

ter it has passed through the minimum is apparently due to the large concentration of HCl in the organic solvent. With the continued increase in solubility of water in the ethereal phase, this layer becomes similar to the denser phase.

While the molar distribution coefficient of HCl between the two layers, which is shown in Fig. 3, increases continuously, the equilibrium HCl concentration reaches a maximum and then decreases. This decrease is due to the enhanced solubility of ether in the aqueous phase. The location of a maximum in the equilibrium hydrochloric acid concentration of the aqueous phase suggests an explanation for the decrease in extraction efficiency of ferric chloride by isopropyl ether when the initial hydrochloric acid exceeds 8.5 molar. The plot shown in Fig. 4 is very similar in shape to a plot of the $\log (Fe)_{Et_2O}/(Fe)_{Aq}$ against the initial concentra-

tion of hydrochloric acid for equal volume extraction given by Nachtrieb and Conway.⁸ The equilibrium concentrations for initial hydrochloric acid of 9.5, 10.5 and 11.5 molar in Fig. 4 have been calculated for equal volume extraction from tie line data on the ternary diagram.

The results of this investigation are being applied in a study of the ferric chloride extraction system.

Acknowledgment.—This investigation is partially supported by the U. S. Atomic Energy Commission under Contract No. AT(30-1)-562. The authors are also indebted to Professors L. G. Bassett, W. H. Bauer and S. E. Wiberley who contributed generously of their time for consultation during the course of this work, and to Mr. J. E. Savolainen who participated in the early stages of the investigation.

TROY, NEW YORK

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BOSTON UNIVERSITY]

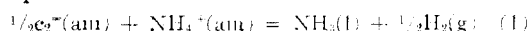
The Thermochemistry of Calcium and Calcium Iodide in Ammonia at -33° ¹

BY SUMNER P. WOLSKY, EDWARD J. ZDANUK AND LOWELL V. COULTER

RECEIVED MAY 29, 1952

For the solution reaction of calcium metal and calcium iodide in liquid ammonia, $\Delta H = -19.7$ and -62.8 kcal., respectively, at -33° . For the reaction of calcium metal with $NH_4^+(am)$, $\Delta H = -99.3$ kcal. From these thermochemical data for calcium metal, $\Delta H = -79.7$ kcal. has been calculated for the reaction: $e_2^-(am) + 2NH_4^+(am) = 2NH_3(l) + H_2(g)$. This result is in agreement with that previously obtained for the same reaction based on the thermochemistry of the alkali metals, and signifies two-electron ionization of the calcium atom in ammonia rather than one-electron ionization and the presence of Ca_2^{++} previously proposed. In ammonia, $S^{\circ}Ca^{++} = -129$ e.u. relative to $S^{\circ}H^+ = 0$. If two-electron ionization of calcium is assumed, the solvation energy difference for the gas ion pair, I^- and e^- , based on the thermochemistry of calcium and calcium iodide is 32.8 kcal. which compares favorably with 31.5 and 31.4 kcal. obtained from the thermochemistry of sodium and potassium and their iodides. The large negative ionic entropy of $Ca^{++}(am)$ and the larger heats of ammoniation of electrolytes compared with heats of hydration are qualitatively correlated with the differences in the nature of the solvents.

Moderately dilute solutions of the alkali metals in liquid ammonia react with $NH_4^+(am)$ according to the equation



with the liberation of 40.4 ± 1 kcal. per equivalent.² The constancy of this value for the alkali metal solutions has confirmed the observed similarity of the state of the electron in these solutions and, in addition, now serves as a basis for comparison of the alkaline earth metal solutions with the alkali metal solutions. This is of particular interest in the case of calcium solutions since the low magnetic susceptibility of these solutions relative to barium solutions³ has been interpreted by Yost and Russell⁴ as an indication of one-electron ionization for the solution reaction, $Ca(s) = \frac{1}{2}Ca_2^{++}(am) + \frac{1}{2}e_2^-(am)$, rather than two-electron ionization, $Ca(s) = Ca^{++}(am) + e_2^-(am)$. As a part of the objective of this research, it has been of interest to make a thermochemical distinction between the two different modes of ionization with the use of the re-

action represented by equation 1. For two-electron ionization in calcium solutions, reaction 1 should liberate 40.4 kcal. per equivalent of calcium, whereas, a considerably lower value would be anticipated for the heat of reaction of the system resulting from one-electron ionization. The direct determination of this heat of reaction has not appeared feasible because of experimental difficulties. As a consequence, we have obtained it indirectly from the heat of solution of calcium in liquid ammonia and the heat of reaction of calcium with $NH_4^+(am)$.

