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**TRITONS AND TRITIDES AS THE SOLUTE AND DIFFUSING SPECIES
IN CERAMIC TRITIUM BREEDERS**

by

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SUMMARY

Intragranular diffusion of tritium is one component of the overall process for tritium release from lithium-containing ceramics that may be used to breed tritium in a fusion reactor. The nature of this transport is reviewed in terms of the understanding established for the mechanism of hydrogen migration in other oxides. In this mechanism, the diffusing species is the proton, which moves from oxide ion to oxide ion, thereby giving rise to apparent hydroxide migration. Analogously, at high oxygen activity, the triton, transiently bonded to successive oxides and forming successive tritoxides, is taken to be the dominant migrating species in ceramic breeders. In addition, tritide is a significant participant in tritium release at low oxygen activity. The relationship of tritons and tritides as the migrating species to the observed release of both reduced and oxidized forms of tritium can be understood in terms of the thermodynamic conditions that prevail. Mechanisms are proposed to rationalize the participation of these species.

INTRODUCTION

Reports on the release of tritium from ceramic breeder materials often deal with release rates that appear to depend on surface or bulk diffusion. Tritium release is described in terms of "tritiated species" that diffuse through the bulk or on the surface of the breeder material. While the phrase "tritiated species" is conservative and consistent with the fact that studies to identify the species in the breeders of interest are rare, the phrase obscures some details and useful concepts that are available both in theory and in experimentation. It is the purpose of this paper to review some of the work that has been done with oxide systems other than tritium breeders in order to provide a basis, at least by analogy, for understanding observations in tritium breeders in terms of tritons and tritide ions. Some original calculations will be presented to help unify the triton and tritide concepts for the breeder LiAlO_2 . These calculations indicate the possibility for two diffusional processes for tritium transport. Surface charge layer effects and their modification by adsorbed gases are reviewed and a suggested connection between them is made to offer a rationale for the impact of hydrogen and oxygen on tritium release. Radiation damage effects are not considered, except for one that is especially important thermodynamically and one that is seen as participating in adsorption-desorption.

REVIEW -- OCCURRENCE OF HYDROXIDE

Hydroxide in Lattice

In 1966, S. Stoz and Carl Wagner published a paper [1] in which earlier understanding for equilibria between $\text{H}_2\text{O}(\text{g})$ and oxidic melts was extended to solid oxides. In the melt, the reaction had been formulated as:

They proposed that for solid oxides the process could be formulated in terms of defect notation as:

where H_i is an interstitial proton, $\text{V}_\text{O}^{\bullet\bullet}$ is an oxide ion vacancy with a net double positive charge, and O_O is an oxide ion in its usual position in the oxide sublattice. They called attention to the dependence of oxide vacancies on temperature and oxygen activity in the coexisting gas phase. This relationship was formulated as:

Here, e' is an electron. This equation indicates that by treating an oxide with a reducing agent or by subjecting it to vacuum to remove O_2 , the reaction will be displaced to the left and will increase the concentration of oxide vacancies, V_O . An additional possibility under reducing conditions was considered, namely, the occurrence of the negatively charged hydrogen ion, the hydride ion, H^- . The H^- ion would occupy an O^{2-} site, producing a site with a net single positive charge. The H^- ion in this situation is represented by H_O . A reaction to describe formation of this hydride species, which would occur under reducing conditions, was written as:

In that 1966 article, Stotz and Wagner did not elaborate on the nature of the interstitial proton. However, they did indicate the usefulness of infrared spectroscopy in clarifying the bonding state of the interstitial proton. Much work since then has dealt with this point. Because the proton is the smallest cation, approximately 10^{-4} Å in size (it is a bare nucleus with no extra-nuclear electrons), its polarizing power is great. In chemical terms, the proton has a very strong tendency for covalent bond formation with oxide ions to produce OH^- . Numerous studies have provided evidence for the OH^- ion as a species existing in solid oxides. The proton is unique in that its interstitial position in a solid oxide is a bonded one in the OH^- ion. The studies have included measurements at high temperatures and room temperature and have included the temperature region that is of interest to fusion reactor science.

