$E_3 - {}^1/_2\, E_7$ of 9.6 ± 1 kcal./mole for the range 60 to 170° was calculated by the method of Noyes and Dorfman.[5] This might be compared to values from 9.5 to 9.7 kcal./mole obtained for methyl attack on acetone.[29] In view of the uncertainty in the quantum yields of formation of diallyl, it does not seem profitable at this time to attempt to evaluate E_4. However, it would seem qualitatively that because of the resonance energy associated with an allyl radical compared to methyl,[30,31] E_4 should be considerably greater than 9.6 kcal./mole. Reaction 5 was included in the mechanism to account for the traces of cyclopropane detected at elevated temperatures.

It is evident from the temperature dependence of the quantum yields of 1-butene, ethane and biallyl that the combination reactions 6, 7 and 8 have activation energies much less than the hydrogen abstraction processes. Actually E_7 is known to be of the order of 0.0 to -1.6 kcal./mole[32,33] and it seems likely that E_6 and E_8 are also close to zero.

The formation of biacetyl, which is indicated by the mass spectrometric evidence, occurred, presumably by 9, at 25° but not at 170°. A similar effect has been well known in acetone photolysis[5] and explained on the basis that the acetyl radical dissociates rapidly by 1 at temperatures above 100°. There is no evidence to date as to whether or not a specific hydrogen atom is removed by radical attack on the parent ketone. Thus, the product of the abstraction processes 3, 4 and 5 has been designated simply as C_5H_7O. At temperatures above 100° R may represent methyl, allyl or C_5H_7O radicals and it is clear that a number of products could be formed by 10. In photolyses carried out near room temperatures the situation is further complicated by the fact that acetyl radicals also probably combine with other radicals, R, as indicated in 11. A very complex mixture of reaction products would be expected to result from 9, 10 and 11, and in view of the very low yields no detailed effort was made to determine each of them.

No "simple" primary or secondary reaction could be devised to explain the ethylene formed. It is interesting to note, however, that Mandelcorn and Steacie[34] also found significant quantities of ethylene in the products of the high temperature photolysis of acetone.

Acknowledgment.—The authors are indebted to the Atomic Energy Commission for generous support through contract AT(11-1)-89, Project No. 4. One of us (I. Norman) was also supported in part by an Eastman Kodak Fellowship and by a grant from the Abbott Fund of Northwestern University.

---

[29] For a comprehensive review see "The Reactions of Methyl Radicals," by A. F. Trotman-Dickenson, *Quart. Rev.*, **VII**, 198 (1953).

[30] M. Szwarc and A. H. Sehon, *J. Chem. Phys.*, **18**, 237 (1950).

[31] D. P. Stevenson, private communication, 1953.

[32] R. Gomer and G. B. Kistiakowsky, *J. Chem. Phys.*, **19**, 85 (1951).

[33] K. U. Ingold and F. P. Lossing, *ibid.*, **21**, 1135 (1953).

[34] L. Mandelcorn and E. W. R. Steacie, *J. Can. Res.*, in press.

EVANSTON, ILLINOIS

[CONTRIBUTION FROM THE MOORE LABORATORY OF CHEMISTRY, AMHERST COLLEGE]

Differential Capacity of Mercury in Aqueous Sodium Fluoride Solutions. I. Effect of Concentration at 25°

BY DAVID C. GRAHAME

RECEIVED APRIL 3, 1954

The differential capacity of mercury in contact with aqueous solutions of sodium fluoride has been studied as a function of concentration at 25°. The results show that from the capacity measurements at any one concentration (but preferably a high one) it is possible to calculate the capacity at all others. This result confirms an hypothesis advanced earlier to the effect that in the absence of specific adsorption the differential capacity of the region lying between the metal and the outer Helmholtz plane depends upon the surface charge density of the metal but not upon the concentration of the electrolyte. The results serve as an additional strong confirmation of the classical theory of the diffuse double layer. They also provide data which can be used for an exacting test of the accuracy of techniques used for the experimental measurement of the differential capacity of the electrical double layer.

The electrocapillary properties of aqueous solutions of fluorides are of special interest because it has been shown[1] that the fluoride ion is unique (in so far as is now known) in that it is not chemisorbed on mercury at 25° even when the latter is positively charged except, perhaps, when the positive charge becomes rather large. Solutions of *sodium* fluoride are particularly convenient for these studies because of the nearly equal mobilities of the ions, which makes for small and reproducible liquid junction potentials.

