[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

CHEMICAL AFFINITY AND ELECTRON AFFINITY

BY ROSCOE H. GERKE

RECEIVED FEBRUARY 9, 1924

Chemical affinity is attributed to the tendency of atoms to form groups of eight electrons in the outer valence shell, according to the theories of Lewis,[1] of Langmuir[2] and of Kossel.[3] Andrade[4] states that Lewis was the first to recognize that the chemical bond can be attributed to the sharing of electrons.

It is the purpose of this paper to exhibit data which indicate that the tendency of an electronegative halide atom to form a group of eight electrons in its outer shell by sharing the electron of an electropositive atom is, in the simple cases, quantitatively measured by the electron affinity of the halide atom.[5] In order to make this relation quantitative, it will be necessary to restrict the discussion to the energies of formation of compounds in the vapor state from atoms in the vapor state. For example, the heat or energy of formation of hydrogen chloride from hydrogen atom and chlorine can be calculated from thermal data, which include the heats of dissociation of hydrogen and of chlorine and the ordinary heat of formation of hydrogen chloride. Equation 3 represents the formation of hydrogen chloride from the atoms and the energy of the reaction is —99.5 Cal. or 4.3 volt-equivalents. The electron affinity[6] of chlorine atom

$$\begin{aligned} {}^1/_2\,Cl_2 &= Cl;\ \Delta E = 35.0\ \text{Cal.} && (1)\\ {}^1/_2\,H_2 &= H;\ \Delta E = 42.5\ \text{Cal.} && (2)\\ H + Cl &= HCl;\ \Delta E = -99.5\ \text{Cal.} && (3)\\ \hline {}^1/_2\,H_2 + {}^1/_2\,Cl_2 &= HCl;\ \Delta E = -22.0\ \text{Cal.} && (4) \end{aligned}$$

is the energy given out when an electron combines with a chlorine atom to produce a negative chlorine ion. Equation 5 represents this process,

$$\cdot + \cdot\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}: \;=\; :\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}: ;\ \Delta E = 3.9\ \text{volt-equivalents} \qquad (5)$$

and the energy given out is 3.9 volt-equivalents which is within experimental error[7] equal to the energy given out when a hydrogen atom combines with a chlorine atom to produce hydrogen chloride. This relation also holds for hydrogen bromide and hydrogen iodide, as shown in Table I.

---

[1] Lewis, THIS JOURNAL, **38**, 762 (1916).

[2] Langmuir, *ibid.*, **41**, 868 (1919).

[3] Kossel, *Ann. Physik*, **49**, 229 (1916).

[4] Andrade, "Structure of the Atom," Harcourt Brace and Co., **1923**.

[5] Gerke, *Science*, **58**, 312 (1923).

[6] The method of evaluating the electron affinity of atoms from continuous spectra is fully discussed by Foote and Mohler, "The Origin of Spectra," Chemical Catalog Co., **1922**.

[7] The thermal data, especially the heat of dissociation of chlorine and of hydrogen, are discordant at least to the extent of 5.0 Cal.

The fact that the energies of formation of the hydrogen halides from atoms are, respectively, substantially equal to the electron affinity of the halide atom is evidence that the tendency of an electronegative atom to share the electron of a hydrogen atom is measured by the electron affinity of the electronegative atom.

TABLE I

ENERGY OF REACTIONS IN VOLT-EQUIVALENTS

Reaction	Energy
$H^{\cdot} + .\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}: = H:\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}:$	4.3
$. + .\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}: = :\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}:$	3.9[8]
$H^{\cdot} + .\overset{\cdot\cdot}{\underset{\cdot\cdot}{Br}}: = H:\overset{\cdot\cdot}{\underset{\cdot\cdot}{Br}}:$	3.4
$. + .\overset{\cdot\cdot}{\underset{\cdot\cdot}{Br}}: = :\overset{\cdot\cdot}{\underset{\cdot\cdot}{Br}}:$	2.9[8]
$H^{\cdot} + .\overset{\cdot\cdot}{\underset{\cdot\cdot}{I}}: = H:\overset{\cdot\cdot}{\underset{\cdot\cdot}{I}}:$	2.9
$. + .\overset{\cdot\cdot}{\underset{\cdot\cdot}{I}}: = :\overset{\cdot\cdot}{\underset{\cdot\cdot}{I}}:$	2.6[8]

