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Ionization Potentials and Electron Affinities in Aqueous Solution

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Abstract: By combining gas-phase proton affinities and aqueous pK_a values, it is possible to obtain free energies of hydration for a large number of cations and anions. With some corrections these numbers can be used to convert gas-phase ionization potentials, I, and electron affinities, A, into the corresponding aqueous solution values, I' and A'. An assumption must be made about the free energy of hydration of H^+, taken as -259.5 kcal/mol. The absolute potential of the hydrogen electrode is then 4.50 V, and values of I' and A' can be converted to standard oxidation or reduction potentials. The absolute electronegativity, $(I' + A')/2$, in solution is estimated and found to be little different from the gas-phase value, $(I + A)/2$. The absolute hardness, $(I' - A')/2$, is much smaller than the gas-phase value, but it is shown that the solution value has little utility. The gas-phase value should be used even in solution.

Two important properties of any molecule, radical, or ion, M, are its gas-phase ionization potential I, and its electron affinity, A. Of potentially even greater importance are the corresponding properties in aqueous solution.

$$M(aq) = M^+(aq) + e^-(g) \qquad I' \qquad (1)$$

$$M(aq) + e^-(g) = M^-(aq) \qquad A' \qquad (2)$$

It is convenient to define I' and A' as the potentials corresponding to the standard Gibbs free energy changes in (1) and (2). The free energy of the electron at rest in the gas phase is set at zero.

These conventions make it impossible to measure I' and A' directly. However, it also makes it possible to calculate them by several independent methods. Reactions 1 and 2 may be coupled to the reaction defining the absolute potential of the hydrogen electrode

$$H^+(aq) + e^-(g) = \tfrac{1}{2}H_2(g) \qquad E^\circ{}_H \qquad (3)$$

The value of $E_H{}^\circ$ has long been debated, but there is now general agreement on a value near 4.50 V at 25 °C.[1,2] This figure corresponds to the Gibbs free energy of hydration of the proton being -259.5 kcal/mol and allows the free energy of hydration of other ions to be calculated.

Adopting these values, we may write

$$M(aq) + H^+(aq) = M^+(aq) + \tfrac{1}{2}H_2(g) \qquad E^{\circ\prime} \qquad (4)$$

$$M(aq) + \tfrac{1}{2}H_2(g) = M^-(aq) + H^+(aq) \qquad E^\circ \qquad (5)$$

The conventional (thermodynamic) value of the oxidation potential for M(aq) is then $E^{\circ\prime} = -I' + 4.50$ V. The reduction potential for M is $E^\circ = A' - 4.50$ V. I' is always positive, and A' is positive when reaction 2 is spontaneous. Standard states for gases are taken as the ideal gas at 1 atm of pressure and 25 °C, and for aqueous solutions as the ideal 1 M solution at 25 °C, in this paper.

Some of the uses for I' and A' may now be appreciated. In electrochemical experiments, they define the reversible potentials at which one electron oxidation and reduction of M will occur. In chemical reactions, they define whether single electron transfers (SET) between different M species are possible. In recent years such SET mechanisms have been recognized as being very important, in both inorganic and organic chemistry.[3]

Other reaction mechanisms also may depend markedly on I' and A'. In nucleophilic substitution reactions, it has been thought for some time that I' helped to determine the nucleophilicity of a series of nucleophiles.[4] Also, A' would partly determine the electrophilicity of the reacting partner. The analogy between SET and S_N2 mechanisms has recently been stressed.[5]

An important case of partial transfer of a pair of electrons occurs in the reaction of Lewis acids and bases. An analysis of the bonding in acid-base complexes shows that I and A for both the acid and the base enter as important parameters, when the reaction is a gas-phase one. Presumably I' and A' could play similar roles for reactions in solution.

Finally the determination of I' and A' allows the absolute electronegativity, χ, and absolute hardness, η, parameters for M to be calculated. These quantities are defined as

$$\chi = (I + A)/2 \text{ and } \eta = (I - A)/2 \qquad (6)$$

for the gas-phase values.[6] Similar equations should exist for processes in solution, but no data have been available.

One might hope that measurements of the ordinary potentials of suitable half-cells would give values E° and $E^{\circ\prime}$. However, reactions 4 and 5 are usually irreversible, either because of slow rates of electron transfer or because of rapid decomposition of the initial products. In other cases rapid follow-up reactions lead to overall reversible potentials of lesser interest, e.g., I^-/I_2. Finally, the solvent water may be oxidized or reduced more readily than M.

Only in a few cases are both partners in a redox couple stable enough so that a reversible potential can be either measured or calculated from thermodynamic data. This has been done for the couples O_2^-/O_2,[7] NO_2^-/NO_2,[8] and ClO_2^-/ClO_2.[9]

If M is a transition-metal complex, then reversible one-electron redox potentials can often be measured or calculated. Such complexes are not considered in this paper because they rarely act as nucleophiles or electrophiles. However, they sometimes can be used to find E° or $E^{\circ\prime}$ for other systems by a kinetic method. A detailed study must be made to find both the forward and reverse rate constants for a reaction such as

$$M' + M^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} M'^- + M \qquad (7)$$

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[1] From the viewpoint of solution thermodynamics see: (a) Noyes, R. M. *J. Am. Chem. Soc.* **1962**, *84*, 513-522. (b) Rossinsky, D. R. *Chem. Rev.* **1965**, *65*, 467-490. (c) Miller, W. A.; Watts, D. W. *J. Am. Chem. Soc.* **1967**, *86*, 6051-6056. (d) Noyes, R. M. *J. Am. Chem. Soc.* **1964**, *86*, 971-979.

[2] For solid-state electrochemistry see: (a) Nosik, A. J. *Annu. Rev. Phys. Chem.* **1978**, *29*, 189. (b) Reiss, H.; Heller, A. *J. Phys. Chem.* **1985**, *89*, 4207-4213. (c) Trasatti, S. IUPAC; Commission I.3 (Electrochemistry), 1984.