Some early studies on the differential capacity of aqueous solutions of sodium fluoride on mercury have already been reported from this Laboratory,[2] but it was emphasized that the measurements were of a preliminary nature, having been made before the techniques of measurement had been fully worked out. It also happens that solutions of sodium fluoride give less reproducible results than most other simple electrolytes, probably because of the greater difficulty associated with the purification of this salt, and because it is less pure to begin with as well. In the present work sufficient purity has been achieved to reduce the errors arising on this account to negligible proportions.

The results to be reported here will be treated in the same theoretical manner as those reported earlier.[2] It will be shown that experiment and theory now agree very satisfactorily except in the most dilute solution studied and except at strongly anodic potentials, where the theory is not expected to ap-

---

[1] D. C. Grahame and B. A. Soderberg, *J. Chem. Phys.*, **22**, 449 (1954).

[2] D. C. Grahame, *Chem. Revs.*, **41**, 441 (1947).

ply very well anyway. With respect to the most dilute solutions it will be shown that the theory is probably more accurate than the measurements.

Experimental

Sodium fluoride was prepared by recrystallization of the C.P. salt from aqueous solution. Because the solubility of sodium fluoride is nearly independent of temperature, it was necessary to remove water by evaporation. The most satisfactory way of doing this is in a vacuum desiccator, and this was most often done. Under these conditions large clear crystals of sodium fluoride were produced, and the solutions to be studied were prepared by dissolving weighed amounts of the dried crystals in conductivity water.

The differential capacity of the mercury–solution interface was measured by methods already described in detail in previous publications.[3] Briefly what was measured was the capacity of a growing pendant mercury droplet immersed in the solution. The potential of the mercury droplet relative to the solution could be varied at will, somewhat as in polarography, and the capacity could be measured on an impedance bridge. The alternating input signal to the bridge could be varied in frequency and in amplitude. It was found that variations in the frequency and in the amplitude of the input signal had no effect upon the measured capacity until the signal became so large that a perceptible distortion of the pattern was visible on the screen of the oscilloscope used to display the amplified output of the bridge. This distortion of the pattern was very characteristic and was easily recognized once it had been seen and identified as the effect of overdriving the bridge. Thus there is almost no danger of accidentally obtaining erroneous reading from this cause. This circumstance makes it possible to increase considerably the amplitude of the a.c. input signal to the bridge over what would heretofore have been considered "safe." In very dilute solutions and at high frequencies this circumstance is especially helpful, since it is otherwise very difficult to maintain sufficient bridge sensitivity.

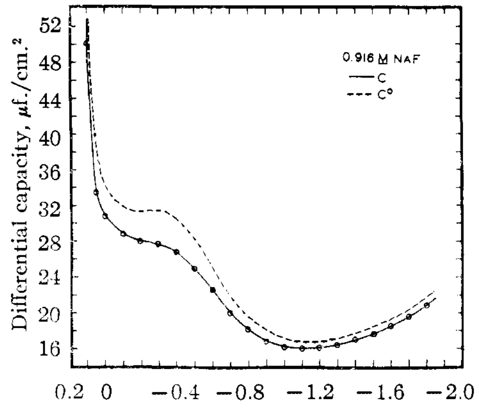

Fig. 1.—Differential capacity of mercury in contact with aqueous 0.916 *M* sodium fluoride solution at 25°. Dashed line represents the differential capacity of that part of the double layer lying between the metallic surface and the outer Helmholtz plane.

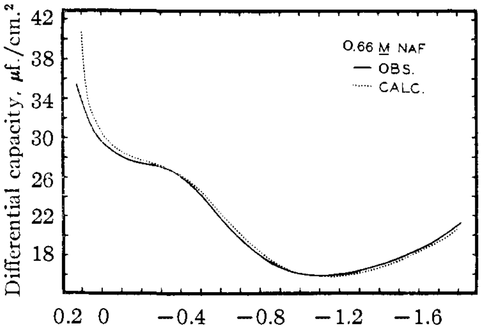

Fig. 2.—Differential capacity of mercury in contact with aqueous 0.66 *M* sodium fluoride solution at 25°.

