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THEORY OF HELIUM DISSOLUTION IN URANIUM DIOXIDE

I. Interatomic Force in Uranium Dioxide
II. Helium Solubility

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THEORY OF HELIUM DISSOLUTION IN URANIUM DIOXIDE

I Interatomic Forces in Uranium Dioxide

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ABSTRACT

Knowledge of the nature of the interatomic forces in uranium dioxide is required for theoretical treatment of phenomena such as radiation damage, adsorption and gas solubility. The Van der Waals and repulsive forces are of particular interest, for these interactions govern the behavior of neutral species in the crystal. The Kirkwood-Müller expression for the coefficients of the $1/r^n$ dispersion forces were employed, and the form of the repulsive potentials were taken from the delta-function model of Mason and Vanderslice. The two disposable parameters in the repulsive potentials were evaluated from data on the atomic properties of the constituent ions and the lattice constant and compressibility of UO_2. The calculated cohesive energy of the UO_2 lattice was in very good agreement with the value obtained from a conventional Born-Haber cycle.

Knowledge of the nature of the interatomic forces in uranium dioxide is required for theoretical calculation of phenomena such as radiation damage, adsorption, and gas solubility. Here we evaluate these forces using data on the atomic properties of the ions and the lattice constant, and compressibility of UO_2 at 0°K.

The UO_2 lattice shown in Fig. 1 is of the fluorite type, and is assumed to be completely ionic in character.[1] The room temperature lattice constant is a = 5.470Å. Extrapolation of thermal expansion data[1] to 0°K yields a value of a = 5.468Å. The cation-anion distance is $r_{OU} = \sqrt{3}\, a/4 = 2.368$Å; the oxygen-oxygen separation is $r_{OO} = a/2 = 2.734$Å, and the distance between uranium atoms is $r_{UU} = a/\sqrt{2} = 3.867$Å.

The cohesive energy represents the energy released when a mole of crystalline UO_2 is assembled from the constituent ions initially at infinite separation. The cohesive energy consists of four components due to attractive forces and a repulsive contribution arising from the overlapping of the electron clouds of adjacent ions. The major attractive components are the Coulomb energy resulting from the interaction of the oxygen and uranium ions and the London or Van der Waals forces arising from the fluctuating induced multipole moments of the ions.[2,3,4,5] All terms except the Coulomb term consist of three components, arising from O^{-2} -O^{-2}, U^{+4}—U^{+4} and O^{-2} -U^{+4} interactions.

The cohesive energy, E_c, as a function of lattice constant, a, is:

$$E_c = -\frac{C_c}{a} + \left[K^r_{OO}\, b_{OO} \exp\left(-\frac{a/2}{\rho_{OO}}\right) + \frac{1}{2} K^r_{OU}\, b_{OU} \exp\left(-\frac{a/\sqrt{2}}{\rho_{OU}}\right) + K^r_{OU}\, b_{OU} \exp\left(-\frac{\sqrt{3}a/4}{\rho_{OU}}\right) \right.$$

$$- \left[K^{(1)}_{OO} \frac{C^{(1)}_{OO}}{(a/2)^6} + \frac{1}{2} K^{(1)}_{OU} \frac{C^{(1)}_{OU}}{(a/\sqrt{2})^6} + K^{(1)}_{OU} \frac{C^{(1)}_{OU}}{(\sqrt{3}a/4)^6} \right]$$

$$- \left[K^{(2)}_{OO} \frac{C^{(2)}_{OO}}{(a/2)^8} + \frac{1}{2} K^{(2)}_{OU} \frac{C^{(2)}_{OU}}{(a/\sqrt{2})^8} + K^{(2)}_{OU} \frac{C^{(2)}_{OU}}{(\sqrt{3}a/4)^8} \right] \quad (1)$$

$$- \left[K^{(3)}_{OO} \frac{C^{(3)}_{OO}}{(a/2)^{10}} + \frac{1}{2} K^{(3)}_{OU} \frac{C^{(3)}_{OU}}{(a/\sqrt{2})^{10}} + K^{(3)}_{OU} \frac{C^{(3)}_{OU}}{(\sqrt{3}a/4)^{10}} \right]$$

The repulsive term has been taken as exponential in form, for reasons to be discussed later.

Following Childs[6] the zero point vibrational energy of the lattice has been considered as a part of the cohesive energy.

The Coulomb energy is represented by the first term on the right of Eq. (1). The constant C_c is given by[7]

$$C_c = Z^2 Me^2 \quad (2)$$

where Z is the charge on the oxygen ion (-2) and M is the Madelung constant for the fluorite structure based on the lattice constant a (11.6365). The numerical value of C_c is 1.55×10^4 kcal/mole -Å.

The coefficients K in Eq. (1) represent the sum of the interactions of a central atom with the other atoms in the lattice. They multiply the potential at the nearest neighbor distance, and are greater than the actual number of nearest neighbors because of the contribution of more distant ions. Numerical values of the K's depend upon the type of lattice and the rapidity with which the particular potential varies with separation distance.

The oxygen ions in the UO_2 crystal form a simple cubic lattice with a nearest neighbor distance of $r_{OO} = a/2$. If $\phi_{OO}(r_{OO})$ denotes the potential energy of a pair of oxygen ions at a separation of r_{OO} due to the repulsive or one of the attractive forces, the contribution of this particular term to the cohesive energy is:

$$\frac{1}{2}(2N_{AV})\left[6\,\phi_{OO}(r_{OO}) + 12\,\phi_{OO}(\sqrt{2}\,r_{OO}) + 8\,\phi_{OO}(\sqrt{3}\,r_{OO}) + \ldots\right] = K_{OO}\,N_{AV}\,\phi_{OO}(r_{OO}) \quad (2)$$

where N_{AV} is Avogadro's number.

