ELECTRODE POTENTIALS AND HYDRATION ENERGIES.
THEORIES AND CORRELATIONS

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CONTENTS

I. INTRODUCTION

A. SCOPE AND CONVENTIONS

The energies involved in the two processes, (a) gas atom → gas ion, and (b) gas atom → aquo-ion, are fundamental to the properties of aquo-ions. The electrode potential and its temperature coefficient provide a large contribution to the energy change in (b) which is termed in this review an aqueous ionization. The process (b)–(a) corresponds to hydration of the gas ion, and theories propounded for the accompanying energy change are considered here. The steps (a) and (b) as individual processes are subsequently examined. Photoionization spectra of ions in solution and thermal reactions involving transfer of charge, being closely related topics, are also included, as are some electrode potentials for unstable ions, derived from interpretations of electron-transfer kinetics or correlations involving process (b).

In the last decade hydration has been considered in reviews (15, 46a, 171, 174a), symposia (80, 124), and numerous textbooks (10a, 90, 151a, 175). Papers on hydration energies often include reviews, but usually only of related treatments. The literature to September 1964 has been inspected; because of the extent of the field, data and interpretations have been included only when closely relevant to processes (a), (b) for monatomic ions. Since hydration energy includes interactions between ion and water molecules which extend to, and disappear only at, infinite distances from the ion in solution, "hydration" properly includes all these interactions. However, compare the following contentions: "the electrical field in the neighborhood of an ion falls continuously with increasing distance and it is therefore arbitrary to regard some of the water molecules as associated with the ion and others as not" (48); on the other hand, "the numbers of molecules moving with the ions as a single kinetic entity . . . we

[Robinson and Stokes (178a)] regard as 'true' hydration numbers." In this review, apart from acceptance of the complete meaning in "hydration energies and entropies," the terms "hydration" and "hydration number" will refer only to those water molecules assumed to lie within a shell 2.8–3 Å. thick about the surface of the monatomic ion, unless "secondary hydration" is specifically mentioned, referring to water in a further shell ~3 Å. thick imagined to surround, or partly penetrate, the "primary" shell. However, some (apparent) hydration numbers, as in Table IV, must refer to only one or two molecules of what is here called the primary shell.

The choice of model for calculation of hydration energies is much wider than that for lattice energies, and even for the well-defined lattice case numerous approaches are in use (207). A concentrated attack on the former problem, in many recent publications, has led to a proliferation of parameters and assumptions, and it has seemed most useful to examine these in detail. While different models might profitably serve in accounting for different varieties of phenomena (or even one phenomenon), these models should not conflict. Agreement in hydration energies from theory and experiment is not difficult to achieve (a brief textual comment on this point thus sufficing, in the present review, in the place of extensive tabulations of variously calculated values). The validity of any model would appear then to rest on some subjective and therefore unscientific assessment. The ultimate goal is, however, not the achievement of an indefinable correctness of model, but the eradication as far as possible of obvious inconsistencies between models, and the comparative approach of the present review is intended to assist toward that end.

For the majority of ions considered here, i.e., cations, both the above components of the hydration cycle, (a) and (b), are oxidations. Thus, despite the desirability of a general conformity with the Stockholm convention (44, 139), American oxidation potentials are used in this review. (Being identical with that for gas phase ionization potentials, a third, quite widespread but now evanescent usage (67, 151d, 214), of writing reduction (Stockholm) potentials with oxidative half-reactions, might have been employed.) Electrode potentials have been clearly defined by Ramsey (173) who suggests as standard state, for the electron appearing in half-reactions, the state of the electrons in the metal connection to the normal hydrogen electrode (cf. 110, 111, 151c). Electrode potentials receive attention in numerous reviews and textbooks (23, 51, 120, 151d), and temperature coefficients have been calculated (21).

B. SYMBOLS

Energies and related quantities:

Y	standard free energy F or enthalpy H or entropy S, at 25°
$\Delta Y_{h\ con}$	conventional thermodynamic value for hydration, referred to gas phase hydrogen ion; for standard states 1 m in solution and 1 atm. gas
$\Delta Y'_{h\ con}$	same as $\Delta Y_{h\ con}$, but referred to gas phase hydrogen molecule
ΔY_h	an "absolute" thermodynamic value for hydration, for conventional standard states, depending on some choice of absolute value for proton hydration
$\Delta Y'_{ai}$	for the process gas atom → aquo-ion, referred to hydrogen molecule; conventional standard states
$\Delta Y'_{aq}$	for formation of ion in 1 m solution, from elements; referred to H_2
U	potential, surface, kinetic, or resonance energy, identified by subscript
I	gas phase ionization potential
I_{aq}	calculated solution phase ionization energy
$E°$	American oxidation potential
ε	electron affinity
ψ	a potential
D	electric displacement
E	field
$\mathfrak{F}$	the faraday, 23.06 kcal./v. equiv.
Q_{int}	internal (electronic) partition function

Dimensions and volumes:

v	volume
V	partial molal volume of ion in solution
V_f	free volume in solution
x	a distance in solution
r	an ionic radius or a radial distance, variously defined (see the following)
$r_c,\ r_{exp},\ r_{qt},\ r_L$	ionic radii derived from different assumptions
$r_{aq},\ r_g$	radial distance from the center of an ion in water, or in the gas phase, respectively, appearing in the Born expression
a	part of r_{aq} arising from dielectric void
r_w	radius of H_2O molecule
$d = r + r_w$	separation between centers of ion and water molecule

Properties of water:

ϵ	low-field dielectric constant (permittivity)
ϵ''	high-field permittivity
n_{ref}	refractive index
α_p	polarizability
$\mu,\ \mu_i$	permanent and induced dipole moments of water
Θ	quadrupole moment of water for ion–water axis

Numbers and parameters:

$A,\ B$	parameters fitting empirical entropy correlations
$Q,\ R$	parameters containing Θ
n	principal quantum number
n_h	hydration number
z	a number, representing the magnitude of ionic charge
Z_{nuc}	nuclear charge
η	electron shell repulsion exponent
λ	a fraction (of charge)

Ions:

M^{z+}	cation with noble gas electronic structure

$\mathfrak{M}^{z+}$ cation lacking noble gas electronic structure
X^{z-} anion

Superscripts:

′   referred to H_2 gas

″   with theoretical correction for dielectric saturation

°   standard state 1 m solution (applied only to entropies S in solution and $E°$)

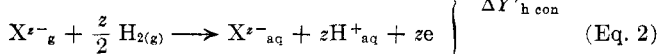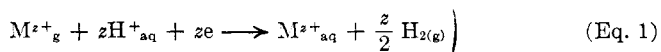*   of activation

Subscripts:

BC   Born charging

g   in the gas phase

aq   in water, or, of formation in water

h   of hydration (absolute value)

h con   of hydration (conventional value)

ai   of aqueous ionization

diss   for formation of halogen gas atom at 1 atm. pressure, from element in standard state

sub, vap   of sublimation, of vaporization

I   of gas phase ionization

un   unitary

tr   of translation

con   conventional value, with that for H^+_{aq} taken as zero ⎫ applied to ionic entropies in solution

abs   absolute value

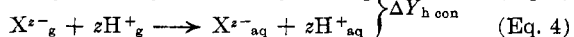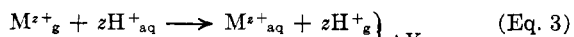(Some symbols appearing only once are defined in the text.)

C. DATA

Methods of evaluating $E°$ (43) include calculation from observed enthalpies and entropies of formation of aquo-ions from elements, as by Latimer (135), who employed predominantly NBS 500 (154) thermal data. The experimental cycle used in evaluations of hydration energies is given in Figure 1.

Conventional values are given with respect to gas phase hydrogen as either the molecule

$$M^{z+}_g + zH^+_{aq} + ze \longrightarrow M^{z+}_{aq} + \frac{z}{2} H_{2(g)} \quad \text{(Eq. 1)}$$

$$X^{z-}_g + \frac{z}{2} H_{2(g)} \longrightarrow X^{z-}_{aq} + zH^+_{aq} + ze \quad \text{(Eq. 2)}$$

$\Delta Y'_{h \text{ con}}$

or as H^+_g

$$M^{z+}_g + zH^+_{aq} \longrightarrow M^{z+}_{aq} + zH^+_g \quad \text{(Eq. 3)}$$

$$X^{z-}_g + zH^+_g \longrightarrow X^{z-}_{aq} + zH^+_{aq} \quad \text{(Eq. 4)}$$

$\Delta Y_{h \text{ con}}$

$(Y = F, H, \text{ or } S)$.

$\Delta Y_{h \text{ con}}$ values, Table I, being free of an inconvenient convention relating $\Delta F'_{h \text{ con}}$, $\Delta H'_{h \text{ con}}$, and $\Delta S'_{h \text{ con}}$ (156), seem preferable. $\Delta F_{h \text{ con}}$ differs from $\Delta F'_{h \text{ con}}$ by $362.5z$ kcal. (from data for $^1/_2H_{2(g)} \longrightarrow H_g^+ + e_g$ (154)). S_g values are properly given by the Sackur–Tetrode equation with additional terms in Q_{int} when $Q_{int} \neq 1$. The tabulated values of $\Delta S_{h \text{ con}}$ are reliable to 0.1–4 e.u., and the energies usually to 1–3 kcal./g.-ion (section IXA). Selected absolute values for H^+ hydration (cf. sections II and IVE) are given in Table II.
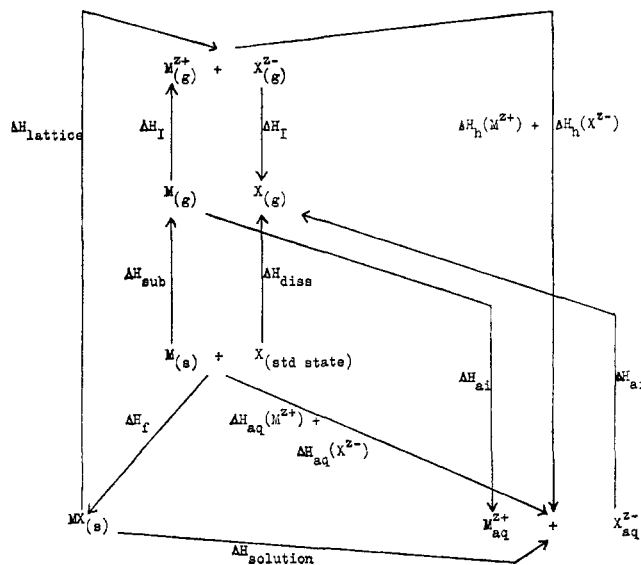

Figure 1.—Experimental cycle for determination of hydration energies.

II. SINGLE-ION HYDRATION ENERGIES AND SURFACE EFFECTS

Experimentally, energy sums for anions and cations, or differences between cation and proton values, are obtained; single-ion values have been estimated by extrapolation procedures involving ionic radii (section IVE) or, less satisfactorily (155), by dividing by two the sum for a selected anion–cation pair, assumed more or less arbitrarily to differ only in charge sign, other single-ion values following from this assignment (Table IX). Separate immersions of a positive and a negative particle, identical apart from charge sign, may however require different amounts of work, (i) because the charge, water-quadrupole interaction energies, if appreciable, would be of opposite sign in the two cases (36, 92) or (ii) because there could be different orientations of H_2O about anions and cations (Table III and Figure 2) or (iii) because of the surface effects considered in the next paragraph. Radii commonly used are estimated contributions to interionic distances in crystals, and application to experimental energies of
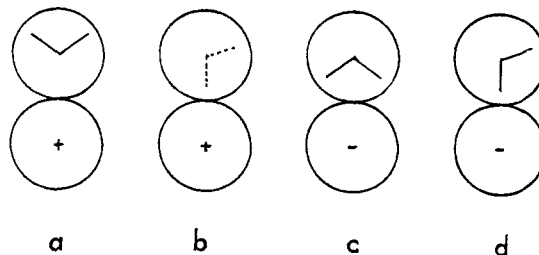

Figure 2.—Suggested orientations of water about ions (100): (a) normal dipole orientation at cation; (b) angled dipole (lone-pair) orientation at cation; (c) normal dipole orientation at anion; (d) linear H bond at anion. ———, O–H bond; ———, lone pair.

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TABLE I

HYDRATION DATA AND IONIC RADII

(Standard states, gas: 1 atm. pressure, 24.47 l./mole; solution: 1 m)

	r_o, Å. (Pauling)	r_o, Å. (Goldschmidt or thermochemical (t))	r_{exp}, Å. (ref. 85)	$S°_{con}$, e.u.	$\Delta H_{h\ con}$, kcal./g.-ion	$\Delta F_{h\ con}$, kcal./g.-ion	$\Delta S°_{h\ con}$, e.u.	$-\Delta F_h$, kcal./g.-ion
H⁺				0.0	0.0	0.0	0.0	260.5ᵃ
Li⁺	(0.60)ʰ	0.78	0.94	3.4	137.7	138.4	−2.4	122.1
Na⁺	0.95	0.98	1.17	14.4	163.8	162.3	5.1	98.2
K⁺	1.33	1.33	1.49	24.5	184.0	179.9	13.6	80.6
Rb⁺	1.48	1.49	1.63	29.7	190.0	185.0	16.5	75.5
Cs⁺	1.69	1.65	1.86	31.8	197.8	192.7	17.2	67.8
Be²⁺	0.31				−73			
Mg²⁺	0.65	0.78		−28.2	62.0	65.5	−11.7	455.5
Ca²⁺	0.99	1.06		−13.2	140.8	140.2	1.8	380.8
Sr²⁺	1.13	1.27		−9.4	176.1ᵇ	175.1ᵇ	3.4	345.9
Ba²⁺	1.35	1.43		3.0	210.1ᵇ	205.9ᵇ	14.1	315.1
Ra²⁺	1.40	1.52			220			
Al³⁺	0.50	0.57		−74.9	−331.6	−321.8	−32.7	1103.3
Sc³⁺	0.81	0.78		(−54.9)ᶜ,ʰ	−153.3ᵇ	−147.8ᵇ	(−18.6)	929.3
Y³⁺	0.93	0.93		(−48.9)ᶜ	−82.1ᵇ	−78ᵇ	(−13.7)	859.5
La³⁺	1.15	1.22			−2.5			
Ga³⁺	0.62	0.62		−83	−337.6	−324.5	−44	1106.0
In³⁺	0.81	0.92		−62	−199.9	−192.7	−24	973.2
Tl³⁺	0.95	1.05			−217.9			
Cu⁺	0.96			(−6)	118.7	(124.3)	(−18.7)	(136.2)
Ag⁺	1.26	1.13			147.1	146.0	3.7	114.5
Tl⁺	1.40	1.49		30.4	182.8	178.5	14.6	82.0
NH₄⁺		1.40 (t)		27.0	185			
Cr²⁺	0.84				79.3			
Mn²⁺	0.80			−20	80.4	83.2	−9.5	437.8
Fe²⁺	0.76	0.83		−26.2ᵈ	59.4ᵇ,ᵉ	64.6ᵇ,ᵉ	−17.2	456.4
Co²⁺	0.74	0.82		−26.6ᵈ	36.3ᵇ,ᵈ	41.5ᵇ,ᵈ	−17.4	479.5
Ni²⁺	0.72			−29.5ᵈ	20.8ᵇ,ᵈ	26.8ᵇ,ᵈ	−19.8	494.2
Cu²⁺		0.82 (t)		−20.4ᵈ	19.9ᵇ,ᵉ	23.3ᵇ,ᵉ	−11.3	498.7
Zn²⁺	0.74	0.83		−25.5	32.8	36.4	−11.9	484.6
Cd²⁺	0.97	1.03		−14.6	89.8	90.5	−2.6	430.5
Hg²⁺	1.10					(84.7)ᵇ		(436.3)
Pb²⁺	1.20	1.32		5.1	167.7	163.2	15.2	357.8
Cr³⁺	0.69	0.65		(−270)				
Fe³⁺	0.64	0.67		−70.1	−264	−254	−33.6	1035.5
Ce³⁺	1.11	1.18			−67			
U³⁺	...			−30				
Tl³⁺	0.95	1.05			−217.9			
Ce⁴⁺	1.01				−508			
U⁴⁺	...			−78				
F⁻	1.36	1.33	1.16	−2.3	−383.1ᶠ	−364.3ᶠ	−63.1	103.8
Cl⁻	1.81	1.81	1.64	13.2	−351.1ᶠ	−336.3ᶠ	−49.5	75.8
Br⁻	1.95	1.96	1.80	19.3	−347.7ᶠ	−333.0ᶠ	−45.8	72.5
I⁻	2.16	2.20	2.05	26.1	−333.9ᶠ	−321.9ᶠ	−40.3	61.4
S²⁻	1.84	1.74		(5.3)	−849.4	(−824.6)	(−83.1)	303.6)
OH⁻		1.40 (t)		−2.5	−371ᵍ			
SH⁻		1.95ᵍ		14.6	−341ᵍ			

$$r_L(M^{z+}) = r_o(M^{z+}) + 0.28 \text{ Å.} \Big\}$$
$$r_L(X^{z-}) = r_o(X^{z-}) - 0.28 \text{ Å.} \Big\} \quad r_c \text{ values from column 3}$$

