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REVIEW OF STATUS OF SELF-DIFFUSION
IN US, UN, UO_2 , AND UC

by

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ABSTRACT

The nature of imperfections and their contribution to the diffusion mechanism are of primary interest in a self-diffusion study. With this in mind, the literature on US, UN, UO₂, and UC was reviewed. The review indicates that very few self-diffusion studies or investigations of other properties related to defects have been performed. The bulk of the work has either been done on impure material with questionable experimental techniques or it has not been performed under equilibrium conditions.

INTRODUCTION¹

General

In a perfect crystal, every atom occupies the site assigned to it on the basis of the crystal structure. None of these sites is empty; therefore atoms may migrate only by direct interchange or by a ring mechanism in which three or more atoms rotate as a group. These two types of migration have never really been confirmed; in general, when appreciable migration occurs, it has been linked to the presence of imperfections. These imperfections include one or more of the following: interstitials, vacancies, and associates. An example of an associate is given on page 5. The nature of these imperfections and their contribution to the diffusion mechanism are of primary interest in a self-diffusion study.

The two phenomena involving mass transport over large distances are:

- (1) Migration due to a concentration gradient; i.e., diffusion.
- (2) Migration due to an electric field; i.e., ionic conduction.

The most straightforward approach for describing the movement of atoms is to follow the movement of the various imperfections (either charged or neutral). We will therefore consider a concentration gradient dC_i/dx of a particular type of imperfection. This gradient produces a flux of imperfections j_i that is related to the diffusion coefficient D_i by the following equation:

$$j_i = -D_i \frac{\partial C_i}{\partial x} \quad (\text{Fick's First Law}).$$

Ionic conduction (σ_i) can be described by

$$\sigma_i = C_i Z_i q v_i,$$

where C_i is the concentration of the imperfection, $Z_i q$ is the effective charge, and v_i is the mobility of the imperfection.

The diffusion coefficient (D_i) and the mobility (v_i) of an imperfection are related in the following way:

$$\frac{v_i}{D_i} = \frac{Z_i q}{kT} \quad (\text{Nernst-Einstein relation}).$$

The actual use of this equation is complicated by the fact that measured conductivity of a material is composed of two terms: (1) the electronic conductivity produced by electrons and electron holes (σ electronic), and (2) the ionic conductivity due to the migration of charged atomic imperfections (σ ionic). The conductivity is then the sum of these two contributions:

$$\sigma = \sigma_{\text{ionic}} + \sigma_{\text{electronic}} = \sum_i C_i Z_i q v_i.$$

Often the contribution of one imperfection to conduction is much in excess of the others, so that the others may be ignored. However, if the contributions of the various imperfections are of the same order, it becomes necessary to determine by additional experiments the relative contribution of each mechanism to the total electrical conductivity.

Although it is convenient to discuss diffusion in terms of migrating imperfections, the quantities that are observed experimentally refer to the diffusing atoms and not directly to the imperfections. It then becomes necessary to relate D_i with the gross diffusion coefficient (D_g) actually observed.

An example of this problem given by Kroger¹ is NaCl containing CaCl_2 . Three different imperfections are present in this material: (1) calcium having an effective plus-one charge on a sodium lattice site (CaNa), (2) sodium vacancies having an effective minus-one charge produced to maintain charge neutrality in the crystal (VNa^1), and (3) the neutral associate (CaNaVNa^1)^x or $(\text{CaNaVNa})^x$. Calcium can diffuse only in the form of the neutral associate, but during this diffusion the following association-dissociation equilibrium must be maintained:

A variation in the concentration C_{as} of the associate, therefore, entails a variation in $CaNa$.

The diffusion flux of the associate is

$$j_{Ca} = -D_{as} \frac{\partial C_{as}}{\partial x} = -D_{as} \frac{\partial C_{as}}{\partial C} \frac{\partial C}{\partial x}.$$

Therefore,

$$D_g = D_{as} \frac{\partial C_{as}}{\partial C},$$

where C is, in this case, the total concentration of calcium. Because the concentration of the associate does not vary linearly with the concentration of calcium, we are led to the conclusion that D_g varies with the concentration, but D_{as} is a constant.

Another complication arises from the interpretation of the diffusion constants of the imperfections on an atomic scale. Because diffusion and conduction take place by jumping on the atomic scale, the quantities v_i and D_i must be interpreted in terms of these jumps.

The simplest behavior is found with interstitial diffusion in which the imperfection and the jumping atom are identical. The diffusion coefficient (D_i) can then be described by

$$D_i = \omega_i a^2,$$

where a is the distance over which the imperfection and the atom jump and ω_i is the jump frequency of the atom. The jump frequency is described by the equation

$$\omega_i = \nu_i e^{-\Delta H/kT},$$

in which ν_i is a frequency having a somewhat questionable physical significance, and ΔH is the activation energy involved in the jump. Interstitial diffusion is represented by our standard Nernst-Einstein relation,

$$\frac{v_i}{D_i} = \frac{Z_i q}{kT}.$$

More complicated relations are encountered when the movement of two (or more) different atoms is involved. In this case, the diffusion constant of the imperfection (D_i) is a function of the jump frequency of the various atoms involved, and the various jumps are not independent and give rise to correlation effects. This leads to a modified Nernst-Einstein relation,

$$\frac{v_i}{D_i} = \frac{1}{f} \frac{Z_i q}{kT},$$

where f is the correlation factor. Typical values of the correlation factor for vacancy-tracer diffusion in various structures are as follows: 0.5 (diamond lattice); 0.656 (simple cubic); 0.722 (body-centered cubic); 0.782 (face-centered cubic and hexagonal close-packed).

