THE DETERMINATION OF ELECTRON AFFINITIES

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I. INTRODUCTION

The problem of determining electron affinities was a subject of considerable interest in the early 1930's, and several novel methods were developed for measuring these quantities for the halogen atoms. These values agreed well with those obtained by the theoretical calculation of ionic lattice energies for the alkali halide crystals. However, it was soon apparent that both experimental and theoretical methods had severe limitations; the experimental methods often break down when applied to molecules rather than atoms, and the theoretical methods are unreliable when the negative ions being considered are not spherically symmetrical. This absence, therefore, of generally applicable experimental and theoretical methods means that there is a large gap in our knowledge of electron affinities, and this lack of data is now becoming a severe handicap to the formulation of most semi-empirical theories of chemical binding.

We will define the electron affinity (E) of an atom, molecule, free radical, or negative ion X by the exothermicity of the reaction

$$X + e \rightarrow X^-$$

at 298°K. in the gas phase, measured in kilocalories per gram-ion or in electron volts (1 e.v. = 23.06 kcal.). Most of the experimental methods lead to a direct evaluation of this quantity, whereas most of the theoretical determinations yield the heat of formation of the X^- ion, and a further assumption as to the heat of formation of X itself is needed in these cases. It is therefore proposed, in such instances, to aim at first obtaining an accurate value for the heat of formation of the negative ion before making any assumptions leading to a value for the electron affinity. All auxiliary thermochemical data are taken from the tables of the Bureau of Standards (128) unless otherwise specifically stated.

The greater portion of the experimental data on electron affinities has been obtained from direct studies on the interaction between electrons and the substance under consideration. These experiments will be considered first and other methods will be discussed subsequently, in approximately the order of decreasing directness.

II. ELECTRON ATTACHMENT PHENOMENA

If a stream of slow electrons (i.e., electrons accelerated by potentials of less than 1 v.) is allowed to drift through a gas under a pressure of a few millimeters of mercury, there will be quite a large probability that the atoms or molecules constituting the gas will take up electrons to form negative ions in cases where those atoms or molecules have positive electron affinities. In the experiments carried out by Bradbury (28) on oxygen, the swarm of electrons was generated photoelectrically at the cathode and was drawn under the influence of a small uniform potential gradient to the anode. The observed current gives the number of electrons plus negative ions reaching the anode. If, now, an "electron filter" is placed in the path of the electron swarm, it is possible to stop the electrons reaching the anode, whilst the comparatively heavy negative ions are unaffected. The electron filter consists of a grid of fine wires so constructed that alternate wires are connected across a radiofrequency oscillator. By suitable adjustment of this radiofrequency field, it is possible to drive all the electrons to one or another of the grid wires, while the negative ions carry on relatively unperturbed. The decrease in anode current gives the ratio of ions to electrons, and by the use of a second filter at a known distance from the first, it is a simple matter to calculate the probability of electron attachment. In the case that the gas under investigation has an affinity for electrons, the probability of formation of negative ions will fall rapidly to a minimum with increasing accelerating voltage, and then rise again as the electron energy becomes large enough to disrupt the molecule into smaller fragments. Considerable discussion of this method, of both practical and theoretical aspects, has been given by Massey and Burhop (110, 112) and Healey and Reed (69), and as it has not been a fruitful source of electron affinities, it will not be further discussed here. From such studies as these, it has been deduced that the molecules CO, NH_3, CO_2, N_2O, H_2O, and H_2S have no affinity for electrons but that the molecules SO_2, NO, Cl_2, Br_2, and I_2 have positive electron affinities (5, 29, 30, 68). From similar work on mercury vapor, Simons and Seward (150) were able to deduce the value of 35.4 kcal./mole for the electron affinity of the mercury atom, and the value of about 50 kcal./mole for the electron affinity of the boron trifluoride molecule (148) (which may be compared with two thermochemical estimates by Skinner (152) of $\geq$ 17 kcal./mole and $\geq$ 40 kcal./mole). The oxygen molecule has also been studied by this method, but discussion of these results will be deferred to a later stage.

III. ELECTRON IMPACT MEASUREMENTS

When a beam of electrons is fired into a gas, a number of reactions take place, resulting in the formation of both positive and negative ions. Experiments which fall into this class usually follow the lines of the general mass-spectrometer techniques, although some of the earliest experiments did not employ magnetic separation of ions. The fundamental difference between these measurements and the previous method lies in the use of a homogeneous electron beam instead of a swarm of electrons in which there is a large variation in electronic velocity; the maintenance of the homogeneity of the electron beam requires much lower working pressures, of the order of 10^{-5} mm. of mercury. Whilst the appearance potentials of positive ions in a mass-spectrometer are usually of the order of 10 or 15 v., the appearance potentials of negative ions may be as low as 1 v., and the peak intensity of negative ions is seldom as much as 1 per cent of the parent positive-ion peak intensity. (The abundance of the negative halogen ions in the mass spectra of the halomethanes is exceptional in this respect (6, 7, 39, 177).) In many cases, negative ions formed in this way possess considerable kinetic energies: for example, the appearance potential of NH_2^- from NH_3 is about 6 v. (109); the endothermicity of the reaction $NH_3 \rightarrow NH_2 + H$, i.e., $D(H—NH_2)$, is about 4 v. but as the reaction $NH_2 + e \rightarrow NH_2^-$ would be expected to be some 1 or 2 v. exothermic, it would appear that the overall reaction $NH_3 + e \rightarrow NH_2^- + H$ is accompanied by the liberation of some 3 or 4 e.v. of kinetic energy (unless one or both of the particles is formed in an excited state). A number of workers, notably Tate and Lozier (106, 167), Hagstrum and Tate (62), and Blewett (19) have improved the method in order to take account of the initial kinetic energy of the ions.

In the application of Hagstrum and Tate, use was made of the fact that ions of the same mass but having differing velocities are deflected by differing amounts in the magnetic field of the mass-spectrometer. By placing a number of slits between the ion source and the collector plate, it was possible to correlate approximately (knowing the geometry of the machine) the collecting efficiency of the apparatus with the initial kinetic energy of the ions. Their results will be discussed later in the section on oxygen ions.

In the experiments carried out by Tate and Lozier and by Blewett, the negative ions had to overcome a retarding potential before they passed into the ion collector; it was then a simple matter to examine the velocity distribution of the negative ions by varying the retarding potential between the ion source and the collector. For example, Blewett has shown that in the reaction $Br_2 + e \rightarrow Br + Br^-$, a retarding potential of 2.3 v. is required to extinguish the Br^- peak; since the kinetic energy is equally divided between the two resulting particles, the total kinetic energy formation in this reaction is 4.6 e.v. Since the appearance potential of the Br^- peak is 2.8 v., it follows that

$$A(Br^-) + E(Br) = D(Br—Br) + \text{K.E.}(Br + Br^-)$$

that is,

$$2.8 + E(Br) = 1.9 + 4.6$$

or

$$E(Br) = 3.7 \pm 0.2 \text{ e.v.}$$

A similar study of the relationship between electron energy and the kinetic energy of the fragments formed from iodine was made by Buchdahl (34), who gave the electron affinity of iodine as 3.0 ± 0.2 e.v.

A considerable body of information on the existence of negative ions (57) has been collected as the result of electron impact studies on the formation of negative ions, although relatively few quantitative determinations of electron affinities have been made. The earliest studies were made by Knipping (94) (see also Henglein (73) and Frank (53)), who studied the energy required to produce the dissociation of HX into H^+ and X^-, giving values for the heat of formation of X^- in good agreement with later studies. Further information on the halogens was obtained by Hogness and Harkness (76) from a mass-spectrometer study of iodine; it was shown that I^-, I_2^-, and I_3^- were stable ions. The reaction $I_2 + e \rightarrow I + I^-$ was shown to be the only primary process producing negative ions and to take place with electrons having zero kinetic energy, i.e., $E(I) > D(I_2)$. I_2^- and I_3^- were formed by secondary collisions. Baker and Tate have observed Cl_2^- in the mass spectrum of carbon tetrachloride (6) and Blewett (19) observed a peak corresponding to Br_2^-. Tüxen (170), using a mass-spectrometer, demonstrated the existence of the ions O^-, O_2^-, NO_2^-, NO_3^-, OH^-, and H^- in discharges in air, oxygen, hydrogen, water vapor, and the inert gases, although no ions of N^-, N_2^-, He^-, Ne^-, or A^- were detected. Further electron beam experiments by Dukel'skiĭ and Ionov (44) on the vapors of selenium, tellurium, antimony, and bismuth seem to have established the existence of the following ions: Se^-, Se_2^-, Se_3^-, Se_4^-; Te^-, Te_2^-; Sb^-, Sb_2^-, Sb_3^-; Bi^-, Bi_2^-, Bi_3^-, and Bi_4^-. In all cases, the appearance of the monatomic ion, presumably by the process $X_2 + e \rightarrow X + X^-$, required less than 1 v. of electron energy. From this it was deduced that in the cases of selenium, antimony, and bismuth, $E(X) \geq [D(X_2) - 1]$ e.v. and that in the case of tellurium, $E(Te) \approx D(Te_2)$.

Recently, measurements similar to those on ammonia by Mann, Hustrulid, and Tate (109) (i.e., without consideration of kinetic energy of the ions) have been carried out on hydrogen sulfide, hydrogen selenide, and phosphine by Neuert and Clasen (129). Apart from demonstrating the existence of the ions HS^-, HSe^-, and PH_2^-, they obtained the appearance potentials of S^- and Se^- in the following reactions,[1] from which the quoted heats of formation are derived:

REACTION	APPEARANCE POTENTIAL	HEAT OF FORMATION
	e.v.	*kcal./mole*
$H_2S + e \rightarrow S^- + 2H$	6.5 ± 1	$\Delta H_f(S^-) \leqslant 41 \pm 25$
$H_2S + e \rightarrow S^- + H_2^+ + e$	24 ± 2	$\Delta H_f(S^-) \leqslant 191 \pm 45$
$H_2Se + e \rightarrow Se^- + H_2^+ + e$	20 ± 2	$\Delta H_f(Se^-) \leqslant 124 \pm 45$
$H_2Se + e \rightarrow Se^- + H + H^+ + e$	29 ± 3	$\Delta H_f(Se^-) \leqslant 270 \pm 70$

These results illustrate the difficulties that are inherent in the determination of electron affinities by simple mass-spectrometer methods; only the first heat of formation quoted is anything like the correct value,—the three others concealing

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[1] There is apparently an error in this paper in the assignment of these reactions.

very considerable amounts of kinetic energy. The experimental uncertainties are large because of the very low peak intensities of these negative ions.

