four temperatures. For every experiment, the value of $(k_{12} - k_{14})$ obtained was divided by the value of k_{12} obtained for the *same run.* For the experiments at 0° and 24.75° the 95% confidence interval is reported for the mean k_{12} values and for the mean 100 k_{14}/k_{12} values.

TABLE I

VALUES OF THE RATE CONSTANT AND THE ISOTOPE EFFECT AT FOUR TEMPERATURES

Temp., °C.	k_{12}, min.$^{-1}$ × 10^4	$(k_{12} - k_{14})$, min.$^{-1}$ × 10^4	$100k_{14}/k_{12}$
0.00 ± 0.05	34.45	4.247	87.68
	34.29	3.544	89.66
	34.50	4.058	88.24
	33.58	3.556	89.41
	33.99	3.501	89.70
	34.98	3.915	88.81
	33.99	3.692	89.14
	34.59	3.996	88.45
	34.30 ± 0.30		88.89 ± 0.52
14.75 ± 0.05	216	19.2	91.12
	221	21.1	90.46
	219		90.79
18.75 ± 0.05	380	34.6	90.89
	359	31.4	91.25
	370		91.07
24.75 ± 0.05	755.6	65.68	91.31
	733.0	63.79	91.30
	730.3	60.85	91.67
	764.1	58.82	92.30
	763.9	72.77	90.47
	749.3 ± 14.8		91.41 ± 0.58

C. Calculation of the Values of ΔE and E.—From the Arrhenium equations for the dehydration of the two species of formic acid, the following expression was derived

$$\ln \frac{k_{14}}{k_{12}} = \ln \frac{A_{14}}{A_{12}} - \Delta E/RT$$

If it is assumed that A_{14}/A_{12} is constant in the temperature range, 0–25°, ΔE was calculated from the slope of the line obtained by plotting the logarithms of each of the seventeen values of k_{14}/k_{12} against $1/T$.

$$\Delta E = 189 \pm 53 \text{ cal. per mole}$$

The 95% confidence interval of this ΔE value was calculated as twice the standard deviation from the line fitted by the method of least squares. In an exactly analogous manner the seventeen values of k_{12} gave

$$E = 20{,}118 \pm 139 \text{ cal. per mole}^4$$

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(4) *Cf.* E. Schierz, THIS JOURNAL, **44**, 447 (1922); E. Schierz and H. Ward, *ibid.*, **50**, 3240 (1928).

OAK RIDGE, TENNESSEE RECEIVED APRIL 27, 1951

[CONTRIBUTION NO. 533 FROM THE CHEMISTRY LABORATORIES OF INDIANA UNIVERSITY]

Heats of Solution and Reaction in Liquid Ammonia. VIII.

BY HARVEY DALE MULDER[1] WITH FREDERIC C. SCHMIDT

Several heats of solution of inorganic salts have been measured. The heat of neutralization of the ammono base, KNH_2, with the ammonium salts of various strong acids, has been determined and yields a value of 26.1 kcal. This heat effect is much larger than the heat of neutralization of strong acids and bases in water. Also heats of formation of Na_2Se and Na_2Se_2 have been measured directly by means of the liquid ammonia calorimeter.

I. Introduction

In the previous paper[2] there were reported the salts of such bases as the alkyl amines. We have extended these measurements to salts of such organic bases as guanidine and hydroxylamine. Heats of solution of potassium amide over a moderate range of concentrations were made as a comparison with the heats of solution of its analog in water, NaOH.

Kraus[3] made one measurement of the heat of neutralization of the ammono base, potassium amide, with ammonium bromide. We have repeated this work by measuring the heat effect of this base with other ammono acids in liquid ammonia; such as NH_4I, NH_4NO_3, NH_4SCN and NH_4Br. The heat of combination of the ammonium ion with the amide ion is 26.1 kcal., which is lower than the value found by the previous workers.[3]

II. Experimental

The calorimeter and procedure were the same as used in previous measurements.[2] However, a larger pipet was constructed to deliver 46.5 ml. of liquid ammonia at −33° in order that the measurements might be made in more dilute regions than formerly.

The guanidine salts were prepared from guanidine carbonate supplied to us by the Nitrogen Division of the American Cyanamid Company at Stamford, Connecticut. All salts used were recrystallized from water. The sodium and potassium were Baker Analytical Reagent Grade and were put into fragile sample bulbs according to the technique of Kraus and Schmidt.[4]

The potassium amide was prepared by reaction of the metal with ammonia. The potassium had previously been put into fragile sample bulbs so that the amide was

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(1) This paper comprises the greater part of the thesis submitted by Harvey D. Mulder in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Department of Chemistry, Indiana University.