Diffusion involving two different atoms is found in the diffusion of calcium in NaCl via the $(Ca_{Na}V_{Na})^x$ associate. The migration of this associate involves both jumps of the neighboring vacancy (jump frequency ω_2) and jumps of the neighboring sodium atoms (jump frequency ω_1) required to position the vacancy in front of the calcium so that a following jump may occur.

Only sodium jumps near the calcium need be taken into account if the associate is strongly bound. The following equation may be developed:

$$\omega_{as} = \frac{\omega_1 \omega_2}{\omega_1 + \omega_2}.$$

When $\omega_1 \gg \omega_2$, $\omega_{as} \approx \omega_2$; and when $\omega_1 \ll \omega_2$, $\omega_{as} \approx \omega_1$. In this case, $\omega_1 \ll \omega_2$; therefore the rate of diffusion is controlled by the host-atom jump frequency.

If the complex $(Ca_{Na}V_{Na}')^x$ is weak, then jumps of the vacancy away from the calcium must be taken into account. This leads to excited states of the associate and finally even to dissociation.

The radioactive tracer-vacancy associate is an example of a weak associate. If diffusion takes place via lattice sites, sodium and chlorine atoms in NaCl can only move if they are adjacent to a vacancy. Therefore the complexing with a vacancy is required of a tracer to detect diffusion. But this is a very weak associate. In fact, the heat of association equals zero, and the associate is formed only as a result of the random distribution of tracers and vacancies. For a weak associate, $\omega_1 \approx \omega_2 \approx \omega$ gives a solution for the diffusion problem with a marked correlation effect varying from $\omega_{as} \approx 0.5\omega$ to $\omega_{as} \approx 0.8\omega$, depending on the crystal structure. Correlation effects in tracer diffusion do not occur, if the tracers diffuse via an interstitial mechanism. They do occur, however, if the tracer diffuses by the interstitialcy mechanism. With this mechanism, a normal lattice atom from a site adjacent to the interstitial tracer jumps into an empty interstitial site, whereupon the tracer, in a coordinated jump, fills the vacancy left behind by the normal atom.

A further complication arises in relation to the diffusion of imperfections charged with respect to the lattice. When a positively charged imperfection begins moving, a negatively charged imperfection must also

move to maintain a local charge uniformity. If this does not occur, then an electric field (diffusion potential) builds up that tends to stop the diffusion. It is, therefore, evident that the diffusion of the oppositely charged imperfection is coupled and that the diffusion will in general be determined by the slower of the two imperfections taking part.

In our example of calcium-doped NaCl, the only charged imperfections are CaNa and VNa , so that the movement of VNa must be accompanied by the migration of CaNa . But CaNa cannot diffuse; therefore VNa also will not contribute to the diffusion, so that only the neutral associates $(\text{CaNaVNa})^x$ diffuse.

Now if an electric field is applied, one might think that calcium does not migrate because single calcium centers CaNa have an effective charge but cannot move, whereas the associates that can move are neutral and are thus not pulled by the field. This is true for strong associates. For weak associates, there is an effect due to the fact that sodium jumps that lead to dissociation of an associate are favored by the field when they take place at the positive side of the pair, whereas sodium jumps that lead to association of a sodium vacancy with a single calcium center are favored at the negative side of the pair. Once a new pair has formed, with the vacancy at the negative side, the calcium can jump into it, following the pull of the field. In this manner, the calcium can make one jump down the field whenever a new associate is created. Therefore, associates with short half-lives (weak associates) will show a greater efficiency of migration of calcium in an electric field, because whenever an associate is formed or reformed it will present the conditions for the calcium to diffuse in the direction of the field.

Nonstoichiometric Compounds

The manner in which diffusion is affected by a deviation from stoichiometry depends on the defect type. It therefore follows that an investigation of diffusion over a range of stoichiometry might aid in clarifying the defect type. As an example of how diffusion measurements can help determine the type of defects, consider the compound PbS. If this compound has Schottky disorder, an excess of lead would be accommodated with the formation of sulfur vacancies, with a corresponding decrease in the concentration of lead vacancies. If the crystal contained excess sulfur, the opposite would occur. The result would be that lead would diffuse fast in sulfur-rich crystals and slow in lead-rich crystals. The diffusion of sulfur would be just the opposite.

