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Molecules with a High Electron Affinity

L.N.Sidorov

Experimental values of the electron affinity of inorganic compounds reported between 1975 and 1980 are systematically examined. The following methods of measuring electron affinity are briefly reviewed: photo-extraction and photoelectron spectroscopy, electron impact, ion-molecule reactions, ionisation by alkali metal atoms, ion-molecule equilibria, and methods based on measuring the frequency for intramolecular charge transfer in the absorption spectra of complexes and on calculations using a thermochemical cycle. Classes of compounds having an electron affinity greater than that of halogen atoms are identified by analysing published data. 166 references.

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I. INTRODUCTION

In the early 1970's very few substances with an electron affinity higher than that of the halogen atoms were known, and it was generally assumed that positive values of the electron affinity must lie in the range 0–4 eV. However, experimental methods of measuring electron affinity were being actively developed[1,2], and the first reports of compounds with very much higher electron affinities were beginning to appear[3]. These compounds are the strongest known oxidising agents, they readily form stable negative ions, and they lower the concentration of electrons in flames and plasmas.

In this paper we shall review experimental methods of measuring electron affinities, their validity when applied to substances with a high electron affinity, and the results obtained in the period 1975–1980. References to earlier work can be found in recent monographs[1,2]. Franklin and Harland's review[4] gives an account of experimental methods of studying negative ions and of the results obtained up to 1974, and it lists earlier reviews on negative ions (published since 1950). The most reliable information on the electron affinity of inorganic and of organic molecules published up to 1975 is summarised by Rosenstock and coworkers[5]. Between 1978 and 1980 four more reviews were published[6–9]; these contain more recent results and they partly overlap the present discussion.

Standard methods of determining electron affinities include the threshold methods, in which the affinities are calculated from the minimum energy of an impinging particle which will lead to the formation or breakdown of a negative ion. Among these methods are the photo-extraction and the electron impact method, and also methods based on the formation of negative ions by ion–molecule reactions or by collisions between neutral particles. Another large group of methods can be described as "equilibrium" methods, because the measurement consists in determining the temperature dependence (or the absolute value) of the equilibrium constant of a reaction involving the negative ion. This group includes the magnetron method and the surface ionisation method, and also the study of equilibria in gases, flames, and plasmas, and the classical effusion method, which was only very recently modified to deal with the special problems met in the determination of electron affinities.

Theoretical calculations of the electron affinity lie outside the scope of this review. The relevant methods are briefly outlined in Refs.1,2, and 7. Recent theoretical calculations of the electron affinity of hexafluorides are reported in Refs.10–12. Some of the more obscure methods which have been used to measure electron affinities are mentioned in Refs.1 and 2. In the latter part of this review we shall discuss two semiquantitative methods for estimating the electron affinity of complex molecules such as hexafluorides. The first is based on a calculation by the Born–Haber thermochemical cycle (see, for example, Ref.1), which includes the heats of reactions between charged particles and neutral particles. This method relies on theoretical calculations of the crystal lattice energy. The second method is based on a study of the absorption spectra of complex molecules, coupled with an experimental determination of the frequency of the transition corresponding to the intramolecular charge transfer process. Theoretically[13] this frequency is related to the ionisation potential of the electron donor and the electron affinity of the acceptor. The electron affinity of the acceptor molecule can therefore be estimated.

II. PHOTO-EXTRACTION AND NEGATIVE ION PHOTOELECTRON SPECTROSCOPY

For a more detailed discussion of the topics examined in this Section the reader is referred to recent monographs[1,2] and papers[14,15]. Both methods depend on a calculation of the energy balance in the photo-extraction of an electron from a negative ion:

$$AB^- + h\nu = AB + e \ .$$

Two distinct approaches have been used. In the first the frequency of the radiation is varied, and the threshold energy for the photo-extraction of the electron is found experimentally; in the second the radiation frequency is fixed and the kinetic energy spectrum of the emitted electrons is recorded. Since the kinetic energy spectrum characterises the energy levels of the negative ion, the term "negative ion photoelectron spectroscopy" has been proposed for

this variant. In the case of atomic anions the interpretation of the results is unambigous, and the experimental values of the frequency and energy of the emitted electrons can be used to calculate the electron affinity of the atom with high precision (Table 1): some workers[16] quote an uncertainty of ±0.0003 eV. For molecular anions the calculated value corresponds to a vertical transition, and in general this is not the same as the electron affinity of the molecule (defined as the energy difference between the ground states of the molecule and the ion). The difference between a vertical and an adiabatic transition can be large, especially in the case of molecules with a large electron affinity.

Table 1. Electron affinities determined by photo-extraction (PE) and photo-electron spectroscopy (PES) methods.

Molecule	E_a, eV	Method	Reference
AsH	1.0±0.1	PE	[20]
As_2	0	PE	[21]
BeH	0.7±0.1	PE	[20]
CD_2O	1.552±0.022	PES	[22]
CD_2S	1.858±0.006	PE	[23]
CH	1.238±0.008	PES	[24]
CH_2	0.21±0.03	PES	[25]
CH_3	0.08±0.03	PES	[26]
CH_3	1.882±0.024	PES	[22]
CH_3O	1.570±0.022	PES	[22]
CH_3O	1.59±0.04	PE	[27]
CH_3	1.86±0.04	PE	[23]
CO_3	2.69±0.14	PE	[28]
CO_3	2.9±0.3	PE	[19]
CO_3	3.26±0.17	PE	[29]
C_2	3.391±0.017	PE	[30]
C_2H	2.97±0.10	PE	[18]
CaH	0.93±0.05	PE	[20]
FeCO	1.26±0.02	PES	[31]
$Fe(CO)_2$	1.22±0.02	PES	[31]
$Fe(CO)_3$	1.8±0.2	PES	[31]
$Fe(CO)_4$	2.4±0.3	PES	[31]
FeO	1.492±0.020	PES	[17]
LiCl	0.61±0.02	PES	[32]
MgH	1.05±0.06	PE	[20]
NH	0.381±0.014	PES	[33]
NO_2	2.5	PE	[34]
O_3	2.102±0.025	PE	[35]
PH	1.028±0.010	PES	[36]
PH	1.00±0.06	PE	[20]
PH_2	1.271±0.010	PES	[36]
PO	1.092±0.010	PES	[36]
P_2	0.65	PE	[21]
S_2	2.00±0.15	PE	[21]
SiH	1.277±0.009	PES	[37]
SiH_2	1.124±0.020	PES	[37]
ZnH	0.95	PE	[20]

Experimental studies of the photo-extraction of electrons from negative ions are fairly complicated, and include a number of steps (not least, the generation of a strong beam of negative ions). The early work was carried out by the crossed beam method[1], in which the source of ions is a glow discharge and the ions emerge from a slit in the anode with an energy of ~ 300–500 eV and an energy spectrum 25–50 eV wide. The ion beam is accelerated, collimated, and after passing through the mass separator it enters the photon interaction region. The light source was either an argon ion laser working at 4880 and 5145 Å (2.5 and 2.4 eV) or a dye laser with a continuously swept frequency in the energy range 1.75–2.4 eV. The experiment consisted in recording the kinetic energy spectrum of the emitted electrons and measuring the threshold value of the photon energy (i.e. the minimum photon energy giving rise to photo-extraction).

