[CONTRIBUTION FROM THE LABORATORIES OF CHEMISTRY AND PHYSICS OF UNION COLLEGE]

Heats of Solution and Heats of Reaction in Liquid Ammonia. V.[1] The Alkali and Alkaline Earth Metals

BY FREDERIC C. SCHMIDT, FRANK J. STUDER AND JOSEPH SOTTYSIAK

In earlier papers in this series a liquid ammonia calorimeter has been described and results of measurements of heats of solution and reaction in liquid ammonia have been published.[2] In the present work, the heats of solution of the alkali and alkaline earth metals have been studied over a fairly wide range of concentrations. Kraus and Schmidt previously measured the heat of solution of metallic sodium in this solvent[2] and found it to have a negative heat of 1385 cal. Metallic lithium also has been studied, but only at quite low concentrations. In this paper the results of the heats of solution of lithium at higher concentrations are reported, as well as those of calcium, barium and strontium, and they show a markedly large change in the atomic heat effect with a change in concentration. Atomic heats of solution of the metals, potassium, rubidium and cesium have also been measured.

Experimental Details

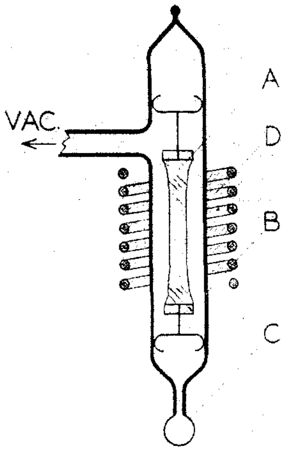

Fig. 1.

A new calorimeter made of "Nonex" glass was used in these experiments. This instrument was the same in all details as the one described by Kraus and Schmidt.[2] The calorimeter constant was determined experimentally by introducing a known amount of heat into water in the calorimeter and noting the difference in the heat introduced and that taken up by the water at 20°. Allowing for the change in the specific heat of the glass with the temperature, this reduces to 9.16 cal. per degree at the boiling point of liquid ammonia. Uncertainties in this value do not affect the precision of the results, as the temperature changes are, for the most part, very small. The radiation constant of the calorimeter was determined and found to be 0.10 cal. per degree per minute. This correction was generally insignificant, due to the short duration of the determinations. The amount of ammonia used in all the determinations was 29.80 g., which was corrected for the ammonia vaporized due to the heat evolved. The following constants were employed: specific heat of ammonia at the boiling point 1.067 cal./deg.,[3] heat of vaporization 327.7 cal./g.[4] In the case of the metals potassium, rubidium and cesium, whose heat effects were zero, the current in the battery circuit of the Queen potentiometer was diminished by means of a resistance so as to spread out the scale readings and catch any small temperature change that might have occurred. The temperature change in all of these measurements was zero to an accuracy of 0.005°.

Preparation of the Metals.—The metals rubidium and cesium were reduced from their respective chlorides by granulated metallic calcium in the apparatus shown in Fig. 1. Twenty-five grams of the chloride was quickly and thoroughly mixed in an atmosphere of dry air with approximately 5% more than an equivalent of the calcium and put into a pure nickel tube (A), the ends of which were folded over. The charged tube was introduced into the apparatus at (B) and supported by nickel wire springs. The apparatus was then sealed off at the top and immediately evacuated. The glass was heated with a hand torch during the evacuation so as to degas the interior as thoroughly as possible. Coil (D) from an induction furnace was used to heat the nickel tube to red heat in order to initiate the reaction. Sufficient heat was maintained by the reaction to carry the reduction to completion. Both rubidium and cesium distilled and exuded from the seams of the nickel tube, free from unreacted salts and calcium chloride, and ran down into the fragile bulb (C) which was then sealed off. The metals were then redistilled into weighed fragile bulbs to be used for the heat measurements. Yields ranging from 35 to 45% were obtained in the case of both metals. Chemical examination of these metals showed no impurities. The potassium used was twice distilled. The lithium and the alkaline earth metals were better than 99.5% pure. In an atmosphere of dry hydrogen, these metals were cut into as large pieces as were permitted by the size of the capillary tubes on the fragile bulbs. The metals were free of their respective nitrides and oxides.

Experimental Results

The heats of solution of lithium, potassium, rubidium and cesium are presented in Table I, and those of the alkaline earth metals, calcium, barium and strontium, in Table II.

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[1] This present investigation was made possible by a Grant-in-Aid from the Society of the Sigma Xi and the Warren Fund of the American Academy of Arts and Sciences.

[2] C. A. Kraus and J. A. Ridderhof, THIS JOURNAL, **56**, 79 (1934); Kraus and Prescott, *ibid.*, **56**, 86 (1934); Kraus and Schmidt, *ibid.*, **56**, 2297 (1934); Schmidt, Sottysiak and Kluge, *ibid.*, **58**, 2509 (1936).

