[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE ENERGY OF SOLUTION OF GASEOUS IONS IN RELATION TO THE EFFECT OF A CHARGE UPON THE DIELECTRIC

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The reaction, ion gas equals ion solution, may be considered as the link by which we can connect the rapidly accumulating information concerning the ionization potential of gaseous atoms with our knowledge of electrode potentials and, in general, the whole subject of the behavior of ions in solution. Born[1] has pointed out that, if the ions be considered as spheres of radius r and charge e, the energy of solution should be given by the expression $\Delta E = (e^2/2r)(1-(1/D))$, where D is the dielectric constant of the solvent. From a consideration of the data then at hand Born concluded that the values of the radii of the positive ions computed from the energies of solution were in general smaller than those calculated by Bragg and Bragg[2] from crystal structures for the effective atomic radii. It would seem, however, from the calculations presented in this paper that a remarkably close agreement exists between the two values for the atomic radii, and that the energy of solution of the positive ions is almost wholly due to the effect of the charge upon the dielectric.

Energies of solution of gaseous ions were first calculated by Fajans.[3] His original work was in error because of the neglect of the photo-electric energy difference which exists between electrons in gas and electrons in metal. However, the values for the alkali metal ions given in his later article are in approximate agreement with those calculated in this paper.

As a typical example we may consider the calculation of the energy of solution of Na^+. The steps involved and the corresponding energies are

$$\begin{array}{ll}
\text{Na(gas)} = \text{Na(metal)} & ;\ \Delta E = -27\ \text{k.cal.}\\
\text{Na}^+\text{(gas)} + \text{E}^-\text{(gas)} = \text{Na(gas)} & ;\ \Delta E = -118\\
\underline{\text{Na(metal)} = \text{Na}^+(1\ M) + \text{E}^-\text{(gas)}} & \underline{;\ \Delta E = \quad 49}\\
\text{Na}^+\text{(gas)} = \text{Na}^+(1\ M) & ;\ \Delta E = -96
\end{array}$$

The energy of the first reaction is obtained from the heat of sublimation with a small correction for the difference, $\Delta(PV)$, between ΔH, the heat, and ΔE, the energy. The energy of the second reaction, the ionization potential of sodium gas, is obtained from spectroscopic data as the energy corresponding to the head of the $(1s-mp)$ series for sodium. The energy of the third reaction is obtained as the sum of three quantities, two of which are not known with great accuracy. In the first place, the absolute values of the single electrodes are based upon the determination of the calomel electrode. The older values from the dropping electrode and the

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[1] Born, *Z. Physik*, **1**, 45 (1920).

[2] Bragg and Bragg, "X-Rays and Crystal Structure," Bell and Sons, London, **1924**.

[3] Fajans, *Ber. physik. Ges.*, **21**, 549 (1919); **21**, 709 (1919).

capillary electrometer gave the mercury as 0.56 volt positive in respect to the solution. The more recent work of Billitzer[4] and of Garrison[5] gives —0.13 volt. Merely as an average the value + 0.22 has been chosen, so we may write $Hg + Cl^- = HgCl + E^-$ (in metal); $\Delta F = 5.1$ k.cal. In order to obtain the energy of removing the electron from the metal to the gaseous state, we will use the long wave-length limit for the photoelectric effect for mercury,[6] $\lambda = 2600$, which gives $\Delta E = 109.3$. Then we obtain $Hg + Cl^- = HgCl + E^-$(gas); $\Delta F = +114.4$ k.cal., neglecting the small difference between ΔF and ΔE for the photoelectric reaction. Combining this reaction with the reaction $HgCl + Na = Hg + Na^+(1\,M) + Cl^-(1\,M)$; $\Delta F = -68.6$ k.cal., we obtain Na (metal) $= Na^+(1\,M) + E^-$(gas); $\Delta F = 45.8$ k.cal.