Thus, Engelking and Lineberger[17] produced a strong beam of FeO^- and O^- ions in a low-pressure electric discharge, struck by burning iron pentacarbonyl in oxygen or nitrous oxide. The ions were accelerated to 680 eV and mass-separated in a Wien filter. The ion beam was crossed with a photon beam of 2.5 eV energy (4880 Å). The emitted electrons were energy-analysed, using an electrostatic monochromator with a resolution of 0.06 eV. The electron energy scale was calibrated by using the O^- ions present in the same discharge. As a result the electron affinity of the FeO molecule was found[17] to be $E(FeO) = 1.492 \pm 0.020$ eV.

In another type of apparatus ion–cyclotron resonance is used. This method does not require an accelerating voltage for mass separation, and the ions move from the source region to the analyser with near-thermal velocities. The time of residence of the ion in the apparatus is of the order of seconds: this is the most attractive feature of the "ion–cyclotron resonance + photo-extraction" method. The use of ion–molecule reactions to generate negative ions becomes possible. The primary negative ions are formed by collisions between neutral molecules and electrons (emitted by a thermionic cathode), and these ions take part in ion–molecule reactions during their subsequent slow drift within the source. The list of negative ions which can be studied has been greatly increased by the advent of this method. Janousek and coworkers[18] determined the electron affinity of the C_2H radical in an apparatus which included a V-5900 ion–cyclotron resonance spectrometer. The pressure in the drift region was 2×10^{-7} mmHg, the life time of the ions was ~ 0.5 s. The C_2H^- anions were obtained by the ion–molecule reaction $C_2H_2 + F^- \rightarrow C_2H^- + HF$. The source of F^- was the dissociative ionisation of nitrogen trifluoride by electron impact ($NF_3 + e \rightarrow NF_2 + F^-$). The electron affinity value obtained in these experiments was $E(C_2H) = 2.94 \pm 0.10$ eV.

A study of negative molecular ions relevant to the chemistry of the *D* layer in the ionosphere was carried out in the molecular physics laboratory of the Stanford Research Institute[19]. This work was aimed mainly at determining the photo-dissociation and photo-extraction cross-sections of ions such as $O_2^-.O_2$, $O_2^-.H_2O$, $O_3^-.H_2O$, CO_3^-, CO_4^-, HCO_3^-, $HCO_3^-.H_2O$, $NO.O_2^-$, $NO.O_2^-.H_2O$, and $NO_2^-.H_2O$. The measurements of cross-section could (in some cases) be interpreted in terms of the threshold values of the photo-extraction energy, and in these cases the electron affinity was calculated. The apparatus used in this work included a mass spectrometer with a drift tube. The negative ions were produced by collision with electrons emitted from a thorium–iridium cathode, and by the subsequent ion–molecule reactions in the drift tube. The ion source and the drift tube were filled with the gas (or gas mixture) at 0.05–1.0 mmHg pressure. The ions drifted (under the influence of a weak electric field) with an average velocity about an order of magnitude lower than the thermal velocity. During their drift time the ions undergo enough collisions with neutral particles to come to thermal equilibrium with the medium, and the excess energy acquired by the ions during their formation relaxes. This is one of the main advantages of the method, since it eliminates errors arising from the presence of ions in excited states and possessing an excitation energy much greater than the thermal energy. Approximately 2 mm beyond the exit slit of the drift tube the ions cross a modulated photon beam generated either by a dye laser with a continuous spectrum in the region of 4250–4600 Å or by an argon or krypton ion laser with a discrete set of lines at 4067–5309 Å. Beyond the exit slit the ions enter the high-vacuum region, which includes a quadrupole mass spectrometer. After mass separation the ions are recorded in a two-channel counter in the presence (I) and in the absence (I_0) of laser radiation. The percentage breakdown of the ions is small, and the I/I_0 ratio is close to unity. Therefore the signal needs to be integrated over a fairly long time: from minutes to hours, depending on the photo-extraction cross-section.

The method has been used also to determine the electron affinity of carbon trioxide[19]: the result was $E(CO_3) = 2.9 \pm 0.3$ eV. Electron affinity values obtained by the photo-extraction and photo-electron spectroscopy method and published between 1975 and 1980 are listed in Table 1.

III. ELECTRON IMPACT

Negative ions can be formed in several ways during electron impact. However, direct electron capture is not very effective because of the need to transfer the affinity energy to a third body, or to dissipate this energy among the internal degrees of freedom of the molecule. Processes leading to the formation of ion pairs have been successful, but only for atoms[1]. Therefore only the dissociative electron capture process has been widely used to measure electron affinities. The most recent review of dissociative electron attachment processes is given in Ref.38, and earlier work is discussed in Refs.4 and 39.

Table 2. Electron affinities determined by the electron impact method.

Molecule	E, eV	Reference	Molecule	E, eV	Reference
AsBr	1.3	[40]	$NaBO_2$	1.43±0.22	[47]
$AsBr_2$	3.5	[40]	$NbCl_4$	1.4	[50]
AsCl	1.3	[40]	PCl_3	0.95	[51]
$AsCl_2$	2.2	[40]	PF_3	3.7	[52]
AsF	1.3	[40]	$SiBr_2$	1.7; 1.9	[46]
AsF_2	0.8—0.9	[40]	$SiCl_2$	0.64; 0.90	[46]
C_2F_3	⩾1.6	[41]	$SnBr_2$	1.33	[53]
C_3F_5	~3.0	[41]	$SnBr_3$	3.31	[53]
ClF	2.37±0.21	[42]	$SnBr_3$	3.08	[51]
ClF_2	⩾0.9±0.2	[42]	$SnCl_2$	1.04	[53]
ClF_2	⩾3.23±0.19	[43]	$SnCl_3$	2.53	[53]
ClF_3	⩾2.40±0.10	[43]	SnF_3	⩾1.2	[53]
ClO	2.35±0.12	[44]	SnI_2	1.74	[53]
ClOF	2.00±0.19	[44]	SnI_3	3.21	[53]
ClO_2	1.80±0.16	[44]	$TaCl_4$	>1.4	[50]
$(CrO_3)_2$	1.6	[45]	$TiBr_3$	0.76	[51]
$(CrO_3)_3$	1.8	[46]	$TiCl_3$	0.61	[51]
$GeBr_2$	1.6; 1.8	[46]	$VOCl_3$	⩾3.6	[54]
$GeCl_2$	2.56	[46]	VOF_3	3.1±0.3	[54]
$GeCl_3$	1.83	[46]	WF_4	2.6	[55]
KBO_2	1.17±0.22	[47]	WF_4	⩾1.0	[56]
NF_2	0.4±0.2	[48]	WF_5	1.25±0.2	[55]
NF_2	⩾0.7±0.2	[49]	WF_5	⩾0.4	[56]
			WOF_3	⩾0.3	[56]

The dissociative electron capture process is described by the reaction $AB + e \rightarrow A + B^-$. The lower limit of the electron affinity of the molecule, $E(B)$, can be found from the threshold value of the electron energy, E_e, if the bond breaking energy $D(A-B)$ is known:

$$E(B) \geqslant D(A—B) - E_e + T ,$$

where T is the combined kinetic energy of the A and B residues. The inequality sign allows for the possible generation of the dissociation products in an excited state. Electron affinity values obtained in 1975—1980 by the electron impact method are listed in Table 2.

