve to indicate the relative magnitude of the various effects entering into the calculations. As an example of an endothermic process, we have the following data for sodium: Na, 0.5364 g.; Δp of solution, 3.35 cm.; Δt of calorimeter, $-0.69°$; Δt Na, $-56.83°$; radiation transfer, −1.16 cal.; specific heat Na, 0.268. On the basis of values of the constants given above, the various heat effects are as follows: ammonia condensed, −6.33 cal.; to cool the sodium, −8.17 cal.; calorimeter liquid, −14.72 cal.; calorimeter, −3.91 cal.; radiation transfer, −1.16 cal.; total, −34.29 cal. Based on the amount of sodium used, this gives −1470 cal./atom for the heat of solution of sodium.

As an example of an exothermic process we have the following data for sodium bromide: NaBr, 1.867 g.; NH_3 vaporized, 0.5369 g.; Δt calorimeter, $+0.34°$; Δt salt and glass (containing salt), $-56.1°$; glass container, 0.1524 g.; specific heat of glass, 0.2; specific heat of sodium bromide, 0.118. With these data and the constants given above, the following are the several heat effects: vaporization of ammonia, +175.6 cal.; temperature change of calorimeter liquid, +6.59 cal.; calorimeter, +1.93 cal.; radiation transfer, +1.5 cal.; temperature change of sodium bromide, −12.36 cal.; temperature change of glass container, −1.68 cal.; net heat effect, +171.58 cal. On the basis of the amount of sodium bromide used, this gives 9460 cal./mole.

It will be noted that in the case of the sodium solutions the greatest heat effect was due to the change in the temperature of the calorimeter. However, the heat effects due to cooling off the sodium and to condensing ammonia are comparable with the calorimeter effect. The corrections, therefore, are more significant in endothermic than in exothermic processes. In the case of sodium bromide, for example, the heat effect due to the vaporization of ammonia was more than ten times the next largest heat effect; indeed, it was approximately ten times the net heat effect due to all other factors. This ratio among the different heat effects is approximately maintained whatever the amount of salt introduced, but, as the molar heat effect diminishes, the correction terms become correspondingly more important.

It will be noted that, with a single exception—potassium nitrate—all salts dissolve in ammonia with evolution of heat, but the order of the salts in respect to their heat effects is very much the same in ammonia as it is in water. Thus, potassium nitrate, which is the only salt having a negative heat effect in ammonia, has the greatest negative heat effect in water, while sodium iodide which has a positive heat effect of nearly 18,000 calories in ammonia, has the highest positive heat effect, 1400 cal., in water. In ammonia, as in water, the nitrates have the lowest heat effect and the iodides usually the highest. Similarly, among the alkali metal and ammonium salts, potassium salts have the lowest heat effects, and lithium salts the highest. There are a number of inversions. The heat effect of potassium iodide in liquid ammonia is markedly higher than that of potassium bromide, while in water, the heat effect of potassium iodide is slightly the lower (as positive heat). The spread of heat effects in liquid ammonia is markedly greater than it is in water. Thus, the heat effect in liquid ammonia varies from −400, for potassium nitrate, to 17,500 cal. for sodium iodide, a spread of 18,000 cal., while in water, for the same salts it varies from −8460 to +1400 cal., a spread of 10,000 cal.

The behavior of silver nitrate is quite exceptional. This salt, which dissolves in water with an absorption of 8800 cal. of heat, dissolves in liquid ammonia with an evolution of 22,000 cal. Without doubt, the tendency of the silver ion to form stable complexes with ammonia has something to do with the large energy effect accompanying its solution in ammonia. The heat of solution of silver iodide, however, is very much lower than that of silver nitrate. This is perhaps not surprising in view of the fact that silver nitrate is a strong electrolyte in liquid ammonia while silver iodide is a weak one.

Sodium dissolves in liquid ammonia with the absorption of approximately 1400 calories of heat. That the heat effect accompanying the solution of this metal should be so near zero is doubtless due to compensation among various terms that enter into the total energy effect. It will be remembered that the molecular volume of sodium dissolved in liquid ammonia is almost twice that of the pure metal and that solutions of sodium in liquid ammonia are lighter than either sodium or ammonia.[9] This indicates a very large expansion which, without doubt, is accompanied by the absorption of considerable heat.

