tion) $aT^{1/2}$ is about $2 \times 10^{11}$ in these units and low values of this magnitude are found for other similar reactions if the assumption is made that the association reaction for $CH_3$ radicals is "normal." If the latter is low the constant for $CH_4$ formation will be reduced even further. For reaction (2) (the rate determining step for $C_2H_6$ formation from $CH_3$ and $Hg(CH_3)_2$), $aT^{1/2}$ is about $7 \times 10^6$, a very low value compared to most other bimolecular reactions.

## Summary

1. The rates of formation of $C_2H_6$ and of $CH_4$ during irradiation of $Hg(CH_3)_2$ have been studied as functions of intensity, pressure, and temperature.
2. At temperatures below 250° $CH_4$ seems to be formed solely by the reaction $CH_3 + Hg(CH_3)_2 = CH_4 + CH_2HgCH_3$.
3. Ethane must be formed by at least two processes, one of which is the combination of $CH_3$ radicals and the other of which is a reaction of $CH_3$ radicals with $Hg(CH_3)_2$ which apparently proceeds through an unstable intermediate addition complex.
4. The pre-exponential factor in the rate constant for $CH_4$ formation is very much smaller than for ethane formation by radical combination.
5. The activation energy for reaction of $CH_3$ radicals with $Hg(CH_3)_2$ to form $C_2H_6$ is very low, about the same as for $C_2H_6$ formation by radical combination, but the pre-exponential factor is so low that the rate is small and a chain reaction is of relatively minor importance.
6. A mechanism consistent with the facts has been proposed.

ROCHESTER, NEW YORK RECEIVED MAY 6, 1949

---

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BOSTON UNIVERSITY]

# The Heats of Reaction of Lithium, Sodium, Potassium and Cesium with Ammonium Ion in Liquid Ammonia at −33°

BY LOWELL V. COULTER AND ROBERT H. MAYBURY

The thermochemistry of oxidation–reduction reactions involving the alkali metals in liquid ammonia is of twofold interest. From a long range view the heats of reaction of the metals with ammonium ion in liquid ammonia, for example

$$M + NH_4^+ = M^+ + NH_3 + {}^1/_2H_2 \qquad (1)$$

may provide basic thermal values which when combined with corresponding free energy changes permit evaluation of relative partial molal ionic entropies in this solvent. In addition to the use of ionic entropies in the calculation of oxidation–reduction potentials not measurable directly, these ionic properties also permit evaluation of relative entropies of solvation of ions in liquid ammonia in a manner developed by Latimer[1] for water solutions. The existing scarcity of accurate free energy data for reactions occurring in liquid ammonia imposes temporary restrictions on the development of a set of reliable ionic entropies for this medium. However, the presumably simpler nature of liquid ammonia as compared with water arising from weaker hydrogen bonding would appear to simplify somewhat the theoretical treatment of the solvation process in this medium and therefore justify the exploration of this solvent.

Of immediate interest is the utilization of thermal data for the above reaction for the comparison of the nature of liquid ammonia solutions of the ammonia soluble metals. Prevailing concepts of these systems, while differing with regard to the equilibria involved in the more concentrated solutions and though incomplete as to the exact nature of the ammoniated electron, agree that the dilute solutions consist of solvated metal ions and single electrons resulting from essentially complete ionization in the dilute range of concentration. An exact similarity for these solutions has been observed by Gibson and Argo,[2] who have reported identical absorption spectra for dilute solutions of lithium, sodium, potassium and cesium. It is to be expected that these systems would likewise possess identical thermochemical properties for reactions involving the solvated electron of these solutions with a common oxidizing agent, as for example

$$e^-_{(am)} + NH_4^+{}_{(am)} = {}^1/_2H_{2(g)} + NH_{3(l)}$$

Direct measurement of the thermal effect associated with this reaction has not seemed experimentally feasible. It may be obtained indirectly, however, as the difference between the heat of solution of the metal in pure liquid ammonia and the heat of reaction of the metal with ammonium ion in liquid ammonia. The latter heat of reaction for solid lithium, sodium, potassium and cesium determined in this research combined with the literature values for the heats of solution of the metals has made possible the evaluation of the heat of this reaction. For dilute solutions of each of these metals we have obtained heats of reaction ranging from 39.7 kcal. for potassium to 41.6 kcal. for cesium with a mean of 40.4 kcal. This we regard as indicative of a common reaction for these solutions involving the solvated electron which energetically appears identical within experimental error in all cases.