Comparison of the nature of calcium and alkali metal solutions may also be accomplished by a consideration of the differences of solvation energy in liquid ammonia of the gas ion pairs, $I^-(g)$ and $e^-(g)$, derived from the appropriate thermochemical data for alkali metal-iodide systems and the corresponding calcium systems. This comparison has entailed the experimental determination of the heats of solution of Ca and CaI_2 in liquid ammonia.

Experimental Procedures

The calorimetric procedure followed in this research has been described previously.² The total heat capacity of the calorimeter varied from 85 to 165 cal. per degree and reaction times varied from 5 to 70 minutes depending upon the experiment. Crystals of calcium metal of appropriate size were selected from a high purity preparation of the metal

(1) Part of this paper was presented before the Division of Physical and Inorganic Chemistry, American Chemical Society Meeting, Cleveland, Ohio, April 11, 1951.

(2) L. V. Coulter and R. H. Maybury, THIS JOURNAL, **71**, 3394 (1949); L. V. Coulter and L. Monchick, *ibid.*, **73**, 5867 (1951).

(3) S. Freed and N. Sugarman, *J. Chem. Phys.*, **11**, 354 (1943).

(4) Don M. Yost and Horace Russell, Jr., "Systematic Inorganic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1941, p. 148.

supplied by the Union Carbide and Carbon Corporation. Analysis by the oxalate method of three randomly selected samples indicated $99.8, 99.8$ and $100.2 \pm 0.2\%$ calcium. All samples were preserved in evacuated fragile ampoules following the removal of oxidized surface.

Anhydrous CaI_2 was prepared by gentle decomposition of $\text{CaI}_2 \cdot 8\text{NH}_3$ with the aid of high vacuum at temperatures below 190° . Octaammoniate containing hydrate as a probable impurity was initially precipitated by mixing liquid ammonia solutions of C.P. $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (40 g./200 ml. NH_3) and C.P. NH_4I (60 g./200 ml. NH_3) in a stoppered un-silvered dewar vessel. Purification of the ammoniate was attained by five recrystallizations which effectively removed nitrate ion as an impurity. All recrystallizations were performed in redistilled, oil-free, commercial anhydrous ammonia. Final recrystallizations were made in ammonia previously dried over sodium amide. Following the removal of the mother liquor of the final recrystallization, the ammoniate was transferred, in the presence of anhydrous ammonia gas, to a deammoniation manifold schematically represented by Fig. 1. Evacuation of the manifold was made through a stopcock "A" which, in a closed position, permitted removal of the manifold from the vacuum line and thus facilitated mechanical transfer of the anhydrous CaI_2 into the desired sample bulbs. Following proper division of the sample in this manner, the bulbs were sealed off under vacuum for analysis or heat of solution measurements.

Deammoniation of the $\text{CaI}_2 \cdot 8\text{NH}_3$ was accomplished by high vacuum pumping for three to four days during which time the temperature was gradually increased to a maximum of 190° . Analysis by standard methods for calcium and iodide on various preparations indicated a purity of $99.5 \pm 0.5\%$.

Results and Discussion

The observed heat effects for the solution of calcium and calcium iodide in liquid ammonia and the reaction of calcium with ammonium ion are summarized in Tables I, II and III. The changes in heat content per mole are tabulated in column 6. The observed change in temperature of the calorimeter for each determination and the associated heat effect are tabulated in columns 3 and 4, respectively. The heat contribution resulting in the vaporization of calorimetric solvent follows in column 5 and is calculated from the specific heat of vaporization and the amount of ammonia vaporized.