An early paper by Soffner [2], referred to in the Stotz and Wagner article, reported infrared bands (measured with a beam chopping technique) for OH^- and OD^- in single crystals of TiO_2 from room temperature to 1000°C . In this system, later work by Bates and Perkins [3] reported infrared data not only for OH^- and OD^- but also for OT^- . The isotope effect on the infrared absorption frequencies enabled Bates and Perkins to inquire into the nature of the hydrogen bonding interactions ($\text{O}\dots\text{H}\dots\text{O}$) that could be accommodated by different models of the atomic vibrations. They concluded that the $\text{O}\dots\text{H}\dots\text{O}$ bonding system in rutile is not linear.

The nonlinearity of the $\text{O}\dots\text{H}\dots\text{O}$ group in rutile apparently does not hold in alumina where the proton has been shown by Borer et al. to be on a line connecting O^{2-} ions [4]. These authors calculated the crystal field potential to gain information on the location of the proton on the O^{2-} - O^{2-} line. They concluded that the proton is located unsymmetrically on this

line, closer to one of the O^{2-} ions. This is tantamount to identifying this proton as present in OH^- .

Data for OH^- in alumina that carry implications of particular significance to breeder materials came from the work by Gruen et al. [5]. They bombarded alumina with 15 keV protons and deuterons and observed infrared absorption bands that attested to the presence of internal (i.e., not surface) hydroxyls and deuterioxyls. These species formed at the end of the range of the bombarding protons or deuterons. In a fusion reactor breeder, therefore, one would expect that the recoil tritons, most of which come to rest within the solid breeder, would form OT^- . (Unless the local oxygen activity is low enough to favor tritide.)

Once the correspondence of the interstitial proton to lattice OH^- is established, it follows that measurements of the solubility of hydroxide in an oxide can be understood as measurements of the solubility of protons. The measurements are often carried out by measuring the uptake of $H_2O(g)$. Such measurements should be regarded as measuring, not the solubility of H_2O , but the solubility of the hydrolytic reaction product, OH^- (or of protons), in the solid oxide. It follows from the nature of this OH^- discussed above that the description of this solubility does not require fitting a "molecule" of $LiOH$ into the lattice of the breeder oxide.

Hydroxide on Surface

Corresponding to the occurrence of protons in the interior of solid oxides in the form of OH^- groups, protons also occur on the surface of solid oxides as $-OH$ groups. Numerous studies on alumina, silica, MgO , and other oxides have dealt with the properties of $-OH$ groups on the surfaces of these materials. For MgO , two types of surface hydroxyl groups were distinguished by means of their infrared stretching frequencies of 3752 and 3610 cm^{-1} [6].

Subsequently, proton magnetic resonance measurements on MgO-bearing adsorbed water confirmed the water to be chemisorbed and showed the distribution of the hydroxyls on the surface to be determined by the structure of the adsorbent lattice [6]. The model applied to the data regards the chemisorption of an H_2O molecule to involve the bonding of OH^- groups to magnesium ions and of protons to neighboring oxide ions to produce overlapping layers of hydroxyl ions.

The behavior of adsorbents on oxides frequently has been discussed in the catalysis literature in terms of Lewis or Brønsted acid and base sites. This is a viewpoint complementary to one based on concepts of solid state defects. For example, OH^- ions on an alumina surface behave as Brønsted acid sites [7]. When two such adjacent OH^- ions combine to liberate an H_2O molecule, one entity left behind is an exposed Al ion, which, because of its electron deficient nature, functions as a Lewis acid site. The remaining oxide site takes on Lewis base character. Infrared spectra of alumina [7] provide evidence of surface heterogeneity, which can be characterized in terms of surface OH^- groups being located in different environments of surrounding oxides and of different bonding situations regarding the aluminum ions.

