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# An estimation of the ionization potentials of actinides from a simple dependence of the aqueous standard potentials on the ionization potentials of elements including lanthanides

R. Heyrovska*

*J. Heyrovsky Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, Dolejskova 3, 182 23 Prague, Czech Republic*

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## Abstract

It was found recently that the ionization potentials and electron affinities of elements in the gaseous state are linked to the standard potentials of their principal oxidation states in aqueous solutions by simple linear relations. These relations are characteristic for each group of elements of the periodic table. In the case of the actinides, in the absence of adequate data on their ionization potentials, the linear relation obtained for the group IIIB elements (including lanthanides) has been found useful for estimating them using the available data on their standard oxidation potentials (obtained in most cases by radio-polarography). © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Metals; Electrochemical reactions; Electronic states; Thermodynamic properties; Valence fluctuations

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## 1. Introduction

The energies involved in removing or adding electrons from (or to) neutral atoms of elements in the gaseous state measured as ionization potentials, $I$ (or electron affinities, $E_A$) are different from the corresponding energies measured as the standard oxidation potentials, $E°$ in aqueous solutions. Therefore water plays a very significant role in the properties of elements involving electron transfer. The difference between $E°$ and $I$ (or $E_A$) is usually explained [1,2] in terms of the energies of sublimation, solvation, work function, etc. In calculating the differences it is to be noted that the zero of both $I$ and $E°$ are arbitrary. $E°$ is referred [1,2] to as the standard hydrogen electrode (S.H.E.) with $E°=0$ and $I=0$ refers to an electron at infinity. Recently, the author found [3] that $E°$ for the principal oxidation states in aqueous solutions and the values of $I$ for the gaseous state of elements of various groups in the periodic table are related to each other in a simple linear way. This linear relation is utilized here to estimate the ionization potentials of actinides by using the available data [2] on the standard oxidation potentials obtained by radio-polarography.

## 2. Method of estimation

The standard oxidation potentials ($E°$) in aqueous solutions [1,2] and the ionization potentials ($I$) [4] of elements of groups IA (except H and Li) ($I = I_1$), IIA (except Be) ($I = I_1 + I_2$) and IIIB (Sc, Y and the lanthanides except Eu) ($I = I_1 + I_2 + I_3$) were recently shown [3] to be related to each other by the simple Eq. (1):

$$E°/I = a - b(I - I_r) \tag{1}$$

In the above equation, $a = (E°/I)_r$ for $I = I_r$, any suitable reference value and $b$ is the slope of the linear plot of $(E°/I)$ vs. $I$. For each group of elements mentioned above, $a$ and $b$ are constants and can be obtained by linear regression. All the data pertaining to Eq. (1) are given in Table 1. The linear dependences of the ratio $(E°/I)$ on $I$ for elements of groups IA, IIA and IIIB (including lanthanides, except Eu) are compared in Fig. 1. The reference values $I_r$ were chosen as the points of intersection of the

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*Fax: +420-2-858-2307.

*E-mail address:* rheyrovs@jh-inst.cas.cz (R. Heyrovska).

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Table 1
Ionization potentials $I$ [4] and standard oxidation potentials in aqueous solutions $E°$ [2] (see Eq. (1))