The reference electrode and the solution under test were held at 25 ± 0.1°. The reference electrode consisted of a

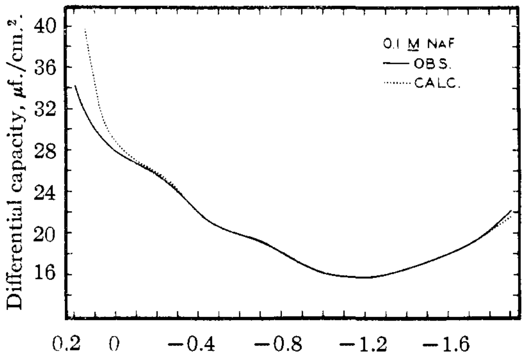

Fig. 3.—Differential capacity of mercury in contact with aqueous 0.10 *M* sodium fluoride solution at 25°.

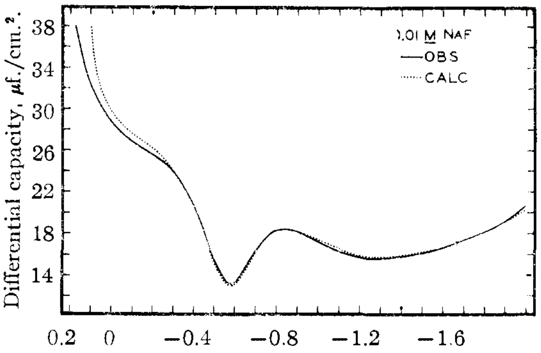

Fig. 4.—Differential capacity of mercury in contact with aqueous 0.01 *M* sodium fluoride solution at 25°.

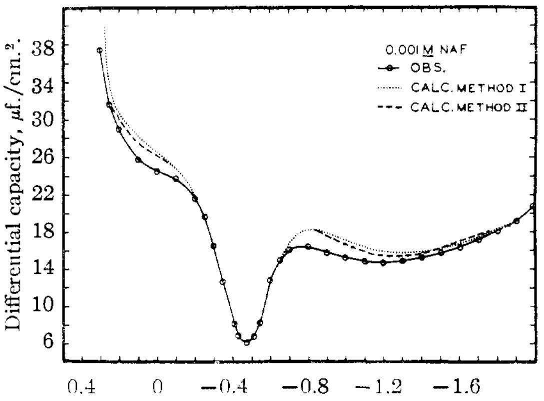

Fig. 5.—Differential capacity of mercury in contact with aqueous 0.001 *M* sodium fluoride solution at 25°.

---

[3] D. C. Grahame, "Comptes Rendus de la III^e Reunion, Comité International de Thermodynamique et de Cinétique Electrochimiques," Berne, August 1951, Carlo Mandredi, Editor, Milan, 1952. Also available as Technical Report No. 6 to the Office of Naval Research, May 25, 1951. The technique described in the above paper differs only in minor technical details from that described in THIS JOURNAL, **71**, 2975 (1949).

TABLE I[a]

SURFACE CHARGE DENSITY, q, FOR MERCURY IN CONTACT WITH AQUEOUS SOLUTIONS OF SODIUM FLUORIDE AT 25°

E,[b] volts	q in microcoulombs per sq. cm.				
	0.916 N	0.66 N	0.10 N	0.01 N	0.001 N	calc.[c] 0.001 N
−1.85	−25.66		−24.42	−23.16	−20.90	
−1.75	−23.56	−23.38	−22.39	−21.22	−19.08	−20.12
−1.65	−21.60	−21.40	−20.50	−19.40	−17.36	−18.34
−1.55	−19.73	−19.53	−18.70	−17.66	−15.73	−16.64
−1.45	−17.96	−17.75	−16.98	−15.98	−14.15	−15.00
−1.35	−16.26	−16.04	−15.32	−14.37	−12.62	−13.43
−1.25	−14.60	−14.38	−13.72	−12.80	−11.12	−11.88
−1.15	−12.98	−12.76	−12.14	−11.24	− 9.64	−10.32
−1.05	−11.38	−11.16	−10.56	− 9.64	− 8.15	− 8.72
−0.95	− 9.76	− 9.54	− 8.94	− 8.04	− 6.62	− 7.05
−0.85	− 8.06	− 7.86	− 7.26	− 6.34	− 5.03	− 5.15
−0.75	− 6.22	− 6.07	− 5.47	− 4.54	− 3.40	− 3.48
−0.65	− 4.20	− 4.09	− 3.55	− 2.70	− 1.79	− 1.81
−0.55	− 1.95	− 1.89	− 1.56	− 1.05	− 0.54	− 0.54
−0.45	+ 0.56	+ 0.54	+ 0.49	+ 0.31	+ 0.14	+ 0.14
−0.35	3.25	3.15	2.68	1.84	1.05	1.05
−0.25	6.03	5.87	5.08	3.86	2.70	
−0.15	8.84	8.62	7.66	6.25	4.86	
−0.05	11.74	11.45	10.31	8.80	7.24	
+0.05	14.86	14.41	13.18	11.48	9.70	
+0.15	20.15		16.20	14.35	12.30	
+0.25				17.57	15.21	
e. c. max., volts	0.4716	(0.4716)	0.4736	0.4735	0.473	

