THE IONIZATION OF SALT VAPORS
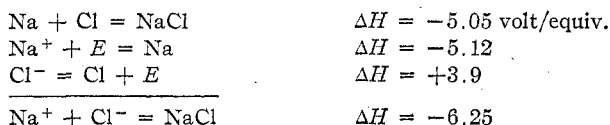
BY WENDELL M. LATIMER

A study of the energies of formation of the simpler chemical compounds seems to offer a promising method of investigating the problems of molecular structure; and now that data are available for the calculation of the heats of ionization of the vapors of the hydrogen and alkali halides, it is important to consider these heats from the standpoints of both the static and dynamic theories of atomic structure. The heats of ionization are also interesting in that they enable us to calculate the degree of ionization of these salt vapors and thus dispel any doubt as to their very slight ionization.

The heat of ionization of a salt vapor may be calculated from the heat of formation of the salt vapor from its elements in the state of monatomic vapors, the ionization potential of the metal and the electron affinity of the negative element. The corresponding equations for sodium chloride are:

$Na + Cl = NaCl$	$\Delta H = -5.05$ volt/equiv.
$Na^+ + E = Na$	$\Delta H = -5.12$
$Cl^- = Cl + E$	$\Delta H = +3.9$
$Na^+ + Cl^- = NaCl$	$\Delta H = -6.25$

In order to obtain the heat of the first reaction the values tabulated by Wortenberg and Schulz[1] were used for the heat of formation of sodium chloride from metallic sodium and molecular chlorine,—99,000 cal., the heats of sublimation of sodium metal, 30,000 cal., and of sodium chloride, 48,000 cal., and the value of Trautz and Stackel[2] for the dissociation of the chlorine molecule into atomic chlorine, 71,000 cal. The change of the heat of the reaction with temperature is less than the experimental error in some of the data and has therefore been neglected. The value for the heat of the reaction in calories, namely, 116,500, has been converted to volt equivalents, since the spectroscopic data which we shall use are more commonly expressed in this unit.

The heat[3] of the second reaction, 5.12 volts, is known accurately as the energy corresponding to the head of the $(1s-mp)$ series of sodium. The electron affinity of chlorine, according to Franck's[4] interpretation of the spectra of the halogens, is given by the head of the series converging at 3180. This value, 3.9 volts, is somewhat in doubt; however, it leads to a heat of

[1] Wortenberg and Schulz, Z. Elektrochem., 27, 568 (1921).

[2] Trautz and Stackel, Z. anorg. Chem., 122, 81 (1922).

[3] Compare Foote and Mohler, "Origin of Spectra," American Chemical Society Monograph, Chemical Catalog Co., 1922, p. 65.

[4] Franck, Z. Physik, 5, 428 (1921). Steubing, Ann. Physik, 64, 673 (1921). Angerer, Z. Physik, 11, 167 (1922).

ionization of hydrogen chloride (see Table I) which is in agreement with the experimental value of Foote and Mohler.[5]

In a similar manner (1) the heats of formation from their elements as atomic gases, and (2) the heats of ionization of the hydrogen and alkali chlorides, bromides and iodides have been calculated and are given in Table I. The electron affinity of bromine, 2.9, and iodine, 2.6, and the other data for the alkali halides have been taken from the same sources as those for sodium chloride, except the values for the dissociation of molecular bromine, 42,000 cal., and molecular iodine, 35,000 cal., which are approximate values taken from the calculations of Lewis and Randall.[6] For the heats of formation of hydrogen chloride, bromide and iodide from their elements as diatomic gases the values of Lewis and Randall have again been used: 22,000, 12,000 and 1500, respectively. The dissociation of hydrogen, 3.1 volts, is that given by Olsen and Glockler.[7]