| Element | Group, $b$ (eV$^{-1}$) | $I = \Sigma I_n =$ | $I$ (eV) | $E°$ (V) | $E°/I$ | $E°/I_{cal}$ | $E°_{cal}$ | $I_{cal}$ |
|---|---|---|---|---|---|---|---|---|
| (H)[a] | IA | $I = I_1 =$ | 13.597 | 0.000 | 0.000 | −0.978 | −13.300 | 13.597 |
| Intersecn. | (IA/IIA) | $I_r =$ | 6.455 | 1.901 | 0.295 | 0.295 | 1.901 | 6.455 |
| Na | IA, $b = 0.1782$ | $I = I_1 =$ | 5.138 | 2.714 | 0.528 | 0.529 | 2.719 | 5.129 |
| K | | $I = I_1 =$ | 4.340 | 2.925 | 0.674 | 0.671 | 2.914 | 4.357 |
| Rb | | $I = I_1 =$ | 4.176 | 2.925 | 0.700 | 0.701 | 2.926 | 4.175 |
| Cs | | $I = I_1 =$ | 3.894 | 2.923 | 0.751 | 0.751 | 2.924 | 3.892 |
| Fr[b] | | $I = I_1 =$ | 3.938 | 2.92 | 0.741 | 0.743 | 2.93 | 3.930 |
| Mg | IIA, $b = 0.0117$ | $I = I_1 + I_2 =$ | 22.679 | 2.36 | 0.104 | 0.104 | 2.35 | 22.748 |
| Ca | | $I = I_1 + I_2 =$ | 17.983 | 2.84 | 0.158 | 0.159 | 2.86 | 17.875 |
| Sr | | $I = I_1 + I_2 =$ | 16.723 | 2.89 | 0.173 | 0.174 | 2.90 | 16.641 |
| Ba | | $I = I_1 + I_2 =$ | 15.215 | 2.92 | 0.192 | 0.191 | 2.91 | 15.258 |
| Ra | | $I = I_1 + I_2 =$ | 15.424 | 2.92 | 0.189 | 0.189 | 2.91 | 15.456 |
| Sc | IIIB, $b = 0.0021$ | $I = I_1 + I_2 + I_3 =$ | 44.11 | 2.03 | 0.046 | 0.049 | 2.14 | 41.80 |
| Y | | $I = I_1 + I_2 + I_3 =$ | 38.97 | 2.37 | 0.061 | 0.059 | 2.31 | 39.92 |
| La | | $I = I_1 + I_2 + I_3 =$ | 35.81 | 2.38 | 0.066 | 0.066 | 2.36 | 36.06 |
| Ce | | $I = I_1 + I_2 + I_3 =$ | 36.62 | 2.34 | 0.064 | 0.064 | 2.35 | 36.39 |
| Pr | | $I = I_1 + I_2 + I_3 =$ | 37.65 | 2.35 | 0.062 | 0.062 | 2.34 | 37.82 |
| Nd | | $I = I_1 + I_2 + I_3 =$ | 38.35 | 2.32 | 0.060 | 0.061 | 2.33 | 38.24 |
| Pm | | $I = I_1 + I_2 + I_3 =$ | 38.79 | 2.29 | 0.059 | 0.060 | 2.32 | 38.33 |
| Sm | | $I = I_1 + I_2 + I_3 =$ | 40.11 | 2.30 | 0.057 | 0.057 | 2.28 | 40.38 |
| (Eu)[a] | | $I = I_1 + I_2 + I_3 =$ | 41.83 | 1.99 | 0.048 | 0.053 | 2.23 | 37.30 |
| Gd | | $I = I_1 + I_2 + I_3 =$ | 38.86 | 2.28 | 0.059 | 0.060 | 2.32 | 38.26 |
| Tb | | $I = I_1 + I_2 + I_3 =$ | 39.40 | 2.31 | 0.059 | 0.058 | 2.30 | 39.52 |
| Dy | | $I = I_1 + I_2 + I_3 =$ | 40.41 | 2.29 | 0.057 | 0.056 | 2.28 | 40.64 |
| Ho | | $I = I_1 + I_2 + I_3 =$ | 40.66 | 2.33 | 0.057 | 0.056 | 2.27 | 41.74 |
| Er | | $I = I_1 + I_2 + I_3 =$ | 40.77 | 2.32 | 0.057 | 0.056 | 2.27 | 41.75 |
| Tm | | $I = I_1 + I_2 + I_3 =$ | 41.92 | 2.32 | 0.055 | 0.053 | 2.23 | 43.63 |
| Yb | | $I = I_1 + I_2 + I_3 =$ | 43.47 | 2.22 | 0.051 | 0.050 | 2.17 | 44.47 |
| Lu | | $I = I_1 + I_2 + I_3 =$ | 40.27 | 2.30 | 0.057 | 0.057 | 2.28 | 40.61 |
| Intersecn. | (IIA/IIIB) | $I_r =$ | 23.73 | 2.17 | 0.091 | 0.091 | 2.17 | 23.74 |

[a] Excluded in regressions. $E°/I_{cal} \sim -1$ if H follows group IA.
[b] $E°$ (approx.) from Ref. [4].

