

ATTACHMENT A PHYSICAL AND CHEMICAL PROPERTIES OF TRITIUM

(Note: The bulk of the information presented in this attachment was adapted from Sections 2.10.1 through 2.10.6 of the U.S. Department of Energy's "Design Considerations" (DOE, 1999). Although some of the information may appear to be somewhat dated, the basic concepts behind the information have not changed since that time.¹ See also the information presented in Attachment B.)

A.1 Sources of Tritium

Tritium is the lightest of the naturally occurring radioactive nuclides. Tritium is produced in the upper atmosphere as a result of cascade reactions between incoming cosmic rays and elemental nitrogen. In its simplest form, this type of reaction can be written as follows:



Tritium is also produced in the sun as a subset of the proton-proton chain of fusion reactions. Although a steady stream of the tritium near the surface of the sun is ejected out into space (along with many other types of particles) on the solar wind, much larger streams are ejected out into space during solar flares and prominences. Being much more energetic than its solar wind counterpart, tritium produced in this manner is injected directly into the earth's upper atmosphere as the earth moves along in its orbit. Regardless of the method of introduction, however, estimates suggest that the natural production rate for tritium is about 4×10^6 Ci/yr, which, in turn, results in a steady-state, natural-production inventory of about 7×10^7 Ci.

Tritium is also introduced into the environment through a number of manmade sources. The largest of these, atmospheric nuclear testing, added approximately 8×10^9 Ci to the environment between 1945 and 1975. Because the half-life of tritium is relatively short (i.e., about 12.3 years—see Section A.3.1, below), much of the tritium produced in this manner has long since decayed. However, tritium introduced into the environment as a result of atmospheric testing increased the natural background levels by more than two orders of magnitude, and, in spite of its relatively short half-life, the natural background levels of tritium in the environment will not return to normal until sometime between the years 2020 and 2030.

Tritium levels in the environment cannot truly return to background levels, however, because of a number of additional manmade sources. Tritium is also produced as a ternary fission product, within the fuel rods of nuclear reactors, at a rate of $1\text{--}2 \times 10^4$ Ci/1,000 megawatts electric. (Although much of the tritium produced in this manner remains trapped within the matrix of the fuel rods, estimates suggest that recovery of this tritium could reach levels of 1×10^6 Ci/yr.) Typical light-water and heavy-water moderated reactors produce another 500–1,000 to 1×10^6 Ci/yr, respectively, for each 1,000 megawatts of electrical power. Commercial producers of radioluminescent and neutron-generator devices also release about 1×10^6 Ci/yr. Thus, tritium facilities operate within a background of tritium from a variety of sources.

¹ Additional Note: Because the bulk of the information presented in this attachment is presented in a paraphrased format, it is suggested that the reader refer directly to DOE 1999 for additional information, which does include all the appropriate references to the original citations.

A.2 The Relative Abundance of Tritium

The isotopes of hydrogen have long been recognized as being special—so special, in fact, that each has been given its own chemical name and symbol. Protium, for example, is the name given to the hydrogen isotope of mass-1, and the chemical symbol for protium is H. Deuterium is the name given to the hydrogen isotope of mass-2; the chemical symbol for deuterium is D. Tritium is the name given to the hydrogen isotope of mass-3. Its chemical symbol is T.

Protium is by far the most abundant of the hydrogen isotopes. Deuterium follows next with a relative abundance of about 1 atom of deuterium for every 6,600 atoms of protium; that is, the D-to H-ratio is about 1:6,600. Tritium is the least common hydrogen isotope. The relative abundance of naturally occurring tritium (i.e., tritium produced in the upper atmosphere and tritium injected directly by the sun) has been estimated to be on the order of 1 tritium atom for every 10^{18} protium atoms. The introduction of manmade tritium into the environment, particularly as a result of atmospheric testing, has raised this level approximately one order of magnitude so that the ambient T-to-H ratio is now approximately $1:10^{17}$.

The names, commonly used chemical and nuclear symbols, atomic masses, and relative natural abundances of the hydrogen isotopes are summarized in Table A-1.