(2) E. Hennelly, D. K. Stevens, M. Warren, H. Zuhr, J. Sottysiak with F. C. Schmidt, THIS JOURNAL, **69**, 1025 (1947).

(3) C. A. Kraus and J. A. Ridderhof, *ibid.*, **56**, 79 (1934).

(4) C. A. Kraus and F. C. Schmidt, *ibid.*, **56**, 2297 (1934).

ready for use. After the metal had been converted to the amide, the bulb was sealed off. The amount of amide was determined by weighing the bulb plus the amide previous to measuring the heat effect, and then weighing the cleaned, dried fragments of the bulb after the calorimeter had been dismantled. However, in carrying out the heats of neutralization of potassium amide with the various ammonoacids, the amide was prepared as above in the calorimeter itself, and the bulb containing the ammonium salt was introduced on the crushing rod, care being taken to keep moisture out of the calorimeter. This was accomplished by keeping a steady stream of dry nitrogen running into the calorimeter while introducing the bulb and plunger.

III. Heats of Solution

Below in Tables I, II and III are given the molar integral heats of solution of several salts. The integral heats of solution of ammonium thiocyanate, potassium thiocyanate, potassium iodide and potassium amide were determined over a fairly large range of concentrations. The heats of solution of potassium amide represents heats in the near concentrated region, due to the low solubility of this compound. It is interesting to note that the integral heats for the guanidine salts are very little different from those of the corresponding ammonium salts at the same concentration.

TABLE I

MOLAR HEATS OF SOLUTION OF SOME GUANIDINE SALTS AND POTASSIUM AMIDE AT −33.4°

Salt	Wt. sample, g.	$m^{1/2}$	ΔH soln., kcal.
Guanidine HCl	(1) 1.0837	0.606	8.56
	(2) 0.8451	.534	8.60
Guanidine HCNS	(1) 0.9642	.512	9.86
	(2) 0.5270	.378	9.93
Guanidine HBr	(1) 1.2325	.534	10.05
	(2) 0.8002	.428	10.02
Guanidine HNO_3	(1) 0.8560	.477	5.45
	(2) 0.7541	.445	5.53
$H_2N-OH\cdot HCl$	(1) 0.6714	.561	16.43
	(2) 0.5922	.526	16.21
Potassium amide	(1) 1.2539	.856	1.48
	(2) 0.7842	.675	1.74
	(3) 0.4736	.525	1.97
Ammonium nitrate	(1) 0.9097	.605	6.75

TABLE II

MOLAR HEATS OF SOLUTION OF AMMONIUM AND POTASSIUM THIOCYANATE AT −33.4°

Ammonium thiocyanate			Potassium thiocyanate		
Sample, g.	$m^{1/2}$	ΔH soln., kcal.	Sample, g.	$m^{1/2}$	ΔH soln., kcal.
1.7422	0.863	9.10	1.5735	0.721	3.86
1.3319	.756	9.29	1.0752	.597	4.58
1.2804	.737	9.39	0.7407	.496	4.80
1.0566	.672	9.71	.5249	.417	4.75
0.9191	.626	9.71		.000	4.78
.7029	.546	9.72			
.6106	.508	9.72			
	.00	9.72			

TABLE III

MOLAR HEATS OF SOLUTION OF POTASSIUM IODIDE AT −33.4°

Weight sample, g.	$m^{1/2}$	ΔH soln., kcal.
4.0833	0.896	6.47
2.5230	.704	6.52
2.4812	.696	6.53
1.7704	.587	6.96
1.0458	.489	7.82
0.9985	.440	7.82
0.8560	.403	7.80
	.00	7.82

IV. Heats of Reaction

In Table IV are given the data pertaining to the heat of neutralization of potassium amide with the four amino acids NH_4Br, NH_4I, NH_4NO_3 and NH_4SCN and in Table V the heat data for the determination of the heats of formation of Na_2Se and Na_2Se.