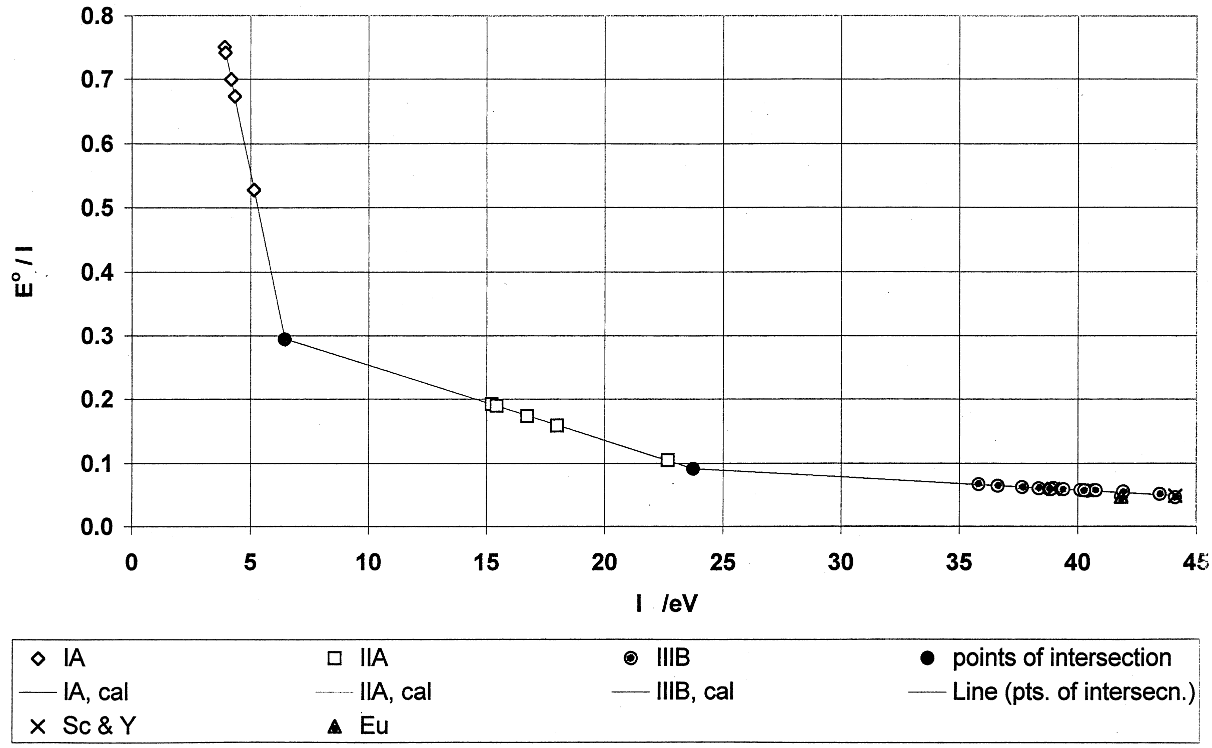

Fig. 1. Comparison of the linear dependence of $E°/I$ on $I$ for elements of groups IA, IIA and IIIB (including lanthanides); see Eq. (1) and Table 1.

