[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF SOUTHERN CALIFORNIA]

Some Ionic Free Energies in Liquid Ammonia[1]

BY KENNETH SCHUG[2] AND HAROLD L. FRIEDMAN

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The free energies of formation of several ions relative to Na^+, all in liquid ammonia solution at 0°, have been determined by measurements upon the position of equilibrium in reactions such as $Na^+(NH_3) + K(Hg) \rightarrow Na(Hg) + K^+(NH_3)$ combined with previously reported results for the free energies of formation of the amalgams. The results are, for ΔF^0 for the reaction $Na^+(NH_3) + M_2(c) \rightarrow Na(c) + M_2^+(NH_3)$ M_2 = K, −3.1; Rb, −2.9; Cs, −5.6; $^1/_2$Sr, −5.4 kcal./mole. Relative ionic entropies are derived from these values together with literature enthalpy data. The free energy values themselves are compared critically with the results of e.m.f. measurements.

The state of our knowledge of the thermodynamic properties of solutions of electrolytes in liquid ammonia has been reviewed recently by Jolly,[3] Coulter,[4] and Latimer and Jolly.[5] For the alkali and alkaline earth metal ions in liquid ammonia there are discrepancies of the order of kilocalories in the molar standard free energies of formation of the ions as calculated from various data. This paper describes the application of the amalgam partition method[6] to this problem. Although the determinations to be described are not of high accuracy, it is believed that they are free of the possibility of severe systematic errors, unlike most of the determinations in liquid ammonia based upon solubility or e.m.f. methods. Incomplete information about the nature of the equilibrium solid phase in the former case and about the reversible cell reaction in the latter may lead to such errors.

The amalgam partition method depends upon the measurement of equilibrium concentrations in the reaction

$$\frac{1}{z_1} M_1{}^{z_1+}(NH_3) + \frac{1}{z_2} M_2(Hg) \longrightarrow \frac{1}{z_1} M_1(Hg) + \frac{1}{z_2} M_2{}^{z_2+}(NH_3) \quad (1)$$

We represent the stoichiometric molal concentrations in the amalgam phase as m_1 and m_2 and the stoichiometric molar concentrations in the ammonia phase as m_{1a} and m_{2a}. The activity coefficients of the solutes in the amalgam phase are given by f_1 and f_2, and the ionic activity coefficients in the ammonia phase by γ_1 and γ_2. Then the equilibrium constant of reaction 1 is

$$K = \left[\left(\frac{m_1 f_1}{m_{1a}}\right)^{1/z_1}\left(\frac{m_{2a}}{m_2 f_2}\right)^{1/z_2}\right] \frac{(\gamma_2)^{1/z_2}}{(\gamma_1)^{1/z_1}} \quad (2)$$

The factor in square brackets in eq. 2, designated as R, is calculated from the experimentally determined equilibrium concentrations and the amalgam activity coefficients previously reported.[7] Extrapolation of R to zero concentration in the ammonia phase yields K.

K may be related to the free energy changes in reactions involving only M_1 or M_2. We have

$$-RT \ln K = \Delta F_1{}^0 = F^0{}_{1m}/z_1 - F^0{}_{2m}/z_2 + F^0{}_{2a}/z_2 - F^0{}_{1a}/z_1 \quad (3)$$

in which $F^0{}_{1m}$ is the standard free energy change of the reaction

$$M_1(c) \longrightarrow M_1(Hg) \quad (4)$$

and $F^0{}_{1a}$ is the standard free energy change of the reaction

$$M_1(c) + z_1H^+(NH_3) \longrightarrow M_1{}^{z_1+}(NH_3) + \frac{z_1}{2} H_2(g) \quad (5)$$

The standard free energies in the amalgams are known[7] so the present results yield the last two terms on the right of eq. 3, that is, the difference of the standard free energies of formation of the positive ions in liquid ammonia. If $M_1{}^{z_1+}$ were $NH_4{}^+$ in any case, then these measurements would yield the standard free energy of formation of $M_2{}^{z_2+}$ relative to $\Delta F_f{}^0(NH_4{}^+) = 0$. Although it seems possible that this may be done by the present method at 0°, the amalgams containing NH_4 decompose rapidly and require faster manipulation than we have been able to manage at this high temperature.

