PORTIONS
OF THIS
DOCUMENT
ARE
ILLEGIBLE

BLANK PAGE

LA-UR-78-1523

TITLE: MIXING RULES FOR AND EFFECTS OF OTHER HYDROGEN ISOTOPES AND OF ISOTOPIC SWAMPING ON TRITIUM RECOVERY AND LOSS TO BIOSPHERE FROM FUSION REACTORS

AUTHOR(S): J. H. Pendergrass (L-5)

MASTER

SUBMITTED TO: 3rd ANS Topical Meeting on the Technology of Controlled Nuclear Fusion (Proceedings) (May 1978)

los alamos
scientific laboratory
of the University of California
LOS ALAMOS, NEW MEXICO 87545

An Affirmative Action/Equal Opportunity Employer

UNITED STATES
[illegible]
[illegible] ADMINISTRATION
[illegible] W-[illegible]-ENG. [illegible]

MIXING RULES FOR AND EFFECTS OF OTHER HYDROGEN ISOTOPES AND OF ISOTOPIC SWAMPING ON TRITIUM RECOVERY AND LOSS TO BIOSPHERE FROM FUSION REACTORS

J. H. Pendergrass

LOS ALAMOS SCIENTIFIC LABORATORY
LOS ALAMOS, NEW MEXICO 87545

ABSTRACT

Efficient recovery of bred and unburnt tritium from fusion reactors, and control of its migration within reactors and of its escape into the biosphere are essential for self-sufficient fuel cycles and for public, plant personnel, and environmental protection. Tritium in fusion reactors will be mixed with unburnt deuterium and protium [illegible] reactions and diffusion into coolant loops from steam cycles. Rational design for tritium recovery and escape prevention must acknowledge this fact. Consequences of isotopic admixture are explored, mixing rules for [illegible] fusion reactor dilute-solution conditions are developed, and a rule of thumb regarding its effects on tritium recovery [illegible]

INTRODUCTION

Present indications are that at least the first generation of fusion reactors will be fueled with [illegible] because [illegible] less [illegible] liber[illegible] ing fus[illegible] reactors[illegible] reactors[illegible] tritium [illegible] though [illegible] relatively [illegible] tium [illegible] and [illegible] logical [illegible]

Eff[illegible] from fusion [illegible] and other [illegible] tion within [illegible] plants is essential for [illegible] cient tritium fuel cycles, [illegible] for natural [illegible] fusion reactors [illegible]

[illegible]

Work done under the [illegible]

Efficient recovery of bred and unburnt tritium is essential for maintaining low tritium inventories. Escape of tritium to the biosphere can be minimized by maintaining low tritium inventories and by providing engineered barriers to tritium escape. Under emergency conditions, the breeding blanket and the main coolant loops are usually considered to represent the greatest hazard, whereas during normal operations, thin, hot reactor components lying across direct paths to the biosphere are critical to tritium escape. Tritium escape into steam cycle loops, and thence into the biosphere, is generally regarded to be the most important [illegible] hazard associated with normal [illegible] covery systems and escape-prevention barriers.

Protium will be generated by [illegible] reactions of [illegible]

[illegible]

[illegible]

and deuterium. Thus, unburnt tritium and deuterium, which constitute the majority of fuel fed to fusion reactors, may not represent the majority of hydrogen isotopes recovered.

Recovery of deuterium, which is relatively abundant in nature and can be obtained at modest cost, is not necessary for economic generation of fusion energy. However, buildup of protium and deuterium within reactor subsystems to excessive levels cannot be tolerated, because of potential deleterious effects on reactor materials of construction. Tritium recovery systems will simultaneously remove protium and deuterium because of their similar physicochemical characteristics, but at a penalty of increased tritium recovery system capacity.

Protium concentrations in thermonuclear reactor fuel streams will probably have to be reduced to 1% or less. The DT isotopic ratio must be adjusted by the addition of makeup deuterium.

Clearly, [illegible] of the tritium [illegible] are affected by the presence of [illegible]

[illegible]

Our discussion will be confined to the dilute-solution conditions anticipated for tritium in fusion reactor breeding blankets, coolant loops, structural materials, and perhaps cavity exhaust streams. Early estimates of rates of tritium escape into steam cycles from coolant loops suggested that tritium concentrations in fusion reactor systems might have to be maintained at 1 ppm or less. As the difficulties of tritium recovery from solutions at such concentrations have become apparent, more effective concepts for prevention of tritium escape have been developed, and the importance of potential tritium hazards relative to other potential fusion reactor hazards have been more accurately assessed, some consideration has been given to operation with tritium concentrations an order or two higher in magnitude. Nonetheless, dilute solution theory will still be applicable, [illegible] concentrations are still quite low.