IV. ION—MOLECULE REACTIONS

When the collision between a negative ion and a neutral particle results in an endothermic reaction it is possible, in principle, to determine the enthalpy of formation of the negative ion and the electron affinity. In the simplest case, when the reaction consists simply in the exchange of an electron, the threshold value of the energy of the mutually repelling particles which leads to charge transfer gives the difference in electron affinity between the molecules taking part in the reaction. The electron affinities of halogen molecules[57] and oxygen compounds[58] have been obtained in this way:

Molecule	F_2	Cl_2	Br_2	I_2	O_2	O_3	NO	NO_2	NO_3
E, eV	3.08	2.38	2.51	2.58	0.48	1.96	0.09	2.04	⩾2.49

The measurements consisted in determining the threshold energy of processes such as $F^- + F_2 \rightarrow F_2^- + F$, which corresponds to the difference in electron affinity between the atom and the molecule.

Charge transfer processes can be accompanied by chemical reactions leading to the formation of new ions and molecules. The threshold energy of the colliding particles gives the enthalpy of the reaction, and the possibility of calculating the electron affinity arises when the enthalpies of formation of all the other participants in the reaction are accurately known. A good illustration of this method is provided by an experimental determination[49] of the threshold energy (found to be 0.64 eV) for reactions of the type of

$$I^- + HNO_3 \rightarrow NO_3^- + HI .$$

This quantity is the enthalpy of the reaction, and since the enthalpies of formation of I^-, HNO_3, and HI are known, the enthalpy of formation of the NO_3^- ion can be calculated: $\Delta H_f^\circ(NO_3^-) = -3.04 \pm 0.09$ eV. In order to determine the electron affinity we must know $\Delta H_f^\circ(NO_3)$. Using the published value of this parameter the authors[49] obtained $E(NO_3) = 3.77 \pm 0.25$ eV.

Another example of the prospects of ion—molecule reactions is provided by a study[60] of the dissociation of negative ions by collisions with inert gas atoms. In this work a more complicated technique was used to produce the beam of negative ions. Whereas in the work described above[49] the range of negative ions was very limited, and only processes giving rise to a single type of negative ion could be used, in Ref.60 a mass separation of the negative ions was carried out as the first stage in the process. As a result, any method of ionisation could be used, including methods which yield a large number of different negative ions. After mass separation the ion beam passed through a 90° electrostatic analyser which selected the ions having a prescribed energy in the range 0.3—170 eV with an energy scatter of 0.2—0.3 eV. These ions have a known kinetic energy when they reach the collision chamber, where they undergo endothermic ion—molecule reactions to form new ions which are detected in a second mass spectrometer. The experiments consist in determining the minimum energy of the colliding ions for which reaction products are formed. The technique has been used[61] to study the dissociation of negative ions on the gases A (Xe, Kr, Ar, Ne, He, and N_2). The average value of the threshold energy for the reaction $N_2O^- + A \rightarrow N_2 + O^- + A$ was 0.43 eV, which can be combined with published data on the bond energy $D(N_2—O)$ and on $E(O)$ to give $E(N_2O) = 0.22$ eV.

Ion—cyclotron resonance apparatus is widely used in studies of ion—molecule reactions, usually for exothermic reactions which take place at thermal energies between the colliding particles. Hence the pair of particles on which the electron affinity is measured must be chosen so that the charge transfer reaction can proceed in one case but not in the other. This allows both the upper and the lower limit of the electron affinity of the given molecule to be determined. The electron affinity of tungsten hexafluoride has been determined in this way[62]. Charge transfer was shown to occur with fluorine but not with chlorine, and hence the value $E(WF_6) = 3.5 \pm 0.1$ eV was obtained.

In an earlier study[63] an attempt was made to measure the threshold energies of ion–molecule reactions directly. A beam of negative UF_6^- ions was produced by surface ionisation of uranium hexafluoride on a rhenium filament at 800–900 K, i.e. at a temperature giving a negligibly small electron emission current. The energy of the UF_6^- anions was varied between 0 and 40 eV, and the threshold values of the energy for the following reactions were identified[63]:

$$UF_6^- + UF_6 \rightarrow UF_7^- + UF_5$$
$$UF_6^- + BF_3 \rightarrow UF_5 + BF_4^- ,$$

leading to the affinities of uranium hexafluoride for electrons and for the fluoride ion shown in Table 3.

Table 3. Electron activities obtained from the threshold energies of ion–molecule reactions.

Molecule	*E*, eV	Reference	Molecule	*E*, eV	Reference
BrO	⩾1.5±0.2	[66]	NaCl	0.77	[71]
Cl	3.4	[67]	NaF	0.42	[71]
CO	1.37	[67]	OCN	3.6±0.2	[64]
CO_3	⩾2.80	[68]	O_3	⩾1.8234	[68]
ClO	⩾1.6±0.2	[66]	O_3	⩾2.26+0[04	[73]
IN	1.3	[69]		−0.06	
IO	2.6	[67]	SF_2	3.4±0.2	[74]
IO	2.3	[70]	SF_5	>3.45	[74]
IO	⩾2.1±0.3	[66]	SO	1.2	[70]
KBr	0.61	[71]	SO_2	1.05	[70]
KCl	0.63	[71]	SO_2Cl	<3.17	[75]
KF	0.23	[71]	SO_2F	<2.34	[75]
NO	0.8±0.2	[69]	UF_5	2.4	[63]
NO_2	2.1	[69]	UF_6	4.9±0.5	[63]
NO_3	3.77±0.25	[59]	UF_6	⩾3.61	[76]
N_2O	0.22±0.11	[61]	UF_6	>5.0	[77]
NaBr	0.94	[71]	UF_7	⩽5.5	[63]
			WF_6	3.51±0.1	[62]

Another possible way of determining thermochemical quantities by using ion–cyclotron resonance apparatus involves measuring the equilibrium constants of ion–molecule reactions. Thus, in an experimental study[64] of the reaction

$$HCO_3^- + HNCO \rightleftarrows OCN^- + HCO_2H$$

the rate constants of the forward (k_f) and of the reverse (k_r) reaction were determined, and the equilibrium constant $K = k_f/k_r$ was calculated. The equilibrium constants obtained in this way agreed exactly with the values directly determined by measuring the concentration ratios of the ions and molecules under conditions giving long residence times of the ions in the reaction zone. By combining the result with published data on the enthalpy of formation of the reactants and products the authors[64] obtained $E(OCN) = 3.62 \pm 0.2$ eV for the electron affinity of the OCN radical.

A new method of calculating electron affinities from studies of electron extraction by glancing-angle impact has been proposed[65]. Negative ions (B^-) having a high kinetic energy (~ 6000 eV) can be converted into B^+ ions by glancing-angle collisions with neutral molecules:

$$B^- + N \rightarrow B^+ + N + 2e \cdot$$

If both B^- and B^+ are in their electronic ground state the difference in their kinetic energies is equal to the sum of the ionisation potential $I(B)$ and the electron affinity $E(B)$ of the B molecule. If $I(B)$ is known, we can calculate the electron affinity by measuring the difference between the kinetic energies of the B^- and the B^+ ion. For example, $E(CN) = 3.3$ and $E(S_2) = 2.15 \pm 0.5$ eV have been determined in this way[65], in good agreement with published data. Electron affinities obtained in 1975–1980 from studies of ion–molecule reactions are given in Table 3.