Further information as to the manner in which a halogen shares the electron of hydrogen may be obtained from the observation[9] that ionization potentials of the three hydrogen halides are practically equal to the ionization potential of the hydrogen atom. The experimentally determined ionization potentials of hydrogen chloride, bromide and iodide are, respectively, 13.7[10] and 14.4,[11] 13.8[11] and 13.4,[11] while the most recent determination of the ionization potential of the hydrogen atom is 13.54[12] volts. The energy necessary to remove a hydrogen nucleus from an electron in a hydrogen atom is approximately equal to that necessary to remove the hydrogen nucleus from its shared electron when the latter is shared by the chlorine atom in hydrogen chloride, if the very probable assumption of Foote and Mohler[6] as to the nature of the products of ionization is true. These two observations lead to a simple explanation of these reactions. If a hydrogen atom combines with a chlorine atom, electron and nucleus as a unit fall into place in such a way that the energy decrease is equal to that which would occur if the electron alone had fallen into the chlorine atom.

In order to test this relationship for halides of metals, the energies of formation have been calculated by a method which is similar to that employed for hydrogen chloride. In Table IIA, Col. 5, are listed the

---

[8] The electron affinities of chlorine, bromine and iodine are those taken from spectroscopic data, as summarized by Angerer, *Z. Physik*, **11**, 167 (1922).

[9] Latimer, THIS JOURNAL, **45**, 2803 (1923), also makes this observation and calculates the ionization potentials of the alkali halides.

[10] Foote and Mohler, *ibid.*, **42**, 1832 (1920).

[11] Knipping, *Z. Physik*, **7**, 328 (1921).

[12] Olmstead and Compton, *Phys. Rev.*, **22**, 559 (1923).

energies of formation in large calories of a few diatomic halides, where X and M, respectively, designate the halogen and the more electropositive atom. By adding the equations heading the first six columns, the equation heading the seventh column results, which is the heat of reaction of the substances in their ordinary state. The values in the fifth column are the energies or heats of reactions of the gaseous atoms to form the gaseous compound. Most of the data in Table II were taken from Lewis and Randall[13] except as mentioned below. The heats of vaporization of metals were calculated with the aid of Trouton's rule and the constant employed was 25 cal. per deg. The heats of evaporation of the halides were taken from the data of Ruff,[14] of Von Wartenburg and Bosse,[15] and of Eastman and Duschak.[16] The heat data for the chloro-iodides and -bromides, sodium bromide and iodide and stannic chloride were taken from Landolt-Börnstein-Roth "Tabellen." The greatest source of error in these data is probably in the heats of dissociation of the diatomic elements. At any rate, the data are consistent and an absolute accuracy

TABLE II

ENERGIES OF REACTIONS

A RELATION BETWEEN ENERGY OF REACTION OF ATOMS AND ELECTRON AFFINITY OF ELECTRONEGATIVE ATOMS

	A ENERGIES OF FORMATION OF DIATOMIC HALIDES						B ENERGY OF REACTIONS IN VOLT-EQUIVALENTS		
Compound	$\frac{1}{2}X_2 = \frac{1}{2}X_2(g)$	$\frac{1}{2}X_2(g) = X(g)$	$\frac{1}{2}M_2 = M(g)$ or $M = M(g)$	$M(g) + X(g) = MX(g)$	$MX(g) = MX$	$\frac{1}{2}X_2 + M = MX$	Energy of formation	Electron affinity	Difference
KCl	...	35.0	25.8	−124.4	−43.1	−106.7	5.4	3.9	1.5
NaCl	...	35.0	28.8	−117.3	−46.6	− 98.1	5.1	3.9	1.2
HCl	...	35.0	42.5	− 99.5	....	− 22.0	4.3	3.9	0.4
TlCl	...	35.0	45.0	−103.2	−25.1	− 48.3	4.5	3.9	0.6
AgCl	...	35.0	55.0	− 75.7	−44.3	− 30.0	3.3	3.9	−0.6
$\frac{1}{2}PbCl_2$	...	35.0	22.7	− 80.4	−20.3	− 43.0	3.5	3.9	− .4
$\frac{1}{4}SnCl_4$	...	35.0	18.5	− 83.4	− 2.1	− 32.0	3.6	3.9	− .3
NaI	7.0	17.1	28.8	− 82.6	−39.4	− 69.1	3.6	2.6	1.0
HI	7.0	17.1	42.5	− 68.0	....	− 1.4	2.9	2.6	0.3
AgI	7.0	17.1	55.0	− 49.7	−44.2	− 14.8	2.2	2.6	− .4
NaBr	3.3	20.5	28.8	− 98.5	−40.1	− 86.0	4.3	2.9	1.4
HBr	3.3	20.5	42.5	− 78.3	....	− 12.0	3.4	2.9	0.5
ICl	...	35.0	24.0	− 57.8	− 7.0	− 5.8	...	...	...
BrCl	...	35.0	23.8	− 52.5	− 7.0	− 0.7	...	...	...