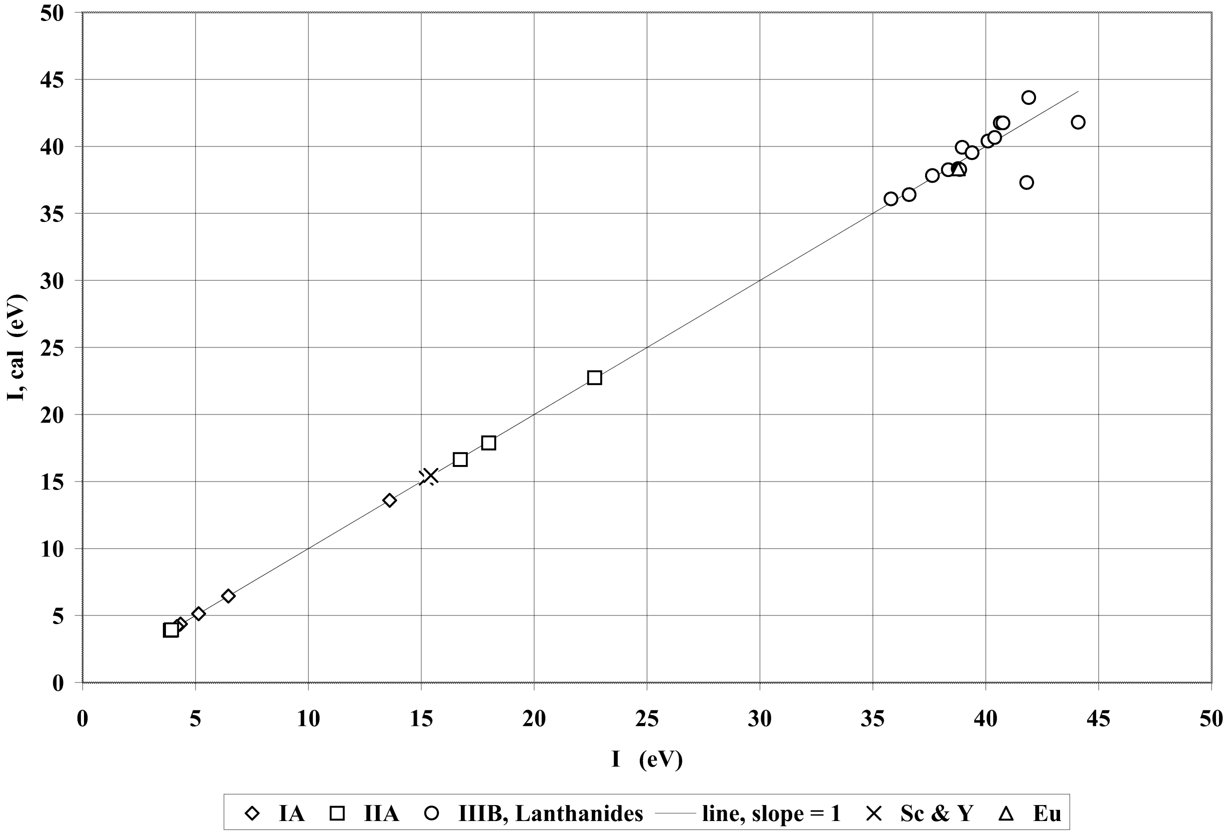

Fig. 2. Comparison of $I_{cal}$ obtained using $E°$ [2] and the constants $a$ and $b$ in Eq. (1) with $I$ [4] for elements of groups IA, IIA and IIIB (including lanthanides); see data in Table 1.

lines for groups IA and IIA and for groups IIA and IIIB as shown in Fig. 1. Eq. (1) reproduces very well the values of $E°$ and $I$ for elements of groups IA and IIA and reasonably well for elements of group IIIB, as can be seen from the columns headed $E°_{cal}$ and $I_{cal}$ in Table 1. Fig. 2 shows the agreement of $I$ with that calculated by using $E°$ [2] and the constants $a$ and $b$ in Eq. (1).

From Eq. (1), one can see that the fraction, $(I - E°)/I$ which indicates the facility of oxidation in the aqueous phase compared to the gas phase also varies linearly with $I$:

$$(I - E°)/I = (1 - a) + b(I - I_r) \quad (2)$$

Another note from the thermodynamic point of view is that the free energy $\Delta G_g = nFI$ (where $F$ is the Faraday constant) is positive (energy is expended) in the gas phase for extracting the $n$ electrons out of the atom, and $\Delta G_{aq} = -nFE°$ is negative (energy is released) in aqueous solutions when the standard oxidation potential $E°$ is positive with respect to the S.H.E. (as in the case of the elements in Table 1).

