ECS Transactions, 25 (23) 159-163 (2010)
10.1149/1.3328519 ©The Electrochemical Society

Aqueous Redox Potentials Found to be Inversely Proportional to the Bohr Radius

Raji Heyrovska

Institute of Biophysics, Academy of Sciences of the Czech Republic,
Kralovopolska 135, 612 65 Brno, Czech Republic;
Email: rheyrovs@hotmail.com

The author found recently that the covalent, van der Waals and valence shell radii of atoms vary linearly with their respective Bohr radii obtained from their gaseous ionization potentials. Earlier, the ratio of the standard redox potential (with SHE = 0) to the ionization potential had been found to vary linearly with the latter. Here, the standard potentials are shown to be indirectly proportional the Bohr radius and directly proportional to the ionization potentials. This yielded the absolute potential of the SHE and thereby the absolute aqueous redox potentials of elements. These have been presented here in a Table.

Introduction

Aqueous standard redox potentials (E^o) are free energies which are the driving forces for electron transfer reactions. Since, by convention, they are referred to that of the standard hydrogen electrode (SHE) as zero, a knowledge of the absolute potential of the latter will give the actual absolute redox potentials. This paper presents the absolute potentials of the SHE and other redox couples of elements. The work originated from the previous findings that linear relations exist (1) between the covalent and other radii of atoms and their Bohr radii a_B obtained from gaseous ionization potentials ($I = 7.2/a_B$ for I in eV and a_B in Å), and also between the ratio E^o/I and I for many Groups of elements (2). Since a_B is the distance between the electron and the positive nucleus, the author was curious to see whether a linear relation exists between E^o and the reciprocal of a_B (similar to the relation between I and a_B).

Standard redox potential and the Bohr radius

By using the available data for E^o and I from (3), it was found that indeed E^o does vary linearly with $1/a_B$ (= I/7.2). The linear relations for redox couples of the Group IA (hydrogen and alkali metals, except Li) and Group VIIA (halogens) elements are shown in Fig. 1. This linear relation implies that actually E^o must vary linearly with I. This was found to be the case, as described below.

Standard redox potential and gaseous ionization potential

The linear dependence of E^o and I is shown for elements of Groups IA, IIA and VIIA in Fig. 2. The straight lines follow the equation,

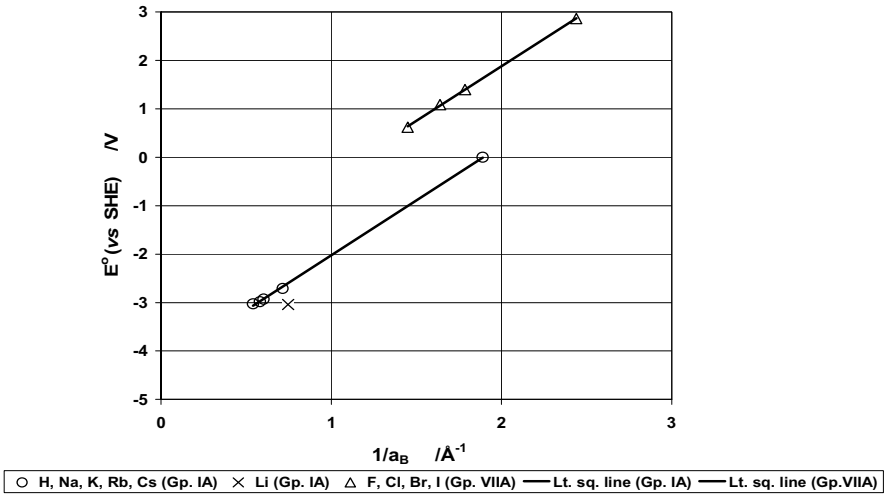

Figure 1. Linear dependence of standard aqueous redox potentials, E^o (SHE = 0) of elements of Groups IA and VIIA on the reciprocal of Bohr radius, a_B.

