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Tritium Effluent Control Project Progress Report: July-September 1975

Carl J. Kershner and John C. Bixel

March 19, 1976

Research and Development Report

MOUND LABORATORY
Miamisburg, Ohio
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MONSANTO RESEARCH CORPORATION
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UNITED STATES ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION
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NOTICE

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Summary

Tritiated Liquid Waste Decontamination (Molecular Excitation)
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The isotopic selectivity of the two-photon dissociation process was examined in more detail. The selectivity or ratio of HTO to H_2O molecules that are photodissociated was found to be on the order of 25. Although this selectivity is sufficient for bench scale proof-of-principle experiments, it is inadequate for application to large scale detritiation projects, e.g., nuclear fuel reprocessing plant waste. The selectivity is such that most of the laser energy is wasted in photodissociation of H_2O. This obstacle may be overcome by pumping more vibrational energy into the HTO molecules. Various schemes towards this end are being considered.

Extensive ab initio calculations on the potential surface for the hydrogen atom-water exchange reaction have been carried out. The results bear out the predictions of the simple qualitative model proposed earlier. The energy barrier is calculated to be $38\frac{1}{2}$ kcal/mole, which implies that the exchange reaction $T + H_2O \rightarrow HTO + H$ is at least 10^9 times slower than the exchange reaction $T + H_2 \rightarrow HT + H$. Calculations were also performed on the analogous hydrogen atom-hydrogen fluoride exchange reaction.

In preparation for experiments on the IR spectrum of HTO a spectrophotometer cell has been modified for use with HTO and a cell loading system has been assembled and tested.

Electrolysis of High Level Tritiated Water In lieu of other disposal methods a system using a General Electric UCT-1 regenerative cell has been assembled and tested. This system should be capable of decomposing pure water into hydrogen and oxygen gases. The tritium from this process can be purified and reused instead of buried.

Catalytic Exchange Detritiation Studies Fabrication and installation of the experimental apparatus were completed, and analytical instruments were integrated into the system. A preliminary economic evaluation was made of the HT/H_2O catalytic exchange detritiation stripping process as it might apply to a 5 metric ton/day nuclear fuel reprocessing plant.

Shipping Container Development for Tritiated Liquid Waste A tritiated water shipping container has been designed and developed for use with the ERDA-DOT approved AL-MI secondary container. The stainless steel container is 23 in. long and 6 3/4 in. in diameter and is capable of containing up to 2 kg of tritiated water immobilized on Type 4A molecular sieve. The design has been based on compatibility with effluent removal or detritiation systems at three ERDA construction sites and with calorimetry and recovery facilities at Mound.

TRITIUM WASTE CONTROL PROJECT

C. J. Kershner, Science Fellow
J. C. Bixel, Project Leader

A December 1970 Commission communique asked that contractors seek to limit their tritium and other radioactive effluent to levels that are "as low as practicable." Subsequent communiques suggest control of radiological release to less than 10% of the Radioactivity Concentration Guide (RCG) for uncontrolled areas and also suggest moving the point of concentration measurement from plant boundary limits to within the effluent stacks.

Beginning in 1970, an intensive tritium emission control effort was put into effect at Mound Laboratory. This effort has as its goal an ultimate objective of approaching zero emissions, and an engineering goal quantified in terms of maintaining stack emission levels at or below 10% of the present RCG values (40 $\mu Ci/m^3$ for HT and 0.2 $\mu Ci/m^3$ for HTO). To accomplish these goals, facility design and operating philosophies were revised to those of containment and recycle as opposed to the past practice of high dilution and release. Over the past five years, implementation of this philosophy through facility modifications and additions and changes in operating procedures has resulted in a 30-fold reduction in the gaseous tritium effluents released from the laboratory. However, reduction of tritium effluent levels to 10% of RCG values at the point of emission and nearly complete recycle pose problems that are beyond ready solution with state-of-the-art tritium control technology.

To meet this advanced technological need, the Tritium Effluent Control Project was initiated in January 1972. The experimental direction of this project is predicated on the results of an initial source and facility evaluation which revealed that as much as 80% of the total annual release to the atmosphere could be attributed to "background" diffusion from glove boxes and other containments to the room ventilation systems which are directly stacked. To treat the voluminous quantities of high humidity room air was deemed to be both economically and technically impractical, so emphasis has been placed on confining the tritium at the source through use of glove box atmosphere detritiation and recovery systems and applying room air treatment only for emergency conditions in the event of accidental releases.

Basic separation and enrichment technology is being developed and applied to gaseous and liquid effluent detritiation and recovery. The major portion of the gaseous effluent treatment development is in the pilot scale phase. A test laboratory, embodying many of the results of the past research phase of the work, has been designed and its construction nearly completed.

TRITIATED LIQUID WASTE DECONTAMINATION (MOLECULAR EXCITATION)

W. R. Wadt, R. E. Ellis

BACKGROUND

Operations involving tritium produce significant quantities of aqueous waste, which must be disposed of in a safe manner. Much of the waste contains a low concentration of tritium. At present, these low-level wastes are processed and buried at relatively high expense. An alternate procedure would be to discharge the waste after dilution to "safe" levels. However, both methods eventually allow some or all of the tritium to enter the environment. A preferable procedure would be to decontaminate the wastes by extracting the small amounts of tritium. The economic feasibility of detritiating large volumes of low-level (10^{-3}-10 $\mu Ci/ml$) water is highly dependent on the separation factor of the elementary isotopic separation process employed. The separation factor for most H/T isotopic systems is quite small - ranging from slightly greater than 1 to approximately 10 for the case of water electrolysis. However, one process, selective photoexcitation, has the potential for orders-of-magnitude higher separation factors and, in principle, requires much less separative work because the separation energy is applied to the minor constituent rather than to the entire feed mixture. In conventional multi-staged separation processes, sufficient energy input is needed for processing the total feed quantity many times to maintain the total cascade flow required for the desired separation. Thus, selective photoexcitation is a very attractive process for an application where one is concerned with the isotopic separation of trace quantities from a voluminous quantity of feed such as in the case of water detritiation or heavy water enrichment.

The goal of this study is to determine the feasibility of decontamination by selective molecular excitation. If the process proves successful, further applications will be considered, such as: 1) extension of the treatment of high-level aqueous wastes, 2) control of the tritium level in the primary coolant of light water reactors, and 3) removal of deuterium from water.

PRIOR WORK

Laser Separation System A plausible scheme to detritiate low-level aqueous wastes by molecular photoexcitation has been formulated. The process, which is carried out in the gas phase, consists of isotopically-selective photodissociation (ISP) of HTO in the presence of H_2 which scavenges the photoproducts. The ISP is achieved by a two-photon process employing an infrared (ir) laser and an ultraviolet (uv) flashlamp. The ir laser selectively excites the OT stretching vibration in HTO at 4.35 μm, while the uv flashlamp is filtered so as to photodissociate only the vibrationally excited HTO molecules. The photoproducts, T and OH, both react rapidly with H_2 to produce HT and H_2O, respectively. By recycling the hydrogen stream the tritium may be significantly enriched relative to the water stream. An analysis of the kinetics indicates that for low-level wastes, the effect of the tritium β decay on regeneration of HTO places a more stringent limitation on the tritium level allowable in the hydrogen stream than does the reaction, OH + HT → HTO + H.

A tunable ir laser developed by Prof. R. L. Byer and co-workers at Stanford University was determined to be the most appropriate for our purposes. The laser consists of an $LiNbO_3$ optical parametric oscillator (OPO) pumped by a Q-switched Nd:YAG laser. The laser is tunable from 1.4 to 4.45 μm with relatively high powers (~1 mj/pulse). Prof. Byer was retained as a consultant on the procurement of a comparable laser system. A Q-switched Nd:YAG laser was ordered from General Photonics Corporation.

The $LiNbO_3$ crystal for the OPO and associated optical components were also procured. Finally, a long-path two-photon absorption cell (Wilks Scientific Corporation) and an appropriate xenon flashlamp (Xenon Corporation) were ordered.

HTO Infrared Spectrum The exact wavelengths and absorption intensities of the HTO molecule in the infrared region around 4.35 μm are necessary for determining parameters for the experiments in water decontamination via molecular excitation. Using HDO as a surrogate very satisfactory spectra were obtained from a Digilab FTS-14 Spectrophotometer.

ACCOMPLISHMENTS

Laser Separation System Experiments performed at Stanford University under the direction of Prof. R. L. Byer revealed that a simple Nd:YAG oscillator does not possess the power required to drive the OPO at 4.35 μm. A 1/4 in. Nd:YAG amplifier must be added to the oscillator to obtain the required power. In addition, a Faraday rotator isolator is required to isolate the oscillator-amplifier chain from feedback in order to maintain stable operation. Consequently, the order for an Nd:YAG oscillator from General Photonics Corporation was modified to include an Nd:YAG amplifier and Faraday rotator isolator.

The isotopic selectivity of the two-photon dissociation process was examined in more detail. The selectivity or ratio of HTO to H_2O molecules that are photodissociated was found to be on the order of 25. Although this selectivity is sufficient for bench scale proof-of-principle experiments, it is inadequate for application to large scale detritiation projects, e.g., nuclear fuel reprocessing plant waste. The selectivity is such that most of the laser energy is wasted in photodissociation of H_2O. This obstacle may be overcome by pumping more vibrational energy into the HTO molecules. Various schemes towards this end are being considered.

Extensive ab initio calculations on the potential surface for the hydrogen atom-water exchange reaction have been carried out at the Aerospace Corporation in conjunction with Dr. N. W. Winter. The results bear out the predictions of the simple qualitative model proposed earlier. The energy barrier is calculated to be 38½ kcal/mole, which implies that the exchange reaction $T + H_2O \rightarrow HTO + H$ is at least 10^9 times slower than the exchange reaction $T + H_2 \rightarrow HT + H$. Calculations were also performed on the analogous hydrogen atom-hydrogen fluoride exchange reaction. The importance of including diffuse functions in the basis set, which had been predicted by simple model considerations, was corroborated by the results. The addition of diffuse functions leads to a nonlinear transition state contravening previous calculations without diffuse functions that predict a linear transition state. This result may have important implications for the rate of vibrational deactivation of HF by H atoms. The latter process is a key element in the design of efficient high-powered HF chemical lasers.

HTO Infrared Spectrum A Barnes Engineering Company spectrometer cell has been modified for use in determining the HTO spectrum in the 4.35 μm region. The system to load this cell was assembled and the active components operationally tested.

DISCUSSION

Laser Separation System

Modifications to the ir laser In the previous quarter a Q-switched Nd:YAG laser was ordered from General Photonics Corporation to drive an $LiNbO_3$ OPO. The output power was specified to be 15 mj/pulse TEM_{00}. However, experiments performed early in June by Prof. R. L. Byer and co-workers at Stanford University revealed that more than 15 mj/pulse TEM_{00} was required to drive the OPO at 4.35 μm, which is far from degeneracy (2.12μm). In order to attain the OPO power threshold at 4.35 μm, a 1/4 in. Nd:YAG amplifier was placed in front of the Nd:YAG oscillator. The oscillator-amplifier chain produced pulses with 50 mj of energy, which was determined to be adequate to drive the OPO at 4.35 μm. In addition, Byer and co-workers found that a Faraday rotator isolator was necessary to protect the oscillator-amplifier chain from feedback. Without the isolator, back-reflected 1.06 μm radiation would be amplified by the 1/4 in. amplifier and produce instabilities in the Nd:YAG oscillator.

Upon notification of these results, we proceeded to modify the purchase order for an Nd:YAG oscillator to include a 1/4 in. Nd:YAG amplifier and a Faraday rotator isolator. The oscillator-amplifier-isolator chain will produce 50 mj, 20 nsec, TEM_{00} pulses at a rate of 10 pps. These modifications have engendered a two to three month delay in the delivery of the laser, and hence, the initiation of the water detritiation experiments.