The bracketed term on the left of Eq. (2) sums the contributions from the six nearest neighbors at r_{OO}, the twelve next nearest neighbors at $\sqrt{2}\,r_{OO}$, etc. This lattice sum is multiplied by twice Avogadro's number (the number of oxygen atoms per mole of UO_2) and by one-half to avoid counting interactions twice. The lattice sums are converging series, the values of which have been tabulated for potentials which vary as $1/r^n$. For $n = 30$, for example, $K_{OO} = 6$, which indicates that only the nearest neighbors are significant contributors; for long-range forces characterized by $n = 6$, however, $K_{OO} = 8.4$, and the ions more distant than the nearest neighbor shell contribute nearly 30% to the total interaction energy.[8]

The uranium ions constitute a face-centered-cubic lattice in UO_2, and their contribution to the total energy is:

$$\frac{1}{2}(N_{AV})\left[6\,\phi_{UU}(r_{UU}) + 6\,\phi_{UU}(\sqrt{2}\,r_{UU}) + 24\,\phi_{UU}(\sqrt{3}\,r_{UU}) + \ldots\right] = \frac{1}{2}K_{UU}\,N_{AV}\,\phi_{UU}(r_{UU}) \quad (3)$$

Tabulations of K_{uu} for $1/r^n$ potentials are also available.[8]

Beginning with a central uranium ion, the lattice sum for the oxygen-uranium interactions is:

$$N_{AV}\left[8\,\phi_{OU}(r_{OU}) + 24\,\phi_{OU}\left(\sqrt{\tfrac{11}{3}}\,r_{OU}\right) + \ldots\right] \simeq 8\,N_{AV}\,\phi_{OU}(r_{OU}) \qquad (4)$$

The first two terms in the brackets of Eq. (4) are identical to the first and fourth terms of the body-centered-cubic lattice sum. Since the second and third terms do not appear, the entire sum can be reasonably approximated by the first (or nearest neighbor) term.

Table 1 summarizes the values of K used in the various terms in Eq. (1).

Table 1. Component Lattice Sum Coefficients[8]

n in $1/r^n$	Interaction	O-O	U-U	O-U
6	dipole-dipole	8.40	14.45	8
8	dipole-quadrupole	6.95	12.80	8
10	quadrupole-quadrupole	6.43	12.31	8
12	repulsive	6.20	12.13	8

Since lattice sums are not available for exponential potentials, the $1/r^{12}$ potential has been used to approximate the K coefficients for the repulsive terms.

Attractive Forces

Several formulae for evaluating dipole-dipole interactions have been proposed.[9] The original London formula is:

$$C_{AB}^{(1)} = \frac{3}{2}\alpha_A\alpha_B\,\frac{h\nu_A\,h\nu_B}{h\nu_A + h\nu_B} \qquad (5)$$

where A and B denote the two molecules, α is the polarizability and $h\nu$ a characteristic energy, usually taken to be the ionization energy.

The theory of Kirkwood and Müller yields:

$$C_{AB}^{(1)} = 6mc^2 \alpha_A \alpha_B \frac{1}{\alpha_A/\chi_A + \alpha_B/\chi_B} \tag{6}$$

where mc^2 is the energy equivalent of the rest mass of the electron (0.51 mev) and χ the susceptibility.

The Kirkwood-Müller formula has been chosen for the following reasons:

First, Eq. (5) (with the characteristic energy taken as the ionization potential) cannot be directly applied to interactions involving the O^{-2} ion, which has a negative ionization potential and is unstable as a free species. Second, Eq. (6) best reproduces the experimentally observed dipole-dipole forces for the rare gases.[10] Since the oxygen ion has the electron structure of neon, and tetravalent uranium that of radon (plus two extra 5f electrons), Eq. (6) would be expected to satisfactorily predict dispersion energies for the constituent ions of UO_2.

The Kirkwood-Müller relation has been used extensively in adsorption calculations[11,12,13,14] which, like this study, involve estimation of interatomic forces in the condensed rather than the gaseous phase.

The Van der Waals forces also include contributions from higher order multipole moments.[2,3,4,5] In addition to the dipole-dipole interactions, dipole-quadrupole forces give rise to a term varying as $1/r^8$. The $1/r^{10}$ term contains contribution from quadrupole-quadrupole and dipole-octupole interactions. The $1/r^{12}$ term includes dipole-fourth order pole and quadrupole-octupole interactions.

Terms higher than the dipole-quadrupole interaction are usually not included in lattice energy computations. However, when the separation

distance between the constituent atoms is sufficiently small, the higher order interactions are not negligible. The $1/r^{10}$ and $1/r^{12}$ terms have been considered by Heller in his study of the loosely bound Hg-rare gas molecules, in which the separation distance is of the order of 3.0-3.5Å.[4] In the UO_2 lattice, the O^{-2} -U^{+4} separation is 2.368Å, and because of the appreciable polarizabilities of the two ions, the higher order multipole forces may be significant. In this study, only terms up to and including the quadrupole-quadrupole interaction will be considered. There is no experimental verification of the accuracy of formulae describing interactions higher than the dipole-quadrupole, but the approximations probably become less valid as the order of the poles involved increases.[3] Furthermore, since the Kirkwood-Müller formula overestimated the dipole-dipole potential by some 50% for rare gases, neglecting contributions of octupoles and fourth order poles tends to compensate for the high interaction energies predicted for the lower order poles.