IV. Heats of Reaction

The energies of the reactions represented by the following equations have been determined calorimetrically

(1) $NH_4Br + NaNH_2 = NaBr\cdot am + 2NH_3$ (liq.) $- 33{,}000$
(2) $NH_4Br + KNH_2\cdot am = KBr\cdot am + 2NH_3$ (liq.) $- 27{,}500$
(3) $PbBr_2\cdot am + 6Na = 2NaBr\cdot am + Na_4Pb - 104{,}400$
(4) $PbBr_2\cdot am + 2Na = 2NaBr\cdot am + Pb - 91{,}200$
(5) $PbBr_2 + 2Na\cdot am = 2NaBr\cdot am + Pb - 123{,}700$
(6) $4Na + 9Pb = Na_4Pb_9\cdot am - 88{,}000$
(7) $2Na\cdot am + S = Na_2S - 89{,}800$
(8) $2Na\cdot am + 2S = Na_2S_2 - 99{,}000$
(9) $2Na + Te = Na_2Te - 82{,}500$
(10) $2Na\cdot am + Te = Na_2Te - 86{,}900$
(11) $Na_2Te + Te = Na_2Te_2\cdot am - 21{,}900$
(12) $Na_2Te_2 + am = Na_2Te_2\cdot am - 4400$
(13) $Na_2Te_2\cdot am + 2Te = Na_2Te_4\cdot am - 1900$

Results and Experimental Details.—In carrying out the reactions, one component was introduced into the calorimeter and the other into the addition tube. When the calorimeter had reached a steady state, the second component was added, the evolved ammonia was absorbed in water as already described, and the temperature indicated by the thermocouple was read until the original pressure was re-established. In reaction (1), sodium amide, prepared according to the method of Kraus and Cuy,[10] was introduced into the calorimeter, care being taken to avoid oxidation or contact with moisture. In reaction (2), metallic potassium was introduced into the calorimeter and was converted to the amide with the aid of a bit of oxidized iron wire. The ammonia was evaporated after preparing the amide to remove hydrogen, after which 20 g. of ammonia was condensed in the calorimeter and the reaction was carried out. In reactions (3) and (4), metallic sodium was cut under oil and introduced into the addition tube in a stream of ammonia vapor. In reaction (6), lead bromide was reduced to metallic lead by means of sodium in liquid ammonia in a special tube. The ammonia was evaporated and the salts were washed out with slightly acid, air-free water. After drying *in vacuo*, this lead was introduced into the calorimeter. Unless the lead is very finely divided, the reaction between sodium and lead in liquid ammonia is not sufficiently rapid to permit of calorimetric measurements. In reactions (7) and (8), sulfur was introduced into the addition tube. Sodium was introduced into the addition tube in reaction (9) and tellurium in reaction (10). In reaction (11), sodium telluride, Na_2Te, was prepared in the calorimeter and an equivalent amount of tellurium was added. In (12), Na_2Te_2 was added from the addition tube. In reaction (13), tellurium, from the addition tube, was added to a solution of sodium ditelluride.

The results are given in Table II. In columns 3 and 5 are given the weights of the materials indicated in columns 2 and 4. The amount of ammonia vaporized is given in column 6.

Example of Calculations.—Complete data necessary for the calculations are not given in Table II. The nature of the effects involved and their general order of magnitude will be clear from an example. Following are the data for reaction (2a): NH_4Br, 0.9479 g.; KNH_2, equivalent to NH_4Br; glass, 0.23; NH_3 vaporized, 0.845; Δt calorimeter and liquid, 0.225°; Δt ammonium bromide and glass, 63.45°; radiation transfer, 0.45 cal.; specific heats: glass, 0.2; NH_4Br, 0.2069. From these data the following heat effects are calculated: vaporization of ammonia, 276.4; change in temperature of calorimeter and liquid, 6.08; radiation transfer, 0.45; temperature change of ammonium bromide and glass, -15.36; net heat effect, 267.4 cal., which corresponds to 27,600 cals. for the heat of the reaction.

This example will serve to show that in the case of reactions where the heat effect is generally greater than it is in processes of solution, the heat effect due to the ammonia vaporized is far greater than the combined effects due to all other causes. The largest correction term is only -15.4 cal., due to cooling the ammonium bromide and its

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(9) Kraus, Carney and Johnson, This Journal, **49**, 2206 (1927).

(10) Kraus and Cuy, *ibid.*, **45**, 712 (1923).