$\Delta Y_{h\ con}$ and $S°_{con}$ values from a tabulation (16) of NBS 500 (154) values, or, when superscripted, NBS 500 data with new values as follows. ᵃ Experimental value (174). ᵇ New (198) sublimation quantities. ᶜ From new (198) estimates of metal entropies, with $\Delta H'_{aq}$ and $\Delta F'_{aq}$ from NBS 500. ᵈ New (123) estimates. ᵉ NBS 500 $\Delta H'_{aq}$ and $\Delta F'_{aq}$ equally adjusted to accommodate new $S°_{con}$ values. ᶠ New (19) (unweighted) electron affinities, converted to enthalpies at 298° following NBS 500 (except for Br⁻, for which $Q_{int}(Br)$ assumed unity). ᵍ From ref. 92. ʰ Values in parentheses are particularly uncertain.

radii derived from erroneous subdivision could give spurious indications of (i)–(iii) (24).

If at a gas–water interface a preferred water-dipole orientation (not at present known) leads to a predomi-

nantly positive or negative surface-charge distribution, a potential difference across the surface, ψ_{H_2O}, will result, and the work done in conveying a charge through the surface will differ in sign for positive or negative charges (164a).[1]

Measurements of (Volta) potential differences between phases separated by gas or vacuum apparently lack the Nernstian reversibility essential to e.m.f. measurements. Pseudo-reversibility at the balance point of measurement can however be established by demonstrating the lack of effect of ionizing the gas in the gap (164b). The single-ion hydration energies obtainable as follows from such measurements seem somewhat less arbitrary than the theoretical assessments to be considered in section IVE.

Randles measured the potential difference ψ between KCl solution, in equilibrium with $Hg_2Cl_{2(s)}|Hg_1$, and mercury at zero potential, the latter forming an axial jet in a tube down the internal wall of which the KCl solution was allowed to flow (174). The two relevant cells, giving rise to ψ and $E^\circ_{K,Cl}$, respectively, were

$$\boxed{Q}\text{---}Hg_1 \text{ (jet)}|N_2|KCl_{aq}|Hg_2Cl_{2(s)}|Hg_1\text{---}\boxed{P}$$
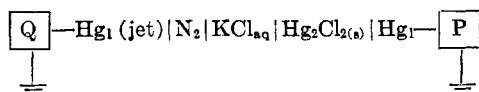
where Q = quadrant electrometer acting as null-point indicator, and P = potentiometer, and

$$K|Hg_1|Hg_2Cl_{2(s)}|KCl_{aq}|K$$
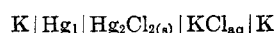
With the known mercury photoelectric limit W (i.e., the lowest free energy necessary to evict an electron

TABLE II

VALUES ACCEPTED IN THIS REVIEW FOR PROTONIC HYDRATION

$$S^\circ_{abs}(H^+) = -5.0 \text{ e.u.} \quad \text{(from section IVD)}$$

$H^+_g \rightarrow H^+_{aq}$	$\Delta F_h(H^+) = -260.5$ kcal. (174)
	$\Delta H_h(H^+) = -269.7$ kcal. (from $\Delta F_h(H^+)$ and $S^\circ_{abs}(H^+)$)
$^1/_2 H_{2(g)} \rightarrow H^+_{aq} + e_g$	$\Delta F'_h(H^+) = 102.5$ kcal. (from $\Delta F_h(H^+)$ and ref. 154)
	$\Delta H'_h(H^+) = 97.4$ kcal. (from $\Delta H_h(H^+)$ and ref. 154)

from the uncharged metal), the following sequence gives the absolute hydration free energy of K^+ provided that (i) correctly represents the reaction in the first cell.

(i)	$^1/_2 Hg_2Cl_{2(s)} + e_{Hg} \longrightarrow Hg_1 + Cl^-_{aq}$		$-\mathcal{F}\psi$
(ii)	$e_{Hg} \longrightarrow e_g$		W
(iii)	$K_s + ^1/_2 Hg_2Cl_{2(s)} \longrightarrow K^+_{aq} + Cl^-_{aq} + Hg_1$	$\mathcal{F}E^\circ_{K,Cl}$
(iv)	$K_s \longrightarrow K^+_g + e_g$		$\Delta F_{sub} + \Delta F_I$
(v)	$K^+_g \longrightarrow K^+_{aq}$		$\Delta F_h(K^+)$

Since (v) = $-$(i) + (ii) + (iii) $-$ (iv), substitution of the known free energies gives $\Delta F_h(K^+) = -80.6$ kcal./g.-ion, the other single-ion values of Table I following directly.

Adsorption of water on the Hg surface could apparently introduce some error into such measurements (74). Henceforth, for simplicity, ψ_{H_2O} is here summarily taken as zero, from an estimate (73) of 0.1 ± 0.1 v.

TABLE III

SUGGESTED ORIENTATIONS[a] OF WATER ABOUT M^+ AND X^-

	M+		X-		
Author	Normal dipole	Angled dipole	Normal dipole	Linear H-bond	Some H-bonding
Bernal and Fowler (18a)	√			(√)	
Eley and Evans (66)	√			(√)	
Verwey (205)		√		√	
Haggis, Hasted, and Buchanan (91)	√				√[b]
Moelwyn-Hughes (151a)	√		√		
Brady (29)	Li+				
Hindman (100)			Cl-, Br-; I-(?)	F-	
Schultz and Hornig (186)					√
Walrafen (208)					√
Vaslow (203)	Cs+ ← {similar stabil- ities} → Cs+; Li+, (Na+)				
Vollmar (206)	Li+; (Al³+)				

[a] Depicted in Figure 2. [b] Dipole assumed to be sufficiently free to orient in an external field.

(1) Terminology (164a): potentials at points in the water phase, calculated with proper inclusion of ψ_{H_2O}, are called "electrochemical potentials," but if ψ_{H_2O} is neglected without justification they are termed "chemical potentials" (unhappily). Single-ion hydration energies are correspondingly termed "real" or "chemical," often in italics. Experimental single-ion values (to be described) appear to take account of the surface effects; differences between values so derived and somewhat arbitrary "chemical" free energies have been used to calculate a value for ψ_{H_2O} of unknown significance (74, 104, 121, 122, 197, 204).

A cycle proposed by Noyes (157) to circumvent present ignorance of ψ_{H_2O} either involves consideration of only the sums of cation and anion hydration energies, thus excluding single-ion values or suggests that the (Born) charge involved in formation of single aquo-ions be considered to originate from the water phase, which still involves an unspecified energy difference for the process, free charge in vacuo to free charge in water.

III. SUMMARY OF THEORETICAL MODELS AND PARAMETERS

A. THEORETICAL PROCEDURES

1. Born Charging

In the simplest formulation (27) the free energy of charging a sphere of radius r_g in vacuo to charge ze is

$$\Delta F_{BCg} = z^2 e^2/2r_g \qquad \text{(Eq. 5)}$$

while in a dielectric of permittivity ϵ, here water, the corresponding free energy is (28)

$$\Delta F_{BCaq} = z^2 e^2/2r_{aq}\epsilon \qquad \text{(Eq. 6)}$$

The difference, which is the Born-charging hydration free energy, is

$$\Delta F_{BCh} = -(1 - \epsilon^{-1})z^2 e^2/2r \qquad \text{(Eq. 7)}$$

$$= -661.0z^2(1 - \epsilon^{-1})/r \qquad \text{(Eq. 8)}$$

(kcal./g.-ion, for r in Å.) if $r_{aq} = r_g = r$. Differentiation with respect to temperature gives

$$\Delta S_{BCh} = \frac{z^2 e^2}{2r\epsilon}\left(\frac{\partial \ln \epsilon}{\partial T}\right)_p \qquad \text{(Eq. 9)}$$

Since they are excluded in this expression, kinetic contributions to the entropies of actual ions have to be estimated and subtracted for comparison with Eq. 9 (section IVD). Similar corrections to experimental ΔF_h, for comparison with ΔF_{BCh}, appear usually to be neglected; here the kinetic contribution is relatively small (92).

Parameters to be selected for the application of this macroscopic law to experimental hydration quantities are as follows: a set of crystal radii, and possible corrections thereto, for the change to a noncrystalline environment; or, if the radical bound to the charge placed on the ion is assumed not to coincide with the physical radius, crystal radii and corrections thereto are replaced by "quasi-theoretical" radii r_{qt} having little connection with observed crystal distances. In addition, ΔF_{BCaq} requires correction since the operative

permittivity differs from the macroscopic ϵ value; the high field about ions during charging is stated (155, 149, and proponents of normal dipole orientation, Table III) to cause in most cases sufficient orientation of first-shell dipoles to render these ineffective in contributing to orientation polarization of the solvent.

2. Molecular Interactions

This heading covers calculations of the energies of interaction of the ionic charge with permanent and induced multipoles of water. Apart from Azzam's (8, 8a), calculations have been confined to first-shell water, second and further shells being treated by Eq. 7 and 9 as a continuum of macroscopic permittivity. Parameters required are radii of ions and of water, the polarizability and multipole moments of water, and a coordination number n_h. (Potential energies ΔU_{pot}, i.e., Coulombic energies, calculated with unit dielectric constant, are so obtained; these are often equated with enthalpies. In fact the corresponding enthalpies are (92) $\Delta H = \Delta U_{pot} + \Delta U_{kin} + \Delta Pv$, ΔU_{kin} probably being small (92).)

3. Structural Theories

Disruption or ordering of water structure, caused by the intrusion of ions, is more or less quantitatively considered, parameters as for section IIIA2 being employed.

B. PARAMETERS

1. Hydration Numbers n_h

By an isotope-dilution technique (168) using $H_2^{18}O$, n_h for Cr^{3+} was accurately established as 6.0, and 5.9 ± 0.1 for Al^{3+} and 4.1 ± 0.2 for Be^{2+} have been found by O^{17} n.m.r. measurements (45). Considerations of symmetry in Raman spectra clearly indicate octahedral water coordination by Cu^{2+}, Zn^{2+}, Mg^{2+}, Ga^{3+}, In^{3+}, and Tl^{3+} (98). Measurements of transport of water with ions (25, 182), activity coefficients (79, 80, 178b), V, and compressibilities (46c, 54, 162, 200, and

TABLE IV

APPARENT HYDRATION NUMBERS FOR UNIVALENT IONS (100)ᵃ

Ion	Activity coefficients		Ion exchange (82)	Mean, several methodsᵇ (25)	Diffusion coefficients (178c)	Permittivity (96) (n_h'')	Proton resonance (100)
	(79)	(80)					
Li⁺	3.4	4.2–4.7	3.3	4	2.3–2.8	6	4
Na⁺	2.0	2.7–3.3	1.5	3	0.7–1.2	4	3.1
K⁺	0.6	1.7–1.8	0.6	2	0.4–0.9	4	2.1
Rb⁺	0	1.5		1		3.5	1.6
Cs⁺	0	1.4	[0]				1.0
F⁻	1.8			3			1.6
Cl⁻	[0.9]	[0.9]		2	0.0–0.5	[0]	0
Br⁻	[0.9]	[0.9]			0.2–0.7	[0]	0
I⁻	[0.9]	[0.9]		0.7	0.7–1.2	[0]	0

ᵃ Assumed values in square brackets. ᵇ From mobility, entropy, compressibility, V.

TABLE V

QUASI-THEORETICAL RADII, r_{qt}, IN Å. (193)

	-2		-1		0		1		2		3
									Ionic charge		
O	2.405	F	1.909	Ne	1.583	Na	1.352	Mg	1.180	Al	1.046
S	2.726	Cl	2.252	Ar	1.918	K	1.671	Ca	1.480	Sc	1.328
Se	2.665	Br	2.298	Kr	2.019	Rb	1.801	Sr	1.625	Y	1.481
Te	2.956	I	2.548	Xe	2.239	Cs	1.997	Ba	1.802	Ra	1.642

references therein) have, *inter alia*, been interpreted in terms of specific hydration numbers of uncertain status; some examples are given in Table IV. HClO₄, depending on concentration, is extracted from water solution as a tetra-, di-, or monohydrate (146), and OH⁻ as a trihydrate (3). Activities in acid solution indicate a relative (primary + secondary) hydration number for H⁺ of 10, at high dilution (167), and a similar value is suggested by heat capacity measurements (but not for identical concentrations) (2). Gaseous $H_9O_4^+$ was identified mass spectrometrically (213). X-Ray diffraction studies do not give unequivocal n_h values (29, 30, *cf*. 61). Ultrasonic vibration potentials promise to establish the masses of the hydrated ion entities (53, 181, 218, 220). Microwave measurements of permittivities of electrolyte solutions (96) have been interpreted in terms of rotationless bonding of n_h'' water molecules of assumed permittivity 5.5, by the use of a simple dielectric mixture formula (91). n_h'' for anions was assumed zero on the basis of an arbitrary model allowing dipole orientation to external fields of hydrational molecules about X⁻.