A means of extending the Kirkwood-Müller theory to the higher order terms in the dispersion energy has been suggested by Kiselev and Poshkus[15], who noted that Eqs. (5) and (6) are identical if the characteristic energy is chosen as

$$\hbar\nu = \frac{4mc^2}{\alpha/\chi} \tag{7}$$

The final expressions are[16,17]

$$C_{AB}^{(2)} = \left(\frac{45\hbar^2}{32\pi^2 m}\right)\alpha_A\alpha_B\left\{\frac{1}{2\left(\frac{\alpha_A/\chi_A}{\alpha_B/\chi_B}\right)+1} + \frac{1}{2\left(\frac{\alpha_B/\chi_B}{\alpha_A/\chi_A}\right)+1}\right\} \tag{8}$$

for dipole-quadrupole interactions, and:

$$C_{AB}^{(3)} = \left(\frac{315\, h^4}{1024\, \pi^4 m^3 c^2}\right) \alpha_A \alpha_B \frac{\alpha_A/\chi_A}{1 + \frac{\alpha_A/\chi_A}{\alpha_B/\chi_B}} \qquad (9)$$

for quadrupole-quadruple interactions.

The polarizability of the oxygen ion and susceptibility of U^{+4} and O^{-2} are available from literature tabulations.[18] The polarizability of tetravalent uranium, however, has not been measured; an estimate based upon screening constants[19] yields a value of 5.0Å^3. To assess the reliability of this figure, the screening constant estimates and literature values for the polarizabilities and susceptibilities of other tetravalent cations is shown in Table 2. The calculated values of the susceptibilities appear to be in reasonable agreement with measurements, particularly for the heavier ions. The polarizabilities, however, exhibit greater discrepancies. The calculated value for Ge^{+4} is lower than the value reported by Tessman et al.[20] while for the remaining ions, the screening constant method yields values which are as much as a factor of 3-4 too large. The polarizability of U^{+4} is probably less than the calculated value of 5.0, but greater than the value of 2.4 for Sn^{+4}. In the following computation, a value of $\alpha_{U^{+4}} = 3.0$ Å^3 will be used.

The polarizability of the oxygen ion has been taken as the average of the two values reported in ref. 18, or $\alpha_{O^{-2}} = 3.3$Å^3. The susceptibilities from the same source are 58×10^{-6}Å^3 and 33×10^{-6}Å^3 for U^{+4} and O^{-2} respectively.

An additional check on the plausibility of the polarizability estimates is offered by the relation between the index of refraction of UO_2 and its molecular polarizability.[20]

$$\alpha_{UO_2} = \alpha_{U^{+4}} + 2\alpha_{O^{-2}} = V_m \frac{n^2-1}{L(n^2-1)+4\pi} \tag{10}$$

Here n is the refractive index and V_m the molecular volume of UO_2. With $L = 4\pi/3$, Eq. (10) is the Lorentz-Lorentz formula; with $L = 0$, Eq. (10) is the Drude formula.[21] Using $V_m = 40.8\text{Å}^3$ from UO_2 density data and $n = 2.35$[1], Eq. (10) yields $\alpha_{UO_2} = 5.9$ for the Lorentz-Lorentz formula and $\alpha_{UO_2} = 14.7$ for the Drude formula. The value of α_{UO_2} corresponding to $\alpha_{U^{+4}} = 3.0$ and $\alpha_{O^{-2}} = 3.3$ is 9.6, indicating that the estimated polarizabilities of the individual ions are not unreasonable.

REPULSIVE FORCES

Most investigations of interionic forces in crystals have utilized a repulsive potential originally suggested by Born and Mayer,[22]

$$\phi^r(r) = b\, e^{-r/\rho} \tag{11}$$

$$b = c\left(1 + \frac{z_A}{n_A} + \frac{z_B}{n_B}\right) \exp\left[\frac{r_A^i + r_B^i}{\rho}\right] \tag{12}$$

In Eq. (12), c is a constant for all ions, z is the valence of the ion, n the number of outer shell electrons, and r^i the ionic radius. From an examination of the cohesive energy of the alkali halides, Born and Mayer found that a single value of $\rho = 0.345\text{Å}$ could be employed. This approach is completely empirical, except that the exponential form is similar to the potentials derived from quantum mechanical calculations for the rare gases.

There are several reasons for not employing the classical method to the present study of UO_2: first, the constant c in Eq. (12) is not specified (it is usually determined by minimizing the cohesive energy at the known

interionic separation distance[23]); second, it is unreasonable to expect that the steepness parameter ρ should be the same for O^{-2} and U^{+4}, or that either be equal to 0.345; third, in order to study adsorption or gas solubility phenomena in UO_2, it is necessary to obtain repulsive potentials between neutral atoms and the ions of the lattice. Eq. (12) obviously cannot be applied to neutral species, and there is no obvious way of "mixing" the Born-Mayer potential with a rare gas potential to obtain the ion-atom interaction.

In this study we will utilize the delta-function model of the repulsive potential originally proposed by Mason and Vanderslice[24] and applied with considerable success to the rare gas interactions. Since the ions in UO_2 are spherically symmetric and have rare gas outer electron configurations, the model should apply to O^{-2} and U^{+4} as well.

The repulsive potential energy-distance relation is implicit in three equations:

$$\phi^{r}(r) = \sqrt{n_A n_B}\, g_A g_B \exp\left[-\tfrac{1}{2}\left(c_A v_A + c_B v_B\right)\right] \tag{13}$$

where n_A and n_B are the total numbers of electrons in the two partners, g_A and g_B are measures of the binding strength of the electrons in the atom or ion, and c and v are given by:

$$c_A = g_A\left(1 - e^{-c_A v_A}\right) \tag{14}$$

$$v_A = R + 2a_A e^{-R/a_A} \tag{15}$$

with similar expression for species B.