---

[1] Latimer, *Chem. Rev.*, **18**, 349 (1936).

[2] Gibson and Argo, THIS JOURNAL, **40**, 1327 (1918).

## Experimental

The calorimeter employed was essentially of the type used by Kraus and Schmidt[3] but differed in size and method of collecting the gaseous products of the reaction, hydrogen and vaporized ammonia. The calorimeter I of Fig. 1 consisted of a Pyrex vacuum-jacketed test-tube capped with a removable top G by means of a ground glass joint. The top was connected through F to a manifold and served as a point of suspension for the thermocouple well E, sample crushing rod K and the reciprocating stirrer B-J suspended by the spring A. Intermittent energizing of the solenoid C provided a stirring rate of 60 strokes per minute.

Sample bulbs of the metals were held near the bottom of the calorimeter in a platinum stirrup L located directly below the sample crushing rod K to which the holder was loosely attached. The crushing rod extended beyond the calorimeter top through a gas tight seal at D. A fine mesh platinum gauze enclosed the sample bulbs and served as a bubble trap whereby continuous contact of metal and solution was prevented and a controlled reaction rate obtained. The calorimeter was thermostated by boiling liquid ammonia contained in the closed Dewar vessel M of Fig. 1.

The gas collecting system consisted of a six-liter flask P thermostated at 25.0 ± 0.1°, and a manometer Q which were connected to the manifold through a small metal needle valve O. Withdrawal of gas from the calorimeter into the evacuated collecting system was made by manual adjustment of the valve during the reaction period. The entire gas collecting system had a total volume of 6715 ml. The connecting lines which were not thermostated amounted to about 1% of the total volume.

For each thermochemical measurement a weighed amount of ammonia, usually between 110 and 120 g., was introduced at N and condensed in the calorimeter to a liquid depth of about 14 cm. as indicated by the dotted line in Fig. 1. Temperature measurements were made with a copper-constantan thermocouple, calibrated at the sublimation point of carbon dioxide and the freezing point of mercury. Potentials were measured with a Type K-2 Leeds and Northrup potentiometer with a matched galvanometer having a sensitivity of 20 mm. per microvolt for a scale at a distance of 15 ft. from the galvanometer.

Commercial anhydrous liquid ammonia of 99.2% purity, according to the supplier, was used for the thermostating liquid. Stock ammonia for the calorimeter reaction medium was prepared by distillation of the ammonia from the large commercial cylinders into a small cylinder containing sodium metal as a drying agent.

The metals employed in the research were of the following grades as indicated by the supplier and were used without further purification except for cesium which underwent a distillation in the process of sample preparation: lithium, Lithaloy, low sodium quality (typical analysis as furnished by the supplier, N, 0.15; Si, 0.05; Fe, 0.02; Al, 0.01; Ca, 0.10; Na, 0.15; K, 0.05%); sodium, Baker, Analytical Reagent; potassium, Baker, C. P.; cesium, Fairmount Chemical Co.; C. P. Baker Analytical Reagent ammonium chloride and bromide dried at 100° were the oxidizing agents in the reactions. Samples of oxide-free sodium and potassium for the reaction were prepared in small thin-walled glass bulbs in the manner described by Kraus.[4] The cesium samples were prepared by a high vacuum distillation of the metal from the shipping ampoules into the weighed sample bulbs. Lithium samples with clean surfaces were prepared by cutting cylinders of the metal from the ingots under oil followed by removal of the oil with dried benzene rinses.

**Procedure.**—The net measured heat effect associated with reaction (1) was a composite of heat absorbed by the vaporization of ammonia during the reaction and the thermal change resulting from the temperature change of the calorimeter and contents. The experimental determination of the first of these quantities involved the withdrawal of gas during the reaction period from the calorimeter manifold into the calibrated gas collecting system through the manually controlled needle valve at such a rate as to maintain a constant pressure in the calorimeter. The second of these quantities was obtained from the measured temperature change of the calorimeter, as determined by the thermocouple measurements, and the total heat capacity of the calorimeter and contents.