We will focus on the development of mixing rules for equilibria of hydrogen isotope mixtures and on the effects that the presence of more than one hydrogen isotope [illegible] has on [illegible] tritium [illegible] systems.

PHYSICAL [illegible] HYDROGEN ISOTOPE MIXTURES IN [illegible]

Most of the [illegible] of fusion reactors will probably [illegible]. Many [illegible] involve [illegible] tritium-[illegible] loops. Clearly, the [illegible] as [illegible] isotopes in metals is [illegible] in [illegible] tritium [illegible] recovery [illegible]. We will [illegible] hydrogen [illegible].

Review of [illegible] and [illegible]

Many careful [illegible] Ricca,[9] Ricca, [illegible] hank,[26],[27] [illegible] and Wu,[10] and [illegible] and Yamashita,[17] have confirmed that the empirical relationship named for A. Sieverts accurately describes the temperature-dependent solubility of protium, deuterium, and tritium in metals at very low concentrations and, in some instances, at relatively high concentrations, for both pure metals and alloys with low surface-to-volume ratios so that adsorption is not a significant factor.

A theoretical justification for Sieverts' empirical law can be developed as follows. We assume, in accord with experimental evidence, e.g., see Isenberg,[28] that a hydrogen isotope exists in solution in metals as an [illegible] [illegible]. For present purposes [illegible] whether the dissociation of gas-phase molecules necessary for dissolution occurs in the gas phase, on the metallic surface, or in the bulk metal. An equilibrium [illegible]

[illegible]

[illegible]

The [illegible]

[illegible]

[illegible]

If temperature [illegible] standard [illegible] ed, then Sieverts' law for the solubility of hydrogen isotopes in metals is obtained:

$$X_{H(s)} = K_{S_H}(T)\left|p_{H_2}/1\ \mathrm{atm}\right|^{1/2}$$

$$K_{S_H}(T) = K^0_{S_H} e^{-Q_{S_H}/RT}, \quad K^0_{S_H} = \frac{f^0_{H(s)}}{\gamma_{H(s)}} e^{\overline{\Delta S^0}/R},$$

$$Q_{S_H} = \overline{\Delta H^0}$$

[illegible]

[illegible] the only other explicit consideration of the problem of predicting solubilities of the individual hydrogen isotopes in a mixture and the gross solubility of the mixture [illegible] Hickman [illegible] that [illegible] should [illegible] chemical species and [illegible] Sieverts' [illegible]:

$$X_{Total} = K_{S_{Total}}(T)\, p^{1/2}_{Total}$$

He [illegible] mixing rule:

$$K_{S_{Total}}(T) = [illegible]$$

Hickman [illegible] of holes [illegible] available for [illegible] dissolution [illegible] both isotopes [illegible] holes.

Hickman [illegible] data for the solubility [illegible] of protium and deuterium [illegible] alloy of palladium and silver. [illegible] the basis of these experimental results, [illegible] the postulated mixing rule [illegible] the solubility of the mixture acceptably well.

Atkins and [illegible] used the mixing rule suggested by Hickman in analyzing the results of experiments which investigated the permeation of similar mixtures through the walls of tubes of the same alloy. They claimed acceptable agreement between their experimental results and those of analysis based on Hickman's suggested mixing rule.

However, the fact that Sieverts' law accurately predicts the solubility of hydrogen isotopes in many metals and allows up to relatively high concentrations, suggests, for systems sufficiently dilute in the dissolved hydrogen isotopes, that the systems are also relatively dilute in comparison to the number of holes in metallic valance bands. The large isotopic differences in solubility, as reflected by differences in Sieverts'-law constants, suggest that a mixture of hydrogen isotopes cannot be treated as a single chemical substance for all purposes. Therefore, the following analysis, which explores the consequences of validity of Sieverts' law for the solution of individual hydrogen isotopes in metals, was performed to develop an alternative, which has some theoretical basis, to Hickman's suggested mixing rule.

On an atomic basis, in solutions sufficiently dilute in all solutes, solute atoms are surrounded by and interact virtually all the time with solvent atoms rather than with other solute atoms. Therefore, in such solutions the solubility of a solute is [illegible] by its properties and by those of the solvent and is [illegible] affected [illegible] by the properties of other solutes. This interpretation should also be valid if the solvent is a mixture of [illegible], [illegible] the ratios of concentrations of the species in the solvent [illegible] constant, e.g., if the solvent is an alloy, dilute or otherwise.