Isotopic selectivity of two-photon dissociation In the previous quarterly reports[1-3] the two-photon photodissociation was assumed to be completely isotopically-selective. This, of course, is not the case. A better idea of the selectivity may be gained from the potential curves for H_2O and HTO in Figures 1 and 2, respectively. The lowest energy electronic absorption in H_2O arises from the transition $X^1A_1 \rightarrow A^1B_1$, which basically corresponds to a one-electron promotion from the oxygen 2p lone pair perpendicular to the molecular plane to a Rydberg 3s orbital centered on the oxygen. The A^1B_1 state is dissociative (cf. Figure 1) so that the electronic absorption is broad and featureless,[4] representing the shape of the ground vibrational state wavefunction. The "bump" or inflection point in the A^1B_1 potential curves arises from a curve crossing between a repulsive valence state (large distances) and an attractive Rydberg state (small distances).[5] An analogous curve crossing in H_3O has been described in more detail previously.[2] Finally, note that the zero-point energy (ZPE) of the A^1B_1 state is non-zero since one OH bond remains intact as the molecule dissociates into H + OH. The ZPE for the dissociative A state is shown in Figures 1 and 2 and is taken into account in calculating the absorption wavelength.

It is clear from Figures 1 and 2 that the vibrational excitation of the HTO molecules shifts the electronic absorption spectrum to longer wavelength relative to that for H_2O. Since we are dealing with a bond-to-continuum transition, the onset of absorption is not sharp but rather is an exponential tail. As a result, completely selective photodissociation of HTO is not possible. Determination of the relative absorption cross-sections for H_2O and HTO*, (the asterisk denotes vibrationally excited HTO) and hence, the selectivity of the photodissociation is complicated by various competing considerations. First, the vibrational energy of the HTO ($2295 + 3771 = 6066\ cm^{-1}$) is greater than that of the H_2O ($4634\ cm^{-1}$) by $1432\ cm^{-1}$, shifting the electronic absorption to longer wavelength. Second, one must consider the changes in the vibrational wavefunction which are mirrored in the absorption spectrum. For $v = 0$ wavefunctions the most probable value for $\Delta r = r - r_e$ is zero, while for $v = 1$ wavefunctions it is nonzero. Consequently, there is an additional increase in the uv absorption cross-sections at longer wavelengths as one goes from $v = 0$ to $v = 1$ states. On the other hand, the probability of finding the molecule at large Δr decreases significantly if hydrogen is replaced with tritium, because of the large mass difference. The extensive ab initio calculations by C. W. Kern and co-workers at Battelle, Columbus, on the ground state potential surface of the water molecule might resolve the problem of comparing the H_2O $v = 0$ and the HTO $v = 1$ wavefunctions.[16] This possibility is being pursued.

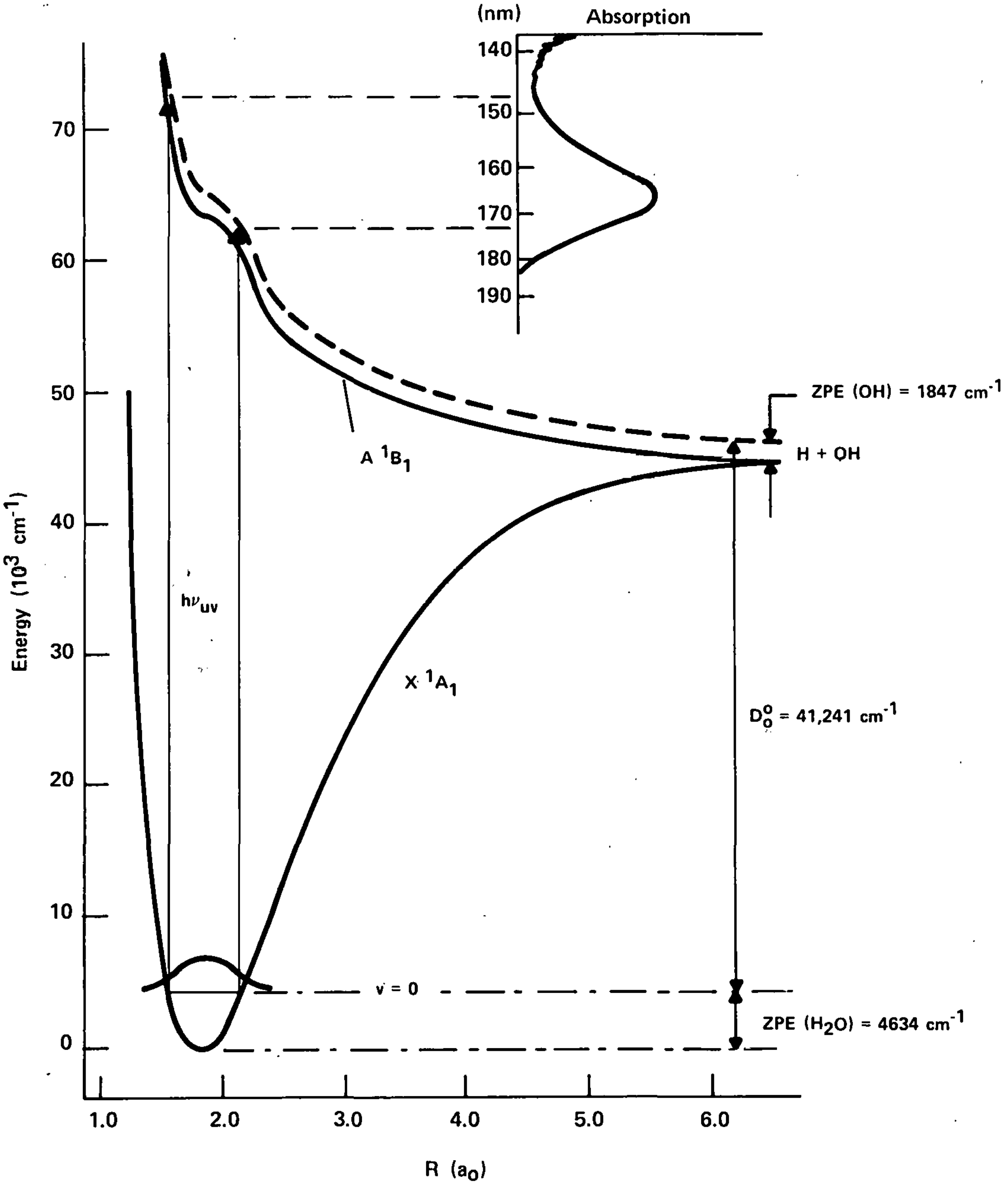


FIGURE 1 - Schematic potential curves for the X^1A_1 and A^1B_1 states of H_2O stretching one OH bond. (NB $1a_0$ = 0.539177Å)

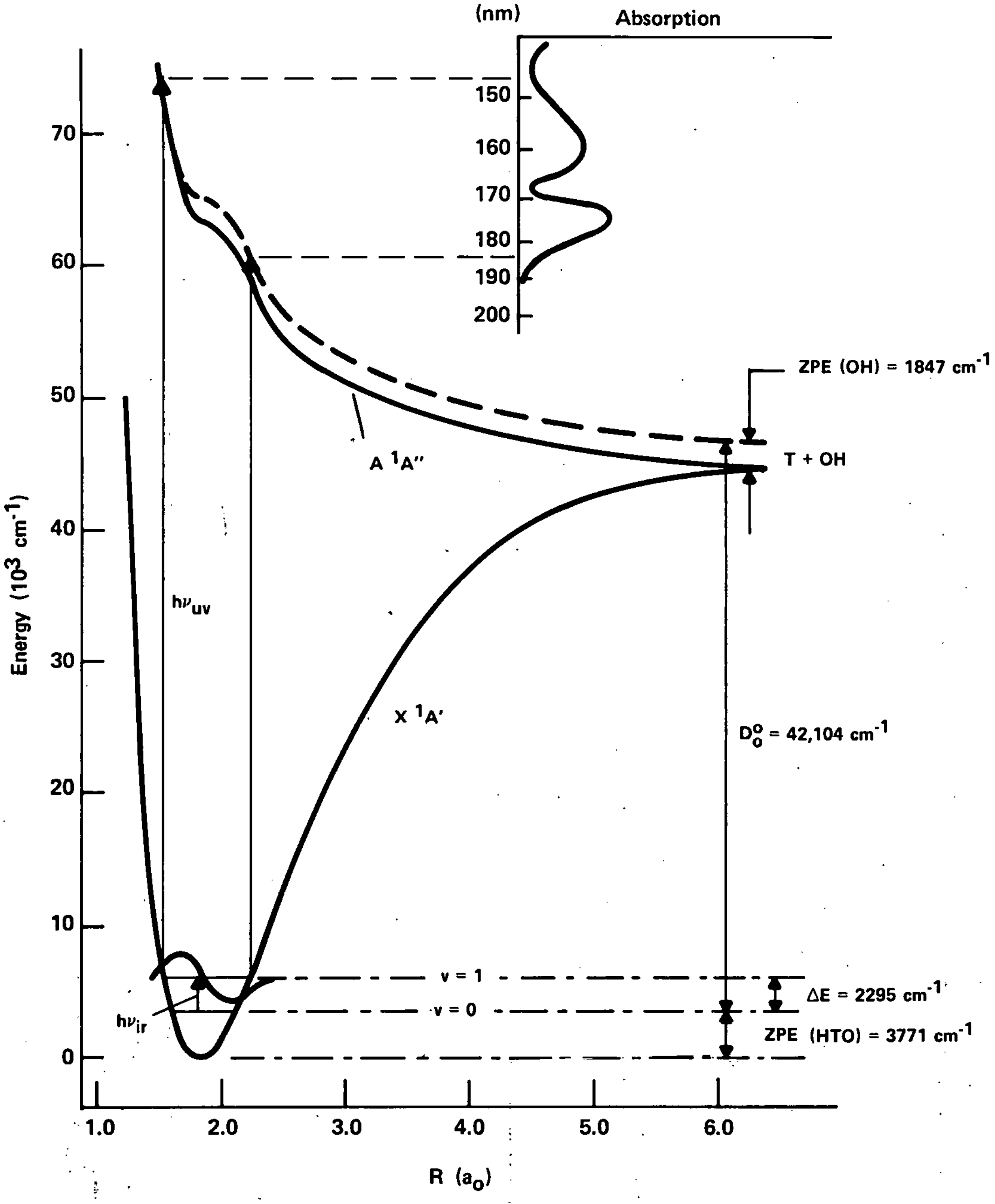


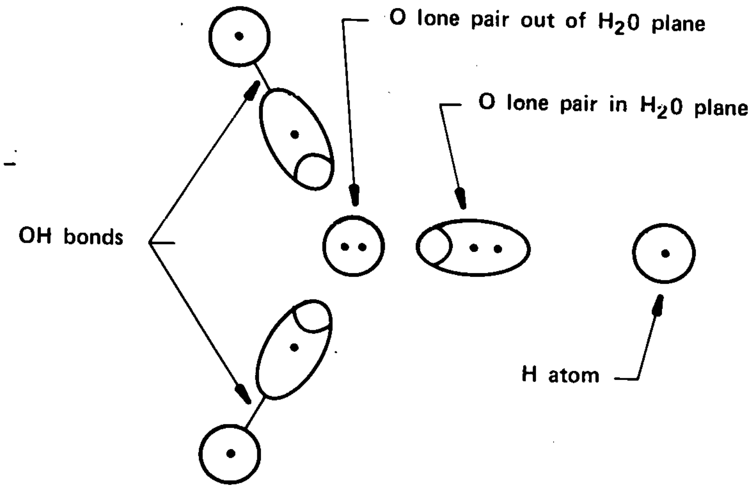
FIGURE 2 - Schematic potential curves for the X^1A' and the A^1A'' states of HTO stretching the OT bond.