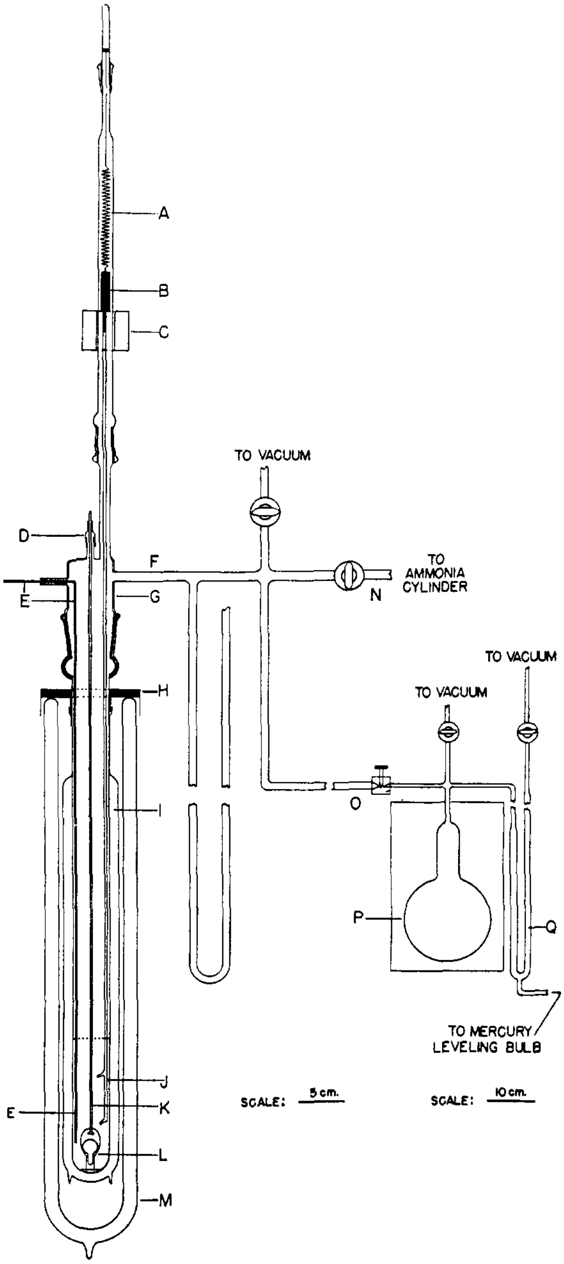

Fig. 1.

Following the assembly of the calorimeter containing the reactants and liquid ammonia the temperature of the calorimeter was allowed to approach a steady state value.

When a constant temperature or temperature drift was attained, usually less than a thousandth of a degree per minute the sample bulb was fractured by a downward thrust of the crushing rod which initiated the reaction. During the reaction period withdrawal of vaporized ammonia and product hydrogen from the manifold into the

---

[3] Kraus and Schmidt, This Journal, 56, 2297 (1934).

[4] Kraus, *ibid.*, 30, 1197 (1908).