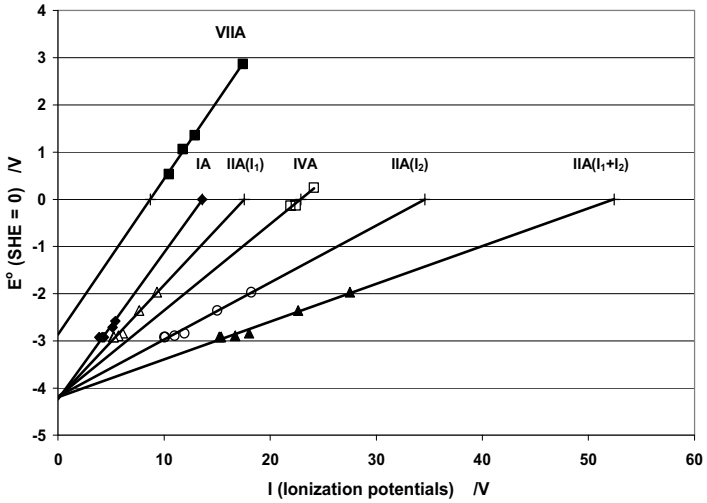

Figure 2. Linear dependence of the aqueous standard potentials, E^o (vs S.H.E.) on the gaseous ionization potentials, I. For Li, the half wave potential (6) fits Gp. IA better than the value in (3). Y-intercepts, average: $-E^o_{I=0}$ = -4.21 (+/-) 0.03 V and VIIA: -2.87 (+/-) 0.005 V. Slopes k_{aq}: IA: 0.311; IIA(I_1): 0.240; IIA(I_2): 0.121; IIA(I_1+I_2): 0.080; IVA: 0.183; VIIA: 0.330. X-intercepts, $I_{E=0}$: VIIA : IA : IVA : II (I_1) : II (I_2) : II (I_1+I_2) = 8.7 : 13.6 (H): 22.9 : 17.6 : 34.6 : 52. 5 V.

$$E^o = k_{aq}I - E^o_{I=0} \quad [1]$$

where k_{aq}, the slope, is a constant characteristic for each Group and $E^o_{I=0}$, the intercept at I = 0, is the absolute potential of the S.H.E. For the Group IIA elements the plots of E^o vs I are linear for the first (I_1) and second (I_2) ionization potentials and for their sum (I_1+I_2). The corresponding slopes, $k_{aq,1}$, $k_{aq,2}$ and $k_{aq,1+2}$ are in the ratio, 1 : ½ : 1/3. This shows that for these elements, $I_1 = I_2/2 = (I_1 + I_2)/3$. The Y and X intercepts are given in the legend for Fig. 2. The results for redox couples of many more Groups of elements of the Periodic Table are given in (4).

The absolute potential of SHE

The straight lines for Groups IA (H, Li, Na, K, Rb, Cs), IIA (Be, Mg, Ca, Sr, Ba, Ra) and IVA (Ge, Sn, Pb) have the same intercept, $E^o_{I=0}$ = 4.21 (+/- 0.03) V. An investigation of the E^o vs I linear dependence for many redox couples (4) gives the average value, 4.20 (+/- 0.03) V. This value is close to the earlier theoretical value suggested by Trasatti (5), 4.44 (+/- 0.02) V for the $H^+/(½)H_2$ equilibrium at the S.H.E. and is almost the same as the recent (5) experimental value, 4.20 (+/- 0.40) V obtained by Donald et al (6) from studies on aqueous nano-drops in the gas phase. For details and more literature on absolute potentials, see (3, 5, 6). For those of Group VIIA (F, Cl, Br, I), Fig. 2 gives a value $E^o_{I=0}$ = 2.87 (+/- 0.01) V), and is the same as in (4). This is close to the sum (2.86 V) of the potential (3) (2.107 V) for $(½)H_2 \rightarrow H(g)$ and the electron affinity (3) (0.75 V) of hydrogen, and forms the absolute potential of the S.H.E. with respect to the $(½)H_2/H^-$ equilibrium.

Thus, the simple linear Eq. [1] between the aqueous standard potentials and the gaseous ionization potentials have afforded, for the first time, unambiguous values of the absolute potential of the SHE.