IV. EQUILIBRIUM MEASUREMENTS

The idea of measuring the equilibrium between atoms, electrons, and negative ions seems to have first been applied by Rolla and Piccardi in 1925 (141). If a fine metallic thread is placed in a flame and heated to red heat, electrons are emitted, and in the presence of certain atoms or molecules, reactions of the type $X + e \rightleftharpoons X^-$ are possible. A thin metal plate held a short distance away at a potential positive with respect to the wire attracts the electrons, giving rise to a small electric current. The introduction of some such substance as methyl iodide into the flame causes a reduction in this current, owing to the formation of iodide ions by the reaction $I + e \rightleftharpoons I^-$, since the iodide ions have a much smaller mobility than free electrons. If it is assumed that the ionic mobility is so small that no iodide ions reach the anode, this reduction in current, together with a knowledge of the rate at which iodine atoms are entering the system, leads to the equilibrium constant for the reaction $K = [e][I]/[I^-]$. The application of this constant to the equation $\log K = -U/RT + C$ (making certain assumptions about the value of C), knowing the temperature T, gives the value of U, which is the electron affinity of the iodine atom. Using methyl iodide, Piccardi (135) obtained the value $E(I) = 82.0$ kcal./mole, and with ethyl bromide, $E(Br) = 86.7$ kcal./mole (136). These results are now known to be some 10 per cent too high, but with the advances taking place in our knowledge of electronics during the early 1930's, a number of other workers were able to apply the idea of measuring these sort of equilibria with a greater degree of precision. Rolla and Piccardi later extended their flame measurements to substances in Group VI of the Periodic Table (137, 142) and were able to derive the following electron affinities: $E(SO_2) = 64.5$, $E(SeO_2) = 53$, and $E(MoO_3) = 63.0$ kcal./mole.

The next significant advance in this field came in 1934, when Sutton and Mayer (162), closely followed by Glockler and Calvin (55), thoroughly reinvestigated the equilibrium between electrons and iodine atoms. Sutton and Mayer constructed a vacuum tube, consisting of a vertical tungsten filament surrounded concentrically by a grid and an anode, mounted coaxially inside an electromagnetic solenoid. When a very low pressure of iodine is admitted to the system, the iodine atoms formed by thermal dissociation on the incandescent filament set up an equilibrium with the electrons being emitted by the hot surface; both the electrons and the iodide ions are drawn towards the anode by the application of a suitable potential difference between the anode and the filament. The anode current is thus carried partially by electrons and partially by negative ions, and it is possible to distinguish these modes by using what is known as the "magnetron effect": when a sufficiently intense magnetic field is set up by the solenoid, it is possible to drive the electrons into concentric circular paths in the space between the filament and anode, so that, in fact, no electrons reach the anode, whilst the heavy negative ions proceed unimpaired. The reduction in anode current in the presence of the magnetic field leads directly to the proportions of the current carried both by the electrons and by the negative ions, and a knowledge of these two quantities, together with the pressure of iodine and the filament temperature, leads to the equilibrium constant for the reaction and so the free-energy change for the reaction at the filament temperature. Combining this with the known entropies and specific heats of the reaction components gives the electron affinity of the iodine atom. The use of this method has been gradually extended to the remaining halogens and to oxygen (which will be considered later). Considerable difficulty was experienced in obtaining consistent results by Mitchell and Mayer (123) in the case of chlorine, but the position was satisfactorily resolved by McCallum and Mayer (119), using both chlorine and stannic chloride as sources of chlorine atoms. Fluorine was studied by Metlay and Kimball (122), but they were unable to reach any conclusion about the electron affinity of the fluorine atom; however, following the acceptance of the new dissociation energy for fluorine (41, 49, 184), it was shown by Bernstein and Metlay (15) that the results were compatible with the value of $E(\mathrm{F})$ proposed by Evans, Warhurst, and Whittle (49).

The method used by Glockler and Calvin resembled that of Sutton and Mayer in that the equilibrium between iodine atoms and electrons was set up on the surface of a thermionic filament, the resultant electrons and negative ions being attracted towards an anode, but their estimation of the relative proportions of electron and negative-ion current depended on a radically different principle. The anode current of a diode is given by the Langmuir–Child space-charge equation:

$$\log i = \log C(e/m)^{1/2} + \tfrac{3}{2}\cdot\log V$$

With the tube completely evacuated, a study of the current–voltage relationship gives the magnitude of the constant C. Now, when the iodine is admitted, the anode current, being carried by both electrons and negative ions, bears a different relationship to the anode voltage, since the mean value of e/m for the current-carrying species is different. This new value of e/m gives at once the ratio of the contributions of the electrons and the negative ions to the anode current, and the calculation of electron affinity from here on follows that of Sutton and Mayer. Table 1 gives a summary of all the significant determinations of electron affinity for the halogens, using direct methods.

A second kind of equilibrium measurement has been used to considerable advantage, again by Mayer (114), and later by Saha, Tandon, and Srivistava (144, 159, 165, 166). When the vapor of an alkali halide is heated to a temperature of the order of 1800°K. in a graphite vacuum furnace, it partially dissociates, and a number of equilibria are set up between the gaseous species MX, M, X, M^+, X^-, and free electrons. Not all these equilibria are independent, but the one that we are interested in is that between MX, and M^+ and X^-, from which the endothermicity (Q_0) of the reaction

$$\mathrm{MX(gas)} \rightleftharpoons \mathrm{M^+(gas)} + \mathrm{X^-(gas)}$$

can be derived. The required pressure of MX vapor was attained by heating some of the salt in a subsidiary electric furnace, whence it passed into the high-temperature region of the graphite furnace where dissociation took place. The products of dissociation effused through a small hole at one end of the furnace to be collected by a Faraday cylinder connected to a cell and galvanometer. The Faraday cylinder was given a small positive or negative potential with respect to the graphite tube in order to collect the negative or positive ions effusing from the furnace. In the case of the negative-ion current, it was necessary to correct for the portion carried by electrons, but in later applications (159) the electrons were deflected away from the Faraday cylinder by a magnetic field. From a knowledge of the area of the effusion hole, the pressure of MX, the two ion currents, and the temperature of the furnace, it was then possible to calculate the equilibrium constant between MX, M^+, and X^-, and thence the free energy of the gaseous dissociation of MX into ions. Making the usual entropy corrections gives Q_0, and the addition to this quantity of the latent heat of vaporization of MX gives the lattice energy of the MX crystal (the lattice energy, U, of a crystal MX is the endothermicity of the dissociation reaction $MX(cryst) \rightarrow M^+(gas) + X^-(gas)$). The results of such measurements are given in table 2. Helmholz and Mayer (71) ascribe a possible error of ±3 kcal. to lattice energies measured in this way. The knowledge of these lattice energies enables us to calculate electron affinities by a thermochemical method, since the heats of formation of crystalline alkali halides and of gaseous

TABLE 1

*Directly determined electron affinities (at 0°K.)**

ATOM	METHOD	AUTHORS	$E_0(X)$
			kcal./mole
I	Flame (CH_3I)	Piccardi	82.0
	Space charge (I_2)	Glockler and Calvin	74.6 ± 3
	Magnetron (I_2)	Sutton and Mayer	72.4 ± 1.5
	Electron impact (I_2)	Buchdahl	69.2 ± 5
Br	Flame (C_2H_5Br)	Piccardi	86.7
	Space charge (Br_2)	Glockler and Calvin (56)	88.0
	Magnetron (Br_2)	Doty and Mayer (42)	80.5 ± 0.4
	Electron impact (Br_2)	Blewett	87.7 ± 5
Cl	Magnetron (Cl_2)	Mitchell and Mayer	92.7 ± 4?
	Magnetron (Cl_2)	McCallum and Mayer	85.84 ± 1.0
	Magnetron ($SnCl_4$)	McCallum and Mayer	85.83 ± 1.0
	Electron impact (Cl_2)	Hanson (63)	92.2 ± 6
F	Magnetron (F_2)	Bernstein and Metlay	82.2 ± 3.9

* These electron affinities may be corrected to room temperature by the addition of about 1 kcal./mole.

metallic positive ions are well known, the heat of formation of the negative ion being given by the equation:

$$\Delta H_f(\mathrm{X}^-) = \Delta H_f(\mathrm{MX}) - \Delta H_f(\mathrm{M}^+) + U$$

Thus, if we also know the heat of dissociation of X_2, which gives $\Delta H_f(\mathrm{X})$, the electron affinity is readily obtainable.

TABLE 2

*Experimental lattice energies of alkali halides (at 0°K.)**

SALT	Q_0	$\lambda_0(\mathrm{vap})$	U_0	$\Delta H_f(\mathrm{MX})$	$\Delta H_f(\mathrm{M}^+)$	$\Delta H_f(\mathrm{X}^-)$	$\Delta H_f(\mathrm{X})$	$E(\mathrm{X})$
	kcal./mole	*kcal./mole*	*kcal./mole*	*kcal./mole*	*kcal./mole*	*kcal./mole*	*kcal./mole*	*kcal./mole*
LiCl...	150.7 (144)	50.6 (131)	201.3	−97.7	162.9	−59.3	29.0	88.3
NaCl..	129.7 (144)	55.0 (118, 131)	184.7	−98.2	146.0	−61.2		90.2
			181.3 (71)					
KCl...	113.5 (144)	52.9 (118, 131)	166.4	−104.2	123.1	−60.9		89.9
NaBr..	124.7 (165)	53.0 (118, 131)	177.7	−86.0	146.0	−54.3	26.7	81.0
KBr...	109.3 (165)	51.9 (118, 131)	161.2	−93.7	123.1	−55.6		82.3
RbBr..			151.3 (71)	−93.0	118.3	−60.0		86.7
LiI....	129.1 (159)	48.8 (128)	177.9	−64.8	162.9	−49.8	25.5	75.3
NaI...	118.8 (166)	47.9 (128)	166.7	−68.8	146.0	−48.1		73.6
KI....	102.4 (166)	49.0 (131)	151.4	−78.3	123.1	−48.9		74.4
	104.6 (114)	49.0 (131)	153.6					
RbI...	99.1 (159)	46.1 (131)	145.2	−78.5	118.3	−51.6		77.1
CsI....	94.8 (114)	(48)	142.8	−80.5	110.1	−47.8		73.3

* The heats of formation, at 298°K., are from reference 128. The latent heats of vaporization were taken from data of Niwa (131) and of Mayer and Winter (118) and from reference 128. In calculating $\Delta H_f(\mathrm{X}^-)$ and $E(\mathrm{X})$, it is assumed that there is no difference between the lattice energies at 0°K. and 298°K., an assumption which is not likely to cause an error of more than 0.5 kcal./mole.