TABLE I

HEATS OF FORMATION FROM ELEMENTS AS MONATOMIC VAPORS AND HEATS OF IONIZATION IN VAPOR STATE

	ΔH Formation	Ionization		ΔH Formation	Ionization		ΔH Formation	Ionization
HCl....	−4.05	13.6	HBr...	−3.0	13.6	HI....	−2.4	13.3
LiCl....	−6.1	7.6	LiBr..	−5.6	8.1	LiI,...	−4.4	7.2
NaCl...	−5.05	6.25	NaBr..	−4.5	6.7	NaI...	−4.0	6.5
KCl....	−5.3	5.7	KBr...	−4.75	6.15	KI....	−4.2	5.9
RbCl...	−5.4	5.7	RbBr..	−4.75	6.05	RbI...	−4.2	5.8
CsCl....	−5.4	5.4	CsBr..	−4.8	5.8	CsI...	−4.2	5.5

It will be observed that for a given halide the heats of ionization are in the same order as the ionization potential of the positive atoms, and that, in general, the work of ionizing a halide from a positive ion is not much greater than that of removing the valence electron. It may also be observed that these compounds do not form, as is often stated, because of the greater affinity of the halide for the electron. Thus, hydrogen and chlorine combine in spite of the fact that it requires 13.54–3.9 or 9.64 volts to take the electron off the hydrogen and put it on the chlorine.

Ionization Constant for Sodium Chloride

The ionization constant for the reaction, $NaCl = Na^+ + Cl^-$, may be calculated from the relation: $-RT \ln K = \Delta H - T\Delta S$. For ΔH, the heat of ionization, we have found 6.25 volts or 144,000 cal. For ΔS, the entropy change of the reaction of 298°K. and 1 atmosphere, the value 22.4 is obtained using for the entropy of Cl^- 36.3, and of Na^+ 35.1, as given by the Sackur equation[8] and for the entropy of sodium chloride 49.0, as given

[5] Ref. 3, p. 186.

[6] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., 1923.

[7] Olsen and Glockler, *Proc. Nat. Acad. Sci.*, 9, 122 (1923).

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

by the approximate equation of Latimer[9] for the diatomic gases. Taking ΔC_p for the reaction as 2.5 cal./deg., ΔS_{1725} is 26.8 at the boiling point of sodium chloride. Then for the equilibrium constant at the boiling point, $-1725 \times 4.59 \log K = 144{,}000 - 1725 \times 26.8$, and for K we find 4×10^{-13}. The partial pressure of either of the ions in the vapor at $1725°K.$ and 1 atmosphere is then 6×10^{-7} atmospheres. In other words, sodium chloride vapor is ionized to about the same extent as liquid water at ordinary temperatures. Indeed, if we calculate in a similar manner the dissociation of sodium chloride vapor into atomic sodium and chlorine, we find this decomposition to be almost a hundred fold greater than the ionization. Using the same method as that employed for sodium chloride, the ionization constant of all the compounds in Table I may be determined. In every case the ionization would be found to be extremely small.

Heats of Ionization and Atomic Structure

The method which Born[10] has used to calculate the energy of the crystal lattice for the alkali halides has been (1) to determine the field of force about an ion, and (2) from the field of force to calculate the energy of combination as due entirely to the change in electrostatic potential of the ions. We wish to consider the validity of this method in connection with the heats of ionization which have been given in Table I.

Spectroscopic data, as interpreted by the Bohr theory, seem at present to offer the only exact method of determining the field of force about an ion. The simplest case is, of course, the hydrogen ion; and here, from the completeness of Bohr's explanation of the hydrogen spectra, we may conclude that the field of force, up to a few tenths of an Ångström unit (10^{-8} cm.), corresponds exactly to the inverse square for a charge equal to, but of the opposite sign to that of the electron.