For lack of information, we will ignore the effect of the vibrational wavefunction and will focus on the shift in the uv absorption spectrum induced by the increased vibrational energy in HTO. A qualitative analysis of the uv spectrum of H_2O^4 predicts that the absorption cross-sections should be larger by a factor of 25 for HTO versus H_2O if one excites along the exponential tail for HTO (i.e., excitation wavelength >185 nm). According to Figure 2, the maximum absorption cross-section for HTO occurs at ~175 nm, but the H_2O cross-section would be at most a factor of five smaller. At first a photodissociation selectivity factor of 25 sounds large, however, it is orders-of-magnitude too small if molecular photoexcitation is to be applied to large scale water detritiation problems, e.g., nuclear fuel reprocessing plant waste. In these cases, the HTO concentration is very low (~0.1 ppm) and large volumes must be handled (~500 l/hr). To photodissociate all the HTO molecules, one must also dissociate 1/25 or 4% of the H_2O molecules. Nearly all of the photon energy must be pumped into the H_2O fraction rather than the HTO fraction, circumventing the basic idea behind molecular photoexcitation. As a result, the power requirements for detritiation of large volumes of low-level aqueous wastes are not competitive with other separative processes such as catalytic exchange.

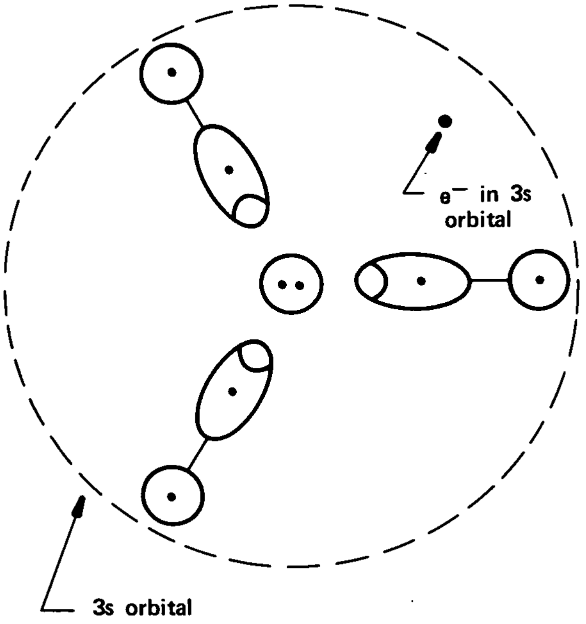
In order to increase the selectivity of the two-photon photodissociation process, the vibrational energy pumped into the HTO molecules must be increased. We are currently investigating ways to increase the vibrational excitation. For example, if the HTO molecules possessed 10,000 cm^{-1} of vibrational energy (in addition to the ZPE), the photodissociation selectivity would be increased to ~10^6. Moreover, the required uv radiation would be at longer wavelengths, ~210 nm, rather than ~190 nm. The latter result greatly enhances the possibility of finding a high-power uv laser to supply the second photon. Preliminary calculations indicate that large-scale detritiation of low-level aqueous wastes would be economically attractive if a photodissociation selectivity of 10^6 could be achieved. A final caveat, vibrational relaxation may severely limit the degree of selectivity.

Ab Initio Calculations on the H + H_2O Potential Surface One of the key reactions in water detritiation by ISP is the regeneration of HTO by back-exchange of the tritium atoms, i.e., T + H_2O → HTO + H. The rate of this reaction is not known experimentally. Semiquantitative theoretical arguments indicate that the activation energy for the exchange reaction should be approximately 20 to 30 kcal/mole[2]. If this is the case, then the exchange reaction will proceed at a very slow rate, which is the key to successful scavenging of the tritium by the hydrogen stream. Therefore, it is imperative to obtain a quantitative theoretical value for the activation barrier. Towards this end, extensive ab initio quantum mechanical calculations on the H + H_2O reaction surface have been and are being performed in conjunction with Dr. N. W. Winter on the CDC 7600 computer at the Aerospace Corporation.[6]

The simple orbital model for the H + H_2O exchange reaction, presented previously,[2] may be used to determine the appropriate basis set and wavefunction(s) to be employed in the calculations. The approach of a hydrogen atom to a water molecule may be represented at large distances (>3 a_0) by the following orbital diagram



where ⬭ denotes an oxygen sp hybrid orbital in the molecular plane, ○ denotes both a hydrogen 1s orbital and an oxygen 2p orbital perpendicular to the molecular plane, tie lines denote bonds, and dots denote electrons. As the hydrogen (or tritium) atom approaches one of the oxygen lone pairs, say the one in the H_2O plane, there is a repulsive interaction analogous to that between a hydrogen and a helium atom. The hydrogen 1s orbital initially mixes in antibonding character to remain orthogonal to the lone pair because of the Pauli Principle and then builds in nonbonding Rydberg 3s character on the oxygen at shorter distances, again maintaining orthogonality to the lone pair. Meanwhile, the oxygen lone pair gradually delocalizes onto the incoming hydrogen atom forming a third OH bond so that the transition state may be represented as shown on the following page.



In order to describe the Rydberg 3s character, diffuse functions must be included in the basis set. Moreover, to obtain good quality results one requires a "double zeta" (DZ) quality basis set including polarization functions on the oxygen (i.e., d functions). All the calculations were performed with the Dunning[7] [3s, 2p/2s] contraction of the Huzinaga[8] (9s, 5p/4s) set of primitive Gaussian basis functions, augmented 1) with one set of d functions on the oxygen with an exponent of 0.91[9] and 2) with one set of diffuse s and p functions with an exponent of 0.028[10]. The basis set is denoted as DZd+R.

Gangi and Bader (GB)[11] previously studied the H_2O potential surface using a comparable basis set and an open-shell restricted Hartree-Fock (HF) wavefunction, i.e., all the orbitals except one are doubly occupied. The HF wavefunction neglects electron correlation, and hence, may introduce errors arising from different correlation energies for H_2O + H and H_3O. It is clear from the orbital diagrams that the major correlation energies arise from the OH bonds. The generalized valence bond (GVB) wavefunction[12,13] can account for a significant fraction of the static correlation energy by replacing the doubly occupied HF orbitals with a pair of non-orthogonal singlet-coupled orbitals.

$$\text{HF: } \phi(1)\ \phi(2)\ [\alpha(1)\beta(2)-\beta(1)\ \alpha(2)]$$

$$\text{GVB: } [\phi_a(1)\phi_b(2)+\phi_b(1)\phi_a(2)][\alpha(1)\beta(2)-\beta(1)\alpha(2)]$$

Therefore, for H_3O, the doubly-occupied HF orbitals describing the three OH bonds are replaced with GVB pairs. As one hydrogen is pulled off to give H_2O + H, one GVB pair changes from an OH bond to an oxygen lone pair.

An ambiguity arises in the description of H_2O + H in that there are two lone pairs on the oxygen and only one is described by a GVB pair. Planar H_3O configurations correspond to splitting the in-plane oxygen lone pair in H_2O + H, while non-planar H_3O configurations correspond to splitting the out-of-plane lone pair. Moreover, the energies of these two descriptions of H_2O + H are different. The energy of the wavefunction with the out-of-plane oxygen lone pair split is 2.76 kcal/mole lower. To be consistent both lone pairs should be split. However, each additional GVB pair greatly increases the cost of determining the wavefunction and the energy, so that only one lone pair was split. The energies of planar H_3O configurations are referred to an H_2O + H calculation with the in-plane lone pair split and the energies of non-planar H_3O configurations are referred to an H_2O + H calculation with the out-of-plane lone pair split.

To simplify the solution for the above wavefunction, two approximations are made:[12] 1) orbitals from different pairs are taken to be orthogonal (strong orthogonality) and 2) the orbitals in each pair are assumed to be singlet coupled (perfect pairing).[14] The resulting wavefunction, designated GVB (3/PP), has the form

$$\Psi=A[\phi_1{}^2\phi_2{}^2(\phi_a\phi_b+\phi_b\phi_a)(\phi_c\phi_d+\phi_d\phi_c)(\phi_e\phi_f+\phi_f\phi_e)\ \phi_3\alpha\beta\ldots\alpha\beta\alpha]$$

When solving for the wavefunction, the equivalent representation of the GVB pairs in terms of two orthogonal natural orbitals is used.[15]

$$\phi_a\phi_b + \phi_b\phi_a = C_1\phi_1^2 - C_2\phi_2^2$$

Configuration interaction (CI) calculations will be carried out to obtain a more quantitative treatment of the potential surface. At present full CI calculations (freezing the oxygen 1s orbital electrons) within the nine orbital space defined by the GVB (3/PP) wavefunction have been performed at a few points. The CI calculation, designated GVB-CI, entails 747 spatial configurations and 1723 spin eigenfunctions. More extensive CI calculations are in progress.

The primary goal of the GVB(3/PP) calculations was to determine the energy barrier for the H + H_2O exchange reaction. Towards this end, calculations were carried out to determine the equilibrium geometry of H_3O. The coordinate system is shown in Figure 3. Initially, a D_{3h} geometry for H_3O was assumed, i.e., planar with the bond angles equal to 120°. The OH bond lengths were varied symmetrically. The results listed in Table 1 (NB energies are referred to separated $H_2O + \overline{H}$) and plotted in Figure 4 lead to an optimum value of $1.87a_o$ for the OH bond length, which is very similar to the 1.86 a_o obtained by GB[11]. Using a near optimum OH bond length of $1.8853a_o$, the bond angle was optimized by considering pyramidal C_{3v} geometries. The results shown in Table 2 and Figure 5 indicate an optimum angle of 106.6° and an energy drop of 5 kcal/mole relative to the planar geometry. GB[11] obtained an optimum bond angle of 111.77° and an energy drop of only 2 kcal/mole.

In the actual exchange reaction one hydrogen attacks an oxygen lone pair forming a new OH bond, while another OH bond breaks forming a new lone pair. To model this process, we constructed a two-dimensional grid in which only two OH bond lengths were varied. The remaining geometrical parameters were fixed at the experimental values for H_2O, i.e., 104.45° for all the angles and $1.8111a_o$ for the third OH bond. In this way, the two-dimensional surface is symmetrical and "dissociates" to H + H_2O in its experimental geometry. Fortuitously, both 104.45° and $1.8111a_o$ are proximate to the optimum values for H_3O, 106.6° and $1.87a_o$, respectively, so that the lowest energy for H_3O calculated on the two dimensional surface will be only ~2 kcal/mole higher than the optimum value. Consequently, the resulting surface would be very suitable for carrying out dynamical calculations on the H + H_2O exchange reaction.

Table 3 and Figure 6 illustrate a cut of the two-dimensional surface in which one OH bond is fixed at $1.8111a_o$. A 5½ kcal/mole hump is obtained in the region of $2.25a_o$ in accord with the work of GB[11]. The hump indicates the region in which the unpaired hydrogen orbital is transforming into an oxygen Rydberg 3s orbital. Therefore, the two-dimensional grid was centered in the region of 1.5 to $2.5a_o$. The results are shown in Table 4, with contour and three-dimensional plots of the surface given in Figures 7, 8, and 9.

Finally, the various ab initio calculations on H_3O are compared in Table 5 at the D_{3h} geometry with the OH bond lengths equal to $1.86a_o$. The basis set of GB[11] included polarization functions on the hydrogens but no diffuse p functions on the oxygen. An RHF calculation with the DZd+R basis employed in this work would lead to energy ~0.01 h above that of Gangi and Bader.

In our simple orbital model for the exchange reaction the hydrogen 1s orbital smoothly changes into an oxygen 3s orbital as the hydrogen atom approaches the water molecule. Analysis of the orbital coefficients at a series of separations bears out the above picture. The oxygen 3s character does not become appreciable until the OH distance is less than $2.5a_o$. The major switch occurs in the region of the hump near $2.25a_o$. Recall that the hump is actually a manifestation of an avoided crossing.[2] Concurrent with the changes in the unpaired orbital, the oxygen lone pair being approached by the atom smoothly transforms into a third OH bond. Orbital plots demonstrating the above metamorphoses are being made.

The energy of H_3O at the bottom of the well in Figure 7 (∠HOH = 104.45°, AO = BO = 1.90 a_o, CO = $1.8111a_o$) is 33 kcal/mole higher than the energy of H + H_2O. The calculated energy barrier is even higher, 38½ kcal/mole, because of the hump. These results are 5 to 6 kcal/mole higher than the values obtained by GB[11], implying that the major correlation effects approximately balance for H_3O and H + H_2O as had been predicted.[2] However, the GVB (3/PP) wavefunction includes only part of the static correlation energy and none of the dynamic correlation energy (i.e., instantaneous correlation of the electron movements). Therefore, CI calculations that include the key portions of the remaining correlation effects must be carried out to determine a quantitative value for the energy power. These calculations are in progress.