The absolute aqueous redox potentials of elements

The absolute aqueous redox potential in aqueous solutions is given by,

$$E^o_{abs} = E^o + E^o_{I=0} = k_{aq}I \quad [2]$$

where $E^o_{I=0}$ = 4.20 (+/- 0.03) V (4) for all Groups except VIIA for which it is 2.87 (+/- 0.01) V, and k_{aq} is a constant for each Group. Thus, by adding the absolute potential of the SHE to the standard potentials (E^o) in (3), the absolute standard potentials (E^o_{abs}) in aqueous solutions have been obtained. The E^o_{abs} values for the redox couples of many elements of the Periodic Table have been presented here in Table I. The electronic structures and the atomic numbers of the elements have also been given in Table I.

TABLE 1. Absolute aqueous redox potentials, $E^{o}_{abs} = E^{0}_{SHE=0} + E^{o}_{abs}(SHE)$ (in V) of elements, ^{Z}X, where Z is the atomic number, $E^{o}_{abs}(SHE) = 2.87$ (+/- 0.01) V for gp. VIIA and 4.20 (+/- 0.03) V for the others. $E^{0}_{SHE=0}$ data are from [3]. The values of n in the redox, O + ne = R are at the head of the columns or in brackets next to E^{0}_{abs}.

Elec.struc.	^{Z}X	E^{o}_{abs}	Elec.struc.	^{Z}X	E^{o}_{abs}	Elec.struc.	^{Z}X	E^{o}_{abs}	Elec.struc.	^{Z}X	E^{o}_{abs}
Gp.IA: s^1		**n=1**	**Gp.IB: s^1**		**n=1**	**Gp.IIA: s^2**		**n=2**	**Gp.IIB: s^2**		**n=2**
$1s^1$	^{1}H	**4.20**									
$[He]2s^1$	^{3}Li	**1.16**				$[He]2s^2$	^{4}Be	**2.23**			
$[Ne]3s^1$	^{11}Na	**1.49**				$[Ne]3s^2$	^{12}Mg	**1.84**			
$[Ar]4s^1$	^{19}K	**1.28**	$[K]3d^{10}$	^{29}Cu	**4.72**	$[Ar]4s^2$	^{20}Ca	**1.36**	$[Ca]3d^{10}$	^{30}Zn	**3.44**
$[Kr]5s^1$	^{37}Rb	**1.28**	$[Rb]4d^{10}$	^{47}Ag	**5.00**	$[Kr]5s^2$	^{38}Sr	**1.31**	$[Sr]4d^{10}$	^{48}Cd	**3.80**
$[Xe]6s^1$	^{55}Cs	**1.28**	$[Cs]4f^{14}5d^{10}$	^{79}Au	**6.03**	$[Xe]6s^2$	^{56}Ba	**1.28**	$[Ba]4f^{14}5d^{10}$	^{80}Hg	**5.05**
$[Rn]7s^1$	^{87}Fr		$[Fr]5f^{14}6d^{10}$	^{111}Rg		$[Rn]7s^2$	^{88}Ra	**1.28**	$[Ra]5f^{14}6d^{10}$	^{112}Cn	
Gp.IIIA: s^2p^1		**n=3**	**Gp.IIIB: s^2d^1**		**n=3**	**Gp.IIIB: $s^2f^xd^1$**		**n=3**	**Gp.IIIB: $s^2f^xd^1$**		**n=3**
$[Be]2p^1$	^{5}B	**3.35**				$[Ba]5d^1$	^{57}La	**1.82**	$[Ra]6d^1$	^{89}Ac	**2.07**
$[Mg]3p^1$	^{13}Al	**2.53**				$[Ba]5d^04f^2$	^{58}Ce	**1.86**	$[Ra]6d^2$	^{90}Th	**2.37(4)**
$[Zn]4p^1$	^{31}Ga	**3.67**	$[Ca]3d^1$	^{21}Sc	**2.17**	$[Ba]5d^04f^3$	^{59}Pr	**1.85**	$[Ra]6d^15f^2$	^{91}Pa	**2.74(4)**
$[Cd]5p^1$	^{49}In	**3.86**	$[Sr]4d^1$	^{39}Y	**1.83**	$[Ba]5d^04f^4$	^{60}Nd	**1.88**	$[Ra]6d^15f^3$	^{92}U	**2.54**
$[Hg]6p^1$	^{81}Tl	**5.45**	$[Ba]5d^1$	^{71}Lu	**1.82**	$[Ba]5d^04f^5$	^{61}Pm	**1.91**	$[Ra]6d^15f^4$	^{93}Np	**2.41**
$[Cn]7p^1$	^{113}Uut		$[Ra]6d^1$	^{103}Lr	**2.07**	$[Ba]5d^04f^6$	^{62}Sm	**1.90**	$[Ra]6d^05f^6$	^{94}Pu	**2.20**