Results are described for systems having Na, K, Rb, Cs and Sr as components (M_1 or M_2). Systems including Li were also investigated, but in these cases equilibrium in reaction 1 lies too far to one side to allow the determination of all of the equilibrium concentrations by the analytical methods employed here.

Experimental

Materials.—Binary and ternary amalgams of various compositions were prepared by the electrolysis of aqueous solutions. The amalgams were dried *in vacuo*, filtered, and stored under NH_3 pressure. The total molality of solutes in the amalgams varied from 0.007 to 0.025. Anhydrous ammonia was purified with sodium immediately before use.

Equilibration.—The equilibrations were carried out in 30 ml. Pyrex vessels fitted with pressure stopcocks. The vessels containing appropriate amounts of salts were dried and charged with amalgam and ammonia on the vacuum line. They were then rotated for 1 to 3 hours in a thermostat at 0.05 ± 0.05° or at −17.80 ± 0.05°. The ammonia and amalgam phases were then sampled, and the ammonia samples evaporated to dryness and taken up with water. The remainder of the analytical procedure has been described.[7] When the concentration of the ammonia solution was very low the initial amalgam composition was adjusted to make the equilibrium ammonia phase concentration of each of the positive ions about equal, in order to facilitate analysis. As in the earlier work, the analytical technique was checked in several cases by performing a complete material balance and by the analysis of blanks.

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(1) (a) This research was supported by the Research Corporation and by the U. S. Atomic Energy Commission; (b) from the thesis submitted by Kenneth Schug to the Graduate School of the University of Southern California in partial fulfillment of the requirements for the Ph.D. degree; (c) presented in part before the Division of Physical and Inorganic Chemistry, American Chemical Society, Minneapolis, Minn., in Sept., 1955.

(2) Department of Chemistry, Illinois Institute of Technology, Chicago 16, Illinois.

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

(4) L. V. Coulter, *J. Phys. Chem.*, **57**, 553 (1953).

(5) W. M. Latimer and W. L. Jolly, THIS JOURNAL, **75**, 4147 (1953).

(6) K. Schug and H. L. Friedman, *ibid.*, **76**, 3609 (1954).

(7) H. L. Friedman and K. Schug, *ibid.*, **78**, 3881 (1956); H. L. Friedman and M. Kahlweit, *ibid.*, **78**, 4243 (1956).

Results

The principal results are reported in graphical form in Figs. 1 to 4.

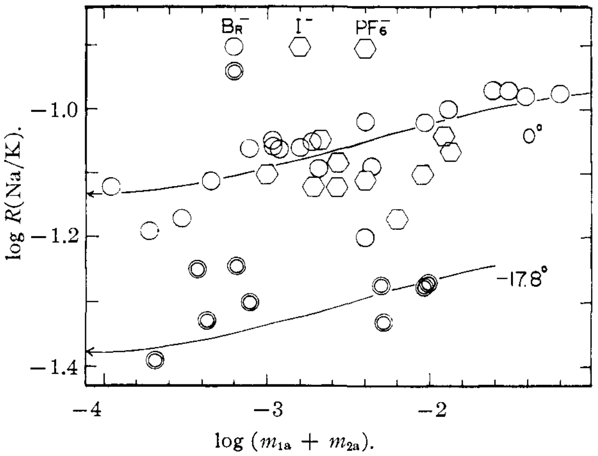

Fig. 1.—m_1 = Na, m_2 = K, the curves are calculated for $K_{DISS}(KBr) = 1.90 \times 10^{-3}$ and $K_{DISS}(NaBr) = 2.90 \times 10^{-3}$.

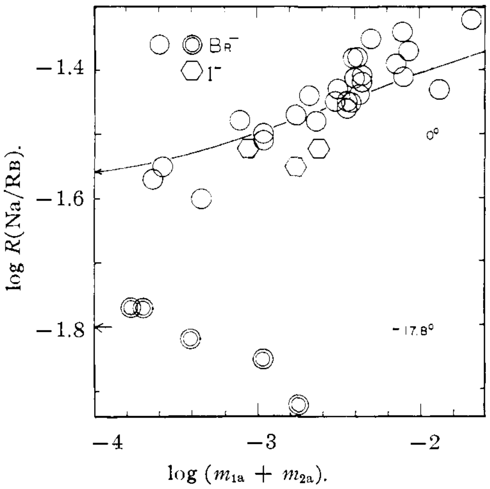

Fig. 2.—m_1 = Na, m_2 = Rb, the curve is calculated for $K_{DISS}(RbBr) = 1.57 \times 10^{-3}$ and $K_{DISS}(NaBr) = 2.9 \times 10^{-3}$.