TABLE I
HEAT OF SOLUTION OF CALCIUM METAL IN LIQUID AMMONIA

G. atom of metal	Moles NH_3 /mole metal	ΔT	$q_1 = \frac{\Delta T}{\times C_p}$	$q_2 = \frac{\text{sp. ht. vap.} \times \text{g. vap.}}{\text{vap.}}$	$-\Delta H$, kcal.
This research					
0.00400	1700	+0.173	+24.9	53.0	19.5
.00406	1690	-.142	-20.8	102.2	20.0
.00408	1700	+.144	+21.4	60.3	20.0
.00397	1760	+.0311	+4.6	71.7	19.2
.00392	1765	+.0623	+9.2	68.8	19.9
.00934	615	+.0737	+9.0	184.4	20.7
.0150	267	+.535	+44.9	305.8	23.4

Measurements by Schmidt, Studer and Sottysiak⁵

G. atom of metal	Moles NH_3 /mole metal	$q_1 + q_2$	$-\Delta H$, kcal.
0.004758	366.0	46.47	9.76
.006163	282.0	62.36	10.12
.006934	251.0	74.77	10.78

In addition to the results of this research, we have included in Table I for comparison the integral heats of solution of calcium obtained by Schmidt, Studer and Sottysiak.⁵ As is to be ob-

(5) F. C. Schmidt, F. J. Studer and J. Sottysiak, *THIS JOURNAL*, **50**, 780 (1938).

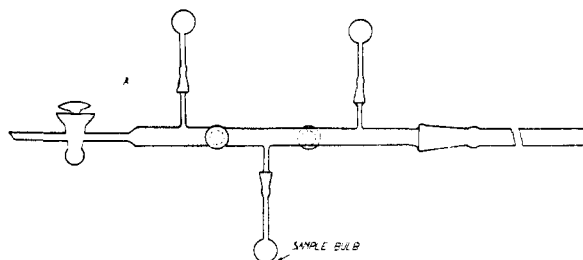
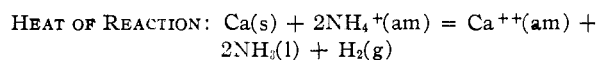


Fig. 1.

served, a large discrepancy exists between their results and the values obtained in this research. In view of the previous agreement obtained on the heat of solution of NH_4Br ,² a substance relatively easy to handle and purify, we are inclined to account for the present difference on the basis of impurities in the calcium employed by Schmidt and co-workers. This appears to be the most plausible explanation in view of our experience with ordinary commercial calcium preparations which have a tendency to be low in free metal.

TABLE II



G. atom of metal	Moles NH_3 /mole metal or salt	ΔT	$q_1 = \frac{\Delta T}{\times C_p}$	$q_2 = \frac{\text{sp. ht. vap.} \times \text{g. vap.}}{\text{vap.}}$	$-\Delta H$, kcal.
This research					
0.000866	7870	-0.391	-56.7	143.2	100.0
.000948	6970	-.548	-76.6	171.4	100.0
.000893	7990	-.366	-56.0	143.0	97.4
.000856	8580	-.352	-55.5	140.9	99.8
.000679	11200	-.472	-75.6	140.6	95.7
.000739	10250	-.468	-76.4	152.4	102.9
Mean					99.3 ± 3

TABLE III

HEAT OF SOLUTION OF CaI_2

G. atom of metal	Moles NH_3 /mole metal	ΔT	$q_1 = \frac{\Delta T}{\times C_p}$	$q_2 = \frac{\text{sp. ht. vap.} \times \text{g. vap.}}{\text{vap.}}$	$-\Delta H$, kcal.
0.00841	770	+0.190	26.5	489.9	61.4
.00605	1170	+.273	40.6	359.0	66.5
.00465	1520	+.083	12.2	279.9	62.8
.00922	810	-.390	-62.0	653.6	64.2
.00340	2200	+.336	53.7	176.9	67.5
.00607	1230	+.173	27.4	373.8	66.2
.00313	2380	+.187	29.5	167.2	62.8
.00179	4250	+.126	20.5	93.7	63.5
.00160	4680	+.0310	4.5	96.2	63.3
.00215	3310	+.104	15.7	118.0	62.2
.00159	4780	+.057	9.4	90.5	62.8
.000653	10980	+.066	9.9	30.7	62.3
	∞				62.8 ± 0.7