TABLE I

SUMMARY OF HEAT EFFECTS

| Expt. | G. atoms of metal or moles of salt | Moles of $NH_4$ salt in soln. | $-\Delta T$, cor. | $C$, (total ht. cap.) | $q_1 = C \times \Delta T$ | G. of $NH_3$ vaporized | $q_2$ = Sp. ht. vap. × G. vap. | Net heat $q_1 + q_2$ | Reacn. time, min. | $-\Delta H$ kcal. per g. atom |
|---|---|---|---|---|---|---|---|---|---|---|
| | Li and $NH_4Br$ | | | | | | | | | |
| F | 0.00240 | 0.00257 | 0.561 | 140.1 | − 78.6 | 0.6070 | 199 | 120 | 5 | 50.3 |
| E | .00248 | .00248 | .361 | 140.0 | − 50.5 | 0.5406 | 177 | 126 | 2 | 51.1 |
| G | .00463 | .00528 | .995 | 139.7 | −139 | 1.133 | 371 | 232 | 5 | 50.3 |
| C | .00615 | .00640 | 1.01 | 136.8 | −138 | 1.381 | 452 | 314 | 1.5 | 51.2 |
| 15 | .01326 | .0227 | 1.083 | 131.8 | −142.7 | 2.450 | 799.3 | 656.6 | 8 | 49.7 |
| 16 | .01447 | .0227 | 1.123 | 140.5 | −157.8 | 2.695 | 882.7 | 724.9 | 7 | 50.3 |
| | Na and $NH_4Cl$ | | | | | | | | | |
| 3 | .004961 | .0283 | 0.525 | 149.6 | − 78.5 | 0.8238 | 269.2 | 190.7 | 1.5 | 38.4 |
| 4 | .00958 | .0115 | 1.316 | 148.6 | −195.6 | 1.748 | 572.4 | 376.8 | 24 | 39.3 |
| 5 | .01050 | .0115 | 1.418 | 143.7 | −203.8 | 1.865 | 612.3 | 408.5 | 19 | 38.8 |
| 2 | .01317 | .0283 | 1.433 | 150.3 | −215.4 | 2.227 | 728.1 | 512.7 | 30 | 38.9 |
| 6 | .02220 | .0254 | 1.474 | 142.9 | −210.6 | 3.242 | 1061.8 | 851.2 | 13 | 38.3 |
| | Na and $NH_4Br$ | | | | | | | | | |
| 9 | .01718 | .0227 | 1.450 | 145.2 | −210.5 | 2.665 | 871.8 | 661.3 | 10 | 38.5 |
| 8 | .02072 | .0227 | 1.391 | 146.4 | −203.6 | 3.059 | 1001.7 | 798.1 | 6.5 | 38.5 |
| | K and $NH_4Br$ | | | | | | | | | |
| 10 | .01053 | .0227 | 1.218 | 146.6 | −178.6 | 1.829 | 598.6 | 420.0 | 9 | 39.9 |
| 11 | .01209 | .0227 | 1.278 | 146.6 | −187.4 | 2.038 | 666.9 | 477.7 | 8.5 | 39.6 |
| 12 | .01542 | .0227 | 1.331 | 146.4 | −194.9 | 2.461 | 805.4 | 610.5 | 9.5 | 39.6 |
| | Cs and $NH_4Br$ | | | | | | | | | |
| H | .005843 | .00641 | 1.13 | 137.6 | −156 | 1.221 | 400 | 244 | 18 | 41.8 |
| I | .008911 | .00986 | 1.17 | 139.3 | −163 | 1.626 | 531 | 368 | 28 | 41.3 |
| | Li | | | | | | | | | |
| J | .0718 | .0000 | −0.089 | 138.8 | 12.4 | 2.064 | 673.7 | 686.1 | 6 | 9.55 |
| | $NH_4Br$ | | | | | | | | | |
| K | .04380 | .0000 | −0.25 | 137.0 | 34.0 | 1.172 | 382 | 416 | 10 | 9.50 |

gas collecting system was accompanied by approximate temperature readings of the calorimeter in order to establish the temperature–time pattern from which the graphically determined mean temperature was calculated. During the post reaction period regular temperature measurements were again recorded for a period of fifteen to thirty minutes during which time a steady temperature drift was apparent. The corrected temperature change taking into account radiation heat gain was calculated from the temperature patterns so obtained in the usual manner for this type of calorimeter.[5] Although the reactions studied were exothermic, a temperature lowering of the calorimeter always occurred because of the release of gaseous hydrogen within the liquid. The mean calorimeter temperature was approximately −33°.

From the known volume, temperature and pressure of the gas collected in the gas collecting system the weight of ammonia vaporized was calculated by means of Berthelot's equation of state and the critical constants for ammonia.[6] The vaporization heat effect was determined from the net amount of ammonia vaporized and the specific heat of vaporization of ammonia[7] at the mean calorimeter temperature. Pressures were determined by a mercury manometer read by a cathetometer to 0.05 mm. Correction was made for the hydrogen gas liberated by the reaction and collected along with the ammonia in the manifold or gas collecting system on the assumption that the hydrogen gas behaved ideally. A correction was also applied to the weight of ammonia vaporized in those experiments having a net pressure change in the calorimeter system.

The heat capacity of the calorimeter was determined in a fashion similar to a heat measurement except that an electric heater was substituted for a sample of metal. To reproduce the temperature pattern as nearly as possible, hydrogen gas was measured into I through a side arm not shown in Fig. 1 and allowed to bubble through the solvent ammonia in the calorimeter simultaneously with the introduction of measured quantities of electrical energy. The dependence of the calorimeter heat capacity on depth was determined electrically at 25° with water in the calorimeter. For a depth of 15 cm. the heat capacity of the calorimeter was 21 cal. per degree at −33°.

Specific heats for liquid ammonia and the alkali metals were taken from the work of Overstreet and Giauque[8] and the compilation by Kelley.[9] A specific heat of 0.2 cal./g. was assumed for Pyrex glass in evaluating the small contributions of sample containers and glass rod to the total heat capacity of the calorimeter.

