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# THE COHESIVE ENERGY OF URANIUM DIOXIDE AND THORIUM DIOXIDE

CRMET-788

BY

B. G. CHILDS

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## ABSTRACT

Theoretical values have been calculated of the heats of formation of uranium dioxide and thorium dioxide on the assumption that the atomic binding forces in these solids are predominantly ionic in character.

The good agreement found between the theoretical and observed values shows that the ionic model may, with care, be used in calculating the energies of defects in the uranium and thorium dioxide crystal structures.

## 1. INTRODUCTION

Although much interest has recently been shown in the physical and technological properties of uranium dioxide and, to lesser extent, thorium dioxide, little attention has so far been paid in the published literature to the fundamental question as to the nature of the forces responsible for cohesion in these solids - that is to the extent to which atomic interactions of various types contribute to the measured binding energies. This subject is not only in itself of considerable fundamental interest but also has important technological implications since, for example, it is basic to the calculation of the energies and behaviour of lattice defects produced in the oxides by neutron bombardment in a nuclear reactor. It is the purpose of this note to examine this question by means of a calculation of the heats of formation of uranium dioxide and thorium dioxide based on the assumption that the binding forces are primarily electrostatic in character.

## 2. THE OBSERVED HEATS OF FORMATION

### 2.1 Uranium Dioxide

The heat of formation of uranium dioxide, $H_T$, - the energy released in the reaction

$$U(s) + O_2(g) \longrightarrow UO_2(s) \quad \text{at } T^oK$$

has been measured by Huber, Holley and Meierkord[1]. They found

$$H = -259.2 \pm 0.6 \text{ kcal mol}^{-1} \text{ at } 298^{\circ}K.$$

It is desirable, in order to avoid introducing lattice vibrational energy and entropy terms into the calculation of binding energy, to correct this value of H from 298°K to 0°K and zero atomic vibrational amplitude by means of the relation

$$H_o = H_T - Z - \int_o^T C_p dt$$ where Z is the zero point energy.

Z is given approximately, using the Debye expression for the vibrational energy of a solid, by $Z = \frac{27}{8} R\theta_D$. $\theta_D$, the Debye temperature, is approximately 680°K for uranium dioxide so that $Z = 4.6$ kcal mol$^{-1}$. The value of $\int_o^T C_p dt$ at 298°K obtained from the specific heat data of Jones and Long[2] is 2.8 kcal mol$^{-1}$. The corrected observed value of the heat of formation for uranium dioxide is thus

$$\underline{H_o = -266.6 \text{ kcal mol}^{-1}}$$

2.2 Thorium Dioxide

For thorium dioxide, Huber, Holley and Meierkord[1] found

$$H = -293.2 \pm 0.4 \text{ kcal mol}^{-1} \text{ at } 298^{\circ}K$$

This agrees well with the value

$$H = -292.6 \pm 1.4 \text{ kcal mol}^{-1} \text{ at } 298^{\circ}K$$

obtained by Roth and Becker[3]. We will adopt the former value since it appears to be slightly the more accurate.

The specific heat measurements of Osborne and Westrum[4] give 2.5 kcal $mol^{-1}$ for the enthalpy of thorium dioxide at 298°K and, since the Debye temperature is approximately 700°K, the zero point energy for thorium dioxide is 5.0 kcal $mol^{-1}$.

The corrected heat of formation for thorium dioxide is therefore

$$H_o = -300.7 \text{ kcal mol}^{-1}$$

## 3. THE BORN-HABER CYCLE

In order to calculate the heats of formation theoretically, it is necessary first to construct a thermodynamic cycle of the Born-Haber type[5]. In this cycle, the atomic and electronic processes leading to the formation of solid oxide in the standard state are imagined to be broken down into a series of steps, each step having associated with it the emission or absorption of a characteristic amount of energy.

The cycle for uranium dioxide considered as an ionic solid is

$$U(s) \xrightarrow{V_o} U(g) \xrightarrow{I} U(g)^{4+} + 4e^-$$

$$UO_2(s) \xleftarrow{H_o} + \qquad + \xrightarrow{E_o} UO_2(s)$$

$$O_2(g) \xrightarrow[D_o]{} 2O(g) \xrightarrow[2A]{} 2O(g)^{2-} - 4e^-$$

where $H_o$ is the heat of formation of uranium dioxide, $V_o$ the heat of sublimation of solid uranium, $D_o$ the heat of dissociation of gaseous molecular to atomic oxygen, I the total heat of ionization of free uranium atoms to the $U^{4+}$ state, A the electron affinity of oxygen for the $O^{2-}$ state and $E_o$ the lattice energy of uranium dioxide. The energies are those appropriate to the formation of one mol of uranium dioxide at $0^{\circ}K$.