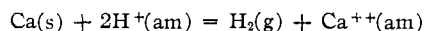
It is to be noted that for the concentration range investigated the heat of solution is dependent on the concentration. Extension of the measurements to higher dilutions was not attempted since the increasing error of the measurements for small heat effects reduces the significance of the results. As a consequence, we have averaged the values in the vicinity of 1700 moles NH_3/Ca and have obtained $\Delta H = -19.7$ kcal., presumably, for the reaction: $\text{Ca(s)} = \text{Ca}^{++}(\text{am}) + e_2^-(\text{am})$. Subtraction of this reaction and the corresponding ΔH from the reaction: $\text{Ca(s)} + 2\text{NH}_4^+(\text{am}) = \text{Ca}^{++}(\text{am}) +$

$\text{H}_2(\text{g}) + 2 \text{NH}_3(\text{l})$, for which $\Delta H = -99.3$ kcal. (see Table II), gives for the reaction: $\text{e}_2^-(\text{am}) + 2 \text{NH}_4^+(\text{am}) = 2 \text{NH}_3(\text{l}) + \text{H}_2(\text{g})$, $\Delta H = -79.6 \pm 3$ kcal. This is to be compared with the corresponding heat of reaction of the alkali metal solutions for which $\Delta H = -80.8$ kcal. per two equivalents has been found.¹ In view of this agreement, we are inclined to regard the state of the electron in calcium metal solutions to be the same as in alkali metal solutions of comparable normality and conclude that two-electron ionization of calcium in liquid ammonia appears to be the case. It then follows that the explanation proposed by Freed and Sugarman,³ rather than the one-electron ionization of calcium as proposed by Yost and Russell,⁴ is the more appropriate for explaining the low magnetic susceptibility of calcium solutions.

The representation of the electron in a paired state in equation 1 for the concentration of 1700 moles NH_3/Ca is somewhat arbitrary and in error since the indications are that some unpairing³ occurs at this concentration. However, in view of the fact that the heat effect associated with the unpairing at this concentration is probably less than 1 kcal.,⁶ we have tentatively written the electron in the paired state and regard the heat of reaction to be for this form of the electron species. Comparison of the ΔH for equation 1 obtained in this research with the value previously reported² for the alkali metals is justified in view of comparable normalities.

The relative partial molal ionic entropy of Ca^{++} in liquid ammonia may now be calculated from the observed ΔH for the reaction: $\text{Ca}(\text{s}) + 2 \text{NH}_4^+(\text{am}) = \text{Ca}^{++}(\text{am}) + 2 \text{NH}_3(\text{l}) + \text{H}_2(\text{g})$, and the corresponding free energy change. From the cell potential data reported by Pleskov⁷ we have calculated $E_{\text{Ca}}^0 = 1.63$ volts relative to $E_{\text{H}_2}^0 = 0$ in ammonia at -50° for NH_4^+ at unit activity. With the aid of the observed heat of reaction at -33° and the free energy change at -50° , we find, approximately, $E_{\text{Ca}}^0 = 1.59$ volts at -33° and $\Delta F_{240^\circ\text{K}}^0 = -73.4$ kcal. Employing the average value of Table II, $\Delta H = -99.3$ kcal., for the standard heat of reaction $\Delta H_{240^\circ\text{K}}^0$ and -73.4 kcal. for the standard free energy change, we finally obtain $\Delta S_{240^\circ\text{K}}^0 = -108$ e.u. and $S_{\text{Ca}^{++}}^0 = -171$ e.u. relative to $S_{\text{NH}_4^+}^0 = 0$ at 240°K . Although this value must be regarded as highly tentative in view of the approximations made in obtaining the standard calcium electrode potential, attention should be called to its large negative value relative to the entropy of the alkali cations,² a situation not encountered to this extent in aqueous systems. This observation is, nevertheless, in agreement with the relatively large energy of ammoniation of Ca^{++} which also signifies a greater net ordering effect in the ammoniation of ions than is observed to be the case for hydration.