Gp.IVA: s^2p^2		**n=2**	**Gp.IVB: s^2d^2**		**n=4**	$[Ba]5d^04f^7$	^{63}Eu	**2.21**	$[Ra]6d^05f^7$	^{95}Am	**2.13**
$[Be]2p^2$	^{6}C	**4.72**				$[Ba]5d^04f^8$	^{64}Gd	**1.92**	$[Ra]6d^15f^7$	^{96}Cm	**2.14**
$[Mg]3p^2$	^{14}Si	**3.39**				$[Ba]5d^04f^9$	^{65}Tb	**1.89**	$[Ra]6d^05f^9$	^{97}Bk	**2.19**
$[Zn]4p^2$	^{32}Ge	**4.45**	$[Ca]3d^2$	^{22}Ti	**3.01**	$[Ba]5d^04f^{10}$	^{66}Dy	**1.91**	$[Ra]6d^05f^{10}$	^{98}Cf	**2.27**
$[Cd]5p^2$	^{50}Sn	**4.06**	$[Sr]4d^2$	^{40}Zr	**2.50**	$[Ba]5d^04f^{11}$	^{67}Ho	**1.87**	$[Ra]6d^05f^{11}$	^{99}Es	**2.20**
$[Hg]6p^2$	^{82}Pb	**4.08**	$[Ba]4f^{14}5d^2$	^{72}Hf	**2.64**	$[Ba]5d^04f^{12}$	^{68}Er	**1.88**	$[Ra]6d^05f^{12}$	^{100}Fm	**2.24**
$[Cn]7p^2$	^{114}Uuq		$[Ra]5f^{14}6d^2$	^{104}Rf		$[Ba]5d^04f^{13}$	^{69}Tm	**1.88**	$[Ra]6d^05f^{13}$	^{101}Md	**2.50**
Gp.VA: s^2p^3		**n=3**	**Gp.VB: s^2d^3**		**n=3**	$[Ba]5d^04f^{14}$	^{70}Yb	**1.98**	$[Ra]6d^05f^{14}$	^{102}No	**3.00**
$[Be]2p^3$	^{7}N	**5.68**				$[Ba]5d^14f^{14}$	^{71}Lu	**1.90**	$[Ra]6d^15f^{14}$	^{103}Lr	**2.20**
$[Mg]3p^3$	^{15}P	**3.70**									
$[Zn]4p^3$	^{33}As	**4.44**	$[Ca]3d^3$	^{23}V	**3.95**						
$[Cd]5p^3$	^{51}Sb	**4.4**	$[Sr]4d^3$	^{41}Nb	**3.10**						
$[Hg]6p^3$	^{83}Bi	**4.52**	$[Ba]4f^{14}5d^3$	^{73}Ta							
$[Cn]7p^3$	^{115}Uup		$[Ra]5f^{14}6d^3$	^{105}Db							
Gp.VIA: s^2p^4		**n=2**	**Gp.VIB: s^2d^4**		**n=3**	**Gp.VIIA: s^2p^5**		**n=1**	**Gp.VIIB: s^2d^5**		**n=2**
$[Be]p^4$	^{8}O	**5.42**				$[Be]2p^5$	^{9}F	**5.74**			
$[Mg]3p^4$	^{16}S	**3.75**				$[Mg]3p^5$	^{17}Cl	**4.23**			
$[Zn]4p^4$	^{34}Se	**4.09**	$[Ca]3d^4$	^{24}Cr	**3.44**	$[Zn]4p^5$	^{35}Br	**3.94**	$[Ca]3d^5$	^{25}Mn	**3.02**
$[Cd]5p^4$	^{52}Te	**3.06**	$[Sr]4d^4$	^{42}Mo	**4.00**	$[Cd]5p^5$	^{53}I	**3.41**	$[Sr]4d^5$	^{43}Tc	**4.60**
$[Hg]6p^4$	^{84}Po	**2.8**	$[Ba]4f^{14}5d^4$	^{74}W	**4.08(4)**	$[Hg]6p^5$	^{85}At	**3.07**	$[Ba]4f^{14}5d^5$	^{75}Re	
$[Cn]7p^4$	^{116}Uuh		$[Ra]5f^{14}6d^4$	^{106}Sg		$[Cn]7p^5$	^{117}		$[Ra]5f^{14}6d^5$	^{107}Bh	
Gp.VIIIA: s^2p^6			**Gp.VIIIB: s^2d^6**		**n=2**	**Gp.VIIIB: s^2d^7**		**n=2**	**Gp.VIIIB: s^2d^8**		**n=2**
$1s^2$	^{2}He										
$[Be]2p^6$	^{10}Ne										
$[Mg]3p^6$	^{18}Ar										
$[Zn]4p^6$	^{36}Kr		$[Ca]3d^6$	^{26}Fe	**3.76**	$[Ca]3d^7$	^{27}Co	**3.92**	$[Ca]3d^8$	^{28}Ni	**3.94**
$[Cd]5p^6$	^{54}Xe		$[Sr]4d^6$	^{44}Ru	**5.24(8)**	$[Sr]4d^7$	^{45}Rh	**4.96(3)**	$[Sr]4d^8$	^{46}Pd	**5.12**
$[Hg]6p^6$	^{86}Rn		$[Ba]4f^{14}5d^6$	^{76}Os	**4.89(4)**	$[Ba]4f^{14}5d^7$	^{77}Ir	**5.36(3)**	$[Ba]4f^{14}5d^8$	^{78}Pt	**5.39**
$[Cn]7p^6$	^{118}Uuo		$[Ra]5f^{14}6d^6$	^{108}Hs		$[Ra]5f^{14}6d^7$	^{109}Mt		$[Ra]5f^{14}6d^8$	^{110}Ds	