Thus we conclude that Sieverts'-law expressions obtained by fitting experimental solubility data for pure isotopes are applicable to individual isotope solubilities when isotopic mixtures are involved. Therefore, for a system containing all three hydrogen isotopes, we write:

$$X_{Total} = X_{H(s)} + X_{D(s)} + X_{T(s)}$$

$$= K_{S_H}(T)\,p^{1/2}_{H_2(g)} + K_{S_D}(T)\,p^{1/2}_{D_2(g)} + K_{S_T}(T)\,p^{1/2}_{T_2(g)}$$

$$= \left[K_{S_H}(T)y_{H_2}^{1/2}+K_{S_D}(T)y_{D_2}^{1/2}+K_{S_T}(T)y_{T_2}^{1/2}\right] P_{Total}^{1/2}$$

$$= K_{S_{Total}}(T)\ P_{Total}^{1/2}\ .$$

In an isotopic mixture there will be isotopic exchange in the gas phase, i.e., in addition to the molecular species $H_2(g)$, $D_2(g)$, and $T_2(g)$ the species $HD(g)$, $DT(g)$, and $TH(g)$ will be present. In addition, the diatomic molecules can dissociate to yield the atomic species $H(g)$, $D(g)$, and $T(g)$. The following set of six gas-phase reactions are independent:
$H_2(g)+D_2(g) \rightleftharpoons 2HD(g)$, $D_2(g)+T_2(g) \rightleftharpoons 2DT(g)$,
$T_2(g)+H_2(g) \rightleftharpoons 2TH(g)$, $H_2(g) \rightleftharpoons 2H(g)$,
$D_2(g) \rightleftharpoons 2D(g)$, and $T_2(g) \rightleftharpoons 2T(g)$.

The corresponding equilibria can be expressed in the forms:

$$\frac{p_{HD(g)}^2}{p_{H_2(g)}p_{D_2(g)}} = \frac{y_{HD}^2}{y_{H_2}y_{D_2}} = K_{HD}(T),$$

$$\frac{p_{H(g)}^2}{p_{H_2(g)}} = \frac{y_H^2}{y_{H_2}} P_{Total} = K_{H_2}(T)$$

with similar expressions for the other reactions. Experimental values for the equilibrium constants are listed in Table I.

In terms of y_H', y_D', and y_T' the equilibrium relationships for the gas phase can be written, in the absence of significant molecular dissociation to form the atomic species, in the form:

$$\frac{\left[(y_H'-y_{H_2})+(y_D'-y_{D_2})-(y_T'-y_{T_2})\right]^2}{y_{H_2}y_{D_2}} = K_{HD}(T)$$

upon substitution of [illegible] as:

$$y_{HD} = (y_H'-y_{H_2})+(y_D'-y_{D_2})-(y_T'-y_{T_2}) .$$

Solution for the mole fractions [illegible] species may [illegible]. Substitution of [illegible] for the diatomic species [illegible] gives an answer in [illegible] y_H', y_D', and y_T'.

If dissociation [illegible] form the atomic [illegible] situation [illegible]

TABLE I

EQUILIBRIUM CONSTANTS $K_{HD}(T)$, [illegible]
$K_{D_2}(T)$, $K_{T_2}(T)$, [illegible]

T,K	$K_{H_2}(T)$*, atm	[illegible](T)*, atm	[illegible]	[illegible]	[illegible]	[illegible]
300	[illegible]$\times10^{-72}$	1.219×10^{-72}	---	3.26	2.60	[illegible]
400	---	---	---	3.48	3.00	[illegible]
500	4.939×10^{-14}	1.171×10^{-31}	---	3.62	3.26	[illegible]
600	---	---	---	3.72	3.45	[illegible]
700	---	---	---	3.79	3.59	[illegible]
800	---	---	---	3.83	3.65	[illegible]
900	---	---	---	[illegible]	[illegible]	[illegible]
1000	5.174×10^{-19}	2.972×10^{-17}	3.0×10^{-17}	[illegible]	[illegible]	[illegible]
1250	---	---	---	[illegible]	[illegible]	[illegible]
1500	3.109×10^{-10}	2.229×10^{-10}	2.44×10^{-10}	3.96	3.93	[illegible]
2000	2.611×10^{-6}	2.227×10^{-6}	2.35×10^{-10}	[illegible]	[illegible]	[illegible]