Comparison with CI calculations on analogous systems O + H_2,[5] OH + H,[5] and HF + H[17] indicates that the energy barrier may drop by as much as 15 kcal/mole. Nevertheless, the activation energy should still be ≳20 kcal/mole, since the changes

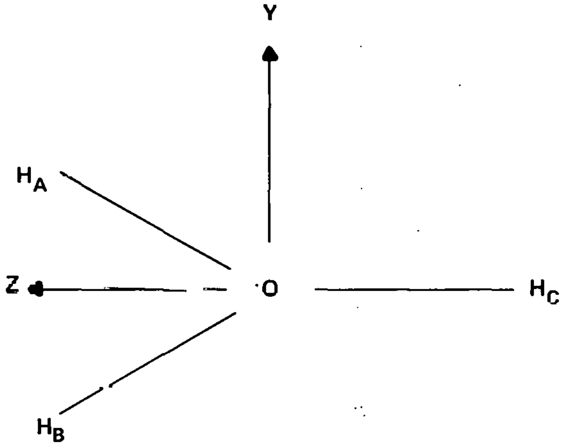


FIGURE 3 - Coordinate system for H_3O.

Table 1

GVB(3/PP) RESULTS FOR PLANAR D_{3h}
$(\angle AOB=\angle AOC=\angle BOC=120°, \overline{AO}=\overline{BO}=\overline{CO}=R)$

$R(a_o)$	E(kcal/mole)
2.0	42.6
1.8853	37.3
1.86	37.3
1.72	48.6*

*Energy relative to that for H_2O + H, -76.58308h

Table 2

GVB(3/PP) RESULTS FOR NONPLANAR C_{3v}
$(\angle AOB=\angle AOC=\angle BOC=\theta, \overline{AO}=\overline{BO}=\overline{CO}=1.8853a_o)$

θ	E (kcal/mole)
120°	37.3
112°	33.1
108°	32.0
104.45°	32.1

Table 3

GVB(3/PP) RESULTS FOR NONPLANAR C_h APPROACH OF H_C
$(\angle AOB=\angle AOC=\angle BOC=104.45°, \overline{AO}=\overline{BO}=1.8111a_o)$

$\overline{CO}(a_o)$	E(kcal/mole)	$\overline{CO}(a_o)$	E(kcal/mole)
10.0	0.0*	2.25	39.4
5.0	0.9	2.0	34.8
3.0	18.4	1.811	34.9
2.5	34.5	1.5	67.6

*Absolute energy for H_2O + H is -76.58748h (NB 1h=27.21165eV).

Table 4

GVB(3/PP) RESULTS FOR NONPLANAR C_1*
$(\angle AOB=\angle AOC=\angle BOC=104.45°, \overline{CO}=1.8111a_o)$

	$\overline{BO}(a_o)$				
$\overline{AO}(a_o)$	1.5	1.8111	2.0	2.25	2.5
1.5	100.5	67.6	67.1	70.1	63.4
1.8111	67.6	34.9	34.8	39.4	34.5
2.0	67.1	34.8	35.2	41.3	37.6
2.25	70.1	39.4	41.3	51.2	
2.5	63.4	34.5	37.6		71.3

*Energies are given in kcal/mole.

Table 5

AB INITIO RESULTS FOR H_3O PLANAR D_{3h}
$(\angle AOB=\angle AOC=\angle BOC=120°, \overline{AO}=\overline{BO}=\overline{CO}=1.86a_o)$

Calculation	Basis Set	Wavefunction	E(h)
Winter[16]	DZ+R(s,p)	RHF	-76.4697
Gange & Bader[11]	POL+R(s)	RHF	-76.4926
This Work	DZd+R(s,p)	GVB(3/PP)	-76.5237
This Work	DZd+R(s,p)	GVB-CI	-76.5889

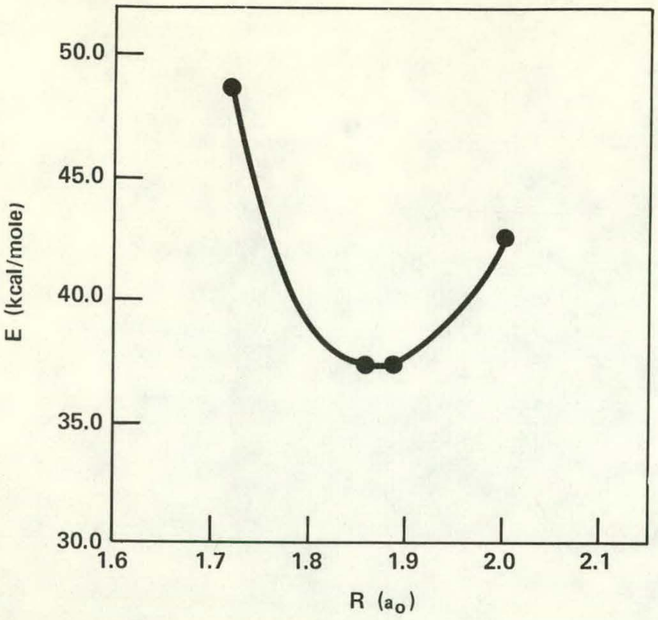


FIGURE 4 - Planar D_{3h} *Stretch*
($\overline{AO}=\overline{BO}=\overline{CO}=R$, $\angle AOC=\angle AOC=\angle BOC=120°$).

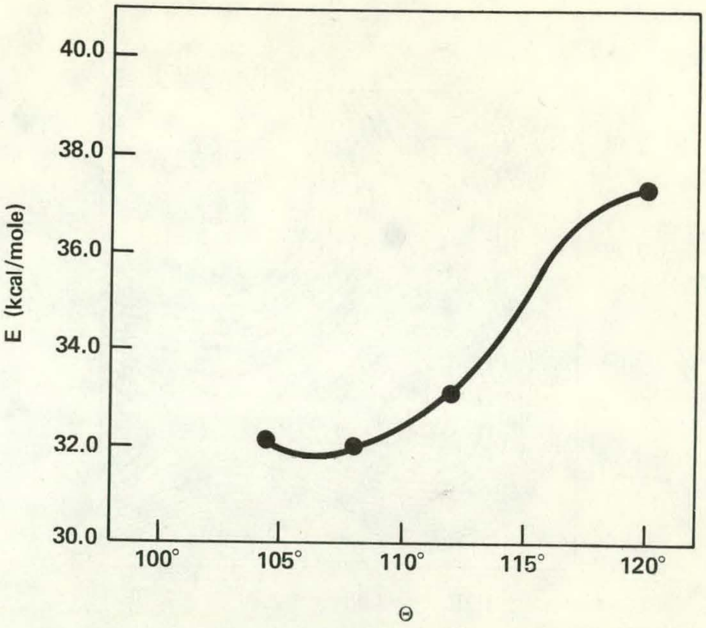


FIGURE 5 - Nonplanar C_{3v} *bend*
($\angle AOB=\angle AOC=\angle BOC=\Theta$, $\overline{AO}=\overline{BO}=\overline{CO}=1.8853a_o$).

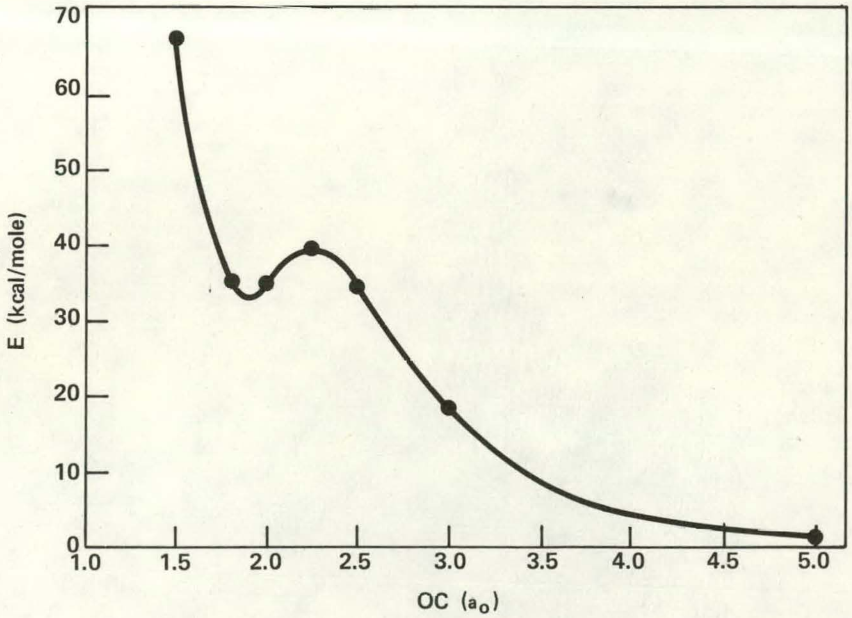


FIGURE 6 - Nonplanar C_h *approach of* H_C($\angle AOB=\angle AOC=\angle BOC=104.45°$,
$\overline{AO}=\overline{BO}=1.8111a_o$).

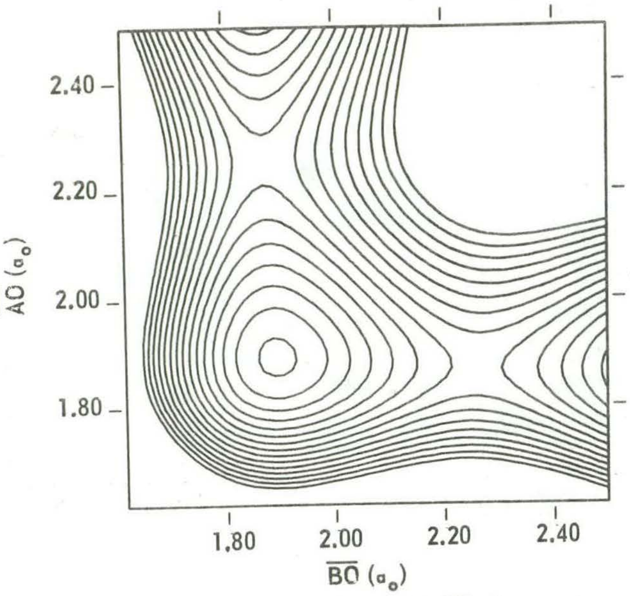


FIGURE 7 - Two-dimensional contour plot for the $H + H_2O \rightarrow H_2O + H$ exchange reaction ($\angle AOB = \angle AOC = \angle BOC = 104.45°$, $\overline{CO} = 1.8111a_0$).

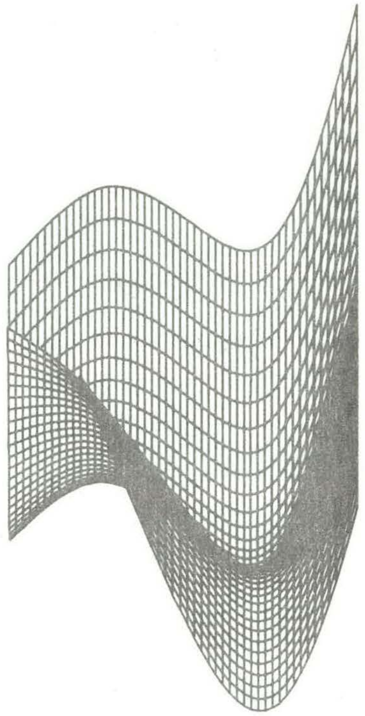


FIGURE 8 - Three-dimensional contour plot for the $H + H_2O \rightarrow H_2O + H$ exchange reaction viewed along the line $AO = 1.94a_0$ ($\angle AOB = \angle AOC = \angle BOC = 104.45°$, $\overline{CO} = 1.8111a_0$)

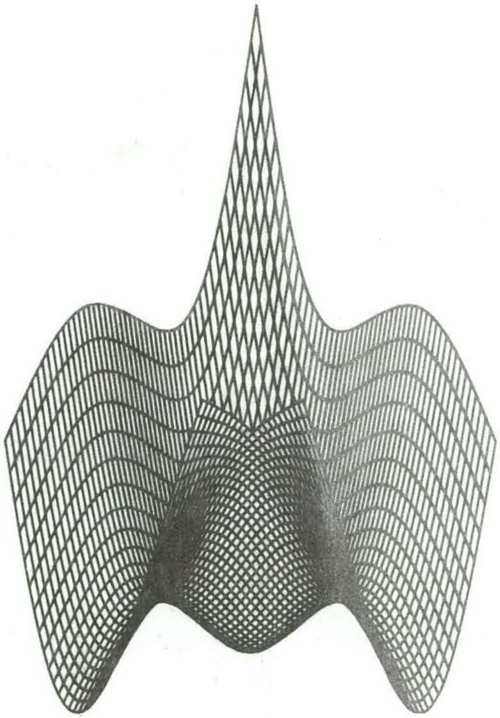


FIGURE 9 - Three-dimensional contour plot for the $H + H_2O \rightarrow H_2O + H$ exchange reaction viewed along the line $AO = BO$ ($\angle AOB = \angle AOC = \angle BOC = 104.45°$, $\overline{CO} = 1.8111a_0$).