Now in order to complete our calculation of ΔE we must know ΔS, the entropy change. For this calculation the difficulty exists that in general we have no values for the absolute entropies of ions in solutions. The calculations were first made on the assumption that ΔS was so small that ΔF could be taken equal to ΔE. Further consideration showed this to be true in many reactions, while in others the difference amounts to a good many kilogram calories. The simple calculation of the sum of the entropies of the ions of a salt in solution shows that these values are less than the corresponding values from the Sackur equation for the ions as gases by a quantity which is roughly proportional to the heats of solution of the ions.[7] An approximate value of the proportionality factor has been chosen from a large number of different salts. We may then write $S_{Na^+(1\,M)} = 3/2(R\,ln \text{ at. wt.}) - (0.014 \times \Delta E_{\text{solution}}) + 25.7$. The approximate value for ΔE of sodium has been used to determine the entropy of sodium ion. This value, 21 entropy units, and the entropies of sodium metal and the electron gas, as summarized by Lewis, Gibson and Latimer[8] then gives $\Delta S = 12$ entropy units; and Na(metal) $= Na^+(1\,M)$; $\Delta E = 49$ k.cal.

Table I gives a summary of the data used in similar calculations for the ions listed. This list includes all the ions whose ionization and electrode potentials are known, with the exception of Hg^+ which has been omitted because of its formula Hg_2^{++} in solution.

The energies of sublimation are based largely upon the values given by Hildebrand.[9] For barium and strontium his rule has been to estimate the heat of vaporization from the approximate boiling points. A slightly

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[4] Billitzer, *Z. physik. Chem.*, **48,** 513 (1904); **51,** 166 (1905).

[5] Garrison, THIS JOURNAL, **45,** 37 (1923).

[6] Pohl and Pringsheim, *Ber. physik. Ges.*, **13,** 474 (1911).

[7] A discussion of the absolute values of the entropy of aqueous ions will be given by the author in a subsequent paper.

[8] Lewis, Gibson and Latimer, THIS JOURNAL, **44,** 1008 (1922).

[9] Hildebrand, *ibid.*, **37,** 970 (1915); **40,** 45 (1918). *Chem. Rev.*, **2,** 395 (1926).

TABLE I

SUMMARY OF DATA USED IN CALCULATING ΔE OF SOLUTION

	ΔE of sublimation	E.m.f. against hydrogen	ΔS of electrode	ΔE of electrode	ΔE of ionization	$-\Delta E$ of solution
H^+	36[a]	0	-7[b]	106	312	242
Li^+	39	2.94	+12	44	124	119
Na^+	27	2.71	12	49	118	96
K^+	21	2.92	11	44	99	77
Rb^+	20	2.92	13	45	97	72
Cu^+	75	-0.51	15	124	177	128
Ag^+	62	-0.80	16	131	174	107
Mg^{++}	35	2.3	-27	102	521	454
Ca^{++}	47	2.8	-20	81	413	379
Sr^{++}	38	2.8	-15	83	383	338
Ba^{++}	32	2.6	-12	93	350	289
Zn^{++}	31	0.76	-28	173	636	494
Cd^{++}	26	0.40	-20	192	606	440
Al^{+++}	56	1.34	-100	200	1205	1061

[a] Heat of dissociation of hydrogen. There seems to be no reliable value at present; 72,000 cal. is taken as an approximate figure, in agreement with the work of Olson and Glockler, *Proc. Nat. Acad. Sci.*, **9**, 122 (1923).

[b] The entropy of hydrogen ion appears to be somewhat larger than the value given by the author's approximate equation.

lower value for lithium, based upon a slightly lower boiling point, has been used. In obtaining ΔE_{298} from the heats of fusion and vaporization small corrections have been made for ΔC_p and $\Delta(PV)$ terms.

The normal electrode potentials have been taken from the tables given by Lewis and Randall,[10] with the exception of magnesium, calcium, barium, strontium and aluminum. The first four are from concordant checks obtained from thermal data for both the oxides and fluorides, together with Tamele's value[11] for the calcium electrode. For aluminum Heyrovský's value —1.34 has been used.[12] These electrode potentials have been checked approximately, using the authors' values for the entropy of the ions.