A third type of equilibrium investigation has been made by Dukel'skiĭ and Ionov (43, 84), who studied the dissociation of molecular beams of alkali halides on a tungsten filament at temperatures around 2500°K. It had been shown by Hendricks, Phipps, and Copley (72) and by Johnson and Phipps (85), that the well-known Saha–Langmuir equation (97), commonly used to describe the ionization of alkali metal atoms on a heated metal filament, could equally well be applied to the surface ionization of sodium and potassium halides. Thus, it appeared that the alkali halides dissociated on the hot surface, the alkali metal atoms thereupon evaporating partly as positive ions; the fate of the halogen atoms was not investigated. It was supposed by Dukel'skiĭ and Ionov that the halogen atoms resulting from the dissociation, having high electron affinities, were able to capture electrons from the hot surface and evaporate partly as negative ions, again according to the Saha–Langmuir equation; this they showed to be the case. A beam of alkali halide molecules was directed towards a tungsten filament, and the resulting positive and negative ions were collected alternately by a Faraday cylinder as in previous applications; the electrons were separated from the negative ions by the application of a magnetic field. For such an experiment, the analog of the Saha–Langmuir equation is:

$$\frac{i_+}{i_-} = \frac{1 + 4 \exp\left(\frac{W - E}{kT}\right) e}{1 + 2 \exp\left(\frac{I - W}{kT}\right) e}$$

where i_+ and i_- are the observed positive-ion and negative-ion currents, e is the electronic charge, I is the ionization potential of the alkali metal, and W

TABLE 3

Electron affinities measured by surface ionization of alkali halides

ELEMENT	SALT (MX)	E(X)	AVERAGE E(X)
		kcal./mole	*kcal./mole*
Fluorine	KF	94.8 ± 3 (W = 4.93) 83.5 ± 3 (W = 4.52)	83.5
Chlorine	NaCl	82.5 ± 3	86.5
	KCl	85.5 ± 2	
	RbCl	87.2 ± 1	
	CsCl	90.6 ± 2	
Bromine	NaBr	77.5 ± 1	81.8
	KBr	83.9 ± 2	
	RbBr	83.9 ± 2	
Iodine	KI	76.3 ± 2	76.3

is the work function of the tungsten filament, the other terms having their usual significance. It is seen that this method gives a direct evaluation of electron affinities without any knowledge of the vapor pressure of the alkali halide, or any other doubtful thermochemical quantities. The agreement with other determinations is in general good, as can be seen from table 3. The only case which calls for any comment is that of potassium fluoride, where the authors considered it necessary to use a higher value of W than usual, i.e., 4.93 e.v. instead of 4.52 e.v. because of the (supposed) conditioning of the surface by the fluoride. This view receives some support from the work of Johnson and Phipps (85), who found difficulty in measuring the work function of a tungsten surface using sodium fluoride, although it may have been that the results were complicated by the attack of sodium fluoride, even when perfectly dry, on all their quartz surfaces. It may or may not be fortuitous that if the normal work function is used in the case of potassium fluoride, the value of E(F) obtained is in close agreement with the present accepted value. In the view of the present author, this value of 83.5 kcal. and the value of 82.2 kcal. obtained from Metlay and Kimball's equilibrium data (15), are genuine determinations of the electron affinity of fluorine, and the fact that the original authors in each case were reluctant to accept these values in face of their divergence from the then accepted value in no way detracts from their significance.

Whilst they do not exactly come under the heading of equilibrium measurements, we shall describe here, because of their superficial similarity to the experiments just described, some studies by which the existence of a number of negative ions has been demonstrated, i.e., ionization of molecular beams on a hot metal surface, followed by conventional mass-spectrographic separation of the resulting ions. Arnot and Milligan (3) showed that Hg^- was formed when a beam of mercury atoms was allowed to fall on a nickel filament, the process being first the ionization to form Hg^+, followed by the abstraction of two electrons from the metal surface. Negative ions formed in this way possess considerable kinetic energy. In such experiments, Arnot (2) observed the ions C^-, CO^-, CO_2^-, O^-, O_2^-, H^-, and N^-, although it is believed from electron attachment studies that carbon monoxide and carbon dioxide have negative electron affinities, and it seems probable from extrapolation and theoretical considerations (see later) that N^- is unstable; it may be, however, that these ions are formed in excited states which may be stable with respect to spontaneous ionization or dissociation. Subsequently, Sloane and Press (156) constructed a double mass-spectrometer in which positive ions formed in the conventional manner are sorted and concentrated on to a chrome-nickel electrode. Negative ions formed by abstraction of electrons from the metal surface are collected and sorted in the second mass-spectrometer section. Using this technique, they were unable to detect Hg^- ions, but Sloane and Love (155) later demonstrated the formation of Li^- from positive lithium ions.

A few equilibrium measurements have also been carried out in solution (see Bent and Keevil (13) for previous references). Bent (12) studied the equilibrium set up between Na^+, R^-, R, and liquid sodium amalgam (where R is a triphenylmethyl radical) when a solution of a known mass of sodium triphenylmethyl in ether was shaken with mercury. Since sodium is present in ether solution only as ions, analysis of the resulting sodium amalgam leads to a knowledge of the concentrations (activities) of Na^+, R^-, and R in the solution, and combining these with the activity coefficient of sodium metal in the resulting amalgam yields the equilibrium constant for the reaction

$$\mathrm{Na(solid)} + \mathrm{R(ether)} \rightleftharpoons \mathrm{R^-(ether)} + \mathrm{Na^+(ether)}$$

from which the free-energy change can easily be obtained. Estimation of the free energies of solution in ether of the reacting species yields the free-energy change of the same reaction in the gas phase, from which it was calculated that the electron affinity of the triphenylmethyl radical is 59 ± 5 kcal./mole. Subsequent work showed that the electron affinities of all triarylmethyl radicals are about 60 kcal./mole. However, Swift (163) pointed out that there was an error in the assumption of the dissociation constant of sodium triphenylmethyl by Bent, and that the correction of this led to an electron affinity of 48 ± 5 kcal. for the triphenylmethyl radical. A similar reduction presumably applies to the other radicals.

V. THE CALCULATION OF LATTICE ENERGIES

It is well known that the energy of interaction of an assembly of one mole of spherical positive and negative ions can be represented to a good degree of approximation by the Born equation (23)

$$U = \frac{ANZ_1Z_2e^2}{R} - \frac{B}{R^m}$$

where N is Avogadro's number, Z_1 and Z_2 are the ionic charges, e is the electronic charge, R is the distance between positive and negative centers, and A, B, and m are constants. The first term represents the coulombic attraction between the positive and negative ions, A, the Madelung constant, being characteristic of the type of crystal lattice. The second term represents the compressional repulsion between the electron clouds of adjacent ions, the value of B being defined by the condition that at the equilibrium distance R, $\mathrm{d}U/\mathrm{d}R = 0$. The constant m usually takes a value between 6 and 9 and may be determined from such data as the compressibility of the crystal lattice (154). The energy of a gaseous ion-pair is better represented by $m = 11$ or 12, because the internuclear distances are much less than in crystals, resulting in increased distortion of the electron's shells and a reduction in the nuclear screening, thereby causing the repulsion curve to be steeper (174).

With the advent of wave mechanics, it became clear that ions could no longer be thought of as compact spheres, but that their surfaces are diffuse, the electron density falling away exponentially with increasing distance from the nucleus. The theory of crystal lattices was subsequently modified by Born and Mayer (27) to take account of the interpenetration of the electron clouds, resulting in the well-known expression

$$U = \frac{ANZ_1Z_2e^2}{R} - be^{-R/\rho}$$

the constant ρ having the value of 0.345, and the value of b again being defined by the condition $\mathrm{d}U/\mathrm{d}R = 0$ when R is equal to the equilibrium separation. Table 4 gives a series of results on the calculation of lattice energies for the alkali halides by a number of authors, beginning with the early calculations by Born and Heisenberg (25) and by Lennard-Jones (102) using the Born expression, followed by calculations by Mayer and Helmholz (116) using the Born–Mayer expression. The later calculations of Verwey and de Boer (173) and of Huggins (77) differ from those of Mayer and Helmholz only in respect of a more refined assessment of van der Waals forces. The electron affinities of the halogens which are calculated in table 4 are based on Huggins' lattice energies, which are here accepted as the best available calculated data. It will be seen that the more recent of the lattice energies in table 4 are in excellent agreement with the experimental lattice energies which are given in table 2, thereby providing a gratifying confirmation of the theoretical treatment. A number of other lattice energies—namely, those of the halides of Tl^+, Cu^+, and Au^+ (1, 115)—give electron affinities for the halogens in fair agreement with the more reliable ones in table 4.

TABLE 4

Lattice energies of the alkali halides and the electron affinities of the halogens at 298°K.

SALT	LATTICE ENERGIES						ELECTRON AFFINITIES				
	Born and Heisenberg (1924)	Lennard-Jones (1927)	Mayer and Helmholz (1932)	Verwey and de Boer (1936)	Huggins (1937)	Kapustinsky (1943)	ΔH_f(MX)	ΔH_f(M^+)	ΔH_f(X^-)	ΔH_f(X)	E(X)
	kcal./mole	*kcal./mole*	*kcal./mole*	*kcal./mole*	*kcal./mole*	*kcal./mole*	*kcal./mole*	*kcal./mole*	*kcal./mole*	*kcal./mole*	*kcal./mole*
LiF.....			240.1	243.0	**243.6**	227.7	−146.3	162.9	−65.6		84.3
NaF....	222	226	213.4	216.1	**215.4**	211.5	−136.0	146.0	−66.6		85.3
KF.....	191	195	189.7	193.5	**192.5**	188.5	−134.5	123.1	−65.1	18.7	83.8
RbF....	163	177	181.6	186.0	**183.0**	181.7	−131.3	118.3	−66.6		85.3
CsF.....	170	175	173.7		**175.7**	170.4	−126.9	110.1	−61.3		80.0
LiCl....			199.2	201.9	**200.2**	192.1	−97.7	162.9	−60.4		89.4
NaCl...	182	179	183.1	186.0	**183.5**	179.9	−98.2	146.0	−60.7		89.7
KCl....	164	161	165.4	168.9	**167.9**	162.7	−104.2	123.1	−59.4	29.0	88.4
RbCl...	156	156	160.7	164.7	**162.0**	158.2	−102.9	118.3	−59.2		88.2
CsCl....	146	142	152.2		**153.1**	149.4	−103.5	110.1	−60.5		89.5
LiBr....			188.3	192.0	**189.5**	183.2	−83.7	162.9	−57.1		83.8
NaBr...	172	172	174.6	178.3	**175.5**	172.3	−86.0	146.0	−56.5		83.2
KBr....	156	156	159.3	163.4	**161.3**	156.2	−93.7	123.1	−55.5	26.7	82.2
RbBr...	149	150	153.5	158.6	**156.1**	149.7	−93.0	118.3	−55.2		81.9
CsBr....	139	138	146.3		**149.6**	143.9	−94.3	110.1	−54.8		81.5
LiI.....			174.1	178.7	**176.1**	170.4	−64.8	162.9	−51.6		77.1
NaI.....	158	163	163.9	168.9	**164.3**	161.0	−68.8	146.0	−50.5		76.0
KI......	145	148	150.8	154.6	**152.4**	146.8	−78.3	123.1	−49.0	25.5	74.5
RbI.....	140	143	145.3	150.3	**148.0**	141.0	−78.5	118.3	−48.8		74.3
CsI.....	131	132	139.1		**142.5**	134.7	−80.5	110.1	−48.1		73.6

The main experimental data required for the calculation of lattice energies are the type of crystal lattice—thereby defining the value of A—and the value of R, which may be derived from x-ray crystal analysis or sometimes (less accurately) from simple density measurements. Kapustinsky (90) has developed an approximation which may be used when the lattice constants are not known, based on the assumption of a NaCl-type lattice of ions having Goldschmidt radii (with coördination number 6). Values for the alkali halides calculated on this basis are also given in table 4, and are seen to be a little low by comparison with the other calculations; the approximation is useful in dealing with more complicated structures. A detailed account of the calculation of lattice energies has recently been given by Partington (133).