V. IONISATION BY COLLISION OF NEUTRAL PARTICLES

Collisions between neutral particles can lead to the formation of ion pairs, thus allowing electron affinities to be determined from the threshold value of the energy of the colliding particles. Under these conditions the threshold energy directly gives the difference between the ionisation potential and the electron affinity of the particles. The formation of ion pairs by collisions between neutral particles is discussed in Ref.78.

Table 4. Electron affinities determined by ionisation with alkali metal atoms.

Molecule	*E*, eV	Reference	Molecule	*E*, eV	Reference
AuF_6	10.0±0.5*	[82]	NO_3	3.7±0.2	[91]
BBr_3	0.8±0.2	[83]	O_2	0.44	[95]
$BClBr_2$	0.9±0.2	[83]	O_3	2.14±0.15	[96]
BCl_2Br	0.7±0.2	[83]	$PBrCl_2$	1.5	[97]
BCl_3	0.3±0.2	[83]	PBr_2Cl	1.6	[97]
BF_3	0.0±0.2	[83]	PBr_3	1.6	[97]
Br_2	2.6±0.2	[84]	PCl_3	0.8	[97]
CCl_2	1.8±0.3	[85]	$POCl_2$	3.8	[97]
CCl_3	1.3±0.3	[85]	$POCl_3$	1.4	[97]
CCl_4	2.0±0.2	[85]	PtF_6	⩾5.1±0.5	[93]
$CFCl_2$	1.1±0.3	[85]	ReF_6	>3.89	[92]
$CFCl_3$	1.1±0.3	[85]	ReF_6	⩾5.1±0.5	[93]
CF_2Cl	1.6±0.3	[85]	SF_3	3.1±0.2	[93]
CF_2Cl_2	0.4±0.3	[85]	SF_4	0.8±0.2	[93]
CF_3	1.9±0.3	[85]	SF_5	2.9±0.1	[98]
CF_3Br	0.9±0.2	[86]	SF_5	2.7±0.2	[93]
CF_3I	1.6±0.2	[86]	SF_6	0.32±0.15	[98]
CF_3I	1.4±0.2	[87]	SF_6	0.46±0.20	[93]
$CHCl_2$	0.0±0.3	[85]	SO_2	1.14±0.15	[96]
CH_3NO_2	0.4±0.2	[86]	SO_3	1.70±0.15	[96]
COS	0.46±0.20	[88]	SbF_6	6.0	[82]
CS_2	1.0±0.2	[88]	SeF_6	2.9±0.2	[93]
CS_2	0.6±0.2	[89]	$SnCl_3$	3.7±0.5	[90]
Cl_2	2.4±0.2	[84]	$SnCl_4$	2.49±0.15	[90]
FCl	1.5±0.3	[85]	TeF_6	3.3±0.2	[93]
$GeCl_3$	>2.61	[90]	$TiCl_4$	2.88±0.15	[90]
HNO_3	0.57±0.15	[94]	UF_5	⩾1.9	[94]
IrF_6	>4.34	[92]	UF_5	4.0±0.4	[99]
IrF_6	⩾5.1±0.5	[93]	UF_6	⩾4.3	[94]
MoF_5	>3.3	[94]	UF_6	5.1	[99]
MoF_5	⩾3.5	[93]	WF_5	1.25	[100]
MoF_6	>3.89	[92]	WF_5	⩾1.8±0.3	[93]
MoF_6	⩾4.5	[94]	WF_6	>4.5	[92]
MoF_6	⩾5.1±0.5	[93]	WF_6	⩾4.9	[94]
NO_2	2.5	[95]	WF_6	3.7	[99]
			WF_6	5.1±0.5	[93]

* Estimated value.

In the collision of neutral particles the main problem is how to control the energy of the collision. In ion–molecule reactions this problem disappears, since the energy of charged particles is readily controlled by an electrostatic field, but in reactions between neutral particles a special solution of this problem must be found. Two different approaches have been used so far to prepare beams of neutral particles having energies of a few electron volts. The first relies on the application of supersonic flow technologies. The technique has been used[79,80] to study the formation of the ion pairs Cs^+ and Cl^-, Cs_2Cl^+ and Cl^-, and Cs^+ and $CsCl_2^-$ by collisions between the molecules CsCl or Cs_2Cl_2 and the atoms Ar, Kr, Xe (or the molecule SF_6) at energies which could be varied from thermal energy to 18 eV. These very high energies (for neutral particles) were obtained by gas-dynamic methods. No numerical values of the electron affinity of molecules have been obtained by this method so far: one possible reason is the formation of ion pairs at energies well in excess of the threshold energy of the reaction.

The second approach uses ionisation by collisions with alkali metal atoms. "Fast" alkali metal atoms can be obtained by transferring charge from M^+ ions which have been accelerated in an electric field to neutral M atoms. This method can yield atomic beams of alkali metals having a high and controlled (to ~ 0.1 eV) energy. Ionisation by alkali metals is widely used to measure the electron affinity of organic[81] as well as inorganic molecules. The method has been intensively developed by several groups of workers, and in recent years it has yielded important information on electron affinities (Table 4).

VI. EQUILIBRIUM METHODS

The electron affinity can be calculated by measuring the equilibrium constant of the reaction $A^- \rightarrow A + e$ at a known temperature T:

$$K_p = p_A p_e / p_{A^-} ,$$

where p_A, p_e, and p_{A^-} are the partial pressures of A molecules, of electrons, and of A^- ions in the system in thermodynamic equilibrium. The electron affinity, numerically equal to the heat ΔH_0° of the reaction at $T = 0$ K, is calculated by the equation

$$E(A) = \Delta H_0^\circ = RT \ln K_p + \Delta\Phi^\circ ,$$

where $\phi^\circ = S_T^\circ - (H_T^\circ - H_0^\circ)/T$ is the reduced Gibbs energy.

For gaseous molecules and ions the quantity ϕ° can be calculated by statistical thermodynamic methods from molecular constants. Unfortunately, very few data are available on the electronic states, structures, and vibration frequencies of negative ions, and practically none on polyatomic ions. Hence the calculations must be based on estimated molecular parameters, which lowers the precision of the results, but to an acceptable extent, since the entropy of the reaction is relatively insensitive to the uncertainty of the molecular parameters of the reactants and products.

In most cases the error in the estimated entropy of the gas-phase reaction is between 1 and 4 e.u., leading to an error of ~ 0.05–0.20 eV in the estimated electron affinity. The main difficulty in the use of this method lies in establishing an experimental procedure which gives reliable values of the equilibrium constant. Different methods have to be combined in order to obtain simultaneous measurements of the partial pressure of molecules, ions, and electrons. The neutral and the charged particles must be sampled from the same place, where local equilibrium is known to exist. The difficulty of simultaneously measuring the relative pressures of negative ions and electrons was solved by an apparatus which has been called the magnetron[101].