2. Radii of Ions

a. Semiempirical Radii r_c

"Semiempirical" radii r_c based on semitheoretical or arbitrary divisions of crystallographic inter-ion distances usually agree, in different sets, to within ~0.1 Å. for any one M^{z+} or X^- ion. These have been given by Zachariasen (219), Goldschmidt (83), Wyckoff (216), and Pauling (166b) (some of the latter's values having been modified by Ahrens (4) in the light of correlations between ionization potentials and other semiempirical radii). Some "thermochemical" values, calculated from experimental lattice energies and the Mayer-Born-Madelung lattice energy expression (116, 207), belong in this group (Table I).

b. Quasi-Theoretical Radii r_{qt}

van Eck (62) obtained r_{qt} values from the assumption $\Sigma I = z^2 e^2 / 2 r_{qt}$. Stokes (193) suggested that the charge on M^{z+} or X^- is bound within a radius apparently corresponding to a van der Waals value (Table V)

$$r_{qt} = K/(Z_{nuc} - s)$$

K is a constant for an isoelectronic series and is determined by substitution, in the equation, of the known

van der Waals radius and ($Z_{nuc} - s$) for the noble gas of the series; ($Z_{nuc} - s$) is the Slater effective nuclear charge (188) for the outermost electron of the ion or noble gas atom. These radii, together with only three further parameters giving effective permittivities, when used in Born-charging calculations, reproduce all $M^{z+}X^-_z$ lattice energies to within about 1% (194). (Correlations with r_{qt} (195) might be further analyzed in terms of the Slater orbital energies (188) to which r_{qt}^2 is inversely proportional in isoelectronic series.)

c. Experimental Radii r_{exp}

Measured electron densities in NaCl (215) show unequivocally that in the crystal a radius of 1.17 Å. is to be attributed to Na⁺, viewed as a sphere, and 1.64 Å. to Cl⁻. Radii which on addition reproduce M⁺-X⁻ crystal distances, and which are consistent with the Na-Cl division, have been tabulated (85). Omitting the Li⁺ value (inconsistently low (4) on the Pauling scale), these experimental cationic radii r_{exp} (Table I) are 0.16 to 0.23 Å. larger than the Pauling values, anionic radii being correspondingly smaller.

Blandamer and Symons (24) have shown that properties of M⁺ and X⁻ ions (*viz*., ΔF_h, S_{un}, and, less exactly, ionic conductances) fall closely on one curve for each property, when plotted as functions of r_{exp}; two curves are necessary for anions and cations, respectively, when r_c values are taken. The novel implication of these correlations is that ion-water interactions are dependent *only* on the radii and not on the charge sign (*cf*. section II).

d. Aquo-Radii r_L from Values for Large Ions

These values, obtained by adding 0.28 Å. to Goldschmidt cationic r_c, and substracting 0.28 Å. from the anionic r_c, were proposed (132) on the ground that in solution the large isoelectronic ions Cs⁺ and I⁻ have equal radii. The assumption $r_c(Cs^+) + r_c(I^-) = r_L(Cs^+) + r_L(I^-)$ gives the 0.28-Å. term, which was subsequently deemed applicable to all other ions (117). All $V(M^+)$ and $V(X^-)$, when plotted against $4/3\pi r_L^3$, fall close to a single curve (117).

e. Ion-Water Distances

Subtraction of r_c from the shortest M^{z+}---OH_2 and X⁻---O crystallographic distances in hydrates (92) indicated a most probable r_w of 1.38 Å. If separated, the cationic data alone give an average of about 1.43 ±

0.1 Å., and the anionic, 1.33 ± 0.05 Å. (taking approximate limits). While the small difference apparently lends support to the use of r_c values in assessing ion–water distances (compression or dilatation of the *ions*, on solution, being invoked to account for the changes from the r_{exp} values established for the anhydrous MX lattices (11)), identification of the geometric with the X-ray center of H_2O is implicit here, and the coincidence of both with the multipole origin was assumed in calculations (92). These assumptions seem to be no better founded than the simpler one of Blandamer and Symons, that the r_{exp} values apply to both lattice and solution (24).

3. Accommodation of Ions in Water

a. Void about Ions

Three types of void space need be considered in connection with the immersion of spherical particles having physical radii r. (We exclude here the effects of charge and mismatching of volumes, *i.e.*, of electrostriction and structural alterations which clearly require separate consideration.) Firstly, the increase in liquid volume Δv, because of the granular nature of the mixing, will be $> \frac{4}{3}\pi r^3$ (17); for insertion into a cubic lattice site, $\Delta v/(\frac{4}{3}\pi r^3) = 1.91$, into a random close-packed structure, 1.72, and into a closest-packed structure, 1.35 (177; *cf.* 48, 97, 153), all three factors applying to the assumed case $r = r_w$. Because the packing of water about ions is not known, the relevant factor cannot be exactly specified. Secondly, owing to the granular nature of the dielectric, a change (increase (81)) in the proportion of void in the dielectric immediately about ions relative to that in the bulk dielectric might be expected. This "dielectric void" is by no means necessarily identical with the "geometric" void, $\Delta v - \frac{4}{3}\pi r^3$, identification of geometric with dielectric void implying a particular definition of the dielectric (*cf.* (81) and (210) with (155) and (193)). Thirdly, the kinetic motion of an ion (presumably predominantly vibrational against surrounding water molecules (170) with, as well, the translational facility of changing sites in the solution) may be represented as translation in a free volume (66, 129, 170) which again would be related only loosely to the previous two volume factors (but *cf.* (118)).

b. Formation of Holes

Some authors contend that the insertion of an ion into water requires work to be done in making a cavity for it. Thus, Noyes (155, 157) considers, and rejects, taking the energy of hydration of isoelectronic noble gases as representing part of this work, favoring instead (157) (as do Mikhailov and Drakin (149), section VA) an energy for the creation of a spherical surface in the water. van Eck (62) took an enthalpy 15

± 5 kcal./g.-ion for the work, and Buckingham, ∼10 kcal., the latent heat (36).

IV. APPLICATION OF THEORIES

A. BORN CHARGING

Laidler and Pegis (131), noting that it is impossible to reconcile both Eq. 7 and 9 with experimental data by adding a constant term a to all r_c in these expressions (a practice which succeeds for $\Delta F_h(M^{z+})$ only—see Table VI), calculate $\Delta F_h''$ and $\Delta S_h''$ with a theory taking account of dielectric saturation. Several theories exist for the variation of water permittivity with distance x from the ion center (35, 81, 130, 149, 162, 176, 185). All give sigmoid variations resembling the examples in Figure 3 for Laidler's (130, *cf.* 162) and Mikhailov and Drakin's (149) theories. (Webb's older calculations (210) based on the Debye internal field (52) indicated dielectric saturation to extend much further out from the ion.) For complete saturation, minimum possible values ϵ_{min}'' of the permittivity at an ion, which have been assumed or calculated, are 4 to 5.69 (176), 2.89 (149), and 1.78 (81, 130, 131). Padova (162) identifies three realms with the structural shells to be considered in section IVC, the ϵ_{min}'' range corresponding with the hydration shell A, the $\epsilon_{min}'' < \epsilon'' < \epsilon$ range with the intermediate B shell, the ϵ range representing bulk water.

Laidler and Pegis proceeded from an adaptation (86, 87) of Booth's theory (26)

$$\epsilon_x'' = \frac{\partial D}{\partial E} = \frac{\epsilon - n_{ref}^2}{1 + bE^2} + n_{ref}^2$$

where $b = 1.08 \times 10^{-8}$ (e.s.u.)$^{-2}$ from experiment (140, 141) and theory (26); E = field at x. Integrating, D, the electric displacement at distance x from ion during charging, is obtained as

$$D = n_{ref}^2 E - \frac{\epsilon - n_{ref}^2}{b^{1/2}} \tan^{-1}(b^{1/2}E) = \lambda e/x^2$$

where λ increases from 0 to z during charging. This relationship between E and λ is used in the following. The potential at x due to the charge on the ion during charging is

$$\psi = \int_\infty^x E dx \qquad \text{(Eq. 10)}$$

The work of charging the ion in solution is given by

$$\Delta F_{BCaq}'' = \int_0^z \psi d(\lambda e) = e \int_0^z \psi d\lambda \quad \text{(Eq. 11)}$$

the limit for x in ψ, Eq. 10, being r_{aq}. The electrostatic hydration free energy is then $\Delta F_{BCh}'' = \Delta F_{BCaq}'' - z^2e^2/2r_g$. Numerous parameters were invoked to represent the effect of temperature on the high-field permittivity in calculating ΔS_h (131).[2]

Since $^4/_3\pi(1.25r_c)^3$ arises as a term contributing to V (48), Laidler and Pegis put $r_{aq} = 1.25r_c$, and justified their assumption that $r_g = 1.25r_c$ on quasi-theoretical grounds ($cf.$ sections IIIB3a and IIIB2a). The best-fitting value of $\Delta F_h(H^+)$ was numerically large (section IVE, Table IX), being determined from predominantly cationic data by the choice of radii.

The view (131) that r_{aq}, if different from r_c, is not necessarily equal to r_g, while incontestable, still allows the insertion of $r_c + a$ in Eq. 7, since, if a represents dielectric void (section IIIB3a), the passage of charge elements through a involves the same amount of work in both gas and solution processes, Eq. 5 and 6. Thus Glueckauf (81a), also using Booth's theory for ϵ'', obtained a fit with experimental data for both ΔH_h (of M^{2+} and I^-) and, less well, ΔS_h (of M^+ and M^{2+}), using $a \approx 0.6$ Å. ΔS_h deviations were attributed to the vibrational, librational, etc., motions of hydrational water (section IVD), but of course these are the very factors governing ϵ'' and $\partial\epsilon''/\partial T$. The a value represents void additional to the already large fraction in the bulk dielectric and may be compared with other values obtained from alternative assumptions (Table VI). Assuming a continuous dielectric, Glueckauf (81c) showed that calculated ϵ'' values were closely consistent, except for Li^+ and I^-, with experimental permittivities of M^+, X^- solutions from microwave measurements ((96) section IIIB1). From a molecular model employing the a values of Table VI and $r_w = 1.55$ Å., together with suitable assumptions concerning the disposition of first- and second-shell water, substitution of ϵ_x'' in a dielectric mixture formula reproduced all the observed permittivities. ϵ_x'', from the continuum calculation for distance x, was here attributed to the whole volume of the H_2O molecule with center at distance x from the ion.

Neglected electrostrictive pressure has an incremental effect on ϵ'' (185). Apart from Glueckauf's molecular adaptation, the calculated ϵ'' values refer to a macroscopic continuous dielectric (185); only small deviations from ϵ are usually predicted to occur beyond

Table VI

a Values Required for Fit of Experimental ΔF_h to
Born-Charging Equations with Various Assumptions
Concerning Permittivity

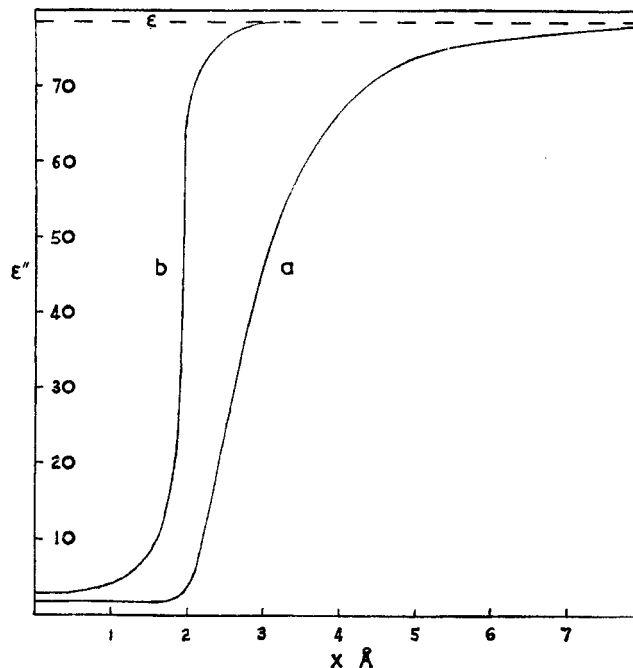| Author	Ions	Permittivity	a, Å.
Webb (210)	M^+	ϵ'' from Webb's theory	0.55–0.50
	X^-	(210) with experimental V	0.44–0.39
Voet (205a)	M^{2+}	ϵ	0.65
Latimer, Pitzer, and	M^+	ϵ	0.85
Slansky (136)	X^-	ϵ	0.1
Laidler and Pegis (131)	All ions	ϵ'' from Booth's theory (26)	$0.25r_c$
Noyes (155)	M^+	ϵ	0.74–0.69
	M^{2+}	ϵ	0.79–0.74
	M^{3+}	ϵ	0.84–0.79
	X^-	ϵ	0.56–0.34
Glueckauf (81a,c)	M^{2+}	ϵ'' from Booth's theory	0.64
	F^-, Cl^-	(26)	0.35
	I^-		0.56

Figure 3.—Variation of permittivity with distance x from univalent ion, for (a) Laidler (130), Grahame (86, 87), Booth (26); (b) Mikhailov and Drakin (149), Anselm (5). For other valencies, abscissa is multiplied by $z^{1/2}$ (81c, 149).

the first shell. Such theories have also been applied to the electron-transfer mechanism (130), ion association (179), V values (46c, 162, 210), activity coefficients (81b), and the salting-out of neutral solutes (47).

Stokes obtained good agreement with experimental ΔF_h values using a modified form of Eq. 7, with $r_g = r_{qt}$ and $r_{aq} = r_c$ (Table V). The value 9.0 was taken for the ϵ'' corresponding to nonrotating bound water, assumed to form one molecular shell about M^+ and Ba^{2+}, two shells about other M^{2+} and M^{3+}, and none about X^-. Experimental support was claimed, for the permittivity assumption for X^-, from the in fact arbitrary model (91) affording n_h'' values (section IIIB1), and in addition the value 9.0 for ϵ'' differs seriously from the 5.5 assumed in the latter.

van Eck's definition of r_{qt} (section IIIB2b) gives for M^{2+}, $\Delta H_{BCh} = -(\Sigma I)(1 - \epsilon^{-1} - \epsilon^{-1}\partial \ln \epsilon/\partial T)$, and he suggested the relationship, from an apparently linear plot of observed values, $\Delta H_h(M^{2+}) + 15 = -(\Sigma I)$, hole formation accounting for the 15 kcal.

Noyes (155, 157) obtained heuristic effective permittivities ϵ_{eff} (Table VII) by substitution of experimental ΔF_h and r_c values directly into Eq. 7, ϵ_{eff} being the parameters to be determined from the equation. The nonelectrostatic part of ΔF_h was taken equal to a value $P\Delta v - T\Delta S$ for (an actually unrealizable) gas compression, at 1 atm. constant pressure, from the gas-phase standard-state volume per mole, 24.47 l., to the solution phase volume of 1 l. (compare the nonisobaric value, $\Delta F = -T\Delta S$, favored in ref. 149), with

an additional small term for cavity surface formation. Corrected ΔS_h values inserted into Eq. 9 yielded $\partial \ln \epsilon_{\text{eff}}/\partial \ln T$ values, but these (as ϵ_{eff}, to a much smaller extent) are critically dependent on Noyes' assumptions concerning ionic translation in solution (157) (section IVD).