In Eq. (15), a_A is the radius of species A obtained from screening constant estimates, and R the separation distance, both in units of a_0,

the Bohr radius. The potential energy is in units of $e^2/a_0 = 627.32$ kcal/mol.

For the separation distances in the UO_2 crystal (~ 2.5Å), R is sufficiently large to render the exponential terms in Eqs. (14) and (15) negligible: $v_A \simeq v_B \simeq R$, $r \simeq g$. Eq. (13) reduces to the simple exponential form of Eq. (11), with b and ρ given by

$$b = 627.32 \sqrt{n_A n_B}\, g_A g_B, \quad \text{kcal/mol} \tag{16}$$

$$\rho = \frac{a_0}{\frac{1}{2}(g_A + g_B)}, \quad \text{Å} \tag{17}$$

Several features of the delta-function repulsive potential are of interest: the prescription for the potential is independent of the radii of the two species (a_A and a_B) in the limit of large separation. The steepness parameter ρ is a function of the two interacting species; the same parameter which determines ρ also influences the magnitude of b; A "mixing rule" is specified: the geometric mean of the ng^2 for b and the reciprocal of the arithmetic mean of the g's for ρ; the formulation is equally valid for ions or atoms provided that appropriate values of g can be determined.

In the application of the delta-function model to rare gas atoms, Mason and Vanderslice found that g should be specified by:

$$g = \sqrt{2}\,\frac{I}{I_H} \tag{18}$$

where I is the ionization potential of the free atom and $I_H = 13.6$ ev is the ionization potential of hydrogen. For UO_2, however, g cannot be obtained for Eq. (18), since the ionization potential of the free O^{-2} ion is negative.

Hence, we will regard the values of g for O^{-2} and U^{+4} as disposable parameters, which will be selected to give the best fit to the lattice constant and the compressibility of UO_2.

DETERMINATION OF THE PARAMETERS IN THE REPULSIVE POTENTIAL

Eq. (1) can be written as:

$$E_c = -E_{coul} - E^{DD} - E^{DQ} - E^{QQ} + E^{r}_{OO} + E^{r}_{UU} + E^{r}_{OU} \tag{19}$$

where E_{Coul} is the magnitude of the electrostatic term in Eq. (1), and E^{DD}, E^{DQ}, and E^{QQ} are the magnitudes of the sum of the multipole interactions (i.e., the terms in the last three brackets in Eq. (1)). The repulsive terms are of the form shown in the first bracketed term of Eq. (1), with b and ρ given by Eqs. (16) and (17).

The condition that the cohesive energy be a maximum at the observed lattice constant is:[23]

$$\frac{dE_c}{da} = 0 \qquad \text{when } a = 5.468\,\text{Å}$$

Using Eq. (1), this force balance is

$$0 = -E_{coul} - 6E^{DD} - 8E^{DQ} - 10E^{QQ} + \left(\frac{a}{\rho_{OO}}\right)E^{r}_{OO} + \left(\frac{a}{\rho_{UU}}\right)E^{r}_{UU} + \left(\frac{a}{\rho_{OU}}\right)E^{r}_{OU} \tag{20}$$

The coefficient of compressibility, β, is related to the second derivative of E_c by:[23]

$$\frac{d^2E_c}{da^2} = \frac{9}{4}\frac{aN_{AV}}{\beta} \qquad \text{when } a = 5.468\,\text{Å}$$

This can be written as:

$$\beta = \frac{9}{4}\frac{a^3N_{AV}}{\beta} = -2E_{coul} - 42E^{DD} - 72E^{DQ} - 110E^{QQ} + \left(\frac{a}{\rho_{OO}}\right)^2E^{r}_{OO} + \left(\frac{a}{\rho_{UU}}\right)^2E^{r}_{UU} + \left(\frac{a}{\rho_{OU}}\right)^2E^{r}_{OU} \tag{21}$$

where
$$\xi_{oo} = \frac{2a_o}{g_o} = \frac{1.058}{g_o} \tag{22}$$

$$\xi_{uu} = \frac{\sqrt{2}\,a_o}{g_u} = \frac{0.749}{g_u} \tag{23}$$

$$\xi_{ou} = \frac{4a_o/\sqrt{3}}{\frac{1}{2}(g_o+g_u)} = \frac{2.44}{g_o+g_u} \tag{24}$$

With the lattice constant fixed at a = 5.468Å, the attractive terms in Eqs. (19)-(21) are known constants. The terms involving the repulsive forces, however, are functions of g_O and g_U. There are three equations for the determination of two unknowns.

The parameters g_O and g_U have been obtained by simultaneous solution of Eqs. (20) and (21), since these two equations are most sensitive to the repulsive potential. Because of the dominant influence of the Coulomb term in Eq. (19), the calculated cohesive energy is quite insensitive to g_O and g_U. The value of B in Eq. (21) has been obtained from the data presented in Ref. 1 and a rough extrapolation to 0°K as 8200 kcal/mole.

From Eqs. (20) and (21), we have obtained $g_O = 1.27$ and $g_U = 1.32$. The oxygen ion has the same number of electrons as neon. Because the nuclear charge in O^{-2} is two less than that of Ne, we would expect the electrons in O^{-2} to be less tightly bound than in Ne. According to the delta-function model, this would be reflected in a smaller value of g for O^{-2} than the value of 2.24 for neon. Conversely, U^{+4} has nearly the same electron structure as the rare gas radon, but the electrons are more tightly bound in U^{+4} because of the four additional nuclear charges. Consequently, we would expect g_U to be somewhat greater than the 1.12 value of g for radon. Both of these expectations are substantiated by the calculations.

The contribution of each of the interactions to the cohesive energy is shown in Table 3. For comparison, the results of the earlier calculation by Childs[6] are also shown. In our figures, the oxygen-uranium interaction contributes most heavily to the Van der Waals and repulsive terms.