Table A-1 The Isotopes of Hydrogen

Name	Chemical symbol	Nuclear symbol	Atomic mass	Natural abundance (%)	Natural abundance (x:H ratio)
Protium	H	${}_1^1\text{H}$	1.007 825 03	99.985%	1:1
Deuterium	D	${}_1^2\text{H}$	2.014 101 78	0.015%	1:6,600
Tritium	T	${}_1^3\text{H}$	3.016 049 26 ^a	Very Low	$1:10^{17}$

^a Calculated.

A.3 Radioactive Decay of Tritium

A.3.1 Generic

As the lightest of the pure beta emitters, tritium decays with the emission of a low-energy beta particle and an anti-neutrino, as follows:



Tritium decays with a half-life of 12.32 years. The specific activity of tritium is approximately 9,619 Ci/gram, and/or 1.040×10^4 grams per Ci. In addition, the activity density (i.e., the specific activity per-unit volume) for tritium gas (T_2) is 2.589 curies per cubic centimeter (Ci/cm^3) under standard temperature and pressure (STP) conditions (i.e., 1 atmosphere of pressure at 0 degrees Celsius ($^{\circ}\text{C}$)), and/or $2.372 \text{ Ci}/\text{cm}^3$ at 25°C . It can also be shown that the former value translates to 58,023 curies per gram-mole and 29,012 curies per gram-atom, under STP conditions.

A.3.2 Beta Emissions

Beta particles interact with matter by colliding with bound electrons in the surrounding medium. In each collision, the beta particle loses energy as electrons are stripped from molecular fragments (ionization) or promoted to an excited state (excitation). The beta particle also loses energy by emitting photons (bremsstrahlung radiation), as it is deflected by the coulomb fields of nuclei. Because the rate of energy loss per unit path length (linear energy transfer) increases as the velocity of the beta particle slows, a distinct maximum range can be associated with beta particles of known initial energy.

The beta decay energy spectrum for tritium is shown below in Figure A-1. The maximum energy of the tritium beta is 18.591 ± 0.059 keV. The average energy is 5.685 ± 0.008 keV. The maximum range² of the tritium beta is 0.58 milligrams per square centimeter (mg/cm^2).

The absorption of energy from beta particles that emanate from a point source of tritium has been shown to occur nearly exponentially with distance. This is a result of the shape of the beta spectrum as it is subdivided into ranges that correspond with subgroups of initial kinetic energies. As a consequence, the fraction of energy absorbed, F , can be expressed as shown in Equation A.3:

$$F = 1 - e^{-(\mu/\rho)(\rho)(x)} \quad (\text{A.3})$$

where μ/ρ is the mass attenuation coefficient of the surrounding material, ρ is the density of the surrounding material, and x is the thickness of the surrounding material. For incremental energy absorption calculations, Equation A.3 can be restated as follows:

$$F = 1 - e^{-\mu x} \quad (\text{A.3a})$$

where μ (i.e., the linear attenuation coefficient) is the product of the mass attenuation coefficient (μ/ρ) and the density (ρ), and x is the incremental thickness of choice. In gases at 25 °C, at atmospheric pressure, for example, the linear attenuation coefficients for the gases hydrogen (H_2), nitrogen (N_2), and argon (Ar), are 1.81 per centimeter (cm^{-1}), 11.0 cm^{-1} , and 12.9 cm^{-1} , respectively. A 5-millimeter thickness of air will absorb 99.6 percent of tritium betas. A comparable thickness of hydrogen (or tritium) gas will absorb only 60 percent of the tritium betas.

Absorption coefficients for other media can be estimated by applying correction factors to the relative stopping power (the scattering probability) of the material of interest. For the most part, these will be directly proportional to ratios of electron densities. Examples of tritium beta ranges are shown below in Table A-2. The values shown for tritium gas and for air are stated as STP values.

² To be technically correct, the term "range" should have the units of distance. In many cases, however, it is more convenient to express the "maximum range" of a particle in terms of the mass per unit area of the absorber needed to stop the particle (with units of mg/cm^2), which is equal to the product of the absorber's density (in units of mg/cm^3) An advantage of expressing ranges in this way is that, as a practical matter, the masses and areas of thin foils, which are often used in range experiments, are easier to measure than their thicknesses.