With recognition of Lewis acid and base sites on an oxide surface, one can understand the adsorption not only of water but of H_2 or O_2 . A study of adsorption of O_2 on MgO has been performed by Nelson et al. [8]. They found the rate of chemisorption to increase with temperature in the 250-550°C range and correlated this activated chemisorption with valence changes in transition metal impurity ions. They also indicated that the observed kinetics of adsorption is consistent with buildup of space charge in the

surface region. Space charge effects are suggested to bear on the rates of release of tritium from a breeder and will be discussed below.

REVIEW -- PROTON MIGRATION

With the background established for the existence of OH^- groups in and on metal oxides and for the role of the proton in forming OH^- groups, the question of migration or diffusion in the oxide can be addressed. One group of authors has recently asserted that "There is ample evidence that the diffusing species in oxides is H^+ (or D^+), and not OH^- ion of H_2 , or H_2O " [9]. As evidence, they indicated that when a crystal of MgO containing OH^- (prepared by heating the MgO in $\text{H}_2\text{O}(\text{g})$) was placed in an electric field at 1100 K and higher, the OH^- concentration increased at the negative electrode, indicating a sweep of the protons. At 1300 K, all protons were swept out [10]. The process is one of protons hopping from one oxide ion to another in the oxide sublattice. This hopping process can be visualized in terms of the hydrogen-bonded structures discussed above, in which the $\text{O}\dots\text{H}\dots\text{O}$ system is the transition state for the proton in moving from one oxide ion to the next.

Protonic conduction occurs in other oxide systems, too. The perovskite-type compounds, e.g., SrCeO_3 , are the basis for solid electrolytes in which proton conductivity appears when measurements are made in atmospheres containing water vapor [11]. The data for proton conductivity as a function of water vapor partial pressure, when interpreted in terms of the Stotz-Wagner formalism, indicated that the protons were present in the interstitial form, i.e., as OH^- . Very recently, an attempt was reported to derive activation energies for proton conduction in materials of this type [12]. The calculations used a lattice simulation approach to map the three-dimensional conduction path of a proton. The dependence of the calculated activation energy for proton conduction on lattice parameter paralleled

observed values but did not agree numerically. Inclusion of additional factors in the theory (e.g., induced dipole energy and changes in effective ionic radii) was seen as potentially offering improved results.

In an earlier survey [13] of existing theoretical approaches, Ajayi et al. recalled that a relevant variable to include in the treatment of migration energies is the polarization of ions in the presence of defects. For fast ion conductors, they calculated the total interaction energy between the lattice and a mobile ion existing in many possible positions. The minimum energy path was dependent on the radius of the moving ion. It is interesting that the activation energy was lowest for intermediate-size ions. This conclusion implies that the proton, with its small size, would not necessarily have the lowest activation energy for diffusion. The most probable position for small ions, which include the proton, is often off-center with respect to site symmetry. These two aspects agree with what would be described, in chemical terms, as a covalently bonded proton breaking and reforming bonds with successive oxide ions. That is, the process presents the appearance of OH^- migration but is really a proton moving about the oxide ion sublattice.

A Chemical View of Proton Migration

The polarization of ions in the presence of defects, mentioned by Ajayi et al., can be applied to understand the driving force for proton movement on the oxide sublattice. Movement of atoms into vacancies is commonly understood to be a step in the diffusion of atoms, but in the case of proton diffusion on an oxide sublattice, one can visualize an indirect aspect to the role of vacancies, not in the oxide sublattice but in the cation sublattice. Since the solid is composed of interpenetrating sublattices of cations and