Similarly, it was found [3] that for elements of groups VIII, IB, IIB, IIIA (except B) and IVA (except C and Si), $E°/I$ varies linearly with $E°$ and that for elements of groups VIA (except O) and VIIA (except F), the ratio $E°/E_A$ varies linearly with $E°$. For elements of the other groups not mentioned above, relevant data for at least three elements were not available for assessing the linearity.

## 3. Results and discussion

Since the above linear relations reproduce the $E°$ and $I$ data reasonably well, they can be used to obtain either of the two from a knowledge of the other. This result comes in handy for the case of the actinide elements, which belong to group IIIB like the lanthanides. The most common oxidation state is +3 (For elements from Th to Np, the +4 state is more stable than the +3 state). The available $E°$ data in Ref. [2] and $I$ data in Ref. [4] show that for the actinides, there are data for the first ionization potential $I_1$ and not for the second and third, $I_2$ and $I_3$ in most cases (except for Th). On the other hand, data on $E°$ (for the trivalent state) are available [2] (in most cases measured using radio-polarographic methods) for all the actinides (except Th and Pa). Therefore, the linear Eq. (1) could be used for estimating $I$, the sum of the first three ionization potentials. For Th, since $E°$ is not available for $Th/Th^{3+}$ oxidation (since the tetravalent state is more stable) $E°$ could be obtained from the known [4] ionization potential sum, $I$ $(= I_1 + I_2 + I_3)$. The estimated values of $I$ (in eV) and other relevant data pertaining to Eq. (1) for the

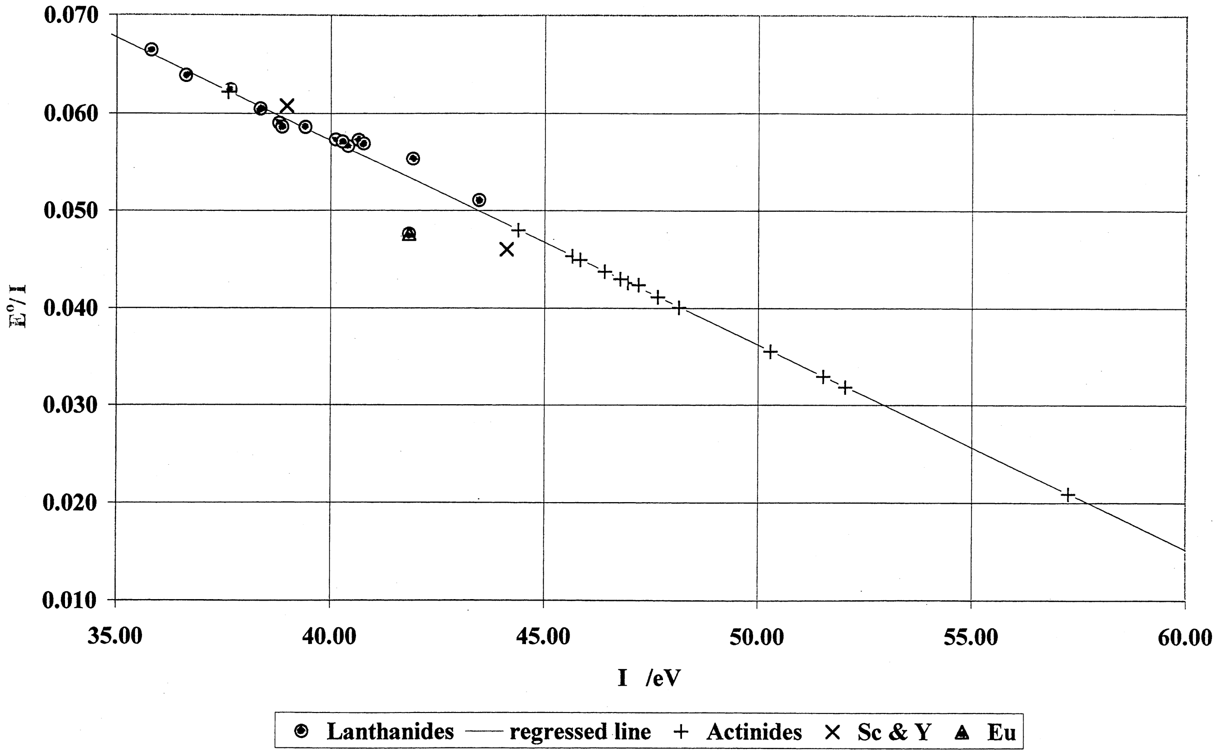

Fig. 3. The linear dependence of $E°/I$ on $I$ for elements of group IIIB, including the values estimated for actinides in Table 2.