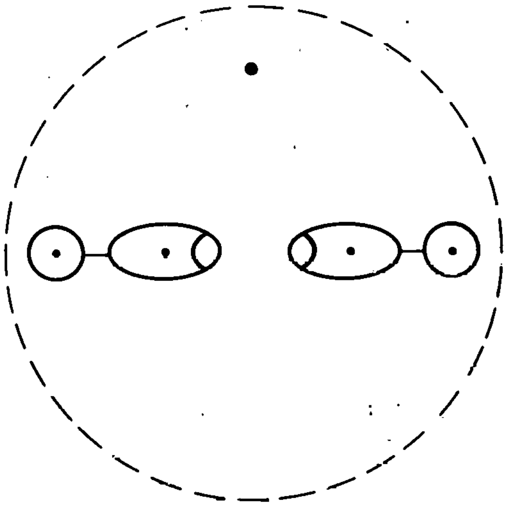
in the zero point energy are not expected to produce any further decrease in the barrier. In conclusion, the partial results on the H + H_2O exchange reaction bear out the earlier predictions that the rate is exceedingly slow, i.e., on the order of 10^{-25} to 10^{-24} cm^3/molecule sec.[2]

Ab Initio Calculations on the H + HF Exchange Reaction In the course of developing a simple model for the H + H_2O exchange reaction, the isoelectronic H + HF exchange reaction was considered.[2] The collinear reaction was treated from the point of view of the orbital phase continuity principle[18] with the result that the unpaired orbital (the hydrogen 1s orbital at infinite separation) would possess significant fluorine 3s character at the transition state. A large activation energy was predicted. Soon after, Bender, Garrison and Schaefer (BGS)[17] reported an energy barrier of 49 kcal/mole, based on extensive CI calculations. However, BGS employed a POL basis set (DZ plus polarization functions) which did not include any diffuse functions. A fluorine 3s orbital would be poorly described by such a basis. If the unpaired orbital did possess significant 3s character at the transition state, the calculated value for the energy barrier would be artifically high (by 5 to 10 kcal/mole). We decided to check the calculations of BGS as to the effect on including diffuse functions on the fluorine.

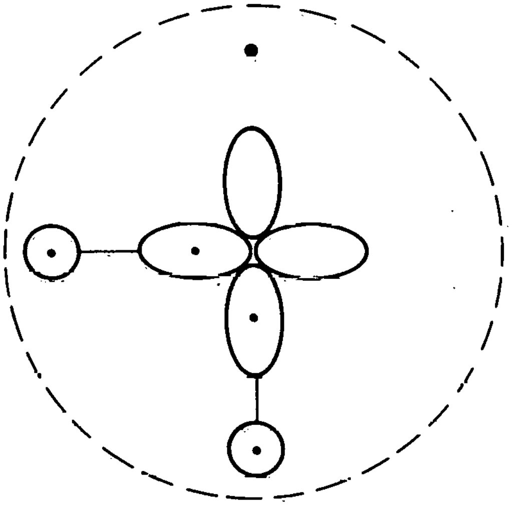
The calculations were performed with the Dunning[7] [3s, 2p/2s] contraction augmented 1) with one set of polarization functions (d's on the fluorine, p's on the hydrogen) all with an exponent of 1.0, and 2) with one set of diffuse s and p functions with exponents of 0.035 and 0.030, respectively. BGS employed a more extensive POL basis set than ours, namely a [5s, 3p, 1d/3s, 1p] contraction of a (9s, 5p, 2d/5s, 1p) set of primitives.[17] In analogy to the H + H_2O calculations, a GVB (2/PP) wavefunction was employed in which both HF orbitals describing the two HF bonds at the transition state were replaced with GVB pairs. At infinite separation of HF + H one of the GVB pairs describes the fluorine 2s lone pair. BGS performed HF calculations and then CI calculations consisting of all single and double excitations from the HF configuration.[17]

GVB(2/PP) calculations were carried out at three points with and without diffuse functions in the basis set: 1) collinear $H_AF + H_B$ with $R(H_AF) = 1.7331\ a_0$, the experimental HF bond length, and $R(H_BF) = 10\ a_0$; 2) collinear H_AFH_B with $R(H_AF) = R(H_BF) = 2.1543\ a_0$, the saddle point calculated by BGS with the CI wavefunction[17]; 3) nonlinear H_AFH_B with $R(H_AF) = R(H_BF) = 2.1543\ a_0$ and $\angle HFH = 90°$. The results are shown in Table 6. For collinear HFH addition of diffuse functions leads to an energy decrease of 5 kcal/mole and for nonlinear HFH the decrease is 11 kcal/mole. In both cases, the effect is significant. Analysis of the orbital coefficients for the unpaired orbital indicate significant utilization of the diffuse s function as expected. The HF calculations of BGS[17] led to a value of 67.8 kcal/mole for the energy barrier, which is 3 kcal/mole smaller than our POL basis set value. The origin of the differences are threefold: 1) the correlation energy in the GVB(2/PP) wavefunction increases the barrier by 0.6 kcal/mole; 2) the HF saddle point geometry is slightly different $R(H_AF) = R(H_BF) = 2.1165\ a_0$; and 3) the BSG POL basis set is better than ours.

The unpaired orbital is expected to have more fluorine 3s character at 90° than at 180°, because the fluorine 2p lone pair can form a stronger HF bond than the fluorine 2s pair can (compare the orbital diagrams below).



180°



90°

Table 6

GVB(2/PP) RESULTS FOR HF + H*

Geometry	POL	POL + R
Collinear HF+H	0.0[a]	0.0[b]
Collinear HFH	70.9	66.1
Nonlinear HFH	73.2	61.9

*Energies are given in kcal/mole.

[a] Absolute energy was -100.570678h.

[b] Absolute energy was -100.570678h.

(NB ∞ denotes a fluorine 2p orbital). The inclusion of diffuse functions leads to a nonlinear saddle point geometry, at least at the GVB(2/PP) level. However, the energy of the 90° HFH configuration should be referred to a GVB(2/PP) wavefunction for HF + H in which a fluorine 2p lone pair is split rather than the 2s. This change of reference should increase the energy of the 90° HFH configuration by 3 to 5 kcal/mole to a value comparable with that for collinear HFH. Calculations will be performed to verify this supposition. In any case, a nonlinear saddle point geometry is still expected, which is in accord with the existing calculations on the fluoronium ion, FH_2^+, that predict a bond angle of 114 ± 2°.[19]

The inclusion of diffuse functions appears to be quite important in describing the HF + H exchange reaction; leading to a nonlinear saddle point geometry. Further calculations are needed to determine the optimum saddle point geometry, which may lead to a decrease on the order of 20 kcal/mole in the energy barrier. Nevertheless, the exchange reaction would still be very slow with an activation energy on the order of 20 to 30 kcal/mole (comparable to that for H + H_2O). On the other hand, the smaller energy barrier and nonlinear saddle point may have a significant effect on the calculated efficiency for deactivation of vibrationally excited HF molecules by H atoms. Since the agreement between the experimental measurements for H atom vibrational deactivation of HF is very poor,[20] good theoretical calculations are needed. Therefore, we plan to generate an accurate potential surface for HF + H, on which dynamical calculations will be performed. The results may have significant implications for the design of more efficient HF chemical lasers, which are based on the vibrational population inversion obtained from the reaction $F + H_2 \rightarrow HF$ $(v \leq 3)$ + H.

HTO Infrared Spectrum A Barnes Engineering Co. spectrophotometer cell has been modified for use in determining the ir spectrum of HTO. A coil of 1/8 in. o.d. stainless steel tubing was connected to the cell to allow condensation of the HTO sample from a flowing helium stream. Welded metal bellows valves were attached to the inlet and outlet of the cell to reduce the possibility of HTO leakage from the cell. All joints in the cell were either welded or brazed with the exception of the transmission windows.

The windows are NaCl and are sealed by rubber O-rings. The modified cell is helium leak tight.

The cell loading system was assembled in the configurations shown in Figure 10. The system shown in Figure 10 is a closed flow loop for preparing controlled amounts of HTO for filling the spectrophotometer cell. The system consists of: 1) a tritium gas inlet system with a 25 cc standard volume and pressure transducers for introducing measured quantities of HT/He mixtures into the flow system, 2) a copper oxide bed for converting the HT to HTO, 3) mass flow and moisture meters for gas flow analyses and 4) a metal bellows type pump for circulating the gas stream at rates as high as 50 cm^3 sec^{-1} at 50 torr. The spectrophotometer cell together with its condenser coil can be isolated and removed from the loading system for installation on the spectrophotometer. The system has been assembled, leak checked, and operational tests initiated.

FUTURE PLANS

There are nine major objectives for the next quarter: 1) completion of the CI calculations on the H + H_2O and H + HF exchange reactions; 2) construction and testing of the H_2O/H_2 flow system and reaction cell; 3) assembly and testing of the tunable ir laser; 4) alignment of the tunable ir laser, uv flashlamp and reaction cell; 5) runing the ir laser to the maximum absorption bond in HTO; 6) initiation of feasibility experiments on water detritiation by two-photon ISP; 7) helium leak testing of the ir spectrophotometer cell loading system; 8) a test run of the cell loading system to obtain the ir spectrum of HDO and 9) recording the ir spectrum of HTO.