A different diffusion behavior would be expected if PbS would have Frenkel disorder. For predominant Frenkel disorder of the lead, excess lead results in lead interstitials and excess sulfur results in lead vacancies. If both defects have a comparable mobility, we would expect an increase of the diffusion of lead with both an increasing excess of lead and an increasing excess of sulfur. If the sulfur had Frenkel disorder, we would expect an

increase in the diffusion of sulfur with both an increasing excess of lead and an increasing excess of sulfur. The preliminary experiments of Anderson and Richards² showed that the self-diffusion of lead in sulfur-rich PbS was faster than in stoichiometric or lead-rich material. This result seemed to indicate Schottky disorder. However, the more recent experiments of Simkovich and Wagner³ showed that the self-diffusion rate of lead was a minimum near the stoichiometric point, which indicated that Frenkel disorder of lead was the predominant defect. This conclusion was substantiated by experiments of silver- and bismuth-doped PbS performed by Seltzer and Wagner.^{4,5} They showed that the self-diffusion of sulfur is fast in sulfur-rich PbS, is much slower in PbS that is stoichiometric or has a small excess of lead, and decreases slightly with further additions of lead. This suggests that an excess of sulfur produces interstitial sulfur as well as the lead vacancies found by the lead-diffusion experiments. The sulfur must then diffuse either interstitially or via lead vacancies. Because the presence of interstitial sulfur indicates Frenkel disorder of the sulfur, the actual defect state in PbS is most probably either a mixture of Frenkel disorder of lead and sulfur with lead predominating (sulfur diffusing interstitially), or mainly lead Frenkel disorder (sulfur diffusing via cation vacancies). But if both lead interstitials and sulfur vacancies exist together, then we might also speak of interstitial disorder with an admixture of Frenkel disorder of the lead. The disorder found by the use of diffusion measurements over a range of compound composition can then be compared with the Kroger-Vink diagram ($\ln$ [sulfur partial pressure, P_{S_2}] vs $\ln$ [concentration of each imperfection]) obtained from chemical equilibrium calculations. This diagram can be used to determine in a quantitative manner which imperfections are responsible for the observed disorder model. The PbS study is a prime example of how the defects in a compound having a range of stoichiometry can be studied by means of diffusion measurements.

MATERIALS INVESTIGATED

Uranium Monosulfide

No information has been reported on self-diffusion in US. Uranium monosulfide does exhibit an appreciable, though as yet not well-determined, range of stoichiometry. The maximum limits of the S/U ratio at room temperature are 0.96 to 1.01 according to Cater,⁶ and 0.96 to 1.03 according to Shalek.⁷ At temperatures above 1700°C, Cater shows essentially a line compound in his schematic phase diagram. The basic problems of oxygen and nitrogen contamination and the limitations of chemical analysis for sulfur make the reported range of stoichiometry in US more questionable than it appears. Shalek also reports a decrease of the lattice parameter on both sides of $S/U = 1.00$, and this decrease could suggest the presence of Schottky disorder. This should also be closely scrutinized, however, because the presence of nitrogen and oxygen impurities (which were found in sizable quantities) appeared to produce significant decreases in the lattice parameter.

Although there is a question about the exact range of stoichiometry (this still has to be determined for high-purity material), it certainly is present. It would, therefore, be of interest to study the self-diffusion of uranium and sulfur, not only to obtain diffusion coefficients per se, but to obtain information about the diffusion mechanism, i.e., atomic disorder. A good isotope of sulfur (S^{35}) having an 87-day half-life and emitting a 0.167-MeV β particle is available for use in tracer measurements. Both the counting of sections and residual-activity methods could be used simultaneously to determine the rate of S^{35} self-diffusion. Uranium does not have an adequate β - or γ -emitting isotope; therefore another method must be used. One can measure the α activity of diffusing U^{235} by the surface-activity decrease method,⁸ measure mass-spectrographically the U^{235} content in a sectioning experiment,⁹ or determine the U^{235} content by fission-counting sections in a neutron environment.⁹ Preferably, the fission counting of removed sections and the determination of α activity with the surface-activity decrease method should be used together. Because of the NaCl structure in US, no problems are expected with anisotropic diffusivities.

This brings us to another problem (oxygen contamination) inherent in working with all uranium ceramic compounds. The uranium monosulfide presently available contains typically about 2000 ppm of oxygen when produced by reacting UH_3 with H_2S gas at 550°C. The product of this reaction is ground to the desired particle size, pressed, and sintered at 1700 to 2050°C. To improve the purity of this material several steps might be taken; e.g.,

1. All operations could be done in inert-gas gloveboxes (many are now, but not all).
2. More care could be exercised in the hydriding of uranium to UH_3 and its subsequent reaction with H_2S .
3. The final pressed and sintered body could be melted in a tungsten crucible in vacuum to drive off oxygen.

Once a product of relatively high purity is obtained, it would then be desirable to grow single crystals. Studies with single crystals are useful in eliminating the possibility of grain boundary diffusion.

The temperatures necessary to obtain sufficiently large diffusion rates to make accurate measurement should be of the order of T_m down to $0.7T_m$ (the melting point of US is $2462 \pm 30^\circ C$ ⁶). The tracer diffusion coefficient of U^{234} in UO_2 has been found to be about $10^{-13} \text{ cm}^2/\text{sec}$ at 1800°C;¹⁰ the melting point of UO_2 is about $2806 \pm 45^\circ C$.¹¹ This suggests that the self-diffusion of uranium in US would probably have to be studied at temperatures above 1500°C.