oxides, it is plausible that vacancy in the cation sublattice, which would bear an effective negative charge, would provide a slightly more negative environment for an oxide adjacent to it. Such an oxide ion can be viewed either as having slightly augmented negative charge, or as having slightly expanded electron orbitals. In either event, the oxide ion would become an attractive center for a proton bonded to the nearest oxide. In effect, the hydrogen-bonded interaction between the oxides, which provides the transition state for the proton transfer, would be altered so that the off-center position of the proton on the oxide-oxide line would shift toward the oxide with the vacancy-induced polarization. The cation vacancy itself, in this view, would not be directly involved as a location for the proton to move into. As the cation vacancy moves about the cation sublattice, proton positions on the oxide sublattice would follow. The process can be described as a cation vacancy-assisted diffusion of protons, or as a cation vacancy-induced migratory polarization of the oxide sublattice which results in proton diffusion on the sublattice. Of course, within the cation sublattice, vacancy migration is counterbalanced by opposite cation migration, and a correlation would be expected between the rates and energetics of cation self-diffusion and proton diffusion. Such a correlation has been pointed out for the Li_2O system by Tam [14]. Experimental data for ionic conductivity and spin-lattice relaxation (nuclear magnetic resonance) to support such a correlation were reported by Ohno et al. [15] for Li_2O , Li_2SiO_3 , and LiAlO_2 .

It is apparent that theoretical treatments for these processes constitute a developing field. A recent review of the hopping process covers not only the activated processes at high temperature, but also the occurrence of quantum mechanical tunneling mechanisms for hopping at low

temperatures [16]. A treatment that is of specific interest to fusion reactor ceramic breeders is being made by Tam [17].

The Role of Tritide in Diffusion

For very low oxygen activities, the additional consideration of the role of hydride and tritide species enters. Our earlier calculations [18] had indicated that these species become significant in the condensed phase at oxygen activities of about 10^{-25} and lower. Experimental evidence has also been reported for the presence of tritide in irradiated Li_2O [19]. In light of the demonstrated formation of elemental lithium in neutron-bombarded lithium ceramics [20,21] (and in LiF [22]), it is of interest to inquire as to the magnitude of tritide and hydride under very low oxygen activities. The paper reporting the evidence for the globules [20] indicated that annealing after irradiation resulted in a decline of evidence for globules above 600 K. This decline occurred after 3 hours of annealing at lower temperatures. The gradual disappearance of globules can be understood to result from increasing dissolution of elemental lithium as temperature rises, and/or from gradual combination of elemental lithium with other damage entities. For tritium release from an ongoing irradiation at a high temperature, it is a question of whether these dynamically competing processes yield a net rate for elemental lithium production that could be sufficiently high to build up a significant activity of lithium. Monte Carlo analyses by Ghoniem and Chou [23] of displacement cascades in neutron-irradiated spinel suggest the possibility of coupling of like metallic atoms along the cascade. In consideration of this theoretical work and the experimental evidence for tritide and lithium globules, the possibility for regions of very low oxygen activity is plausible and justifies a thermodynamic calculational survey.

Thermodynamic calculations have been performed for LiAlO_2 over a range of decreasing oxygen activities at 800 K. The calculations (by the SOLGASMIX computer code) are for the same ideal solution system that was treated earlier [24]. Figure 1 shows the calculated ratio of the concentration of tritoxide to the concentration of tritide in LiAlO_2 as a function of oxygen activity; the activity of zero-valent lithium is also shown. It is seen that the mole fractions of tritoxide and tritide are equal at a critical oxygen activity of about 10^{-45} , and that the concentration of tritide at lower oxygen activities becomes much greater than that of tritoxide. At higher oxygen activities, tritoxide dominates. The concentration of elemental lithium at 800 K at the critical oxygen activity is only about 10^{-9} mole fraction, or about 10^{-3} mole ppm. In view of the findings, elemental lithium can be expected within a lithium ceramic. For example, for a lithium activity of 2.5×10^{-2} , which does not yet correspond to globules but to a dilute solution of elemental lithium, the oxygen activity is 10^{-75} and the $\text{OT}^-:\text{T}^-$ ratio is 4×10^{16} .