A few authors have attempted to calculate lattice energies by wave-mechanical methods, with a fair degree of success, as follows:

AUTHOR	COMPOUND	U
		kcal.
Hylleraas (82)	LiH	218.6
Löwdin (105)	LiCl	187.7
Löwdin (105)	NaCl	183.2
Landshoff (96)	NaCl	182
Löwdin (105)	KCl	166.9

The values for sodium and potassium chlorides are very close to those in table 4, but that for lithium chloride is some 5 per cent low. Hylleraas' value for U(LiH) compares favorably with the 218.2 kcal./mole obtained by Bichowsky and Rossini, using the Born approximation (17), and gives $\Delta H_f(\text{H}^-) = 34.1$ kcal. in good agreement with the values obtained by direct quantum-mechanical calculations.

Table 5 contains the lattice energies, calculated by the Born equation, of some salts of the more important negative ions. The lattice energies of the alkali cyanides were calculated by Sherman (149) and lead to an electron affinity for CN of about 85 kcal., assuming that the ΔH of formation of the CN radical is 92.7 kcal./mole (120). A crude spectroscopic extrapolation estimate by Lederle (101) (see Section VIII) gives $E(\text{CN}) = 92$ kcal., which is in fair agreement with the lattice energy data; recent electron impact measurements on cyanogen have been shown to be consistent with a value of $E(\text{CN}) \approx E(\text{Br})$ (39). The ΔH of formation of CN^- given in table 5 agrees only moderately with the value of 17 kcal. derived from Knipping's electron impact data (95), although his figures were subsequently corrected by Frank (53), giving $\Delta H_f(\text{CN}^-) = 5$ kcal. From lattice energies calculated by Kapustinsky's method, Yatsimirskiĭ (186) obtained the value $\Delta H_f(\text{CN}^-) = 16.3$ kcal./mole.[2] From such data, one can only conclude that the value of $\Delta H_f(\text{CN}^-) = 10 \pm 5$ kcal. is an optimistic assessment of the situation.

The data on amides are derived from the density data given by Juza (87), but the value of about 15 kcal. obtained for NH_2^- is considerably at variance with Yatsimirskiĭ's value of 45 kcal./mole for $\Delta H_f(\text{NH}_2^-)$ (186). Since the ΔH of formation of the NH_2 radical is 43 kcal./mole (146, 164), one may conclude, in view of the demonstrable stability of free NH_2^- ions (109), that the former value is more reasonable, since it leads to a positive value for the electron affinity of the NH_2 radical. The density measurements correspond to an ionic radius of 1.75 ± 0.1 Å., whereas Yatsimirskiĭ used 1.30 Å. Juza and Opp (88)

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[2] Yatsimirskiĭ's figures are based on heats of formation for positive ions taken from Bichowsky and Rossini's earlier compilation, but some of these values are as much as 10 kcal. in error, causing errors of up to 5 kcal. in the heats of formation of the negative ions. Here, and elsewhere in this paper, Yatsimirskiĭ's figures have been corrected by an amount (3.5 kcal.) representing the mean difference between his and the present values for the halogens.

TABLE 5

The lattice energies of some cyanides, amides, hydrosulfides, and carbonates

SALT	U	ΔH_f(MX)	ΔH_f(M^{+n})	ΔH_f(X^{-n})
	kcal./mole	*kcal./mole*	*kcal./mole*	*kcal./mole*
NaCN	170.6	−21.5	146.0	3.1
KCN	156.1	−26.9	123.1	6.1
RbCN	150.3	(−26)*	118.3	6.3
CsCN	142.5	(−26)	110.1	6.5
$LiNH_2$	200	−43.5	162.9	−6.4
$NaNH_2$	185	−28.4	146.0	10.6
KNH_2	168	−28.3	123.1	16.6
$RbNH_2$	162	−25.7	118.3	18.0
$CsNH_2$	153	−25.4	110.1	17.6
NaSH	168	−56.5	146.0	−34.5
KSH	155	−63.2	123.1	−31.3
RbSH	150	−62.4	118.3	−30.7
CsSH	143	−62.9	110.1	−30.0
$MgCO_3$	771	−266	561.8	−57
$CaCO_3$	701	−288.5	463.6	−51
$ZnCO_3$	775	−194.2	664.9	−84
$CdCO_3$	715	−178.7	627.1	−91
$MnCO_3$	747	−213.9	601.5	−68
$FeCO_3$	762	−178.7	650.7	−67

* The heats of formation in parentheses are estimates.

TABLE 6

The lattice energies of oxides, sulfides, and selenides of Group II metals

SUBSTANCE	SHERMAN (1932)	MAYER AND MALTBIE (1932) (117)	de BOER AND VERWEY (1936) (22)	KAPUSTINSKY (1943)	MEAN	ΔH_f(MX)	ΔH_f(M^{++})	ΔH_f(X^{--})
	kcal./mole	*kcal./mole*	*kcal./mole*	*kcal./mole*	*kcal./mole*	*kcal./mole*	*kcal./mole*	*kcal./mole*
BeO			1080, 1030		1055	−135.0	714.9	215
MgO	940.1	939	936, 920	914.3	930	−143.8	561.8	224
CaO	824.1	831	830, 825	825.5	831	−151.9	463.6	215
SrO	790.9	766	784, 780	768.9	778	−141.1	427.7	209
BaO	747.0	727	740, 735	730.6	736	−133.4	395.7	207
MgS	778.3	800	790*	786.3	789	−83.0	561.8	144
CaS	721.8	737	710*	719.5	722	−115.3	463.6	143
SrS	687.4	686	680*	675.8	682	−108.1	427.7	146
BaS	655.9	647	640*	645.6	647	−106.0	395.7	145
CaSe	698.8			683.7	690	−81.8†	463.6	145
SrSe	667.1			644.1	655	−83.4†	427.7	144
BaSe	637.1			616.8	625	−81.3†	395.7	148

* From van Arkel and de Boer (1).

† From Bichowsky and Rossini (17).

have recently shown that the radius of the NH_2^- ion is 1.67 Å., thereby confirming the data derived from density measurements.

The lattice energies for the hydrosulfides are those of West (181), which yield a ΔH of formation of SH^- in relatively good agreement with the -24.3 kcal. obtained by Yatsimirskiĭ (186).

The data on carbonates, due to Lennard-Jones and Dent (103), represent the earliest attempt to calculate the lattice energies of divalent ions from x-ray data; the results are surprising in that they lead to a markedly negative ΔH of formation for an ion containing two excess electrons. Unlike other doubly negative molecule ions, CO_3^{--} is stable with respect to any possible decomposition other than those involving ionization, i.e., $O_2^{--} \rightarrow 2O^-$ is 100 kcal. exothermic, whereas $CO_3^{--} \rightarrow CO + 2O^-$ is 100 kcal. endothermic, suggesting that we may ascribe a considerable resonance energy to the carbonate ion. By far the greatest proportion of work on the lattice energies of crystals containing divalent negative ions has been done on the oxides, sulfides, and selenides of the Group II metals. The position in this field is summarized in table 6. A number of earlier calculations on oxides and sulfides due to van Arkel and de Boer (1) have been omitted, but these, with single exceptions, give values for $\Delta H_f(O^{--})$ and $\Delta H_f(S^{--})$ in excellent agreement with those derived in table 6.

Finally, mention must be made of the extensive compilation of lattice energies made by Sherman (149) in a review of the subject in which he discusses critically the position of the Born equation at that time (1932). However, apart from the values taken from this paper in tables 5 and 6, most of the data refer to lattice energies of mixed oxides and mixed halides which do not help in determining additional electron affinities.

VI. HEATS OF SOLVATION OF IONS

It was shown by Born (24) (see also Bernal and Fowler (14)) that there was a relationship between the free energy of solution of a gaseous ion of radius R, in a medium of dielectric constant ϵ, of the form:

$$-\Delta F = \frac{e^2}{2R}\left(1 - \frac{1}{\epsilon}\right)$$

The entropies of gaseous ions may be calculated from the Sackur equation and the entropies of a large number of aqueous ions have been determined by Latimer, Powell, Pitzer, and Smith (99, 139), so that it is an easy matter to calculate the heat of solution of gaseous ions in water if R is known. If we are interested in a negative ion X^-, its heat of formation can be obtained by the application of Hess's Law to the process

$$H^+(\text{gas}) + X^-(\text{gas}) + \text{aq} \rightarrow [H^+(\text{aq}) + X^-(\text{aq})]$$

assuming values are known for (*a*) the heat of formation of completely dissociated HX in water and (*b*) the heat of hydration S_{H^+} ($= -\Delta H_{\text{soln}}$) of a gaseous proton. In the case of a strong acid HX, the first requirement presents no difficulty; the method of dealing with weak acids has been outlined by Briegleb (31). Thus, we are dependent only on the heat of hydration of gaseous

H^+, the value of which has been the subject of controversy for many years. Almost the only method of obtaining this quantity is to make use of the calculated heats of hydration of the positive alkali metal ions. The difficulty arises because water cannot be considered as a fluid of uniform dielectric constant in the vicinity of an ion, and, in effect, the apparent radius of the ion is not the same as its radius in the gas phase or in a crystal. Therefore, considering the alkali halide MX, the sum of the lattice energy of MX plus the heat of solution of solid MX in water is divided into two parts for each MX, producing a set of self-consistent, but interdependent, values for S_{X^-} and S_{M^+}; if it is possible to fix a value for one of these ions, the rest follow automatically. For a long time this was done on the assumption that $S_{K^+} = S_{F^-}$ (46), but more recently, both Verwey (171, 172) and Latimer, Pitzer, and Slansky (98), from detailed studies of the problem, produced independently and simultaneously two almost identical sets of heats of hydration of these ions. Their values, which are based on slightly different sets of lattice energies, are in kilocalories per gram-ion:

Ion	Li^+	Na^+	K^+	Rb^+	Cs^+	F^-	Cl^-	Br^-	I^-
Verwey	120	94.5	75	69	61	122	89.5	83	73.5
Latimer	121.2	94.6	75.8	69.2	62.0	122.6	88.7	81.4	72.1

It follows from these values and the Born equation that a correction must be made to R of +0.85 Å. for positive ions and +0.1 Å. for negative ions when considering heats of solution of ions in water. Following Fajans (52), S_{H^+} may be calculated in the following manner:

$$\begin{array}{lll}
\text{Li(cryst)} + H_2O\text{(liq)} \rightarrow \text{Li}^+\text{(aq)} + OH^-\text{(aq)} + \tfrac{1}{2}H_2\text{(gas)} & & +53.0\text{ kcal.} \\
H^+\text{(aq)} \quad + OH^-\text{(aq)} \rightarrow H_2O\text{(liq)} & & +13.7\text{ kcal.} \\
\hline
\therefore \text{Li(cryst)} + H^+\text{(aq)} \rightarrow \text{Li}^+\text{(aq)} + \tfrac{1}{2}H_2\text{(gas)} & & +66.7\text{ kcal.} \\
\text{also Li(cryst)} + H^+\text{(gas)} \rightarrow \text{Li}^+\text{(gas)} + \tfrac{1}{2}H_2\text{(gas)} & & +204.2\text{ kcal.} \\
\hline
\therefore H^+\text{(aq)} \quad + \text{Li}^+\text{(gas)} \rightarrow H^+\text{(gas)} + \text{Li}^+\text{(aq)} & & -137.5\text{ kcal.}
\end{array}$$

$$\text{i.e., } S_{H^+} - S_{Li^+} = 137.5\text{ kcal.}$$

which, using Latimer, Pitzer, and Slansky's value for S_{Li^+}, gives $S_{H^+} = 258.7$ kcal. Calculations from the other alkali metal ions yield values from 256.9 to 259.5 kcal./gram-ion for S_{H^+}. Briegleb (32) quotes an estimate of 263 kcal. derived from electrode potentials; we will therefore accept 260 kcal./gram-ion as the heat of hydration of a proton.