Another experimental condition that must be mentioned at this point is the necessity of maintaining the diffusion specimen at a given stoichiometry through the duration of an experiment. To do this, the specimen

must be held at equilibrium with the surrounding atmosphere so that there will be no net exchange between the specimen and the atmosphere. A standard method applied to maintaining a given partial pressure of $S_2(g)$ is the use of H_2S/H_2 mixtures. At a given temperature and H_2S/H_2 ratio, the S_2 partial pressure is defined by the reaction $H_2 + (1/2) S_2 \rightleftharpoons H_2S$. The equilibrium constant,

$$K_{H_2S} = \frac{P_{H_2S}}{P_{H_2}(P_{S_2})^{1/2}},$$

for this reaction has been thoroughly studied and is well-defined.¹² The equilibrium partial pressure of sulfur over US with various compositions, however, has not been measured. We can estimate the partial pressure of sulfur over US from the work of Cater (for US of unknown stoichiometry). He found for the reaction

that

$$\Delta G = -109,000 + 23.0T \text{ cal/mole } (298-1405^\circ K).^{6,13}$$

Extending this equation and using the plot of Richardson and Jeffes¹⁴ make it possible to estimate the sulfur vapor pressure and H_2S/H_2 ratios. The results are given in Table I.

The free energy obtained by using $U(S) + (1/2) S_2 \rightarrow US(S)$ does not, of course, strictly hold above $1405^\circ K$ (the melting point of uranium); but

TABLE I. Estimated PS_2 and H_2S/H_2 Ratio for US from Thermodynamic Data

Temp, °C	PS_2 , atm	H_2S/H_2 Ratio
1200	10^{-22}	$\frac{1}{10^{10.5}}$
1400	10^{-18}	$\frac{1}{10^9}$
1600	10^{-15}	$\frac{1}{10^{7.5}}$
1800	10^{-13}	$\frac{1}{10^{6.5}}$
2000	10^{-11}	$\frac{1}{10^6}$

because of the small break in the free-energy curve at the uranium melting point, we should still be able to use our ΔG equation for estimating equilibrium pressures without serious error.

It is apparent that the very small H_2S/H_2 ratios in Table I are not very practical experimentally. Problems with thermal diffusion and proper gas-mixing eliminate H_2S/H_2 mixtures as equilibrium atmospheres for uranium monosulfide. We must, therefore, use another technique to

establish an equilibrium atmosphere over US. This can be accomplished by using another sulfide whose sulfur pressure is known at various temperatures. A fairly large amount of the other sulfide can be held in one part of a closed system at a temperature giving the desired $S_2(g)$ pressure, while the US specimen is held in another part of the system at the test temperature. Because both materials are in the same closed system, the partial pressure of S_2 over US is the same as the known partial pressure of S_2 over the other sulfide. While making all measurements, one must maintain the temperature of the whole system above the boiling point of sulfur (444.6°C)¹⁵ so that condensation of the S_2 gas will not occur. If condensation were to occur, equilibrium would be difficult to obtain.

This has fairly well described what needs to be done to obtain self-diffusion measurements in US. At this point, it would be useful to look at some other properties of US that could yield information on the type of diffusion mechanism to be expected in US.

Let us first examine the electronic properties of US (by using electrical resistivity, Seebeck coefficient, and Hall coefficient) to get a picture of the proposed electronic band structure. By measuring resistivity and Seebeck coefficient up to 1000°C , Tetenbaum¹⁶ found that US is semimetallic in nature. Its resistivity increases nonlinearly from $286\ \mu\text{ohm-cm}$ at room temperature to about $328\ \mu\text{ohm-cm}$ at 850°C . Its Seebeck coefficient (thermoelectric power) is positive (hole conduction), with a value of $50\ \mu\text{V}/^\circ\text{C}$ at 25°C ; it increases to a maximum of $59.2\ \mu\text{V}/^\circ\text{C}$ at 300°C , and gradually decreases to $43.5\ \mu\text{V}/^\circ\text{C}$ at 1000°C (the highest temperature tested). Kanter and Kazmierowicz¹⁷ found that the Hall effect is positive and, therefore, the current is carried by holes. They found a temperature-dependent Hall coefficient, which yielded the following carrier density values: $n \approx 1.2 \times 10^{21}\ \text{cm}^{-3}$ at 25°C , and $n \approx 1.6 \times 10^{21}\ \text{cm}^{-3}$ at 90°C .

The band model suggested by Tetenbaum and Kanter and Kazmierowicz assumes that two of the uranium valence electrons form bonds with sulfur, and in a cubic crystalline field, the uranium f states will be split into a singlet and two triplet groups, and two of the remaining uranium valence electrons will fill the lowest singlet state. We are then left with a fairly broad s conduction band, which is almost filled, and overlapping it near the top of the nearly filled conduction band is one of the f bands associated with one of the triplet states. We would expect the partially filled f band to be narrow and one in which the density of states would be higher than in the s band. For such a model, current transport will be primarily by holes in the s band, and the relaxation time will be largely determined by the narrow f band. The weak temperature dependency of resistivity found in US might be attributed to a mutual cancellation of the following factors over a wide temperature range:

- (1) An increase in the number of phonons with rising temperature, tending to give an increase in resistivity with temperature.
- (2) An increase in the number of charge carriers with temperature, tending to give a decrease in resistivity with temperature.
- (3) A shift of the Fermi level toward a region of lower density of states, resulting in a lower density of final states for s-f scattering, and hence tending to give a decrease in resistivity with increasing temperature.