TABLE IV

HEATS OF NEUTRALIZATION OF POTASSIUM AMIDE WITH NH_4I, NH_4NO_3, NH_4SCN, NH_4Br

Moles KNH_2	Acid, mole	Heat of reaction, kcal.
Reaction of KNH_2(am.) with NH_4I		
0.00638	0.00304	39.5
.00572	.00349	39.4
	Mean heat of reaction	39.4
Reaction of KNH_2(am.) with NH_4NO_3		
0.00409	0.00252	33.34
.00454	.00376	32.15
	Mean heat of reaction	32.8
Reaction of KNH_2(am.) with NH_4SCN		
0.005466	0.00367	35.9
.007170	.00376	35.9
	Mean heat of reaction	35.9
Reaction of KNH_2(am.) with NH_4Br		
0.00483	0.00329	36.0
.00519	.00352	35.4
	Mean heat of reaction	35.7

Combining the heat of solution of the various ammono acids used (NH_4I, NH_4NO_3, NH_4SCN, NH_4Br) with the heats of reaction at equivalent concentration as shown in Table IV, we get the heats of neutralization of the base KNH_2 as illustrated below.

$$(1)\begin{cases} NH_4I + KNH_2\cdot\text{am.} \longrightarrow KI\ \text{am.} + 2NH_3 & 39.4\ \text{kcal.} \\ NH_4I + \text{am.} \longrightarrow NH_4I\ \text{am.} & 13.3\ \text{kcal.} \end{cases}$$

$$(2)\begin{cases} NH_4I\ \text{am.} + KNH_2\ \text{am.} \longrightarrow KI\ \text{am.} + 2NH_3 & 26.1\ \text{kcal.} \\ NH_4NO_3 + KNH_2\ \text{am.} \longrightarrow KNO_3\ \text{am.} + 2NH_3 & 32.8\ \text{kcal.} \\ NH_4NO_3 + \text{am.} \longrightarrow NH_4NO_3\ \text{am.} & 6.7\ \text{kcal.} \\ NH_4NO_3\ \text{am.} + KNH_2\ \text{am.} \longrightarrow KNO_3\ \text{am.} + 2NH_3 & 26.1\ \text{kcal.} \end{cases}$$

$$(3)\begin{cases} NH_4SCN + KNH_2\ \text{am.} \longrightarrow KSCN\ \text{am.} + 2NH_3 & 36.4\ \text{kcal.} \\ NH_4SCN + \text{am.} \longrightarrow NH_4SCN\ \text{am.} & 9.7\ \text{kcal.} \end{cases}$$

$$(4)\begin{cases} NH_4SCN\ \text{am.} + KNH_2\ \text{am.} \longrightarrow KSCN\ \text{am.} + 2NH_3 & 26.7\ \text{kcal.} \\ NH_4Br + KNH_2\ \text{am.} \longrightarrow KBr\ \text{am.} + 2NH_3 & 35.5\ \text{kcal.} \\ NH_4Br + \text{am.} \longrightarrow NH_4Br\ \text{am.}[5] & 10.4\ \text{kcal.} \\ NH_4Br\ \text{am.} + KNH_2\ \text{am.} \longrightarrow KBr\ \text{am.} + 2NH_3 & 25.1\ \text{kcal} \end{cases}$$

This value (26.5 kcal.) is not in agreement by some 6.1 kcal. with the value determined by Kraus and Ridderhof[3] of 19.4 kcal. It is true that these investigators ran their one determination at a

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(5) F. C. Schmidt, J. R. Sottysiak and H. Kluge, THIS JOURNAL, 58, 2509 (1936)

fairly high concentration of 122 moles of ammonia per mole of salt formed while our measurements were made at a concentration of some 500 moles of solvent per mole of salt. However, the discrepancy cannot be due entirely to a heat of dilution effect. These investigators made only one determination using ammonium bromide and potassium amide.

Selenium

Selenium combines with sodium in anhydrous liquid ammonia to form insoluble Na_2Se and soluble Na_2Se depending on the number of equivalents used.

The heats of reaction measured in this investigation, shown in Table IV, are represented by the equations

(1) $2Na\cdot am. + Se \longrightarrow Na_2Se \quad \Delta H = 84.7$ kcal.

(2) $2Na\cdot am. + 2Se \longrightarrow Na_2Se_2\ am. \quad \Delta H = 100.0$ kcal.

(3) $2Na + NH_3 \longrightarrow 2Na\cdot am.^4 \quad \Delta H = -2.7$ kcal.

TABLE V

MOLAR HEATS OF REACTION OF SODIUM WITH SELENIUM IN ANHYDROUS LIQUID AMMONIA

Gram atom Na	Gram atoms Se		ΔH reaction, kcal.
	Na_2Se		
1.24×10^{-2}	6.25×10^{-3}		84.3
9.3×10^{-3}	2.5×10^{-3}		85.9
1.4×10^{-2}	2.4×10^{-3}		83.9
		Mean	84.7
	Na_2Se_2		
1.16×10^{-2}	1.16×10^{-2}		100.00

Subtracting equation (3) from equation (1), the heat of formation of solid Na_2Se from its elements at $-33.5°$ is found to be 82.0 kcal. Kraus[3] measured the heat of formation of solid Na_2Te from its elements in essentially the same manner and found it to be 84.3 kcal.