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[4] Hudson, R. F. *Chimia (Aarau)* **1962**, *16*, 173-177. The Edwards equation had introduced oxidation potentials of nucleophiles as measured of reactivity as early as 1954. However, they were used as a substitute for polarizabilities. Edwards, J. O. *J. Am. Chem. Soc.* **1954**, *76*, 1560-1547.

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[6] Parr, R. G.; Pearson, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 7512-7516.

[7] Meisel, D.; Czapski, G. *J. Phys. Chem.* **1975**, *79*, 1503-1509.

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where M′ is the metal complex. Setting $k_1/k_{-1} = K_{eq}$ allows a calculation of $E°$ for the M^-/M couple. This method has been used for SCN^-/SCN,[10] I^-/I,[10] and N_3^-/N_3.[11]

The most general method for estimating $E°$ or $E°'$ consists of the use of thermodynamic cycles, in which, unfortunately, at least one quantity must be estimated from models. The earliest use of this method seems to be that of Eberson, who estimated $E°'$ for several carboxylate anions.[12] Berdnikov and Bazhin made similar calculations for ten common anions.[13] Ritchie has recently added several more anions to the list.[14] He also has made the important step of including a few neutral molecules.

The present paper greatly extends the available results for molecules and also adds a number of anions. For consistency the earlier examples are recalculated. A simpler approach to the necessary thermodynamic cycles is used, more realistic approximations are made for unknown quantities, and advantage is taken of a larger and more reliable data base.

The Calculation of I' for Anions

It is convenient to treat anions, X^-, in terms of their ionization potentials in aqueous solution, rather than the electron affinities of the corresponding radicals, X. We have

$$X^-(g) = X(g) + e^-(g) \qquad I \tag{8}$$

$$X^-(aq) = X(aq) + e^-(g) \qquad I' \tag{9}$$

I is equal to $\Delta G°$ for the reaction 8 at the absolute zero, if small corrections due to electronic multiplicities are ignored. Neglecting changes in the vibrational frequencies of $X^-(g)$ and $X(g)$ which cause small changes in entropy, I is also equal to $\Delta G°$ at 25 °C. I' is defined as $\Delta G°$ for reaction 9. We now need the free energies of hydration at 25 °C for X^- and X, $\Delta G°_{X^-}$ and $\Delta G°_X$.

The former may be readily found from proton affinity (PA) data in the gas phase and pK_a values in solution, since $\Delta G°_{H^+}$ is −259.5 kcal/mol.

$$HX(g) = H^+(g) + X^-(g) \qquad PA - 7.5 \text{ kcal} = \Delta G°_{(g)} \tag{10}$$

$$HX(aq) = H^+(aq) + X^-(aq) \qquad 2.303RT(pK_a) = \Delta G°_{(aq)} \tag{11}$$

The gas-phase free-energy change, or the gas-phase basicity, is given by PA − 7.5 kcal, where the 7.5 kcal is a good approximation to $T\Delta S°$ for reaction 10.[15,16] Finally we have

$$-\Delta G°_{X^-} = PA - 267 - \Delta G°_{HX} - 1.36pK_a \tag{12}$$

Fortunately many values of $\Delta G°_{HX}$, the free energies of hydration of the neutral molecules HX, are available in the literature.[17,18] Unknown values may usually be estimated with an accuracy consistent with the reliability of the other data in (12), that is, ±2 kcal. The useful compilation by Hine and Mookerjee gives rules for constituent effects.[18]

Table I. Some Properties of Selected Anions, X^-

X^-	I^{a}	PA^{e}	pK_a^{g}	$\Delta G°_{HX}$^{k}	$-\Delta G°_{X^-}$^{m,t}	$I'^{o,u}$
$C_6H_5CH_2^-$	0.88	378	41	1.0	57	3.40
CH_3^-	0.08	417	48^{h}	4.0	80	3.73
PH_2^-	1.25	387	27	2.5	65	4.18
$C_6H_5^-$	1.10^{b}	398	43	1.0	72	4.27
O_2^-	1.40	351	4.7	−3.5	85	4.31^{q}
CH_2CN^-	1.51	372	25	−2.0	73	4.59
H^-	0.74	400	31^{i}	4.0	87	4.68
NH_2^-	0.79	404	34^{i}	−2.4	93	4.72
HSe^-	2.21	339	3.9	1.0	65	5.12
$CH_3COCH_2^-$	1.76	371	19.1	−1.9	79	5.14
n-$C_3H_7S^-$	2.00	354	10.8	0.6	74	5.24
$C_6H_5S^-$	2.47	339	6.5	−0.7	65	5.26
HO_2^-	1.19^{c}	376^{c}	11.7	−6.8	99	5.33
NO_2^-	2.30	338	3.4	(−3.0)	70	5.39
$C_6H_5O^-$	2.35	346	9.9	−4.6	70	5.42
ClO_2^-			2.0			5.43^{p}
HS^-	2.32	352	6.9	1.2	74	5.58
CH_3O^-	1.59	378	15.0	−3.2	93	5.60
I^-	3.06	314	−12^{j}	1.0^{j}	61^{n}	5.69
$CF_3CH_2O^-$	2.22	364	12.5	(−1.0)	81	5.78
N_3^-	2.70^{d}	344^{d,f}	4.7	−1.5	72	5.77
SCN^-			0.9			6.16^{r}
HC_2^-	2.94	375	25	3	71	6.18
OH^-	1.83	391	15.7	−4.4^{l}	104	6.22
Br^-	3.36	324	−10^{j}	1.2^{j}	70^{n}	6.35
$CH_3CO_2^-$	3.29	344	4.8	−4.8	75	6.54
NO_3^-	4.00	325	−1.4	(−4.0)	63	6.78
Cl^-	3.62	333	−8^{j}	1.4^{j}	75^{n}	6.81
CN^-	3.82	349	9.3	−1.2	75	7.02
F^-	3.40	371	3.5	−5.6	105^{s}	7.88