An explanation of the temperature dependency of the thermoelectric power was not offered, but it should be emphasized that the thermoelectric power depends quite sensitively on the detailed shape of the conduction band and on the detailed energy dependence of carrier relaxation time.

With the exception of the rather preliminary work of Shalek on the lattice parameters of US, nothing has been done that might lead us to the principal disorder present. We must, therefore, conclude that the nature of disorder in uranium monosulfide is completely unstudied and that self-diffusion experiments could yield some very pertinent results.

Uranium Mononitride

Progress on the determination of properties pertinent to self-diffusion studies in UN has generally not advanced as far as in US. No information has been reported on self-diffusion in UN. Uranium mononitride has a large range of stoichiometry above 1200°C (about $\text{UN}_{0.96}$ at 1500°C and $\text{UN}_{0.80}$ at 2000°C for the lower limits, and $\text{UN}_{1.01 \pm 0.02}$ at 1600°C for an upper limit).¹⁸ Below 1200°C, the stoichiometry range is very narrow and appears in the partial phase diagram as a line compound. The measurement of lattice parameters in UN is not too helpful in looking for the principal type of disorder because of side effects produced by oxygen contamination. This is very similar to the US problem. As a matter of fact, many of the problems found in US are also common to UN, namely, preparation of high-purity material, production of single crystals, and the general lack of pertinent properties necessary for a comprehensive self-diffusion study.

The self-diffusion of uranium would be determined by using the techniques described for US. The diffusion of nitrogen, however, is a different matter. Because no useful radioactive isotope is available, another technique must be used. One that comes to mind is an isotope-exchange experiment with the two naturally occurring isotopes of nitrogen (N^{14} and N^{15}). The general method consists of annealing UN made with nitrogen depleted in N^{15} (natural nitrogen consists of 99.634% N^{14} and 0.366% N^{15}) in an atmosphere enriched with N^{15} . One then analyzes the gas atmosphere periodically with a mass spectrometer and, from the changing $\text{N}^{14}/\text{N}^{15}$ ratio, calculates the self-diffusion coefficient of nitrogen.

More details as to this method and some of its shortcomings will be discussed in the section on uranium dioxide (page 15) to which it has already been applied. There is also a possibility of applying an activation analysis to nitrogen self-diffusion.

The temperatures necessary to obtain diffusion rates of sufficient magnitude to make accurate measurements should be above 1800°C (the congruent melting point is about $2835 \pm 30^\circ\text{C}$).²⁰

To maintain the diffusion specimen at a given stoichiometry through the entire experiment, the specimen must be held in equilibrium with the surrounding atmosphere. This could be accomplished by maintaining a NH_3/H_2 atmosphere around the specimen, or by defining the nitrogen partial pressure in the system through the presence of another nitride whose equilibrium nitrogen partial pressure at various temperatures is well-known.

Knowing that for the reaction,

$$\Delta G = -70,000 + 20.5T \text{ cal/mole } (298-1405^\circ\text{K}),^{13,19}$$

we can estimate the nitrogen pressure necessary to maintain equilibrium. Begin with the equation

$$\Delta G = -RT \ln K,$$

where K can be taken to equal $1/(\text{P}_{\text{N}_2})^{1/2}$. Rearranging

$$\Delta G = RT \ln \text{P}_{\text{N}_2}^{1/2}$$

results in

$$2\Delta G = RT \ln \text{P}_{\text{N}_2},$$

or

$$\text{P}_{\text{N}_2} = e^{2\Delta G/RT}.$$

Table II presents the results when we insert the proper values for ΔG and T .

Since the pressures listed in Table II are considerably higher than those estimated for US, they may be more readily attainable by using NH_3/H_2 mixtures (than by using $\text{H}_2\text{S}/\text{H}_2$ mixtures in the case of US) with the equilibrium

TABLE II. Estimated P_{N_2} for UN from Thermodynamic Data

Temp, °C	P_{N_2} , atm
1600	10^{-7}
1800	10^{-6}
2000	10^{-5}

If the required pressures are not obtainable with NH_3/H_2 mixtures, then a nitride having a known equilibrium partial pressure of N_2 at various temperatures can be used, just as in the case of US. The advantage with nitrides is that nitrogen will not condense at room temperature but sulfur will. This makes the experimental setups somewhat less clumsy.

Little has been done on characterizing chemical bonding in UN. From the high electrical conductivity (resistivity of $176 \mu\text{ohm-cm}$ at 200°C and a positive temperature coefficient have been reported),¹⁸ UN like US must have a reasonable degree of metal-metal bonding, while the characteristically high melting point implies that the metal-nonmetal bonds are substantial. Allbutt *et al.*,²⁰ suggest from magnetic measurements that bonding in uranium nitrides, phosphides, and carbides has considerable covalent character but US is somewhat ionic. This ionic character of US suggested by Allbutt is somewhat complicated according to a band model proposed by Tetenbaum and Kanter and Kazmierowicz.

As in the case of US, nothing is known about the defect character of UN. For this reason, it would be of interest to study self-diffusion in UN to gain some knowledge of the migration mechanism and perhaps relate this to the basic understanding of the entire group of uranium compounds having a NaCl structure (UC, US, UN, UP, etc.).