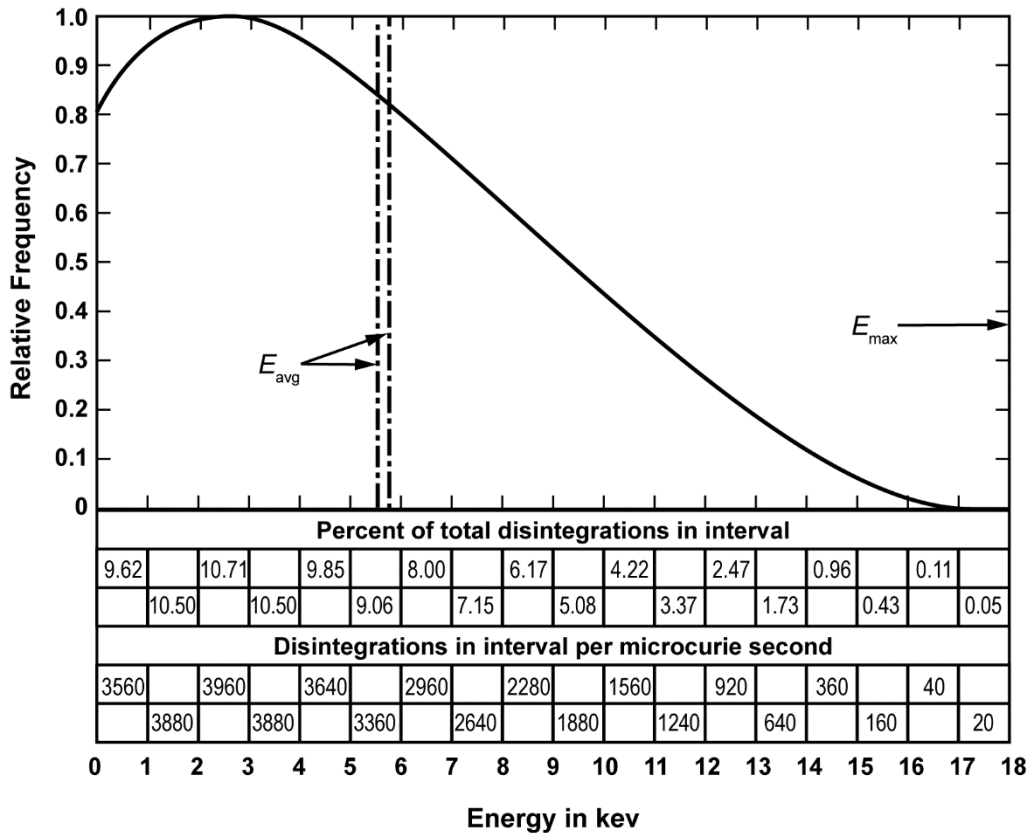


Figure A-1 Tritium Beta-Decay Energy Spectrum
Table A-2 Approximate Ranges of Tritium Betas

Material	Beta	Range
Tritium gas	Average	0.26 cm
Tritium gas	Maximum	3.2 cm
Air	Average	0.04 cm
Water (liquid)	Average	0.42 μ m
Water (liquid)	Maximum	5.2 μ m
Stainless Steel	Average	0.06 μ m

A.3.3 Photon Emissions

No nuclear electromagnetic emissions (gamma emissions) are involved in the decay scheme for tritium, although it is worth noting that tritium does produce bremsstrahlung (braking radiation) as its beta particles are decelerated through interactions with nearby matter. For purposes of this document, however, the production of tritium bremsstrahlung radiation can be ignored.

A.4 The Chemical Properties of Tritium

A.4.1 Generic

Although the chemical properties of tritium have been described in great detail, three distinct types of chemical reactions, and one underlying principle in particular, are worth noting here. The reaction types are solubility reactions, exchange reactions, and radiolysis reactions. The

underlying principle is Le Châtelier's Principle. An overview of these types of reactions and of Le Châtelier's Principle is presented below.