It will be seen from this cycle that two hypothetical routes for the formation of solid uranium dioxide may be considered: either by direct reaction of solid uranium with oxygen or by the formation of free gaseous uranium and oxygen ions and their subsequent combination. Since the total energy involved should be the same for either route we have

$$H_o = E_o + I + V_o + 2A + D_o$$

where a positive sign indicates the absorption of energy in the reaction step.

The two terms on the extreme right of the expression are common to the calculation for both uranium and thorium dioxides. A has been estimated by Sherman[7] to be - 166.5 kcal $mol^{-1}$. This estimate was based upon a calculation of lattice energies for alkaline earth oxides. An independent estimate by de Boer and Verwey[8] gave a value of - 173 kcal $mol^{-1}$. Since the two estimates agree closely we will take the mean value

$$A = -170 \text{ kcal mol}^{-1}$$

$D_o$ is known with fair accuracy[9] to be

$$D_o = 117.2 \text{ kcal mol}^{-1}$$

The remaining terms in the expression are dealt with in the following sections.

## 4. THE HEATS OF SUBLIMATION OF URANIUM AND THORIUM

The heat of sublimation of uranium at 0°K has been calculated from vapour pressure data by Rauh and Thorn[10]. They found

$$\underline{V_o = 116.6 \text{ kcal mol}^{-1}} \text{ for uranium.}$$

In the case of thorium, no reliable values exist for the vapour pressure of the solid metal. The heat of vaporization of thorium at the melting point, 1970°K, calculated from the vapour pressure data reported for the liquid metal by Martini[11] is 130.4 kcal mol$^{-1}$. To correct this to $V_o$, we assume first that the latent heat of fusion of thorium, in line with that of other body centred cubic metals of similar melting points, is close to 3.5 kcal mol$^{-1}$. The enthalpy of solid thorium at 1970°K calculated from the specific heat data of Griffel and Skochdopole[12] and Jaeger and Veenstra[13], is 19.3 kcal mol$^{-1}$ so that

$$\underline{V_o = 153.2 \text{ kcal mol}^{-1}} \text{ for thorium.}$$

## 5. THE IONIZATION POTENTIALS OF URANIUM AND THORIUM

One of the largest terms in the energy expression is the heat of ionization - the sum of the first four ionization potentials for free uranium and thorium atoms. In the case of thorium, values have been determined from spectrographic data[14, 15] for the third and fourth potentials $Th_{III}$ and $Th_{IV}$, while a reliable estimate has been made by Finkelnburg[16] for $Th_{II}$. These values are

| | II | III | IV | |
|---|---|---|---|---|
| Th | 11.5 | 20.0 | 28.7 | e.v. |

In the case of uranium, only the first potential, $U_I$, has been measured[17], the value being 4.7 e.v.

Despite this lack of information, it is possible to estimate the missing values with quite a high level of confidence using Finkelnburg's method[16]. In this, advantage is taken of the fact that, for a series of ions having the same outer electron configuration, a simple relation exists between the atomic number of the ion, Z, and the screening constant, S. S is given by

$$S = Z - Z_e = Z - n\sqrt{\frac{I_i}{R}}$$ where $Z_e$ is the effective nuclear charge acting on the outermost electron, $I_i$ is its ionization potential and R is the Rydberg constant, 13.595 e.v. Examples of such isoelectronic ion series are 1. Ra, $Ac^+$, $Th^{2+}$, $Pa^{3+}$, $U^{4+}$ and 2. Fa, $Ra^+$, $Ac^{2+}$, $Th^{3+}$, $Pa^{4+}$, $U^{5+}$. Measured values of the appropriate ionization potentials in addition to $Th_{III}$ and $Th_{IV}$ also exist for $Ra_I$ and $Ra_{II}$ while $Ac_{II}$ and $Fa_I$ have been estimated by Finkelnburg. Plotting s against Z for the two series