The use of heats of solvation of ions in this way is not a very accurate method of estimating electron affinities, largely because of the uncertainties associated with the absolute value of S_{H^+} and in the determination of the effective radius of the ion concerned, although if $S_{H^+} = 260$ kcal. is used, a number of heats of hydration given by Yatsimirskiĭ (187, 188) lead to heats of formation of the negative ions in close agreement with those obtained from calculations of lattice energy.

A number of experiments in which electron-transfer spectra are observed in solution lead to the quantity $(E + S)_X$, i.e., the electron affinity of X plus the heat of solvation of X^- (see, e.g., reference 47). An estimate of S_{X^-} then leads directly to $E(X)$. The quantity $(E + S)_X$ is the difference between the heat of formation of gaseous X and solvated X^-, and a rough estimate of the latter quantity is often enough to establish the thermodynamic feasibility or otherwise of a postulated reaction mechanism involving the species X^- in solution. The point that the electron affinity of an atom is greater in solution than in the gas phase was recently raised by Massey (111), who discussed the stability of O^{--} ions in aqueous solution in terms of "cluster formation" of the polar solvent molecules with the ions. We may restate this principle in more familiar terms: the electron affinity of an atom in solution will be greater than in the gas phase by an amount representing the difference between the heats of solvation of the atom and of the negative ion; since the heat of solvation of a neutral particle is usually very small, whereas the heat of solvation of an ion is of the order of hundreds of kilocalories per gram-ion, the addition of an electron to a particle is a much more profitable process in solution than in the gas phase.

VII. THE KINETICS OF ELECTRODE PROCESSES

Recent experiments by Hush and Oldham (80, 132) on the behavior of benzyl iodide solutions at a dropping mercury electrode led to the formation of large quantities of benzylmercuric iodide. Subsequent investigations on alkylmercuric halides showed that the reduction occurred in two one-electron stages, and that the second reduction wave corresponded almost exactly to the second wave for the corresponding alkyl iodide in those cases where this was also a two-stage process. Evidence has been accumulated that this two-stage reduction process is

$$\mathrm{RHgX} \rightleftharpoons \mathrm{RHg^+} + \mathrm{X^-}$$

followed by

$$\mathrm{RHg^+} + e \rightarrow \mathrm{RHg} \qquad (1)$$

where the RHg radical is adsorbed on the mercury electrode surface,—in all probability as free R radicals, since the latent heat of vaporization of mercury (14.5 kcal.) is greater than $D(\mathrm{R{-}Hg})$ which for R = CH_3, C_2H_5, and i-C_3H_7 is about 6 kcal./mole (65, 124). These radicals are then reduced according to

$$\mathrm{R(adsorbed)} + e \rightarrow \mathrm{R^-} \qquad (2)$$

and from a comparison of the half-wave potentials of these reactions at infinite dilution, they have established an electron affinity scale for hydrocarbon radicals relative to that of the triphenylmethyl radical (2.1 e.v.). A number of assumptions are involved, which will be discussed in detail by these workers in a later publication, but a provisional list of electron affinities is as follows: $E(i\text{-}C_3H_7) = 0.5$; $E(n\text{-}C_3H_7) = 0.8$; $E(C_2H_5) = 0.9$; $E(CH_3) = 1.1$; $E(C_6H_5) = 1.6$; $E(\alpha\text{-naphthyl}) = 1.6$; $E(\text{benzyl}) = 1.8$; $E(\text{allyl}) = 2.1$ e.v. The figure obtained for $E(\mathrm{CH_3})$ is very close to an intuitive estimate of 20 kcal./mole by Baughan, Evans, and Polanyi (11).

An attempt has also been made by Lyons (107) to derive electron affinities of molecules from electrode kinetic data. It had been shown by Maccoll (108) that there was a correlation between the half-wave potential for the reduction of a hydrocarbon and the energy of the lowest vacant orbital in the molecule. Representing the reduction process as

$$\begin{array}{lll} \mathrm{Hg} \rightarrow \mathrm{Hg^+(aq)} + e & - 4.52 \text{ e.v.} \\ \mathrm{R} + e \rightarrow \mathrm{R^-} & + E \\ \mathrm{R^-} + \mathrm{aq} \rightarrow \mathrm{R^-(aq)} & + S_{\mathrm{R^-}} \end{array}$$

the half-wave potential is given by $(4.52 - E - S_{\mathrm{R^-}})$ if the process is reversible. Calculation of $S_{\mathrm{R^-}}$ leads to a value for E, the electron affinity of the gaseous hydrocarbon molecule. However, the problem of calculating these electron affinities may not be as simple as this, since the kinetics of the reduction process are as yet unknown.

VIII. SPECTRAL AND EXTRAPOLATION METHODS

A number of attempts have been made to derive electron affinities from spectroscopic data, but with varying degrees of success. Many of them depend on extrapolation or interpolation from existing data which at the time appeared to be reasonable but which are now known to be faulty. For example, the so-called "electron affinity spectra" or electron-transfer spectra, which consist of the ultraviolet absorption bands of solvated negative ions, have been reviewed by Rabinowitch (140), who showed that there was a close parallelism between the frequencies of the absorption maxima and the electron affinities of the gaseous radicals in the sequence $\mathrm{SH^-}$–$\mathrm{I^-}$–$(\mathrm{CNS^-})$–$\mathrm{Br^-}$–$\mathrm{OH^-}$–$\mathrm{Cl^-}$; if $\mathrm{OH^-}$ is put in its correct place, the correlation is broken. There still remains, however, a strong correlation between the frequencies of the absorption maxima and $(E + S)_{\mathrm{X}}$ values (47), which were discussed above, and these values, used in conjunction with estimates of heats of solvation, represent a useful source of approximate data on electron affinities. Lederle (101) correlated the ultraviolet absorption maxima of the methyl halides, methanol, and methyl cyanide, and from the known electron affinities of Cl, Br, and I, deduced that the electron affinities of F, OH, and CN were about 95, 88, and 92 kcal., respectively; the first two are much higher than would now be accepted, but the CN value may be of the right order.

A second type of spectroscopic method has been described by Hellmann and Mamotenko (70), who studied the complex emission spectra of carbon, nitrogen, oxygen, and fluorine atoms and derived interpolation formulae between the respective term values which enabled them to estimate electron affinities. Their value for oxygen is 15 kcal. too low, and the value for fluorine (which is confirmed by Wu (185), using the same method) is too high by nearly the same amount; actually, several extrapolation methods lead to a value of about 95 kcal. for the electron affinity of fluorine (100, 101, 145, 153, 169).

A set of electron affinities for the halogens which have often been quoted are those of Lederle (100), which are based on the ultraviolet absorption spectra of the gaseous alkali halides. These (electron-transfer) spectra are due to the dissociation of a gaseous ion-pair M^+X^- into neutral atoms (140), and such information does not lead to any knowledge of the heats of formation of free negative ions. Lederle made use of Born and Heisenberg's calculations of lattice energies (25), and the fact that his final answers are reasonable merely illustrates the essential consistency of the auxiliary thermochemical data used to calculate electron affinities from lattice energies. The internal consistency of his results is fortuitous, as pointed out by Kuhn (95). Thus it appears that no direct spectroscopic determination of electron affinities has yet been accomplished; the position in this respect is adequately discussed elsewhere (57).

A method of estimating electron affinities from dipole moments was suggested by Sklar (153). The dipole moments of the methyl halides were interpreted in terms of a partial charge transfer from the methyl to the halogens, and the amounts of negative charge residing on each halogen atom were plotted against $E(X)$ (with $E(F) = 95$), giving a straight line. On extrapolation back to zero charge separation the electron affinity of the methyl radical was derived as 1.8 e.v. Further calculations on this basis yield electron affinities for the ethyl radical of 1.4 e.v., for the two propyl radicals of 1.0 e.v., and for NO_2 and CN, the values of 6.5 and 7.0 e.v., respectively (113). The calculated values for NO_2 and CN are larger than our accepted figures by a factor of about 2, and it is probable that this method is without foundation, as it makes use of an erroneous value for the electron affinity of fluorine. Moreover, modern views on the origin of dipole moments imply that no simple correspondence exists between the dipole moment and the extent of charge transfer (37, 38).

One of the most widely used extrapolation methods for the estimation of electron affinities of atoms depends on the knowledge of the ionization potentials of a series of isoelectronic positive ions. It is well known that a plot of $I^{1/2}$ against atomic number for a series of isoelectronic positive ions gives a straight line, but that the extrapolation of this line back through the neutral atom to the corresponding negative ion always gives an overestimate for the ionization potential of that negative ion. Glockler (54), and more recently Bates (8), have shown that for the lighter elements, the ionization potentials (I) of a series of isoelectronic species of nuclear charge Z are well represented by

$$I_z = a + bZ + cZ^2$$

where a, b, and c are constants. Using the experimental ionization potentials for systems having $(n + 1)$ electrons with $Z = (n + 1)$, $(n + 2)$, and $(n + 3)$ leads to the solution

$$I_n = 3I_{n+1} - 3I_{n+2} + I_{n+3}$$

where I_n is the ionization potential of the isoelectronic negative ion having a nuclear charge n, i.e., the electron affinity of the n^{th} atom in the Periodic Table. Table 7 presents a comparison of Glockler's original results, those recalculated by Bates, and a new series recalculated by the same method on the basis of the latest spectroscopic data (127). The results represent very small differences between large numbers and are subject to considerable uncertainties in some cases; furthermore, when systems containing more than eighteen electrons are considered, the method loses its general applicability. In those cases where it is possible to make comparisons with other determinations (see table 10), the method always underestimates the electron affinity; Bates favors the idea that these values are to be regarded as lower limits.