A method which avoids the need to measure the concentration of electrons can be based on surface ionisation, in which two ion currents are measured as a function of the surface temperature of the ion source. The result of this experiment is the difference in electron affinity between two atoms or molecules. If one of the electron affinities is known, the other is easily calculated. The surface ionisation method is widely known, and fully described in Ref.102. The latest developments in surface ionisation techniques in relation to the determination of electron affinities are discussed in Ref.103. The sample is evaporated from the surface of the ion source by means of a beam of positive ions rather than by a molecular beam (as in the conventional form of the method). This improvement offers very good control of the purity of the surface and of the thickness of the evaporated layer. The positive ions are neutralised, and the resulting molecules can undergo electron capture[103].

The most serious shortcomings of the magnetron method and of the surface ionisation method are due to the presence of temperature and concentration gradients between the bulk of the gas phase and the surface of the hot filament, and also to the large variations in the local value of the work function[104], which can lead to incorrect values of the electron affinity[1].

A more direct approach to the measurement of electron affinity relies on measuring the concentrations or pressures of ions, electrons, and molecules in a gas[64,105,106], vapour[107,108], flame[109], or plasma[110,111]. The experimental procedures developed for exploiting the drift of ions in a carrier gas have been used in studies of ion-molecule reactions and of the rate constant of electron removal by a bimolecular reaction such as $O_2^- + O_2 \rightarrow e + 2O_2$[105] or $NO^- + NO \rightarrow e + 2NO$.[106] At the same time the rate constants of the electron capture reactions in three-body collisions (i.e. in the reverse reaction) were also measured. Knowing the rate constants for the forward and the reverse reaction, the equilibrium constant and the electron affinity were calculated for the O_2[105] and the NO molecule[106]. Another example of the determination of equilibrium constants was mentioned in Section III above: the measurement of the rate constants of the forward and the reverse reaction by using ion–cyclotron resonance. The electron affinity of the OCN radical was calculated[64] from the equilibrium constant measured in this way.

Table 5. Electron affinities determined by measuring the equilibrium constants of ion–molecule reactions.

Molecule	E, eV	Reference	Molecule	E, eV	Reference
BO	$\geqslant$2.49	[109]	PO_2	3.0	[110]
BO_2	4.07±0.21	[109.112]	PO_3	3.5	[110]
CeF_4	3.6±0.3	[124]	PtF_4	5.25±0.20	[128]
CrO_3	2.38±0.52	[109.144]	PtF_5	6.5	[128]
FeF_3	4.25±0.20	[124]	PtF_6	8.0±0.3	[126]
FeF_4	5.40±0.20	[124]	ReO_3	2.85±0.55	[109]
FeO_2	2.85	[110]	ReO_4	4.45	[115]
$HCrO_3$	4.04±0.52	[109.114]	UF_5	3.30±0.16	[129]
$HMoO_3$	4.25	[109.176]	UF_6	4.89±0.25	[129]
HWO_4	4.15	[109.113]	WF_6	5.5	[111]
MnF_2	4.36±0.15	[127]	WO_3	3.64±0.41	[109.113]
MnF_3	5.27±0.20	[128]	WO_2	3.6	[111]
MoO_3	2.58±0.41	[109.116]	MoF_5	3.63±0.20	[72]
PO_2	3.68±0.41	[115]	MoF_6	3.68±0.20	[72]

A series of papers[112–116] describes ion–molecule equilibrium studies in flames consisting of hydrogen, nitrogen, and oxygen. The aim of the work was to study electron capture processes by additives assumed to have a very high electron affinity. Tungsten was introduced into the flame as $W(CO)_6$ or WF_6, chromium as $Cr(NO_3)_3$ or $Cr(CO)_6$, and rhenium as an aqueous solution of a rhenium salt or as ReF_6. Atomic potassium or caesium were also added as electron donors. The experiment consisted in measuring the equilibrium constants of the reactions involving molecules, ions, and electrons:

$$e + H_2WO_4 \rightarrow HWO_4^- + H$$

$$HWO_4^- + H \rightarrow WO_3^- + H_2O$$

$$WO_3 + e \rightarrow WO_3^- .$$

The concentrations of negative ions and of electrons were determined with a mass spectrometer and microwave resonator; the concentrations of neutral molecules or atoms were

calculated from standard thermodynamic formulae by using the heat of formation and the total concentration of the additive (i.e. the weights of chromium, molybdenum, tungsten, or rhenium introduced). From the equilibrium constants obtained in this way the heats of the reactions and the heats of formation of the negative ions were calculated. The electron affinities were determined as the difference between the heats of formation of the negative ion and those of the corresponding neutral molecule. The results are given in Table 5.

Some recent attempts to study electron affinities by measuring the electrical conductivity of plasmas have been reported[110-111]. The method depends on the large decrease in the electrical conductivity of the plasma caused by the formation of molecules and radicals with a high electron affinity. Model calculations suggest that the decrease can be as high as 10–40%, depending on the type and concentration of the additive: for example, oxides of iron, aluminium, and phosphorus lead to the formation of the ions FeO_2^-, PO_2^-, PO_3^-, and AlO_2^-.[110] The electrical conductivity of the plasma has been measured[111] as a function of the type and concentration of the additives. We see from the results (Table 5) that some hexafluorides have extremely high electron affinities (~ 5 eV).

The effusion method was first used in 1971–1974 to measure electron affinities[107,108,117] by studying the equilibrium between negative ions and neutral molecules in a Knudsen cell. The cell had to be heated to ~ 2000 K in order to give measurable concentrations of negative ions. The experimental substances were placed (at lower temperatures) in separate temperature-controlled compartments. By heating these compartments the experimental substances were transferred through connecting channels to the mixing chamber, where they underwent partial dissociation into neutral particles and charged particles. The neutral particles were monitored by conventional high-temperature mass spectroscopic methods. The negative ions present in the vapour of the experimental substances were also monitored mass spectroscopically after being "extracted" from the effusion cell by an electrostatic field.

Table 6. Heats (ΔH°_{298}) of the gas-phase reaction $MF_n + F^- = MF_{n+1}^-$.

Molecule	$-\Delta H^0_{298}$, eV	Reference
AlF_3	5.16±0.10	[120,123,130]
BeF_2	4.07±0.19	[131]
CeF_3	4.76±0.09	[124]
FeF_2	4.57±0.11	[124,132]
FeF_3	4.55±0.10	[124,132]
HfF_4	4.22±0.09	[131]
KF	2.26±0.06	[133]
LaF_3*	4.94±0.35	[122]
MnF_2	4.45±0.13	[124,132]
MnF_3	4.55±0.13	[124,132]
ScF_3	5.05±0.13	[133]
UF_4	4.26±0.09	[130]
UF_5	4.83±0.35*	[122]
ZrF_4	4.23±0.13	[124]

* Calculated from published data[122].

The equilibrium constants of several ion–molecule reactions involving negative ions were successfully measured, and the electron affinity (eV) of the following molecules and radicals was determined: AlF_2 (2.30), BF_2 (2.20)[117]; BO (3.12), BO_2 (3.47)[107]; AlO (3.68), AlO_2 (4.11).[108] It was subsequently discovered that the use of very high temperatures (2000–2500 K) to obtain measurable concentrations of negative ions is not essential.

Negative ions were detected in the saturated vapour of a large number of inorganic salts and their binary systems at temperatures as low as 700–1200 K.[118-122] This observation led to the rapid development of studies of ion–molecule equilibria and to the determination of affinities for the electron and for the F^- anion. Many workers[110-123] have reported experimental tests of the existence of ion–molecule equilibrium under the conditions of a real effusion experiment and have developed methods of measuring the activity of neutral components from measurements of the partial pressures of negative ions. The fullest description of these techniques is given in Ref. 124 and 125, where the effect of the extracting field on the effusion process and on the electronic work function of the inner surface of the effusion cell is also discussed.