A.4.2 Solubility Reactions

Elemental hydrogen, regardless of its molecular form (i.e., H₂, hydrogen deuteride (HD), deuterium gas (D₂), HT, deuterium tritium (DT), and/or T₂), can be expected to be soluble, to some extent, in virtually all materials. On the atomic or molecular scale, hydrogen-like atoms, diatomic hydrogen-like species, or larger, hydrogen-like-bearing molecules tend to dissolve interstitially (i.e., they diffuse into the crystalline structure, locating themselves inside the normal lattice work of the internal structure). Schematically, such reactions can easily be described in terms of the generic reactions shown in Equations A.4a, A.4b, and A.4c:



Theoretically, however, the underlying mechanics are much more complex. For example, of the generic reactions shown above, none are shown as being reversible. From a chemical perspective, none of these reactions is technically correct because, in most dissolution reactions, the solute that goes in can be expected to be the same solute that comes out. From an operational standpoint, however, experience has shown that, regardless of the tritiated compound that enters into the reaction, an HTC (i.e., a tritiated water vapor) component can be expected to come out. Presumably, this is due to catalytic effects and/or exchange effects that derive from the outward migration of the tritiated species through the molecular layers of water vapor that are bound to the downstream surface of the material.

A.4.3 Exchange Reactions

Driven primarily by isotope effects, exchange reactions involving tritium can be expected to occur at a relatively rapid pace. Moreover, the speed at which reactions of this type can occur can be further enhanced by the addition of energy from radioactive decay. For tritium, therefore, reactions similar to those shown in Equations A.5 and A.6 can be expected, and they can be expected to reach equilibrium in time frames that range from seconds to hours:



Equation A.5 describes the preferential form of tritium, as it exists in nature, in the earth's upper atmosphere. Equation A.6 describes the preferential form of tritium, as it exists in nature, in the earth's lower atmosphere (i.e., in a terrestrial environment).

Equation A.6 is particularly important because it describes the formation of tritiated water vapor (i.e., HTO) without the involvement of free oxygen (i.e., with no free oxygen gas (O₂)). A comparable reaction that would involve free oxygen would take the form of a classic inorganic chemical reaction, such as shown in Equation A.7:



But, because a classic inorganic chemical reaction like that depicted in Equation A.7 can be expected to reach equilibrium in a time frame that ranges from many hours to several days under the conditions normally found in nature, classic inorganic chemical reactions of this type are not necessary for this discussion.

A.4.4 Radiolysis Reactions

It was noted previously in Section A.3.2 that the range of the tritium beta is very short. As a consequence, it follows that virtually all the energy involved in tritium beta decay will be deposited in the immediate vicinity of the atoms undergoing decay. When the medium surrounding the decaying atoms is tritium gas, tritiated water, or tritiated water vapor in equilibrium with its isotopic counterparts, reactions such as those presented in Equations A.8 and A.9 below can be expected to dominate. When the medium surrounding the decaying atoms is not a medium that would normally be expected to contain tritium, however, an entire spectrum of radiolysis reactions can be expected to occur.

For typical, day-to-day operations, the most common type of radiolysis reactions in the tritium community can be expected to occur at the interface between the air above a tritium-contaminated surface and the tritium-contaminated surface itself. For these types of reactions, some of the energy involved in the tritium-decay process can be expected to convert the nitrogen and oxygen components in the air immediately above the surface (i.e., the individual N_2 and O_2 components in the air) into the basic generic oxides of nitrogen, such as nitric oxide, nitrous oxide, and nitrogen peroxide (i.e., NO , N_2O , and NO_2 , respectively). As the energy deposition process continues, it can also be expected that these simpler oxides will be converted into more complex oxides, such as nitrites and nitrates (i.e., NO_2s and NO_3s , respectively). Because all nitrite and nitrate compounds are readily soluble in water (and/or water vapor), it can further be expected that a relatively large percentage of the available nitrites and nitrates in the overpressure gases will be adsorbed into the monomolecular layers of water vapor that are actually part of the surface (see Section A.6, below). With the available nitrites and nitrates now an integral part of the monomolecular layers of water vapor, it can finally be expected that the most common type of radiolysis-driven reactions should result in the gradual, low-level buildup of tritiated nitrous and nitric acids on the surfaces of most tritium-contaminated materials.