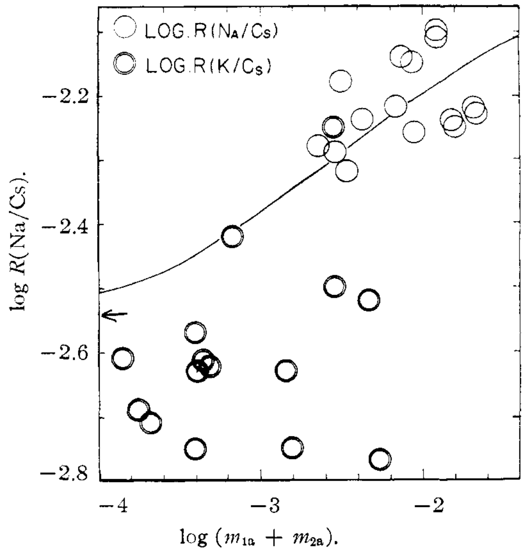

Fig. 3.—m_1 = Na, m_2 = Cs, the solid curve is calculated for $K_{DISS}(CsBr) = 0.9 \times 10^{-3}$, $K_{DISS}(NaBr) = 2.9 \times 10^{-3}$.

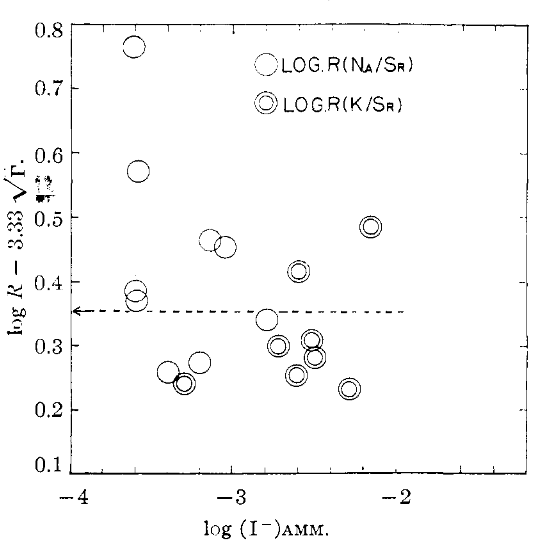

Fig. 4.—m_1 = Na or K, m_2 = Sr; iodide solutions.

Errors.—Most of the experimental points are within 0.1 unit (log *R*) of the smooth curve, corresponding to an uncertainty of about ±13% in *R*. This is attributed to analytical errors and to imperfect separation of the phases. There is no reduction of the solvent by the amalgams in periods of 10 to 20 hours, as shown by experiments in which the equilibration was carried out in a vessel with conductivity electrodes sealed into the vessel and with no added salt. There is no difficulty in attaining equilibrium in reaction 1 as shown by the observed lack of dependence of *R* upon equilibration time in the range 1 to 3 hours, and upon the direction of approach to equilibrium.

Effect of Water.—In two experiments at 0° in the Na/K system, 10% by volume of water was present in the solvent. For these experiments, with log $(m_{1a} + m_{2a}) = -1.91, -1.95$ and $\log R = -1.02, -0.99$, respectively, the results coincide with those for anhydrous ammonia (Fig. 1). For Na/K in pure water (reaction 1 with water in place of ammonia) it is found that $\log R = 0.1$[7] and it would be interesting to see in what range of solvent composition log *R* changes.

Dependence upon Anion.—For the systems in which M_1 and M_2 are both alkali metals the ionic strength contribution to γ_1/γ_2 cancels out and what is left may be regarded as specific ion interaction. It is likely that in liquid ammonia in the low concentration range of interest here, this interaction arises mainly in the pairing of ions of opposite sign. Unfortunately there are no conductimetric determinations of the ion-pair dissociation constants that are needed here. As an approximation, the results of Hnizda and Kraus[8] for NaBr and KBr at −33° have been assumed to apply here, and values for RbBr and CsBr have been assumed to give agreement with the partition data. For given values of K_1 and K_2 for M_1Br and M_2Br, values of γ_1/γ_2 can be calculated and the shapes of the curves in Figs. 1 to 3 have been obtained in

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[8] V. F. Hnizda and C. A. Kraus, This Journal, **71**, 1565 (1949).

this way. The vertical position of each curve was chosen to make the curve pass as well as possible through the experimental points for the bromide solutions.