In the last two or three years the effusion method has been used to measure the affinity for the electron and for the F^- anion of a large number of inorganic fluorides (Tables 5 and 6). The most important of these results was the first experimental determination of the electron affinity of platinum hexafluoride: the highest electron affinity ever reported[126].

VII. CALCULATION OF ELECTRON AFFINITY FROM THERMOCHEMICAL DATA AND FROM THE ABSORPTION SPECTRA OF COMPLEXES

The difficulty of the direct experimental determination of electron affinity has led to the development of several methods by which the electron affinity can be estimated from measurements of related quantities. Typical of this approach is the calculation by a Born–Haber thermochemical cycle in which reactions involving both the charged and the neutral particles are included.

In order to calculate the electron affinity by this cycle we need to measure the heat of formation $\Delta H^\circ_{0f}(AB)$ of the crystalline compound AB from the gaseous components A and B, and to calculate theoretically the crystal lattice energy U of the compound. The energy U is equal to the heat of reaction (1) ($U = -\Delta H^\circ_0(1)$):

$$A^+(g) + B^-(g) \rightarrow Ab(cr) . \quad (1)$$

The heat of formation of the crystalline compound AB from gaseous A and B is equal to the heat of reaction (2), $\Delta H^\circ_0(2)$:

$$A(g) + B(g) \rightarrow AB(cr) . \quad (2)$$

The electron removal and addition reactions are written

$$A \rightarrow A^+ + e \quad (\Delta H^0_0(3) = I(A)) , \quad (3)$$

$$B + e \rightarrow B^- \quad (\Delta H^0_0(4) = -E(B)) , \quad (4)$$

where $I(A)$ is the ionisation energy (potential) of A and $E(B)$ is the electron affinity of B. The ionisation energy is usually known, and the electron affinity is calculated as the algebraic sum of the heats of reactions(1), (2), and (3):

$$\Delta H^0_0(4) = \Delta H^0_0(2) - \Delta H^0_0(1) - \Delta H^0_0(3) \quad (5)$$

or

$$E(B) = I(A) - U - \Delta H^0_0(2) .$$

Measurements of the heats of formation of molybdenum and tungsten pentafluorides and of the complexes MWF_6 and $MMoF_6$ (where M = Li–Cs) have been reported[134-136]. The crystal lattice parameters were determined, and used to calculate the energy of formation of crystalline MWF_6 and $MMoF_6$ from the M^+ and MoF_6^- (or WF_6^-) ions. By combining

the results with the known heats of formation of the pentafluorides, the electron affinities of the hexafluorides and the affinities for the F^- anion of the pentafluorides were calculated. In a more recent paper[136] an improved calculation of the crystal lattice energy is presented and a slightly different value of the electron affinity is obtained (see Table 7).

Table 7. Electron affinities calculated from thermochemical and spectral data.

Molecule	*E*, eV	Reference
HO_2	1.85±0.12	[138]
IBr_2	4.94	[139]
ICl_2	5.35	[139]
ICl_4	3.98	[139]
I_3	5.27	[139]
IrF_6	7.85 (6.8)*	[137]
MoF_6	5.36±0.06	[134]
MoF_6	5.77 (4.8)*	[137]
ReF_6	<6.33 (5.3 *	[137]
UF_6	<5.81 (4.8)*	[137]
WF_6	5.08±0.05	[134]
WF_6	4.63	[136]
WF_6	4.51 (3.5)*	[137]

* Calculated from the absorption spectra of the complexes by using the most recent value[62] of the electron affinity of WF_6; $E(WF_6) = 3.5$ eV. The other entries are thermochemical calculations.

The first attempt to calculate the electron affinities of the transition metal (W, Mo, U, Re, Ir) hexafluorides from the absorption spectra of their complexes was reported[137] in 1978. New frequencies were observed in the visible and near u.v. regions of the absorption spectra of the crystals formed by the hexafluorides with xenon at liquid-nitrogen temperatures. They were assigned to intermolecular charge transfer between xenon and the hexafluoride:

$$Xe + MF_6 \xrightarrow{h\nu} Xe + MF_6^- .$$

The theory of charge transfer in complexes[13] leads to the expression

$$h\nu = I(Xe) - E(MF_6) + G ,$$

where $I(Xe)$ is the ionisation potential of the donor (Xe), $E(MF_6)$ is the electron affinity of the acceptor (MF_6), and G is a constant determined empirically by using a standard ($XeWF_6$ crystals). The energy $h\nu$ was determined experimentally, and the constant G was calculated by combining this value with published data on the ionisation potential of xenon and on the electron affinity of tungsten hexafluoride. From the G value, and the measured charge transfer frequencies of the xenon complexes, the electron affinities of five hexafluorides were calculated (Table 7). We note that the most recent value[62] of $E(WF_6)$ is 3.5 ± 0.1 eV, whereas the value 4.5 eV was used in Ref.137. Therefore all the results quoted in that paper should be lowered by ~ 1 eV.

VIII. COMPOUNDS HAVING AN ELECTRON AFFINITY GREATER THAN 3.0 eV

Each of our Tables (1–7) includes electron affinity values measured by one particular method. By comparing these results we can assess the relative merits of different approaches to the problems presented by the study of molecules with a high electron affinity.

Photo-extraction occupies a leading place among existing experimental methods of measuring electron affinity, and no other method can compete with the precision of its results. Measurements by negative ion photo-electron spectroscopy are usually claimed to have a precision of 0.01–0.02 eV, and in some cases (for example, for the carbon atom) the precision is as high as 0.0003 eV.[16] In photo-extraction experiments where the percentage breakdown of the anions is fixed a precision of 0.02–0.10 eV is usually quoted. The results are more difficult to interpret, since allowance is needed for the difference in energy between adiabatic and vertical transitions. Negative ion photo-electron spectroscopy gives a direct measurement of the lowest photon energy capable of generating a free electron. This energy corresponds to a vertical transition and is higher than the energy of the adiabatic transition which is equal (by definition) to the electron affinity. The numerical importance of these differences can be assessed only by comparing the results with those obtained by independent methods.

The photo-electron spectroscopy method can also be used to determine the enthalpies of formation of gaseous compounds having a high electron affinity. These compounds readily form stable negative ions in the gas phase, and it is experimentally easier to determine the enthalpy of formation of the negative ion than that of the corresponding neutral molecule or radical. Many examples can be quoted, and in some cases (e.g. AlF_4^- and HfF_4^- (Table 6), WF_7^- (Ref.62), and UF_7^- (Ref.63)) the enthalpy of formation of the negative ion is reliably determined while the existence of the corresponding neutral radical remains doubtful. Evidently, the enthalpy of formation of these radicals could be determined from measurements of the enthalpy of formation of the negative ions and the energy of extraction of an electron.