Uranium Dioxide

In contrast to US and UN, self-diffusion studies in UO_2 have been performed. Auskern and Belle²¹ measured the self-diffusion of oxygen in UO_2 from 300 to 780°C by an isotope-exchange method. They obtained diffusion coefficients by annealing powders of UO_2 in an atmosphere of CO_2 enriched with O^{18} over a stoichiometry range of $UO_{2.002}$ to $UO_{2.092}$ (Fig. 1). In these experiments, no attempt was made to maintain the annealing atmosphere in equilibrium with the UO_2 of a given composition. They analyzed the powders after annealing to determine if any oxidation had occurred. No evidence was

Fig. 1. Self-diffusion of Oxygen in Uranium Dioxide, after Auskern and Belle²¹

found for an increase in the oxygen content of the UO_2 . They added hydrogen to the CO_2 atmosphere so as to sharply reduce the O_2 partial pressure produced by the reaction

They reported that no significant change by the reaction $\text{H}_2 + (1/2) \text{O}_2 \rightleftharpoons \text{H}_2\text{O}$ in oxygen self-diffusion rates was found when the H_2/CO_2 mixtures were used. It does, however, seem strange that some oxidation at the surface of the powders did not occur. One would expect a change in the self-diffusion rate if an appreciable amount of surface oxidation had occurred because of the large rate increase that was found with increasing oxygen content. A number of errors are inherent in the isotope-exchange experiment. Some of the more important errors are the estimation of the powder's surface area, the nonsphericity of the particles, the range of particle size, and the packing of the particle bed. These are all experimental difficulties that could theoretically be overcome by refinements in technique. Recently, however, a very large shortcoming of this method was confirmed. Diffusing O^{18} into BeO , Holt²² found, on using a proton activation technique and sectioning, that the reported values for self-diffusion of oxygen are in serious error (much too large). It is reasoned that, because the powders contain many cracks, grain boundaries, and dislocations, what people have been measuring with isotope-exchange experiments is not volume diffusion, but various types of surface diffusion. The result of this very significant experiment is to make questionable the usefulness of all isotope-exchange experiments. This could very easily be reflected in the results of Auskern and Belle. Aronson *et al.*²³ showed that the oxidation of UO_2 to U_3O_8 is controlled by diffusion of oxygen through the uranium dioxide lattice. In the temperature range investigated, 160 to 350°C, the diffusion coefficients for oxygen during oxidation can be represented by the equation

$$D = 5.5 \times 10^{-3} \exp(-26,300/RT).$$

This appears to be at least qualitatively consistent with Auskern and Belle's results near the limit of the UO_2 phase region ($\text{UO}_{2.063}$, where $D = 2.06 \times 10^{-3} \exp[-29,000/RT]$).

The strong dependence of the oxygen self-diffusion rates on oxygen concentration suggests that the diffusion-current carriers are either interstitial oxygen or uranium vacancies. Willis,²⁴ using neutron diffraction, confirmed that in UO_2 , which has a CaF_2 structure, excess oxygen is present interstitially.

Auskern and Belle consider the diffusion step in nonstoichiometric UO_2 to be one in which an interstitial ion and a lattice ion move in combination, the lattice ion moving into an available neighboring interstitial site, and the interstitial ion moving into the vacated lattice site. This mechanism (discussed on page 8) is interstitialcy diffusion,²⁵ and Auskern and Belle feel it is more reasonable than direct interstitial-lattice exchange. If in UO_2 the formation of diffusion current carriers takes place thermally, then either anti-Frenkel (O vacancies and O interstitials) or anti-Schottky (O interstitials and U interstitials) disorder is present.

The diffusion measured in stoichiometric UO_2 ($\text{UO}_{2.004}$) may have been due to the presence of impurities (extrinsic diffusion), which would completely swamp out the intrinsic diffusion due to the thermally activated defects. Inasmuch as the purity of the powders was not given in the report, the powders may have been relatively impure and the diffusion measured in $\text{UO}_{2.004}$ from 550 to 780°C was quite possibly extrinsic. Auskern and Belle make a simple calculation to determine the energy to form an anti-Frenkel defect (which is the disorder that appears to be present in the temperature range investigated). The calculation results in a value of 70 kcal/mole. No other work has been reported on the self-diffusion of oxygen in UO_2 .

Fig. 2. Self-diffusion of Uranium in UO_2 , after Auskern and Belle¹⁰

Auskern and Belle¹⁰ also measured the self-diffusion of uranium in pressed and sintered (99.97% pure), 98% dense, stoichiometric UO_2 (no oxygen composition given). In the temperature range of 1450-1785°C, the uranium diffusion can be represented in Fig. 2 by the equation

$$D = 4.3 \times 10^{-4} \exp(-88,000/RT) \text{ cm}^2/\text{sec}.$$

The experimental methods used in their studies are fraught with uncertainty. They used the surface-activity-decrease technique to determine the diffusion coefficients because penetrations of only a few microns were found (Fig. 3). It is somewhat questionable that they could grind off 0.2- μ layers with reasonable certainty. They used semi-infinite couples with a coating of highly enriched U^{235}O_2 on one surface. They found no evidence for a bound tracer layer, but did have problems with surface evaporation of the tracer material before diffusion into the sample occurred.