The interpretation of the concentration dependence of log R in terms of ion association seems to be satisfactory for the data of Fig. 1. It is gratifying that the points for I^- and PF_6^- solutions, for which K_1 and K_2 are presumably larger[8] than for Br^- solutions, show less concentration dependence than the points for Br^- solutions.

The log R values of Fig. 2, 0°, exhibit a concentration dependence which is consistent with the values of K_1 and K_2 chosen. The implication that KBr is a stronger electrolyte than RbBr reflects the same order, found in the dissociation of the nitrates at $-40°$ by Monosson and Pleskov.[9]

The concentration dependence of the Na/Cs system proved to be more difficult to investigate because the small value of R (of the order of 0.005) tends to make the concentration of Cs^+ (NH_3) too small to measure at low electrolyte concentration. In an attempt to fill this gap measurements were also made upon the K/Cs system, for which $R \sim 0.03$. As shown in Fig. 3, the values of R obtained from measurements of the K/Cs equilibrium are somewhat lower than expected on the basis of the Na/K and Na/Cs data. The cause for this discrepancy is not understood. Again the data imply that the lighter alkali metal ion forms the stronger electrolyte, namely, RbBr stronger than CsBr, and again the same trend for the nitrates may be deduced from the data of Monosson and Pleskov.[9]

The discrepancies found in the measurements involving Cs ought not to be construed as indicating the same low order of accuracy in the other data. Thus, good checks are obtained upon comparison of the separate Na/K and Na/Rb data with the results of direct measurements on the K/Rb system

log R(K/Rb)	$-$log $(m_1a + m_2a)$	Est. log (γ_1/γ_2)	Calcd. log K(Na/K)
-0.50	2.46	0.03	-1.02
$-$ .48	2.53	.03	-1.04

The last column was calculated from these data using log K(Na/Rb) $= -1.55$, and is to be compared with the value from Fig. 1, log K(Na/K) $= -1.13$.

Solutions Containing Sr.—Systems in which M_1 is Na or K and M_2 is Sr also have been investigated, with the results shown in Fig. 4. The observations have been corrected for the ionic strength effect in the ammonia phase and in the case of the K/Sr data a further correction for the Na/K equilibrium constant has been made so that the two sets of data may be directly compared. The validity of the ionic strength correction depends upon the assumption that SrI_2 and NaI are both strong electrolytes under the experimental conditions. This is perhaps unlikely, but the correction amounts to at most 0.1 in log R and is therefore small compared to other errors. The effect of ion-pairing has been neglected for lack of conductivity data for Sr salts in liquid ammonia, but it presumably contributes to the downward trend of log R with increasing concentration of I^- in the ammonia phase.

Equilibrium Constants.—On the basis of the concentration dependence of log R, as discussed in the preceding paragraphs, the values indicated by the arrows on the figures are estimated as the log K values for the respective systems. The results are summarized in Table I, with the uncertainties estimated from the precision of the data as illustrated by the graphs and the cross-checks discussed above.

TABLE I

EQUILIBRIUM CONSTANTS FOR REACTION 1

M_1/M_2	Na/K	Na/Rb	Na/Cs	Na/Sr
Log K, 0°	-1.13	-1.56	-2.5	0.35
Log K, $-17.8°$	-1.38	-1.8	...	..
Uncertainty, in log K, 0°	0.1	0.2	0.3	0.3

For the Na/K system, the temperature coefficient may be expressed in terms of ΔH_1, the enthalpy increase in reaction 1, which is 4.8 kcal./mole.[4,7] Then from the $-17.8°$ value of log K we calculate

$$\log K_{0°} = -1.38 + 4800(1/255 - 1/273)/4.56 = -1.11$$

in good agreement with the directly observed value.

In the same way, for the Na/Rb system we utilize $\Delta H_1 = 6.2$ kcal./mole[4,7] and from the $-17.8°$ value of log K we calculate

$$\log K_{0°} = -1.45$$

which is in fair agreement with the directly observed value.

