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STANDARD REAL FREE ENERGIES OF IONIZATION OF SINGLE ATOMS AND IONS IN AQUEOUS MEDIA

By

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Abstract

The standard real free energies of ionization I(aq) of single atoms and ions in aqueous media have been estimated for 87 elements on the basis of the absolute electromotive forces of the associated redox couples and of the hydrated electron which are referred to the standard state of the gaseous electron. The ionization potential I_p(aq) of a series of divalent cations of the transition metal calculated from I(aq) have been compared with the light quantum of the long-wave edge of the electron transfer spectra of these ions observed by Dainton and James in aqueous media.

Introduction

The photochemical oxidation and reduction processes of cationic and anionic species have been extensively studied in aqueous media in the field of photochemistry.

Franck and Scheibe[1] suggested as early as 1928 that the ultraviolet absorption spectra of the halogen ions in aqueous media were to be electron affinity spectra of a water molecule in the hydration layer. Farkas and Farkas[2] also discussed the primary process of the water decomposition by photo-excitation of ions in aqueous media. Dainton and James[3] observed ultra-violet absorption spectra of divalent cations of the elements of the first long period from vanadium to nickel and found a linear correlation between the longwave edges of the absorption spectra and the electrode potentials of the redox systems associated with photochemical oxidation processes, on which basis they predicted a linear relation between the ionization potential of the dissolved cation and the magnitude of the light quantum necessary for the excitation of the cation. The formation of the hydrated electron by illumination of aqueous solutions of various anions was verified to occur through a dissociation of the excited state of hydrated anionic species.[4,5]

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The mechanism of the photochemical processes was discussed mainly based on the energetics of the ionization of atoms in aqueous media[1,2] or on the identification of the products by the chemical method combined with the spectroscopic data and the scavengers of the hydrated electron or radicals.[4,5] However, the mechanism of the photochemical primary processes was not settled because of the deficiency of the information on the energetics of the ionization of atoms and the solvation of ions in aqueous media in the sense of the absolute scale.

The absolute values of the free energies of ionization of atoms and solvation of ions in aqueous media as well as the absolute electromotive forces of the associated redox systems referred to the standard state of the gaseous electron will be the physical quantities which are essential for the elucidation of the mechanism of the photochemical primary processes and also of the electrochemical processes of the photo-excited states of atoms and ions.

The standard real free energy of hydration of electron which can be identified with the absolute electromotive force of the hydrated electron has been estimated by Rotenberg[6]. The standard real free energies of solvation of monoatomic ions and the absolute electromotive forces of the associated redox systems have recently been estimated in our laboratory for a number of elements in aqueous and non-aqueous media.[7,8,9,10] It may therefore be possible to estimate the standard ionization free energies of atoms in aqueous media from the comparison of the absolute electromotive forces of the hydrated electron and the associated redox couples.

In the present work the ionization free energies of atoms in aqueous media at 25°C will be estimated on the basis of the absolute electromotive forces reported previously,[8] and the linear relation found by Dainton and James[3] will be discussed using the ionization free energies obtained for divalent cations.

Formulation of the standard free energy of ionization I(aq) of an atom in aqueous media

The standard real free energy of ionization I(aq) of an atom in aqueous media may be defined as the standard free energy of formation of the hydrated ion $\mathbf{M}^z$(aq) and the hydrated electron e^-(aq) from the atom $\mathbf{M}$(g) in the gaseous state as

$$I(\mathrm{aq}) = \bar{\mu}^0_{\mathrm{M}^z(\mathrm{aq})} + z\bar{\mu}^0_{\mathrm{e}^-(\mathrm{aq})} - \mu^0_{\mathrm{M(g)}} , \qquad (1)$$

where $\bar{\mu}^0$'s are the electrochemical potentials of the specified species with

subscripts in the standard state and z is the valency of the ion including positive or negative sign. It can readily be seen from the definition of $I(\mathrm{aq})$ that $I(\mathrm{aq})$ is expressed by the difference of the absolute electromotive forces between the redox couple $\mathbf{M}^z/\mathbf{M}(\mathrm{g})$ and the hydrated electron $\varphi^0_{\mathbf{M}^z/\mathbf{M}(\mathrm{g})}$ and $\varphi^0_{\mathrm{e}^-(\mathrm{aq})}$