*Woolley, et al.(37)
**Jones(38)

expressions for y_{HT}, y_{DT}, and y_{TH} for substitution into the first three equilibrium relations are now of the form:

$$y_{HD} = (y_H \cdot y_{H_2})^{1/2} (y_D \cdot y_{D_2})^{1/2} (y_{T_2} \cdot y_{T_2})^{1/2}$$

$$\cdot \left[\sqrt{y_{H_2} \frac{K_{H_2}(T)}{P_{Total}}} + \sqrt{y_{D_2} \frac{K_{D_2}(T)}{P_{Total}}} + \sqrt{y_{T_2} \frac{K_{T_2}(T)}{P_{Total}}} \right].$$

To obtain a meaningful comparison with the intuitive mixing rule of Hickman, we consider a mixture of protium and deuterium only at temperatures sufficiently low and pressures sufficiently high that dissociation to form the atomic species can be neglected, but temperatures [illegible] that the [illegible] of $K_{i_2}(T)$ [illegible] negligibly [illegible] the high-temperature limit. Based on these assumptions, solution for the molecular mole fractions gives:

$$y_{H_2} [illegible]^2 + y_{D_2} [illegible]^2 .$$

Substitution of these results into the [illegible] mixing rule yields [illegible] that of the mixing rule [illegible]. [illegible] rule [illegible] mixing rule. [illegible] for which [illegible] protium and deuterium [illegible] results [illegible] positively [illegible] empirical [illegible] mixing rule [illegible].

ISOTOPIC SWAMPING

The introduction of large amounts of protium into fusion reactor systems has been advocated to promote recovery of tritium so that lower tritium concentrations, and thus lower inventories and escape rates, can be maintained. This process, referred to as isotopic swamping, can be beneficial if:

- required capacities of tritium recovery and isotopic separation systems are not increased inordinately as a result of isotopic swamping,
- isotopic swamping significantly decreases residual tritium concentrations or enhances the effectiveness of barriers to tritium escape by mechanisms not otherwise available,
- the use of tritium recovery methods which are inherently less expensive, e.g., whose capital and/or operating costs are less, is made feasible through isotopic swamping.

These characteristics represent the basis upon which a rule of thumb for a *priori* assessments of potential beneficial effects of isotopic swamping on fusion reactor tritium recovery methods can be formulated. Many processes have been proposed for recovery and/or concentration of bred tritium from tritium-breeding blanket and coolant-loop streams, and unburnt tritium from cavity exhaust streams. The effects of isotopic swamping on all these proposed processes cannot be discussed here, and we are forced to concentrate on only a few. In particular, we will discuss effects of isotopic swamping on recovery of tritium by means of tritium windows and cold trapping of liquid-metal pumping cycle and secondary coolant loops and on escape of tritium into the biosphere by permeation through metallic barriers.

Isotopic Swamping Effects on a Light Metal Diffusive [illegible]

Hickman[illegible] examined the effects of isotopic swamping on tritium-window processes for tritium extraction from liquid lithium, which possessed the following characteristics:

- Sieverts' law of solubility of hydrogen isotopes in metals and Hickman's mixing rule for dissolution of hydrogen isotopes in metals are both applicable.
- The only significant resistance to permeation through the window is the resistance to diffusion of the bulk metal of the window membrane.
- Tritium extraction is performed under steady state, isothermal conditions.

- Equilibrium with respect to isotopic interchange between diatomic molecular hydrogenic species in the gas phase is attained at all times, the high-temperature limiting values of the isotopic interchange equilibrium constants are applicable, and molecular dissociation to give the atomic species can be neglected.

The stated assumptions imply that expressions for the permeation fluxes of protium and tritium through the tritium window can be written in the forms:

$$J_{T_2} = \frac{\phi_{T_2}(T)}{\delta}\left(p_{T_2,1}^{1/2} - p_{T_2,2}^{1/2}\right) = \frac{\phi_{T_2}(T)}{\delta}\left[\left(y_T^{\prime 2} p_{Total}\right)_1^{1/2} - \left(y_T^{\prime 2} p_{Total}\right)_2^{1/2}\right] = \frac{\rho_M}{M_M}\,\frac{D_{T_1}(T)}{\delta}\left(x_{T_1,1} - x_{T_1,2}\right)$$

$$= \frac{\phi_{T_2}(T)}{\delta}\left[\left(y_{T_2} p_{Total}\right)_1^{1/2} - \left(y_{T_2} p_{Total}\right)_2^{1/2}\right]$$

$$\phi_{T_2}(T) = \frac{\rho_M}{M_M}\, D_2(T)\, s_T(T) .$$

If all three hydrogen isotopes are present and/or if dissociation of the molecular species to give the atomic species in the gas phase cannot be neglected, then the analysis will be more complex, but similar.