Comparison with the Data of Pleskov and Monosson.—These investigators measured[10] the e.m.f.'s at $-35°$ of cells of the type

$$M(Hg)|M(NO_3)_2,\ 0.1\ N|KNO_3,\ \text{satd.}|Pb(NO_3)_2,\ 0.1\ N|Pb$$

with electrolytes in liquid ammonia solution. If it is assumed that the reaction at the amalgam electrode is

$$M(Hg) \longrightarrow M^{z+}(NH_3) + ze^-(Hg)$$

and that the liquid junction potential does not depend upon M, then the potential of a given cell of this type minus the potential of a cell in which M = Na gives the free energy change of reaction 1. In this way the data may be compared with ours as directly as possible.

The steps of the calculation are outlined in Table II. (a) Correct the measured e.m.f.'s to 1 m amalgam concentrations, neglecting amalgam activity coefficients, to obtain E^1. (b) Convert E^1 to free energy in kcal./equivalent and correct for the non-ideality of the amalgam used, expressed as[7] F_2^{rel}, giving ΔF_{cell}. (c) Subtract ΔF_{cell} for Na from that for the other metals, giving ΔF_1^0 $(-35°)$. (d) Convert this to ΔF_1^0 (0°) using ΔH_1^0 obtained from the amalgam data and the heats of solution of the metals in liquid ammonia.[4,7]

The last row of Table II shows our results for $\Delta F_1^0(0°)$, calculated from Table I. The agreement for Na/K and Na/Rb is surprisingly good, in

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[9] A. M. Monosson and W. A. Pleskov, *Z. physik. Chem.*, **156A**, 176 (1931).

[10] W. A. Pleskov and A. M. Monosson, *Acta Physichochim. U.R.S.S.*, **2**, 615 (1935); W. A. Pleskov, *ibid.*, **6**, 1 (1937); W. A. Pleskov, *ibid*, **20**, 163 (1946).

TABLE II

REDUCTION OF PLESKOV AND MONOSSON E.M.F. DATA

All free energies expressed in kcal./mole

	Li	Na	K	Rb	Cs	Ca
E, −35°, v.	1.658	1.3375	1.2873	1.230	1.0785	1.108
Amalgam, m	0.0258	0.0413	0.0566	0.02666	0.0145	0.00070
E^1, v.	1.732	1.4029	1.3461	1.3044	1.1652	1.182
F_2^{rel}	0.07	0.17	0.44	0.32	0.28	0.0 (est.)
ΔF_{cell}	−39.86	−32.18	−30.58	−29.75	−26.58	−27.25
$\Delta F^0{}_{,1}$ −35°	− 7.68	0.00	1.60	2.43	5.60	4.93
$\Delta F^0{}_{,0}$ 0°	− 7.12	0.00	1.12	1.87	4.94	6.3
$\Delta F^0{}_{,1}$ 0°, this work	.....	0.00	1.41	1.95	3.14	− 0.44[a]

[a] For Sr, not Ca.

TABLE III

CALCULATION OF IONIC ENTROPIES

Heats and free energies in kcal./mole, entropies in cal./mole deg.

	Li	Na	K	Rb	Cs	Sr
ΔF_1^0 0°	− 7.12	0	1.41	1.95	3.14	− 0.44
$F^0{}_{\mathrm{im}}$ 0°	−20.2	−18.56	−23.11	−23.36	−27.29	−47.07
ΔF_6^0 0°	− 8.76	0	− 3.14	− 2.85	− 5.59	− 5.41
ΔH_6^0 0°	−11.1	0	− 1.4	− 1.4	− 1.4	−11.05
ΔS_6^0 0°	− 8.6	0	6.4	5.3	15.3	−20.6
$\frac{1}{z_i} S^0(\mathrm{M}^{z_i+}) - S^0(\mathrm{Na}^+)$						
This work, 0°	−14.0	0	9.4	9.7	22.9	−14.9
Coulter, −33°	−18.7	0	11.4	7.2	5.4	−77[a]
Latimer and Jolly, 25°	− 6.9	0	6.3	13.9	13.9	−25.6[a]

[a] For Ca, not Sr.

view of the assumptions necessary to interpret the e.m.f. data. Although the amalgam partition data for Na/Cs and K/Cs are the least precise of the alkali metal pairs, the uncertainty in the partition data is far less than the difference between the partition and e.m.f. data. The difference between the partition result for Sr and the e.m.f. result for Ca also is large and is in the opposite direction from that expected from the trend in the alkali metal series. In this case the correction of the e.m.f. data to 0° is made upon the assumption that the heats of solution of Ca and Sr in Hg are the same. However it seems likely that this does not account for the discrepancy, but that Pleskov's e.m.f. measurements with Ca(Hg) electrodes are not consistent with the amalgam partition results with Sr.