<div style="text-align:center">TABLE VII</div>

ϵ_{eff} VALUES BASED ON PAULING r_c RADII (155, 157) (IN GROUPS)

Li$^+$–Cs$^+$	1.79	2.32	2.98	3.33	3.72
Be^{2+}–Ra^{2+}	1.37	1.80	2.31	2.38	2.80 2.86
Al^{3+}, Sc^{3+}, Y^{3+}, La^{3+}	1.58	2.04	2.15	2.50	
F$^-$–I$^-$		10.0	12.4	13.3	15.3

The smallness of the ϵ_{eff} values was attributed to dielectric saturation. Some high ϵ_{eff} values, such as that obtained for Ag$^+$, 7.61, were attributed to specific bonding of H_2O. Three cases of high ϵ_{eff} should thus arise: (i) where minimal H_2O orientation occurs because the field at the (necessarily large) ion is weak, (ii) where quantum mechanical interaction leads to strong bonding, or (iii) where the allowed packing of water about the ion (section IVC) facilitates a stronger electrostatic interaction of a point-charge center in the H_2O with the ionic charge. Explanation (iii) was invoked (155) to explain the higher range derived for $\epsilon_{\text{eff}}(X^-)$, Table VII; clearly, a closer equivalence of values for M$^+$ and X$^-$ would be obtained by the use of r_{exp} in Noyes' procedure.

In summary, the additive a term introduced by Latimer is *not* due to dielectric saturation alone as far as can be judged from modern, but still essentially macroscopic, dielectric saturation theories exemplified by Glueckauf's work. Its neglect in Noyes' approach results in low ϵ_{eff} values. The dielectric void explanation may be obviated by the invocation of r_{qt} values (those considered above being $> r_c$ or r_{exp}) which cannot be lightly dismissed, since, e.g., the negative charge removed from a real atom to form a cation is at least in part distributed beyond the crystal radius. Thus, for Born charging as applied to real ions

$$\Delta F_{\text{BCh}}'' = -\frac{z^2 e^2}{2(r_e + a)} + \frac{z^2 e^2}{2(r_e + a)f(\epsilon'')} \quad \text{(Eq. 7a)}$$

where r_e represents the radial distance at which the ionic charge effectively resides, a represents any dielectric void, and $f(\epsilon'')$ is that function of ϵ'' at present calculated by the Laidler–Glueckauf method or estimated in molecular terms as by Stokes. Despite the present theoretical inseparability of the r_e and a values, Eq. 7a does embody for the first time all the modifications to the macroscopic law hitherto suggested.

B. MOLECULAR INTERACTIONS

The comprehensive irreducible interactions treatment of Stecki (191), lacking the requisite hydration parameters, has been applied only to the case of a hard

spherical ion in a nonpolar hard-sphere solvent. While some terms in the complete expression can be grouped together to give a single term, $(z^2 e^2/2)(r_{\text{ion}} + r_{\text{solvent}}) \cdot (1 - \epsilon_{\text{solv}}^{-1})$, which clearly has affinities with Eq. 7, this does not seem to justify inserting $r_c + r_w$ into the Born expression for hydration; $r_{\text{ion}} + r_{\text{solv}}$ appears to be the smallest possible dimension allowed in the given formulation. Most formulations of the first approximation primary-shell treatments fundamentally follow those of Garrick (75, 76) and van Arkel and de Boer (6), with various choices of model (Table III).

For H_2O assumed to have permanent and induced dipoles μ and μ_i—the latter being calculable from the field at the water molecule—and ions with radii r_c (assumed by all authors in this section except Blandamer and Symons (24)), interaction with M^{s+} having normal dipole orientation of six coordinated water molecules is given by (10a)

$$\Delta U_{\text{pot}} = -6ze(\mu + \mu_i)/d^2 + $$
$$6(1.19)(\mu + \mu_i)^2/d^3 + 6\mu_i^2/2\alpha_p + 6B_{\text{rep}}/d^s \quad \text{(Eq. 12)}$$

for charge–dipole, dipole–dipole, μ_i formation, and electron-shell repulsion energies. 1.19 is a geometrical factor and B_{rep} is eliminated by differentiation for equilibrium separation d. Basolo and Pearson (10a) add further terms ΔU_{CF} for the crystal field stabilization of transition-metal ions and $\Delta H_{\text{BCh}}(\mathfrak{M}(OH_2)_6^{z+})$ for interaction with the remaining solvent; thus

$$\Delta H_h = \Delta U_{\text{pot}} - \Delta U_{\text{CF}} + \Delta H_{\text{BCh}}(\mathfrak{M}(OH_2)_6^{z+}) + 6\Delta H_{\text{vap}}(H_2O)$$

$6\Delta H_{\text{vap}}(H_2O)$ represents the energy of liberation of the six coordinated molecules from bulk water (76). (η however is obtained as ~6 from consideration of the concomitant perturbation by the crystal field of both r and U (105–107).)

For transition-metal ions, minima in plots of $\Delta H'_{h\,\text{con}}$ vs. Z_{nuc} are explained as being due to crystal field stabilization, $\Delta H'_{h\,\text{con}} + \Delta U_{\text{CF}}$ showing a monotonous correlation with Z_{nuc} for both $\mathfrak{M}^{2+}$ and $\mathfrak{M}^{3+}$ (10a, 51b, 77, 101, 161).

The oft-stated view that the positive protonic end of the water dipole can get closer to anions than the negative end can to cations (11, 95, 155) has been expressed in alternative form by Buckingham (36). The ionic-charge, water-quadrupole interaction, assuming normal dipole orientation, introduces terms $\pm n_h ze\mu/2d^3$ (+ for cations, − for anions), and additional terms in d^{-4} for water–water interactions. This leads to differences $\Delta H_h(M^+) - \Delta H_h(X^-)$, for M$^+$ and X$^-$ having the same r_c and $n_h = 4$, of

$$Q/d^3 + R/d^4 = 4\frac{e\Theta}{d^3} - \frac{135\sqrt{2}}{32\sqrt{3}}\frac{\mu\Theta}{d^4} \quad \text{(Eq. 13)}$$

and for $n_h = 6$

$$Q/d^3 + R/d^4 = 6\,\frac{e\Theta}{d^3} - \frac{9(6\sqrt{2}+11)}{8}\,\frac{\mu\Theta}{d^4}$$

Quantum mechanical calculation (59) gives $\Theta \approx 0.43 \times 10^{-26}$ e.s.u., but from ΔH_h for K^+ and F^- (of equal r_c), Buckingham derived a Θ about five times higher. Values so derived depend on the assumed n_h, the assumed dipole orientation, the use of r_c values, and (203) the choice of the center of H_2O as multipole origin. Using Buckingham's value of Θ, Vaslow (203) calculated that an angled dipole orientation was stablest for Li^+, but for Cs^+ a wide range of orientations were approximately isoenergetic (Table III). No equivalent calculations for anions were performed; these would be of interest.

In opposition to the view that cations and anions are subject to different interactions with H_2O, Blandamer and Symons (24), favoring r_{exp} values (section IIIB2c), point out that anion H-bonding has its analog for M^+ in cation, lone-pair interaction, thereby emphasizing "peripheral" water interactions rather than the central forces invoked in the preceding paragraphs (see also section IVF).

Such peripheral interactions are given more weight when the central multipoles of the water molecule are replaced, in calculation, by an internal point-charge distribution, as by Bernal and Fowler (18), Eley and Evans (66), and Verwey (205), whose calculations and models (Figure 2 and Table III) have been thoroughly discussed (46). While each proton was allocated a fractional positive charge, however, the negative constituent of the dipole was treated as a single point charge, close to or at the center of the H_2O molecule; separate foci of negative charge, for each lone pair, would correspond more closely with the symmetry of cation–OH_2 and anion–H_2O interactions suggested by Blandamer and Symons.

C. WATER STRUCTURE ABOUT IONS

In order to explain experimental quantities other than hydration energies (1, 18, 46, 70, 124), aquo-ions have been represented (70) as having about them first, a shell A of oriented H_2O, then a disordered shell B of water having fewer H bonds per molecule than bulk water, and then C, structurally normal water. Shell A is said to be obliterated by B for structure-breaking ions Cs^+ and I^- (70, 124) (and possibly for K^+, Rb^+, Cl^-, and Br^- as well (29, 30, 90)). If shell B is rendered insignificant by A, the ion is said to be structure-making (with the implication of ice structure) (124).

Calculations of the tendency of primary shell water to normal dipole or angled dipole orientation (203), and of second-shell water to orientation as in the bulk or as determined by the ionic field (8, 8a), have been made; earlier calculations are summarized in ref. 46. Interpretations of new experimental work (171) (freez-

ing effects (172), proton resonance (68, 95, 187, cf. 100), infrared (37, 38, 102) and Raman (40, 186, 208, 209) spectra) do not unequivocally resolve the much-debated question of orientation. Only for $EuCl_3$ (71) and $ErCl_3$ (31) solutions has it been possible to interpret X-ray data directly in terms of ice-like structure, but H bonding clearly occurs with X^- (186, 208, 209). For Li^+, normal dipole orientation and a large B shell is strongly favored in Vollmar's interpretation of NO_3^- (aq) Raman spectra (206).

Possibly too inflexible a picture of water structure is implied by the foregoing, since "it is difficult to pack units of tetrahedral symmetry in a three-dimensional lattice with any economy of space. Several solutions to the problem are almost equally good and no one is much better than any of the others" (124). In conformity with this view, a linear correlation has been found (32) between α, the relative compression or dilatation of the solvent about an ion, and β, the relative viscosity about the ion. α is deduced as $(V - 4\pi r_c^3/3)/1000$, and $\beta = B_{visc} - {}^3/_4\pi r_c^3/400$, B_{visc} being the viscosity B-coefficient (113). Negative α with positive β is taken to indicate a compressive ion (Na^+, M^{2+}, and La^{3+}); positive α with negative β, a dilative ion (K^+ and larger M^+, and X^-). Li^+ does not conform (α just negative, β large and positive), and data for F^-, and further M^{3+}, are lacking. Structure making and breaking is thus replaced by the concept of a smooth transition between compression and dilatation.

The following, based on some fresh considerations, appears to represent as close a reconciliation of views on first-shell orientation as the disparities will allow; several remain. Concerning its anomalous, large V (90c), "Li^+ is just structurally different from other ions" (17). Packing in crystalline group-O solids (49) shows that He is also different, its true sphericity with $1s^2$-shell outer electrons, allowing hexagonal close-packing; other noble gases have outer tetrahedral (sp^3) lobes, the interactions of which apparently induce cubic packing (49). If similar arguments may be applied to M^{z+}, Li^+ and Be^{2+} would be best suited, by their electronic sphericity, in being able to induce the most favorable water structure. Also, since small ions should "see," and interact accordingly with, the detailed charge distribution in H_2O, which must surely approximate to a point dipole only for larger ions, the angled dipole lone-pair orientation (Figure 2) seems probable about Li^+ and Be^{2+}. (Cf. fully developed σ-bonding in B^{III} as $B(OH)_3$, and a discussion of its structure (60).) A water molecule in the first shell is generally assumed to retain its tetrahedral electronic structure (100) (trigonal splitting of oxygen orbitals has, however, been suggested (111a)). Then the large V for Li^+ is attributable to tetrahedron building based on first-shell H_2O (78). With increase in ionic size, normal dipole orientation should set in, with small but

structurally important decreases in H-bond concentration, and for the largest ions, weak dipole orientation and volume mismatching should cause first-shell structure breaking. Structural effects of intraionic tetrahedral charge distributions might be superimposed by somewhat tenuous analogy with group-O solids. For F^- to I^-, conceptual separation of the bending of H bonds (which are presumably linear for F^-), the trend towards normal dipole orientation, and structure breaking, is difficult, but something like the sequence suggested for M^+ should hold. The observed correlations with r_{exp} could be construed as confirming this assumption (section IIIB2c).

While the models employed in deriving the n_h values in Table IV omit the effects of structure breaking, the lower (0 to 2) values particularly must represent a number of H_2O actually bound, diminished by the effects of structure breaking (i) among other, unbound, water molecules also occupying the primary shell, and (ii) in outer shells, but other effects undoubtedly contribute to an unknown extent. Association of large ions with $z = 1$ has been attributed to the consequent reduction of the structural disturbance (55). A kinetic approach to hydrational structure is favored by Samoilov (184).

D. ENTROPIES

In $S°_{con}(M^{z+}) = S°_{abs}(M^{z+}) - zS°_{abs}(H^+)$, and $S°_{con}(X^-) = S°_{abs}(X^-) + zS°_{abs}(H^+)$, the value of $S°_{abs}(H^+)$ appears to lie between -6 and -2 e.u. (46b, 84, 90a), from empirical correlations and thermal e.m.f. measurements. (Interpretations of the latter, however, conflict (32a, 46, 84).) These absolute entropies contain an entropy of mixing (the cratic entropy (90b)) which, if the solution were a lattice, would be given by R ln 55.5 (90b, cf. 66), 55.5 being the water molality in the conventional standard state. Then

$$S_{un} = S°_{abs}(M^{z+} \text{ or } X^{z-}) - R \text{ ln } 55.5$$

S_{un}, the unitary entropy (90b), is then independent of the choice of standard state. S_{un} may be construed as the sum of "translational" entropy S_{tr} for ionic motion in some free volume in solution (see section IIIB3a) and the dielectric entropy arising from the modification of the motions of solvent molecules by the field of the ion (155, 157).

Eley and Evans (66) performed exhaustive calculations of the dielectric entropy involving all the possible modes of motion of coordinated water; their choice of model (Table III) has however been contested (205) and some disagreement with newer experimental values noted (16). For the Sackur–Tetrode calculation of S_{tr} (cf. 46d for correction of a misprint) they took as model a particle, having the reduced mass of ion-plus-one-H_2O molecule, performing gas-like translation in a free volume of 0.04 cc./g.-ion. Laidler (129)

made a best-fit estimate of V_f (Eq. x, Table VIII) for translation of ion alone but later included it only as one contribution to an adjustable parameter (Laidler and Pegis (131), section IVA).

Various expressions and treatments of entropies are summarized in Table VIII. The bracketed term in (x) and (xii) represents the Sackur–Tetrode equation for ionic translation in the free volume V_f, which is formally expressed in (xii) as an undetermined parameter (cf. 170).

The alternative to splitting the nonelectrostatic entropy into configurational and free volume translational terms is to assume with Noyes (157) and Moelwyn-Hughes (151b) that the whole volume of solution (1 1.), per mole of ions, specified by the chosen standard state, is available for gas-like translation of the ion. (Noyes (155, 157) however made no allowance for a corresponding translational contribution to ΔF_h.) Krestov (127) attempted to separate the terms contributing to ΔS_h by assuming that the nonelectrostatic part may be represented by the value for hydration of isoelectronic noble gases (cf. section III-B3b and (124)).