[a] Gas-phase electron affinities of X in eV. Data from 21, except as noted. [b] De Puy, C. H.; Bierbaum, V. M.; Damrauer, R. *J. Am. Chem. Soc.* **1984**, *106*, 4051–4053. [c] Bierbaum, V. M.; Schmitt, R. J.; De Puy, C. H.; Mead, R. D.; Schulz, P. A.; Lindberger, W. C. *J. Am. Chem. Soc.* **1981**, *103*, 6262–6263. [d] Jackson, R. L.; Pellerite, M. J.; Brauman, J. I. *J. Am. Chem. Soc.* **1981**, *103*, 1802–1805. [e] Gas-phase proton affinities in kcal/mol. Data from ref 23, except as noted. [f] D_0 for H–N$_3$ equal to 92.5 kcal/mol, ref 22. [g] For HX in water at 25 °C. Values for organic acids from the following: Stewart, R. *The Proton: Applications to Organic Chemistry*; Academic: New York, 1985, Chapter 2. Others from the following: Albert, A.; Serjeant, E. P. *Ionization Constants of Acids and Bases*; Methuen; London, 1962. [h] This value is quite uncertain. See footnote *i*. [i] From experimental values in THF–crown ether: Buncel, E.; Menon, B. *J. Am. Chem. Soc.* **1977**, *79*, 4457–4461; *J. Organomet. Chem.* **1977**, *141*, 1–5. Four pK_a units have been subtracted to approximately correct to water. See: Jaun, B.; Schwarz, J.; Breslow, R. *J. Am. Chem. Soc.* **1980**, *102*, 5741–5748. [j] These values calculated from known free energies of hydration of anions (ref 1c) and the assumption that $\Delta G°_{H,X} = \Delta G°_{CH_3X}$. [k] Free energies of hydration at 25 °C in kcal/mol. Data from ref 17 and 18. Estimated values in parentheses. [l] Standard state for liquid water is one molar. [m] Free energies of hydration of anions, X^-, in kcal/mol. Calculated from eq 12. [n] Reference 1b,c. [o] Ionization potentials in aqueous solution in eV. Calculated from eq 13. Subtract 4.50 eV to get $E°'$. [p] Reference 9. [q] Reference 7. [r] Reference 10. [s] Agrees with independent value in ref 1c. [t] The uncertainty is ±2 kcal·mol, unless the pK_a is a very large positive number. [u] While the values have been calculated to 0.01 V, they are subject to an uncertainty of ±0.15 V.

Note that the free energy of hydration of neutral molecules is given by $RT \ln (P/C)$, where P is the vapor pressure of the solute in atmospheres at 25 °C and C is the concentration of the solute in mol/L, if activity coefficients are ignored. For slightly soluble solutes, P may be set equal to the vapor pressure of the pure solute and C to the concentration in a saturated solution. For ordinary covalent molecules, the range of free energies of hydration at 25 °C is a rather narrow one: from +5.0 kcal/mol for an insoluble gas like helium to −6.5 kcal/mol for a nonvolatile, but hydrophilic, solute like glycerol.

Table I contains the essential data for a number of common anions and the values of $\Delta G°_{X^-}$ calculated from these data. To find I' in aqueous solution from I in the gas phase, we still must estimate $\Delta G°_X$, the free energy of hydration of the radicals. Ritchie[14] has suggested that $\Delta G°_X = \Delta G°_{HX}$ be used as a good approximation. While true in some cases, it cannot be valid for very polar H–X bonds, where strong hydrogen bonding will occur. For example, HF has an experimental value of $\Delta G°_{HX}$ of −5.6 kcal/mol, while the value for the F atom is sometimes estimated as +4.5 kcal/mol, which is that for neon.

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Table II. Free Energies of Hydration of Some Neutral Molecules at 25 °C[a]

molecule	$\Delta G°_{HX}$	molecule	$\Delta G°_{HX}$
HF	-5.6	NH_3	-2.4
CH_3F	+1.7	CH_3NH_2	-2.7
H_2O	-4.4	$(CH_3)_2NH$	-2.4
CH_3OH	-3.2	CH_4	+4.1
$(CH_3)_2O$	0.0	C_2H_6	+4.0
CH_3CO_2H	-4.8	H_2S	+1.2
$CH_3CO_2CH_3$	-1.4	CH_3SH	+0.6
		$(CH_3)_2S$	+0.4

[a] Values in kcal/mol, data from ref 17 and 18.

In one case at least an experimental test is possible. Since $E°'$ is known for the O_2^-/O_2 couple, we can calculate a value of $\Delta G°_{O_2^-}$ from the electron affinity of gaseous O_2 (10 kcal) and the free energy of hydration of O_2 (+3.9 kcal). The resulting value is -86 kcal/mol, which agrees very well with independent estimates, using other data.[19] From the proton affinity in the gas phase, and the pK_a in water, a value of -3.5 kcal/mol for the free energy of hydration of HO_2 can be calculated. This differs substantially from that of O_2, given above, and from that of H_2O_2, -6.8 kcal/mol.

Table II shows some values for free energies of hydration of neutral molecules which support the idea that CH_3X be used as a model for X.[20] In brief, for low-polarity H-X bonds the free energies of hydration are essentially the same for CH_3X and HX. For the polar bonds, O-H and F-H, hydrogen bonding is lost on replacing H by CH_3. Thus the methyl group acts like a hydrogen atom which is nonpolar. If a nonpolar H atom mimics the odd electron of the radical X, then a methyl group should do as well.

Accordingly, for all donor atoms but O and F, Ritchie's hypothesis is used and $\Delta G°_{HX}$ is used in place of $\Delta G°_X$. For O and F, $\Delta G°_{CH_3X}$ replaces $\Delta G°_{HX}$. With these approximations, values of I' are calculated by

$$I' = I + \Delta G°_{X^-} - \Delta G°_X \qquad (13)$$

The results are included in Table I. To obtain $E°'$ values, smply subtract I' from 4.50 V.