[a] Complete tables available in ref. 4. [b] Potentials measured relative to normal calomel electrode. [c] Obtained by integration of capacity values calculated by method II. Values in this column are believed to be more accurate than those in the column next left.

hydrogen electrode in a solution of sodium fluoride at the concentration under test to which a suitable phosphate buffer had been added to produce a stable *p*H of 7.10. Conversion to a normal calomel electrode scale was effected by subtracting 0.700 volt from the observed potential. Suitable provision was made to avoid the contamination of the pure sodium fluoride solution under test by the phosphate buffer.

Results and Discussion

The investigations which were carried out in this work were concerned with the effects upon the differential capacity of the concentration of the electrolyte and of its temperature. The effects of concentration at a constant temperature of 25° will be discussed in this part. The effects of temperawill be discussed in a part II.

The experimental results at 25° are shown in Figs. 1–5 along with calculated results obtained in a manner to be described below. These results are qualitatively the same as those reported earlier,[2] but differ quantitatively by a considerable amount. The differences are to be attributed to the much better technique of the present measurements. At concentrations of 0.01 N and below there is a pronounced minimum at the potential of the electrocapillary maximum (e.c.max.). A slight dip in the capacity is noted at this potential even in the tenth-normal solution. The same thing can be discerned in the capacity curves of certain other electrolytes whose anions are little or not at all adsorbed at the potential of the e.c.max. It is caused, of course, by the fact that the capacity of the diffuse double layer goes through a minimum at the potential of the e.c. max.

Integration of the capacity with respect to the potential gives values of q, the surface charge density on the mercury.[2] Table I lists a few of the values obtained.[4] These values are needed for the calculations to be described.

For all but 0.001 N solutions of sodium fluoride the potential of the e.c.max. has been estimated by comparison with our accurately determined values for sodium chloride.[5] We have used for this purpose our method VII, which has been found to work well for 0.1 N potassium fluoride. The uncertainty in these results amounts to about a millivolt or two. For 0.001 N sodium fluoride the minimum in the capacity curves gives the potential of the e.c.max. with an accuracy which is believed to be better than that of any other method.

It has been found as expected (see Table I) that the potential of the e.c.max. is independent of concentration within the limits of error of the measurements. This fact serves to remove a minor anomaly in the less accurate measurements reported earlier (ref. 2, Table I). It also serves to confirm our belief in the absence of chemisorption of fluoride ion on mercury at the potential of the e.c.max. at 25°.

The calculated values of the capacity shown in Figs. 2–5 (called method I in Fig. 5) were obtained as follows[6]: It was assumed, first, that the fluoride

---

(4) Tables of C and of q at 10-millivolt intervals are contained in the author's Technical Report No. 14 to the Office of Naval Research, dated Feb. 18, 1954. This report also contains complete tables of data corresponding to the figures appearing in ref. 1. This report is available at the Library of Congress, Washington, D. C., or from the author on request.

(5) D. C. Grahame, E. M. Coffin and J. I. Cummings, Technical Report No. 2 to the Office of Naval Research, Aug. 11, 1950. Also available in abbreviated form in THIS JOURNAL, **71**, 2978 (1949); *ibid.*, **74**, 1207 (1952).