as shown in Figure 1, we obtain two straight lines which, extrapolated to $U^{4+}$ and $U^{5+}$ give values for $U_V$ and $U_{VI}$, the fifth and sixth potentials of uranium, of 44.2 and 58.8 e.v. respectively. We now have values for three of the first six ionization potentials for uranium. To estimate $U_{II}$, $U_{III}$ and $U_{IV}$, we note that in the uranium atom which has six electrons outside the rare gas core it is not necessary to break into the outermost full shell (6p) in going from U to $U^{6+}$. There should, therefore, be no great discontinuity in the series $U_I$ - $U_{VI}$ the chief factor responsible for the increasing energy being the increasing electrostatic attraction between the electron and the ion due to the increasing ionic charge.

In the case of the transition elements Cr, Mo, V and Nb, which have 6, 6, 5 and 5 electrons respectively outside the closed shell, the ionization potential for the removal of the outer electrons is given quite well by the relation $(I_m)^{1/2} = km$ where m is the order of the ionization potential and k is a constant. This relation is also obeyed quite well for $Th_{II}$ - $Th_{IV}$ and for Ce, a rare earth. We would thus expect a similar relation to hold in the case of uranium and in fact in the graph of $(I_m)^{1/2}$ against m for uranium (Figure 2) the points for $U_I$, $U_V$ and $U_{VI}$ fall on a straight line. Thus by interpolation from this line we can estimate the values $U_{II}$, $U_{III}$ and $U_{IV}$ required. The estimated values for the first six ionization potentials of uranium are accordingly.

| | I | II | III | IV | V | VI | |
|---|---|---|---|---|---|---|---|
| $U_i$ | 4.7 | 10.8 | 19.4 | 30.8 | 44.2 | 58.8 | e.v. |

As would be expected, by analogy with the rare earth series, these are much the same as the corresponding potentials of thorium and other members of the actinide series, where values are available for comparison.

We thus have for the heat of ionization

$$I = \sum_{I-IV} U_i = \underline{1515 \text{ kcal mol}^{-1}} \text{ for uranium.}$$

The missing potential for thorium, $Th_I$, is found immediately from Figure 2 to be 5.3 e.v. so that the heat of ionization

$$I = \sum_{I-IV} Th_i = 1511 \text{ kcal mol}^{-1} \text{ for thorium.}$$

## 6. THE LATTICE ENERGY

### 6.1 Uranium Dioxide

The lattice energy of uranium dioxide considered as an ionic solid includes the sum over the lattice of the electrostatic attractive and repulsive potentials of the $U^{4+}$ and $O^{2-}$ ions together with the repulsive potential arising from the overlap of the charge clouds from neighbouring ions. These two terms account almost entirely for the resultant lattice energy: however, in exact calculations it is necessary also to allow for the smaller contribution from the van der Waals forces which arise from the fluctuating polarization interactions of the ions. The lattice electrostatic potential, the summation of the potential energies of individual ions i and j at distance $r_{ij}$ is

$$E_{eo} = \sum_{ij} \frac{e_i e_j}{r_{ij}} = -N \frac{A e^2 Z^2}{2}$$

where N is Avogadro's number, A = 11.637 is the Madelung constant for the uranium dioxide lattice (fluorite structure) relative to the lattice constant, a, and Z = 2 for uranium dioxide.

Thus

$$E_{eo} = -\frac{1.553}{a} \times 10^{-4} \text{ kcal mol}^{-1} = -2821 \text{ kcal mol}^{-1}.$$

The energy contribution from the van der Waals forces is also negative since they assist the electrostatic forces in maintaining cohesion. An expression for the van der Waals potential, w, between two atoms or ions at distance r apart has been developed by London[18]. He showed that the principal term comes from the time average of the interaction between the electric dipole induced by atom (1) on atom (2) with that induced by (2) on (1). This potential which varies rapidly with r is

$$W_{12} = \frac{-3h}{2r^6} \frac{\nu_1 \nu_2}{\nu_1 + \nu_2} \alpha_1 \alpha_2$$

where $\alpha_1$ and $\alpha_2$ are the polarizabilities and $\nu_1$ and $\nu_2$ are characteristic excitation frequencies of the ions in the solid. The total van der Waals contribution to the lattice energy is the sum of w over the lattice