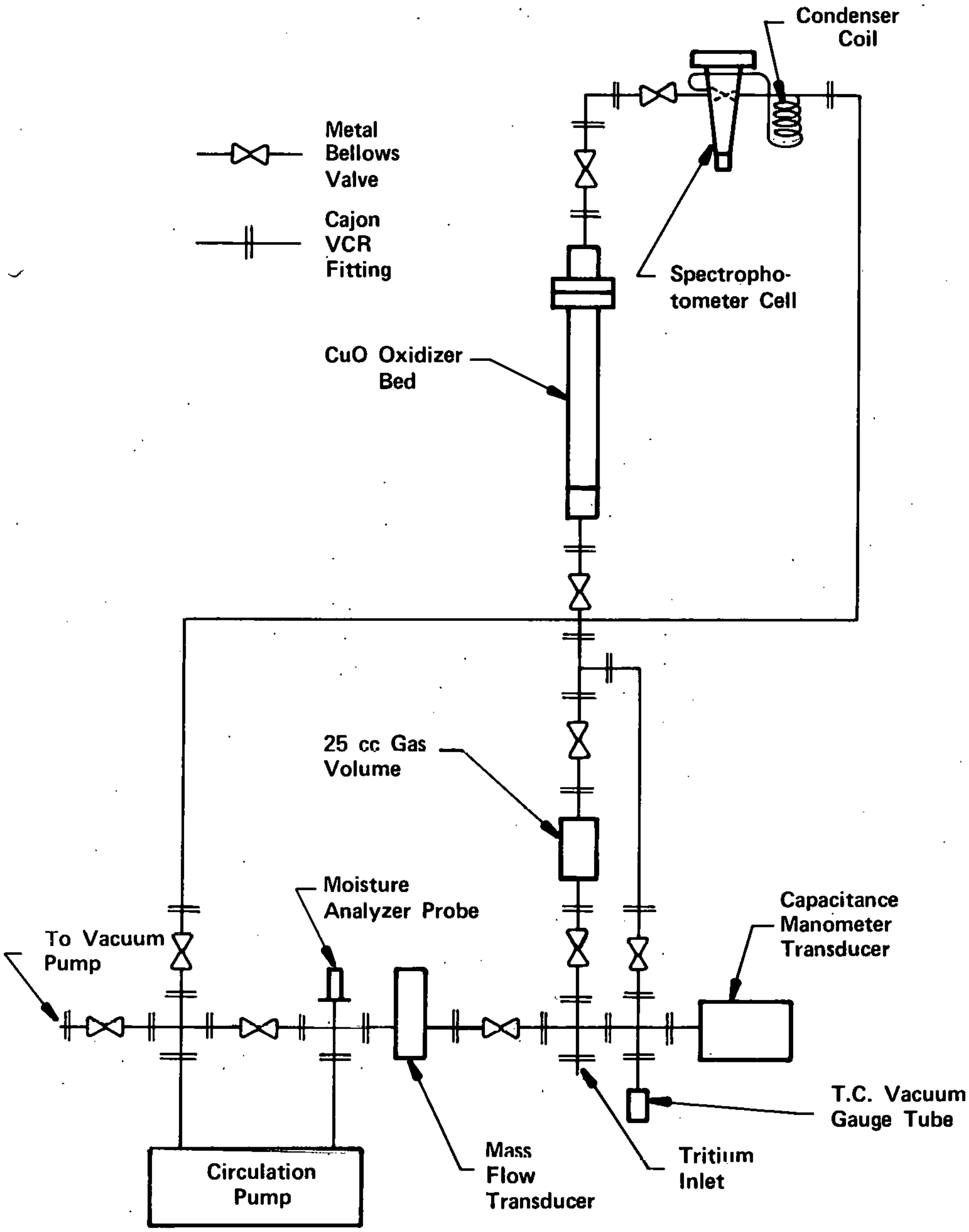


FIGURE 10 - Spectrophotometer cell loading system.

BACKGROUND

Operations involving tritium produce a significant quantity of high and low-level liquid wastes, composed mostly of water, which must be disposed of in a safe manner. In the past, these liquids have been absorbed on solids or diluted to specified levels and buried; or they have been diluted to low enough levels to be discharged as "uncontaminated" water. All of these methods eventually allow tritium to enter the environment. A preferable method would be to decontaminate such wastes (without dilution) to near the natural level before discharge. Demonstrations of the feasibility and development of such decontamination techniques are the goals of this work.

PRIOR WORK

The General Electric UCT-1 regenerative cell was previously operated in the electrolysis mode to decompose HDO for measurement of the H/D separation factor. Since the experimental separation factor was relatively low (~1.6) this work was discontinued.

ACCOMPLISHMENTS

Using a General Electric UCT-1 regenerative cell as the active element, an apparatus to dissociate pure, high-tritium-content water was built.

DISCUSSION

Small quantities of high level tritiated water are being generated for use in a program currently being pursued at Mound Laboratory. Because of the problems involved with disposing of the waste products of this program, consideration is being given to converting the high level water to H_2-T_2 gas mixture via electrolysis. Due to the low quantity (tens of cubic centimeters) and very high tritium content, the General Electric UCT-1 regenerative fuel cell appeared to be a prime candidate. This cell is not only on hand but uses a solid polymer electrolyte which decreases the actual conversion system volume. Accordingly the UTC-1 plumbing has been modified to allow complete processing of small quantities of water. A schematic of the system as modified is shown in Figure 11.

In operation the feed water can be brought into the system by the detachable reservoir or directly through the VCR fitting on top of the "wash water" reservoir valve. The feed water is transferred to the O_2 side of the cell using vacuum and argon pressure appropriately. After electrolysis has taken place several additional volumes of pure H_2O will be electrolyzed in order to flush most of the remaining tritium from the system. The H_2-T_2 gas mixture will be stored in a metal tank (~5 liters) and the O_2 will be pumped to the ERS (Effluent Recovery System). The O_2 reservoir tank is necessary to maintain a pressure differential of <100 psi across the cell membrane (the solid polymer electrolyte) per the manufacturer's specifications.

Control of the amount of water electrolyzed is critical since the cell must not become too dry otherwise the electrolyte membrane will suffer heat damage. The only method presently available for such control is to accurately measure the time and current of electrolysis. From these data the exact quantity of water electrolyzed can be determined.

The maximum current for cell operation is 5 amperes, which corresponds to 0.093 moles or ~1.67 cc of water per hour. Since about 10 cc of wash water will be used to "flush" out the cell, roughly 8 hours continuous running would be required to process 1.67 cc of highly contaminated feed. Only 10 cc of flush water would be required for large amounts of feed so the processing time is not linearly dependent on the quantity of contaminated feed.

The electrolysis cell has been operated satisfactorily (using H_2O) in the system shown in Figure 11. It will be necessary to disassemble the system at the VCR fittings in order to install it in a glovebox for the tritium work. The tritium storage tank and access to the required services will also be inside the glovebox.

FUTURE PLANS

The system shown in Figure 11 will be installed in a glovebox and test runs made on small quantities (1 cc) of highly purified tritiated water.

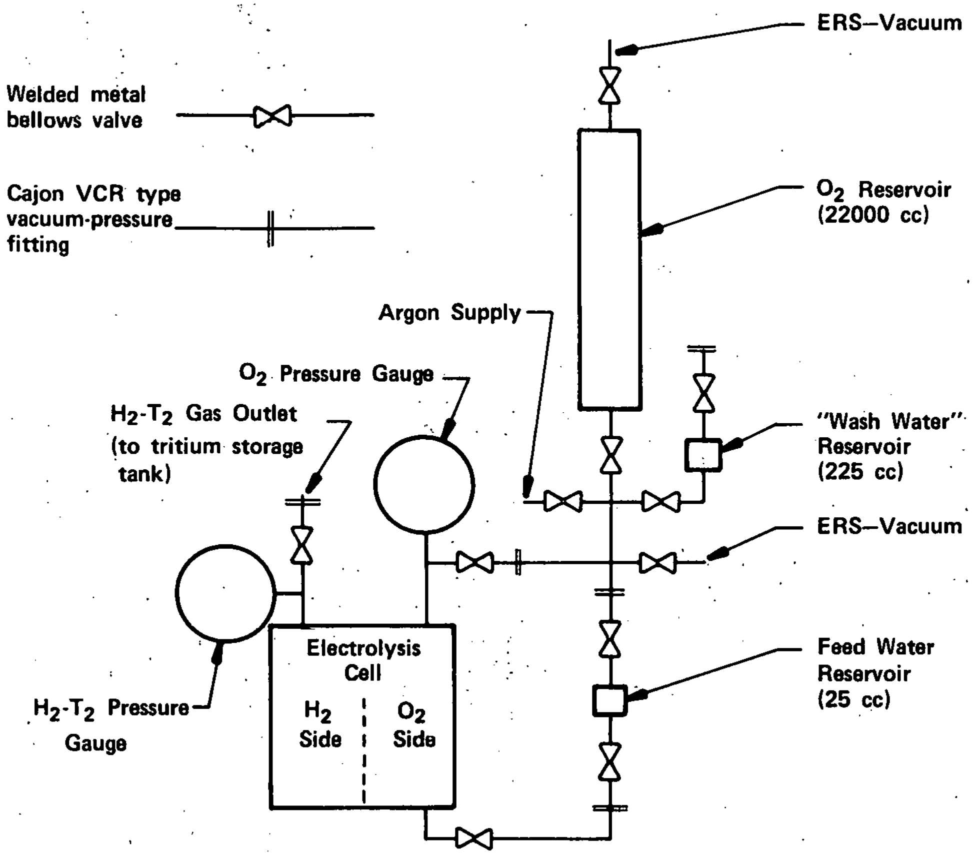


FIGURE 11 - System for high level tritiated water electrolysis.

CATALYTIC EXCHANGE DETRITIATION STUDIES

J. C. Bixel, B. W. Hartzel, and W. K. Park

BACKGROUND

With the exception of tritium, all the radioisotopes produced in the operation of a light water reactor are amenable to some form of chemical or physical separation process for removal from the effluent water streams. The detritiation of these aqueous wastes, however, requires development of isotopic separation processes. Over 100 ideas have been considered for effecting the isotopic separation of tritium from water. Alternative methods have been discussed in a review by Ribnikar and Pupezin.[21] A number of technical and economic feasibility studies have been carried out on possible detritiation schemes - mostly based on experience and data from heavy water (D_2O) separation processes.[24-25]

Many of the basic separation methods used for heavy water production processes are technically feasible for detritiating water. Detritiation, however, requires larger stripping and recovery factors than does heavy water production. To be capable of obtaining the needed high recovery, a feasible detritiation process will require a high isotopic separation factor.

The hydrogen-water chemical exchange process has the required high isotopic separation factor and is uniquely suited to a water feed. In addition, the technical feasibility of hydrogen isotopic enrichment through the exchange between hydrogen and water is not questioned. The process has been employed to produce heavy water on a large scale.[26] The HT/H_2O catalytic exchange process was selected on the basis of high isotopic separation factor and technical feasibility to be the most likely process for development and demonstration of waste water detritiation.

The objectives of this study are:

- Determination of technical and economic factors of HT/H_2O exchange as a possible detritiation process for treating tritium contaminated water from power reactor and fuel reprocessing plant operations.
- Determine suitability of hydrophobic exchange catalysts for use in water detritiation systems, and
- Through pilot scale testing, establish design criteria for detritiation systems capable of meeting the tritium control needs of the U.S. power reactor industry and ERDA site operations.

PRIOR WORK

An apparatus and procedure were developed for measuring reaction rates of HT/H_2O chemical exchange with hydrophobic catalysts. This apparatus will be used to obtain reaction rate data needed for further development of the process.

Preliminary process designs were made for both a dual temperature separation cascade and a countercurrent single column enrichment and stripping scheme.

ACCOMPLISHMENTS

Fabrication and installation of the experimental system were completed, and analytical instruments were integrated into the apparatus. The system was leak checked and operational checks were performed. All electrical hook-ups were traced and verified. The system was loaded with water and helium and operated for three days. Several problems with the basic operation of the system were identified, and corrective actions were initiated.

A literature search is continuing to keep abreast of on-going research and to gather kinetic and thermodynamic data applicable to the HT/H_2O exchange process. A computer program was made operational for calculating concentrations of various molecular species at thermodynamic equilibrium.

A preliminary economic evaluation was made of the HT/H_2O catalytic exchange detritiation stripping process as it might apply to a 5 metric ton/day nuclear fuel reprocessing plant.

DISCUSSION

Work in progress is directed toward development of an improved version of the basic HT/H_2O catalytic exchange process, and demonstration of the separation of tritium for the particular concentrations and types of low level aqueous wastes (LLAW) obtained from light water reactors and fuel reprocessing plants. The process will also apply to the removal of tritium from heavy water (D_2O) used as the moderator and coolant in several research and all U.S. government production reactors.

The improved approach to HT/H_2O catalytic exchange is based on the use of antiwetting, hydrophobic catalysts which permit the chemical exchange reactions between liquid water and gaseous hydrogen in direct contact, thus eliminating problems of catalyst deactivation and the complexity of reactor design normally associated with current catalytic exchange techniques[27-29] involving gas-phase catalysis. Use of hydrophobic catalysts was first reported[30] in relation to studies directed toward an improved heavy water process. The catalyst consists of platinum on an alumina substrate with a coating of semipermeable, water repellent material such as silicone or teflon.

The highest isotopic separation factors for HT/H_2O exchange are obtained at low temperatures due to the nature of the chemical equilibrium,

$$HT + H_2O \rightleftarrows HTO + H_2$$

with a value of the isotopic separation factor of about 6 at 25°C. The processes involving steam-hydrogen reactions in the vapor state require higher temperatures to prevent water condensation and are faced with the resulting lower isotopic separation factors.