$$I(\mathrm{aq}) = zF(\varphi^0_{\mathbf{M}^z/\mathbf{M}(\mathrm{g})} - \varphi^0_{\mathrm{e}^-(\mathrm{aq})}), \qquad (2)$$

or using $\varphi^0_{\mathbf{M}^z/\mathbf{M}(\mathrm{p})}$ of the redox couple $\mathbf{M}^z/\mathbf{M}(\mathrm{p})$ where $\mathbf{M}(\mathrm{p})$ is the element in the standard state of pure solid or liquid or gas at 25°C and the value of $\varphi^0_{\mathrm{e}^-(\mathrm{aq})} = 1.56$ v estimated by Rotenberg[6]

$$I(\mathrm{aq}) = zF(\varphi^0_{\mathbf{M}^z/\mathbf{M}(\mathrm{p})} - 1.56) - \Delta F^0_{\mathbf{M}(\mathrm{g})} \text{ ev}, \qquad (3)$$

where $\Delta F^0_{\mathbf{M}(\mathrm{g})}$ is the standard free energy of atomization of $\mathbf{M}(\mathrm{p})$.

It can be seen from Eq. (3) that the ionization free energy of an ion $\mathbf{M}^n$ to $\mathbf{M}^{n+z}$ in aqueous media is also given by the equation

$$I(\mathrm{aq}) = zF(\varphi^0_{\mathbf{M}^{n+z}/\mathbf{M}^n} - 1.56) \text{ ev}. \qquad (4)$$

$I(\mathrm{aq})$ can be estimated numerically on the basis of Eq. (3) or (4) using the values of $\varphi^0_{\mathbf{M}^z/\mathbf{M}(\mathrm{p})}$ or $\varphi^0_{\mathbf{M}^{n+z}/\mathbf{M}^n}$ reported in the previous work[8] and the values of $\Delta F^0_{\mathbf{M}(\mathrm{g})}$ quoted from the thermodynamical data.[11,12,13,14]

Results and Discussion

The values of $I(\mathrm{aq})$ estimated on the basis of Eq. (3) or (4) are listed in Table I. In this table the values of φ^0 without asterisk are quoted from the previous work[8] and those with a single asterisk are calculated by the relation $\varphi^0 = E^0 + 4.42$ v from the standard electrode potential E^0 referred to the standard hydrogen electrode quoted from the references mentioned in the column of E^0 in this Table. The values of $I(\mathrm{aq})$ with double asterisks in Table I are those estimated from the additivity law of the ionization free energies of the consecutive ionization processes because of the lack of experimental data for the standard electromotive force of the associated redox couple. For convenience, the values of $I(\mathrm{aq})$ of the consecutive ionization processes of atoms are listed in Table II, as in the case of the ionization potentials of the gaseous atoms.

It can be seen from Table I or II that the free energy of ionization of an atom in aqueous media is much lower than that in the gas phase as expected from the high solvation energy of the ion in water and falls in the region of the visible and ultra-violet absorption spectra.

The negative sign of $I(\mathrm{aq})$ as seen in the case of alkaline and alkaline-

TABLE I. Absolute electromotive forces φ^0, standard free energies of atomization $\Delta F^\circ_{M(g)}$ of pure substances of element **M**, standard free energies of ionization of single atoms and ions I(aq) in aqueous media at 25°C