TABLE II

HEATS OF REACTION IN LIQUID AMMONIA

React.	Subst. (1)	Wt. (1)	Subst. (2)	Wt. (2)	NH_3 vap.	Net heat effect	Heat of reaction	Mean
(1)	NH_4Br	1.7524	$NaNH_2$	Equiv.	1.810	591.2	− 33,000	
(2a)	NH_4Br	0.9479	KNH_2·am	Equiv.	0.845	267.4	− 27,600	− 27,500
(2b)	NH_4Br	.5759	KNH_2·am	Equiv.	.508	160.2	− 27,300	
(3a)	$PbBr_2$	1.2267	Na	0.4915[a]	1.067	349.2	−104,500	−104,400
(3b)	$PbBr_2$	1.2335	Na	.4877[a]	1.071	350.1	−104,200	
(4)	$PbBr_2$	0.9872	Na	.1240	0.734	245.4	− 91,200	
(5)	$PbBr_2$	1.1470	Na	.1430	1.180	386.5	−123,700	
(6)	Pb	Excess	Na	.6429	1.878	614.9	− 88,000	
(7a)	Na	0.6108	S	.4257	3.698	1210	− 90,500	− 89,800
(7b)	Na	.7762	S	.5422	4.622	1512	− 89,100	
(8)	Na	.7793	S	1.0874	5.226	1709	− 99,000	
(9)	Na	.3636	Te	1.0134	1.976	652.3	− 82,500	
(10a)	Na	.3649	Te	1.0124	2.118	689.4	− 87,100	− 86,900
(10b)	Na	.6205	Te	1.7215	3.622	1179	− 87,400	
(10c)	Na	.8022	Te	2.2235	4.624	1501	− 86,100	
(11)	Na_2Te	2.4145	Te	1.7743	0.768	304.4	− 21,900	
(12)	Na_2Te_2	4.6913	...	....	.247	66.6	− 4,400	
(13)	Na_2Te_2	4.1830	Te	6.7018[a]	.133	26.5	− 1,900	

[a] In excess.

glass container. All other effects are positive, bringing the net correction down to 9.0 cal., about 3% of the effect due to vaporization of ammonia. The higher the heat effect of the process, the smaller are the corrections, relative to the main measured effect due to vaporization.

Check determinations were run in reactions (2), (3), (7) and (10). For heats of reaction ranging from 27,500 to 104,400 cal., the maximum deviation from the mean in the four reactions was, respectively, 0.55, 0.15, 0.8 and 0.92%. It seems that the measurements are reproducible within about 1%. The heat effects measured range as high as 1700 cal., in which case the correction terms become quite small. In reaction (7b) the net correction amounted to 12 cal. out of 1512 cal. due to vaporization of ammonia, and the highest single correction term, due to heat introduced by the sulfur, amounted to only 6.1 cal.

Heat of Formation of Liquid Ammonia.—Introducing the energy change accompanying the solution of sodium bromide in liquid ammonia (−9500 cal.) into equation (1), we have the energy equation

$$NH_4Br + NaNH_2 = NaBr + 2NH_3 \text{ (liq.)} - 23{,}500 \text{ cal.}$$

The heats of formation of ammonium bromide, sodium amide and sodium bromide ("I. C. T."), are, respectively, 64.7, 32.2 and 86.3 kilogram cal. Introducing these values, we have for the heat of formation of liquid ammonia at −33.4° the value 17,000 cal.

Thomsen and Berthelot[11] give 11,890 cal. and 12,200 cal. for the heat of formation of gaseous ammonia at 18 and 15°, respectively. Haber,[12] from his measurements at higher temperatures, computes 10,950 cal. for the heat of formation of gaseous ammonia at 0°.

According to Osborne and Van Dusen,[13] the heat of vaporization of liquid ammonia at 0° is 301.8 cal./g., or 5140 cal./mole. The mean specific heat of liquid ammonia between its boiling point and 0° is approximately 1.1 cal./deg. and the difference between the heat capacities of liquid ammonia and of 0.5 mole of nitrogen and 1.5 moles of hydrogen is approximately 5 cal./deg./mole. This will bring the heat of formation of liquid ammonia at 0° to 16,850 cal. Allowing for the heat of vaporization and for the change in pressure from 4.238 atmospheres to one atmosphere[14] (782 cal.), gives for the heat of formation of gaseous ammonia at 0° under standard conditions, 10,930 cal. This value is practically identical with that of Haber.

Heat of Neutralization of Potassium Amide.—Combining the energy equation for the solution of ammonium bromide, whose heat effect is 8100 cal., with equation (2), whose heat effect is 27,500 cal., we obtain the equation

[11] Landolt-Börnstein, "Physikalisch-chemische Tabellen," Julius Springer, Berlin, 1923, [5] Vol. 2, p. 1490.

[12] Haber, *Z. Elektrochem.*, **21**, 191 (1915).

[13] Osborne and Van Dusen, Bureau of Standards, Scientific Papers, No. 315, issued Dec. 31, 1917; THIS JOURNAL, **40**, 14 (1918).

[14] Cragoe, Meyers and Taylor, Bureau of Standards, Scientific Papers, No. 369, issued Apr. 10, 1920.

$$NH_4Br{\cdot}am + KNH_2{\cdot}am = KBr{\cdot}am + 2NH_3 - 19{,}400 \text{ cal.}$$

The heat of neutralization of an ammono acid by an ammono base in liquid ammonia is, then, 19,400 cal. for the acid and the base here used and at the concentration of the measurement. This heat effect is much larger than the heat of neutralization of strong acids and bases in water.