The Calculation of I' for Neutral Molecules

For neutral molecules, B, we have

$$B(g) = B^+(g) + e^- \qquad I \qquad (14)$$

$$B(aq) = B^+(aq) + e^- \qquad I' \qquad (15)$$

As already described, we have good data for the free energy of hydration of B, $\Delta G°_B$. The problem is that of estimating the unknown values of $\Delta G°_{B^+}$ where B^+ is a radical cation. As models, we will calculate the free energies of hydration, $\Delta G°_{BH^+}$, of the corresponding onium ions of B.

Analogous to eq 10, 11, and 12, we have

$$BH^+(g) = H^+(g) + B(g) \qquad PA - 7.5 = \Delta G°_{(g)} \qquad (16)$$

$$BH^+(aq) = H^+(aq) + B(aq) \qquad 2.303RT(pK_a) = \Delta G°_{(aq)} \qquad (17)$$

$$-\Delta G°_{BH^+} = -PA + 267 - \Delta G°_B + 1.36pK_a \qquad (18)$$

Table III shows a number of values for $\Delta G°_{BH^+}$ for a sampling of common molecules, calculated by means of eq 18. The necessary auxiliary data are also given.

Aue, Webb, and Bowers have already calculated a number of free energies of hydration for substituted ammonium ions from measured values of the gas-phase basicity.[16] For consistency these values have been recalculated by using the approximation $T\Delta S° = 7.5$ kcal/mol. All proton affinities, PA, come from the recent and extensive compilation by Lias, Liebman, and Levin.

Ritchie has suggested using the approximation $\Delta G°_{B^+} = \Delta G°_{BH^+}$, which again may be good in some cases but is not valid in others. For example, a better model for NH_3^+ would seem to be H_3O^+, rather than NH_4^+. Table III shows a very large difference between the values $-\Delta G°_{H_3O^+} = 102$ kcal/mol and $-\Delta G°_{NH_4^+} = 77$ kcal. Fortunately, in this case an experimental result is available.

The radical cation NH_3^+ may be made in aqueous solution by ionizing radiation. From a study of its behavior as a function of pH, a value of $pK_a = 6.70$ may be inferred.[24] The proton affinity of NH_2, the conjugate base of NH_3^+, may also be calculated.

$$NH_2(g) + H^+(g) = NH_3^+(g) \qquad PA = 182 \text{ kcal} \qquad (19)$$

The necessary data are the bond dissociation energy of NH_3 to form NH_2[22] and the ionization potential of NH_3.[25] From the above results a value of $-\Delta G°_{NH_3^+} = 96$ kcal/mol may be calculated, much closer to the H_3O^+ than the NH_4^+ figure.

The solvation energy of anion depends on the net charge and on the size primarily, but there is an important contribution due to any internal dipole moment, and lesser contributions due to higher multipoles.[26] The NH_3^+ ion, like H_3O^+, must have a strong dipole moment whereas NH_4^+ has none. Note that, for cations at least, hydrogen bonding does not appear to play any significant role. Thus K^+ and NH_4^+ have nearly the same ionic size and nearly the same free energies of hydration.

The radical cation $(CH_3)_2NH^+$ has also been studied in water, and a pK_a of 7.0 has been deduced.[27] The proton affinity in the gas phase can also be calculated,[22,25] as for ammonia, and a value of 220 kcal/mol is found. These results lead to a free energy of hydration for $(CH_3)_2NH^+$ of -59 kcal, almost the same as that for $(CH_3)_2NH_2^+$, -61 kcal, as seen in Table III. The Ritchie hypothesis is valid in this case, presumably because of more nearly equal internal dipoles, coupled with the insulating effect of the alkyl groups.

Table IV gives some calculated values for $\Delta G°_{BH^+}$ showing the effect of alkyl substitution on the onium ions. As expected, the difference between an ammonium ion and the related oxonium ion becomes smaller as hydrogen atoms are replaced by methyl groups. The residual effect for $(CH_3)_2NH_2^+$ compared to $(CH_3)_2OH^+$, for example, reflects the smaller size of the latter, as well as the greater polarity of an OH bond. Similar effects account for the reduced differences between phosphonium ions and sulfonium ions.

The radical cation H_2O^+ is expected to have a somewhat larger net dipole moment than H_3O^+, based on vector addition rules. While there is no direct evidence available, a value of -112 kcal/mol for the free energy of hydration of H_2O^+ seems reasonable, compared to -102 for H_3O^+. The proton affinity of OH may be calculated as 142 kcal/mol, leading to a value of the pK_a of H_2O^+ equal to -11. When this ion is formed in the radiolysis of water, it immediately dissociates as predicted by this pK_a.

$$H_2O^+(aq) + H_2O \rightarrow H_3O^+(aq) + OH(aq) \qquad (20)$$

In view of the above discussion and Table IV, the free energies of hydration of the radical cations of primary alkyl amines (including $N_2H_4^+$) are taken as 10 kcal/mol more negative than those of the corresponding ammonium ions. For alcohols and carboxylic acids, the correction is taken as 5 kcal/mol. While these corrections are rather arbitrary, they are probably much better than no corrections at all. For bases in which the donor atom is P or S, the corrections are assumed to be only half as large as for their

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(28) Estimated from the ionic radius of PH_4^+ (1.71 Å) and the trends shown in Table IV. This value leads to a pK_a for PH_4^+ of -3. The older value, -14, usually quoted, leads to a value of $-\Delta G°_{PH_4^+} = 58$ kcal/mol, which is unreasonable.