The very much smaller dipole-dipole term obtained by Childs is due in part to his use of a polarizability of U^{+4} of 0.9Å^3, (calculated as the cube of the ionic radius). In addition, the characteristic energy of the oxygen ion was assumed equal to the ionization energy of Cl^{-1} (4 ev). The characteristic energy of O^{-2} from Eq. (7) is 20.4 ev. The repulsive terms in Childs' analysis were computed from Eqs. (11) and (12) with ρ = 0.345Å. By comparison, the steepness parameter ρ_{OU} obtained from Eq. (17) with the computed values of g_O and g_U is 0.406Å. Childs computed a value of B = 14,800 kcal/mole, which is 80% greater than the experimental value.

Using a conventional Born-Haber cycle, the cohesive energy of UO_2 has been estimated by Childs as -2356 kcal/mole. While our figure of -2340 is closer to this than Childs', the dominant influence of the Coulomb energy precludes use of calculated cohesive energies as a method for assessing the validity of various potential functions.

The large Van der Waals energies calculated here are in part due to the close interionic spacing resulting from the strong Coulombic attraction of the di- and tetravalent ions of the lattice. The value of $C_{OU}^{(1)}$ calculated from Eq. (6) is somewhat greater than the analogous constant for CsBr.[25] The dipole-dipole contribution in CsBr is 11 kcal/mole compared to ~ 300 kcal/mole in UO_2. This thirtyfold difference is due primarily to the much smaller anion-cation separation in the UO_2 lattice (2.37Å in UO_2 compared to 3.71Å in CsBr).

Although the estimates of the repulsive parameters g_O and g_U calculated here appear reasonable, it is difficult to ascertain whether the reduction of the original potential expressions of the delta-function model to the simple exponential form is valid. We can however, compare the potential energy computed from Eqs. (13)-(15) to that obtained from the Eq. (11) with b and ρ given by Eqs. (16) and (17).

Consider two oxygen ions a distance of 2.74Å apart, each interacting with a repulsive parameter $g_O = 1.27$. If we take as the radius of the oxygen ion the screening constant estimate of 0.69Å,[19] the exponential approximation yields a potential energy which is 5% greater than that obtained from the full expression. If the O^{-2} radius is taken as the ionic radius of 1.37Å, the discrepancy increases to a factor of 2.4. In any case, the approximate exponential form of the delta-function model can be regarded as semiempirical description of the repulsive potential depending on one disposable parameter, g.

Of all the parameters required for the calculation of g_O and g_U, the estimate of the polarizability of U^{+4} is least secure. The effect of this parameter on the results presented here has been evaluated by re-solving Eqs. (20) and (21) with $\alpha_U = 2.0 Å^3$ instead of 3.0. The value of g_O decreased from 1.27 to 1.06 and g_U increased from 1.32 to 1.62. The Van der Waals energies decreased by ~ 70 kcal/mole and the repulsive contribution increased by this amount. The computed cohesive energy remained essentially unchanged.

Table 2. Polarizabilities and Susceptibilities

Ion	α, Å^3		$\chi \times 10^6$, Å^3	
	Calc.	Lit.	Calc.	Lit[18]
Ti^{+4}	0.63	0.19, 0.24[20]	12	8
Ge^{+4}	0.73	0.95[20]	17	12
Zr^{+4}	1.79	0.37, 0.8[18]	23	17
Sn^{+4}	3.6	2.4[20]	35	27
Ce^{+4}	3.4	0.73, 1.2[18]	35	28
Hf^{+4}	1.9	---	29	27
Pb^{+4}	6.3	---	46	43
U^{+4}	5.0	---	53	58
O^{-2}	2.2	2.75, 3.88[18] 0.9-3.2[20]	22	33

Table 3. Components of the Cohesive Energy of UO_2 (in kcal/mole)

Interaction	This Work	Childs[6]
Coulomb	-2835	-2820
Dipole-Dipole	- 301	- 22
Dipole-Quadrupole	- 72	---
Quadrupole-Quadrupole	- 8	---
Repulsive	+ 876	+ 411
Cohesive Energy	-2340	-2431

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THEORY OF HELIUM DISSOLUTION IN URANIUM DIOXIDE

II Helium Solubility

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ABSTRACT

The solubility of helium in uranium dioxide was calculated directly from atomic properties and compared with experiment. The calculations were based upon a statistical mechanical formula which assumes dissolved helium to behave as a simple harmonic oscillator in an interstitial site in the UO_2 lattice. Knowledge of the interactions between helium and the oxygen and uranium ions of the lattice permits computation of the heat of solution and the vibration frequency, which yield the Henry's Law constant. The calculated solubility of 6.6×10^{-4} cc (STP)/gm-atm at 1200°C was in good agreement with the experimental measurements, but the heat of solutions differed appreciably. This discrepancy was attributed to experimental errors, for the very large observed heat of solution ($\sim$ -30 kcal/mole) could not arise from purely physical interactions.

The release of appreciable amounts of helium from irradiated fuel elements has recently been demonstrated.[1] The helium appears to result from ternary fission, and because of its high diffusivity, is the primary constituent of the released gases after short exposures. Measurements of helium solubility in UO_2 by Bostrom[2] and Rufeh et al.[3,4] differ by an order of magnitude.

The calculation of helium solubility is based upon the following model:

1. The uranium and oxygen ions are fixed at their equilibrium positions in a perfect crystalline lattice.

2. The only places available for dissolved helium atoms are the unoccupied uranium sites in the UO_2 lattice (dashed circles in Fig. 1 of Part I). The number of such sites is equal to the number of uranium atoms.