Electrode Reaction	φ° (V)	E° vs. SHE (V)	$\Delta F^\circ_{M(g)}$ (eV)	I(aq) (eV)	Electrode Reaction	φ° (V)	E° vs. SHE (V)	$\Delta F^\circ_{M(g)}$ (eV)	I(aq) (eV)
1 a					La^{3+}/La	2.05		4.08	−2.61
$H^+/\frac{1}{2}H_2$	4.42		2.11	0.75	Ce^{3+}/Ce	1.94		4.47	−3.33
Li^+/Li	1.40		1.33	−1.49	Ce^{4+}/Ce	2.96			1.13
Na^+/Na	1.71		0.80	−0.65	Ce^{4+}/Ce^{3+}	5.86*	1.443 (11)		4.30
K^+/K	1.50		0.63	−0.69	Pr^{3+}/Pr	1.95*	−2.47 (18)	3.62	−2.45
Rb^+/Rb	1.43		0.56	−0.69	Nd^{3+}/Nd	1.98		3.04	−1.78
Cs^+/Cs	1.40		0.52	−0.68	Pm^{3+}/Pm	2.00*	−2.42 (18)	2.38	−1.06
1 b					Sm^{3+}/Sm	2.01		1.79	−0.44
Cu^+/Cu	4.94		3.10	0.28	Eu^{3+}/Eu	2.01*	−2.41 (18)	1.46	−0.11
Cu^{2+}/Cu	4.77			3.32	Eu^{3+}/Eu^{2+}	3.99*	−0.43 (16)		2.43
Cu^{2+}/Cu^+	4.58*	0.159(15)		3.02	Gd^{3+}/Gd	2.02		3.75	−2.37
Ag^+/Ag	5.22		2.55	1.11	Tb^{3+}/Tb	2.03*	−2.39 (18)	3.65	−2.24
Ag^{2+}/Ag				5.95**	Dy^{3+}/Dy	2.07*	−2.35 (18)	2.87	−1.34
Ag^{2+}/Ag^+	6.40*	1.98 (16)		4.84	Ho^{3+}/Ho	2.10*	−2.32 (18)	2.66	−1.04
Au^+/Au	6.12		3.38	1.18	Er^{3+}/Er	2.12*	−2.30 (18)	2.51	−0.83
Au^{3+}/Au	5.92			9.70	Tm^{3+}/Tm	2.14*	−2.28 (18)	2.20	−0.46
Au^{3+}/Au^+	5.71*	1.29 (16)		8.30	Yb^{3+}/Yb	2.15*	−2.27 (18)	1.23	0.54
2 a					Lu^{3+}/Lu	2.17		4.01	−2.18
Be^{2+}/Be	2.72		3.00	−0.68	Ac^{3+}/Ac	1.8*	−2.6 (17)	3.60	−3.0
Mg^+/Mg	1.76*	−2.659(17)	1.17	−0.97	Th^{3+}/Th				−8.1**
Mg^{2+}/Mg	2.08			−0.13	Th^{4+}/Th	2.52		5.50	−1.66
Mg^{2+}/Mg^+				0.84**	Th^{4+}/Th^{3+}	8.1*	3.7 (17)		6.5
Ca^+/Ca	1.40*	−3.02 (11)	1.48	−1.64	U^{3+}/U	2.62		4.62	−1.44
Ca^{2+}/Ca	1.55			−1.50	U^{4+}/U	2.92			0.82
Ca^{2+}/Ca^+				0.14**	U^{4+}/U^{3+}	3.81*	−0.61 (16)		2.25
Sr^{2+}/Sr	1.53		1.35	−1.41	U^{5+}/U				4.70**
Ba^{2+}/Ba	1.52		1.70	−1.71	U^{5+}/U^{3+}				6.14**
Ra^{2+}/Ra	1.50		1.09	−1.21	U^{5+}/U^{4+}	5.44*	1.02 (11)		3.88
2 b					U^{6+}/U				7.34**
Zn^{2+}/Zn	3.66		0.99	3.21	U^{6+}/U^{3+}				8.78**
Cd^{2+}/Cd	4.02		0.80	4.12	U^{6+}/U^{4+}	4.82*	0.4 (16)		6.52
$\frac{1}{2}Hg_2^{2+}/Hg$	5.21*	0.793(16)	0.33	3.32	U^{6+}/U^{5+}	4.48*	0.063 (11)		2.92
Hg^{2+}/Hg	5.27			7.09	Np^{3+}/Np	2.56*	−1.86 (16)	3.66	−0.66
$Hg^{2+}/\frac{1}{2}Hg_2^{2+}$				3.77**	Np^{4+}/Np				2.35**
3 a					Np^{4+}/Np^{3+}	4.57*	0.147 (16)		3.01
Al^{3+}/Al	2.75		2.96	0.61	Np^{5+}/Np				5.95**
Ga^{2+}/Ga	3.97		2.48	2.34	Np^{5+}/Np^{3+}				6.61**
Ga^{3+}/Ga	3.90			4.54	Np^{5+}/Np^{4+}	5.16*	0.739 (11)		3.60
Ga^{3+}/Ga^{2+}	3.77*	−0.65 (16)		2.21	Np^{6+}/Np				9.95**
In^+/In	4.17		2.16	0.45	Np^{6+}/Np^{3+}				10.61**
In^{2+}/In	2.76*	−1.66 (19)		0.24	Np^{6+}/Np^{4+}				7.60**
In^{2+}/In^+	4.07*	−0.35 (16)		2.51	Np^{6+}/Np^{5+}	5.56*	1.137 (11)		4.00
In^{3+}/In	4.08			5.40	Pu^{3+}/Pn	2.35*	−2.07 (16)	3.11	−0.74
In^{3+}/In^+	4.02*	−0.40 (11)		4.92	Pu^{4+}/Pu				3.10**
In^{3+}/In^{2+}	3.97*	−0.45 (16)		2.41	Pu^{4+}/Pu^{3+}	5.40*	0.982 (11)		3.84
Tl^+/Tl	4.08		1.53	0.99	Pu^{5+}/Pu				7.06**
Tl^{2+}/Tl				6.69**	Pu^{5+}/Pu^{3+}				7.80**
Tl^{2+}/Tl^+				5.70**	Pu^{5+}/Pu^{4+}	5.52*	1.099 (11)		3.96
Tl^{3+}/Tl	5.13			9.18	Pu^{6+}/Pu				10.92**
Tl^{3+}/Tl^+	5.67*	1.25 (16)		8.22	Pu^{6+}/Pu^{3+}				11.66**
Tl^{3+}/Tl^{2+}	4.05*	−0.37 (11)		2.49	Pu^{6+}/Pu^{4+}	5.47*	1.052 (11)		7.82
3 b					Pu^{6+}/Pu^{5+}	5.34*	0.9184(11)		3.78
Sc^{3+}/Sc	2.34		3.50	−1.16	Am^{3+}/Am	2.04*	−2.38 (17)	2.18	−0.74
Y^{3+}/Y	2.05		3.97	−2.50	Am^{4+}/Am				4.50**