TABLE 7

Electron affinities calculated by extrapolations from ionization potentials

ATOM	LINEAR EXTRAPOLATION	QUADRATIC EXTRAPOLATION		
		Glockler	Bates	This review
	e.v.	*e.v.*	*e.v.*	*e.v.*
H	0.4	0.76	0.74	0.73
He		−0.53	−0.53	−0.53
Li	0.7	0.34	0.47	0.38
Be	0.3	−0.57	−0.8	−0.81
B	1.1	0.12	−0.1	−0.09
C	2.2	1.37	0.9	0.83
N	1.5	0.04	−0.6	−0.10 ± 1.0
O	3.0	3.80	1.0	0.70
F	5.0	3.94	2.9	2.93
Ne	0.2	−1.20	−1.2	−1.24
Na	1.1	0.08	0.0	−0.08
Mg	0.4	−0.87	−0.9	−0.91
Al	1.3	−0.16	0.2	0.50 ± 0.4
Si	2.8	0.60	1.7	2.70 ± 0.5
P	2.0	0.15	0.3	0.57
S	3.3	2.06	1.5	2.17 ± 1.0
Cl	4.8	3.70	3.1	3.05

In connection with their experimental determination of the electron affinity of carbon, Glockler and Sauseville (58) suggested a linear extrapolation formula; they showed that the ionization potentials of isoelectronic series could be represented by

$$(I_z)^{0.575} = aZ + b$$

where a and b are constants. Extrapolation of this line back to the negative ion leads to

$$(I_n)^{0.575} = 2(I_{n+1})^{0.575} - (I_{n+2})^{0.575}$$

The electron affinities (I_n) obtained in this way are also listed in table 7, but, with the single exception of the carbon atom, the method gives poor results. This extrapolation must fail in certain cases because it cannot predict a negative value for I_n; it also fails for systems containing more than eighteen electrons.

IX. QUANTUM-MECHANICAL CALCULATIONS

In a few cases quantum-mechanical methods have been applied to the calculation of electronic binding energies of negative ions, the most extensively studied being the negative hydrogen ion. Quantum-mechanically, H^- presents the same problem as the helium atom except that the nuclear charge is one unit, and a number of variational treatments of differing degrees of approximation have been carried out (16, 74, 81, 160, 183). There is complete agreement between all these calculations, the most accurate being those due to Heinrich, who gave $E(H)$ as 0.7466 e.v. Hylleraas (83) has shown that the excited (2*s*) state of the hydrogen atom has an electron affinity of 0.2876 e.v. The variation method was extended by Wu (185) to the study of He^- and Li^-, showing that He^-, as one would expect, is unstable, but that the lithium atom has an electron affinity of 0.54 v., in good agreement with the values given in table 7. Negative ions of lithium, and also of sodium and potassium, have been reported from mass-spectrometer measurements (40, 45, 155).

The extension of this method to more complicated atoms is scarcely practicable in view of the computational difficulties, and in such cases the only method available is that of the self-consistent field, which has been applied so successfully to atoms and positive ions by Hartree. Self-consistent field calculations on negative ions are in general more tedious than for atoms and positive ions, so that relatively few calculations have been carried out. However, Hartree and Hartree (66, 67) predicted the stability of O^-, but they obtained only a small negative value for N^- and small positive values for Na^- and K^-, which were within the limits of error of the method and so were not conclusive. Recently, Thaler (168) has improved the calculations on sodium and potassium and has established the positive nature of their electron affinities. A more detailed discussion of this subject is given by Massey in Chapter 1 of *Negative Ions* (110).

A third-order perturbation calculation recently carried out on the fluoride ion by Johnston (86) gave for its ionization potential, i.e., the electron affinity of fluorine, 73 kcal./gram-atom, a value which is only 10 kcal. below the best available figure.

The only attempt to calculate the energy of a negative molecular ion was made by Eyring, Hirschfelder, and Taylor (51) for H_2^-. This molecule presents exactly the same problem as the ground state of He_2^+, and by using exactly the same type of treatment as for He_2^+, they showed that whilst H_2 has a negative electron affinity, H_2^- is stable with respect to dissociation into $H + H^-$.

X. THE ELECTRON AFFINITIES OF O, O_2, O_3, AND OH

The discussion of these quantities has been treated separately because of the difficulty that has in general attended their elucidation, and because of their specific applications to astrophysics (10, 182) and to kinetics in aqueous solutions; it cannot, in fact, be claimed that all of them have yet been finally settled.

The exothermicity of the addition of one electron to an oxygen atom to give O^- has been the subject of much research and some controversy, with values ranging from 1 to 3 v. Vier and Mayer (175), using the magnetron equilibrium technique for gaseous oxygen, obtained the value of 70.8 ± 2 kcal. for the addition of one electron to an oxygen atom. At the other end of the range, Bates' extrapolation of ionization potentials gives 1.0 e.v., and values of 1.0 and 1.55 e.v. are given by spectroscopic term value interpolations by Bacher and Goudsmidt (4) and Hellmann and Mamotenko (70), respectively. Thirdly, there is a formidable body of electron impact data which favors an electron affinity for the oxygen atom of just over 2 v. Hagstrum and Tate (62) and Mann, Hustrulid, and Tate (109) have studied the formation of negative oxygen ions on electron impact with oxygen and water molecules, using their energy discrimination technique, and Lozier (106) has investigated the dissociation of O_2 into O^- plus either a normal or an excited oxygen atom, using his retarding potential method. (Hagstrum (61) has recently repeated most of these determinations, obtaining results in complete accord with the earlier measurements.) Thus, the following equations represent processes in which the products are formed with zero kinetic energy, the first being due to Mann, Hustrulid, and Tate, the second to Hagstrum and Tate, and the last two to Lozier:

$$\begin{array}{rll}
H_2O + e \rightarrow 2H + O^- - 7.5 \pm 0.3 \text{ e.v.}; & \therefore \Delta H_f(O^-) = 11.0 \pm 6.9 \text{ kcal.} \\
O_2 + e \rightarrow O + O^- - 3.0 \pm 0.4 \text{ e.v.}; & \therefore \Delta H_f(O^-) = 10.0 \pm 9.2 \text{ kcal.} \\
O_2 + e \rightarrow O + O^- - 2.9 \pm 0.2 \text{ e.v.}; & \therefore \Delta H_f(O^-) = 6.7 \pm 4.6 \text{ kcal.} \\
O_2 + e \rightarrow O^* + O^- - 12.0 \pm 0.2 \text{ e.v.}; & \therefore \Delta H_f(O^-) = 6.6 \pm 4.6 \text{ kcal.}
\end{array}$$

The latter value is derived on the assumption that O^* is $O(^5S)$, whose heat of formation is derived from spectroscopic data (127). A number of other reactions producing O^- from carbon monoxide and nitric oxide have been studied by Hagstrum and Tate and by Hanson (63), but here we are dependent on uncertain values for the latent heat of vaporization of carbon and the dissociation energy of nitrogen, and in fact these reactions have been used to try to establish more firmly these important quantities. Recent spectroscopic evidence (143) points to a value of $D(N—O) = 5.29$ e.v., which, combined with Hanson's data, leads to $E(O) = 2.1$ e.v., in close agreement with values from other electron impact determinations.

Furthermore, following Born and Heisenberg (25) and Hund (78), Briegleb (33) has calculated the proton affinity of O^-, i.e., the heat of the process $O^- + H^+ \rightarrow OH$, which is of the form

$$P_{O^-} = \frac{4}{5}\frac{e^2}{r_{OH}} + \frac{1}{5}\frac{\alpha_{\text{eff}}}{2} \cdot \frac{e^2}{r_{OH}^4} + \frac{e^2(\alpha_{O^-} - \alpha_{\text{eff}})}{2r_{O^-}^4}$$

where r_{OH} is the bond distance in OH, r_{O^-} and α_{O^-} are the ionic radius and polarizability of O^-, respectively, and α_{eff} is defined from the dipole moment of OH by

$$\mu_{OH} = er_{OH} - \alpha_{\text{eff}} \cdot \frac{e}{r_{OH}^2}$$

P_{O^-} works out to be 356 kcal./mole, which leads to a ΔH of formation for O^- of 1 kcal./gram-ion, with an uncertainty of at least ±10 kcal./gram-ion.

Finally, Metlay and Kimball (121) reinvestigated the equilibrium between electrons and oxygen atoms by the same method as Vier and Mayer (175). Using nitrous oxide as their source of oxygen atoms, they obtained an electron affinity of 53.8 ± 0.8 kcal. (i.e., $\Delta H_f(O^-) = 5.4 \pm 0.8$ kcal.) and this led them to further investigate the same process, deriving their oxygen atoms from molecular oxygen, as did Vier and Mayer. They showed that the oxygen was not completely dissociated into atoms at the temperature of the filament, and that negative ions were being formed by a process of addition of electrons to oxygen molecules with an exothermicity of 65.5 ± 2.5 kcal./mole. It would therefore appear that the electron affinity of oxygen atoms has definitely been established to be something of the order of 2.2 e.v., and Metlay and Kimball's equilibrium value is accepted here as being the most accurate.

TABLE 8

Lattice energies of peroxides

CRYSTAL	U	$\Delta H_f(MO_2)$	$\Delta H_f(M^{+n})$	$\Delta H_f(O_2^{-n})$
	kcal./mole	*kcal./mole*	*kcal./mole*	*kcal./mole*
CaO_2	735	−157.5	463.6	114
SrO_2	698	−153.6	427.7	117
BaO_2	647	−150.5	395.7	101
KO_2	172.2	−67	123.1	−17.9
RbO_2	168.2	−63.1	118.3	−13.2
CsO_2	164.5	−62.1	110.1	−7.7

There is little doubt as to the quantity $\Delta H_f(O^{--})$, which has been derived in table 6 from calculations of lattice energy, and it will not be considered further; there are no other data available from which this quantity could be derived.