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

[4] Roy Overstreet and W. F. Giaugue, *ibid.*, **59**, 254 (1937).

TABLE I

ATOMIC HEATS OF SOLUTION OF METALLIC LITHIUM, POTASSIUM, RUBIDIUM AND CESIUM

Wt., g.	Moles NH_3 per atom	Obsd. ht. effect, cal.	Atomic heat effect, cal.
	(A) Lithium		
0.1056	102.8	120.9	7961
.1769	67.6	202.9	7962
.2953	39.7	346.6	8144
.4100	28.2	487.9	8260
.4822	23.6	585.1	8421
.5448	20.9	646.4	8380
	(B) Potassium		
1.2918	52.9	0.00	0.0
1.7200	39.8	.00	.0
	(C) Rubidium		
0.4837	309.6	0.00	0.0
.6375	233.7	.00	.0
1.0689	139.6	.00	.0
	(D) Cesium		
1.0800	215.2	0.00	0.0
3.3963	68.4	.00	.0

TABLE II

ATOMIC HEATS OF SOLUTION OF CALCIUM, BARIUM AND STRONTIUM

Sample	Moles NH_3 per atom	Observed ht. effect, cal.	Atomic ht. of soln., cal.
	(A) Calcium		
0.1907	366.0	46.47	9,764
.2470	282.0	62.36	10,116
.2779	251.0	74.77	10,780
	(B) Barium		
0.3850	621.0	30.90	11,024
.5477	435.0	50.03	12,547
.7469	319.0	77.53	14,258
.9011	262.0	93.80	14,298
1.3658	173.0	160.32	16,124
	(C) Strontium		
0.3000	507.0	59.40	17,351
.3831	397.0	78.44	17,940
.6606	248.0	125.98	18,200
.9720	155.0	214.90	19,380

Discussion

As will be noted upon examination of Figs. 2 and 3, the atomic heats of solution of lithium and the alkaline earth metals vary regularly over the range of concentrations measured, decreasing with a decrease in concentration. The high heats of solution of these metals are due, in part, to a heat of reaction to form an ammoniated metal ion. The other metals measured, potassium, rubidium and cesium, do not form solvated ions. The atomic heats of solution of lithium and calcium in liquid ammonia were calculated by Kraus from vapor pressure measurements and found to be 8698 and 10,230 cal., respectively, for their saturated solutions at 0°.[5] Our measurements of these metals were made at the boiling point of the solvent and in the concentrated region agree very well in magnitude with the calculated values at the higher temperatures.

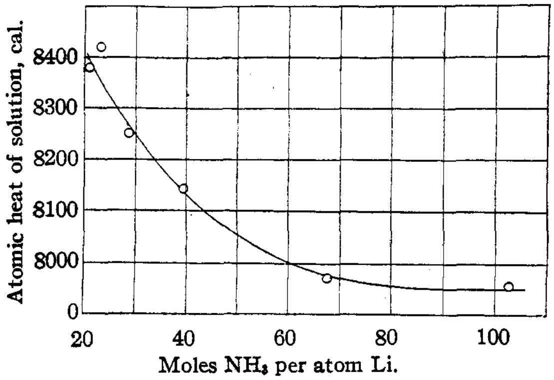

Fig. 2.—Atomic heats of solution of lithium in anhydrous liquid ammonia.

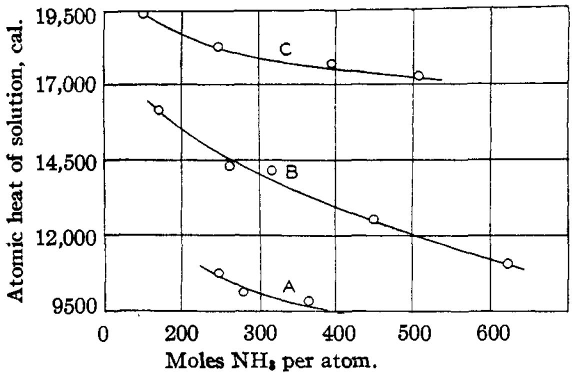

Fig. 3.—Atomic heats of solution of calcium, barium, and strontium.

In the case of the solution of metallic calcium in anhydrous liquid ammonia two phases are formed, one of which is quite dilute and one of which is quite concentrated.[5] There are no data regarding such happening in the case of the metals barium and strontium, but in all probability similar two phase systems are formed. It would seem that such a phenomenon would show as a break in the atomic heat of solution–concentration curves of these metals. Examination of these curves in Fig. 3 shows that apparently such is not the case in the region of the concentrations studied.

Summary

A method is described for the extraction of pure rubidium and cesium from their respective halides in good yields.

[5] C. A. Kraus, THIS JOURNAL, 30, 653 (1908).

The atomic heats of solution of potassium, rubidium and cesium have been measured over a fairly wide range of concentrations and found to be zero.