The fields of force for the more complicated ions are not so simple. However, even in these cases, considerable information can be gained from spectroscopic data. Thus, for lithium, the energy of the atom with the electron in the first external, circular orbit may be found from the head of the $(2p-ms)$ series as 3.53 volts. The energy for the corresponding orbit of hydrogen, the 2_2 orbit, is 3.38 volts; and we may calculate from the Bohr theory that the radius of the orbit is 2.08 Å., and at that distance, the field about the lithium ion corresponds to an effective positive charge of 1.02. For the energy levels at greater distances the effective charge approaches unity very closely. For the interval between 2.08 Å. and the inner electrons, the field of force cannot as yet be determined. However, in order to get an approximate value for this field, we may calculate an average position of the two inner electrons in respect to the nucleus

[9] Latimer, THIS JOURNAL, **43**, 818 (1921).

[10] Born, *Verb. Physik. Fes.*, **21**, 13 (1919); **21**, 679 (1919).

of 3 positive, Fig. 1, that would give an effective charge of 1.02 at a distance of 2.08 Å., along a: $3 - 2 \times \dfrac{2.08^3}{(2.08^2 + b^2)^{3/2}} = 1.02$. This gives b equal to 0.17 Å.[11] Without attempting to attach more than a qualitative significance to the result, the curve for lithium in Fig. 2 has been drawn for the change in the effective charge as the ion is approached along the line "a." Actually, the effective charge must increase somewhat more rapidly than indicated by this approximate treatment.

Likewise, for sodium, we may calculate the energy of the electron in the first external energy level, the 3_3 orbit. In this case it is given by the head of the series at 12,274, and the energy is 1.515 volts. This value corresponds to a radius of 4.8 Å. and an effective charge on the kernel of 1.005 at that distance. If the electrons in the outer shell of the sodium ion were located in definite fixed positions, this value just obtained would serve as a very useful starting point to determine exactly the field at closer distances. At present, although we are confident that the field becomes more positive closer to the ion, we are not in a position to determine it exactly.
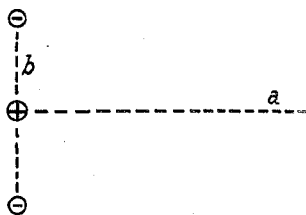
Spectroscopic data are available for similar calculations for all of the alkali metals.[12] However, in the heavier atoms, the first external orbit is out so far, as was the case for sodium, that the field is practically unity, and we are unable to judge the nature of the field closer to the atom. As yet the spectra of the halides have not been worked out sufficiently to give any definite knowledge in regard to the fields of force about the negative ions. However, we may safely say that at a distance, a chloride ion, for example, acts as a unit negative charge, and at closer distances the sign of the field changes to positive.

Fig. 1

Now let us consider the problem of determining the heats of ionization from the fields about the ions. From our knowledge in regard to the quan-

[11] We may also make use of the assumption that the orbits of the two inner electrons are the same as in helium, in order to obtain an idea of their size. The ionization potential of the first electron of He is 24.5 volts and of the second 54.1. Hence, we may write $78.6 = 2 \times 13.54 \, (2 - \alpha)$. This gives for α, the screening constant, 0.296. Using this same screening constant for lithium ion, the radius of the orbit would be $\dfrac{0.53}{3 - 0.296}$ or 0.2Å. if the orbits were circular. Hence, it would seem that the value obtained for b above is reasonable. It is also interesting to note that if we use this same screening constant for hydride ion we obtain 0.14 volts as the electron affinity of hydrogen. This is about the value to be expected from the stability of the hydride ion.

[12] Birge and Brackett, paper read before the American Physical Society, April, 1923. The relation which these authors have traced between the external and internal orbits seems to give quite accurately the field of force acting upon the electrons of the atomic kernel. It does not, however, give the force acting upon an additional electron.

tum relations in the dynamic atomic systems, it might be predicted that the total decrease in potential energy of the system would be divided equally between the increase of kinetic energy of the electrons and the energy liberated.   In such a case it would be meaningless to calculate the heats of ionization in terms of the effective charges on the ions.   It is of interest, however, to overlook such an *a priori* assumption and see how far we can go toward calculating the heat of ionization from the fields of force and the assumption that the energy is due to the change in electrostatic potential of the ions.