Consider the CO_3 molecule and the CO_3^- ion. The bond energy $D(O_2C-O^-)$ for the ion is accurately known, the most recent value[29] being 2.258 ± 0.007 eV. The electron affinity of the oxygen atom is known[5] to an even higher accuracy: $E(O) = 1.462 \pm 0.003$ eV. For the neutral CO_3 molecule the bond energy data are less reliable: $D(O_2C-O) = 0.46 \pm 0.17$ eV.[140] Since $E(CO_3) = D(CO_2-O^-) + E(O) - D(O_2C-O)$, we obtain $E(CO_3) = 3.26 \pm 0.17$ eV. Direct determination of the electron affinity by the negative ion photo-electron spectroscopy method should give a value of $E(CO_3)$ accurate to a few hundredths of an electron volt, and therefore a back-calculation should give a better value of the bond energy $D(O_2C-O)$ for the molecule. Unfortunately, the first attempt was unsuccessful[35], possibly because the intensity of the CO_3^- beam was insufficient, and the photo energy was adequate only for electron affinities lower than 3.1 eV.

There is little doubt that increasing the photo energy should provide the desired result and give more accurate values not only of the electron affinity but also of the heat of formation of the CO_3 molecule. Unfortunately, up to the present all the results obtained by the photo-extraction method lie between 0 and 3 eV (see Table 1). There are no fundamental obstacles to an extension of the measurements to higher energies, though of course some practical difficulties can be expected. The further development of the photo-extraction method and its application to the study of molecules with a high electron affinity should increase very substantially our understanding of the thermochemistry of negative ions and that of their related molecules and radicals.

The electron impact method occupies the second place in relation to the number of results obtained (see Table 2). Nearly all the results were derived from the appearance potentials of negative ions during dissociative electron capture

processes involving the molecules of interest. Inspection of Table 2 shows that in most cases uncertainty limits are not quoted, and occasionally only an upper limit is given. Some results obtained by the electron impact method have been criticised by Mathur and coworkers[90]. The dissociative electron capture method is applicable to the determination of electron affinity in compounds of higher valency only if the molecules undergoing ionisation are even more complex, e.g. $KMoF_6$ or KWF_6. In this case the electron affinity of MF_6 can be determined if MF_6^- ions are formed by dissociative electron capture. Unfortunately, no such results have yet been reported, and an attempt to prepare the AlF_4^- ion by dissociative electron capture from the $NaAlF_4$ molecule was unsuccessful.

Studies of ion–molecule reactions (Section IV) have revealed only 10 substances with an electron affinity higher than 3 eV. The affinity was calculated from the threshold energy of an endothermic ion–molecule reaction[59,61], from the threshold energies of two exothermic ion–molecule reactions[62], or by measuring the rates of the forward and the reverse reaction, i.e. from the equilibrium constant[64]. The latter variant is considered in Section VI, devoted to equilibrium methods. Studies of ion–molecule reactions have yielded relatively few electron affinity data, and the precision of the results usually lies in the range 0.1–0.3 eV (see Table 3).

Relatively few studies of ion–molecule reactions involving negative ions had been reported until recently. The limitation lay both in the method of producing negative ions and in the inadequacy of the available thermochemical data (mainly, on heats of formation). The position has shown a marked improvement in recent years, with a rapid increase in the number of negative ions which can be obtained in the gas phase and in the list of known heats of formation. A good example are the anions (Table 6) which are easily formed by heat treatment of complex salts of the $MAlF_4$ type, where M is an alkali metal[120]. The use of these anions in studies of endothermic ion–molecule reactions should make an important contribution to the acquisition of thermochemical data on fluorine compounds.

In Section V we examine a method based on the formation of an ion pair by the collision of a molecule with an alkali metal atom. Ionisation can be induced by collisions with Cs, K, and Na atoms, and the upper limit of the electron affinities measurable by this method is 5.14 eV, i.e. the ionisation potential of the sodium atom. There is effectively no lower limit. During the last 5 years this method has yielded the greatest number of results: 73 affinity values, 21 of which were higher than 3.0 eV. The method is being actively developed by several groups of workers (see Table 4), who claim a precision between 0.15 and 0.30 eV. There are a number of inconsistencies between the results reported from German and American laboratories, for example in the case of WF_6[93,100]. The high values of the internal excitation energy are surprising.[141] Unfortunately, for most of the hexafluorides the electron affinity is only given as "higher than 5.14 eV", since negative MF_6^- ions are formed even from sodium atoms at thermal energies.

The determination of thermochemical quantities from the absolute values of the equilibrium constants is one of the main experimental methods of chemical thermodynamics. In studies of equilibria involving the gas phase this is one of the principal methods, giving heats of reaction accurate to ~ 4–12 kJ $mole^{-1}$ (0.05–0.15 eV). Therefore experimental methods of measuring the constants of ion–molecule equilibria involving negative ions have been intensively developed during the past 10 years, including work on flames[109], plasmas[110,111], and on the formation of clusters on negative ions[142,143].

The application of the classical effusion method to these problems had only limited success at first, because of the high value of the work function of the inner surface of the Knudsen effusion cell and of the low concentration of negative ions[144]. However, in the case of molecules with a high electron affinity (i.e. for $E > 3$ eV) these problems are less important. A method of lowering the work function of the inner surface of the Knudsen cell during the effusion measurement was also discovered[125]. As a result, the effusion method can now be used to measure electron affinities $E > 3$ eV, and work now in progress may result in a lowering of this limit. The method has no upper limit, since the higher the electron affinity, the easier it is to obtain measurable concentrations of negative ions in the effusion cell.

During the period 1979–1981 this method has been used to determine the electron affinities of iron, manganese, platinum, uranium, and cerium fluorides, and the affinities for the F^- anion of a series of fluorides (see Table 6). The precision of the results is 0.1–0.3 eV, and is often limited by the uncertainty in the heats of formation of the corresponding neutral compounds. The range of substances suitable for investigation by this method can easily be widened to include other halides, oxide halides, oxides, and salts of oxygenated acids. This type of measurement can yield the affinity for other anions as well as the electron affinity. For example, the affinities of the BeF_2 molecule for the following anions have been measured[131]: F^-, BeF_3^-, $Be_2F_5^-$, AlF_4^-, and $BeAlF_6^-$. This work has much in common with the study of cluster formation on negative ions by the method which has been called high-pressure mass spectrometry[142]. Keesel and coworkers[142] determined the heats of formation of $A(SO_2)_n$ clusters on A ions (Cl^-, I^-, NO_2^-), with $n = 1$–4, and Nikitin and coworkers[131] determined the heats of formation of $F^-(BeF_2)_n$ clusters, where $n = 1$, 2, and 3.

We note that the Knudsen effusion cell in addition to its normal purpose (the generation of equilibrium conditions) can also be used as an efficient source of negative ions in methods such as photo-extraction, photo-electron spectroscopy, and other threshold methods of determining electron affinities. When used as an ion source the effusion cell offers the simplest way of applying such methods to the study of those negative ions, which play an important role in high-temperature systems.