Some implications for the diffusion processes arise from these low oxygen activities. Under reducing conditions, the concentration of oxide vacancies, $V_O^\bullet$, will increase by virtue of the reversal of equation 3. At the same time, tritide will be formed by the reducing action of elemental lithium and will occupy some of these vacancies on the oxide sublattice, represented by T_O . Vacancies on the lithium sublattice, V_{Li}' , will also be filled with lithium ions, represented by Li_{Li} . The overall reaction with zero-valent lithium atoms can be described by combining the half-reactions:

Tritoxide : Tritide Ratio
and Lithium Activity
 LiAlO_2 , 800K

Fig. 1. Calculated Tritoxide: Tritide Ratio and Lithium Activity for LiAlO_2 at 800 K as a Function of Oxygen Activity.

to yield the overall reaction:

With oxygen activity declining below the critical level for the solid state, increasing dominance by tritide as the diffusing species may be expected. Triton migration would become correspondingly minor, if not insignificant. (There is also a different critical oxygen activity for the gaseous state dividing dominance of oxidized or reduced gaseous forms; see reference [18].) Vacancies in the lithium sublattice were seen in the earlier discussion to assist in triton migration, but that was a situation expected to prevail for an oxygen activity above the critical value. For oxygen activities below 10^{-45} , tritide migration would increase on the oxide sublattice with the tritide moving into oxide vacancies, and the concentration of oxide vacancies rather than lithium vacancies would directly influence the tritium movement.

The observations of metallic lithium globules in neutron-irradiated lithium ceramics, which are evidence of one kind of radiation damage, suggest that one can regard the ceramic as containing volume elements with a high lithium activity, whether globules or just regions of relatively high lithium concentration. It follows that there is a gradient of oxygen activity within a particle of ceramic, which is depicted in Fig. 2. This gradient extends from a very low value of oxygen activity at and near the volume element to a higher value at the gas-ceramic surface. Because of the gas phase, the higher value is almost certain to be high enough for triton diffusion to dominate in the approach to the surface. For example, a reducing gas stream with 1% H_2 and 1 ppm H_2O will have an oxygen activity at 800 K of about

Gas, 800K.

He + 1% H_2 + 1 ppm H_2O : Oxygen Activity = 3×10^{-35} .

Reduced gaseous species dominant.

Surface

Oxygen Activity = 3×10^{-35} .

H^+ and T^+ dominant species, as OH^- and OT^- .

Mechanism: Proton and triton hopping on oxide lattice assisted by cation vacancies.

////////////////////////////////////

Transition Zone. Oxygen Activity 10^{-45} +/-

H^+ , H^- , T^+ , T^- , H_2 , HT , T_2 .

////////////////////////////////////

Oxygen Activity 10^{-75} ; Lithium Activity 2.5×10^{-2} .

H^- and T^- dominant species.

Mechanism: Hydride and tritide diffusion via anion vacancies.

Fig. 2. Oxygen Activity Gradient Through Solid from Regions of Zero-Valent Lithium to the Surface with Consequent Change in Dominance by Tritide Ions to Dominance by Tritons.

3×10^{-35} . For this oxygen activity, the triton:tritide ratio near the surface is 4×10^4 . However, tritide diffusion would dominate near the high-lithium-activity volume element. It follows that tritium present as tritide would experience a change in diffusion process, from tritide migration to triton migration, as it moves from the volume element toward the surface. Furthermore, there is implicit in this transition the chemical oxidation from the -1 to the +1 oxidation state. If this oxidation proceeds by two single-electron steps, then the intermediate zero oxidation state opens the possibility for T_2 formation and growth of bubbles containing T_2 . Of course, in the transition region where concentrations of tritons and tritides are nearly equal, a triton-tritide interaction is also conceivable, yielding T_2 . This gas could form bubbles in its own right or join helium bubbles.

The rate of tritide diffusion can be expected to be different from the rate of triton diffusion. We are not aware of data bearing on the point, but the tritide diffusion rate would probably be correlated with the rate of $V_O^{\bullet}$. The T^- ion is a large one, with a radius of $2.08 \text{ \AA}$.