Their counting technique also lent itself to sizable errors. It is somewhat difficult to accurately count, in 0.2 μ increments, α particles having a range in UO_2 of about 10 μ . The counting was done with a ZnS scintillator separated from the UO_2 with a small air gap and a Mylar window. The range that the ZnS crystal would detect, including the window, air gap, and energy-discrimination level at

Fig. 3. Activity and Concentration Profiles for U^{235} Diffusion in UO_2

which the counter was operating, made possible an estimate of the UO_2 range in their experiment. However, at best this estimate is only good to $\pm 25\%$.

There was also some evidence, as one would expect, that grain-boundary penetration occurred in these polycrystalline pressed-and-sintered samples.

Auskern and Belle assumed that in stoichiometric UO_2 , the predominant thermal disorder in the cation lattice is also due to Frenkel defects. There appears to be no good basis for this assumption, however,

because they have no data on nonstoichiometric material. At high temperatures (above 1700°C ²⁶), UO_2 can be nonstoichiometric with either an excess of uranium or oxygen; below 1700°C , only an excess of oxygen is found.

Fig. 4. Self-diffusion of Uranium in UO_2 , after Lindner²⁷

The self-diffusion measurements of uranium into uranium dioxide performed by Lindner²⁷ show in Fig. 4 an increase in the diffusion kinetics with increasing oxygen content (argon presumably had a higher oxygen partial pressure than did the hydrogen). Lindner used an α -absorption technique with U^{233} as the tracer material. His experimental technique

and its problems are very similar to Auskern and Belle's. The significant thing in these studies is that the diffusion rate increases with an increase in oxygen. Because of the low temperature of investigation, Lindner may have just been measuring extrinsic diffusion. However, if the results in argon were due to UO_2 having a relatively large oxygen excess, then the results should represent intrinsic diffusion.

The quantities reported in all these diffusion studies are really isotope-diffusion coefficients. True self-diffusion coefficients could not be reported because the exact mechanisms of diffusion are unknown. This, therefore, makes it impossible to apply correlation corrections.

Scott et al.,²⁸ in a plastic deformation study of UO_2 , found that the activation energy (Q) for creep in UO_2 appears to vary with the oxygen/uranium ratio, being about 72 kcal/mole for $\text{UO}_{2.06}$, 65 kcal/mole for $\text{U}_{2.16}$, and ≥ 95 kcal/mole for $\text{UO}_{2.0}$. The value for $\text{UO}_{2.0}$ is approximately the same as that determined for the self-diffusion of uranium in $\text{UO}_{2.0}$ by Auskern and Belle and Lindner. Similar activation energies for creep have been found by Armstrong et al.^{29,30} Scott was not able to propose a creep mechanism but suggested it was related to the uranium-diffusion mechanism.

In his sintering studies on stoichiometric and nonstoichiometric UO_2 , Araos³¹ found that the activation energies for sintering were 110 kcal/mole for $\text{UO}_{2.005}$ and 75 kcal/mole in the range of $\text{UO}_{2.02}$ to $\text{UO}_{2.16}$. These values agree with those obtained for uranium diffusion in UO_2 by Auskern and Belle and Lindner, which suggests that UO_2 sintering is a volume-diffusion process controlled by the diffusion of uranium. Araos was also unable to arrive at the sintering mechanism in UO_2 but suggested that it was related to the diffusion of uranium.

A property closely related to mass transport in semiconductors like UO_2 is charge transport. It is, therefore, useful to look at some electrical-conductivity measurements made on this material. Several investigators³²⁻³⁸ have studied electrical conductivity and thermoelectric power chiefly to correlate the electrical properties with excess oxygen content. The interpretation of Willardson et al.³⁷ was based on the assumption that UO_2 is a classical semiconductor and that a band picture is valid. Aronson et al.³⁸ assumed that UO_{2+x} is a simple ionic crystal containing U^{4+} and U^{5+} cations, and lattice and interstitial O^{--} anions. Heikes and Johnston³⁹ explained the electrical conduction in UO_{2+x} as an activated jumping of localized holes between U^{5+} and U^{4+} , and thus he introduced the concept of the hopping mechanism of conduction in UO_2 . Hartmann,⁴⁰ Hasiguti and Kiyoura⁴¹ found large Hall mobilities and a temperature dependence, both of which seemed to support ordinary band semiconduction. Electrical measurements on pressed and sintered specimens have, in general, only a limited significance because the conductivity is at least partially determined by the resistance of many intergranular boundaries, which in as easily oxidized a semiconductor as UO_2 have a different composition from the bulk material.

The most recent study in this area was performed by Nagels et al.⁴² on single-crystal uranium dioxide having compositions in the range of $\text{UO}_{2.000}$ to $\text{UO}_{2.007}$. The conduction was investigated by means of electrical conductivity and Hall measurements. Using a.c. and d.c. methods, Nagels et al. were unable to detect any Hall effect between 200 and 950°K. From the sensitivity of the apparatus, this result indicates that at room temperature the Hall mobility has to be less than $0.015 \text{ cm}^2 \text{ volts}^{-1} \text{ sec}^{-1}$ at room temperature (the sensitivity of the experiment). Electrical conductivity measured between 90 and 800°K yields an activation energy for conduction which decreases from 7.9 to 4.4 kcal/mole with increasing excess-oxygen content. Nagels et al.

concluded that the small-polaron theory seems to be most adequate to describe the conduction mechanism in UO_2 . Under certain nonideal conditions, these small polarons might contribute to the conductivity by means of a Ferrei mechanism. Under these circumstances, Nagels' results confirm Aronson's assumption of the hopping motion of holes in uranium dioxide.