The heat effect associated with the crushing of an evacuated sample bulb containing no sample was determined in a manner identical with the reaction heat measurements. No pressure or temperature change (±0.01°) was found associated with the process.

## Discussion

The observed heat effects for each of the thermochemical measurements are summarized in Table I. The total heat capacity and corresponding corrected temperature change of the calorime-

---

(5) W. P. White, "The Modern Calorimeter," Chemical Catalog Co. (Reinhold Publishing Corp.), New York, N. Y., 1929, pp. 40-42.

(6) "International Critical Tables," McGraw–Hill Book Co., Inc., New York, N. Y., Vol. III, 1928, p. 234.

(7) Osborne and Van Dusen, *Bur. of Standards, Bull.* **14**, 439 (1917).

(8) Overstreet and Giauque, THIS JOURNAL, **59**, 254 (1937).

(9) Kelley, *Bur. of Mines, Bull.*, **434** (1940).

ter resulting from the reaction are tabulated in columns 4 and 5. The thermal effect, $q_1$, associated with the temperature change follows in column 6. The vaporization effect, $q_2$, listed in column 8 has been calculated from the grams of ammonia vaporized, tabulated in column 7 and the specific heat of vaporization of ammonia at the mean reaction temperature. The total net heat effect per sample and the change in heat content per gram atom for eq. (1) appear in columns 9 and 11, respectively. The values for the latter have been corrected only in the case of lithium for an effective 0.5% impurity.

Comparison of the heats of reaction fail to reveal any significant dependence of the reaction heat on concentration in the range investigated. In the case of lithium the mean of the values for experiments F and E is almost identical with the mean of G and C in which the concentrations were more than doubled. A further increase in concentration does appear, however, to give a slightly decreased reaction heat as evidenced by the mean of experiments 15 and 16 which is about 1.5% less. An analogous trend is to be observed for sodium. Experiment 6, for example, has a heat of reaction about 2% smaller than experiments 4 and 5 in which the dilution was greater. However, in view of an experimental error of at least 1% which must be assigned these values, we are inclined at the present to regard the dilution heat effects to be within the final experimental error to be assigned these measurements. By analogy with similar aqueous systems it is to be noted that dilution heat effects arising from differences in relative heat contents at these concentrations, approximately 400 moles of solvent per mole of solute, are considerably less than 1% of the heats of reaction measured in this research. We shall, consequently, employ these values at this time as the heats of reaction for infinite dilution. On this assumption the heats of reaction for each metal have been averaged and summarized in column 2 of Table II.

TABLE II

| Reactants | $\Delta H_1$, kcal. per g. atom | $\Delta H_2$, kcal. per g. atom | $\Delta H_3$, kcal. per equiv. |
|---|---|---|---|
| Li and $NH_4Br$-1 | −50.5 | (−8.0)[a] | (−42.5) |
| Li and $NH_4Br$-2 | −50.5 | −9.6[b] | −40.9 |
| Na and $NH_4Br$ | −38.5 | +1.40[a] | −39.9 |
| Na and $NH_4Cl$ | −38.8 | +1.40[a] | −40.2 |
| K and $NH_4Br$ | −39.7 | 0[c] | −39.7 |
| Cs and $NH_4Br$ | −41.6 | 0[c] | −41.6 |

[a] Kraus and Schmidt, THIS JOURNAL, 56, 2298 (1934). [b] This research. [c] Schmidt, Studer and Sottysiak, *ibid.*, 60, 2780 (1938).

The heats of solution of the alkali metals in pure liquid ammonia at low concentrations have been determined by Kraus and Schmidt,[10] and Schmidt, Studer and Sottysiak[11] at −33° and are tabulated for convenience in column 3 of Table II as $\Delta H_2$ values. Subtraction of the solution reaction

$$M_{(s)} = M^+_{(am)} + e^-_{(am)} \quad (2)$$

and the associated heat of solution, $\Delta H_2$, from our measured heats of reaction, $\Delta H_1$, has given for each metal solution the molar heat effect, $\Delta H_3$, for the common reaction

$$e^-_{(am)} + NH_4^+{}_{(am)} = NH_{3(l)} + {}^1/_2H_{2(g)} \quad (3)$$

These values are tabulated in the last column of Table II.