(6) NOTE ADDED IN PROOF.—At the suggestion of Dr. J. Ross Macdonald, we have repeated our calculation of C from C^0 using the more nearly complete theory of the diffuse double layer (including di-

ion is not specifically adsorbed (chemisorbed) on mercury at 25°. Then the observed differential capacity can be represented as the resultant of two capacitances in series, C^0 and C^d.[2] C^d is the differential capacitance of the diffuse double layer, whose value can be calculated for any desired conditions from the classical theory of the diffuse double layer.[2] C^0 is the capacitance of the region lying between the metallic surface and the outer Helmholtz plane. The latter is defined as the plane of closest approach of the electrical centers of the cations. C^0 has been calculated from the observed values of C in 0.916 N NaF together with the calculated values of C^d using the familiar equation for the capacity of two condensers in series. These values of C^0 are plotted in Fig. 1, along with the values of C from which they were obtained. C^0 is now regarded as a function of q, the surface charge density, as shown in Fig. 6. It is assumed that this functional dependence is *independent of concentration.* This assumption is inherently reasonable, since the region between the metallic surface and the outer Helmholtz plane is in essentially the same electrical condition, for a given value of q, whatever may be the state of affairs on the other side of the outer Helmholtz plane.[7] It should be mentioned, however, that C^0 is not expected or found to be altogether independent of the nature of the cation, and probably not of the anion either, although this point is more difficult to test experimentally.

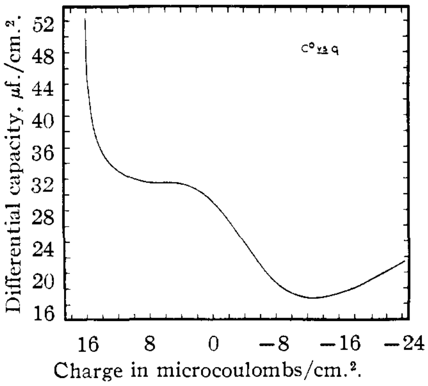

Fig. 6.—Differential capacity of the region lying between the metallic surface and the outer Helmholtz plane. Calculated from data on 0.916 M NaF at 25°.

From the observed dependence of C^0 upon q, one can calculate C at other concentrations, using values of C^d calculated from the classical theory of the diffuse double layer, and using as before the equation for the capacity of condensers in series. These are the values plotted in Figs. 2–5 along with the observed values. In Fig. 5 the capacity calculated by the method described above is labeled "method I." The agreement is seen to be very good in all but certain parts of the curve for 0.001 N NaF, and except under conditions of strong anodic polarization, where the assumption of the complete absence of chemisorption may be breaking down. Alternatively, the assumption that C^0 is solely a function of q may be slightly in error under these conditions, a fact which might arise from the ability of the fluoride ion to penetrate beyond the outer Helmholtz plane (*i.e.*, closer to the metal), thereby introducing some error into the calculation of the properties of the diffuse double layer.

The agreement achieved in these calculations represents a marked improvement over that achieved earlier (ref. 2, Figs. 12–14) by the same method but using inferior data.

The calculated and observed results at the potential of the e.c.max. at four different concentrations are presented in Table II. Here the agreement is good even in 0.001 N solution. In this solution the good agreement extends from about −0.2 to −0.65 volt, as Fig. 5 shows.

TABLE II

CALCULATED AND OBSERVED VALUES OF THE DIFFERENTIAL CAPACITY OF THE ELECTRICAL DOUBLE LAYER AT A MERCURY–SOLUTION INTERFACE AT THE POTENTIAL OF THE E.C.MAX., SODIUM FLUORIDE SOLUTIONS AT 25°

Concn., N	C Obsd.	C Calcd.
0.916	25.71	
.66	24.83	25.18 (method I)
.10	20.66	20.76 (method I)
.01	13.06	12.81 (method I)
.001	6.00	5.76 (method I)
.001	6.00	6.11 (method II)

It is easier and more accurate to measure a small capacitance than a large one under the conditions of our measurements in a very dilute solution, and hence it is to be expected that the minimum capacity on the curve for 0.001 N NaF would be the most accurately determined point. The relatively high specific resistance of the 0.001 N solution severely taxes the accuracy of the method, and it was therefore suspected that the calculated values might be more nearly correct than the observed values where the two disagree. To test this point a second method of calculation was devised. This method, to be called method II, is very nearly one of pure thermodynamics; it makes only the added assumption that specific adsorption is absent. Since it has been shown[1] that this assumption is in surprisingly good agreement with experiment in 0.1 N potassium fluoride, it is surely not very risky to apply it to still lower concentrations of sodium fluoride. What was done was to calculate values of $(\partial C/\partial \mu)_{E^-}$ (where μ is the chemical potential) from two thermodynamic equations derived earlier in this program (equations 15 and 25 of reference 1). Enough values of $(\partial C/\partial \mu)_{E^-}$ were computed for each value of E^- to permit an integration of the function with respect to chemical potential. This gave a value of ΔC, the difference between the differential capaci-

---

electric saturation effects) worked out by us earlier [*J. Chem. Phys.*, **18**, 903 (1950)] taking the index m equal to 2. As one would anticipate, the values of C so obtained differ by no more than a few tenths of one per cent. from those calculated in the simpler manner described in the text because the "correction" made for dielectric saturation comes into the calculation twice with opposite effects of essentially the same magnitude.