Comparison with the Data of Sedlet and DeVries.—These authors measured[11] the potentials of cells of the constitution

$$\mathrm{M(Hg},\ m)|\mathrm{MCl(NH_3}\ m_a)|\mathrm{ZnCl_2{\cdot}6NH_3(s)}|\mathrm{Zn(Hg,\ 2\ phase)}$$

in which M was Na or K, m was fixed for each M, and m_a was varied over a wide range in each case. This allows extrapolation to infinite dilution in the ammonia phase (neglecting the small saturation concentration of $ZnCl_2$) and this the authors have done, leading to values of E^{01}, the potential of the cell with the real amalgam used, but with the electrolyte in the hypothetical 1 molal state. Their results at −36° are

M	Na	K
m	0.0870	0.0704
E^{01}, v.	0.2208	0.1052

These data may be handled in exactly the same way as those of Pleskov and Monosson in Table II, to obtain $\Delta F_1^0 = 2.29$ kcal. at 0° for $M_1 = \mathrm{Na}$, $M_2 = \mathrm{K}$. The discrepancy between this value and those in Table II is not a result of differences in reduction of the data, but is apparent in comparing the observed cell potentials of Sedlet and DeVries with those of Pleskov and Monosson.

The Thermodynamic Properties of the Alkali Metal Ions and Sr^{++} in Liquid Ammonia at 0° Relative to Na^+.—The first row of Table III presents the standard free energy change of reaction 1, derived from the present work except in the case of Li which is calculated from the data of Pleskov and Monosson, as described above. The limits of error may be derived from Table I, except for Li, and are at worst ±0.4 kcal./mole.

In the second row of Table III are the ΔF^0 values for reaction 4, designated $F^0{}_{\mathrm{im}}$ in the Introduction. Combining these data with those in the first row according to eq. 3, we obtain $F^0{}_{\mathrm{ia}}/z_i - F^0{}_{\mathrm{Na,a}}$ (the latter term is $\Delta F^0{}_5$ with $M_1 = \mathrm{Na}$), which is the free energy change in reaction 6

$$\frac{1}{z_i}\,\mathrm{M_i(c)} + \mathrm{Na^+(NH_3)} \longrightarrow \frac{1}{z_i}\mathrm{M_i}^{z_i+}\mathrm{(NH_3)} + \mathrm{Na(c)} \quad (6)$$

The quantity in the fourth row is defined in an analogous way in terms of ΔH^0 for reaction 5 and is evaluated from the calorimetric data of Coulter,[4] neglecting the change in $H^0{}_{\mathrm{ia}}/z_i - H^0{}_{\mathrm{Na,a}}$ from −33 to 0°. Subtracting the third row from the fourth and dividing by T gives the corresponding entropy quantity (row 5). Finally, combination with the standard entropies of the crystalline metals at 0° gives the standard entropies of the ions in liquid ammonia relative to $S^0(\mathrm{Na^+, amm}) = 0$. Relative entropies calculated from the results of Coulter[4] and Latimer and Jolly[5] are included in the table for comparison.

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[11] J. Sedlet and T. DeVries, THIS JOURNAL, **73**, 5808 (1951).

On the whole the present results for the ionic entropies seem to be more consistent with those of Latimer and Jolly than with those of Coulter. The differences are mainly in the choice of free energy values rather than a result of the temperature differences. Although the molar entropy of Ca^{++} in liquid ammonia is expected to be more negative than that of Sr^{++} the difference can hardly be expected to be so great as that (124 e.u.) obtained if Coulter's result for Ca^{++} and the present result for Sr^{++} are both correct. The former result is based upon some e.m.f. measurements by Pleskov (*cf.* Table II) and this comparison supports the view that these e.m.f. measurements are inconsistent with our amalgam partition measurements involving Sr.