Teble I. Continued

Electrode Reaction	φ^o (V)	E^o vs. SHE (V)	$\Delta F^o_{M(g)}$ (eV)	I(aq) (eV)	Electrode Reaction	φ^o (V)	E_o vs. SHE (V)	$\Delta F^o_{M(g)}$ (eV)	I(aq) (eV)
Am^{4+}/Am^{3+}	6.80*	2.38 (17)		5.24	Cr^{3+}/Cr	3.71		3.65	2.80
Cm^{3+}/Cm^{2+}	0.0*	−4.4 (17)		−1.6	Cr^{3+}/Cr^{2+}	4.01*	−0.41 (16)		2.45
Cm^{4+}/Cm^{2+}				4.7**	Mo^{3+}/Mo	4.2*	−0.2 (16)	6.3	1.5
Cm^{4+}/Cm^{3+}	7.9*	3.5 (17)		6.3	W^{6+}/W^{5+}	4.68*	0.26 (19)		3.12
Bk^{3+}/Bk^{2+}	1.0*	−3.4 (17)		−0.6	7 a				
Bk^{4+}/Bk^{2+}				3.8**	$\frac{1}{2}F_2/F^-$	7.07		0.65	−6.16
Bk^{4+}/Bk^{3+}	6.0*	−1.6 (16)		4.4	$\frac{1}{2}Cl_2/Cl^-$	5.78		1.09	−5.31
Cf^{3+}/Cf^{2+}	2.8*	−1.6 (17)		1.2	$\frac{1}{2}Br_2/Br^-$	5.49		0.85	−4.78
Cf^{4+}/Cf^{2+}				7.2**	$\frac{1}{2}I_2/I^-$	4.95		0.73	−4.12
Cf^{4+}/Cf^{3+}	7.6*	3.2 (17)		6.0	7 b				
Es^{3+}/Es^{2+}	2.87*	−1.55 (17)		1.31	Mn^{2+}/Mn	3.37		2.47	1.15
Fm^{3+}/Fm^{2+}	3.3*	−1.1 (17)		1.7	Mn^{3+}/Mn				5.52**
Md^{3+}/Md^{2+}	4.27*	−0.15 (17)		2.71	Mn^{3+}/Mn^{2+}	5.93*	1.51 (16)		4.37
No^{3+}/No^{2+}	5.87	1.45 (17)		4.31	Tc^{2+}/Tc	4.82*	0.400 (19)	6.57	−0.05
4 a					Re/Re^-	4.02*	−0.400 (19)	7.51	−9.97
Sn^{2+}/Sn	4.28		2.77	2.67	Re^+/Re^-	4.17*	−0.25 (19)		5.22
Sn^{4+}/Sn				8.69**	Re^+/Re				−4.75**
Sn^{4+}/Sn^{2+}	4.57*	0.15 (16)		6.02	Re^{3+}/Re^-	4.55*	0.125 (19)		11.96
Pb^{2+}/Pb	4.29		1.69	3.77	Re^{3+}/Re	4.72*	0.300 (19)		1.97
Pb^{4+}/Pb				12.87**	Re^{3+}/Re^+				6.72**
Pb^{4+}/Pb^{2+}	6.11*	1.69 (16)		9.10	Re^{5+}/Re^-				17.96**
4 b					Re^{5+}/Re				7.97**
Ti^{2+}/Ti	2.67		4.42	−2.20	Re^{5+}/Re^+				12.72**
Ti^{3+}/Ti	3.21*	−1.21 (19)		0.53	Re^{5+}/Re^{3+}	4.56*	0.14 (19)		6.00
Ti^{3+}/Ti^{2+}	4.05*	−0.37 (16)		2.49	8				