3. A helium atom in an interstitial position in UO_2 behaves as a simple harmonic oscillator with three vibrational degrees of freedom and characterized by a single frequency.

4. There is no interaction between dissolved helium atoms; the solution is dilute.

These assumptions yield the following expression for the Henry's Law constant (see appendix):

$$k_H = \frac{n_s}{p} = 10^6 \frac{N_s (kT)^{1/2}}{(2\pi m \nu^2)^{3/2}} \exp\left[-\frac{E(0)}{RT}\right] \qquad (1)$$

k_H is the Henry's Law constant in cc (STP) of dissolved helium per gram of UO_2 per atm. n_S is the amount of dissolved He in cc (STP)/gm UO_2

and p is the helium pressure in atmospheres. N_S is the number of sites available (equal to 2.23×10^{21} sites/gm UO_2 or 83.0 cc (STP)/gm UO_2. m is the mass of the helium atom, ν is the frequency of oscillation of the dissolved helium, T the absolute temperature and R the gas constant, k is Boltzmann's constant. E(o) is the heat of solution in kcal/mole.

A helium atom on an interstitial site in UO_2 is in a cell or cage formed by 8 oxygen atoms at a distance of $\sqrt{3}$ a/4 and 6 uranium atoms at a distance of a/2, where a is the lattice constant of UO_2 at the temperature T. The heat of solution is the potential energy of the helium (referred to the free atom) when located at the center of the cell. At a distance r from the central position, the energy is denoted by E(r). According to the simple harmonic oscillator model, the actual potential energy curve is fit to the quadratic form:

$$E(r) = E(0) + \frac{1}{2} \varkappa r^2 \tag{2}$$

The vibration frequency is related to the force constant $\varkappa$ by:

$$\nu = \frac{1}{2\pi} \sqrt{\frac{\varkappa}{m}} \tag{3}$$

In order to calculate the solubility (or the Henry's Law constant) the energy curve E(r) must first be computed and shown to be reasonably well approximated by Eq. (2).

The function E(r) is given by:

$$E(r) = -\left[8 \frac{C^{(1)}_{HeO}}{(\sqrt{3}a/4)^6} m^{(1)}_{HeO}(r) + 6 \frac{C^{(1)}_{HeU}}{(a/2)^6} m^{(1)}_{HeU}(r)\right] - \left[8 \frac{C^{(2)}_{HeO}}{(\sqrt{3}a/4)^8} m^{(2)}_{HeU}(r)\right.$$

$$\left. + 6 \frac{C^{(2)}_{HeU}}{(a/2)^8} m^{(2)}_{HeU}(r)\right] - \left[8 \frac{C^{(3)}_{HeO}}{(\sqrt{3}a/4)^{10}} m^{(3)}_{HeO}(r) + 6 \frac{C^{(3)}_{HeU}}{(a/2)^{10}} m^{(3)}_{HeU}(r)\right]$$

$$+\left[8\, b_{HeO} \exp\left(-\frac{\sqrt{3}\,a}{4\rho_{HeO}}\right) m^{r}_{HeO}(r) + 6\, b_{HeU} \exp\left(-\frac{a/2}{\rho_{HeU}}\right) m^{r}_{HeU}(r)\right] \tag{4}$$

The four brackets in Eq. (4) represent dipole-dipole, dipole-quadrupole, quadrupole-quadrupole and repulsive interactions respectively. Each of the bracketed terms contain two components: the first from He-O^{-2} interaction and the second from He-U^{+4} interactions. In each case, the lattice sums have been approximated by the number of nearest neighbors. Relative to the oxygen ions, helium occupies a lattice position analogous to that of a uranium ion. According to the discussion of part I, this lattice sum can be replaced by the number of nearest neighbors.

In summing the interaction between He and U^{+4}, the first term comes from interaction between a central helium atom and the 6 nearest U^{+4} ions at a distance of a/2. There are 8 next nearest neighbors at a distance of $\sqrt{3}$ a/2, followed by 24 U^{+4} ions at a distance of $\sqrt{5}$ a/2. For a $1/r^6$ potential, the third term is ~15% of the second, and the second term is ~5% of the first. Since the next nearest neighbor term contributes at most 5% to the total He-U^{+4} lattice sum, the entire series has been approximated by the first term for all potentials.

The dependence of E(r) upon distance from the center of the cell are given by the eight m(r) function. The potential energy of a helium atom within a cell is dependent upon angle as well as radial position because the host ions are point centers of force located at discrete positions (e.g. at the 8 corners of a cube in the case of $O^{(-2)}$. To eliminate the dependence upon angular position, we utilize the "sphericallization" procedure employed in the cell model for liquids.[5]

The angle-averaged potential between a helium atom and one of the nearest neighbors is:

$$\bar{\phi}(r) = \frac{1}{4\pi}\int_0^{2\pi} d\psi \int_{-1}^{1} d\mu\, \phi(R) = \frac{1}{2}\int_{-1}^{1} \phi(R)\, d\mu \tag{5}$$

where

$$R = (r^2 + d^2 - 2dr\mu)^{1/2} \tag{6}$$

With the origin at the center of the cell, d is the distance between the origin and the nearest neighbor ($\sqrt{3}$ a/4 for O^{-2}, a/2 for U^{+4}), r the distance of the He atom from the center and R is the distance between the He atom and the nearest neighbor. μ is the cosine of the angle between <u>r</u> and <u>d</u> and ψ is the azimuthal angle.