The hydrophobic low-temperature mixed-phase system potentially has many advantages over the gas phase system; for example, higher isotopic separation factor, lower energy consumption, higher throughput rate, and simpler equipment.

There are two major alternative applications of the HT/H_2O catalytic exchange process to detritiation of LLAW (low-level aqueous waste). The first alternative is to apply the process to the total waste stream and deplete the tritium to a degree that the resulting detritiated waste stream may be dispersed to the environment. This alternative has been referred to by Ribnikar and Pupezin[21] as the <u>stripping</u> scheme. The second alternative application would produce a similar enriched tritium stream, but the water is detritiated to a lesser degree and returned to the reactor (or plant), thus maintaining a desired steady tritium concentration in accord with applicable regulations for in-plant exposure of operating personnel. Ribnikar and Pupezin[21] have called this alternative the <u>recycling</u> scheme. Of course, a wide spectrum of options exist within either scheme when selecting a design basis for the detritiation system. For example, regulatory factors and in-plant parameters such as LLAW throughput quantity and tritium concentration levels could affect the size of the system and the necessary degree of separation and enrichment of the tritium.

The throughput required for removal of tritium from LLAW could vary over a wide range depending on the application. Likewise the degree of separation and recovery required could vary considerably. For example, the internal flow of water in a PWR cooling water recycling detritiation application could be on the order of 10-50 liters/hr with an overall separation factor requirement of 100 to 1000. In comparison, application of the stripping scheme to the flow of LLAW from a fuel reprocessing plant could require a throughput of 500-2500 liters/hr with an overall separation requirement of 10^{11} to 10^{13}. Since the costs associated with detritiation of water increase with increased throughput and also increase with increased overall separation factor, the application of the stripping scheme to the fuel reprocessing plant would be the least favorable from a cost viewpoint, as both throughput and separation requirement are a maximum for the fuel reprocessing LLAW stripping application.

The fuel reprocessing plant application of the waste water detritiation process was chosen for economic evaluation on the basis of being the most stringent, and most costly, application in the fuel cycle. Preliminary economics of this scheme as it might apply to the Allied-Gulf Nuclear Services, Barnwell, S.C., fuel reprocessing plant are discussed briefly below.

PRELIMINARY ECONOMICS

A preliminary economic evaluation was made of the HT/H_2O catalytic exchange detritiation stripping process as it might apply to the Allied-Gulf Nuclear Services (AGNS), Barnwell, S.C., 5 metric ton/day nuclear fuel reprocessing plant. A schematic of the stripping process is given in Figure 12. This processing scheme would detritiate approximately 500 liters/hr of LLAW containing 0.2 Ci/liter of tritium to an extremely stringent degree. Of the tritium contained in the aqueous waste stream (750,000 Ci/yr) 749,999.925 Ci/yr would be concentrated in a quantity of water which would be only 47.3 cc/hr, or the equivalent quantity of gaseous hydrogen isotopic mixture - 5900 cc/hr of gas. The remainder of the 500 liters/hr feed stream would be detritiated to such a degree that it would be below the newly proposed EPA drinking water standard of 20,000 pCi/liter.[31]

Operation cost estimates are given in Table 7. The operating cost of $1,180,000 per year may be compared to the projected cost of biological damage due to released tritium from a 5 metric ton/day reprocessing plant. Using the recent tentative

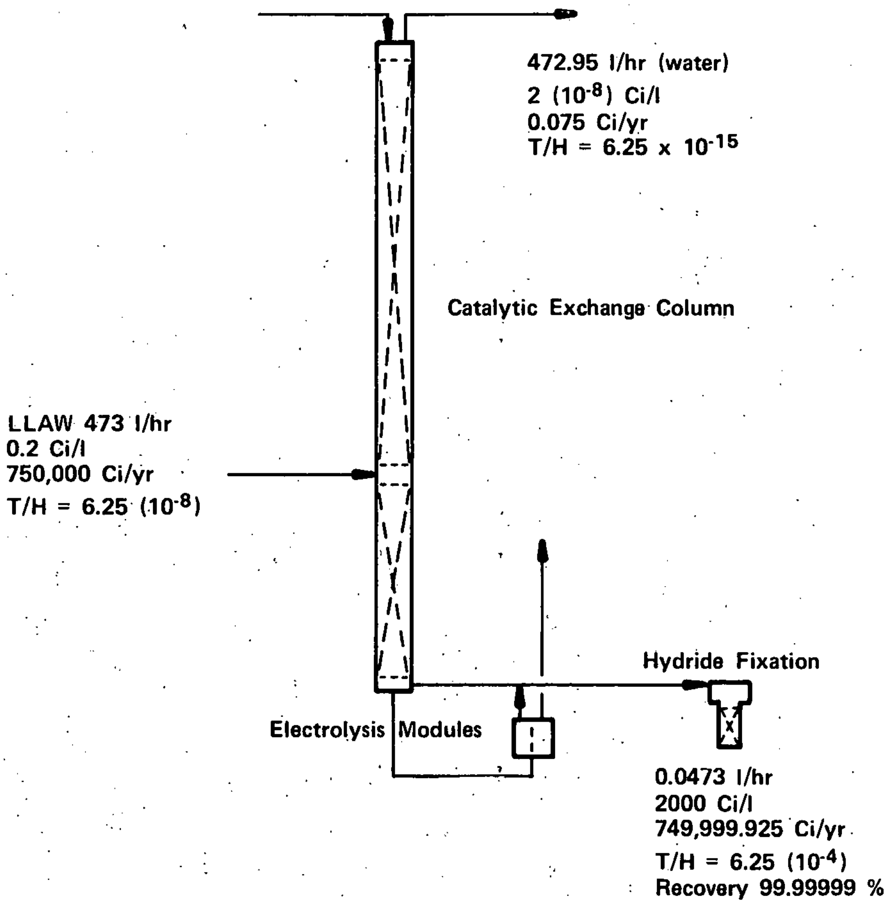


FIGURE 12 - AGNS LLAW detritiation.

assignment of \$1000 per total-body man-rem by the NRC,[32] and the whole body dose for tritium from a 5 metric ton/day fuel reprocessing plant of 3,700 man-rem per year, as projected by the EPA;[33] a cost for biological damage due to release of tritium of \$3,700,000 per year is obtained. Thus the estimated operating cost of \$1,180,000 per year is well below the cost-benefit balance point. Presumably, application of the process in a recycling scheme or other less stringent applications than chosen for the above analysis, would be even more favorable from a cost viewpoint.

On the basis of the above preliminary economic evaluation, the HT/H_2O catalytic exchange detritiation process is judged worthy of further research and development effort.

EXPERIMENTAL

A bench-scale experimental apparatus was built for operation in a controlled glovebox[34,35,36] under recirculating helium atmosphere.

The experimental system is comprised of a low-temperature (20-70°C) reactor (3.8 cm i.d. x 28 cm), a high-temperature (100-500°C) reactor (3.8 cm i.d. x 28 cm), support equipment, and analytical instruments. The low-temperature reactor packed with hydrophobic platinum-coated catalyst (0.48 cm dia.) was designed for a liquid gas countercurrent flow, and tritium is enriched in the liquid water (i.e., $H_2O_{(l)} + HT \text{ cold} \rightleftarrows \text{hot } HTO_{(l)} + H_2$), and the high-temperature reactor with regular nonhydrophobic platinum-coated catalyst (0.32 cm dia. x 0.32 cm) was built for a gas-gas cocurrent flow, and the tritium is depleted from the water vapor (i.e., $H_2O_{(g)} + HT \text{ cold} \rightleftarrows \text{hot } HTO_{(g)} + H_2$). Hence, with these two reactors combined in a system consisting of an evaporator, condenser, phase separator, pumps, etc., a complete closed-loop experimental apparatus involving gas-phase and liquid-phase tritium exchange reactions is obtained. This apparatus is capable of continuous recycling of the enriched and depleted water and hydrogen streams. Operating parameters, such as flow rate and temperature, may be adjusted and steady state conditions may be obtained. Reaction rates are then measured.

Table 7

OPERATION COST ESTIMATE AGNS LLAW DETRITIATION

Detritiated Water - 3.75 (10^6) l/yr
750,000 Ci/yr @ 0.2 Ci/liter
On Stream 330 days/yr
Recovered Tritium 749,999.925 Ci/yr
375 liter/yr @ 2000 Ci/liter

Unit Investment:	
On Site	\$ 3,817,000
Off Site	1,336,000
Total	5,153,000

Item	Quantity/yr	Cost/unit	Cost/yr	Cost/Ci
Variable Costs:				
Cooling H_2O	60,300 kgal	\$ 0.02	\$ 1,000	
Electricity	4.17 (10^7) kWh	0.010	414,000	
Catalyst	950 lb	20.00	19,000	
Total Variable Costs			\$434,000	\$ 0.578
Fixed Costs:				
Direct Labor 8,760 man hr @ \$6.00			\$ 53,000	
Supervision @ 20% DL			10,000	
Maintenance @ 4% PI			153,000	
Supplies @ 10% Maintenance			15,000	
Payroll Burden @ 30% DL			19,000	
Taxes and Insurance @ 3% PI			114,000	
Depreciation 10% Straight Line			382,000	
Total Fixed Costs			\$ 746,000	\$ 0.995
Total Operating Costs			\$1,180,000	\$ 1.573

The experimental apparatus assembly, before installation in the glovebox, is shown in Figure 13.

Initial experiments will be conducted with tritium levels ranging from 0.1 to 10 $\mu Ci/cm^3$, but higher level experiments will be conducted in the future. Tritium levels in the hydrogen steams are monitored by two on-line ion chambers (Overhoff and Associates), and the tritium levels in the water are continuously monitored by two flow-through liquid scintillation counter cells (Packard).

FUTURE PLANS

Experiments will be conducted, and kinetic and thermodynamic performance data will be obtained and evaluated. More detailed economic feasibility studies will then be made. If the catalyst evaluation tests are successful, a multistage pilot detritiation system will be evaluated before proceeding to a field demonstration.

SHIPPING CONTAINER DEVELOPMENT FOR TRITIATED LIQUID WASTE

T. B. Rhinehammer

BACKGROUND

The constraints on the shipment of tritiated liquid wastes are becoming increasingly severe whether for disposal by burial or for tritium recovery and recycle. Containers and methods of packaging are more critical for shipping liquids since the contents are easily lost to the atmosphere if the primary package is ruptured allowing the contents to be exposed to the air. By nature of its physical form (HTO), tritium loss can also be extremely high in case of fire. Hence, multiple containment and fixation of the tritiated liquid waste into an inert form appear to be mandatory needs in achieving absolute containment in any hypothetical or real shipping accident.

In past years tritium waste generation has been totally within ERDA organizations and relatively small in quantity with the waste receiving special handling and disposal. Due to the potentially large quantities of liquid wastes from reactors, fuel reprocessing plants and CTR experiments through the 1980's and the associated risk of population exposure when shipping high level HTO wastes, a shipping package must be developed which will withstand the most severe accident conditions. Initially, it is conceived that not only primary containment but secondary and perhaps tertiary containment may be necessary to achieve the required safety. A study, therefore, is necessary to provide the technical information and limits pertinent to container requirements, development, compatibility, construction, use and safety.

PRIOR WORK

A small in-house study was started in 1975 to develop a small shipping package for intersite shipment of high-level tritiated water wastes. This work was initiated internally as a supplement to Mound Laboratory's basic assignment of tritium recovery from solid and gaseous wastes. A reusable shipping container for tritium recovery and recycle, rather than burial, was initially chosen for development because of the potential availability of high-level wastes and the economic feasibility of recycle. CTR experiments and new ERDA tritium facilities are expected to generate waste requiring disposal. High-level waste will be available for tritium recovery as a result of the water detritiation-enrichment technology now under study and development at Mound for application to low level waste from PWR's, HWR's and fuel reprocessing plants.