Molecular oxygen forms two negative ions, O_2^- and O_2^{--}, the latter being stable only in ionic lattices. Calculations of lattice energy are available in both cases, although these are not as conclusive as usual because these ions lack spherical symmetry, and consequently there is some difficulty in the assessment of the Madelung constant for the lattice. Table 8 gives the lattice energy data of Evans and Uri (48) for both these ions. In the case of O_2^{--} this table represents the only available data, but the electron affinity for the addition of only one electron to an oxygen molecule has been the subject of much discussion. There is convincing evidence in favor of a value of about 1 v. for $E(O_2)$, but this has to be reconciled with Metlay and Kimball's figure of 65.5 kcal. (121), and with some extremely low-energy electron attachment processes. It is difficult to see what the figure of 65.5 kcal., which is derived from thermionic equilibrium measurements on oxygen gas, actually represents, for although it is possible to write at least two mechanisms involving O_3^- having exothermicities very close to this figure, both would seem to be ruled out by other thermodynamic considerations. Evans, Hush, and Uri (47) have recalculated the lattice energy data for the alkali metal peroxides, giving $E(O_2) = 16$ kcal., and Kazarnovskiĭ (91) has again repeated this work, obtaining 22 ± 1.5 kcal., with a maximum possible error of ±10 kcal./mole. It is also possible to estimate the electron affinity of the oxygen molecule, since, according to the empirical rules formulated by Mulliken (125), the binding energy of a homonuclear diatomic molecule comprised of atoms of the first long row of the Periodic Table is 2.5 e.v. per valence bond, this being defined as the difference between the number of pairs of bonding and antibonding electrons. The ground state $(^2\pi_g)$ of the O_2^- ion will be $(z\sigma_g)^2(y\sigma_u)^2(x\sigma_g)^2(w\pi_u)^4(v\pi_g)^3$, dissociating into a normal atom plus an O^- ion (9). Since only $z\sigma_g$, $x\sigma_g$, and $w\pi_u$ orbitals are bonding, the number of homopolar valence bonds is 1.5. Thus, the dissociation energy is approximately $1.5 \times 2.5 = 3.8$ e.v., which leads to a value for $E(O_2)$ of about 0.9 e.v. (*ca.* 21 kcal.). It would therefore appear to be fairly conclusively established that the electron affinity of the oxygen molecule is about 20 kcal./mole, but the position is complicated by the fact that electron attachment experiments by Bloch and Bradbury (20) and by Loeb (104) show that the oxygen molecule adds an electron with an exothermicity of less than 0.19 e.v. and less than 0.34 e.v., respectively. It has been postulated (see Bates and Massey (9) for a critical discussion of this subject) that the O_2^- ion possesses an excited vibrational energy level only a fraction of a volt below the ground state of the neutral oxygen molecule, and that it is this transition that has been observed in the electron swarm experiments. However, Biondi (18), as a result of microwave studies on the removal of thermal electrons by oxygen molecules, has raised doubts about this interpretation; the collision cross-section for the oxygen molecule is more in keeping with radiative capture than with the Bloch–Bradbury mechanism for capture by vibrational excitation. Whilst a satisfactory interpretation of these phenomena has not yet been suggested, it seems fairly certain that the electron affinity of the oxygen molecule is of the order of 20 kcal./mole, and that electron attachment, which takes place with almost zero exothermicity, leads to an excited state of O_2^- which is stabilized either by collision or by radiation of the excess energy.

Quite recently a new oxide of potassium, KO_3, has been prepared (92), and its ΔH of formation was found to be -62.1 ± 0.9 kcal./mole; from x-ray crystallographic studies its lattice energy has been calculated to be 149 kcal./mole (130). This means that the ΔH of formation of O_3^- is -32.5 kcal./gram-ion, and since $\Delta H_f(O_3) = 34.0$ kcal., the electron affinity of the ozone molecule is 66.5 kcal./mole. This at first appears very surprising, but it is interesting to note that both sulfur dioxide and selenium dioxide, which have similar electronic structures and similar geometric dispositions, have electron affinities of 64.5 and 53 kcal./mole, respectively.

At one time it was thought that the electron affinity of the OH radical was about 88 kcal./mole, this value resulting from a heat of hydration estimate by Weiss (178), Lederle's spectroscopic interpolation method (101), and some lattice energy calculations by Goubeau (59). However, on the whole, lattice energy data would appear to point to a lower value for E(OH). The lattice energies of the alkali metal hydroxides have been calculated from crystallographic data by Born and Kornfeld (26), Kapustinsky (89), and Goubeau and Klemm (60), the latter (an improvement on Goubeau's work) taking into account the dipole moment of the OH^- ion, although there is little divergence between any of these determinations. These coincide almost identically with lattice energies estimated from the specific gravity measurements of Juza (87) for the alkali metal hydroxides, with which they are compared in table 9. Yatsimirskiĭ (186) quotes the figure $\Delta H_f(OH^-) = -37.0 \pm 0.5$ kcal. (corrected), derived from lattice energies calculated by Kapustinsky's method (90). These figures correspond to an electron affinity of about 50 kcal./mole for the OH radical.

TABLE 9

Lattice energies of the alkali metal hydroxides

MOLECULE	U_C*	U_D	ΔH_f(MOH)	$\Delta H_f(M^+)$	$\Delta H_f(OH^-)_C$	$\Delta H_f(OH^-)_D$
	kcal./mole	*kcal./mole*	*kcal./mole*	*kcal./mole*	*kcal./mole*	*kcal./mole*
LiOH	234	231	−116.4	162.9	−45.4	−48.4
NaOH	202	205	−102.0	146.0	−46.0	−43.0
KOH	184	184	−101.8	123.1	−40.1	−40.1
RbOH	176	176	−98.9	118.3	−41.2	−41.2
CsOH	168	168	−97.2	110.1	−39.3	−39.3

* The subscripts C and D refer to crystallographic and density data, respectively.

However, there is some conflicting experimental evidence on E(OH). Recently Smith and Sugden (157), using a flame technique, have studied the equilibrium between OH radicals, electrons, and OH^- ions. In a hydrogen–air flame they estimated the electron concentration from the attenuation of centimetric radio waves by the flame, and the concentration of heavy ions, i.e., OH^- ions, was measured by studying the variation of the dielectric constant of the flame at frequencies of the order of 100 Mc./sec.; the flame temperature was measured optically. The concentration of OH radicals in the flame is not known, but can be estimated from previous work on the kinetics of hydrogen–air flames. Thus, the equilibrium constant $[OH][e]/[OH^-]$ can be calculated, and the knowledge of the flame temperature leads to a figure of 62 kcal./mole for the electron affinity of OH, with a possible error of ±6 kcal. This is hardly compatible with the value derived from lattice energies, which one would not expect to be in error by more than about 5 kcal./mole. In order to reduce the experimental value by 10 kcal., it would be necessary to assume that the observed flame temperature was in error by some 300°K. or that the equilibrium constant obtained is out by a factor of 10; the former would not seem credible, in spite of the discrepancy between the optically observed temperature and that calculated from the electron concentration, whereas the second alternative is not entirely out of the question in view of the approximations made in determining [OH] and [OH$^-$].

The resolution of these differences is not an easy matter at the present time, although it could be argued that one would not expect E(OH) to be very different from E(O) because the ionization potentials of O and OH are identical; pending further investigation, we will therefore accept provisionally the value derived from lattice energies, bearing in mind that it might be some 10 kcal. too low.

TABLE 10

Electron affinities of atoms

ATOM	METHOD*	REFERENCE	ΔH_f(X)	ΔH_f(X$^-$)	E(X)
			kcal./g.-atom	*kcal./g.-atom*	*kcal./g.-atom*
H($1s \rightarrow 1s^2$)	C	(74)	52.1	34.9	**17.22**
H($2s \rightarrow 2s2p$)	C	(83)	287.2	280.6	**6.63**
Li	C	(185)	37.1	24.6	**12.5**
Na	C	(168)	26.0	−2	**28**
K	C	(168)	21.5	5.5	**16**
Hg	E.A.	(150)	14.5	−20.9	**35.4**
C	A		138 ± 6	90 ± 14	48 ± 20
N	S.I.	(70)	85	101	**−16**
Sb	E.I.	(44)	60.8		**$\geqslant$47** ?
Bi	E.I.	(44)	49.7		**$\geqslant$17** ?
O	A		59.2	5.4	53.8 ± 0.8
S	E.I.	(129)	65.0	**$\leqslant$41**	$\geqslant$24
Se	E.I.	(44)	48.4		**$\geqslant$40** ?
Te	E.I.	(44)	47.6		**50** ?
F	A		18.7	−64.8	83.5 ± 2
Cl	A		29.0	−59.2	88.2 ± 1.5
Br	A		26.7	−54.9	81.6 ± 1.5
I	A		25.5	−49.1	74.6 ± 1.5
$O \rightarrow O^{--}$	L.E.	Table 6	59.2	**215**	−156 ± 10
$O^- \rightarrow O^{--}$					−210
$S \rightarrow S^{--}$	L.E.	Table 6	65.0	**145**	−80
$S^- \rightarrow S^{--}$					−($\geqslant$104)
$Se \rightarrow Se^{--}$	L.E.	Table 6	48.4	**145**	−97
$Se^- \rightarrow Se^{--}$					−($\geqslant$137) ?
$N \rightarrow N^{-3}$	S.I.	(70)	85	632	**−547**
$C \rightarrow C^{-4}$	S.I.	(70)	138	846	**−708**

* A = this review; C = calculation; E.A. = electron attachment; E.I. = electron impact; S.I. = spectral interpolation; L.E. = lattice energies; H.H. = heat of hydration; E = equilibrium; F = flame.

XI. DISCUSSION

Tables 10, 11, and 12 present a list of electron affinities for atoms, molecules, and free radicals, respectively, which have been determined or estimated by the methods described in the preceding sections. Figures in bold-face type represent the quantity directly determined by the method quoted, the others being calculated from these in conjunction with the heats of formation of the neutral species (if known) which are given in column 4 of each table. Errors are quoted where a reasonable assessment can be made. These figures call for a few brief comments. For the atoms Cl, Br, and I, there are in each case about ten independent experimental determinations, in addition to lattice energy data, from which the figures quoted have been derived. The evidence in favor of the values for F, O, H, and H_2 seems also to be quite conclusive, and those for O_2, Li, Hg, OH, SH, NH_2, CN, and $C(C_6H_5)_3$ may be regarded as fairly reliable, whilst at best the rest of the data can only be considered as tentative.

TABLE 11

Electron affinities of molecules

MOLECULE	METHOD*	REFERENCE	$\Delta H_f(X)$	$\Delta H_f(X^-)$	$E(X)$
			kcal./mole	*kcal./mole*	*kcal./mole*
H_2	C	(51)	0	16.5	**−16.5**
Cl_2	E.I.	(6)	0	− (**⩽39.2**)	⩽39.2
O_2	A		0	−20	20 ± 3
O_3	L.E.	(130)	34.0	**−32.5**	66.5
SO_2	F	(137)	−71.0	−135.5	**64.5**
SeO_2	F	(137)	?		**53** ?
MoO_3	F	(142)	?		**63.0** ?
NO	E.A.	(29)	21.6		**>0**
NO_2	L.E.	(186)	8.1	**−29.2**	37.3
NO_3	L.E.	(186)	13	**−76.5**	89.5
ClO_2	H.H.	(180)	24.7	**−54**	79
ClO_3	L.E.	(186)	37.0	**−54.3**	91.3
ClO_4	L.E.	(186)	(46)†	**−88.0**	134
BF_3	E.A.	(148)	−265.4	−315.4	**50**
$O_2 \rightarrow O_2^{--}$	L.E.	Table 8	0	**110**	−110
$O_2^- \rightarrow O_2^{--}$					−130
$C_2 \rightarrow C_2^{--}$	L.E.	(75)	?	**245**	

* See footnote to table 10.

† Assuming $\bar{D}(Cl—O)$ = 55 kcal./mole.