Table III. Some Properties of Selected Molecules, B

B	I[a]	PA[d]	pK_a[e]	ΔG°_B[h]	$-\Delta G^\circ_{BH^+}$[i,n]	I'[j,o]
$C_6H_5NH_2$	7.70	210	4.6	-3.0	66	4.96
$C_6H_5N(CH_3)_2$	7.12	223	5.1	(-1.0)	52	4.91
N_2H_4	8.74	205	7.9	-7.4	80	5.15
$(CH_3)_3N$	7.80	225	9.9	-1.3	54	5.21
$(C_2H_5)_3N$	7.50	232	10.7	-1.1	51	5.33
$(C_6H_5)_3P$	7.36	230	2.7	(0.0)	41	5.57
n-$C_3H_7NH_2$	8.78	222	10.6	2.4	61	5.80
pyrollidine	8.41	225	11.3	-1.2	57	5.91
$(C_2H_5)_2S$	8.43	205	-5.2	0.6	54	6.06
$(CH_3)_2S$	8.69	201	-5.4	0.5	59	6.11
NH_3	10.17	205	9.3	-2.4	77	6.11
$(C_2H_5)_3P$	8.18	232	8.7	(0.0)	47	6.14
dioxane	9.13	194	-3.2	-3.2	72	6.15
piperidine	8.70	226	11.2	-0.8	55	6.25
C_2H_5SH	9.29	191	-6.6	0.6	67	6.27
$(CH_3)_3P$	8.60	227	8.7	(1.0)	51	6.34
$(C_2H_5)_3As$	8.30	213	-6.6[l]	(0.0)	45[m]	6.34
imidazole	8.96[c]	220	6.7	(-4.0)	60	6.53
THF[b]	9.42	199	-2.0	-1.5	67	6.56
C_6H_6	9.25	186	-14.0[f]	1.1	61	6.56
$P(OCH_3)_3$	8.92	221	2.6[g]	(-1.0)	51	6.75
$(C_2H_5)_2O$	9.50	200	-3.6	0.1	62	6.79
α-picoline	9.02	225	6.5	-2.7	54	6.79
$HCON(CH_3)_2$	9.12	212	-1.2	(-3.0)	56	6.82
pyridine	9.27	220	5.2	-2.8	57	6.92
$(CH_3)_2CO$	9.69	197	-7.2[k]	-1.9	62	7.06
CH_3CO_2H	10.35	190	-6.0[k]	-4.8	75	7.10
CH_3OH	10.85	185	-3.0	-3.2	81	7.25
CH_3CHO	10.22	189	-8.0[k]	-1.6	69	7.29
$C_6H_5NO_2$	9.86	193	-12.0	-2.2	60	7.34
$(CH_3)_2SO$	9.90	211	0.0	(-4.0)	60	7.46
$CH_3CO_2C_2H_5$	10.10	201	-6.5	-1.2	59	7.60
H_2O	12.62	167	-2.0	-4.4	102	7.94
CH_3NO_2	11.13	193	-11.7	-1.8	60	8.65
CH_3CN	12.19	188	-10.0	-2.0	67	9.35

[a] Gas-phase ionization potentials in eV. Reference 25. [b] Tetrahydrofuran. [c] Ramsey, B. G. *J. Org. Chem.* **1979**, *44*, 2093–2097. [d] Proton affinities in kcal/mol. Reference 23. [e] For BH^+ in water. Values from the following: Arnett, E. M. *Prog. Phys. Org. Chem.* **1963**, *1*, 223–401. Stewart, R. *The Proton: Application to Organic Chemistry*; Academic: New York, 1985; Chapter 3. [f] Assuming benzene is a 100 times weaker base than hexamethylbenzene. [g] Schuster-Woldan, H. G.; Bosolo, F. *J. Am. Chem. Soc.* **1966**, *88*, 1657–1663. [h] In kcal/mol. References 17 and 18. Estimated values in parentheses. [i] Free energies of hydration of BH^+ ions in kcal/mol. Calculated from eq 18. [j] Ionization potentials in aqueous solution in eV. Calculated from eq 21. [k] These numbers are uncertain. See: Stewart, R. op. cit. [l] Calculated from free energy of hydration of $(C_2H_5)_3AsH^+$ and PA. [m] Extrapolated from values from $(C_2H_5)_3NH^+$ and $(C_2H_5)_3PH^+$. [n] Values reliable to ±2 kcal/mol, unless the pK_a is a large negative number. [o] The uncertainty in these numbers may be as large as 0.3 V.

Table IV. Free Energies of Hydration, $\Delta G^\circ_{BH^+}$, for Some Onium Ions at 25 °C

ion	$-\Delta G^\circ_{BH^+}$, kcal/mol	ion	$-\Delta G^\circ_{BH^+}$, kcal/mol
NH_4^+	77	H_3O^+	102
$CH_3NH_3^+$	68	$CH_3OH_2^+$	83
$(CH_3)_2NH_2^+$	61	$(CH_3)_2OH^+$	68
$(CH_3)_3NH^+$	57		
$C_6H_5NH_3^+$	66	$C_6H_5OH_2^+$	67
$CH_3CONH_3^+$	64	$CH_3CO_2H_2^+$	75
PH_4^+	71[a]	H_3S^+	85[b]
$CH_3PH_3^+$	64	$CH_3SH_2^+$	72
$(CH_3)_2PH_2^+$	55	$(CH_3)_2SH^+$	59
$(CH_3)_3PH^+$	51		

[a] Reference 28. [b] Assuming $pK_a = -8$.

N or O analogues. For all other molecules in Table III the Ritchie assumption is used, $\Delta G^\circ_{B^+} = \Delta G^\circ_{BH^+}$.

The values of the ionization potentials in aqueous solution may now be calculated.

$$I' = I + \Delta G^\circ_{B^+} - \Delta G^\circ_B \qquad (21)$$

The results are shown in the last column of Table III. As before, the oxidation potential with respect to the hydrogen electrode is found by subtracting I' from 4.50 V.

Estimation of A' for Neutral Molecules

Determining solution-phase electron affinities for neutral molecules is considerably more difficult than determining ionization potentials. The difficulties of direct experimental methods are about the same, and the calculation from other measurements is less certain. In a few cases electron affinities in solution have been derived from polarographic half-wave potentials, but not in aqueous solution.[29]

One difficulty with indirect methods has been that, until recently, only a few gas-phase electron affinities for neutral molecules were known. Happily, recent work was added many new results and promises to add many more. The direct determination of the equilibrium constant for electron transfer reactions

$$B'(g) + B^-(g) = B'^-(g) + B(g) \qquad (22)$$

enables positive values of A to be found.[30] This appears to be a rapid, accurate, and routine method for many molecules.