$$E_w = \sum_{12} w_{12}$$

In the case of uranium dioxide, the values for $\alpha$ and $\nu$ are not known with any certainty. For the $U^{4+}$ ion

$$\alpha \simeq R^3 = 0.9 \times 10^{-24} \text{ cm}^3$$

where R is the ionic radius, and $\nu$ calculated from the fifth ionization potential for uranium is approximately $1.07 \times 10^{16}$ cycle $\text{sec}^{-1}$. For the $O^{2-}$ ion

$$\alpha = 2.74 \times 10^{-24} \text{ cm}^3$$

but no value for $\nu$ seems readily available in the literature. Since the van der Waals term represents only a very small fraction of the lattice energy, no serious error should be introduced if we take for $\nu$ the value appropriate to the $Cl^-$ ion, $9.1 \times 10^{14}$ cycle $\text{sec}^{-1}$(11). Summing over the lattice for the van der Waals interaction between each ion and its nearest and next nearest neighbours we have

$$E_w = -21.5 \text{ kcal mol}^{-1} .$$

For the repulsive, overlap potential between two ions we use the semi-empirical expression of Born and Mayer(19)

$$\epsilon_r = C \exp(-r\rho^{-1})$$

in which $\rho$, which is approximately constant for all ions, has a value of $0.345 \times 10^{-8}$ cm. The constant C is given by

$$C = b\left(1 + \frac{Zi}{ni} + \frac{Zj}{nj}\right) \exp\left[(R_i + R_j)\,\rho^{-1}\right]$$

where Zi, Zj are the valencies, ni, nj the numbers of valence

electrons (eight for ions having rare gas configurations) and Ri, Rj are the radii of the ions i and j.

The constant b which is also independent of the type of ion considered can be found from the equilibrium condition $(\frac{dE}{da}_{a_o}) = 0$.

Summing over the lattice for nearest and next nearest neighbours, we have

$$E_r = b\,(5.80 \exp(-1.255 \times 10^8 a) + 2.00 \exp(-2.048 \times 10^8 a) + 6.08 \exp(-1.449 \times 10^8 a)) \times 10^{28}.$$

Using the condition

$$\left(\frac{dE}{da}\right)_{a_o} = \left[\left(\frac{dE_{eo}}{da}\right) + \left(\frac{dE_w}{da}\right) + \left(\frac{dE_r}{da}\right)\right]_{a_o} = 0$$

with

$a_o = 5.47 \times 10^{-8}$ cm ,

we have $b = 4.99 \times 10^{-23}$

and $E_r = 411$ kcal mol $^{-1}$ .

The total lattice energy of uranium dioxide in the absence of covalent binding is therefore

$$E_o = E_{eo} + E_w + E_r = \underline{-2431} \text{ kcal mol}^{-1}$$

6.2 Thorium Dioxide

The electrostatic energy of thorium dioxide is, on account of its larger lattice constant, somewhat less than that of uranium dioxide:

$$E_{eo} = -2774 \text{ kcal mol}^{-1}$$

The van der Waals potential, in contrast, is slightly larger both because of the greater size and hence polarizability of the $Th^{4+}$ ion

$$\alpha = 1.06 \times 10^{-24} \text{ cm}^3 ,$$

and also since the fifth ionization potential of thorium, which involves breaking into the outer closed shell of the radon configuration, must be considerably greater than that of uranium. A reasonable estimate for $Th_V$ based on the trend shown for the fifth potential in the series Si, Ti, Zr, Ce, all of which have four electrons outside the rare gas shell, is 60 e.v. thus giving a value for $\nu$ of $1.45 \times 10^{16}$ cycle $sec^{-1}$.

Taking the same values for the polarizability and excitation frequency of the oxygen ions as before we obtain

$$E_W = -21.9 \text{ kcal mol}^{-1}.$$

In the calculation of the repulsive potential the constant b is $5.08 \times 10^{-23}$ and

$$E_r = 398 \text{ kcal mol}^{-1} .$$

Thus

$$E_o = E_{eo} + E_w + E_r = \underline{-2398 \text{ kcal mol}^{-1}} \text{ for thorium dioxide.}$$

7. THE CALCULATED HEATS OF FORMATION

The calculated values for $H_o = E_o + I + V_o + 2A + Do$ are thus

$$-2431 + 1515 + 117 + 340 + 117 = \underline{-342 \text{ kcal mol}^{-1}} \text{ for uranium dioxide}$$

and

$$-2398 + 1511 + 153 + 340 + 117 = \underline{-270 \text{ kcal mol}^{-1}} \text{ for thorium dioxide.}$$

These values are, respectively, 75 kcal $\text{mol}^{-1}$ greater and 24 kcal $\text{mol}^{-1}$ less numerically than the observed values.