Now let the total pressure on the low-pressure side be negligible and consider the addition of protium to a system containing initially only tritium. Then the ratio of the tritium flux to its initial value is:

$$J_{T_2}/J_{T_2}^0 = y_T'\left(p_{Total_1}/p_{Total_1}^0\right)^{1/2}$$

whereas the ratio of the effective system tritium inventories under the same conditions is:

$$C_T/C_T^0 = \left(p_{T_2} + \tfrac{1}{2} p_{HT}\right)/p_{T_2}^0 = y_T' p_{Total_1}/p_{Total_1}^0 ,$$

$$C_T/C_T^0 = p_{T_2}/p_{T_2}^0 = y_T'^2 p_{Total_1}/p_{Total_1}^0$$

respectively, for a gas-phase and a liquid-metal phase constituting the principal tritium reservoir.

If the system tritium inventory is maintained constant, then, respectively, for the two cases:

$$y_T' = p_{Total_1}^0/p_{Total_1} ,\quad y_T' = \left(p_{Total_1}^0/p_{Total_1}\right)^{1/2}$$

$$J_{T_2}/J_{T_2}^0 = y_T'^{1/2} < 1 ,\quad J_{T_2}/J_{T_2}^0 = 1 .$$

In the first case, although the system tritium inventory has not been reduced, the tritium window area will have to be increased to remove tritium from the system at the same total rate. In the second case the isotopic swamping has not affected the required tritium window area. Thus, depending on what type of phase represents the principal tritium reservoir, the tritium window area required for a constant total rate of tritium recovery is either increased or not affected for a constant tritium inventory, but clearly is increased if the tritium inventory is to be reduced.

If, instead, the total hydrogen isotope pressure is maintained constant, then:

$$J_{T_2}/J_{T_2}^0 = y_T' = \lambda$$

in both cases, while respectively:

$$C_T/C_T^0 = y_T' ,\quad C_T/C_T^0 = y_T'^2 .$$

Thus, in both cases, the tritium window area required to effect the indicated inventory decrease at a constant tritium recovery rate is increased by the factor 1/λ, but the tritium inventory reduction is greater in the second case.

It is also clear that isotopic swamping will either enhance or not affect the performance of barriers to tritium migration for all the cases considered. Note also that the increase in tritium window area required for removal of tritium at a constant rate when no protium is added is 1/λ when the tritium inventory level is reduced by the factor λ in either a gas phase or a liquid-metal phase.

Isotopic Swamping Effects When Surface Processes are Rate Determining

Hickman(35) and Maroni(36) examined another case of tritium recovery through a tritium window from a fluid stream that had been isotopically swamped with protium. This case involved the postulate that the permeation rate-limiting step was a slow surface process, the recombination of hydrogen isotope atoms followed by desorption from the low tritium partial-pressure side of the membrane. Adsorption-desorption processes, even if consideration is restricted to adsorption and desorption of hydrogen isotopes only, can be complex and there is a vast, often contradictory literature concerning this topic. Therefore, we can only briefly touch upon the subject. If the adsorption and dissociation step on the upstream side of the barrier is permeation rate controlling then a similar approach can be used in the analysis.

This particular step in the permeation process is carefully examined because there is evidence that, under projected thermonuclear reactor conditions, the recombination and desorption of tritium atoms may indeed be rate-limiting. For example, Goodall, et al,(37) explained the results of their experiments concerned with permeation of hydrogen isotopes from liquid lithium through niobium membranes on the basis of such a rate-limiting step.

The model for hydrogen isotope permeation which we shall consider involves the following assumptions, and approximations:

- All resistances to permeation other than those due to the desorption process are negligible.
- The partial pressures of tritium and protium on the low partial pressure side of the barrier are so small that the adsorption rate on that side of the barrier is negligible in comparison to the desorption rate.
- The simple Langmuir adsorption theory with a single class of active sites adequately describes the adsorption process.
- Dissociation in the gas phase to form the atomic hydrogen isotope species from the diatomic molecular species can be neglected.
- The adsorptive characteristics of the high and low partial-pressure barrier surfaces do not differ significantly.
- The permeation occurs under steady-state, isothermal conditions.