The methods discussed in Section VII occupy a special position, because they cannot be classified among the direct experimental methods of determining electron affinities, and they are used mainly to obtain approximate estimates of the affinities. For this reason the results quoted in Table 7 are only tentative, but they are nevertheless of interest because of the increasing importance of this class of compounds in investigations of the reality of electron affinity values in the range 4–8 eV. At present the following values have been reliably established:

Molecule	WF_6	MoF_6	UF_6
E, eV	3.5 ± 0.1 [62] 3.7 ± 0.2 [100] 4.89 ± 0.25 [129]	3.6 ± 0.2 [72]	4.9 ± 0.5 [63] $\geqslant 5.14$ [99]

By comparing these values with those of Table 7 we note discrepancies often greater than 1 eV. The most serious inconsistencies arise with the data obtained from the absorption spectra of complexes. The disagreement affects not only the absolute values of electron affinities (which could be due to an incorrect choice of standard) but also their differences: for example, the difference $E(MoF_6) - E(WF_6)$ according to these data is 1.3 eV, as compared with only 0.1–0.3 eV according to the results obtained by other methods. We conclude that the data of Table 7 should only be used as a rough estimate of the electron affinity, with a precision not better than ~ 1.5 eV.

The experimental results summarised in Tables 1–7 characterise the electron affinity of a large number of inorganic molecules and allow us to identify the classes of compounds for which numerical values of the electron affinity higher than those of the halogen atoms can be expected. Inspection of Table 5 shows that higher-valency oxygen compounds have an electron affinity in the range 3.5–4.3 eV (the BO_2, PO_3, WO_3, HWO_4, $HMoO_4$, and ReO_4 radicals). Even higher values (5.25–5.40 eV) are obtained for the tetrafluorides of the transition metals (FeF_4, MnF_4, PtF_4). Measurements on cerium tetrafluoride gave a value of 3.6 eV, believed to be typical of the tetrafluorides of the lanthanum group. Still higher values were obtained in studies of the hexafluorides.

Bartlett's prediction[145], made in 1968, has been confirmed experimentally: the electron affinities of all the hexafluorides of transition metals in the second and the third series are higher than 3.5 eV, and in the case of platinum hexafluoride the electron affinity is higher than 6.8 eV. According to existing data, $E(PtF_6) = 8.0 \pm 0.3$ eV.[126] For the ReF_6 and IrF_6 molecules the reported value is $E > 5.14$ eV, and for WF_6 and MoF_6 values of 3.5,[62] 3.7,[100] and 3.6 eV[72] have been obtained. Hence the higher fluorides (and probably also the oxide fluorides) of the second and third series of transition metals are a class of compounds showing the highest electron affinity values so far reported. Uranium hexafluoride has an electron affinity of ~ 5 eV, and similar values can be expected for the hexafluorides of the transuranic elements. The high values of electron affinity in this class of compounds probably persist in halides (and oxide halides) other than the fluorides.

The data in Table 6 can be used to calculate the enthalpies of formation of the negative ions BeF_3^-, AlF_4^-, ScF_4^-, LaF_4^-, ZrF_5^-, and HfF_5^-. Similar data are available for the anions WF_7^- [69] and UF_7^-.[63] For the UF_7 radical the energy of addition of the seventh fluorine atom is positive[63], i.e. the potential energy curve of the UF_6–F system has a minimum. For the AlF_4, ScF_4, LaF_4, ZrF_5, HfF_5, and WF_7 radicals this information is not yet available, and the minimum in the potential energy curve may be absent in some of the systems. The enthalpies of formation of these radicals are not known, and only a rough estimate of their electron affinity is possible (5–8 eV[147,149]). Some estimates suggest even higher values of the electron affinity: the record is held by gold hexafluoride, for which a value of 10 eV has been proposed[93]. Of course, there are no direct experimental data, and the compound itself has not yet been synthesised. An analogous situation exists in many instances of high (expected) electron affinity. A good example are the hexafluorides of iron, cobalt, and nickel, whose synthesis has not yet been achieved in spite of repeated attempts.

The compounds with a high electron affinity are the strongest known oxidising agents. They have a strong influence on the concentration of free electrons in flames and plasmas, and they greatly simplify the problem of generating strong beams of negative ions.

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New information on the affinity of compounds for electrons and for the F^- ion has appeared while the manuscript was being prepared for the press.

Photo-extraction and photo-electron spectroscopy methods have been used to obtain the electron affinities of the following compounds: $E(CH_2) = 1.055 \pm 0.0 \pm 5$,[148] $3.374 \leq E(C_2) \leq 3.408$,[166] $E(HO_2) = 1.19 \pm 0.01$,[150] $E(HS) = 2.314 \pm 0.003$ eV.[151] In addition to these experimental papers, a review entitled "Laser spectroscopy of negative ion beams" has also appeared[152]. The electron impact method has been used to show that $E(OF) \geq 2.2$, $E(NF) \cong 0.5$, $E(ClO_3) \geq 3.2$, $E(ClO_2F) \geq 2.3$ eV,[153] and also $E(CCl_2) = 2.5 \pm 0.3$ and $E(CCl_3) = 2.58 \pm 0.20$ eV.[154]

Studies of endothermic ion–molecule reactions have yielded values of the affinity for the electron and for the fluoride anion (E_F^-), and also of the energy of the removal of an oxide anion ($D(MO_n-O^-)$): $E(SF_5) \geq 3.70 \pm 0.3$, $E_F^-(SF_3) = 2.60 \pm 0.16$, $E_F^-(SF_4) \geq 2.60 \pm 0.16$, $E_F^-(SF_5) = 1.10 \pm 0.21$[155]; $D(N-O^-) = 5.0 \pm 0.1$, $E(NO) = 0.02 \pm 0.10$, $D(O-O^-) = 4.1 \pm 0.1$, $E(O_2) = 0.44 \pm 0.1$, $D(NO-O^-) = 4.0 \pm 0.1$, $E(NO_2) = 2.4 \pm 0.1$, $D(N_2-O^-) = 0.43 \pm 0.1$, $E(N_2O) = 0.22 \pm 0.1$, $D(CO_2-O^-) = 2.0 \pm 0.1$, and $E(CO_3) = 3.1 \pm 0.2$ eV.[156]

Ionisation by potassium atoms has been used to prepare negative D_2S^- and H_2S^- ions. The corresponding values of the electron affinity were found to be negative: $E(D_2S) = -1.5 \pm 0.2$ eV and $E(H_2S) = -1.6 \pm 0.2$.[157]

Measurements of the equilibrium constant of ion–molecule reactions have yielded additional information on the thermochemical characteristics of negative ions. Pyatenko and coworkers[158] have obtained $E(UF_5) = 3.78 \pm 0.40$ and $E(UF_6) = 6.33 \pm 0.50$ eV, and Chilingarov and coworkers[159] reported $E(RhF_4) = 5.0 \pm 0.3$ eV. The affinity for the F^- anion was measured, with the following results: $E_F^-(LaF_3) = 4.42$,[160] $E_F^-(VF_3) = 4.9 \pm 0.1$,[161] and $E_F^-(ThF_4) = 4.2 \pm 0.1$ eV.[162] Similar measurements have been reported also for the oxide fluorides of molybdenum and tungsten: $E_F^-(MoO_2F_2) = 4.08 \pm 0.17$ and $E_F^-(WO_2F_2) = 4.30 \pm 0.17$ eV.[163] A detailed description of the determination of the electron affinity of cerium tetrafluoride (including the procedure) is given in Ref. 165. It is interesting to compare these results with experimental data for the hexafluorides of molybdenum[72], tungsten[62], and platinum[126]. These experimental and theoretical results were obtained, independently, in the period 1979–1981, and it is very instructive to compare them with earlier data.

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Lomonosov Moscow State University,
Chemistry Faculty