E. THEORETICAL ESTIMATES OF $\Delta Y_h(H^+)$

From Eq. 3 and 4

$$\Delta Y_{h \text{ con}}(M^+) = \Delta Y_h(M^+) - \Delta Y_h(H^+)$$
$$\Delta Y_{h \text{ con}}(X^-) = \Delta Y_h(X^-) + \Delta Y_h(H^+)$$

With assumed corrections in ΔF_h (section IVA) for nonelectrostatic terms, Noyes (155) put, in these equations

$$\Delta F_h = -163.9/r_c + P/r_c^2$$

where the first term on the right is exactly the Born term, Eq. 7, and the second term is introduced to account for deviations; the constant, P, differs for anions and cations. Substitution of experimental $\Delta F_{h \text{ con}}$ values, for K^+ to Cs^+, and F^- to I^-, then gives seven equations for extrapolative least-squares evaluation of three unknowns, P(cations), P(anions), and $\Delta F_h(H^+)$. $\Delta Y'_h(H^+)$ values were in fact so evaluated, and some procedural amendments later introduced (157).

For hypothetical M^+ and X^- of identical r_c, if differences in ΔH_h are attributed to charge-quadrupole interactions (36, 92)

$$\Delta H_{h \text{ con}}(M^+) - \Delta H_{h \text{ con}}(X^-) =$$
$$-2\Delta H_h(H^+) + Q/d^3 + R/d^4 \quad \text{(Eq. 14)}$$

Values of $\Delta H_{h \text{ con}}(M^+) - \Delta H_{h \text{ con}}(X^-)$ for several choices of d were read off from the two-line plot, $\Delta H_{h \text{ con}}(M^+)$ vs. d^{-3} and $\Delta H_{h \text{ con}}(X^-)$ vs. d^{-3}, and used in Eq. 14a with the corresponding d values, to extrapolate to $d = \infty$ for $\Delta H_h(H^+)$ (92). Several assumptions for Q and R ($n_h = 4$, or $n_h = 6$, for hard ions (section IVB); $n_h = 6$, for soft ions) gave closely concordant values

TABLE VIII

TREATMENTS OF ENTROPIES

	Applicable to	Std. state in solution for $S°$	r, Å. (section IIIB2)	Other parameters	Authors
i. $\Delta S_h = -A/(r_c + a) + B$	M+, X-	1 m (1 M)ᵃ	Pauling r_c	$a = 0.85$ Å. for M+ and 0.1 Å. for X- / B differs for M+ and X-	Latimer, Pitzer, and Slansky (136)
ii. $\Delta S_h = -80z/r + B$	$M^{z+}, \mathfrak{M}^{z+}$	1 m (1 M)	$r = r_c + a$ as in i? (cf. viii)	B varies with z	Coulter and Latimer (47a)
iii. $S°_{con} = -Az/r_c + B$	$M^{z+}, \mathfrak{M}^{z+}$, and X-	1 m	Goldschmidt r_c	A and B vary with sign and size of charge	Kapustinskii (114, 115)
iv. $S°_{con} = -270z/(r_c + a)^2 + {}^{3}/_{2}R \ln M + 37$	$M^{z+}, \mathfrak{M}^{z+}$, and X^{z-}	1 m	Pauling r_o	$a = 2.00$ Å. for cations, 1.00 Å. for anions	Powell and Latimer (169)
v. $S°_{abs} = -A(z/r_c)^{1/2} + B$	$M^{z+}, \mathfrak{M}^{z+}$, and X^{z-}	1 m	Thermochemical and Goldschmidt r_c	Different A, B, for anions and cations	Kapustinskii, Drakin, and Yakuszewski (117)
vi. $S°_{abs} = -A(z/r_L)^{1/2} + B$	$M^{z+}, \mathfrak{M}^{z+}$, and X^{z-}	1 m	r_L	A, B constant for all ions	Kapustinskii, Drakin, and Yakuszewski (117)
vii. $S°_{con} = -154z/(r_c + a)^2 + 47$	$M^{z+}, \mathfrak{M}^{z+}$, and X^{z-}	1 m	Pauling r_o	$a = 1.3$ Å. for cations, 0.4 Å. for anions	Powell (170)
viii. $\Delta S_h = -Az/(r_c + a) + B$	Two lines necessary for all $M^{z+}, \mathfrak{M}^{z+}$, and X^{z-}	1/24.47 m (1/24.47 M)	Pauling r_c	Two sets of A, B; $a = 0.85$ Å. for cations and 0.1 Å. for anions	Latimer (134)
ix. $\Delta S_h = -45.0z/r_L + 11.5$	$M^{z+}, \mathfrak{M}^{z+}$	1 m (1 atm.)	r_L	Compare section VA	Drakin and Mikhailov (57)
x. $S°_{abs} - R \ln 55.5 = -11.6z^2/r + ({}^{3}/_{2}R \ln M + R \ln V_f + 2.9)$	$M^{z+}, \mathfrak{M}^{z+}$	1 m	Pauling covalent r	$V_f = 0.73$ cm.³/mole for all cations	Laidler (129)
xi. $S°_{abs} - R \ln 55.5 = f(1/r_{exp})$	M+, X-	1 m	r_{exp}	f is the same function for M+ and X-	Blandamer and Symons (24)
xii. $S°_{abs} - R \ln 55.5 - ({}^{3}/_{2}R \ln M + R \ln V_f + 2.9)$		1 m			
(a) $= (z^2 e^2/2r\epsilon)(\partial \ln \epsilon/\partial T)_p$ (i.e., $-9.65z^2/r$ e.u.)	Macrosphere		r of macrosphere in Å.	Macroscopic ϵ and T dependence	From Born (27) and section IIIA
(b) $= (z^2 e^2/2r_{eff})(\partial \ln \epsilon_{eff}/\partial T)_p$	$M^{z+}, \mathfrak{M}^{z+}$, and X^{z-}		General three-parameter expression in V_f, r, and ϵ_{eff}		Present review based on Noyes (157) and Laidler (129)

ᵃ In parentheses, standard state for gas.

$\Delta H_h = -260.7 \pm 2.5$ kcal., $\Theta = (1.4$ to $2.0) \times 10^{-26}$ e.s.u.

If n is the principal quantum number of the lowest vacant ionic orbital, the several values of the right of the equation ($n = 3, 4, 5, 6$)

$$\Delta F_h(Li^+) = \Delta F_{h\,con}(Li^+) + {}^{1}/_{2}\{\Delta F_{h\,con}(M^+)_n - \Delta F_{h\,con}(X^-)_n\}$$

obtained by taking isoelectronic pairs $(M^+)_n$, $(X^-)_n$, may be extrapolated against $1/n^2$ to $1/n^2 = 0$, to give $\Delta F_h(Li^+)$ (or, analogously, $\Delta F_h(H^+)$ or any $\Delta F_h(M^+)$ or $\Delta F_h(X^-)$) (108). With increasing n, radii of isoelectronic anions and cations should tend to equalize, and, if ΔF_h is only radius-dependent, an interesting alternative to inverse-radius extrapolations is obtained;

ΔY_h values obtained from both methods agree to within 1–2 kcal. (108). (Numerous extrapolations presented (108) are in fact all repetitions of the same calculation.) The line extrapolated is, however, a curve which is an unknown function of n.

Water molecules completely freed by structure breaking appear to be in the situation, which of course is an extreme exaggeration of what could exist about any real M+ or X-, for which a dielectric constant of 31 has been calculated (190); if this value conforms with a smooth incremental trend from ϵ_{min}'' to ϵ with increasing r, then extrapolations based on Born charging of $\Delta Y_{h\,con}(M^+, X^-)$ to $1/r = 0$, to obtain $\Delta Y_h(H^+)$, are justified; otherwise some uncertainty is introduced into $\Delta Y_h(H^+)$ by an extrapolation not to macroscopic

TABLE IX

ABSOLUTE VALUES FOR PROTONIC HYDRATION (FROM REF. 92 WITH ADDITIONS)

Authors	Ref.	Method	Parameters	Applied to	$-\Delta F_h(H^+)$
Fajans	92				262
Latimer	133	Experimental	(Volta potential)	Hg, Cl^-_{aq}; K^+	250
Klein and Lange	121, 122	Experimental	(Volta potential)	Hg, Cl^-_{aq}	...
Hush	104	Experimental	(Volta potential)	Hg, Cl^-_{aq}	259.5
Kviat and Miscenko (cf. 117)	128	Experimental	(Volta potential)	Hg, Cl^-_{aq}	259.6
Randles (cf. 20, 109)	174	Experimental	(Volta potential)	Hg, Cl^-_{aq}	260.5
Webb	210	Born charging	ϵ'', r_{aq} from V	Na^+, K^+	261.5ᵃ
Latimer, Pitzer, and Slansky	136	Born charging	ϵ, $(r_c + a)$ (Table VI)	Cs^+, I^-	259
Verwey	92, 204	$1/r_c$ extrapolation		M^+, X^-	250
Kortum and Bockris (cf. 193)	126	$\Delta F_h(K^+) = \Delta F_h(F^-)$			262.2
Laidler and Pegis	131	Born charging	ϵ'', $1.25r_c$	M^{z+}, $\mathfrak{m}^{z+}$, X^{z-}	292
van Eck	62	Born charging	ϵ, r_{qt}	M^{z+}, $\mathfrak{m}^{z+}$, X^{z-}	274
Noyes	155	Born charging + empirical r_c^{-2} term	ϵ, r_c	M^+, X^-	257.7
Noyes	157	Born charging + empirical r_c^{-2} term	ϵ, r_c	M^+, X^-	258.7
Ismailov	108	Empirical extrapolation	$1/r_c$ of isoelectronic M^+, X^-	M^+, X^-	258.0
Ismailov	108	Empirical extrapolation	$1/n^2$ of isoelectronic M^+, X^-	M^+, X^-	256.5
Blandamer and Symons	24	$\Delta F_h(Rb^+) = \Delta F_h(Cl^-)$	(Table I values)		260.7
Glueckauf	81a	Born charging	ϵ'', $(r_c + a)$ (Table VI)	M^{z+}	257
					$-\Delta H_h(H^+)$
Garrick	75, 76	ΔU calculation	μ, $r_c + r_w$, α_p	M^{z+}, X^{z-}	...ᵇ
van Arkel and de Boer	6	ΔU calculation	μ, $r_c + r_w$, α_p	M^{z+}, X^{z-}	260.6
Bernal and Fowler (cf. 12, 66)	18b, 92	ΔU calculation	μ, $r_c + r_w$, α_p	K^+, F^-	281
Verwey	92, 205	ΔU calculation	μ, $r_c + r_w$, α_p	M^+, X^-	258
Rice	175	$\Delta H_h(I^-) = \Delta F_{BCh}(I^-)$, Eq. 7			253
Miscenko (cf. 149)	150	$\Delta H_h(Cs^+) = \Delta H_h(I^-)$			264.5
Buckingham	36	ΔU calculation	μ, $r_c + r_w$, α_p, Θ		...
Moelwyn-Hughes	151a	$\Delta H_h(Na^+) = \Delta H_h(F^-)$			271
Azzam	8	ΔU calculation	μ, $r_c + r_w$, α_p		...
Grahn	88	Approximate quantum mechanical calculation			>305
Halliwell and Nyburg	92	ΔU calculation	μ, $r_c + r_w$, α_p, Θ	Ions with $z = 1$	260.7
Ismailov	108	Empirical extrapolation	$1/n^2$ of isoelectronic M^+, X^-		264.0
Glueckauf	81a	Born charging	ϵ'', $(r_c + a)$ (Table VI)	M^{z+}	273
Oshida and Horiguchi	92				267

ᵃ For this and succeeding values, ψ_{H_2O} assumed zero. ᵇ Where no $\Delta Y_h(H^+)$ is given, only a range of values is deducible.

conditions, but to those of increasingly disturbed water. Molecular interaction extrapolations similarly neglect effects of structure breaking, which Vaslow's calculations (section IVB) might be assumed to illustrate (203); his conclusions, applied to the extrapolation with Θ outlined above, would indicate that absolute energies for cations with smaller r_c were numerically somewhat underestimated.

However, the smallness of variations in energy due to structural differences about M^+ and X^- ions, in relation to the large total ΔF_h or ΔH_h values, must render such extrapolations comparatively insensitive to assumptions about hydrational structure, only extreme assumed differences in M^+-water and X^--water interactions (18, 66) causing large deviations from the experimental $\Delta Y_h(H^+)$ values.

F. NONAQUEOUS SOLVENTS

Ismailov (108) contends that the solvation energies with different solvents (Table X), obtained by the $1/n^2$ extrapolation of the previous section, are comparable in value because of similar donor–acceptor ion–solvent interactions. While advocates of Born charging might conceivably suggest interpretation in terms of ϵ'' for

TABLE X

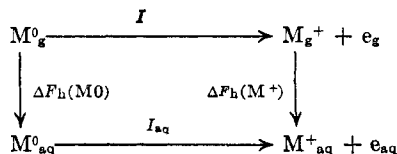NUMERICAL VALUES (108) FOR ABSOLUTE FREE ENERGIES OF SOLVATION (KCAL./G.-ION)

	H_2O	CH_3OH	C_2H_5OH	NH_3
H^+	256.4	252.2	251.6	278.0
Li^+	117.0	115.0	113.0	121.2
K^+	77.0	75.0	72.5	77.0
Cl^-	74.5	73.0	70.5	68.0

each solvent, the proposal that charge–dipole or charge–dielectric interactions are less important than the interaction of the ion with the peripheral charges of the solvating molecule merits note.

V. AQUEOUS IONIZATION ENERGIES

A. DIELECTRIC CONTINUUM MODEL

Commendable emphasis (149) is placed on I_{aq} in the cycle (138) shown here for a univalent cation

$$M^0_g \xrightarrow{\ \ I\ \ } M_g^+ + e_g$$

with $\Delta F_h(M0)$ and $\Delta F_h(M^+)$ on the left and right descending arrows, and

$$M^0_{aq} \xrightarrow{\ \ I_{aq}\ \ } M^+_{aq} + e_{aq}$$

Taking $\Delta F_h(M0)$ and $\Delta F_h(e) \approx 0$, Lee and Tai (138) calculated I_{aq} from a highly simplified model, assuming a Coulombic attractive energy for electron(s) and ion of $-(z)e^2/x\epsilon$, opposed at small separations by a repulsion term A/r^{η}. η are Born–Mayer lattice exponents ($\eta = 5$ to 12) (207). A was eliminated by reference to assumed equilibrium at an ion-electron separation $x = r_c$. Hence

$$I_{aq} = \frac{(z)e^2}{\epsilon r_c}\left(1 - \frac{1}{\eta}\right)$$

Mikhailov and Drakin's modification (149) was to take r_L instead of r_c (section IIIB2d), to calculate I_{aq} with allowance for dielectric saturation (5) about M^{z+} (Figure 3) (neglecting the superposition of the free-electron field) and to introduce a term for surface work in making an aqueous cavity, $\Delta U_{surf} = 4\pi r_L^2\sigma$. σ, the effective energy per unit surface area of water about the cavity, not being the ordinary macro value which includes orientational work already catered for in the dielectric-saturation calculation, was obtained from the approximate rule of Stefan (151c) that $\sigma \times$ (molecular surface area) for an individual solvent molecule is $^1/_2\Delta H_{vap}$. Hence $\Delta U_{surf} = 6.81r_L^2$ kcal./g.-ion (with r_L in Å.). In Table XI the calculated values of $\sum_1^z I_{aq}$

and ΔH_{surf} are compared with the corresponding experimental energies $\Delta F_{ai} = \Delta F_h + \sum^z I$, given by the authors (149). Quoted (149) percentage deviations in ΔF_h are flattering, large $\sum^z I$ values being added, in such an assessment, to both columns 4 and 5.[3] Much larger deviations between ΔF_{ai} and $\Sigma I_{aq} + \Delta U_{surf}$ (20–180 kcal., depending on z) are found for nearly all M^{z+} ions.