The essence of the elementary Langmuir theory of adsorption may be stated as follows. Adsorption of molecules from the gas phase onto solid surfaces can occur only at certain active "sites" on the surface which have an affinity for the species being absorbed, are uniformly distributed, and have equal affinities for the adsorbed species. Each such site is assumed to be capable of adsorbing only a single atom or molecule of the adsorbed species and, because the forces that are responsible for the adsorption are short range, the adsorption at any site is assumed to be independent of whether or not an adjacent site is occupied. If the adsorption involves a dissociation, say of a diatomic molecule, such as tritium molecules, to form the atomic species, then the adsorption process is assumed to involve a reaction between the diatomic molecule and two adjacent sites on the solid surface. The number of pairs of adjacent sites, based on the above listed characteristics of the active sites, is proportional to the square of the number of unoccupied sites, which can be represented in terms of a fractional occupancy of active sites by the adsorbed species, often called the surface coverage by the adsorbed species. In terms of the surface coverage by the adsorbed species and the partial pressure of the gas phase molecular form, a kinetically third-order expression for the rate of adsorption is postulated:

$$r_{T_2Ads} = k_{T_2Ads}(T)(1-\theta_T)^2 p_{T_2} \ .$$

Similarly, the desorption reaction is assumed to involve the kinetically second order reaction of two adsorbed atoms on adjacent active sites whose number is taken as proportional to the square of the fractional coverage and, in terms of surface coverage by the adsorbed species, a rate expression is written as:

$$r_{T_2Des} = k_{T_2Des}(T)\theta_T^2 .$$

Under conditions of adsorption equilibrium, the two rate expressions for adsorption and desorption can be equated and solved for θ_T to obtain:

$$\theta_T = \frac{\left[\dfrac{k_{T_2Ads}(T)}{k_{T_2Des}(T)}\, p_{T_2}\right]^{1/2}}{1+\left[\dfrac{k_{T_2Ads}(T)}{k_{T_2Des}(T)}\, p_{T_2}\right]^{1/2}} .$$

Although other, more complex theories may describe the adsorption behavior in a particular system more accurately, the results obtained with the simple Langmuir theory should be representative and may be the most accurate in some cases, e.g., see Smith.(38) Examples of other types of models for hydrogen isotope adsorption on, and desorption from metals are those of Bucur, et al,(39) and Bucur(40) for adsorption of protium on palladium films. They considered multiple types of active sites and surface reactions and there are many other such treatments. The general approach to analyzing of adsorption or desorption-step-limited permeation processes by using more complex adsorption and desorption models is similar.

The listed assumptions imply that the permeation flux, when only tritium is present, is given by the Langmuir expression for the rate of desorption of tritium from the downstream barrier surface. The surface coverage in the absence of significant upstream surface adsorption and bulk barrier metal diffusive resistances is that corresponding to equilibrium with the upstream molecular tritium partial pressure. The rate expression is therefore:

$$J_{T_2} = \frac{k_{T_2Ads}(T)\,p_{T_21}}{\left\{1+\left[\dfrac{k_{T_2Ads}(T)}{k_{T_2Des}(T)}\, p_{T_21}\right]^{1/2}\right\}^2} .$$

A similar analysis based on the same assumptions when both tritium and protium are present, can be summarized as follows. The rate expressions are of the form:

$$J_{T_2} = k_{T_2Des}(T)\theta_{T2}^2 + \frac{1}{2}\, k_{HTDes}(T)\theta_{T2}\theta_{H2} ,$$

and the absorption equilibrium expressions are of the form:

$$k_{T_2Ads}(T)\theta_{T2}^2 + \frac{1}{2}\, k_{HT_{Des}}(T)\, \theta_{T2}\theta_{H2}$$

$$= k_{T_2Ads}(T)(1-\theta_{T2}-\theta_{H2})^2 p_{T_21}$$

$$+ \frac{1}{2}\, k_{HT_{Ads}}(T)(1-\theta_{T2}-\theta_{H2})^2 p_{HT1} .$$

The preceding adsorption equilibrium expression and the gas-phase isotopic interchange equilibrium expression can be solved for the diatomic protium and tritium and HT partial pressures in terms of the protium and tritium atom fractions in the gas phase and of the total hydrogen isotope partial pressure, although the solution may have to be obtained by numerical techniques, and the results inserted into the rate expressions. The presence of the third hydrogen isotope, deuterium, and significant dissociation of the molecular species to form the atomic species in the gas phase further complicate the problem, but the same principles are applicable.

If the tritium is isotopically swamped with protium, we have:

$$p_{H_2} \gg p_{HT} \gg p_{T_2},\ \theta_H \gg \theta_T ,$$

and the rate and adsorption equilibrium expressions become, respectively:

$$J_{T_2} \approx \frac{1}{2}\, k_{HTDes}(T)\theta_{T2}\theta_{H2},\quad J_{H2} = k_{H_2Des}(T)\theta_{H2}^2$$

and:

$$\frac{1}{2}\, k_{T_2Des}(T)\theta_{T2}\theta_{H2} = \frac{1}{2}\, k_{HTDes}(T)(1-\theta_{H2})^2 p_{HT}$$

[illegible]

Clearly, the rate of [illegible] strongly affected. The [illegible] will be [illegible] so that the [illegible] effect [illegible] the [illegible]

[illegible]

which would release the surface area, e.g., by [illegible] [illegible] has reported the results of [illegible]

[illegible]

[illegible] of liquid sodium, liquid potassium, and a solid sodium-potassium alloy (NaK) coolant streams and will present the [illegible] in terms of [illegible] of [illegible]. The analysis for [illegible] is [illegible].