For the most part, this particular type of reaction sequence does not normally present itself as a problem in day-to-day tritium operations, because (i) the overall production efficiency for these types of reactions is relatively low, and (ii) the materials used for the construction of most tritium-handling systems are not susceptible to attack by nitrous and/or nitric acids. By contrast, however, it should be noted that other types of radiolysis-driven reactions can be expected to occur with tritium in the presence of compounds containing chlorides and/or fluorides, and that these can easily lead to chloride/fluoride-induced stress-corrosion cracking (see, for example, the discussion on materials compatibility issues in Section A.7, below).

One additional point that is worth noting about radiolysis-driven reactions is that their long-term potential for causing damage should not be underestimated. Although the overall production efficiency for these types of reactions might be expected to be relatively low, the generation of products from these types of reactions can, on the other hand, be expected to occur continuously over relatively long periods of time (e.g., 10–20 years, or more). As a consequence, the long-term effects from these types of reactions can be difficult to predict, especially because very little is known about the long-term, synergistic effects of low-level, tritium microchemistry (see Sections A.7 and A.8, below).

A.5 Le Châtelier's Principle

A chemical restatement of Newton's Third Law of Motion, Le Châtelier's Principle states that when a system at equilibrium is subjected to a perturbation, the response will be such that the system eliminates the perturbation by establishing a new equilibrium. When applied to situations like those depicted in Equations A.5 and A.6 above, Le Châtelier's Principle states that, when the background tritium levels are increased in nature (by atmospheric testing, for example), the reactions will be shifted to the right in order to adjust to the new equilibrium conditions by readjusting to the naturally occurring isotopic ratios. Thus, we get reactions of the type shown in Equations A.5a and A.6a:



The inverse situation also applies in that, when the background tritium levels are decreased in nature, the reactions will be shifted back to the left, by again readjusting to the naturally occurring isotopic ratios, as shown in Equations A.5b and A.6b:

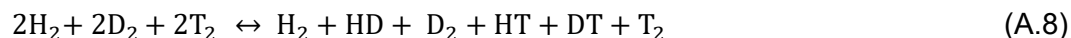


By itself, Le Châtelier's Principle is a very powerful tool. When applied singularly, or to a sequential set of reactions like those depicted in Equations A.5, A.5a, and A.5b or A.6, A.6a, and A.6b, Le Châtelier's Principle shows that exchange reactions of the types depicted above tend to behave as springs, constantly flexing back and forth, constantly readjusting to changing energy requirements, in a constantly changing attempt to react to a new set of equilibrium conditions.

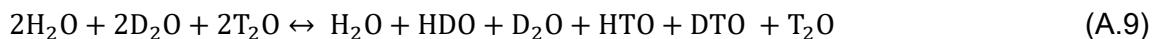
Since elemental hydrogen, regardless of its molecular form (i.e., H_2 , HD, D_2 , HT, DT, and/or T_2), can be expected to dissolve to some extent in virtually all materials, Le Châtelier's Principle can be expected to work equally as well on solubility reactions, like those shown above in the generic Equations A.4a, A.4b, and A.4c. These will be covered in more detail in Section A.6.4, below.

A.6 Modeling the Behavior of Tritium

Any model of the behavior of tritium starts with the assumption that all three hydrogen isotopes coexist in nature, in equilibrium with each other, in the nominal isotopic ratios described above in Table A-1. To this is added the consequences Le Châtelier's Principle predicted. From both, we get the fundamental relationship shown in Equation A.8:



In a terrestrial environment, virtually all the tritium that exists in nature exists as water or water vapor. Correcting this situation for the natural conversion to water and/or water vapor, Equation A.8 becomes Equation A.9:



It can also be assumed that the surfaces of all terrestrially bound objects are coated with a series of monomolecular layers of water vapor. In the final step, it can be assumed that the innermost layers of water vapor are very tightly bound to the actual surface, that the intermediate layers of water vapor are relatively tightly to relatively loosely bound, and that the outermost layers of water vapor are very loosely bound. (See Figure A-2.)