Plumbides.—Subtracting equation (4) from equation (3), we have

$$4Na + Pb = Na_4Pb - 13{,}200 \text{ cal.}$$

There are no data in the literature on the heat of formation of sodium plumbides. The state of the lead after reduction with four atoms of sodium is somewhat uncertain. Without doubt, a considerable quantity of the compound Na_4Pb is present as a solid phase, but Kraus and Kurtz[15] have shown that an equilibrium exists between Na_4Pb and a solution containing a more complex plumbide and free sodium. Judging by the magnitude of the heat effect, much of the sodium must be present in the free state in solution.

Introducing energy values for the heat of solution of sodium (1415 cal./at.) and of sodium bromide (9500 cal./mole) into equation (5), we have

$$PbBr_2 + 2Na = 2NaBr + Pb - 101{,}900 \text{ cal.}$$

The energy of this reaction corresponds to the difference between the heats of formation of 2NaBr and $PbBr_2$. From data in the literature ("I. C. T."), the value is 106,400 cal.

Subtracting equation (4) from equation (5), and introducing the value for the heat of solution of sodium (1415), we have for the heat of solution of $PbBr_2$ the value 29,800 cal. This is a remarkably large heat effect for a process of solution. It is, perhaps, not unexpected, since the heat of solution of silver nitrate is 22,400 cal.

Reaction (6) is of interest in that it yields the heat effect (88,000 cal.) accompanying the formation of a solution of the polyplumbide, Na_4Pb_9.[16] Per atom of sodium, the heat effect is 22,000 cal., indicating a rather high stability for this compound. No data are available for the heats of formation of any plumbides, but the heat of formation of $NaSn_2$ is 15,000 cal. ("I. C. T."). The heat of solution of Na_4Pb_9 is not known. Even if this were considerable, the heat of formation of the polyplumbide would still be relatively high, indicating a considerable stability of the anion complex of this compound.

Sulfides.—Introducing the value of the heat of solution of sodium in liquid ammonia in equations (7) and (8), we obtain for the heat of formation of sodium monosulfide and disulfide the values 87,000 and 96,200, respectively. (It should be noted that both Na_2S and Na_2S_2 are only slightly soluble in liquid ammonia according to Bergstrom.)[17] According to the literature, the heat of formation of sodium monosulfide is 89,800 cal. No data are given in the literature for the heat of formation of the disulfide, although the heat of formation of its aqueous solution is given at 104,500 cal. The heat of solution of the disulfide is not known so that exact comparison with our own values is not possible.

Tellurides.—From reaction (9), the heat of formation of sodium monotelluride is directly found to be 82,500 cal. Introducing the value for the heat of solution of sodium in equation (10), the heat of formation of Na_2Te is found to be 84,300 cal. The latter value is the result of three determinations which are in excellent agreement and are doubtless more trustworthy than the value obtained in reaction (9). There are no values given in the literature for the heat of formation of any tellurides.

Reaction (12) gives 4400 cal. for the heat of solution of sodium ditelluride and introducing this value into equation (11) we obtain 17,500 cal. for the heat of reaction between sodium telluride and tellurium to form sodium ditelluride. Assuming the heat of formation of the normal telluride to be 84,300 cal., we obtain 101,800 cal. for the heat of formation of sodium ditelluride. The heat of formation of the ditelluride which we have obtained is markedly higher than that of the disulfide. In reaction (13), sodium ditelluride was treated with an excess of tellurium. According to Kraus and Chiu,[18] the ratio of tellurium to sodium, in a liquid ammonia solution in equilibrium with metallic tellurium, changes slightly with concentration and approaches a value of 2.0 at higher concentrations. At the concentration of the above measurements, the ratio is 2.0. The heat effect of 1900 calories is due to interaction between tellurium and the ditelluride in solution to form the tetratelluride in solution. Whereas the ditelluride is a relatively stable compound, as indi-

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[15] Kraus and Kurtz, THIS JOURNAL, **47**, 43 (1925).

[16] Kraus, *ibid.*, **29**, 1557 (1907); Smyth, *ibid.*, **39**, 1299 (1917); Zintl, Goubeau and Dullenkopf, *Z. physik. Chem.*, **154A**, 1 (1931); Zintl and Harder, *ibid.*, **154A**, 47 (1931).

[17] Bergstrom, THIS JOURNAL, **48**, 146 (1926).

[18] Kraus and Chiu, *ibid.*, **44**, 1999 (1922).

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.

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[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.

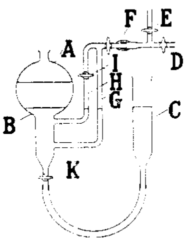

Fig. 1.—Absorption flask.

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.

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