In a cold trap, the liquid metal is passed through [illegible]

[illegible] experiments involving only a single hydrogen isotope.

Assume now that NaH(c) and NaT(c) form an ideal solution. Then, by definition:

[illegible]

In view of the [illegible] of the two [illegible], this should be a good approximation.

For the more dilute liquid-phase solutions [illegible]

and [illegible] the [illegible]
[illegible]
of the [illegible]

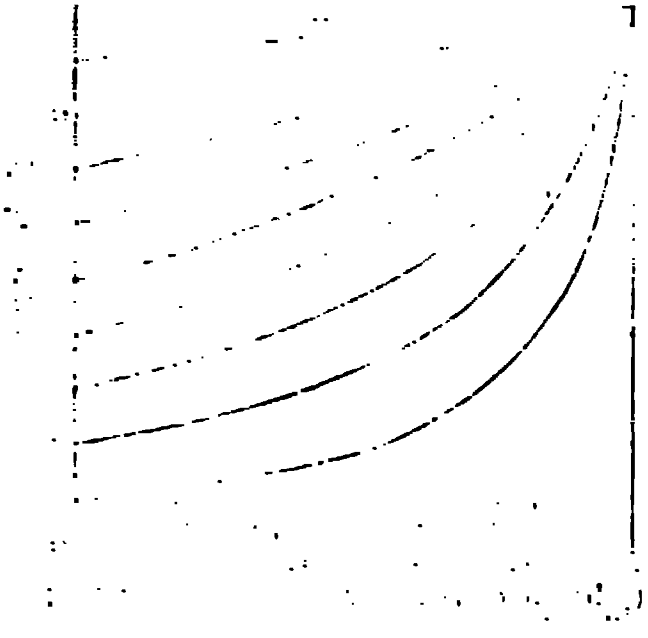
[illegible]

given by [illegible]

[illegible]

[illegible]

[illegible]



[illegible]

- **If tritium recovery system performance is determined primarily by transport rates, then isotopic swamping probably is not cost-effective and may be completely useless.**
- If tritium recovery system performance is **determined primarily by equilibrium considerations,** then isotopic swamping may be cost effective, but there is no guarantee that this will be the case.
- Isotopic swamping will either not significantly affect or will enhance the performance of barriers to tritium escape into the biosphere for a specified tritium concentration level.

The judgment of cost effectiveness must, of course, involve consideration of changes in, e.g., required recovery system capacity, requirements for isotopic separation, benefits arising from reductions in tritium inventories and in rates of escape of tritium into the biosphere, effects on other fusion reactor systems, potential use of less expensive construction materials or lower energy consumption, and [illegible] of a unit of recovery system capacity.

CLOSURE

Because of limitations imposed on the length of papers, we were unable to discuss the effects of the unavoidable presence of other hydrogen isotopes and of isotopic swamping on other fusion reactor tritium recovery systems and tritium migration mechanisms within and from fusion power plants. Examples of tritium recovery processes and migration mechanisms for which interesting analyses using similar methods can be performed include:

- the gas kinetic-limited permeation process discussed by Levin and Stickney,(50)
- the nonequilibrium permeation process described by Shapo and Stickney,(51)
- high-temperature lithium distillation for tritium recovery suggested by Ihle and Wu,(31)
- the molten-salt extraction process for tritium recovery from liquid lithium described by Maroni, et al,(52)
- permeation through potential nonmetallic materials of construction for fusion reactors, e.g., organic polymeric materials used for, e.g., gaskets and seals, and ceramics, such as those discussed by Fowler, et al,(53) and oxide or other corrosion layers that are potentially useful as tritium barriers, as discussed by Strehlow and Savage,(42) and
- thermal diffusion processes discussed by Pendergrass(30).