Considering the size and uncertainty of several of the terms this agreement between theory and experiment must be regarded as quite satisfactory and certainly consistent with the assumption of a considerable amount of ionic binding in the uranium and thorium dioxide structures.

The terms in the expression most likely to be in error by an appreciable amount are the heat of ionization, I, and the repulsive

potential $E_r$. An increase of 3 e.v. in the sum of the first four ionization potentials for uranium (65.7 e.v.) would be sufficient to remove the discrepancy for uranium dioxide and this is not out of the question.

## 8. THE COMPRESSIBILITIES OF URANIUM DIOXIDE AND THORIUM DIOXIDE

It is interesting to compare the bulk compressibilities of the two oxides calculated from the lattice energy expression using the relation

$$\beta = \frac{9Na_o}{4}\left[\frac{\partial^2 E}{\partial a^2}\right]^{-1}_{a_o}$$

Since this relation involves the second derivative of the lattice energy, the calculated compressibility is very sensitive to the exact form and parameters of the energy expression.

### 8.1 Observed Values

Only two experimental determinations of the elastic constants of the oxides have been made. Ryshkewitch[20] using two samples of "high grade purity" thoria "fired to cone 40" (1880°C) found mean values for the rigidity modulus, Young's modulus and Poisson's ratio of $0.58 \times 10^{12}$ dyne $cm^{-2}$, $1.37 \times 10^{12}$ dyne $cm^{-2}$ and 0.17 at room temperature. The bulk compressibility calculated from these results is

$\beta = 1.45 \times 10^{-12}$ $cm^2$ $dyne^{-1}$ at 300°K for thorium dioxide.

An investigation by Lang[21] of the Young's Modulus of two uranium dioxide specimens over a temperature range from 25 to 825°C gave a value of $1.82 \times 10^{12}$ dyne $cm^{-2}$ for 93% dense material at 20°C. The value decreased to $1.62 \times 10^{12}$ dyne $cm^{-2}$ at 825°C so that, making a rough extrapolation, it should be about $1.9 \times 10^{12}$ dyne $cm^{-2}$ at 0°K.

Assuming that Poisson's ratio is the same for uranium dioxide as for thorium dioxide, which has a similar melting point, we obtain

$\beta = 1.04 \times 10^{-12}$ $cm^2$ $dyne^{-1}$ at 0°K for uranium dioxide.

8.2 Calculated Values

The calculated values are $\beta = 0.385 \times 10^{-12}$ $cm^2$ $dyne^{-1}$ at 0°K for thorium dioxide and $\beta = 0.36 \times 10^{-12}$ $cm^2$ $dyne^{-1}$ at 0°K for uranium dioxide - about one third of the observed values. This agreement is about as good as could be expected. The discrepancy occurs largely as a result of uncertainty in the expression for the repulsive potential. In the calculation of lattice energy this term plays a relatively minor role being only one seventh of the electrostatic term; however, in the compressibility expression the repulsive term is over three times as large as the electrostatic term, due to the rapid variation with interatomic distance of the repulsive forces, so that errors in it are of much greater importance. Furthermore, since the two terms are opposite in sign, the error in their sum is still greater. To obtain agreement the repulsive contribution to the calculated compressibility would have to be about one half of that calculated from the Born-Mayer function.

The only parameter which could be adjusted to give such a change is the exponent $\rho$ and even this would have to assume unreasonably large values to give agreement. It thus seems - as is not surprising - that the actual form of the semi-empirical function assumed for the repulsive overlap forces is incorrect so far as its second differential is concerned.