For pair potential functions of the type $\phi(R) = C/R^n$ and $b\, e^{-R/\rho}$, Eq. (5) can be integrated to yield:

$$\bar{\phi}(r) = \phi(d)\, m(r) \tag{7}$$

For a $1/r^6$ potential:

$$m^{(1)}(r) = (1+y^2)/(1-y^2)^4 \tag{8a}$$

For a $1/r^8$ potential:

$$m^{(2)}(r) = (1+\tfrac{10}{3}y^2+y^4)/(1-y^2)^6 \tag{8b}$$

For a $1/r^{10}$ potential:

$$m^{(3)}(r) = (1+7y^2+7y^4+y^6)/(1-y^2)^8 \tag{8c}$$

and for an exponential potential:

$$m^{r}(r) = \frac{\left[1 + (1-y)\frac{d}{\rho}\right]e^{yd/\rho} - \left[1 + (1+y)\frac{d}{\rho}\right]e^{-yd/\rho}}{2y(d/\rho)^2} \tag{8d}$$

where

$$y = r/d \tag{9}$$

all of these functions are unity at r = 0.

The total potential energy of a helium atom at position r in the cell for a particular interaction is obtained by multiplying Eq. (7) by the number of nearest neighbors. When this is done for the three attractive interactions and the repulsive terms and the results summed, Eq. (4) is obtained.

The coefficients C and b and the steepness parameters ρ in Eq. (4) have been computed from Eqs. (6), (8), (9), (16), and (17) of Part I. The values of g_O and G_U employed were those obtained previously ($g_O = 1.27$ and $g_U = 1.32$), while g_{He} was computed from Eq. (18) of Part I as 2.56. The polarizability and susceptibility of He were taken as 0.206 $Å^3$ and 3.12×10^{-6} $Å^3$ respectively.

For T = 1200°C, the lattice constant was estimated from thermal expansion data as 5.525 Å. Table 1 shows the potential energy of the helium atom as a function of displacement from its equilibrium position and Table 2 shows the components of the energy at the equilibrium position.

Despite the complexity of the m(r) functions of Eq. (8), the last column of Table 1 shows that E(r) can be quite satisfactorily approximated by Eq. (2) for displacements up to $\sim$0.8 Å from the equilibrium position.

For $r > 0.8$ Å, the calculated potential energy begins to decrease, due to the rapid growth of the dipole-quadrupole and quadrupole-quadrupole forces. We do not believe that this behavior is realistic, since the expressions for the Van der Waals forces are valid only at large separations. The force constant at 1200°C computed from the first six figures in the last column of Table 1 is 23.8 kcal/mole -Å^2, and the vibrational frequency is 7.9×10^{12} sec^{-1}. The solubility can then be calculated from Eq. (1).

A comparison of the experimental and theoretical Henry's Law constants is shown in Table 3 for various temperatures.

The effect of temperature on the solubility appears in three places. It occurs explicitly in the exponential and pre-exponential terms in Eq. (1); a second order temperature effect results from the variation of the lattice parameter with temperature. A change in the lattice constant will alter the various components of E(r) by different amounts. For example at T = 800°C, the lattice constant is estimated at 5.504Å, the heat of solution is -2.49 kcal/mole, and the vibrational frequency is 8.0×10^{12} sec^{-1}. The heat of solution is smaller at 800°C than at 1200°C because the contraction of the lattice increases the repulsive forces more than the attractive forces. If one were to accept E(0) = -2.63 kcal/mole at 1200°C as the heat of solution and neglect the other temperature effects, the solubility at 800°C would be 26% greater than at 1200°C. However, when the $\sqrt{T}$ term in Eq. (1) and the effect of temperature on E(0) and ν are considered, the predicted solubility of 800°C is 1.5% smaller than at 1200°C. The effective heat of solution between these two temperatures is positive rather than negative, as would be suggested by the negative values of E(0).

The magnitude of the theoretical values in Table 3 are in reasonably good agreement with the measurements of Rufeh, et al.[3]. There exists, however, a large discrepancy in the heats of solution. Table 4 summarizes measurements and calculations on helium solubility in silicon, germanium, and quartz. The heats of solution for Ge and Si are positive; for quartz, it is slightly negative. The large negative values observed by Rufeh and Bostrom for UO_2 are surprising and cannot be explained by the theoretical model employed here. The Van der Waals attractive forces are simply not strong enough to give net binding energies of 10-30 kcal/mole. Heats of solution of this magnitude are more characteristic of some form of homopolar or chemical binding, behavior which one would not expect from helium.

Table 4 also indicates the wide variation in the solubilities of helium in various materials. Notable is the nearly six order of magnitude discrepancy between measurement and theory in Ge.

The order of magnitude agreement between the calculated and experimental solubilities appears to substantiate the assumptions upon which the model is based. The major uncertainty in the calculation (in addition to the four assumptions listed at the beginning of this paper) is the value of the polarizability of tetravalent uranium. If instead of $\alpha_U = 3.0\text{Å}^3$, a value of 2.0Å^3 had been employed, the calculated helium solubilities in Table 3 would have been reduced by a factor of 2.5. This extreme sensitivity of the calculated solubility on the parameters of the attractive and repulsive forces is due to the fact that E(0) is a small difference between large repulsive and attractive energies which are nearly equal (see Table 2). A small percentage change in one component produces a large change in the difference. This sensitivity is evident when the model is applied to the calculation of neon solubility in UO_2. Using the known atomic properties of neon and a

repulsive parameter $g_{Ne} = 2.24$ (from Eq. (18) of part I), an unrealistic E(0) of -16.6 kcal/mole is computed, and the potential function E(r) has a maximum rather than a minimum at r = 0. If, however, g_{Ne} is reduced by 7%, the calculated potential well E(r) has the same shape and depth as that for He and the calculated solubility of Ne in UO_2 is then of the same order of magnitude as that of He. Bostrom[2] has reported that neon is $\sim 1/30$ as soluble as helium, although this figure is based upon only one measurement at the limit of the sensitivity of the method. In SiO_2, neon and helium exhibit nearly equal solubilities.[9,10]

For the heavier rare gases, the balance of energies tips in favor of the repulsive components; the E(0) values become more positive and the solubility decreases. This behavior corresponds to decreasing repulsive parameters, which for Ar, Kr, and Xe are 1.64, 1.46, and 1.26 respectively.