The relatively large negative value for the entropy of Ca^{++} is also apparent from a comparison with H^+ in ammonia. As in aqueous systems, we may write

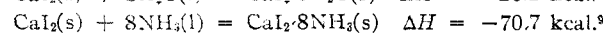
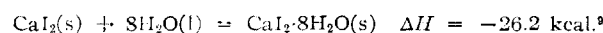


for which $\Delta H_{240^\circ\text{K}}^0 = -99.3$ kcal., $\Delta F_{240^\circ\text{K}}^0 = -73.4$ kcal., and $\Delta S_{240^\circ\text{K}}^0 = -108$ kcal. Assuming $S_{\text{H}^+}^0(\text{am}) = 0$, we then find $S_{\text{Ca}^{++}}^0 = -129$ which is to be compared with $S_{\text{Ca}^{++}}^0 = -13$ relative to $S_{\text{H}^+}^0(\text{aq}) = 0$ for aqueous solutions at 298°K . This large difference in the entropy of Ca^{++} in the two solvents is probably accounted for, in part, by a difference in the absolute values of the $S_{\text{H}^+}^0$ in the two solvents as well as by the temperature difference. Nevertheless, it does appear that the entropy of Ca^{++} is still much more negative in ammonia than in water, even if the absolute entropy of $\text{H}^+(\text{am})$ is considerably less than zero.

On the basis of the results presented in Table III, we have obtained -62.8 ± 0.7 kcal., for the ΔH of solution of CaI_2 at infinite dilution. We have neglected any heat of dilution to infinite dilution and have averaged the heat effects for the five highest dilutions which cover the concentration range 3300 to 11,000 moles NH_3/CaI_2 with essentially no indication of a heat of dilution. Although the average ΔH of solution at dilutions less than 3000 is about 3% greater in comparison with the more dilute range, a dependence on concentration is uncertain in view of the greater experimental error for these measurements resulting from a more vigorous solution reaction.

It is instructive to compare the heats of solution of electrolytes in ammonia and water from the standpoint of the solvation process. Generally speaking, the ΔH of solution of mono-monovalent electrolytes is 3 to 12 kcal. more negative in ammonia than in water. A more striking effect prevails with CaI_2 which liberates 28 kcal. upon solution in water but in ammonia releases 62.8 kcal. Since the sum of ion-dipole interactions and energy of Born charging have been estimated to be essentially the same or less in liquid ammonia than in aqueous systems, it becomes apparent that greater energy is absorbed in the hydration process in the depolymerization of solvent clusters than is required in ammonia. This is, of course, to be expected since the hydrogen bonds are much weaker in ammonia than in water.

At the suggestion of Professor K. S. Pitzer,⁸ further evidence of this greater solvation energy by ammonia has been obtained from a comparison of the heats of solvation of anhydrous CaI_2 in the solid state for the reactions



Since each of these reactions comprises the important step that distinguishes hydration from ammoniation in the total solution reaction, it is to be expected that a comparable difference will be found for the heats of these reactions which is seen to be the case. In making this comparison, it has been assumed that the crystal energies (except for the $\text{Ca}^{++}-\text{NH}_3$ and $\text{Ca}^{++}-\text{H}_2\text{O}$ ion-dipole interaction) of the solvates are essentially the same.

(8) K. S. Pitzer, private communication.

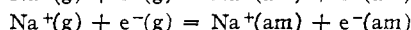
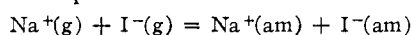
(9) F. R. Bichowsky and F. D. Rossini, "The Thermochemistry of the Chemical Substances," Reinhold Publishing Corp., New York, N. Y., 1936.

(6) G. Candela, unpublished results.

(7) V. A. Pleskov, *Acta Physicochim. U.R.S.S.*, **6**, 1 (1937).

Further understanding of the greater solvation energy of ions in ammonia has been obtained from an approximate calculation of the solvation energy of gas ion pairs in this solvent. Following the general procedure employed by Eley and Evans¹⁰ and Eley and Pepper,¹¹ it has been possible to account for the ammoniation energy of the alkali halide and calcium iodide gas ion pairs from electrostatic considerations alone, thereby removing any requirements of partial covalent bond character as part of the interaction.