Differentiation (57) of the theoretical expression for ΔF_h allows calculation of theoretical ΔS_h values which can be represented by the ad hoc least-squares equation ($cf.$ Eq. ix, Table VIII)

$$\Delta S_h = 18.0 - 46.0z/r_L$$

ΔY_h values for unstable cations, e.g., Mg$^+$, Ca$^+$, and anions, have been similarly calculated (58). The problem of allocating r values for Born charging has

[3] In this connection, the significance of a linear correlation observed (119) between ΔH for (apparently) $M_g^{z+} + ze \rightarrow M_{metal}$, and $\Delta H_h(M^{z+})$, is obscured because both ΔH values consist largely of ΣI.

TABLE XI

CALCULATED AND EXPERIMENTAL AQUEOUS IONIZATION
FREE ENERGIES (KCAL./G.-ION) (149)

	$\sum^z I_{aq}$	ΔU_{surf}	Sum	Exptl. values, $\Delta F_h + \sum^z I$
Li$^+$	10.2	7.6	17.8	5.8
Na$^+$	6.0	10.8	16.8	23.4
K$^+$	2.2	17.0	19.2	22.6
Rb$^+$	1.9	21.4	23.3	24.6
Cs$^+$	1.5	25.4	26.9	25.0
Be^{2+}	173	3	176	(61.0)
Mg^{2+}	62	8	70	78
Ca^{2+}	37	12	49	47
Sr^{2+}	25	16	41	45
Ba^{2+}	19	20	39	43
Al^{3+}	236	5	241	146
Y^{3+}	102	12	114	66
La^{3+}	79	15	94	62

thus been obviated here by characterizing the electron "orbit" in solution by η and r_L, and the medium by ϵ'' and σ. In addition to the severe approximations made for ΣI_{aq}, an estimate (14) of $\Delta F_h(e)$ (section VI) gives -40 kcal. in contrast to the value zero assumed here. Frumkin considers the use of σ in more detail (74). Some analogy is discernible between the preceding theory, and that for electron-transfer reactions given in section VIIB, both purporting to calculate electron-removal energies in solution. Sacher and Laidler's (183) model, for the kinetic case, of electron tunneling between two ions, the height and shape of the barrier being determined by local permittivity and an approximate orbital energy of the electron, has in fact much in common with Mikhailov and Drakin's.

B. CORRELATION WITH IONIZATION POTENTIALS: TRANSITION-METAL IONS

The effect of ligands on electrode potentials (51a) has been discussed in an extensive review of the stabilization of oxidation states by complex formation (158) and analyzed in terms of the relative crystal field stabilizations in oxidant and reductant $\mathfrak{M}$ ions participating in half-reactions (10b).

George and McClure (77) have shown that for transition-metal ions, a plot of ionization potential I for $\mathfrak{M}^{2+}_g \rightarrow \mathfrak{M}^{3+}_g + e$ against Z_{nuc} almost superimposes on that of electrode potentials for

$$\mathfrak{M}^{2+}_{aq} \rightarrow \mathfrak{M}^{3+}_{aq} + e \qquad \text{(Eq. 15)}$$
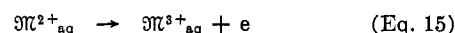
$vs.$ Z_{nuc}, if the E° values are corrected for individual crystal field stabilizations ΔU_{CF} ($cf.$ 217). In Figure 4, $-\mathfrak{F}E^\circ + \Delta U_{CF}(\mathfrak{M}^{3+}_{aq}) - \Delta U_{CF}(\mathfrak{M}^{2+}_{aq})$ is plotted against I, as an alternative presentation of the correlation. Entropy changes in the aqueous ionization were assumed constant for all pairs $\mathfrak{M}^{II}$, $\mathfrak{M}^{III}$ involved (77).

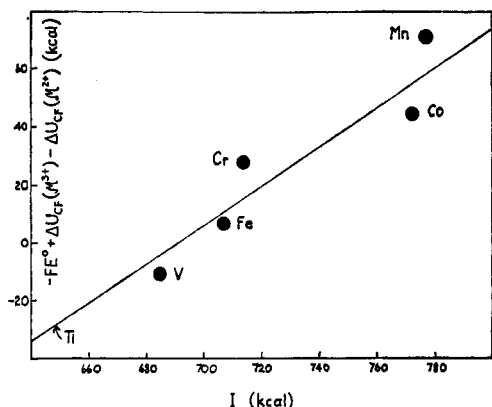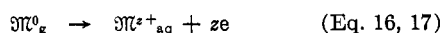Figure 4.—Crystal field corrected oxidation potential against gas phase ionization potential for $\mathfrak{M}^{II} \to \mathfrak{M}^{III} + e$, reaction 15a. Least-squares slope, $1/(1.5 \pm 0.3)$. Data from Tables XII and XIII.

Figure 5.—$\Delta H'_{ai} + \Delta U_{CF}$ against ΣI for (a) trivalent ions, reaction 17a (top and left-hand scales), slope $1/1.78$; (b) divalent ions, reaction 16a (bottom and right-hand scales), slope $1/2.11$. Data from Table XIII.

A similar correlation might be expected between ΣI for $\mathfrak{M}^0_g \to \mathfrak{M}^{z+}_g + ze$ and the energy for $\mathfrak{M}^0_{aq} \to \mathfrak{M}^{z+}_{aq} + ze$, or (if the energy for $\mathfrak{M}^0_g \to \mathfrak{M}^0_{aq}$) is approximately constant for all $\mathfrak{M}$), the energy for

$$\mathfrak{M}^0_g \to \mathfrak{M}^{z+}_{aq} + ze \qquad \text{(Eq. 16, 17)}$$

Experimental data are available only for reactions 16 and 17; the aqueous ionization enthalpies are given by

$$\Delta H'_{ai} = \Delta H'_{aq} - \Delta H_{sub} \quad \text{(for cations)}$$
$$\Delta H'_{ai} = -(\Delta H'_{aq} - \Delta H_{diss}) \quad \text{(for anions; following sections)}$$

For cations the variables involved are related to ΔH_h by $\Delta H_h \approx \Delta H'_{ai} - \overset{z}{\Sigma} I - z\Delta H'_h(H^+)$. Figure 5, from

the data in Tables XII and XIII, shows how far the above contention is supported.[4]

C. CORRELATION WITH CHARGE-TRANSFER SPECTRA

The extrapolated long wave length edge (extinction coefficient 0.1) of the assumed charge-transfer band, for

$$\mathfrak{M}^{II}OH_2 \overset{h\nu}{\to} \mathfrak{M}^{III}OH_2(e) \quad \text{or} \quad \mathfrak{M}^{III}(OH^-)H$$
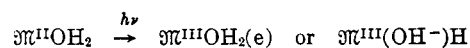
is proportional to $-\mathfrak{F}E^\circ$ for reaction 15, $\mathfrak{M}^{2+}_{aq} \to \mathfrak{M}^{3+}_{aq} + e$ (50, 160), as illustrated in Figure 6. The $h\nu$ coincides with absolute values for the aqueous ionization enthalpy of reaction 15 based on a reasonable assumed value of $\Delta H'_h(H^+)$ (50). This coincidence requires a cancellation of or correction for the opposing effects of Franck–Condon "strain" (112) and solvation (or protonation) of the ejected electron. ΔH for $\mathfrak{M}^{3+}_{aq} + OH^- \to \mathfrak{M}^{3+}OH^-$ (or for $\mathfrak{M}^{3+}_{aq} + e \to \mathfrak{M}^{3+}OH_2(e)$) is presumed approximately constant for all $\mathfrak{M}^{3+}$ involved (50).

TABLE XII
CRYSTAL FIELD STABILIZATIONS AND AQUEOUS IONIZATION
ENERGIES (IN KCAL./G.-ION)

$$\mathfrak{M}^{2+}_{aq} \to \mathfrak{M}^{3+}_{aq} + e \qquad \text{(Eq. 15)}$$
$$\mathfrak{M}^0_g(3d^n4s^2) \to \mathfrak{M}^{2+}_{aq}(3d^n) + 2e \qquad \text{(Eq. 16)}$$
$$\mathfrak{M}^0_g(3d^n4s^2) \to \mathfrak{M}^{3+}_{aq}(3d^{n-1}) + 3e \qquad \text{(Eq. 17)}$$

	ΔU_{CF}-$(\mathfrak{M}^{2+}_{aq})^a$	ΔU_{CF}-$(\mathfrak{M}^{3+}_{aq})^a$	$-\mathfrak{F}E^{\circ b}$ reaction 15	$\Delta H'_{ai}{}^c$ reaction 16	$\Delta H'_{ai}{}^c$ reaction 17
Ca	0	0	...	-172.0	...
Sc	0	0	...	...	-230.8
Ti	24.5	23.2	See section VI	See section VI	-205^d
V	40.8	35.7	-5.9	-177^d	-192^d
Cr	24.0	61.2	-9.5	-150^d	-178^d
Mn	0	36.0	34.8	-119.0	-94^d
Fe	11.4	0	17.7	-120.7^e	-111.2
Co	19.9	22.0	41.9	-115.2^e	$-81^{d,e}$
Ni	29.3	...	...	-114.2^e	...
Cu	22.2	...	...	-98.2^e	...
Zn	0	...	...	-67.6	...

[a] From spectroscopic data (152) except for Ti²⁺, calculated (77). [b] Ref. 135c. [c] All ΔH_{sub} from (198); $\Delta H'_{aq}$ from (154) except for d and e. [d] From $\Delta F'_{aq}$ from (135) (or (154), for Cr³⁺ and Cr²⁺), together with the assumption $S^\circ_{con}(\mathfrak{M}^{2+})$ and $S^\circ_{con}(\mathfrak{M}^{3+})$ constants (77). [e] $\Delta H'_{aq}(\mathfrak{M}^{2+})$ calculated as for Table I.
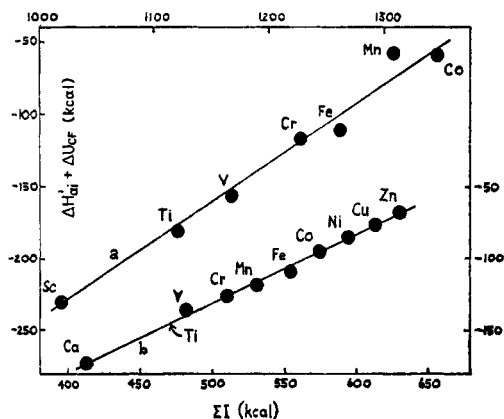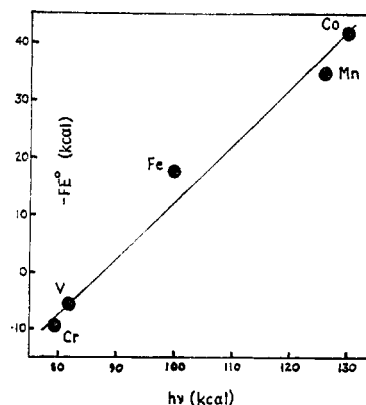

Figure 6.—$h\nu_{min}$ for long wave length edge of charge-transfer spectrum of $\mathfrak{M}^{2+}_{aq}$ against $-FE^\circ$, both in kcal./g.-ion. Data from Tables XII and XIV. Line drawn with unit sloe [at unit sfe per].

(4) Roman numerals in the tables refer to oxidation states, not to be confused (cf. 33) with spectroscopic states.

TABLE XIII[a]

CRYSTAL FIELD CORRECTED AQUEOUS IONIZATION ENERGIES AND GAS PHASE IONIZATION POTENTIALS (IN KCAL./G.-ION)

$$\mathfrak{M}^{II} \rightarrow \mathfrak{M}^{III} + e \qquad \text{(Eq. 15a)}$$

$$\mathfrak{M}^0(3d^n4s^2) \rightarrow \mathfrak{M}^{II}(3d^n) + 2e \qquad \text{(Eq. 16a)}$$

$$\mathfrak{M}^0(3d^n4s^2) \rightarrow \mathfrak{M}^{III}(3d^{n-1}) + 3e \qquad \text{(Eq. 17a)}$$

| | Reaction 15a | | Reaction 16a | | Reaction 17a | |
	I	$-\mathfrak{F}E^\circ + \Delta U_{CF}(\mathfrak{M}^{3+})$ $- \Delta U_{CF}(\mathfrak{M}^{2+})$	ΣI	$\Delta H'_{ai} + \Delta U_{CF}(\mathfrak{M}^{2+}{}_{aq})$	ΣI	$\Delta H'_{ai} + \Delta U_{CF}(\mathfrak{M}^{3+}{}_{aq})$
Ca			414.4	−172.0		...
Sc			...	...	1019.0	−230.8
Ti	648.7	?	471.7	?	1120.4	−181
V	684.8	−11.0	482.7	−136	1167.5	−156
Cr	713.5	27.7	511.0	−126	1227.5	−117
Mn	776.7	70.8	531.9	−119.0	1308.6	−58
Fe	706.4	6.3	555.1	−109.3	1261.5	−111.2
Co	772.1	44.0	574.3	−95.3	1346.4	−59
Ni			594.4	−84.9		
Cu			613.8	−76		
Zn			630.5	−67.6		

[a] Ionization potentials I from ref. 152; other values from Table XII.