Even more important, it seems that electron transmission spectroscopy can be used to measure negative electron affinities.[31] That is, the energies of metastable anion states can be found. There is a drawback in that usually only vertical electron affinities can be found in this way. Still, much useful information on the lowest energy empty, and antibonding, orbitals of common

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(32) Ritchie's calculations (ref 14) are based on a standard state of one molar aqueous solution for H_2.

Table V. Electron Affinities, *A* and *A'*, for Some Representative Molecules

molecule	A,[a,e] eV	model[b]	A',[d] eV
O_2	0.44	O_2^-	4.3
SO_2	1.1	NO_2^-	4.1
$C_1H_5NO_2$	1.1	$C_6H_5NO_2H^+$	3.6
HNO_3	0.57	NO_3^-	3.1
CH_3NO_2	0.45	$CH_3NO_2H^+$	3.0
C_6H_5OH	−1.0	$C_6H_5OH_2^+$ [c]	1.7
C_5H_5N	−0.6	$C_5H_5NH^+$	1.7
$C_6H_k5NH_2$	−1.1	$C_6H_5NH_3^+$	1.6
C_6H_6	−1.2	$C_6H_7^+$	1.5
CH_3COCH_3	−1.5	$(CH_3)_2COH^+$	1.1
C_2H_2	−2.6	C_2H^-	0.6
CH_3CN	−2.8	CH_3CNH^+	0.0
$(CH_3)_3As$	−2.7	$(CH_3)_3AsH^+$	−0.3
$(CH_3)_2S$	−3.3	$(CH_3)_2SH^+$	−0.5
$(EcH_3)_3P$	−3.1	$(CH_3)_3PH^+$	−0.8
$(CH_3)_3N$	−4.8	$(CH_3)_3NH^+$	−2.5
$(CH_3)_2O$	−6.0	$(CH_3)_2OH^+$	−3.0

[a] Positive values from 30; negative values from ref 31. [b] Ion used to estimate $\Delta G°_{B^-}$. [c] $\Delta G°_{BH^+} = -67$ kcal/mol. [d] Calculated from eq 23. [e] Negative values correspond to vertical electron affinities.

molecules has become available.

Table V gives a number of results for representative molecules. They are intended to give an idea of the range that exists. To convert the values of *A* to solution values, *A'*, requires free energies of hydration for the ions B^-. A second difficulty is now evident. Brønsted pK_a data do not provide such convenient models as for X^- and B^+.

The best that we can do at present is to make use of the fact that for sufficiently large ions the monopolar contribution to the free energy of hydration does not depend on the sign of the ionic charge but only on its magnitude. There can still be contributions due to the distribution of charge, but these will be smaller. Thus we look for the best models for B^- that we can find among the available X^-, B^+, or BH^+ ions in Tables I and III.

Specifically, a model for CH_3CN^- might be CH_2CN^- or CH_3CN^+ (assumed the same as CH_3CNH^+). The free energy of hydration for CH_2CN^- is −74 kcal/mol, and for CH_3CNH^+ it is −67 kcal. On the basis of size considerations, the latter is more reasonable. While not very accurate, an estimate can now be made for the solution value for the electron affinity of CH_3CN. The general equation is

$$A' = A - \Delta G°_{B^-} + \Delta G°_{B} \qquad (23)$$

where the free energy of hydration of the model is used for $\Delta G°_{B^-}$. Table V shows the results that are obtained in this way.

The calculation of *A'* for many cations of interest is faced with an apparently insuperable problem. For simple metal cations estimates of *A'* would be possible since the gas-phase data are readily available, and much is known about hydration energies of such ions. Reasonable estimates of free energies of hydration of metal atoms could no doubt be made. But cations such as CH_3^+, Cl^+, and NO_2^+ when placed in water would immediately become $CH_3OH_2^+$ (or CH_3OH), HOCl, and HNO_3. Thus the species of interest do not exist in water, just as H^+ does not.

Discussion

When the *I'* values for anions in Table I are converted to oxidation potentials, $E°'$, good agreement is found with experimental values, where known. These are −0.15 V for O_2^-,[7] −0.99V for NO_2^-,[8] −1.33V for I^-,[10] and −1.33 V for N_3^-.[11] The results are also in agreement with earlier calculations, with a few exceptions. Agreement is taken to mean better than 0.2 V, considering possible errors in the primary data used. The Russian workers used an old value for the heat of formation of cyanide ion,[13] and their number for the CN^-/CN couple is too small. Ritchie's values for anions, including CN^-, are in agreement with Table I, except for the changes in $\Delta G°_X$ discussed earlier.[14]

Eberson[12] calculated a value of −2.41 V for the $CH_3CO_2^-/CH_3CO_2$ couple, compared to −2.04 from Table I. The discrepancy lies in his assumption that $\Delta H°_X$ for CH_3CO_2 is equal to 0. This apparently harmless assumption leads to an error of 9 kcal/mol. All heats of hydration for molecules must be negative, from −1.0 kcal for H_2 to −13 kcal for acetic acid. Since all entropies of hydration are negative, in the range −18 eu for H_2 to −25 eu for CH_3CO_2H,[33] Eberson's assumption that $\Delta S°_X$ is the same for CH_3CO_2 as for CH_3CO_2H is not unreasonable. However, the further reasonable assumption that the free energy change for CH_3CO_2 is the same as for $CH_3CO_2CH_3$ leads to a value of −9 kcal/mol for $\Delta H°_X$.