Ti^{4+}/Ti				3.35**	Fe^{2+}/Fe	3.98		3.84	1.00
Ti^{4+}/Ti^{2+}				5.55**	Fe^{3+}/Fe	4.38			4.62
Ti^{4+}/Ti^{3+}	4.38*	−0.04 (16)		2.82	Fe^{3+}/Fe^{2+}	5.19*	0.771 (16)		3.63
Zr^{4+}/Zr	2.89		5.87	−0.55	Ru^+/Ru				−2.44**
Hf^{4+}/Hf	2.72		6.85	−2.21	Ru^{2+}/Ru	4.87		6.17	0.45
5 a					Ru^{2+}/Ru^+	4.45*	0.03 (18)		2.89
As^{3+}/As	4.72		2.69	6.79	Ru^{3+}/Ru				3.56**
Sb^{3+}/Sb	4.66		2.30	7.00	Ru^{3+}/Ru^+				6.00**
Bi^{3+}/Bi	4.62		1.75	7.43	Ru^{3+}/Ru^{2+}	4.67*	0.2487 (18)		3.11
5 b					Os^{2+}/Os	5.12		7.70	−0.58
V^{2+}/V	3.24		4.84	−1.48	Co^{2+}/Co	4.14		3.94	1.22
V^{3+}/V				1.12**	Co^{3+}/Co	4.82			5.84
V^{3+}/V^{2+}	4.16*	−0.255 (16)		2.60	Co^{3+}/Co^{2+}	6.24*	1.82 (16)		4.68
Nb^{3+}/Nb	3.32		7.02	−1.74	Rh^+/Rh	5.0*	0.6 (18)	5.3	−1.9
Nb^{5+}/Nb	3.46*	−0.96 (20)		2.48	Rh^{2+}/Rh	5.0*	0.6 (18)		1.5
Nb^{5+}/Nb^{3+}	4.10*	−0.324 (20)		5.08	Rh^{2+}/Rh^+				3.4**
Ta^{5+}/Ta	3.30*	−1.12 (20)	7.66	1.04	Rh^{3+}/Rh	5.22			5.68
6 a					Rh^{3+}/Rh^+				7.58**
$\frac{1}{2}O_2/O^-$	5.65*	1.229 (16)	2.40	−6.49	Rh^{3+}/Rh^{2+}				4.18**
S/S^{2-}	3.91*	−0.508 (16)	2.47	−7.17	Rh^{4+}/Rh				9.97**
Se/Se^{2-}	3.64*	−0.78 (16)	1.94	−6.10	Rh^{4+}/Rh^+				11.87**
Te/Te^{2-}	3.50*	−0.92 (16)	1.63	−5.51	Rh^{4+}/Rh^{2+}				8.47**
Te^{2+}/Te	4.82*	0.40 (21)		4.89	Rh^{4+}/Rh^{3+}	5.85*	1.43 (18)		4.29
Te^{4+}/Te	4.99			12.09	Ir^{3+}/Ir	5.58*	1.156 (18)	6.41	5.65
Te^{4+}/Te^{2+}				7.20**	Ni^{2+}/Ni	4.17		3.98	1.24
Po/Po^{2-}	3.0*	−1.4 (21)	1.11	−3.9					
Po^{2+}/Po	5.07			5.91					
Po^{3+}/Po	4.98			9.15	Pd^{2+}/Pd	5.41		3.52	4.18
Po^{3+}/Po^{2+}	4.75*	0.33 (21)		3.19	Pt^{2+}/Pt	5.62		5.39	2.73
6 b					OH/OH^-	6.42			−4.86
Cr^{2+}/Cr	3.52		3.65	0.27					