REFERENCES

1. P. S. Rohwer and W. H. Wilcox, "Radiological Aspects of Environmental Tritium," Nuclear Safety 17, 216 (1976).
2. D. G. Jacobs, "Sources of Tritium and Its Behavior upon Release to the Environment," TID-24635 (December 196[illegible]).
3. A. D. LeClaire, "Some Comments on the Mass Effect in Diffusion," Phil. Mag. 14, 1271 (1966).
4. Y. Ebisuzaki, W. J. Kass, and M. O'Keeffe, "Quantum Mass Effects in Diffusion," Phil. Mag. 15, 1071 (1967).
5. Y. Ebisuzaki, W. J. Kass, and M. O'Keeffe, "Isotope Effects in the Diffusion and Solubility of Hydrogen in Nickel," J. Chem. Phys. 46, 1373 (1967).
6. M. J. Stern and P. C. Vogel, "Relative Tritium-Deuterium Isotope Effects in the Absence of Large Tunneling Factors," J. Am. Chem. Soc. 93, 4664 (1971).
7. A. M. Stoneham and C. P. Flynn, "On the Quantum Theory of Isotope Effects in [illegible] migration and [illegible] Interstitials," J. Phys. F: Metal Phys. [illegible] (1973).
8. H. J. Bauer, J. [illegible], and [illegible], "Reversed Kinetic [illegible] tration of Cathodic Hydrogen [illegible] NiCu30 Alloy," Z. [illegible]
9. T. A. Giorgi and F. Ricca, "Thermodynamic Properties of Hydrogen and Deuterium in Zirconium," Suppl. Nuovo Cimento [illegible]
10. E. Baker, "Hydrogen and Deuterium in Palladium and Pd-Ag Alloy," J. Less-Common Metals 49, 111 (1976).
11. S. Gohr and H. C. Birnbaum, "On the Isotope Effect in Hydrogen Interstitial [illegible]," IU-IA-303 (1976).
12. G. Schaumann, J. Völkl, and G. Alefeld, "The Diffusion Coefficients of Hydrogen and Deuterium in V, Nb, and Ta," Phys. Stat. Sol. 42, 401 (1970).
13. B. Pegel, "On the Isotope Effect in Interstitial Diffusion," Phys. Stat. Sol. [illegible] (1967).
14. B. Pegel, "On the Isotope Effect in Interstitial Diffusion II. Extended Model," Phys. Stat. Sol. 22, K45 (1967).
15. B. Pegel and D. Lepski, "On the Isotope Effect in Interstitial Diffusion III. Quantum Corrections," Phys. Stat. Sol. 23, [illegible]
16. Yu. I. Belyakov and N. I. Ionov, "The Permeation of Hydrogen and Deuterium through a Nickel Membrane at 250-600°C," Sov. Phys. Tech. Phys. 6, 146 (1961).

17. [illegible] Hydrogen and Deuterium in [illegible] J. Less-Common Metals [illegible]

18. [illegible]

19. [illegible] Phys. Rev. [illegible]

20. [illegible]

21. [illegible]

22. [illegible]

23. [illegible]

24. [illegible]

25. [illegible]

26. [illegible]

27. [illegible]

28. [illegible]

29. [illegible]

30. [illegible]

31. [illegible]

32. [illegible]

33. [illegible]

34. [illegible]

35. [illegible] with Neutrons [illegible] Symp. [illegible]

36. [illegible] Migration of [illegible] Thermonuclear [illegible] J. Nucl. Mater. [illegible]

37. [illegible]

[illegible]

53. J. D. Fowler, D. Chandra, R. A. Causey, and T. S. Elleman, "Tritium Diffusion in Ceramic CTR Materials," [illegible]

54. R. A. Strehlow and [illegible], "Preparation and Use of [illegible] to Impede [illegible] of Metals," [illegible]

NOMENCLATURE

C	Concentration
D	Diffusivity
f, f^0	Fugacity, standard state fugacity
G^0	Standard Gibbs free energy change
H^0	Standard enthalpy change
H	Protium swamping and recovery rate
J, J^0	Permeation flux[illegible]
k	Adsorption or desorption rate constant
[illegible]	Equilibrium constants
K_s	Solubility constant
K_S	Sieverts' law constant
K_S^0	Sieverts' law preexponential constant
M	Molecular weight
N_{Na}, N^0_{Na}	Sodium flow rates
p, P	Pressure
Q_S	Sieverts' law exponential constant
r	Adsorption or desorption rate
R	Ideal gas constant
S^0	Standard entropy change
T	Absolute temperature
T^0	Tritium recovery rate
X	Mole fraction
y, y'	Mole, atom fractions

Greek Letters

δ	Tritium window or permeation barrier thickness
γ	Activity coefficient
θ	Fractional surface coverage by adsorbed species
λ	Tritium concentration level
ρ	Density
ϕ	Permeability