In the gaseous molecule of hydrogen chloride the atomic centers are separated 1.27 Å., as determined from the band spectra[13] of the molecule. If unit positive and negative charges separated by infinity were brought up to this distance, the decrease in potential energy, eE/d would be 11.3
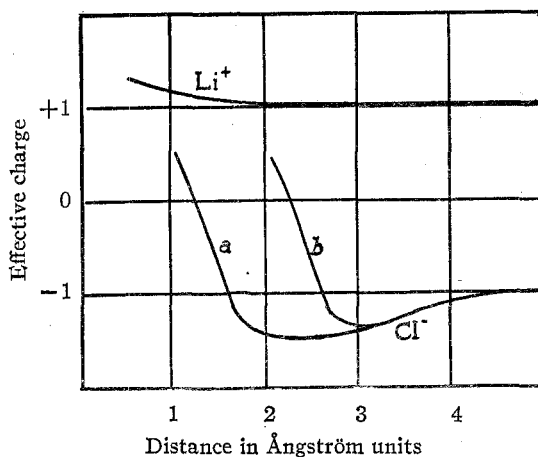

Fig. 2

volts.   Experimentally, we have found 13.6 volts for the ionization of hydrogen chloride.   This larger value might be accounted for by assuming an increase in the effective charge of the chloride corresponding to Curve a, Fig. 2.   However, from a consideration of the heat of ionization of lithium chloride, we obtain quite a different effective charge for the chloride.   The closest approach of a lithium ion and chloride ion in the solid is 2.55 Å. The band spectra for the lithium chloride are not known but, in general, the diameters of gaseous molecules are approximately 10% less than in the solid.[13b]   Using 2.3 Å. as the separation of atomic centers, in order to obtain a change of potential energy of 7.3 volts, we should have to assume that the curve for the effective charge on the chloride ion corresponds roughly to b, Fig. 2.

    [13] (a) Reiche, *Ann. Physik,* **58,** 657 (1919).   (b) Urey, THIS JOURNAL, **45,** 1445 (1923).

In other words, the presence of a positive ion affects the whole structure of the chloride ion. It is obvious, then, that the total energy change cannot be found from the change in potential energy of the ions as a whole considered as rigid structures, but must take into account the changes of potential (and probable kinetic) energy of the electrons in each ion as well.

The approximate treatment of the electrons in a dynamic atom, as located in definite positions, may be justified on the ground that these positions represent time average or effective positions.[14] The greatest objection, however, to the treatment of Born and his associates is the assumption of a rigid structure and thus a complete neglect of changes in energy due to the distortion of the electronic arrangement. It would seem that further attempts in this direction are not likely to be profitable.

Summary

A tabulation has been made of the heats of ionization in the gaseous state of the hydrogen and alkali chlorides, bromides and iodides.

The ionization constant of sodium chloride at its boiling point has been found to be 4×10^{-13}.

From a consideration of the fields of force about the ions and the molecular diameters it would seem that the heats of ionization cannot be calculated by any method which treats the ions as rigid structures of electrons about a positive center.

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A THEORY OF CHEMICAL REACTIVITY

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The influence of temperature on the rate of chemical change is so marked that it is obviously a very important factor in any theory of chemical reactivity. Explanations for the high temperature coefficients of chemical reactions usually center round the empirical equation of Arrhenius[1] connecting velocity of reaction and temperature, which in the integrated form is $2.3026 \log k_1/k_2 = \dfrac{Q}{R}\left(\dfrac{1}{T_2} - \dfrac{1}{T_1}\right)$. Considering the hydrolysis of cane sugar by hydrochloric acid in aqueous solution, Arrhenius suggested that the cane sugar was present in two forms, active and inactive, in mass-action equi-

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[14] Thus, the fundamental idea of G. N. Lewis' theory of valence, that in non-polar compounds a chemical bond consists of a pair of electrons, remains essentially the same whether we consider the electrons as actually located between the atoms or rotating in orbits with that position as their effective location.

[1] Arrhenius, Z. physik. Chem., 4, 226 (1889).