In the approach to the ceramic-gas phase surface, triton migration would dominate and the rate of movement close to the surface would be affected by the charge-layer effects discussed above. The final steps in escaping to the gas phase would depend on the oxygen activity in the gas phase. In any case, surface $-OT$ groups would be involved. Combination of adjacent surface tritoxides to liberate T_2O ,

is the process most easily understood and would be favored by gas phase oxygen activities higher than about 10^{-25} at 800 K. HTO would result from adjacent OT^- and OH^- :

Lower gas phase oxygen activities, such as provided by a gas containing H_2 , favor T_2 and HT liberation. In this case, possible mechanisms include gas phase reduction of freshly evolved HTO or T_2O , or a surface reaction between adsorbed H_2 and surface OT^- :

In more detail, the surface process at low oxygen activity can be conceived as involving a reaction with adsorbed H_2 , forming surface OH^- and F^+ centers. An F^+ center is an electron occupying an oxide vacancy and is shown here by $e\dot{V}_O$ (and with OH^-) to form T_2 (and HT) and an oxide:

SPACE-CHARGE LAYER EFFECTS

Proton movement between the bulk and the surface is potentially influenced by another factor that has not yet received much attention with respect to ceramic tritium breeders. It was shown in 1953 by Lehovc [25] that an electric potential exists between the surface and the bulk of ionic crystals. This potential arises, for example, if the energy of formation of interstitial cations is less than the energy of formation of interstitial anions so that more interstitial cations are formed initially than interstitial anions and there develops a preponderance of cations diffusing into the interior. The result is establishment of a steady state condition with a positive space-charge layer and a negative charge at the crystal surface. Lehovc reported that impurities were influential in determining the

space-charge potential. The thickness of the space-charge layer, λ , for NaCl crystals was estimated as 1.3×10^{-6} cm at 900 K and 2.2×10^{-5} cm at 600 K.

More recently, Slifkin [26] has further confirmed surface-charge concepts and effects, both theoretically and experimentally, and has indicated the universality of the phenomena for all ionic materials. The development of the effect is also a function of impurities, surface topography, and adsorbed species. The magnitude of the electric field just under the surface can be 10^4 - 10^5 V/cm. In a statement that has important implications for tritium breeder irradiation experiments, Lehovec suggested that the space-charge layer could affect diffusion measurements for crystals that are of a size similar to λ . We note that some irradiation experiments from which diffusion coefficients in tritium breeders were derived have involved crystals of such a size.

POLARIZATION EFFECTS OF ADSORPTION

The process described by Lehovec and by Slifkin is an autogenous development of a surface and near-surface space-charge layer. As they observed, environmental factors such as adsorption can affect the charge layer. Surface charge effects influenced by the environment of a chemical system were the basis for Rochow's proposals for a new process which he called alternosorption [27,28]. He noted that earlier observations of the changes in the nature of the charge carriers in semiconducting oxides were understandable in the following terms. If an n-type semiconductor adsorbed an electron-acceptor gas (oxygen is an example), there would be a transfer of electrons from the surface and adjoining layers toward the adsorbed layer. This would result in a positive charge region extending into the solid. Rochow proposed that imposing an external electric field on the solid could, by virtue of this phenomenon, enhance the adsorption of gaseous (electron-acceptor) electro-

negative reactants. Furthermore, if the field is an alternating one, adsorption and desorption could be facilitated in a cyclic manner; hence the name "alternosorption." Experimental confirmation of alternosorption was provided [28]. This phenomenon was seen to offer advantageous control of reactants and products for catalytic processes, but it can also be conceived to offer means for controlling tritium release from a ceramic tritium breeder.

IMPLICATIONS FOR TRITIUM RELEASE RATES

In-pile irradiation and tritium release experiments typically show that a sweep gas containing H_2 enhances HT release. This was observed in the TRIO experiment [29], but that experiment also revealed that a sweep gas containing O_2 essentially halted tritium release. A thermodynamic explanation for this difference was given earlier. However, at least two kinetic explanations can also be advanced for these findings, one based on a mass action effect and one based on the surface charge effect. Both involve adsorption of the dopant gas, H_2 or O_2 .