Acknowledgments

The author is grateful to the Institute of Biophysics of the Academy of Sciences of the Czech Republic (ASCR) for support by institutional research plans Nos. AV0Z50040507 and AV0Z50040702 grants of the ASCR.

References

1. R. Heyrovska, a) *Philippine J. Sci*., **137**, 133 (2008); b) http://arxiv.org/ftp/arxiv/papers/0708/0708.1108.pdf
2. R. Heyrovska, a) *J. Alloys Compds.*, **323 - 324**, 614 (2001); b) 198th Meeting of the Electrochemical Society, USA, Phoenix, Arizona, October 2000, Extended abstract No. 957; http://www.electrochem.org/dl/ma/198/pdfs/0957.PDF
3. A. J. Bard, R. Parsons, J. Jordan, *Standard Potentials in Aqueous Solutions*, (Marcell Dekker, NY, 1985)
4. R. Heyrovska, a) *Electrochem. Solid-State Lett.,* **12** (issue 10), F29-F30 (**2009)**; b) http://precedings.nature.com/documents/3395/version/1
5. S. Trasatti, *Pure & Appl. Chem*. **58**, 955 (1986).
6. W. A. Donald, R. D. Leib, J. T. O'Brien, M. F. Bush and E. W. Williams, *J. Am. Chem. Soc*., **130,** 3371 (2008).
7. J. Heyrovsky and J. Kuta, *Principles of Polarography*, (Publishing House of the Czechoslovak Academy of Sciences, Prague, 1965).