TABLE XIV

ENERGIES FROM CHARGE-TRANSFER SPECTRA OF $\mathfrak{M}^{2+}{}_{aq}$,
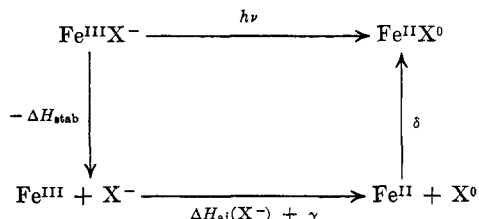$FeX^{2+}{}_{aq}$, AND $X^-{}_{aq}$ (IN KCAL./G.-ION)

	$h\nu$ (min.)		ΔH_{stab}	$h\nu$ (max.)
V^{2+}	82	FeF^{2+}	7.5	120
Cr^{2+}	79.5	$FeCl^{2+}$	8.5	91.5
Mn^{2+}	126	$FeBr^{2+}$	6.1	76
Fe^{2+}	100	Cl^-	...	158
Co^{2+}	130	Br^-	...	143
Ni^{2+}	136	I^-	...	126
(Ref. 50)		(FeX²⁺ data: ref. 112)		
		(X⁻ data: ref. 72)		

Values of $h\nu$ for the absorption maximum in the process

$$Fe^{III}X^-{}_{aq} \xrightarrow{h\nu} Fe^{II}X^0{}_{aq}$$
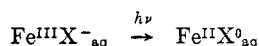
where X = F, Cl, Br, have been suggested (112) as a basis for estimating the electron affinity $\mathcal{E}$ (F) of fluorine; the calculation, however, was a circular one, requiring as a known term a value of ΔH_h (F⁻) for which a choice of electron affinity had already been made. The factors involved are properly related by the cycle (cf. 72) (all steps referring to aqueous solution)

$$Fe^{III}X^- \xrightarrow{h\nu} Fe^{II}X^0$$

(cycle diagram)

$-\Delta H_{stab}$ ... δ

$$Fe^{III} + X^- \xrightarrow[\Delta H_{ai}(X^-) + \gamma]{} Fe^{II} + X^0$$

where γ and δ are assumed constant for all X. Both contain the Franck–Condon energy term (112), γ comprising, as well, ΔH for $X^0{}_g \rightarrow X^0{}_{aq}$, and $-\Delta H$ for $Fe^{2+}{}_{aq} \rightarrow Fe^{3+}{}_{aq} + e$. A plot of $h\nu$ vs. $(\Delta H'_{ai}(X^-) - \Delta H_{stab})$ is presented in Figure 7, together with a plot of $h\nu$ vs. $\Delta H'_{ai}(X^-)$ for the photoionization $X_{aq}^- \xrightarrow{h\nu} X_{aq} + e$. Both lines have slopes close to unity. Many
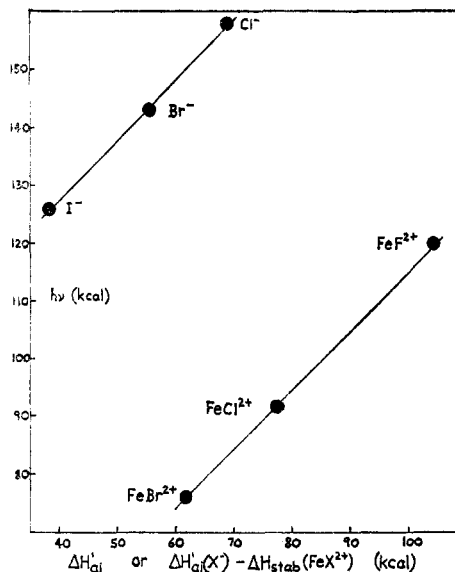

Figure 7.—(a) $h\nu_{max}$, for charge-transfer spectrum of FeX^{2+}, against $\Delta H_{ai}(X^-) - \Delta H_{stab}$; and (b) $h\nu_{max}$, for charge-transfer spectrum of $X^-{}_{aq}$, against $\Delta H_{ai}(X^-)$. Data from Tables XIV and XV; slope (a) 1.04; (b) 1.05.

photoionizations in solution (147) follow the approximate relationship $h\nu \approx I - \mathcal{E} + $ constant (I and $\mathcal{E}$ referring to species oxidized and reduced in the ionization, respectively), but the observed slopes $\partial(h\nu)/\partial I$, for say constant reductant, are in fact often <1 (147).

The relationships in sections VB and VC can be considered in the light of the simple qualitative ideas underlying Drakin and Mikhailov's model (section VA). Where the energy of a photoionization in solution (Figures 6 and 7) is compared with the corresponding thermal value, the observed unit slopes result from the approximately equal effects of the dielectric in both processes. On the other hand, the energies of gas phase
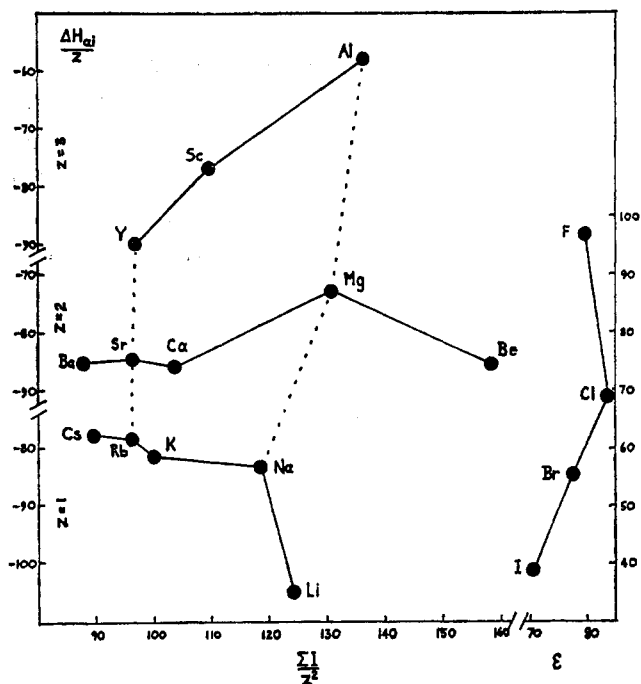
Figure 8.—$\Delta H'_{ai}/z$ against $\Sigma I/z^2$ for M, and $\Delta H'_{ai}$ against $\Sigma I/z^2$ for X$^-$ (right ordinate). Data from Table XV (division by z and z^2 for scaling purposes only). Dotted lines link some iso-electronic ions.
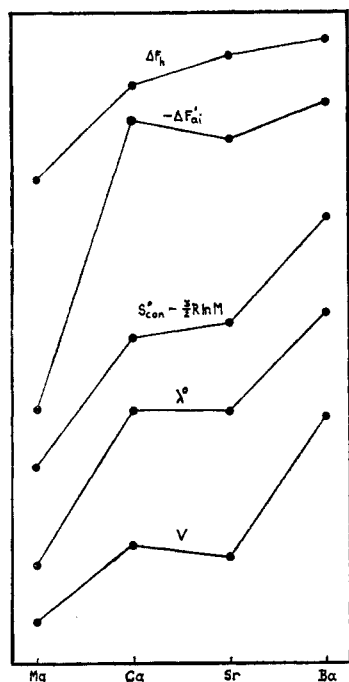

Figure 9.—Properties of M$^{2+}_{aq}$. Values for Mg^{2+} and Ba^{2+}, respectively, are as follows: ΔF_h, -455.5 and -315.1 kcal./g.-ion (Table I); $\Delta F'_{ai}$, -136.3 and -168.2 kcal./g.-ion (154, 198); $S°_{con} - {}^3/_2 R$ ln M, -37.7 and -11.7 e.u. (154); $\lambda°$, 53.06 and 63.6 conductance units (178d); V, -20.3 and -11.7 cc./g.-ion (48).

ionizations are reduced, in the presence of the dielectric, by a constant factor evinced by the slopes of Figures 4 and 5. This latter result is found presum-

ably because the constitution of the dielectric, determined by the orientation of the hydration molecules, remains effectively constant throughout each series considered.

D. RELATIONSHIP WITH IONIZATION POTENTIALS: NOBLE GAS-LIKE IONS

Plots of $\Delta H'_{ai}$ vs. ΣI or ε (Figure 8) for M^{z+} and X$^-$ do not show the simple relationships found for $\mathfrak{M}^{z+}$ except in the case of M^{3+}, for which presumably the high charge ensures a radius-independent constancy of dipole orientation and thus of dielectric constitution. The variations of $\Delta H'_{ai}$ for the other ions in Figure 8 are, at least for M^{2+}, of real significance, since several properties of M^{2+} are shown, in Figure 9, to follow the sequence of $-\Delta F'_{ai}$ (or $-\Delta H'_{ai}$), but not of ΔF_h, ΔH_h, or $1/r_c$. Deviations from linearity in Figure 8 should be at least partially a consequence of the structural disturbances of the dielectric summarized in section IVC, though the effects of differences in the internal electronic structures of the ions (e.g., Sr^{2+} has a filled d shell, Ca has not), may to some extent be superimposed.

TABLE XV

AQUEOUS IONIZATION ENTHALPIES AND GAS PHASE IONIZATION POTENTIALS FOR M AND X$^-$ (IN KCAL./G.-ION)

M^{z+}	ΣI^a	$\Delta H'_{ai}{}^b$	M^{z+}	$\Sigma I^{a\ c}$	$\Delta H'_{ai}{}^{b,c}$
Li$^+$	124.2	-105.0	Al^{3+}	1228	-202.9
Na$^+$	118.5	-83.2	Sc^{3+}	(989)	(-260.8)
K$^+$	100.0	-81.5	Y^{3+}	871	-300.0
Rb$^+$	96.3	-78.5			
Cs$^+$	89.75	-77.9			
			X$^-$	ε^d	$\Delta H'_{ai}{}^b$
Be^{2+}	634	-170.9	F$^-$	79.5	97.0
Mg^{2+}	522.8	-146.0	Cl$^-$	83.3	69.0
Ca^{2+}	414.4	-172.0	Br$^-$	77.5	55.6
Sr^{2+}	385.4	-169.5	I$^-$	70.6	38.85
Ba^{2+}	350.7	-170.4			

^{a} Ref. 152. ^{b} $\Delta H'_{aq}$ from ref. 154; ΔH_{sub} or ΔH_{diss} from ref. 198. ^{c} For reactions M$^0(n - 1)$p$^6 n$s$^2 n$p$^1 \rightarrow$ M$^{III}(n - 1)$p^6 + 3e; excitation energy for Sc^0 from Y^0 value (152) (other terms corresponding closely). ^{d} Ref. 19.

Considering only dielectric effects, in Figure 8, Be$^{2+}_{aq}$ and Li$^+_{aq}$ probably receive excessive stabilization from the H$_2$O lone-pair interaction, and Mg^{2+} and Ca^{2+}, from the positive slope between the points, appear to have similar dielectric environments, possibly with normal dipole orientation. The $z = 2$ sequence is reflected in a very distorted manner by that for $z = 1$, and Na$^+_{aq}$ may well have a similar H$_2$O orientation (section IVC); from the absence of any positive slope in the $z = 1$ sequence, no two successive M$^+$ ions appear to have the same dielectric environment. Structure breaking from Ca^{2+} to Ba^{2+}, and Na$^+$ to Cs$^+$, resulting in diminished charge compensation by the dielectric (18b), could then be responsible for the erratic sequences and negative slopes observed; the $\mathfrak{M}^{II}$

ions in Figure 5 have radii which, from this analysis, do not induce structure breaking. The slope ~2.4 for the X⁻ ions (excepting F⁻, where the deviation could arise from excessively strong H bonding—*cf.* Li⁺ above) is explicable if structure breaking increases or H bonding weakens from Cl⁻ to I⁻, in the reaction $X^-_{aq} \rightarrow X^0_g + e$.

TABLE XVI

AQUEOUS IONIZATION ENTHALPIES AND GAS PHASE IONIZATION POTENTIALS FOR GROUND-STATE $\mathfrak{M}$ AND X^{2-} (IN KCAL./G.-ION)

	ΣI^a	$\Delta H'_{ai}{}^b$		ΣI^a	$\Delta H'_{ai}{}^b$
Ga³⁺	1319	−115.4	Tl⁺	140.8	−41.6
In³⁺	1214	−80.7	Sn²⁺	506.3	−74.4ᶜ
Tl³⁺	1299	3.8ᶜ	Pb²⁺	517.2	−46.4
Cd²⁺	597	−44.0	La³⁺	834.2	−275.8
Hg²⁺	672.8	26.9ᶜ	Gd³⁺		−168.8
Cu⁺	177.9	(−68.7)		$\mathcal{E}^d$	$\Delta H'_{ai}$
Ag⁺	174.5	−43.1	S²⁻	−93	(48.2)ᶜ
Au⁺	212.4	(−46)ᶜ	Se²⁻	−101	(19.1)ᶜ

ᵃ Ref. 152. ᵇ All ΔH_{sub} or ΔH_{diss} from ref. 198; $\Delta H'_{aq}$ from ref. 154 except for c. ᶜ $\Delta H'_{aq}$ from ref. 135. ᵈ Ref. 13.

This brief examination is obviously incomplete, particularly for the M²⁺ ions, and is inapplicable to the more complex sequences in Table XVI. However, as Jørgensen emphasizes (111), ΔH_{ai} values deserve more consideration as measures of the strength of ion–water interactions than has hitherto been given.

VI. OXIDATION POTENTIALS FOR UNSTABLE SPECIES

From the correlations in Figures 4 and 5, free energies and electrode potentials may be estimated for Ti²⁺. The conformity of the Ti³⁺ point with the $\mathfrak{M}^{3+}$ line supports Latimer's (135b) assumptions in deriving $\Delta F'_{aq}(Ti^{3+})$, and the $\mathfrak{M}^{2+}$ line (Figure 5) gives a $\Delta F'_{aq}(Ti^{2+})$ corresponding to $E^° = 1.15$ v. for $Ti_{metal} \rightarrow Ti^{2+} + 2e$ (*cf.* 1.63 v. (135b)). The value of $E^°$ for $Ti^{2+}_{aq} \rightarrow Ti^{3+}_{aq} + e$, on which Latimer's (135b) $\Delta F'_{aq}(Ti^{2+})$ depends, was first erroneously (159) estimated as 0.37 v. (69), but a newer assessment (159) of 2 v. was obtained by adding to the Ti(II, III) electrode potential in acetonitrile the difference between the Cr(II, III) electrode potentials in acetonitrile and water (125), without regard for ΔU_{CF} differences in the two solvents. George and McClure (77) suggested 2.3 v., from their superimposition plot (section VB). Our $\Delta F'_{aq}(Ti^{2+})$ together with Latimer's $\Delta F'_{aq}(Ti^{3+})$ gives 1.32 v. A quite independent calculation, from extrapolation to the Ti²⁺, Ti³⁺ ionization potential, of the least-squares line in Figure 4, gives 1.18 v. The weighted mean of the last two values, 1.29 ± 0.15 v., may now be proposed as the best assessment.

Care is needed in such procedures, since, from $h\nu_{min}$ for Ni²⁺_{aq} obtained as for Figure 6, Dainton and James (50) estimated $E^°$ for Ni²⁺ → Ni³⁺ + e as −2.2

v., while George and McClure predicted ~ −5.5 v. for this half-reaction, and ~ −4.7 v. for Cu²⁺ → Cu³⁺ + e (77). From chemical evidence, Latimer (135c) estimated the latter value as being more negative than −1.8 v., but, as there is also kinetic evidence for the existence of Cu^{III}_{aq} (9), it is most unlikely to be more than ~1 v. more negative. These discrepancies arise because in superimposing gas phase I values on (crystal field corrected) $E^°$ values (section VB), George and McClure imply a slope of unity for Figure 4 which is clearly too high; their values then effectively consist of extrapolations of Figure 4 values using this choice of slope. The smaller values above are thus preferable.