TABLE II. Standard free energies of consecutive ionization of atoms in aqueous media at 25°C in electron volt

(1)

	Atom. no.	−1 ←	0 →	1 →	2 →	3 →	4 →	5 →	6
	1 H		0.75						
Ia	3 Li		−1.49						
	11 Na		−0.65						
	19 K		−0.69						
	37 Rb		−0.69						
	55 Cs		−0.68						
IIa	4 Be		−0.68						
	12 Mg		−0.97	0.84					
	20 Ca		−1.64	0.14					
	38 Sr			−1.41					
	56 Ba			−1.71					
	88 Ra			−1.21					
IIIa	21 Sc				−1.16				
	39 Y				−2.50				
	57 La				−2.61				
IVa	22 Ti			−2.20	2.49	2.82			
	40 Zr					−0.55			
	72 Hf					−2.21			
	90 Th				−8.20	6.50			
Va	23 V			−1.48	2.60				
	41 Nb				−1.74		5.08		
	73 Ta						1.04		
VIa	24 Cr			0.27	2.45				
	42 Mo				1.50				
	74 W								3.12
VIIa	25 Mn			1.15	4.37				
	43 Tc			−0.05					
	75 Re	−9.97	−4.75		6.72		6.00		
VIII	26 Fe			1.00	3.63				
	27 Co			1.22	4.68				
	28 Ni			1.24					
	44 Ru		−2.44	2.89	3.11				
	45 Rh		−1.90	3.40	4.18	4.29			
	46 Pd			4.18					
	76 Os			−0.58					
	77 Ir				5.65				
	78 Pt			2.73					

(2)

	Atom. no.	−2 ←	− 1 ←	0 →	1 →	2 →	3 →	4
Ib	29 Cu			0.28	3.02			
	47 Ag			1.11	4.84			
	79 Au			1.18			8.30	
IIb	30 Zn				3.21			
	48 Cd				4.12			
	80 Hg			3.32	3.77			

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	Atom. no.	−2 ←	− 1 ←	0 →	1 →	2 →	3 →	4
IIIb	13 Al						0.61	
	31 Ga					2.34	2.21	
	49 In				0.45	2.51	2.41	
	81 Tl				0.99	5.70	2.49	
IVb	50 Sn					2.67		6.02
	82 Pb					3.77		9.10
Vb	33 As						6.79	
	51 Sb						7.00	
	83 Bi						7.43	
VIb	8 O		−6.49					
	16 S	−7.17						
	34 Se	−6.10						
	52 Te	−5.51				4.89		7.20
	84 Po	−3.90				5.91	3.19	
VIIb	9 F		−6.16					
	17 Cl		−5.31					
	35 Br		−4.78					
	53 I		−4.12					