In comparing the nature of the solvated electron with other large ions in ammonia, Ogg¹² has called attention to the small solvation energy of the electron by a comparison of the heats of the reactions



from which the solvation energy difference may be obtained for the expression

$$\text{I}^-(\text{g}) - \text{e}^-(\text{g}) = \text{I}^-(\text{am}) - \text{e}^-(\text{am})$$

From the appropriate thermochemical data^{2,5,8,13} for each alkali metal and its iodide, and the corresponding calcium systems, we have calculated the differences in solvation energy of the gas ion pair and have presented the results in Table IV. Strictly

(10) D. D. Eley and M. G. Evans, *Trans. Faraday Soc.*, **34**, 1093 (1938).

(11) D. D. Eley and D. C. Pepper, *ibid.*, **37**, 581 (1941).

(12) R. A. Ogg, Jr., O.N.R. Report, "Electronic Processes in Liquid Dielectric Media. The Constitution of Metal-Ammonia Solutions," Stanford University, California, 1947.

(13) C. A. Kraus and F. C. Schmidt, *THIS JOURNAL*, **56**, 2298 (1934); C. A. Kraus and J. A. Ridderhof, *ibid.*, **56**, 79 (1934); F. C. Schmidt, J. Sottyslak and H. D. Kluge, *ibid.*, **58**, 2509 (1936).

speaking, the energy of unpairing of the solvated electron pair is required to make the calculated values correct and meaningful in an absolute sense. However, since it is an additive constant for each case, it may be omitted for use of the results in a relative manner. On the assumption of two-electron ionization of calcium in ammonia, we observe that good agreement is exhibited among sodium, potassium and calcium systems for the solvation energy differences of the iodide ion and the electron which confirms our earlier conclusion. The low value obtained for lithium solutions probably arises from an uncertainty in the thermochemistry of LiI since previous studies² have shown that lithium metal solutions are entirely comparable with the other alkali metal solutions.

TABLE IV

DIFFERENCE IN AMMONIATION ENERGY OF $\text{I}^-(\text{g})$ AND $\text{e}^-(\text{g})$

Systems	$-\Delta H$, kcal./equivalent
LiI and Li	20.8
NaI and Na	31.5
KI and K	31.4
CaI ₂ and Ca	32.8

Acknowledgment.—We are indebted to the Research Corporation for a Frederick Cottrell grant-in-aid of research for partial support of this research. We are also indebted to the Electro Metallurgical Division of the Union Carbide and Carbon Corporation for the sample of high purity calcium employed in the research.

BOSTON, MASS.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, AND RADIATION LABORATORY, UNIVERSITY OF CALIFORNIA, BERKELEY]

The Entropy of Ionization of Protonic Solvents

BY WILLIAM L. JOLLY

RECEIVED JUNE 17, 1952

The heat of ionization of anhydrous acetic acid has been found to be $\Delta H^\circ = 5700$ cal./mole. Combining this heat with the known ionization constant, one calculates an entropy of ionization, $\Delta S^\circ = -38.6$ cal./deg. mole. This entropy of ionization, like the corresponding values for liquid ammonia, methanol and ethanol, is much more negative than the entropy of ionization of water.

Studies of ionic entropies in methanol¹ and ammonia² have led to the suggestion that ionic entropies in water are abnormally high. The entropies of ionization of water, ammonia, methanol and ethanol are in agreement with this hypothesis. Table I gives the thermodynamic constants for the self-ionization of these solvents. It is apparent that the entropy of ionization of water is much more positive than that for the other three solvents. An explanation may be given in terms of entropies of solvation and the high degree of hydrogen bonding in water. When an ion enters water, more disorder is created than when it enters another, less hydrogen bonded, solvent.

The present work was carried out to determine

(1) W. M. Latimer and C. M. Slansky, *THIS JOURNAL*, **62**, 2019 (1940).

(2) W. L. Jolly, *Chem. Revs.*, **50**, 351 (1952).

whether acetic acid, an acidic solvent, parallels other non-aqueous solvents by having an entropy of ionization much more negative than that of water.

The free energy of ionization of anhydrous acetic acid has been measured by various investigators, and so in order to determine the entropy of ionization, it was necessary to merely determine the heat of ionization. This was accomplished by indirectly measuring the heat of neutralization of a strong acid (perchloric acid) and a strong base (sodium acetate) in anhydrous acetic acid. Two heats were determined, corresponding to the reactions