The gaseous ionization potentials are taken from the Bulletin of the National Research Council,[13] with the exception of the three ionization steps for aluminum. These values, 5.96, 18.08 and 28.3, are obtained from spectra data by Fowler[14] and by Paschen.[15]

Table II gives a comparison of the experimental energies of solution and

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[10] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, **1923**.

[11] Tamele, *J. Phys. Chem.*, **28**, 502 (1924).

[12] Heyrovský, *J. Chem. Soc.*, **117**, 27 (1920).

[13] *Nat. Research Council Bull.*, **9**, 94 (1924).

[14] Fowler, *Proc. Roy. Soc. (London)*, **103A**, 413 (1924).

[15] Paschen, *Ann. Physik*, **71**, 142 (1923).

TABLE II

COMPARISON OF EXPERIMENTAL AND CALCULATED ENERGIES OF SOLUTION

	ΔE of solution		Radius of ion $\times$ 10^8 cm.	
	Exptl.	Calcd. from R	Bragg and Bragg	Calcd. from ΔE
H^+	242	225	0.73[a]	0.68
Cu^+	128	119	1.38	1.28
Li^+	119	110	1.40–1.60	1.38
Ag^+	107	116–96	1.42–1.72	1.53
Na^+	96	94	1.75	1.71
K^+	77	78	2.10	2.13
Rb^+	72	72	2.28	2.28
Zn^{++}	494	486	1.35	1.33
Mg^{++}	454	453	1.45	1.45
Cd^{++}	440	410	1.60	1.49
Ca^{++}	379	375	1.75	1.78
Sr^{++}	338	337	1.95	1.94
Ba^{++}	289	305	2.15	2.27
Al^{+++}	1069	1070	1.38	1.38

[a] From the crystal-structure data on ice.

those calculated from the crystal structure radii of Bragg and Bragg,[16] using the expression $\Delta E = (e^2/2r)(1-(1/80))$. A comparison is also given of the values of the radii given by the reverse calculation. The agreement is indeed surprising. The results appear to lead definitely to the conclusions (1) that specific energy of combination of the various ions with water is small in comparison with the effect of the ion as a charged particle upon the water as a dielectric, and (2) that the effective size of the ions in terms of the distance of approach of a water molecule corresponds very closely to the effective sizes as calculated from crystal data. The agreement is of course somewhat fortuitous considering the uncertainty in the values of the absolute potential of the calomel electrode and the photo-electric limit for mercury. However, the case of aluminum, where these quantities are small in comparison with the ionization potential lends considerable weight to the belief that the general conclusions are correct. The effective size of the positive ions has, of course, no significance in respect to the actual size of the outer electron shell of the kernel. It is rather the distance at which the forces of attraction and repulsion for a negative ion just balance. For many of the ions this effective size is remarkably constant in all of the compounds. On the other hand, silver, for example, forms two series of compounds with radii of 1.42 and 1.72. Since silver oxide, Ag_2O, has the radius 1.42, this seems to be the logical value to use for comparison in water solutions, but the calculated radius falls between the two.

Although it would seem that specific effects of the solvent are relatively small, they must be fairly large in some instances. Thus silver chloride

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[16] Ref. 2, p. 170.

is readily soluble in ammonia with a dielectric constant of 16, whereas its predicted solubility is less. It may be that this abnormality is due to the formation of a definite non-polar bond between the silver and ammonia or to a slight ionization of the silver chloride in liquid ammonia; on the other hand, it may be connected with the abnormality of silver in possessing a seemingly variable effective radius. The alkali metals with the exception of lithium show no such variation in their compounds, and the alkali halides are slightly soluble in ammonia as predicted.

An interesting check would be the calculation of the potential of an electrode in a solvent other than water. Unfortunately there appear to be no data at present to use for a comparison. Likewise the data on solubilities and heats of solution of polar compounds in other solvents are extremely meager. In general, polar compounds do not dissolve in solvents of low dielectric constant. There are a few cases of great solubility[17] but the salt molecule highly hydrated is un-ionized. It is hoped that the extension of the calculations to other solvents may be made shortly.