(3)

Lanthanide

Atom. no.	0 →	1 →	2 →	3 →	4
57 La			−2.61		
58 Ce			−3.33	4.30	
59 Pr			−2.45		
60 Nd			−1.78		
61 Pm			−1.06		
62 Sm			−0.44		
63 Eu		−2.54	2.43		
64 Gd			−2.37		
65 Tb			−2.24		
66 Dy			−1.34		
67 Ho			−1.04		
68 Er			−0.83		
69 Tm			−0.46		
70 Yb			0.54		
71 Lu			−2.18		

Actinide

Atom. no.	0 →	1 →	2 →	3 →	4 →	5 →	6
89 Ac			−3.00				
90 Th			−8.10	6.50			
92 U			−1.44	2.25	3.88	2.92	
93 Np			−0.66	3.01	3.60	4.00	
94 Pu			−0.74	3.84	3.96	3.78	
95 Am			−0.74	5.24			
96 Cm			−1.60	6.30			
97 Bk			−0.60	4.40			
98 Cf			1.20	6.00			
99 Es			1.31				
100 Fm			1.70				
101 Md			2.71				
102 No			4.31				

earth metals shows that these atoms readily liberate electron in aqueous media, as verified experimentally.[5]

Dainton and James[3] observed the charge transfer spectra in aqueous media for a series of divalent cations of the transition metal $\mathbf{V}^{2+}$, $\mathbf{Cr}^{2+}$, $\mathbf{Fe}^{2+}$, $\mathbf{Mn}^{2+}$, $\mathbf{Co}^{2+}$ and $\mathbf{Ni}^{2+}$ and obtained a linear relation between the light quantum $h\nu$ which corresponded to the long-wave edge of the absorption spectra and the standard electromotive force E^0 of the $\mathbf{M}^{3+}/\mathbf{M}^{2+}$ couple with a gradient equal to unity

$$h\nu = FE^0 + 3.70\,, \qquad \text{ev.} \tag{5}$$

They predicted from Eq. (5) that $h\nu$ would be proportional to the ionization potential in aqueous media. Although they pointed out that the constant in Eq. (5) included a term related to the absolute value of E^0 and the standard entropy change of the oxidation process of the cation, it was not possible for them to conclude whether the hydrated electron was formed by one step of photo-excitation or through the excited state of the cation. Now it is possible to express Eq. (5) in terms of the electrode potential in the absolute scale using $E^0 = \varphi^0_{M^{3+}/M^{2+}} - 4.42$ v,

$$h\nu = F\varphi^0_{M^{3+}/M^{2+}} - 0.72 \qquad \text{ev}, \tag{6}$$

The ionization potential $I_p(\text{aq})$ in aqueous media from $\mathbf{M}^{2+}(\text{aq})$ to $\mathbf{M}^{3+}(\text{aq})$ may be given by the equation

$$I_p(\text{aq}) = I(\text{aq}) + T\Delta S^0 \tag{7}$$

since the standard enthalpy change may be identified with the ionization potential. The standard entropy change ΔS^0 changes very slightly in the cation series and is assumed to be approximately equal to -40 cal/deg. g-ion at 25°C from the Powell and Latimer's equation[22] in accordance with Dainton and James. In this way $I_p(\text{aq})$ is given by the equation

$$I_p(\text{aq}) = F\varphi^0_{M^{3+}/M^{2+}} - 2.08\,, \qquad \text{ev} \tag{8}$$

From the comparison of Eqs. (6) and (8) it is found that $h\nu$ is proportional to $I_p(\text{aq})$ with a proportionality constant equal to unity as predicted by Dainton and James, but the value of $h\nu$ is higher than that of $I_p(\text{aq})$ by 1.36 ev. The difference 1.36 ev between $h\nu$ and $I_p(\text{aq})$ suggests that the ion $\mathbf{M}^{2+}$ is electronically excited by the absorption of light quantum and then the excited electron transfers to the hydrated state.

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