---

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

[14] Ruff and Mugden, *Z. anorg. allgem. Chem.*, **117,** 147 (1921).

[15] Von Wartenburg and Bosse, *Z. Elektrochem.*, **28,** 384 (1921).

[16] Eastman and Duschak, *Bur. Mines Tech. Paper*, **225** (1919).

of 10 Cal. is sufficient for the present purpose. Heats of fusion and the effects due to change of temperature have been neglected. The calculated energies of formation (in the fifth column, Table II A) of the compounds have been divided by the factor, 23.0, to convert Cal. to volt-equivalents. In Table II B these energies of formation of the gaseous molecules and electron affinities of the electronegative atoms are tabulated together with the difference between these quantities.

Discussion

In general, it will be observed from the data in Table II B that the energies of combination of halide atoms with metal or hydrogen atoms are nearly the same as the electron affinities of the halide atoms. The closest agreement exists in the case of the hydrogen halides, which are the simplest molecules of this type. The alkali halides exhibit positive deviations, whereas the halides of the less electropositive elements such as the silver, lead and tin exhibit negative deviations. These deviations seem to be real in a qualitative rather than in a quantitative sense. Latimer[9] has discussed the positive deviations from the standpoint of the fields of force about the charged atoms at close distances. The viewpoint that the atoms react as a unit, however, would modify such a discussion. It seems that in the cases of the alkali halides there is a distortion of the arrangement of the electrons in the molecule in such a direction that the electron affinity of the halide atom is greater in the molecule than in a negative ion. The negative deviations may be due to a different cause. Thus, if the silver atom possessed some electron affinity, it may be that the electron affinity of chlorine would not be as completely satisfied as in the case of hydrogen chloride, in which the hydrogen atom may be regarded as possessing little or no electron affinity. It is possible that the close agreement of the energy of formation of thallous chloride with that of hydrogen chloride is accidental and is due to a balancing of positive and negative deviations.

Evidence of considerable distortion of the octets is found in the energy of formation of molecules from two atoms possessing electron affinity. When two chlorine atoms, each tending to satisfy their electron affinity, unite forming the chlorine molecule, the actual energy evolved per atom is 35.0 Cal., whereas if the electron affinity of each was satisfied the energy evolved would be 90.0 Cal. The difference of 55.0 Cal., which was not evolved, may be ascribed to a distortion of the octets, due possibly to a combination of the two effects described above. In Table III are shown these differences for the three halogens. It will also be observed that the energies of formation of bromine chloride and iodine chloride are roughly equal to one-half the sum of the energies of dissociation of their constituents, which may mean that the distortion of the octets around chlorine is the same in bromine chloride and iodine chloride as in molecular chlorine.