The electron affinity values for C and CH are based on the value of $L(C)$ = 138 ± 6 kcal./mole for the latent heat of sublimation of carbon, for which there is an increasing body of electron impact evidence, because this value leads to the most reasonably consistent electron affinities. If the interpretation of the appearance potential of C^- in the mass spectrum of methane is correct (158), we then have $E(C) = 2.0 \pm 0.8$ e.v. as the *lower limit*, in fair agreement with the extrapolation values (table 7) and an estimate of ≤ 1.7 e.v. by Massey (110). The higher values of $L(C)$ would lead to unreasonably high values for the electron affinity of both the carbon atom and the CH radical. (This assumption leads to the conclusion that the formation of the CH_2^- ion is accompanied by about 2 v. of kinetic energy.) Further evidence in support of this conclusion is afforded by the direct equilibrium measurements made by

TABLE 12

Electron affinities of free radicals

RADICAL	METHOD*	REFERENCE	$\Delta H_f(X)$	$\Delta H_f(X^-)$	$E(X)$
			kcal./mole	*kcal./mole*	*kcal./mole*
OH	A		10.1	−40 ± 3	50
SH	L.E.	(181, 186)	32	**−28 ± 4**	60
SeH	L.E.	(181)	35	**−12**	47
NH_2	A		43	15	28
CN	A		92.7 ± 4	10 ± 5	83 ± 9
CNO	L.E.	(188)		**−44**	
CNS	L.E.	(186)		**−8**	
ClO	H.H.	(151, 180)	25†	**−42**	67
BrO_3	L.E.	(188)		**−41**	
IO_3	L.E.	(188)		**−77**	
HSO_4	L.E.	(186)		**−243**	
HCO_3	L.E.	(186)		**−176.5**	
$CO_3 \rightarrow CO_3^{--}$	L.E.	Table 6		**−70 ± 20**	
HCOO	L.E.	(186)		**−104**	
CH_3COO	L.E.	(186)		**−119**	
$C_{15}H_{31}COO$	L.E.	(161)		**−96** ?	
HO_2	S.I. + H.H.	(47, 178)	16	−54	**70**
OC_6H_5	S.I. + H.H.	(80)			**27**
N_3	S.I. + H.H.	(35, 179)			**54**
CH	E.I.	(158)	108	**~70**	~38
CH_2	E.I.	(158)	68	**~90**	?
CH_3	A		32.6		~25
$C(C_6H_5)_3$	E	(12, 163)			**48 ± 5**
$SiCl_2$	E.I.	(176)			**⩾60**
BF_4	L.E.	(21)		**−402**	

* See footnote to table 10.

† $D(Cl—O) = 63$ kcal./mole (138).

Glockler and Sauseville (58) on carbon. Using a carbon filament as their source of both thermionic electrons and carbon atoms, they studied the equilibrium between electrons, carbon atoms, and (presumably) C^- ions by the magnetron technique, and were able to derive a series of values for $E(C)$ depending on what assumption was made for the latent heat of vaporization of carbon, *viz*:

$L(C)$	169	136	124	107 kcal./gram-atom
$E(C)$	4.0	2.8	2.1	1.4 e.v. (±0.3 e.v.).

Clearly, it is only the lower values for $L(C)$ which lead to a reasonable assessment of the electron affinity of carbon.

A brief discussion of the dissociation energies of hydrogen sulfide and sulfur (S_2) is relevant at this point. Pyrolysis of methyl mercaptan (147) leads to the ΔH of formation for the SH radical of 32 ± 4 kcal./mole. This means that $D(H—SH)$ is 89 kcal./mole, and if $D(S_2) = 101$ kcal. is used, $D(H—S)$ becomes 85 kcal./mole. $D(H—S)$ has been measured by Porter (138) and found to be 84.9 kcal./mole; this confirms the highest of the alternatives for $D(S_2)$, which is the value used in these tables. (These conclusions are not in agreement with the values recently derived by Evans and Wagman (50).) The difference between the first and second dissociation energies in water is about 18 kcal./mole, and in hydrogen sulfide about 4 kcal. One would expect this difference to approach zero as the H—X—H bond angle approaches 90°, and on this basis $D(H—SeH)$ is taken to be equal to $D(Se—H) = 65$ kcal. It thus follows in table 12 that $E(SH)$ is greater than both $E(OH)$ and $E(SeH)$, just as $E(Cl)$ is greater than $E(F)$ and $E(Br)$, in agreement with the conclusions of Evans, Warhurst, and Whittle (49). This behavior is also characteristic of the electron affinities of lithium, sodium, and potassium (see table 10); furthermore, if the linear extrapolation of ionization potentials (see table 7) has any physical significance, it is worthy of note that with the single exception of chlorine (where the linearity is beginning to break down) the electron affinity of a second row element is always calculated to be greater than that of the corresponding first row element.

A knowledge of electron affinities is essential in the discussion of ionic-covalent resonance; for example, if a molecule is considered to be a hybrid between covalent A—B and ionic A^+B^-, whilst it is possible to construct potential-energy curves for both these species without much difficulty, the separation between the two curves, which is the important criterion in ionic-covalent resonance, depends directly on the values of the ionization potential of A and the electron affinity of B. Much use has been made in such fields of isoelectronic extrapolation estimates (which are extremely sensitive to small errors in ionization potential data) and in consequence misconceptions have arisen: for example, it has often been assumed that with the exception of lithium, the alkali metals have zero electron affinity—by inference from the figure for sodium in table 7 (quadratic exrrapolation). Hence Hurd (79) states that in the majority of the alkali metal hydrides the electron affinities of the metals are so small in comparison with the electron affinity of hydrogen that the chemical bonds should be predominantly M^+H^-. Since, as table 10 shows, the alkali metals may have electron affinities as large, if not larger than that of hydrogen, this argument breaks down, and the nature of the bonding has to be considered not in terms of electron affinities, but in terms of electronegativities.

However, the lack of electron affinity data is felt very acutely when the strengths of chemical bonds are considered in relation to the electronegativities of the bonded species. We have two main definitions of electronegativity: Pauling (134) used the departure from thermoneutrality of reactions $A_2 + B_2 \rightarrow 2AB$ as a measure of the electronegativity difference between A and B, and Mulliken (126) has defined electronegativity as a function of $\frac{1}{2}(I + E)$, where I is the ionization potential of the particle being considered. The second definition would appear to be the more general but suffers from the disadvantage that so few electron affinities are accurately known. A scale of relative electronegativities for the alkyl radicals has been set up (see, e.g., Kharasch and Flenner (93)) from a study of the series of reactions

$$\begin{tikzcd} & \mathrm{R'HgCl} + \mathrm{R''H} \\ \mathrm{R'HgR''} + \mathrm{HCl} \arrow[ur] \arrow[dr] & \\ & \mathrm{R''HgCl} + \mathrm{R'H} \end{tikzcd}$$

It was supposed that it was the electronegativity of the radical R which governed whether it tended to remain linked to the mercury atom or to associate itself with the hydrogen atom, and on this assumption, by quantitative analysis of the reaction products (i.e., the ratios of R'HgCl and R''HgCl) it was possible to draw up a qualitative electronegativity series for the hydrocarbon radicals.

Studies on the thermochemistry of the mercury alkyls (36, 65, 124) have shown that $D(\mathrm{R{-}HgX})$, where X is a halogen, is greater than $D(\mathrm{R{-}HgR})$ by an amount which is a function of the electronegativities of both X and R. The more electronegative X, the bigger this difference, and the more electronegative R (in Kharasch's sense), the smaller is the difference. In other words, the greater the difference between the electronegativities of R and X, the greater is the difference $[D(\mathrm{R{-}HgX}) - D(\mathrm{R{-}HgR})]$. In the studies of mercury alkyls the analogy of Pauling's criterion for electronegativities is the heat of the gas-phase redistribution reaction:

$$\mathrm{HgR_2} + \mathrm{HgX_2} \rightarrow 2\mathrm{RHgX} + Q$$

As in the simple diatomic case, one would expect the heat of these reactions to be greater, the greater the electronegativity difference between R and X, and this is indeed the case, using again the order of electronegativities of hydrocarbon radicals obtained from Kharasch's experiments. The extension of Pauling's criterion for electronegativities to this case leads to the expression

$$Q = 23.06 \times 2(x_{\mathrm{X}} - x_{\mathrm{R}})(x_{\mathrm{XHg}} - x_{\mathrm{RHg}})$$

where Q is in kilocalories per mole, and the x terms represent the electronegativities of X atoms, and of R, XHg, and RHg radicals, respectively. Assuming that the difference $(x_{XHg} - x_{RHg}) = 0.325$ for all X and all R, it is possible to calculate relative values for Q with considerable precision. Electronegativity values[3] for the halogens are taken as $(I(X) + E(X)/5.56)$, i.e., $x_{Cl} = 3.03$, $x_{Br} = 2.77$, and $x_I = 2.46$, and the values of x_R are chosen to give the best fit between the calculated and the experimental values of Q. (The constant 5.56 is introduced to make electronegativities calculated from both Pauling's and Mulliken's expressions numerically coincident (38).) The calculated and experimental heats are compared in table 13. It is possible to derive, using

$$x_R = \frac{I(R) + E(R)}{5.56}$$

an electron affinity for each R radical from the value of x_R that is assumed in table 13. For the methyl radical, this leads to $E(CH_3) = 1.8 \pm 0.8$ e.v., to be compared with 1.8 e.v. from dipole moment extrapolations and 1.1 e.v. from half-wave potentials. It is not profitable to pursue this idea further at the present time because the thermochemical uncertainties are too large, 1 kcal./mole error in Q leading to an uncertainty of 0.4 e.v. in $E(R)$. Thus it is possible to extend Pauling's treatment for diatomic molecules to a discussion of the bonding in more complicated structures, and such an extension demonstrates that the electronegativities of atoms and radicals are fundamental to such a discussion; in this we are severely restricted by our lack of knowledge of electron affinities for many important free radicals.

TABLE 13

The heat of the reaction $HgR_2 + HgX_2 \rightarrow 2RHgX$

ALKYL	x_R (ASSUMED)	$HgCl_2$		$HgBr_2$		HgI_2	
		Calculated	Experimental	Calculated	Experimental	Calculated	Experimental
		kcal./mole	*kcal./mole*	*kcal./mole*	*kcal./mole*	*kcal./mole*	*kcal./mole*
$Hg(\alpha\text{-}C_4H_3S)_2$	2.75	4.2	4.1*	0.3	0.6*	−4.3	
$Hg(C_6H_5)_2$	2.36	10.0	10.0	6.1	6.0	1.5	1.6
$Hg(CH_3)_2$	2.14	13.4	13.2	9.1	9.5	4.8	6.5
$Hg(C_2H_5)_2$	2.08	14.3	14.5	10.3	10.4	5.7	5.4
$Hg(n\text{-}C_3H_7)_2$	2.10	13.9	13.9	10.0	10.0	5.4	5.4
$Hg(i\text{-}C_3H_7)_2$	1.90	16.9	15.0	13.0	12.9	8.4	8.3

* The figures for mercury di-α-thienyl are obtained from preliminary measurements by Hartley (64).

The determination of further electron affinities is not an easy matter; it is possible that the electronic equilibrium methods could be extended to a few more elements, but at the temperatures involved, molecules and radicals would be decomposed. The only reasonable hope of estimating the electron affinities of radicals would seem to lie in a study of the appearance potentials of negative ions, and the determination of their kinetic energies, although it must be borne

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[3] Neglecting, for simplicity, any considerations of valency state.

in mind that a careful search of the mass spectrum of methane has failed to reveal the existence of a CH$_3^-$ ion (158).

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