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[UNIVERSITY OF CALIFORNIA, LOS ALAMOS SCIENTIFIC LABORATORY]

The Heats of Combustion of Magnesium and Aluminum[1-3]

BY CHARLES E. HOLLEY, JR., AND ELMER J. HUBER, JR.

Precise measurements of the heats of combustion of magnesium and aluminum have been made. The results are: for magnesium, heat of combustion in 25 atm. oxygen = 5895.6 ± 4.8 cal./gram; heat of formation of MgO, $\Delta H_{25°} = -143.70 \pm 0.12$ kcal./mole; for aluminum, heat of combustion in 25 atm. oxygen = 7403.4 ± 5.7 cal./gram; heat of formation of Al_2O_3, $\Delta H_{25°} = -400.29 \pm 0.31$ kcal./mole. A comparison of these results with those of other investigators is made.

Introduction

In connection with work on the heats of formation of the oxides of some of the rare earth elements and of some of the elements of high atomic number it was decided to set up an oxygen bomb calorimeter. Experiments were run on magnesium and aluminum to test the apparatus and to gain experience in its use. We believe the results obtained on these two metals are sufficiently interesting to be worth reporting.

Method.—The method involved the determination of the heat evolved from the burning of a weighed sample of the metal in question in an atmosphere of oxygen of known pressure. The energy equivalent of the calorimeter was determined from the heat of combustion of standard benzoic acid and the heat of combustion was evaluated from this value and measurement of the temperature rise per unit mass of metal. Dickinson's method[4] was used in correcting the temperature rise for heat interchange with the surroundings. The completeness of combustion was determined by treating the combustion products with 6 *N* hydrochloric acid and measuring the amount of hydrogen evolved from any unburned metal present.

Apparatus.—The combustion bomb was a Parr oxygen bomb in which the electrodes were replaced with shorter platinum electrodes. In the end of each was a small hole in which the fuse wire was held by a platinum peg. The volume of the bomb was about 360 ml. On the outside of the bomb a heater was wound of No. 26 Advance wire and cemented in place with clear Glyptal varnish. The calorimeter can was provided with a lid made of silver sheet.

A convection shield made of 0.005 inch silver sheet was provided as recommended by White.[5] By its use the distance between calorimeter and thermostat could be increased to 3 cm. The calorimeter can was completely surrounded, including top and bottom, by the convection shield.

The water thermostat was a covered copper vessel containing approximately 70 liters of water in which the temperature was maintained constant to ±0.005° at about 27°. It was enclosed in an air thermostat in which the temperature was maintained at 25 ± 0.5°.

The temperature of the calorimeter was measured to 0.001° with a precision platinum resistance thermometer and a L and N Type G-2 Mueller Bridge. The resistance thermometer was calibrated by comparing it at several temperatures with a standard resistance thermometer which had been calibrated by the National Bureau of Standards.

The heater wound on the bomb was used for the electrical calibration. The voltage was measured directly by means of a volt box and a Rubicon Type B potentiometer. The potential leads were placed outside the convection shield but as close to it as possible. The current was determined by measuring the potential drop in a precision 0.1 ohm resistor. The time of heating was measured by counting the cyles of a precision 60-cycle tuning fork with a scaling circuit run off the output of the fork. A special switch turned heater and counter on and off simultaneously.

The electrical energy used in igniting the fuse wire was calculated from measurements of the resistance of the firing circuit, the resistance of the fuse wire, the voltage of the batteries, and the time during which the current was on.

The oxygen, furnished by Linde Air Products Corp. as at least 99% O_2, was treated to remove any traces of combustible gases by passing over heated palladized asbestos followed by a drying train. Atmospheric nitrogen was removed by flushing with the purified O_2. All runs were made at 25 atm. O_2 pressure.

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(1) This work was done under the auspices of the A. E. C.

(2) Presented before the Division of Physical and Inorganic Chemistry at the 119th Meeting of the American Chemical Society, Cleveland, Ohio, April 12, 1951.

(3) For material supplementary to this article order Document 3330 from American Documentation Institute, 1719 N Street, N. W., Washington 6, D. C., remitting $1.00 for microfilm (images 1 inch high on standard motion picture film) or $1.00 for photocopies (6 × 8 inches) readable without optical aid.

(4) H. C. Dickinson, *Bull. Bur. Standards*, **11**, 189 (1914).

(5) W. P. White, "The Modern Calorimeter," The Chemical Catalog Co., Inc., (Reinhold Publ. Corp.), New York, N. Y., 1928, p. 169.