It has been assumed in writing the foregoing equations that essentially complete dissociation of the metals and electrolytes involved occurs in liquid ammonia. That such may not be the case with electrolytes is indicated by their conductance in liquid ammonia. Gur'yanova and Pleskov[12] have found the Debye–Onsager theory inadequate for these systems and have accounted for conductance properties with some success on the basis of ion pairs. However, as is to be seen from a comparison of the reaction heats of sodium with the two ammono acids, ammonium chloride and ammonium bromide, appreciable differences in ionic association leading to energy effects are not revealed in the concentration range investigated. This is also evident from the apparent independence of the heats of reaction on concentration in general.

Calculation of $\Delta H_3$ for the lithium solution based on the heat of solution reported by Kraus and Schmidt,[10] and Schmidt and co-workers,[11] led to the value −42.5 kcal. designated as lithium–ammonium bromide-1 in Table II, differing by about 6% from the mean obtained for sodium and potassium. Since this appeared to exceed a reasonable experimental error of 1 to 2% on the basis of a similarity for all alkali metal solutions we redetermined the heat of solution of lithium in pure liquid ammonia and obtained a heat of solution of 9.55 kcal. (see expt. J of Table I) which when combined with $\Delta H_2$ gave for $\Delta H_3$ −40.9 kcal. in better agreement with the values for sodium and potassium solutions. Further measurements in connection with other work now in progress substantiate this observation. We have not been able to account for this discrepancy in the heat of solution of lithium in a satisfactory manner.

The possibility that a heat of amide formation was contributing to our heat of solution does not appear likely in view of the observed stability of the solution. The nature of the temperature–time pattern for the heat of solution of the metal in comparison with other reactions likewise gave no indication of a significant side reaction.

Since our disagreement with previous workers on the heat of solution of lithium could be accounted for on the basis of instrumental and procedural differences, we remeasured the heat of solution of ammonium bromide which has also

---

[10] Kraus and Schmidt, THIS JOURNAL, **56**, 2298 (1934).

[11] Schmidt, Studer and Sottysiak, *ibid.*, **60**, 2780 (1938).

[12] Gur'yanova and Pleskov, *J. Phys. Chem.* (*U. S. S. R.*), **8**, 345 (1936).

been studied by Schmidt and co-workers[13] in the same calorimeter employed for the lithium measurements. We have obtained 9.50 kcal. for the exothermic heat of solution of ammonium bromide at a concentration of 147 moles of ammonia per mole of ammonium bromide. This value is 2.5% lower than the interpolated value of 9.76 obtained from a large scale plot of values obtained by Schmidt. Since these two values are essentially in agreement on the basis of a 1% error for each value, it does not appear that the difference for lithium amounting to about 20% can be ascribed to instrumental differences. It is our intention, however, to redetermine the heat of solution of this metal along with others in a larger calorimeter now under construction which will afford an opportunity to examine these heat effects at much lower concentrations and at the same time eliminate any radiation effect on the solution reaction which might conceivable be involved with the partially jacketed calorimeters employed so far in liquid ammonia studies.

The slightly higher values obtained for $\Delta H_3$ of the cesium solution, $-41.5$ kcal., which exceeds the mean for lithium, sodium and potassium, $-40.2$ kcal., by 3% may be indicative of some difference between this solution and the other alkali metals. However, in view of the fact that a few tenths of a per cent. impurity of one of the lighter alkali metals or calcium can account for this observed deviation, it does not appear appropriate to assign any uniqueness to the dilute ammonia solutions to cesium at this time.

In general, then, it appears that all of the dilute alkali metal solutions investigated in this research are energetically identical within about 1 kcal. Weighting all values equally we obtain for the reaction represented by eq. (3) at $-33°$: $\Delta H = -40.4 \pm 1$ kcal.

This heat of reaction will now furnish a basis for the investigation of the nature of solutions of the alkaline earth metals, calcium in particular. On the basis of the absorption spectra[2] and the magnetic susceptibility[14] of dilute calcium ammonia solutions, a difference appears to exist between calcium and the alkali metals in the first instance and between calcium and barium in the second. Measurements are now in progress to determine whether or not the heat of reaction of the calcium solution with ammonium ion indicates normal ionization of calcium or the formation of $Ca_2^{++}$ and one electron ionization per gram atom of calcium as proposed by Yost and Russell.[15]

The relative partial molal ionic entropies of the alkali metal ions in liquid ammonia may now be calculated from the measured heats of reaction for eq. 1 and the corresponding free energy changes derived from cell measurements by Pleskov and Monoszon.[16] These values appear in column 3 of Table III along with our measured heats of reaction from which the partial molal ionic entropies relative to $\bar{S}^0_{NH_4^+} = 0$ at $-33°$ have been calculated in the usual manner.[1] It does not appear that the free energy changes employed in the calculation are above criticism because of the presence of liquid junction potentials in the cells employed by Pleskov and Monoszon and in view of the approximation of activity coefficients made for the solutes in the cell solutions in obtaining the standard electrode potentials.