## 9. DISCUSSION

The only published discussion of the nature of the binding forces in uranium and thorium dioxides appears to be that of Zachariasen[22]. He has calculated a revised set of radii for ions having rare gas electron configurations as well as a complimentary set of values of the correction constants necessary to allow for the effect of differences in the cation coordination in various ionic crystals. For the large majority of crystals known to have predominantly ionic binding, excellent agreement is obtained between the observed interatomic distances and those calculated using Zachariasen's table. However, for the quadrivalent salts of the "thoride" series, in particular thorium and uranium dioxides, this agreement breaks down and the calculated interatomic distances are greater than the observed ones. For uranium dioxide, the calculated O-U distance is 2.47A while the observed distance is 2.36A. Zachariasen concludes from this that the binding in the oxides is predominantly covalent in character.

On studying Zachariasen's radii in more detail, however, the validity of his conclusion becomes less obvious. For example, in

the series of caesium halides from caesium fluoride to caesium iodide, it is generally agreed that the character of the binding changes from being almost purely ionic to being partially covalent. Nevertheless, the calculated interatomic distance shows no systematic deviation from the observed distance as expected but instead the two agree very closely throughout the whole series. Similarly, the interatomic distances predicted for the salts of barium - the most electropositive alkaline earth - with elements of group 6 in the perodic table show no systematic trend relative to the observed distances on going from barium oxide to barium telluride despite the considerable decrease in anion electronegativity through the series. In addition, in many salts, for example beryllium telluride, silicon tetraiodide, magnesium selenide and silicon disulphide, in which covalent binding would be expected to predominate, the interatomic distances calculated from Zachariasen's radii show the same close agreement with the observed distances as occurs for purely ionic crystals.

Considering now the transition and rare earth elements, titanium, zirconium and cerium which, like thorium, have four electrons outside the rare gas configuration, we find once again that in the series titanium dioxide, disulphide, diselenide and ditelluride where the decreasing anion electronegativity would be expected to result in a progressive increase in the covalent character of the binding, no systematic trend in the calculated "ionic" distance relative to the observed distance occurs. In this case, however, instead of a close coincidence between these

quantities, a roughly constant discrepancy of 0.1A is found, the ionic distances being the larger. The same discrepancy also occurs in the series zirconium dioxide, disulphide and ditelluride and for cerium dioxide.

Thus, in all the fourvalent salts of titanium, zirconium and cerium with oxygen, sulphur, selenium and tellurium for which crystallographic data are available, the same discrepancy occurs despite the differences which must exist in the binding.

We are thus led to the conclusion that Zachariasen's radii are not a sufficiently sensitive criterion to decide the extent to which covalent or ionic binding predominates in a given substance and that the discrepancy noted for the fourvalent salts may well have some other origin than that the binding is covalent. That this same discrepancy of 0.1A in interatomic distance occurs for thorium and uranium dioxides cannot therefore be taken as certain evidence as to the nature of the binding in these substances.

It must certainly be true that the oxides are not perfect ionic solids and that at least some admixture of covalent binding must be present. This is apparent from the fact that they are both intrinsic semi-conductors, indicating electron mobility and thus the presence of some form of resonant electronic structure - a conclusion which is inconsistent with a model in which each type of atom or ion has a characteristic non-interacting charge distribution. Nevertheless, it seems likely that their binding tends more toward the ionic than the covalent extreme. Thus, on general chemical grounds[24], the electronegativities of uranium and thorium

are found to be close to that of beryllium - 1.5 on the scale devised by Pauling.[6] Oxygen, in contrast, is one of the most electronegative elements and is second only to fluorine with a value of 3.5. The difference of 2.0 in the electronegativity values, which according to Pauling[6] determines the extent of the ionic character of the bonding, is comparable with that shown for Li - Cl, Na - Cl and K - Br bonds and corresponds in the uranium dioxide structure, where each uranium atom is surrounded by 8 oxygen neighbours, to an average ionic character per bond of 95%.

This figure would intuitively seem rather high were it not, however, consistent with the conclusion to be drawn from the lattice energy values for if a large amount of covalent binding existed, the calculated lattice energy - using the simple ionic model and including the van der Waals potential - would be too small leading to an underestimate of the heat of formation.

Sherman[23] has calculated the lattice energies of 50 simple compounds using the ionic model. In 15 of these - oxides and fluorides being prominent examples - adjustments of less than 3% in lattice energy were needed to give agreement, suggesting the assignment of an extreme ionic character to their structure, while for the remaining 35 compounds, the discrepancy was greater indicating some degree of electron pairing.

In our case, the calculated lattice energy is numerically too large for uranium dioxide by 2.9% and for thorium dioxide it is 1.3% too small.