Three ERDA contractors and one commercial tritium user have expressed an interest in using a standardized approved shipping container for disposal of their tritiated water waste and are designing their detritiation or tritium recovery systems to be compatible with the container currently under development. The main problem foreseen at this time is capacity of the container to provide the versatility desired. This indicates the need, perhaps, for a family of approved containers. For recovery and recycle, the ideal containers must be economical, reusable, comply with ERDA-DOT shipping regulations, standardized in concept of use, compatible with ERDA detritiation systems and multi-capacity.

Funding was made available in the second quarter of FY-1976 for continued development of this container and also for work on the determination of requirements and the development of containers for shipment and burial of tritiated liquid wastes.

ACCOMPLISHMENTS

Design constraints for a reusable primary container included: 1) weight not to exceed 60 lbs; 2) sized for use in an

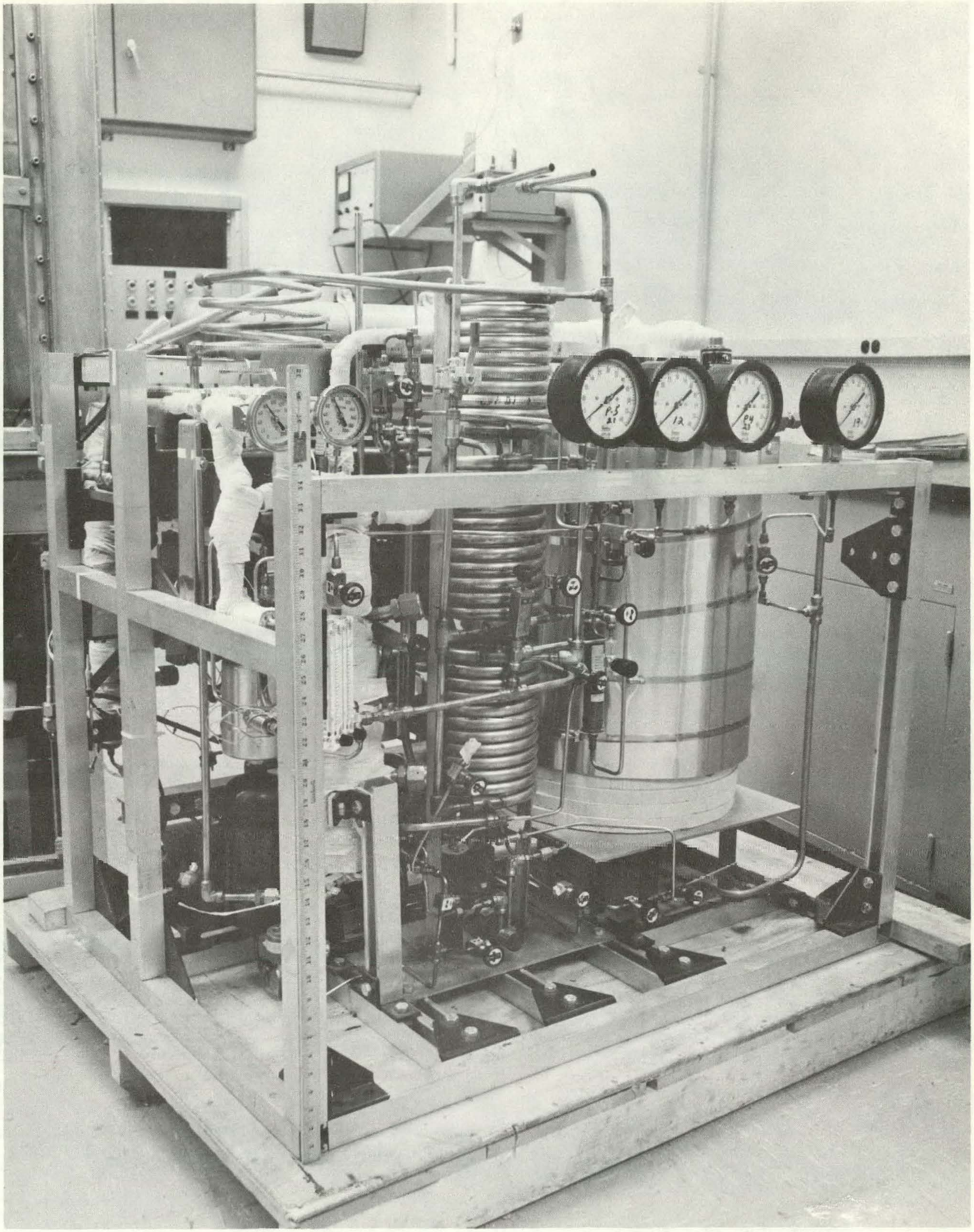


FIGURE 13 - Experimental apparatus assembly.

existing approved ERDA-DOT outer shipping container; 3) sized to be accommodated in the largest calorimeter feasible for tritium measurements; 4) not subject to corrosion over the pH range of 4-11; 5) contain suitable adsorbent which would permit shipment of the water as a "solid", repeated regeneration and indefinite use; 6) permit being heated to 600°F for regeneration of the adsorbent and recovery of the tritiated water, 7) be easily decontaminated; 8) provide double containment in all openings, valves, etc. to the primary container; and 9) satisfy requirements of the safety analyses review for packaging.

A container, meeting most of these requirements, has been designed and developed for use with the AL-M1 secondary shipping container, a specially constructed 55-gal steel drum which is a form of containment approved by ERDA-ALO and DOT for shipment of plutonium-239 and uranium-235. This free-standing container, fabricated of 316L stainless steel to obtain maximum corrosion resistance, weighs less than 45 lbs and can be accommodated in a calorimeter for the purpose of tritium accountability. The calorimeter to be used for this container (30 in. long x 7 in. diam.) was recently constructed and is the largest diameter, air calorimeter built to date. The container as shown in Figure 14 is fabricated from standard off-the-shelf components e.g., standard Schedule 10 stainless steel pipe and pipe caps (preformed dome end sections), to assure economy of construction and material availability. The top of the container is fitted with two standard bellows valves which serve as inlet and outlet ports for loading and emptying the container. Each valve terminates in a Cajon fitting and also in a filter within the container. In this prototype an extra Cajon-sealed port was provided for filling the container with adsorbent. A stainless steel pressure gage (-30 in. Hg to 100 psi) is also provided for monitoring the pressure buildup during storage and shipment. The bourdon type pressure gage is the most likely point of leakage since the gage is vulnerable to mechanical damage and rupture from corrosion and pressure. As an alternative, an economical 0-150 psia all-welded, 316 s.s. pressure transducer terminating in a Cajon fitting has been found which will provide improved primary integrity as well as secondary containment. A thermowell through the top end cap and terminating in the center of the container is provided so that the temperature may be controlled during regeneration of the adsorbent. An O-ring sealed cap attaches to the top of the container to provide secondary containment and physical protection of the valves and gage. Two quick disconnect fittings in the top of the cap permit the space within the cap around the valves to be monitored for tritium leakage before the cap is removed.

The finished container is 23 in. in length and 6 3/4 in. in diameter. The size for this initial container was controlled by two factors: the maximum calorimeter diameter available (7 in. i.d.) and the inner height of the previous ERDA-DOT approved outer shipping package. The active volume of the container is about 10 liters. Up to 2 kg of tritiated water contained on Type 4A molecular sieves to preclude the presence of free liquid can be shipped in the container. The container may be used indefinitely because water can be removed by regenerating the adsorbent to very low tritium and dew-point background with heat and vacuum. Use of the container merely involves connection of an effluent removal or detritiation system to the inlet and outlet valves of the container by means of Cajon fittings.

Engineering drawings have now been completed with the exception of changes in which the pressure gage will be replaced with a transducer.

FUTURE PLANS

General guidelines on the usage of this container must now be established. The pressure drop (ΔP) across the container as a function of gas flow rates and water loading, heat of hydration, rise in temperature with varying loading rates, and the effect of loading rates on the effluent dewpoint and capacity will be determined. These data are necessary for those applications (contractors) where the container is to be connected directly in the generation loop of detritiation or recovery systems. Many of these parameters have already been requested by potential users. The feasibility and problems of direct transfer of waste water consensate to the shipping container will also be evaluated.

A safety analysis test and review of the primary waste container assembled in the AL-M1 outer shipping container will be done during the next two quarters. These data will become a supplement to the existing safety analysis report for packaging (SARP) originally prepared for the AL-M1 nuclear shipping package (MLM-1981, Nov. 30, 1972).

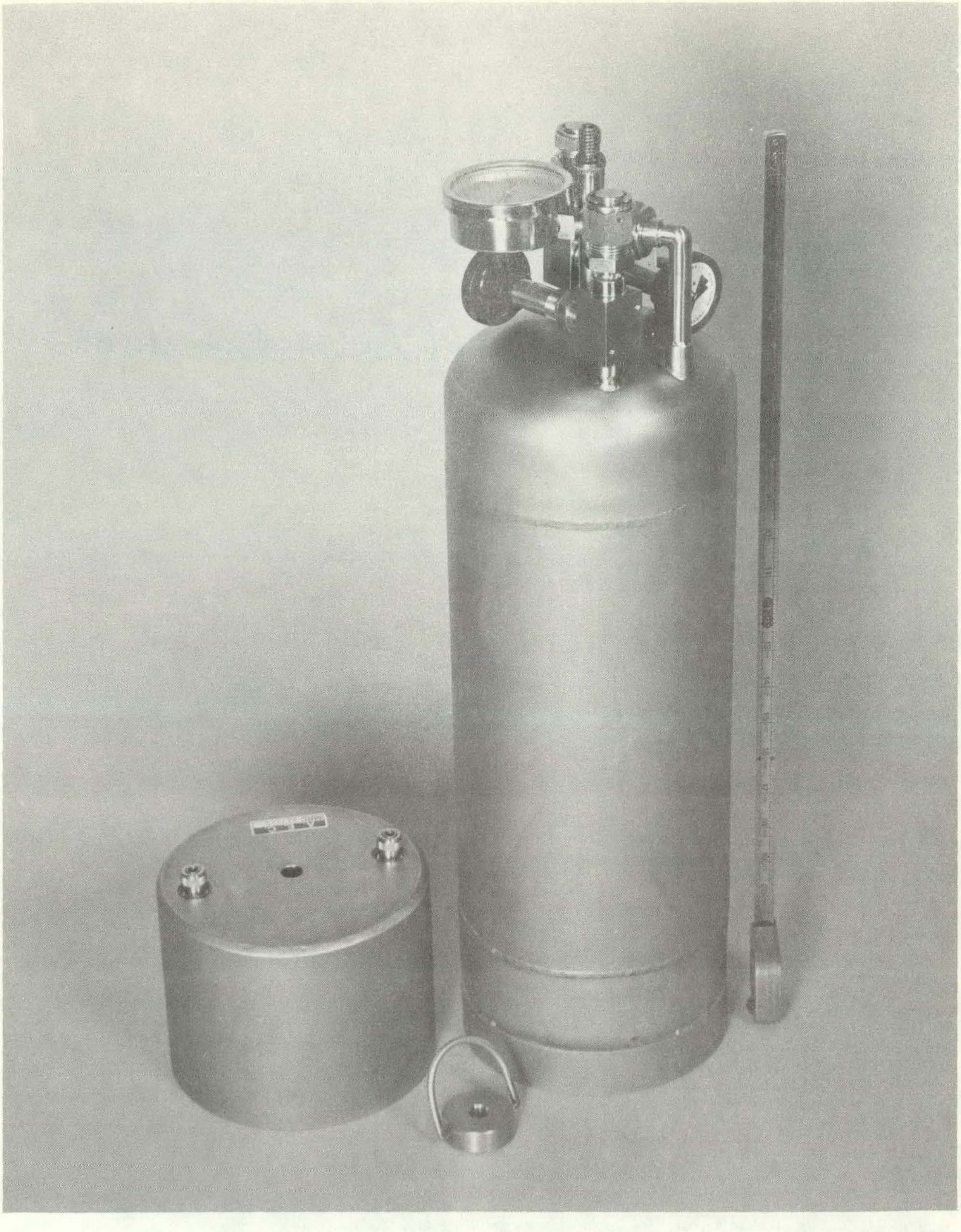


FIGURE 14 - Tritiated water shipping container.

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