TABLE III

IONIC AND SOLVATION ENTROPIES IN LIQUID AMMONIA AT $-33°$

| Ion | $\Delta H^0$ kcal. | | $\Delta F^0$ kcal. | $\bar{S}^0_{240}$°K. cal./deg. | $\Delta S$ of solvation cal./deg. |
|---|---|---|---|---|---|
| $Li^+$ | $(-66.380)^a$ | $-50.6$ | $-51.4$ | $-26.8$ | $-52$ |
| $Na^+$ | $(-57.520)^a$ | $-38.7$ | $-42.4$ | $-9.5$ | $-38$ |
| $K^+$ | $(-60.340)^a$ | $-39.7$ | $-45.6$ | $+2.6$ | $-27$ |
| $Rb^+$ | $(-61.210)^a$ | $-40.0^b$ | $-44.4$ | $-2.4$ | $-34$ |
| $Cs^+$ | $(-62.040)^a$ | $-41.6$ | $-44.9$ | $-3.0$ | $-42$ |

[a] Corresponding values for the reaction $M + H_3O^+_{(aq)} = M^+_{(aq)} + {}^1/_2H_2 + H_2O$ at 25° [Latimer, *Chem. Rev.*, 18, 349 (1936)]. [b] Estimated from value for potassium.

Comparison of the ionic entropies obtained for the metal ions indicates a departure of $\bar{S}^0_{Rb^+}$ and $\bar{S}^0_{Cs^+}$ from the consistent and expected trend for lithium, sodium and potassium. This is emphasized in a consideration of the relative solvation entropies of each of the ions in the last column of Table III, where $\Delta S$ of solvation $= \bar{S}_{M^+} - S_{(gas\ ion)}$. Although smaller negative values for the solvation entropy of $Rb^+$ and $Cs^+$ are expected in comparison with $K^+$ because of the larger ionic radius and consequently less ordering effect on the solvent, the reverse occurs. The admitted uncertainties in the standard potentials undoubtedly will account for these inconsistencies. It is of interest that solvation entropies of the lithium, sodium and potassium ions appear to be linearly dependent on the reciprocal of the ionic radius as already observed for aqueous ions by Latimer[1] and Buffington[17] and that the slope of the curve is approximately the same as obtained for these ions in water solution.[1]

For comparison purposes we have included in Table III the reaction heats of the alkali metals with hydronium ion in water solution. These values appear in parentheses with the corresponding values in column 2 obtained in this research for the reaction represented by eq. (1). It is to be noted that in both systems a minimum value is obtained for $-\Delta H$ for the sodium reaction. Although the difference between the reaction heats in the two systems is about constant at 20 to 21 kcal. for potassium, rubidium and cesium, the dif-

---

(13) Schmidt, Sottysiak and Kluge, THIS JOURNAL, 58, 2509 (1936).

(14) Freed and Sugarman, *J. Chem. Phys.*, 11, 354 (1943).

(15) Yost and Russell, "Systematic Inorganic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1944, p. 148.

(16) Pleskov and Monoszon, *J. Phys. Chem.* (*U. S. S. R.*), 4, 696 (1933); *Acta Physicochim.* (*U. R. S. S.*), 2, 615 (1935).

(17) Latimer and Buffington, THIS JOURNAL, 48, 2297 (1926).

ference in the case of lithium amounts to only 16 kcal., thereby indicating a relatively greater interaction energy of the lithium ion with ammonia than with water.

**Acknowledgment.**—We wish to express our appreciation to the Research Corporation for a Frederick Cottrell grant in aid of research which made this investigation possible. We are also indebted to the Sigma Xi for an earlier grant supporting exploratory work. We acknowledge the assistance of Mr. Sumner P. Wolsky who performed some of the calibration experiments.