For the mass-action effect, adsorption of H_2 will increase the surface OH^- concentration (see reaction 13). If the evolution reaction proceeds as in equation 15 and is first order in each of OH^- and OT^- and is expressed as

$$d[HT]/dt = k[OH][OT],$$

then the HT release rate will be enhanced. For HTO release, equation 9 suggests a similar rate equation, though this condition can only prevail at oxygen activities higher than 10^{-25} at 800 K.

The mass-action view is a simple one and is perhaps adequate for many purposes. However, the surface-charge effect and the adsorption polarization effect can provide a more general kinetic rationale for the observed differences in tritium release rates from irradiated breeder materials, depending on the chemical nature of the sweep gas. A possible picture of the

action of the two effects is shown in Fig. 3. Details of charge distribution still need to be confirmed for various parts of the mechanism.

Let us assume that the solid will develop, in the absence of adsorbents, a surface charge layer that is positive relative to a more negative bulk region. The boundary between the two regions is shown with slanted line shading and the unperturbed situation is shown on the left side of the figure. A proton or triton (on an oxide) in this region experiences the normal resistance to hopping through the positive surface charge layer to the surface. However, where a H_2 molecule is adsorbed, the electropositive (electron donating) nature of this molecule diminishes the effective positive charge in the surface layer and provides a lowered barrier for hopping of a proton out to the surface. The polarization involved here is shown by the δ charges in the figure. Once on the surface, the tritons and protons can diffuse as usual until the bimolecular interaction between them evolves HTO. Evolution of HTO or T_2O is enhanced relative to the rate in the absence of H_2 in the gas phase. Conversely, adsorption of O_2 is predicted to have the opposite effect, i.e., inhibiting release of HTO or T_2O , because it would, as explained by Rochow, induce formation of a positive charge layer, which would be an additional electrostatic potential barrier to repel outward diffusing protons and tritons. Generalization of this concept suggests that any molecule regarded as an electron-donor would be expected, on adsorption, to exert an effect qualitatively similar to that of H_2 . According to this, a non-hydrogenic electron donating adsorbent could provide a means for testing the mass-action and surface-charge mechanisms. An example is carbon monoxide, CO. Such materials, of course, are also reducing agents and there would be a simultaneous effect from reduced oxygen activity to consider.

Combined Surface Charge Layer and Adsorption Polarization Effects

Fig. 3. Schematic View of Suggested Combined Effects of Surface Charge Layer and Adsorption Polarization was to Rationalize Observed Influence of O_2 or H_2 on Tritium Release.

The adsorption and associated charge-layer processes, therefore, provide a basis for understanding, in terms of the kinetics of triton transport, the observed dependencies of tritium release on gas phase composition. Earlier, we had introduced a thermodynamic rationale for the same observations [24]. The thermodynamic argument is that high oxygen activities (greater than about 10^{-25} to 10^{-15} , depending on temperature) favor the HTO and T₂O gaseous forms which are strongly adsorbed on the surface. Low oxygen activities, on the other hand, favor the reduced forms, which are weakly adsorbed and easily released. Since a hydrogen-containing atmosphere provides a reducing environment and, conversely, an oxygen containing atmosphere provides an oxidizing environment, it follows that the thermodynamic and kinetic aspects of the release process work together.

CONCLUSIONS

There is adequate basis for dealing with "tritiated species" as tritons and tritides, depending on oxygen activity, and for viewing the movement of tritons as hopping on the oxide lattice. In the analysis of tritium release rates in irradiation experiments for the purpose of deducing diffusion coefficients for tritium, it appears that some previously unrecognized factors deserve attention. One is the possible presence of two different diffusing species with different rates of diffusion, in different parts of the sample, and with different boundary conditions to be applied to each part. Another is the possibility of surface adsorption polarization effects either alone or combined with surface charge-layer effects. Surface charge-layer effects have been predicted to be of special significance for small particles.

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