For the most part, a detailed consideration of these results is deferred pending the resolution of several uncertainties in the auxiliary data, particularly those relating to the energetics of formation of rubidium amalgam from the elements. However one observation may be made independently of these data. By comparing the equilibrium constant of reaction 1 at 0° with that for the same reaction at 0°, but with H_2O in place of NH_3 as the solvent,[7] we can calculate ΔF^0 for the reaction

$$\frac{1}{z_i}\,\mathrm{M_i}^{z_i+}(\mathrm{H_2O}) + \mathrm{Na}^+(\mathrm{NH_3}) \longrightarrow \frac{1}{z_i}\,\mathrm{M_i}^{z_i+}(\mathrm{NH_3}) + \mathrm{Na}^+(\mathrm{H_2O}) \qquad (7)$$

In this way we obtain

Mi	K	Rb	Cs	Sr
ΔF_i^0	1.55	1.91	2.35	−1.06 kcal./mole

These results are clearly the opposite of what one would expect on the basis of the simple Born charging equation, which predicts that the smaller, more highly charged ion should show the greater preference for the solvent of higher dielectric constant.

LOS ANGELES, CALIFORNIA

[CONTRIBUTION FROM SPECTROSCOPY LABORATORY, THE DOW CHEMICAL COMPANY]

The Donor Characteristics of the Carbonyl Group

BY DENYS COOK

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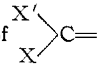
The donor characteristics of molecules containing the carbonyl group are examined in terms of the ionization potential (IP), the carbonyl stretching frequency ($\nu_{C=O}$), the value of the fundamental stretching frequency of HCl (ν_{HCl}), dissolved in such solvents, and the value of the acetylenic C–H stretching frequency of C_6H_5CCH (ν_{CH}) in solution in such solvents. Empirical relationships have been found between these quantities for a large number of carbonyl compounds. Donor strengths are discussed in quantitative terms. Modifications of the carbonyl group of  $\mathrm{X'}\mathrm{X}{>}\mathrm{C{=}O}$ in terms of the properties of X are examined. The experimental evidence presented suggests that such carbonyl compounds can be divided into two clearly distinguishable classes, (A) where no conjugation between X and C=O exists, and (B) where there is such conjugation.

There have been several studies of the relationship between $\nu_{C=O}$ and carbon–oxygen distance, and other fundamental properties of the carbonyl bond.[1] The important result from such studies is that short bonds have high stretching frequencies and force constants and *vice versa.* The emphasis in such studies has been placed on the electrons in the C=O bond, and little or no attention has been paid to the lone pair electrons.

The carbonyl group consists of a C atom hybridized in its sp^2 state with three planar σ-bonding orbitals, the interbond angle being 120°. The fourth orbital is a p orbital at right angles to the sp^2 hybrids. The carbonyl bond is formed by overlapping one of the sp^2 hybrids of the C atom with a p orbital of the O atom to form the σ-bond, the other p orbital of the O atom forming the π-bond with the C p orbital. On account of the greater electronegativity of the O atom the π electrons will not be equally shared. The O atom $2s^2$ and $2p^2$ have so far not been assigned. A hypothetical model which, however, remains to be confirmed by precise quantum-mechanical calculations, can be set up, wherein these electrons belong to two lone pair orbitals (each doubly filled and non-bonding) in a plane at right angles to the π-bond, with a probable angle of 120° between the lone pair orbitals and the carbon–oxygen σ-bond. Indirect evidence for this arrangement comes from the structure of compounds containing groups capable of hydrogen bonding to the carbonyl group.[2]

The carbonyl group lone pair electrons are responsible for many of the physical properties of such compounds as the carboxylic acids and amides. Thus all simple primary amides, with the exception of formamide, are solids due to intermolecular hydrogen bonds. The corresponding N,N-dialkyl amides, where no such hydrogen bonding can take place, usually have much lower melting points than the unsubstituted amide. The carboxylic acids, except in the gas phase at elevated temperatures, consist of hydrogen bonded dimers or chains. Other carbonyl compounds like ketones, esters and acid halides appear to behave normally because of the lack of an acidic hydrogen atom. Hydrogen bonding has been postulated for aldehydes but its existence seems controversial.

Little is known in quantitative terms of the donor strength of lone pair orbitals. It is the pur-

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(1) See E. M. Layton, R. D. Kross and V. A. Fassel, *J. Chem. Phys.*, **25**, 138 (1956), for a comprehensive bibliography.

(2) W. G. Schneider, *ibid.*, **23**, 26 (1955).