Part II.

Table 1. Potential Energy if a Helium in an Interstitial Site in UO_2 as a Function of Displacement from Equilibrium Position (T = 1200°C)

r, Å	E(r), kcal/mole	$2[E(r)-E(0)]/r^2$
0	-2.63	---
0.122	-2.45	24.2
0.245	-1.93	23.4
0.367	-1.04	23.6
0.490	0.24	23.8
0.612	1.90	24.2
0.734	3.83	24.0
0.857	5.66	11.3
0.979	6.46	9.5
1.101	3.91	---
1.224	-7.53	---

Table 2. Components of E(0), kcal/mole at T = 1200°C

	$He-O^{-2}$	$He-U^{+4}$
dipole-dipole	-12.39	-5.00
dipole-quadrupole	- 3.42	-0.73
quadrupole-quadrupole	- 0.46	-0.05
repulsive	12.62	6.80

Table 3. Comparison of Measured and Calculated Solubilities

T, °C	$k_H \times 10^4$ cc(STP)/gm UO_2 - atm	
	Theoretical	Experimental
800	6.5	2.4[2]
1000	7.0	1.1[2]
1200	6.6	6.7[3]
1300	6.5	3.2[3]

Table 4. Helium Solubility in other Crystals

Crystal	Solubility atoms/cc	Heat of Sol'n kcal/mole
Si[6]	$1\text{-}2 \times 10^{13}$	11.0
Si[7]	---	7.8 (calc.)
Ge[8]	10^{18} (calc.)	1.6 (calc.)
Ge[6]	$3\text{-}5 \times 10^{12}$	13.0
Ge[7]	---	8.1 (calc.)
SiO_2[9]	$2\text{-}6 \times 10^{17}$	- 1.2
UO_2[3]	$3\text{-}6 \times 10^{17}$	-34.0
UO_2[2]	$1\text{-}2 \times 10^{17}$	-11.0
UO_2 (This work)	2×10^{17} (calc.)	- 1.0 (calc., 1000-1300°C)

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Appendix - Derivation of Eq. (1)

The condition of equilibrium between helium in the gaseous and dissolved states is:

$$F(g) = F(s) \tag{A-1}$$

or.

$$H(s) - TS(s) = H(g) - TS(g) \tag{A-2}$$

F, H, and S are the molar Gibbs free energy, enthalpy and entropy, respectively. g and s denote the gaseous and dissolved states. By the assumption of a dilute solution, the partial molar quantities in the dissolved state have been replaced by molar quantities.

Since helium is an ideal gas, its enthalpy is:

$$H(g) = \frac{5}{2} RT \tag{A-3}$$

The entropy of an ideal gas is given by the Sackur-Tetrode equation[11,12]:

$$S(g) = R \ln \left[\left(\frac{kT}{10^6 p} \right) \left(\frac{2\pi m \, kT}{h^2} \right)^{3/2} \right] + \frac{5}{2} R \tag{A-4}$$

where p is the pressure in atm and $10^6 p$ the pressure in dynes/cm^2.

The enthalpy of He in the dissolved state is the sum of the enthalpy of vibration of a simple harmonic oscillator with three degrees of freedom and the potential energy at the equilibrium position in the UO_2 lattice:

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(11) G. N. Lewis, M. Randall, K. S. Pitzer and L. Brewer, "Thermodynamics", Chap. 27, 2nd edition, McGraw-Hill (1961).
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$$H(s) = H_{vib} + E(o) \tag{A-5}$$

where H_{vib} is given by[12]

$$H_{vib} = 3RT \left[T\left(\frac{\partial \ell n\ Q_{vib}}{\partial T} \right)_v + \left(\frac{\partial \ell n\ Q_{vib}}{\partial v} \right)_T \right] \tag{A-6}$$

Q_{vib} is the vibrational partition function. The derivative with respect to v is zero since Q_{vib} is independent of volume.

The entropy of helium in the dissolved state is the sum of the entropy of mixing and the entropy of vibration:

$$S(s) = S_{vib} + S_{mix} \tag{A-7}$$

S_{vib} is given by:[11]

$$S_{vib} = 3R \left[\ell n\ Q_{vib} + T \left(\frac{\partial \ell n\ Q_{vib}}{\partial T} \right)_v \right] \tag{A-8}$$

S_{mix} is related to the number of distinguishable arrangements of n_s atoms on N_s sites by:

$$S_{mix} = R\ \ell n \left[\frac{N_s!}{n_s!\ (N_s - n_s)!} \right] = R\ \ell n \left(\frac{N_s - n_s}{n_s} \right) \tag{A-9}$$

For a simple harmonic oscillator with one degree of freedom, the vibrational partition function is:[12]

$$Q_{vib} = \frac{e^{-u/2}}{1-e^{-u}} \approx \frac{1}{u} \tag{A-10}$$

where

$$u = \frac{h\nu}{kT} \tag{A-11}$$

For the system considered here ($T \approx 1200°C$, $\nu \approx 0.8 \times 10^{13} sec^{-1}$), u is on the order of 0.25 and the approximate form of Eq. (A-10) is accurate to one part in 400.

With $n_s/N_s \ll 1$, substitution of Eqs. (A-3) through (A-1) into Eq.(A-2) yields Eq. (1).

An expression similar to Eq. (1) has been utilized for adsorption studies.[13]

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