actinides are given in Table 2. In Table 2, Pa is not included since only $I_1$ is available for this element and no data could be found for the $E°$ for the +3 state which is least stable. Fig. 3 shows the linear graph of $E°/I$ vs. $I$ for group IIIB elements including actinides.

## 4. Conclusions

In the literature, there is a lack of data on the ionization potentials of actinide elements for obvious reasons of their instability. Recently, a simple linear relation was shown to hold between the ionization potentials and the standard aqueous oxidation potentials for the principal oxidation states of elements including lanthanides of the periodic table. This linear relation [see Eq. (1)] has been used here for estimating the ionization potentials of the actinides by using the existing data on their oxidation potentials obtained by radio-polarography.

Table 2
Group IIIB: actinides, standard oxidation potentials $E°$ [2] and ionization potentials $I$ ($= I_1 + I_2 + I_3$) from Eq. (1)

| Actinides | $E°$ (V) | $I$ (eV) | $E°/I =$ | $= a + b(I_r - I)$<br>$b = 0.0021$ |
|---|---|---|---|---|
| Ac ($I_3$ ?) | 2.13 | 44.39 | 0.0480 | 0.0480 |
| Th[a] ($E°$ ?) | 2.34 | 37.60 | 0.0622 | 0.0622 |
| U ($I_3$ ?) | 1.66 | 52.05 | 0.0319 | 0.0319 |
| Np ($I_2$, $I_3$ ?) | 1.79 | 50.29 | 0.0356 | 0.0356 |
| Pu ($I_2$, $I_3$ ?) | 2.00 | 46.95 | 0.0426 | 0.0426 |
| Am ($I_2$, $I_3$ ?) | 2.07 | 45.65 | 0.0453 | 0.0453 |
| Cm ($I_2$, $I_3$ ?) | 2.06 | 45.84 | 0.0449 | 0.0449 |
| Bk ($I_2$, $I_3$ ?) | 2.01 | 46.77 | 0.0430 | 0.0430 |
| Cf ($I_2$, $I_3$ ?) | 1.93 | 48.15 | 0.0401 | 0.0401 |
| Es ($I_2$, $I_3$ ?) | 2.00 | 46.95 | 0.0426 | 0.0426 |
| Fm ($I_2$, $I_3$ ?) | 1.96 | 47.65 | 0.0411 | 0.0411 |
| Md ($I_2$, $I_3$ ?) | 1.70 | 51.53 | 0.0330 | 0.0330 |
| No ($I_2$, $I_3$ ?) | 1.20 | 57.26 | 0.0210 | 0.0210 |
| Lr ($I_1$, $I_2$, $I_3$ ?) | 2.03 | 46.41 | 0.0437 | 0.0437 |
|  |  | $I_r = 60$ |  | $a = 0.0152$ |

[a] For Th, $I$ is from Ref. [4] and $E°$ is the estimated value.

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## References

[1] W.W. Latimer, The Oxidation States of the Elements and their Potentials in Aqueous Solutions, Prentice-Hall, Englewood Cliffs, NJ, 1956.

[2] A.J. Bard, R. Parsons, J. Jordan (Eds.), Standard Potentials in Aqueous Solutions, IUPAC Commission on Electrochemistry and Electroanalytical Chemistry, Marcel Dekker, New York, 1985.

[3] R. Heyrovska, in: Extended Abstract No. 957, 198th Meeting of the Electrochemical Society, Phoenix, Arizona, USA (October), 2000.

[4] Mark Winter, University of Sheffield, Document modification date: 23 March 2000. Copyright 1993–2000. http://www.webelements.com/webelements/elements