It does not necessarily follow from the agreement obtained with the positive ions that equal agreement exists for the negative ions. As yet we have no reliable data for the electron affinity of the negative elements. It seems worth while, however, to assume that the negative ions behave similarly to the positive ions and use the crystal structure data to calculate the electron affinities of chlorine, bromine and iodine.

TABLE III

SUMMARY OF DATA USED IN CALCULATING ELECTRON AFFINITY

	$r \times 10^{-8}$	$-\Delta E$ of solution	E.m.f. against hydrogen	ΔE of reaction	ΔE of dissociation	Electron affinity
Cl^-	1.02	161	1.4	143	35	17
Br^-	1.17	140	1.1	136	21	17
I^-	1.35	122	0.5	124	17	19

Table III summarizes the data used and the results of the calculation. The calculated electron affinities are considerably less than the values obtained by Born from crystal-lattice energies. However, great reliability cannot be accredited to these values of Born.[18] At present there appears to be no check upon these calculations of electron affinity.

By means of the author's equation for the dependence of the entropy of ions upon the heat of hydration, a rough confirmation may be obtained for the heat of solution of the halides. Thus the sum of the entropies of the sodium and chloride ions in 1 *M* solution is approximately 40 entropy units. Using 96 for ΔE of the sodium ion and 161 for ΔE of the chloride ion, we calculate 35 entropy units as the sum of the entropies of the two

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[17] See Latimer and Rodebush, THIS JOURNAL, **42**, 1529 (1920).

[18] See Born and Gerlach. *Z. Physik.* **5**, 433 (1921); and Latimer, THIS JOURNAL, **45**, 2803 (1923).

ions. Moreover, the entropies of bromides and iodides in 1 *M* solution, after correcting for the mass, are approximately 3 and 6 units, respectively, less than those of the chlorides, which is in agreement with the differences in the heats of solution.

It may also be pointed out that the results presented in this paper offer strong support to the Debye treatment of solutions of strong electrolytes, although the values which he calculates for the radii of influence of the ions are considerably larger.

Summary

The energies of solution of fourteen ions have been calculated.

The radii of the ions calculated from the relation $\Delta E = (e^2/2r)(1-(1/D))$ are found to agree very closely with the values of Bragg and Bragg for ionic radii.

Approximate values for the entropies of ions in aqueous solution have been given.

Values for the electron affinities of chlorine, bromine and iodine have been calculated.

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[CONTRIBUTION FROM THE LABORATORIES OF THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH]

DISSOCIATION OF POLYVALENT SUBSTANCES
I. RELATION OF CONSTANTS TO TITRATION DATA

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I. Notation.—The notation used in this article is as follows.

Constants.—K_1', K_2', K_3'. etc. = "Dissociation constants" of a polyvalent acid base or ampholyte, not corrected for activity, and representing the "*steps*" in formation of more negative ions from less negative ions (or molecules). These constants do not refer to groups.

G_1', G_2', G_3', etc. = "Titration constants" obtained by calculating the titration data as if the solution contained monovalent acids in equivalent quantities.

K_1, K_2, K_3, etc. = Dissociation constants corrected for activity.

G_1, G_2, G_3, etc. = Titration constants corrected for activity.

K_0^{I}, K_0^{II}, K_0^{III}, etc. = "Intrinsic constants" of the individual *groups*.

Concentrations (lower case letters).—α_1, α_2, α_3, = Probabilities of dissociation according to G_1', G_2' and G_3'. respectively.

u = Fraction of a substance in un-ionized form.

m = Fraction of a substance in mono-ionic form (mono-ion singly charged ion).

d = Fraction of a substance in di-ionic form (di-ion doubly charged ion).

t = Fraction of a substance in tri-ionic form (tri-ion triply charged ion).

n = Fraction of a substance in the more negative form (predominating at a lower P_{H} than P_{K}).

p = Fraction of a substance in the more positive form (predominating at a higher P_{H} than P_{K}).