(7) This statement assumes that the discrete nature of the ions which go to make up the charge of the diffuse double layer and the discrete nature of the images of these charges lying in the metallic phase do not materially alter the potential gradient within the region lying between the metallic surface and the outer Helmholtz plane. The experimental agreement between the observed and calculated values of the capacity reported in this paper lends support to this otherwise rather dubious assumption.

ties at the two concentrations whose chemical potentials represent the limits of the integration. What was done was to find the capacity of 0.001 *N* NaF from the experimental data for 0.01 *N* NaF using this method. The result is presented in Fig. 5. As anticipated, the two kinds of calculated values agree with one another fairly well even at those potentials where the observed and calculated values (by method I) disagree. It is gratifying to note that where the results calculated by method I agree with the observed values, the results calculated by method II agree with both.

These results tend to confirm our belief that outside of the voltage range -0.2 to -0.65 v. the experimental data in 0.001 *N* NaF show the effect of overstepping the limits of concentration and potential at which the experimental method used by us may be considered to be sufficiently accurate. It should be realized that this situation is inevitable in any series of measurements which is carried to the limits of which the apparatus is capable. Because we now have *calculated* results on which we believe we can rely for 0.001 *N* sodium fluoride over a larger voltage range, it should be possible to use these results as a guide toward the further development of the experimental method.

Perhaps the most important conclusion to be drawn from the agreement between the calculated and observed values of the differential capacity is that the classical theory of the diffuse double layer is more reliable in practice than has generally been supposed or than one might expect from the rather dubious character of the assumptions upon which it is based. In particular the theory assumes that the work needed to transport an ion of charge $z_i\epsilon$ from the interior of the solution to a region of potential ψ is $z_i\epsilon\psi$. The potential ψ is assumed to vary along one coördinate only and is assumed to be uninfluenced by the approach of the ion in question. These are the assumptions inherent in the use of the Poisson–Boltzmann equation and are therefore fundamental to the Debye–Hückel theory of interionic attraction as well. The success of that theory gives added proof of the practical validity of the above-stated assumptions, regardless of their debatable logical foundation.

All of the applications of the Poisson–Boltzmann equation agree in showing that the proper value of the dielectric constant to be used is the "normal" value for the solvent, not corrected for dielectric saturation effects. This also agrees with the conclusions of Latimer, Pitzer and Slansky.[8] This does not mean that dielectric saturation does not occur in the diffuse double layer, but only that the effects of dielectric saturation in the diffuse part of the double layer do not make themselves felt in quantities which are susceptible to measurement. The region lying between the metallic surface and the outer Helmholtz plane is subjected to much greater field strengths and undoubtedly is strongly influenced by dielectric saturation effects. With this the theory of the diffuse double layer is not concerned, but it should be understood that the calculations employed in this paper do not ignore it. It is taken into account implicitly through the introduction of the capacity C^0 whose value is ascertained empirically.

Conclusion

The success of the calculations by method I go far toward proving the validity of the assumptions which underlie them. In particular it seems to be demonstrated rather conclusively that in the absence of specific adsorption the differential capacity of the region between the metallic surface and the outer Helmholtz plane is a function of q, the surface charge density, and not of the concentration of the adjacent electrolyte. There is as yet no way of applying this concept in the presence of specific adsorption. It is once again demonstrated that the classical theory of the diffuse double layer is in agreement with the observable facts.

Acknowledgments.—This work has been supported by the Office of Naval Research. The author is indebted to Mary F. Fitzpatrick for carrying out the calculations herein described.

AMHERST, MASSACHUSETTS

---

(8) W. M. Latimer, K. S. Pitzer and C. M. Slansky, *J. Chem. Phys.*, **7**, 108 (1939).