There are few earlier results to compare with the data in Table III. Ritchie has calculated numbers related to $E°'$ for H_2O, n-$C_3H_7NH_2$, and piperidine.[14] The result for H_2O is consistent with the data in Table III. However, the results for the two amines are dubious since they depend on obviously wrong values of D_0 for the reaction

$$BH^+(g) = B^+(g) + H(g) \qquad D_0 \qquad (24)$$

At absolute zero, the heat of reaction 24 must satisfy the equation

$$D_0 = PA - 313.6 + I \qquad (25)$$

where all values are in kcal.

For reasons already discussed, the values of $E°'$ from the tables will not usually be equal to measured oxidation potentials. But there are many cases where a relationship exists. For example, the "half-wave" potential for the oxidation of aniline in water at a carbon electrode is 0.96 V with respect to the hydrogen electrode.[34] The reversible potential calculated from Table III is 0.46 V. There is an overvoltage of 0.5 V probably due to slow electron transfer to the electrode. The ion $C_6H_5NH_2^+$ also rapidly decomposes.

For a series of substituted anilines, however, it is found that the irreversible "half-wave" potentials vary in just about the way that $E°'$ would.[34] This is a fairly general result. It has been shown that a plot of $E_{1/2}$ vs. *I* is linear for a large number of organic molecules, when oxidized at smooth platinum electrodes in acetonitrile.[35] The slope is nearly unity, as expected from eq 21. The maximum value of *I'* for acetonitrile in Table III is consistent with its use as a solvent for electrochemical oxidations.

The kinetic method has been used to set a limit for the $N_2H_4/N_2H_4^+$ couple,[21] $E°' \geqslant -0.73$ V. This agrees with the value calculated from Table III of −0.65 V. However, $E°'$ would have been calculated as −1.08 V if the free energy of hydration of $N_2H_4^+$ had not been assumed to be 10 kcal more negative than that of $N_2H_5^+$. This assumption is seen to be justified.

Considering Tables I and III together, it is interesting to see how similar are the ranges for anions and neutral molecules. This contrasts with the results in the gas phase, where I is always much greater for neutrals. The role of the solvent water is to make *I'* lower than *I* by 2–4 eV for molecules and to raise *I'* above *I* by a similar amount for anions.

There are some surprises in the tables. It is unexpected to find that CH_3O^- is oxidized more readily than I^-, or that OH^- is discharged more easily than Br^- or Cl^-. It is also unexpected to see that amines are the most easily oxidized molecules, and not phosphines or arsines. It seems peculiar that dioxane should be the most oxidizable O-donor molecule, followed by THF.

Table V shows that electron affinities of neutral molecules are favored in solution by 2–4 eV. Electron affinities of cations would be disfavored by similar amounts. In a few cases even anions, e.g., SO_4^-, would have positive electron affinities in solution. No double negative ions are stable in the gas phase.

Absolute Electronegativities

One use for solution-phase values of *I'* and *A'* is to calculate absolute electronegativities, χ', and hardness parameters, η', in solution.

$$\chi' = (I' + A')/2 \text{ and } \eta' = (I' - A')/2 \qquad (26)$$

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(33) These entropy changes are similar to the entropies of condensation for pure liquids.

(34) Bacon, J.; Adams, R. N. *J. Am. Chem. Soc.* **1968**, *90*, 6596–6599.

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Note that the meaning of χ' and η' is not quite the same as for χ and η. The former are measures of changes in free energy with change in the number of electrons, and the latter relate to changes in electronic energy.[6] Since I and A in the gas phase are defined as energy changes at absolute zero,[25] they are also free energy changes. Conversely, however, I' and A' are not changes in internal energy only but include significant entropy changes.

For neutral molecules, a consideration of Table V shows that for sufficiently large molecules changes from I to I' will be equal and opposite to changes from A to A'. Therefore, the numerical value of χ' will be the same as that for χ. The solvent has no effect on the absolute electronegativity, a useful result.

Even for smaller molecules this should be approximately true. Monatomic anions have larger free energies of hydration than monatomic cations of the same size. For example, compare F^-, ionic radius of 1.36 Å and $\Delta G° = -106$ kcal/mol, and K^+, ionic radius 1.33 Å and $\Delta G° = -80$ kcal. This property helps counteract the fact that M^- will be larger than M^+.

The value of χ is chiefly useful in determining the net direction of spontaneous election transition when two molecules interact.[36] The difference in χ values also determines, in part, the amount of electron transfer that occurs.[37] This, in turn, determines in part the bonding energy between two molecules. It is most useful for neutral molecules where simultaneous electron transfer in both directions is possible (σ and π bonding).[37]

For cations and anions χ is less useful because electron transfer is primarily in one direction: anions are electron donors and cations are electron acceptors. In these cases I and A become the effective electronegativities, respectively.[37] The effect of solvent is now pronounced. Anions are poorer electron donors in solution, and cations are poorer electron acceptors.

For neutral molecules the value of η', $(I' - A')/2$, becomes very small, approaching zero. Technically, this implies that molecules in solution are much softer than those in the gas phase. If a plot of free energy as a function of N, the number of electrons in the molecule, is drawn, the curvature $(\partial^2 G/\partial N^2)$ is close to zero.[6] However, these low values of η' have little practical utility.

A consideration of the known uses of $(I - A)/2$ will make this point clear. It is convenient to use the concepts of MO theory.[37] In the most common case, I and A are related to the one-electron orbital energies of the HOMO and LUMO, respectively.

$$-I = E_{\text{HOMO}} \text{ and } -A = E_{\text{LUMO}}$$

Then $(I - A)$ is simply the difference in energy between the HOMO and the LUMO. Soft molecules have a small energy gap.

(a) When this energy gap is small, both σ and π bonding by partial transfer of electrons are favored.[37] Low I makes a better electron donor and large A makes a better electron acceptor.

(b) Using the second-order Jahn-Teller effect as a basis, it can be shown that a large energy gap is the hallmark of a stable molecule.[38] A small gap indicates instability toward isomerization or dissociation. Hard molecules in general are more stable than similar soft molecules.