The atomic heats of solution of metallic lithium, calcium, barium and strontium have been measured over a range of concentrations and have been found to have a negative heat of dilution.

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The Kinetics and Mechanism of α-Aminoisobutyronitrile Formation

BY T. D. STEWART AND CHOH-HAO LI

Introduction

The α-amino nitriles are generally obtained by the reaction of equimolecular proportions of an alkali cyanide and an amine salt with an aldehyde or ketone in aqueous or aqueous alcoholic solution,[1] or by the reaction between equimolecular proportions of a cyanohydrin and an amine.[2] The main reaction is

$$R_2C(OH)CH + R_2NH \rightleftarrows R_2C(NR_2)CN + H_2O \quad (1)$$

This equation implies that the oxygen is removed from the cyanohydrin and is replaced by the amino group directly; but in view of the following argument this path is extremely unlikely.

When a cyanohydrin is placed in an alkaline medium, such as a solution of an amine, the following equilibria are rapidly established

$$R_2C(OH)CN \rightleftarrows R_2CO + HCN \quad (2)$$

$$HCN + R_2NH \rightleftarrows R_2NH_2CN \rightleftarrows R_2NH_2^+ + CN^- \quad (3)$$

The rapid appearance of cyanide ion demonstrates an apparent high reactivity of the carbon–cyanide bond in the cyanohydrin and shows the improbability of the hydroxyl group being dissociated or exchanged in alkaline solution. Ultee[3] showed that this reactivity was not a property of the cyanohydrin as such, because in acidic medium prussic acid was not formed.

The mechanism[4] of the dissociation in alkali can be expressed

$$R_2C(CN)OH + OH^- \rightleftarrows R_2C(CN)O^- + H_2O \quad (4)$$

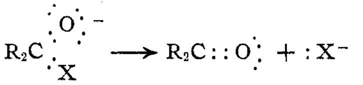
$$R_2C(CN)O^- \rightleftarrows R_2CO + CN^- \quad (5)$$

in which both reactions are rapid and reversible. Equations (4) and (5) are of particular interest inasmuch as a similar effect of alkali has been noted in other cases, namely, aldehyde bisulfite and formocholine dissociations.

$$C_6H_5CH(SO_3)OH^- \underset{}{\overset{-OH^-}{\rightleftarrows}} C_6H_5CH(SO_3)O^= \longrightarrow C_6H_5CHO + SO_3^= + H_2O \quad (6)$$

$$(CH_3)_3\overset{+}{N}CH_2OH \overset{-H^+}{\rightleftarrows} CH_3)_3\overset{+}{N}CH_2O^- \longrightarrow (CH_3)_3N + CH_2O \quad (7)$$

In each case[5] the rate of appearance of cyanide ion, sulfite ion or trimethylamine, respectively, is proportional to the hydroxide ion concentration which in turn governs the concentration of the intermediate ion. In each case the intermediate takes the form



$$R_2C\genfrac{}{}{0pt}{}{\vdots\ddot{O}\vdots^-}{\cdot X} \longrightarrow R_2C::\ddot{O}: + :X^- \quad (8)$$

in which the electron pair bonding the radical X is replaced by an unshared electron pair of the charged oxygen; the dissociation is therefore a substitution reaction and not an ionization in the ordinary sense, and as such would be a relatively rapid reaction.[6] The alkaline catalysis of sugar mutarotation as well as alkaline catalysis of diacetone alcohol dissociation[7] may be represented similarly. It is clear that in an acidic medium the concentration of the intermediate ion would be reduced and hence the rate of dissociation inhibited; in alkali neither the cyanohydrin as such nor the intermediate ion could be expected to dissociate hydroxyl or react to replace it by the amine group.

A clue as to the path by which the oxygen (Eq. 1) is removed is given by the known reactions of the α-amino alcohols and their ethers. Lapworth and his co-workers[8] have pointed out

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[1] "Organic Syntheses," John Wiley and Sons, Inc., New York, 1931, Vol. XI, p. 4.

[2] Zelinski and Stadnikoff, *Ber.*, **39**, 1722 (1906).

[3] A. J. Ultee, *Rec. trav. chim.*, **28**, 248 (1909).

[4] A. Lapworth, *J. Chem. Soc.*, **85**, 1206 (1904).

[5] (a) T. D. Stewart and L. H. Donnally, THIS JOURNAL, **54**, 2333 (1932); (b) T. D. Stewart and H. P. Kung, *ibid.*, **55**, 4813 (1933).

[6] A. R. Olson, *J. Chem. Phys.*, **1**, 418 (1933).

[7] F. H. Westheimer and H. Cohen, THIS JOURNAL, **60**, 90 (1938).

[8] (a) W. Cocker, A. Lapworth and A. Walton, *J. Chem. Soc.*, **111**, 449 (1930). (b) T. D. Stewart and W. E. Bradley, THIS JOURNAL, **54**, 4172 (1932).