The energy of formation[17] of mercuric chloride from the atoms is 5.1 volt-equivalent, which is less than the electron affinity of two chlorine atoms by 2.7 volt-equivalent. In other words, there are 2.7 volt-equivalents of energy which are not given out by the reaction. This result leads to the suspicion that the mercury atom possesses an electron affinity, which prevents the chlorine atom from completely satisfying its electron affinity. Wood[18] and Child[19] have reported that mercury will yield a continuous spectrum which was produced by fluorescence of the mercury vapor, the spectrum extended from the yellow into the ultraviolet according to the photographs of Wood. Child produced the glow by electric means and found that "when the conditions are at their best the red is also visible." Taking 7000 Å. as an approximate value for the long wave length limit of the continuous spectrum and proceeding as in the case of the halogens,[8] the value 1.8 volt-equivalent is found for the electron affinity of mercury. Reverting to the apparent discrepancy in the case of the mercuric chloride, it is evident that this discrepancy is greater than 1.8 volt-equivalent, the provisional electron affinity of mercury, by 0.9 volt-equivalent. Therefore, if the mercury has an electron affinity of about 1.8 volts, the discrepancy between the energy of formation of mercuric chloride and twice the electron affinity of chlorine is largely explained.

TABLE III

ENERGIES OF REACTION IN LARGE CALORIES

	Dissociation	Electron affinity	Difference
$^1/_2$ Cl_2	35	90	55
$^1/_2$ BrCl	26	..	..
$^1/_2$ Br_2	20	67	47
$^1/_2$ ICl	29	..	..
$^1/_2$ I_2	17	60	43

In conclusion it may be stated that the chemical affinity of halide atoms for hydrogen atoms or the tendency of the halide atom to fill up its outer valence shell by sharing the electron of the hydrogen atom as calculated from thermal data is within experimental error measured by the electron affinity of the halide atom, and also that the halide atom shares the electron of the hydrogen atom in such a manner that the energy necessary to remove the hydrogen nucleus from its shared electron in the hydrogen halide is equal to that necessary to separate the hydrogen nucleus from its electron

---

[17] These data were obtained from Landolt-Börnstein-Roth, "Tabellen." The values used for the heat of vaporization of mercury, the heat of vaporization of mercuric chloride and the heat of formation of mercuric chloride were 13.0, 18.0 and —53.0 Cal., respectively.

[18] Wood, *Phil. Mag.*, [6] **18**, 240 (1909).

[19] Child, *Astrophys. J.*, **55**, 329 (1922).

in the normal hydrogen atom.[20] These relationships are approximately quantitatively true in a number of varied examples, inasmuch as the energies of formation of AgCl, $^1/_2$ $PbCl_2$ and $^1/_4$ $SnCl_4$ are all less than the electron affinity of chlorine by only about 0.5 volt-equivalent. There are two classes of distortion of the octets. In one the energy of formation is greater than the electron affinity of the halide atom. In the other, which represents the combination of two electronegative atoms, the electron affinities of the two electronegative atoms are not completely satisfied. These relationships, which are derived by a comparison of thermal data with available spectroscopic data, do not permit a choice of the exact dynamic model of these molecules, but perhaps the study of these molecular spectra will lead to a model of these molecules and also to a picture of the electron bond.

Summary

1. Energies of formation of some diatomic halides from atoms have been calculated from thermal data.

2. The energies of formation of the hydrogen halides from their atoms are substantially equal to the electron affinity of the halide atom.

3. In the case of metallic halides both positive and negative, but not inappreciable, deviations are found to exist, which are discussed from the viewpoint of distortion of the valence octet of electrons.

4. In spite of lack of precision in the thermal data, especially the energies of dissociation of the halogens, and the uncertainty in interpretation of the spectroscopic data on electron affinity, there exists an interesting general relationship between energy of reaction and electron affinity.

CAMBRIDGE 39, MASSACHUSETTS

NOTE

Permanent Filter Mats in Gooch Crucibles.—Preliminary work in this Laboratory has shown that a porcelain Gooch crucible fitted with a permanent porcelain mat can be made at a very low cost. Such a crucible has most of the advantages of the more expensive Munroe crucible.[1]

The chemist is often deprived of the convenience of the Monroe crucible because of its great cost. To supply the demand various types of porous crucibles and filter cones have been devised. Those made from sintered aluminum oxide are familiar. The disadvantages of these are that the sides as well as the bottoms are porous and the liquid adsorbed in the sides is not easily removed by washing. Considerable difficulty is often experi-

---

[20] It may be well to mention that the equations used to represent changes in state are not intended to represent the mechanism but only differences in energy, since it seems that in some cases atoms and molecules must be activated before actual reaction can take place.

[1] THIS JOURNAL, **31**, 456 (1909).