## Summary

The heats of reaction of lithium, sodium, potassium and cesium metals with dilute solutions of ammonium bromide and ammonium chloride have been determined in a liquid ammonia calorimeter at −33°. Combination of these heats of reaction with the known heats of solution of the metals in pure liquid ammonia has given the heat of reaction of each dilute metal solution with ammonium ion. Exothermic heats of reaction varying from 39.7 to 41.6 kcal. (mean 40.4 ± 1 kcal.) indicate within experimental error an identical reaction in each case and, therefore, a close similarity in the nature of the dilute solutions of the alkali metals in liquid ammonia. A redetermination of the heat of solution of lithium in liquid ammonia gave −9.6 kcal. for $\Delta H$ instead of the reported value −8.0 kcal. From the measured heats of reaction and corresponding free energy changes relative partial molal ionic entropies and entropies of solvation of the alkali metal ions in liquid ammonia have been calculated.

BOSTON, MASS. RECEIVED JANUARY 5, 1949

---

[CONTRIBUTION FROM THE LABORATORY FOR THE STUDY OF HEREDITARY AND METABOLIC DISORDERS AND THE DEPARTMENTS OF BIOLOGICAL CHEMISTRY AND MEDICINE, UNIVERSITY OF UTAH COLLEGE OF MEDICINE]

# The Relationship between Homoserine and its Lactone[1]

BY MARVIN D. ARMSTRONG

The preparation of the optical isomers of homoserine ($\alpha$-amino-$\gamma$-hydroxybutyric acid) was described in a previous publication[2] and a brief review was made of its earlier literature. Since the first synthesis of homoserine by Fischer and Blumenthal in 1907[3] little appeared to have been added to our knowledge of the physical and chemical properties of the compound and its derivatives. The purpose of the present investigation was to examine some of these properties, particularly the relationship of homoserine to its $\gamma$-lactone and its diketopiperazine.

The early studies of homoserine by Fischer and Blumenthal indicated that in acid solutions it possibly existed only in the lactone form; the conversion to a lactone is in analogy with the behavior of homocysteine which forms the corresponding thiolactone.[4] Fischer and Blumenthal also prepared free $\alpha$-aminobutyrolactone from its hydrochloride and found that it reacts with itself to form a diketopiperazine. The formation of a diketopiperazine is likewise similar to the reaction of homocysteine thiolactone which reacts with itself in neutral solution to form homocysteine diketopiperazine.[5] It thus was of interest to find whether homoserine could exist in the open form in acid solutions and whether the lactone of homoserine reacted in aqueous solution to form the corresponding diketopiperazine as well as opening to form homoserine.

The nitrous acid amino nitrogen determination showed both homoserine and its lactone to contain the calculated amount of amino nitrogen; homoserine diketopiperazine showed no amino nitrogen under the conditions of the determination. Solutions, ranging from 1 $N$ in sodium hydroxide to 6 $N$ in hydrochloric acid, of the free acid after standing for several days suffered no loss in their content of amino nitrogen; this indicated that no measurable amount of diketopiperazine was formed from homoserine itself. Solutions of the lactone behaved somewhat differently; in the presence of even a slight amount of base the lactone ring opened to form homoserine, and its solutions showed no loss of amino nitrogen. Dilute (1%) neutral or slightly acidic (less than 1 mole of acid/mole of lactone) solutions of the lactone did not show the formation of any significant amount of diketopiperazine; more concentrated neutral or slightly acidic solutions of the lactone, however, showed the formation of a mixture of homoserine and its diketopiperazine. The formation of homocysteine diketopiperazine in good yield from homocysteine thiolactone may be understood to occur as a result of the much greater insolubility of this diketopiperazine in water; this would speed the formation of diketopiperazine at the expense of the reaction forming homocysteine.

The availability of optically active homoserine and its lactone hydrobromide made it appear likely that the relationship of the free amino acid to its lactone could be studied polarimetrically,

---

[1] This research was supported by a grant from the United States Public Health Service. Presented in part before the Division of Biological Chemistry at the 112th meeting of the American Chemical Society, New York, September 16, 1947.

[2] M. D. Armstrong, THIS JOURNAL, **70**, 1756 (1948).

[3] E. Fischer and H. Blumenthal, *Ber.*, **40**, 106 (1907).

[4] B. Riegel and V. du Vigneaud, *J. Biol. Chem.*, **112**, 149 (1935-1936).

[5] V, du Vigneaud, W. I. Patterson and M. Hunt, *J. Biol. Chem.*, **126**, 217 (1938);