## 10. CONCLUSION

It appears, therefore, that the ionic model of uranium and thorium dioxides may be a reasonably good approximation to the truth and that, using it, the energies of structural defects of various types may be calculated with some confidence. In these calculations, however, care will be necessary to allow for the effects on the defect energies of the static polarization of oxygen ions in cases where unbalanced electric fields occur.

## 11. ACKNOWLEDGEMENT

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FIGURE 1

THE SCREENING CONSTANT S AS A FUNCTION OF ATOMIC NUMBER FOR IONS OF SERIES 1 AND 2

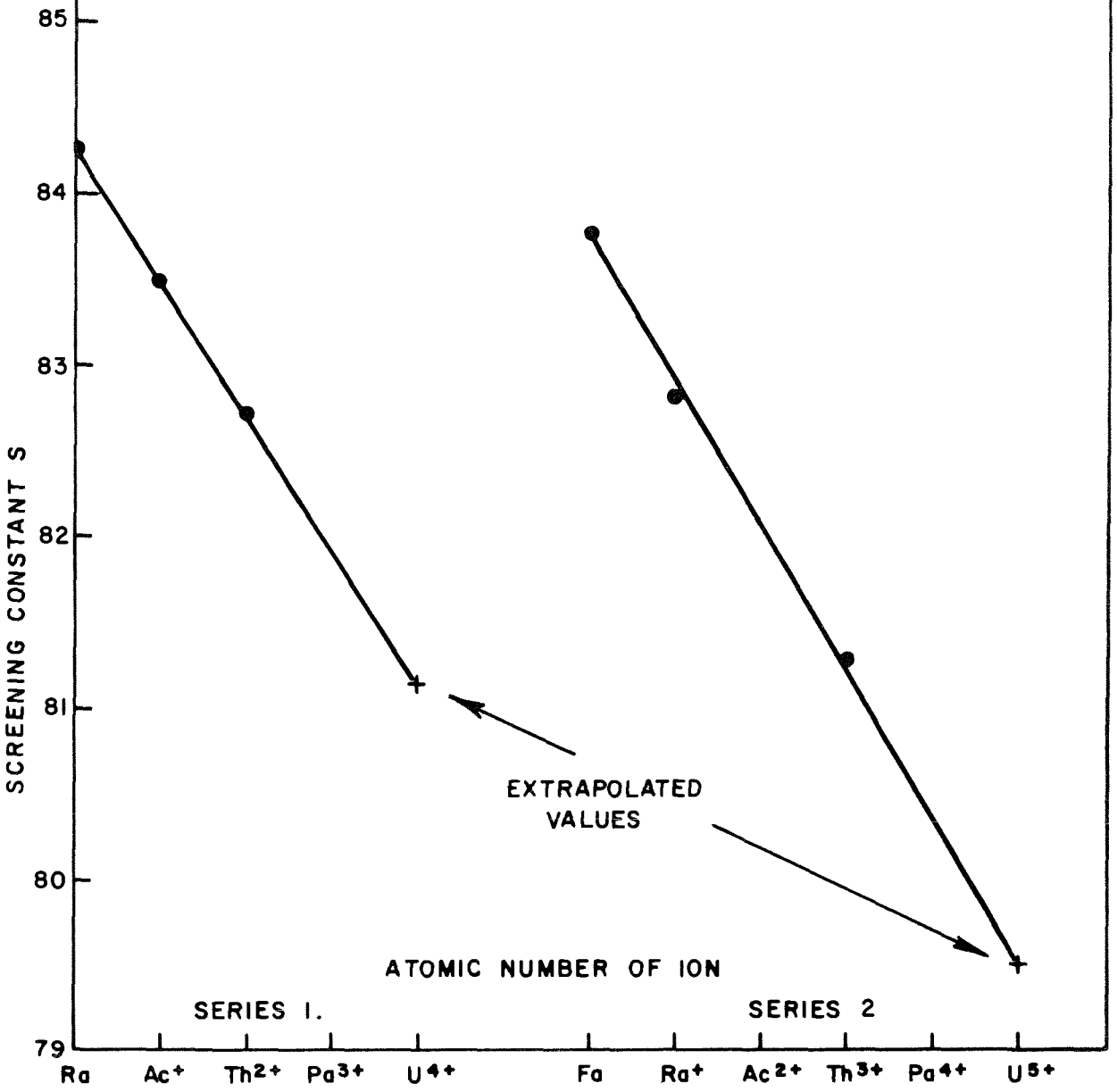
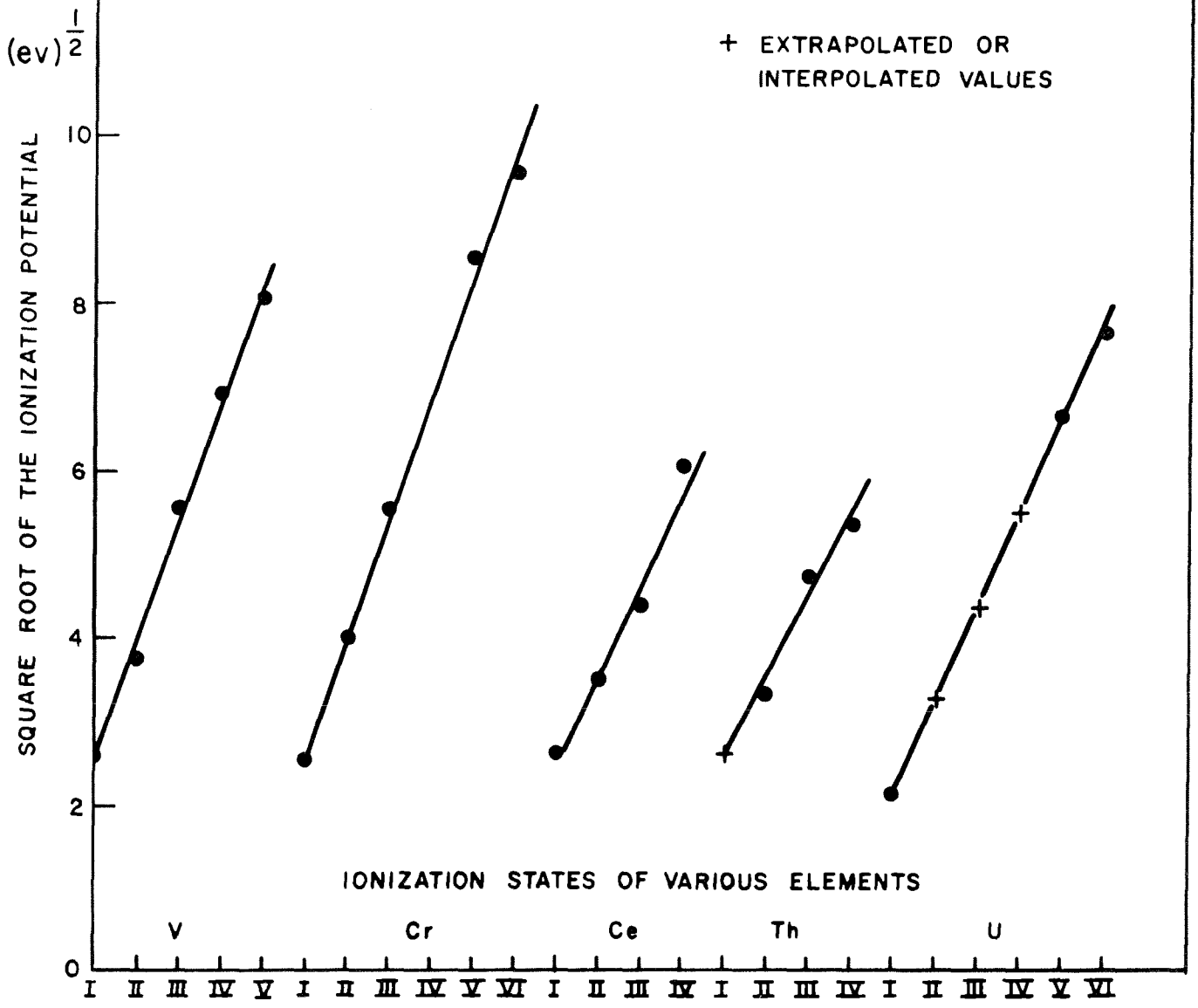


FIGURE 2

THE SQUARE ROOT OF THE IONIZATION POTENTIAL AS A FUNCTION OF THE IONIZATION STATE FOR VARIOUS ELEMENTS



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