Oxidation potentials for other unstable ions, obtained from consideration of electron-transfer mechanisms, are given in Table XVII. The approximate (41) value listed for e_{aq} requires the assumption (14) that ΔF for $H_{aq} \rightarrow 1/2 H_{2(aq)}$ is equal to the value for the reaction in the gas phase. Potentials for the reaction $M^{(z-1)+}_{aq} \rightarrow M^{z+}_{aq} + e_{aq}$ are then 2.7 v. more negative than American oxidation potentials. $\Delta F_h(e)$ for hydration of the electron is derived as −40 kcal. (14).

TABLE XVII

$E^°$ VALUES FOR UNSTABLE KINETIC SPECIES IN ACID SOLUTION

Couple	$-E^°$, v.ᵃ	Reaction(s)	Ref.
Cr^V → Cr^{VI} + e	$\gtrsim 0.62$	Cr^{VI} + Fe^{II} and other Cr^{VI} oxidations	212
Cr^{III} → Cr^V + 2e	$\gtrsim 1.75$	Cr^{VI} + Fe^{II} and other Cr^{VI} oxidations	212
Cr^{IV} → Cr^{VI} + 2e	<1.3 or ≪1.3	Cr^{VI} + Fe^{II} and other Cr^{VI} oxidations	212
Cr^{III} → Cr^{IV} + e	~1.5	Cr^{VI} oxidations and As^V + Cr^{II}	5a, 212
Tl^{II} → Tl^{III} + e	1.00	Tl^I + Tl^{III}; elaborated	106d
Tl^I → Tl^{II} + e	1.50	Eq. 18, section VIIB	
Tl^{II} → Tl^{III} + e	<1.1	Pt catalysis of 2Fe^{II} + Tl^{III}	99; *cf.* 42
Tl^I → Tl^{II} + e	>1.4		
½H_{2(g)} → e_{aq} + H⁺_{aq}	2.7	e_{aq} + H₂O → H_{aq} + OH⁻_{aq}	14

ᵃ Tabulation of the negative of the oxidation potentials avoids ambiguity in the use of > and <.

VII. OXIDATION POTENTIALS AND KINETICS

A. DISPLACEMENT REACTIONS

Edward's use of $E^°$ for $R^- \rightarrow 1/2 R_2 + e$ (64), as a measure of the nucleophilicity of reagent R in ΔF^* correlations for displacement reactions at C, N, and O centers of various substrates, has been likened (211) to a scale of ionization potentials of free radicals. While in water, ΔH_{ai} more closely represents an aqueous ionization energy; justification for the use of Edwards' ($E^°$, pK_a) scale for rate correlations is found in the demonstration that, for X⁻, with $E^°$ as defined above

$$0.059 pK_a - E^° \approx (N_X - N_H)^2$$

N representing Pauling electronegativity (148, 166a). Further developments of Edwards' treatment (65, 103) are reviewed in (211) and (39), respectively.

B. ELECTRON-TRANSFER REACTIONS

ΔF^* for oxidations are closely related to electrode potentials of the reactants (50, 144) and, since calculations of ΔF^* represent a reasonably successful quantitative application of the theories of hydration considered in sections IV and VA, a concise presentation follows. Several reviews exist (93, 196, 199, 201).

The reaction of, e.g., $\dagger \mathfrak{M}^{2+} + \mathfrak{M}^{3+}$ ($\dagger$ representing isotopic labeling) may be broken down into steps: approach to within a few Ångstroms, $\mathfrak{M}-OH_2$ bond length adjustments to a value of d^* intermediate between d^{II} and d^{III} (being cheaper in energy than e-transfer between the ground-state configurations (183)), resonance of the transferring electron between reactant orbitals, and ionic separation with e transferred to the initially oxidant orbital (106b, 143). The associated energies are, respectively, $\Delta F_{app} = z^{II}z^{III}e^2/\epsilon x$, ΔF_{reorg} (calculable from Eq. 12, section IVB (183)), and ΔU_{res}.

The resonance has an oscillation period $\sim h/2\Delta U_{res}$ (94, 106c) and results in an average fraction λ of electronic charge being associated with the oxidant for large enough values of ΔU_{res}. λ is known a posteriori to be $\sim^1/_2$, in the transition states of most one-electron transfer reactions (106e, 144, 145, 199b). The total activation free energy may then be written

$$\Delta F^* = \Delta F_{app} + \Delta F_{reorg} + \begin{Bmatrix} \Delta U_{res} \\ \Delta F_{diel} \\ \Delta F_{trans} \end{Bmatrix} \quad \text{(Eq. 18)}$$

In the following paragraph, a division into classes of mechanism emphasizes, for each class, only one of the terms in braces. $\Delta F_{trans} = -RT \ln \kappa$, and κ, the transmission coefficient, i.e., the probability of the transfer being completed when the ions are suitably juxtaposed, is given approximately by $\kappa = 1 - \exp[-4\pi^2\Delta U_{res}^2/hv\Delta s]$, v being the velocity of crossing, and Δs, the difference of the energy-profile slopes on either side of the potential barrier (221). ΔF_{diel} is still to be defined.

Since ΔU_{res} is not readily calculable (106b, 199a), assumptions concerning its value determine the assumed class, (i)– (iii), of mechanism. Thus, (i) $|\Delta U_{res}|$ < 0.01 kcal. (93b) requires ΔF_{trans} to be calculated for electron tunnelling through a barrier depending on ΔU_{res}; such a calculation (183), for $Fe^{II} + Fe^{III}$, includes allowance for dielectric saturation in ΔF_{app}. (ii) $|\Delta U_{res}|$ > 1 kcal. may be assumed in cases where an anion bridge is known to form between $\mathfrak{M}^{II}$ and $\mathfrak{M}^{III}$, allowing more facile electron transfer by conduction (93d) with diminution of the values of the other ΔF terms of Eq. 18. (iii) 0.01 kcal. < $|\Delta U_{res}|$ < 1 kcal. (the "adiabatic" assumption (93b, 106a, 144)) gives ΔF_{trans} ≈ 0 and allows neglect of ΔU_{res} itself. For an outer-sphere mechanism (106, 144) it is assumed that for ΔF_{app}, $x = d^{II} + d^{III} + 2r_w$. During the time fraction λ of the resonance, when the transferring electron is associated with the oxidant orbital, only the electronic

polarizability of the outer dielectric (i.e., second and further shells) can be in equilibrium with the rapidly oscillating charge (106c); the corresponding permittivity is n_{ref}^2 (106c, 142). The maximum of the potential barrier is thus attained by a transfer of $^1/_2e$ from the equilibrium dielectric of permittivity ϵ about the reductant aquo-ion (radius $d^* + r_w$), to the dielectric of permittivity n_{ref}^2 about the oxidant, of similar radius. Application of simple Born charging to this transfer gives the final barrier as

$$\Delta F_{diel} = \frac{(^1/_2e)^2}{2(d^* + r_w)} \left\{ \frac{1}{n_{ref}^2} - \frac{1}{\epsilon} \right\}$$

hence ΔF^*, from Eq. 18 (106c, 143), $\partial/\partial T$ of which gives ΔS^* and hence ΔH^* (106). The transition-state value of λ is obtained from a more general derivation by the original authors (106, 143) without having to be assumed as $^1/_2$.

For oxidation reactions of corresponding charge type, e.g., $\mathfrak{M}_1^{II} + \mathfrak{M}_2^{III}$, where the accompanying thermodynamic free energy change ΔF_{12} is obtainable from electrode potentials (106e, 144, 145, 199c)

$$\Delta F_{12}^* \approx {}^1/_2\Delta F_1^* + {}^1/_2\Delta F_2^* + {}^1/_2\Delta F_{12} \quad \text{(Eq. 19)}$$

ΔF_1^* is the observed isotopic-exchange value for $\dagger\mathfrak{M}_1^{II} + \mathfrak{M}_1^{III}$, and ΔF_2^* is similarly defined. The last term may be interpreted as arising from the partial (λ) electronic occupancy, in the transition state, of the oxidant transfer orbital. This relationship is predicted to hold when $|\Delta F_{12}|$ is not too large (144), and $\Delta F_{reorg\ 12}$ $\approx {}^1/_2(\Delta F_{reorg\ 1} + \Delta F_{reorg\ 2})$ was assumed in its derivation (144, 199c).

Elaborated forms of Eq. 18 and 19 give reasonably good agreement (within 1–3 kcal.) with observed activation enthalpies or free energies for isotope exchanges between anions (143), between cations (106d), and for oxidation reactions (56). For $V^{2+} + V^{3+}$ and $Co^{3+} + Fe^{2+}$ the calculated ΔH_1^* and ΔF_{12}^*, respectively, are much too low (56, 106d). However, the implicit Born–Oppenheimer approximation (that the nuclei do not move during the interorbital transfer) might not always be adequate; the assumed frequency $2\Delta U_{res}/h$, of electronic motion, is in fact quite close to the $\mathfrak{M}-OH_2$ vibrational frequencies calculable from Sacher and Laidler's potential energy curves (183), and the separate treatment of electronic and nuclear motions, as above, remains to be justified (7, 106e, 180). Finally, although mechanism (ii) is often self-evident, the above preference for (iii) over (i) is somewhat arbitrary (183). A rough estimate of ΔU_{res} (e.g., from Slater orbitals (188), assumed unperturbed by the presence of water molecules) should indicate the more probable path, though both may operate concurrently.

VIII. Concluding Remarks

The failure of the macroscopic Born model to predict electrode potentials and hydration energies is well known (51c) and molecular-scale adaptations, which at least usefully summarize experimental data, introduce parameters which cannot yet be uniquely interpreted. Unless a sort of correspondence principle in reverse can be found (86), to separate the r_e and a terms in Eq. 7a, further analyses may fail to avoid a mere reshuffling of old assumptions, but improved dielectric saturation theories will have obvious applications. Little attempt appears to have been made to check assumptions in Born charging against lattice energies, using lattice permittivities. There seems to be no objection in principle, and lattice permittivities should be free of the dielectric saturation problems arising with a polar medium. r_{exp} should be acceptable here as true ionic radii.

Charging processes restricted to the solution phase alone (as by Güntelberg (89)) give highly successful predictions of variations of free energy with permittivity and temperature. Indeed, the Debye–Hückel and Bjerrum theories employ just the Born model for aquo-ions (34), and progress towards unequivocal interpretation of ion-contact distances appearing in the former theories must depend to an appreciable extent on improvements in the latter; this factor alone justifies the detailed examinations reviewed here. Interestingly, however, the ΔF_h values used for Born-charging cycles appear, for M^{2+}, to be less relevant to some aquo-ion properties than do the ΔF_{ai} (section VD).

While the internal (59, 63) and external (100) bonding of water is partly understood, the range of parameters chosen for molecular-interaction calculations of ΔY_h (8a, 66, 92) have been no better justified than those in Born charging. Again, semiempirical expressions have been usefully applied, e.g., to electron-transfer reactions, but structure breaking eludes a satisfactory quantitative assessment.

In no case is agreement of calculated with experimental ΔY_h values to be taken as completely justifying the assumptions underlying a calculation (cf. 203). The simplification to be gained by using r_{exp} values must give rise to some doubt concerning the admissibility of r_o values. In particular, Θ derived from ΔF_h and r_{exp} would be reduced to a value nearer the quantum mechanical (sections IVB and IVE).

IX. Appendix

A. Sources of ΔY_{con} Values

Table I values were chosen for reasons appearing in the following comments. Some newer data mentioned here, postdating Table I, do not affect any conclusions of this review.

Noyes' compilation (155) taken from NBS 500 values (154) showed that in many unexplained cases, S°_{con} $(M^{z+}) - S_g(M^{z+}) + {}^1/_{2z}S_g(H_2)$ failed to equal $[\Delta H'_{h\ con}$ $(M^{z+}) - \Delta F'_{h\ con}(M^{z+})]/T$.

Benjamin and Gold (16), also using NBS 500 data, omitted from their compilation, again without explanation, several $\Delta S_{h\ con}$ and $\Delta F_{h\ con}$ values, even when the requisite data were available (154). The inconsistencies (and omissions) arose because the NBS 500 values for the variables appearing in the equation

$$S_g(\text{metal atom}) - S(\text{metal}) = (\Delta H_{sub} - \Delta F_{sub})/T$$

in the cases noted, fail to conform with the equation. New and consistent ΔY_{sub} values (198) were thus used in Table I to repair Benjamin and Gold's omissions.

NBS 500 (154) often gives no specific reference to the experimental data used in deriving S°_{con} values (192), most of which are identical with Powell and Latimer's set (169). The latter authors give Kelley (118a) as their source. Kelley (118a) and Kelley and King (118b), in fact, almost exclusively quoted Latimer, Pitzer, and Smith's values (137) which differ often by ~ 2 e. u. from Powell and Latimer's (169). Unfortunately, Latimer (134, 135) later quoted only NBS 500 as his source.

Halliwell and Nyburg (92) proposed new values of $\Delta H_{h\ con}$ for M^{z+} and X^-, some being based on a new source of experimental heats of salt formation, which differ by 1–3 kcal. from NBS 500 values for most, and up to 14 kcal. for some, ions. Parson's (165) values of ΔH_{aq} appear to be taken from Bichowsky and Rossini's tabulation (22) but the accompanying $\Delta Y_{h\ con}$ values are from Benjamin and Gold (16, 154). A compilation of ΔH_h by Russian workers (202), using mainly NBS 500 data in two supposedly different computational procedures, is consistent within 1–2 kcal. with Benjamin and Gold's (16). ΔS_h values were used with ΔH_h to afford ΔF_h, to the exclusion of any direct experimental ΔF data. Unfortunately some S°_{con} values calculated from empirical relationships were included (e.g., for Tl^{3+}). Tabulated (202) entropies of gas ions, calculated with Q_{int}, are formally preferable to Conway and Bockris' values (46b), which are for translation only.

B. Multiplet Levels of Gas Ions

NBS 500 values of ΔH_I appear to have been calculated from $\Delta H_I = \sum_1^z I + {}^5/_{2z}RT$ (157), with terms in the temperature derivative of Q_{int} when $Q_{int} \neq 1$. However, account can be taken of multiplet-level contributions, e.g., in transition-metal ions, by the alternative method of adding to $\sum^z I + {}^5/_{2z}RT$ a "valence state preparation energy" P^+ (19, 77, 189), where

$$P^+ = \sum^J(2J + 1)U_J/\sum^J(2J + 1)$$

U_J being the energy difference between the lowest and the J level of the ion. The two averages (employing either Q_{int} or P^+) can differ by some 5 kcal.; the use of P^+ seems preferable if hydration energies are to be analyzed in terms of the Born model (27), where a smoothed charging process, completely neglecting the statistical distribution of charge in quantum levels, is involved.

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