Although self-diffusion studies of both the cation and anion have been done in UO_2 , they appear to be somewhat unreliable. It is questionable as to what the diffusion mechanism is, especially for uranium migration. Oxygen diffusion might be done by a sectioning method in which an activation analysis for diffusion O^{18} is used. Uranium self-diffusion should be done by the sectioning fission counting and surface-decrease methods described earlier in this report. To get reasonable diffusion coefficients ($10^{-12} \text{ cm}^2/\text{sec}$ or larger), the experiments would probably have to be run above 1800°C . As mentioned earlier, there is evidence for both hypo- and hyperstoichiometric, single-phase UO_2 above 1800°C . It would, therefore, be interesting to study the diffusion of uranium in hypo- and hyperstoichiometric UO_2 to determine its mechanism and the general type of disorder present in the compound. Preceding studies suggest that the uranium disorder may be Frenkel (U interstitials and U vacancies) or anti-Schottky

(U interstitials and O interstitials), but experiments should be performed on high-purity single crystals of UO_2 (Ref. 43) in equilibrium with an atmosphere having the correct partial pressure of oxygen to hold the UO_2 at a desired composition. The equilibrium between UO_2 and O_2 has been studied by a number of investigators,^{26,44-47} but the highest temperature was 1600°C . The results of two more useful studies are shown in Figs. 5 and 6. Before diffusion studies can be done above 1600°C , it will be necessary to establish the partial pressures of oxygen in equilibrium with UO_2 of various compositions.

Fig. 5. Relation of Oxygen Pressure and Temperature to Compositions between $\text{UO}_{2.00}$ and $\text{UO}_{2.63}$, after Chapman and Meadows²⁶

The determination of the self-diffusion mechanism for uranium should be helpful in arriving at the mechanisms for sintering and creep in UO_2 . It should also give valuable information on the type of disorder present. The understanding and control of this disorder will be very useful in altering key properties such as thermal conductivity and melting point, which are dependent on stoichiometry.

Fig. 6. Relation of Oxygen Partial Pressure and Temperature to UO_2+x , after Hagemark⁴⁴

Uranium Monocarbide

Self-diffusion of uranium and carbon in polycrystalline UC having excess carbon has been measured by Chubb *et al.*⁴⁸ by using U^{235} and C^{14} tracers. These measurements were made in the 1200-2120°C range, and the results are given in Figs. 7 and 8. There is some question as to the fundamental significance of the diffusion coefficients obtained because, in the temperature interval studied, UC has an appreciable range of nonstoichiometry⁴⁹ (both hyper- and hypostoichiometric, with respect to carbon). It is therefore possible that, during testing, the composition and the defect concentration could change. This aspect of diffusion was not considered by Chubb *et al.* The predominant defects in UC are not known, but we might guess them to be interstitial carbon atoms in

Fig. 7. Self-diffusion of Carbon in UC, after Chubb *et al.*⁴⁸

Fig. 8. Self-diffusion of Uranium in UC, after Chubb *et al.*⁴⁸

material having excess carbon. If carbon is diffusing by an interstitial mechanism, one would expect the diffusion rate of carbon to increase as interstitial carbon content increases. The uranium diffusion could also be affected by this change in carbon-defect concentration through the equilibrium maintained between the carbon interstitials and, say, uranium vacancies. Similar arguments could be used for UC containing excess uranium.

In all fairness to Chubb *et al.*,⁴⁸ it should be pointed out that obtaining diffusion measurements under equilibrium conditions in UC is experimentally very difficult. Because carbon has such a low vapor pressure, it might be necessary to maintain the UC in equilibrium with given partial pressures of uranium. This would have to be done by holding uranium or one of its compounds at a temperature at which the vapor pressure is known and annealing the UC at some higher temperature in the same closed system. This is similar to the second technique described for defining the sulfur partial pressure over US. It would be necessary to determine the equilibrium partial pressure of uranium over UC at various stoichiometries before conducting the diffusion experiments. Because of these problems, UC is a very disagreeable material to study, and it would probably be difficult to improve on Chubb's data to the point where we would have more than merely diffusion rates obtained under nonequilibrium conditions on material of uncertain composition. It therefore seems unlikely that information on defects and diffusion mechanism could be obtained with a reasonable amount of effort on UC by means of tracer techniques.

CONCLUSIONS

Little is known about the defects that produce nonstoichiometry and alloy atom migration in US, UN, and UC, and studies of anion and cation diffusion would be very helpful in determining the nature of these defects. There would, however, be serious experimental difficulties associated with investigating these materials (especially UC).

The state of knowledge of UO_2 is much more advanced than it is for the other materials considered. Electrical-conductivity measurements have been performed, and much is known about the conduction mechanism. Work has been done on the determination of the principal disorder by using neutron diffraction, electrical conductivity, and self-diffusion measurements, but the defect picture is still unclear, especially with respect to uranium ion diffusion and the recent discovery that UO_2 can exist with excess uranium at high temperature. Information on both oxygen and uranium ion diffusion under equilibrium conditions would help to establish the proper defect model for UO_2 .

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