(c) If the difference in energy between HOMO and LUMO is small, then a manifold or excited states must exist, not far above the ground state. These excited states can be used to polarize a molecule, reducing van der Waals' repulsion energies when two molecules interact.[38]

(d) In simple MO theory $(I - A)$ determines the lowest energy transition in the vis-UV spectrum.[39] Thus I and A values for molecules give information about electronic spectra and, conversely, spectra give information about η values.

(e) For radicals and atoms, I and A often refer to removing an electron from, or adding an electron to, the same orbital. In these cases $(I - A)$ is the mean interelectronic repulsion. It is one of the factors which determines the polarity of a bond between two radicals or atoms.[38]

All of these uses of $(I - A)$ depend mainly on internal properties of the molecule and the gas-phase values of I and A. Solvent effects would not be 0, but they would be small. In no case would the net charge on the molecule, or pair of interacting molecules, be changed. Without a change in the net charge, the large solvent effects leading to I' and A' would not occur.

An estimate of solvation effects could be made by measuring the shifts in absorption maxima in the vis-UV spectra on going from the gas phase to solution.[40] However, it is likely that solvent effects will be different for each of the effects a–e mentioned above. In the absence of any definite information, it seems clear that $(I - A)/2$ would be a much better approximation to use, even in solution, than $(I' - A')/2$.

Note Added in Proof. It appears that phenol is protonated on the ring in the gas phase and that O-protonation is 15 kcal less exothermic (De Frees, D. J.; McIver, Jr., R. T.; Hehre, W. J. *J. Am. Chem. Soc.* **1977**, *99*, 3853). This makes $\Delta G°_{BH^+}$ for $C_6H_5OH_2^+$ equal to 82 kcal/mol, requires a correction for $C_6H_5NH_2^+$, and makes I' for aniline 4.53 V in Table III.

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Registry No. $C_6H_5CH_2^-$, 18860-15-6; CH_3^-, 15194-58-8; PH_2^-, 13937-34-3; $C_6H_5^-$, 30922-78-2; O_2^-, 11062-77-4; CH_2CN^-, 21438-99-3; H^-, 12184-88-2; NH_2^-, 17655-31-1; HSe^-, 16661-43-1; $CH_3COCH_2^-$, 24262-31-5; n-$C_3H_7S^-$, 20733-14-6; $C_6H_5S^-$, 13133-62-5; HO_2^-, 14691-59-9; NO_2^-, 14797-65-0; $C_6H_5O^-$, 3229-70-7; ClO_2^-, 14998-27-7; HS^-, 15035-72-0; CH_3O^-, 3315-60-4; I^-, 20461-54-5; $CF_3CH_2O^-$, 24265-37-0; N_3^-, 14343-69-2; SCN^-, 302-04-5; HC_2^-, 29075-95-4; OH^-, 14280-30-9; Br^-, 24959-67-9; $CH_3CO_2^-$, 71-50-1; NO_3^-, 14797-55-8; Cl^-, 16887-00-6; CN^-, 57-12-5; F^-, 16984-48-8; HF, 7664-39-3; CH_3F, 593-53-3; H_2O, 7732-18-5; CH_3OH, 67-56-1; $(CH_3)_2O$, 115-10-6; CH_3CO_2H, 64-19-7; $CH_3CO_2CH_3$, 79-20-9; $C_6H_5NH_2$, 62-53-3; $C_6H_5N(CH_3)_2$, 121-69-7; N_2H_4, 302-01-2; $(CH_3)_3N$, 75-50-3; $(C_2H_5)_3N$, 121-44-8; $(C_6H_5)_3P$, 603-35-00; n-$C_3H_7NH_2$, 107-10-8; $(C_2H_5)_2S$, 352-93-2; $(CH_3)_2S$, 75-18-3; NH_3, 7664-41-7; $(C_2H_5)_3P$, 554-70-1; C_2H_5SH, 75-08-1; $(CH_3)_3P$, 594-09-2; $(C_2H_5)_3As$, 617-75-4; THF, 109-99-9; C_6H_6, 71-43-2; $P(OCH_3)_3$, 121-45-9; $(C_2H_5)_2O$, 60-29-7; $HCON(CH_3)_2$, 68-12-2; CH_3CHO, 75-07-0; $C_6H_5NO_2$, 98-95-3; $(CH_3)_2SO$, 67-68-5; $CH_3CO_2C_2H_5$, 141-78-6; CH_3NO_2, 75-52-5; CH_3CN, 75-05-8; NH_4^+, 14798-03-9; $CH_3NH_3^+$, 17000-00-9; $(CH_3)_2NH_2^+$, 19497-23-5; $(CH_3)_3NH^+$, 16962-53-1; $C_6H_5NH_3^+$, 17032-11-0; $CH_3CONH_3^+$, 34053-88-8; PH_4^+, 16749-13-6; $CH_3PH_3^+$, 28602-10-0; $(CH_3)_2PH_2^+$, 28604-50-4; $(CH_3)_3PH^+$, 19287-79-7; O_2, 7782-44-7; SO_2, 7446-09-5; HNO_3, 7697-37-2; C_6H_5OH, 108-95-2; C_2H_2, 74-86-2; $(CH_3)_3As$, 593-88-4; $C_6H_5NO_2H^+$, 19154-80-4; $CH_3NO_2H^+$, 19154-77-9; $C_6H_5OH_2^+$, 19527-06-1; $C_5H_5NH^+$, 16969-45-2; $C_6H_7^+$, 38815-08-6; $(CH_3)_2COH^+$, 43022-03-3; CH_3CNH^+, 20813-12-1; $(CH_3)_3AsH^+$, 103884-15-7; $(CH_3)_2SH^+$, 18683-32-4; $(CH_3)_2OH^+$, 17009-82-4; pyrrollidine, 123-75-1; dioxane, 123-91-1; piperidine, 110-86-1; imidazole, 288-32-4; α-picoline, 109-06-8; pyridine, 110-86-1.

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(40) Such effects are often quite small. Even for charge-transfer bands, the shifts are less than 1 eV. See: Reichardt, C. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 29–40.