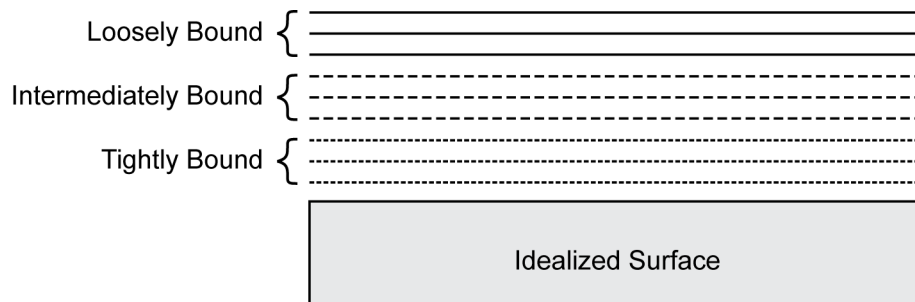
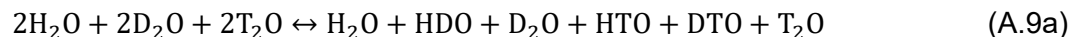


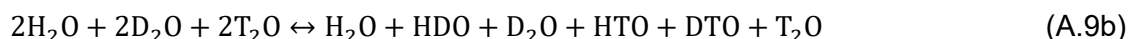
Figure A-2 Idealized Surface Showing Idealized Monomolecular Layers of Water Vapor

A.6.1 Surface-Contamination Modeling

When an overpressure of tritium is added to the system (i.e., the surface, in this case), a perturbation is added to the system, and Le Châtelier's Principle tells us that the tritium levels in the monomolecular layers of water will be shifted to the right, as shown in Equation A.9a:



Tritium is incorporated first into the loosely bound, outer layers, then into the intermediate layers, and finally into the very-tightly-bound, near-surface layers. When the overpressure is removed, the system experiences a new perturbation. In this case, however, the perturbation is in the negative direction, and the system becomes the entity that contains the excess tritium. Le Châtelier's Principle, in this case, indicates that the tritium levels in the monomolecular layers of water will be shifted back to the left, as shown in Equation A.9b:



The tritium that had previously been incorporated into the monomolecular layers now begins to move out of the layers, in an attempt to return to background levels.

The movement of tritium into the monomolecular layers of water vapor is generically referred to as "plate-out." The movement of tritium out of the monomolecular layers of water vapor is generically referred to as "outgassing."

A.6.2 Plate-Out Expectations

When the concentration gradients have been small and/or the exposure times have been short, only the outermost, loosely bound, monomolecular layers of water vapor will be affected. Under such circumstances, the surface-contamination levels will range from no detectable activity to very low levels, that is, up to a few tens of disintegrations per minute per 100 square centimeters (dpm/100 cm²). Since only the outermost monomolecular layers are affected, and

since these layers are easily removed by a simple wiping, the mechanical efforts expended to perform decontamination on such surfaces will, if any, be minimal.

When the concentration gradients have been relatively large and/or the exposure times have been relatively long, the affected monomolecular layers will range down into the intermediately bound layers (i.e., the relatively tightly-to-relatively-loosely-bound layers). Under these circumstances, the surface contamination levels will range from relatively low to relatively high (i.e., from a few hundred to a few thousand dpm/100 cm²). Because the tritium has now penetrated beyond those levels that would normally be easily removed, the mechanical efforts expended to decontaminate such surfaces will be more difficult than those described above.

When the concentration gradients have been large and/or the exposure times have been long, the affected monomolecular layers will range all the way down into the very-tightly-bound layers. The tritium will have penetrated down into the actual surface of the material, itself (see Section A.6.4, below). Under such circumstances, the surface contamination will range from relatively high-to-very-high levels (i.e., from a few tens of thousands to several hundred thousand dpm/100 cm²), and the mechanical efforts expended to decontaminate such surfaces could be very difficult.

A.6.3 Outgassing Expectations

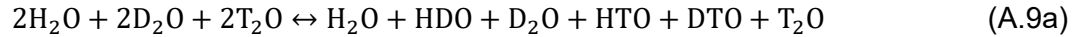
The phenomenon of outgassing is rarely a problem under the first of the exposure situations described above, i.e., situations in which the concentration gradients have been small and/or the exposure times have been short.

However, when systems that have been exposed to even small amounts of tritium for long-to-very-long periods of time are suddenly introduced to room air, or any sudden change in its equilibrium situation, Equations A.5, A.5a, and A.5b; Equations A.6, A.6a, and A.6b; and Reactions A.9, A.9a, and A.9b can be thought of as *springs*, and the initial phenomenon of outgassing can be described as damped harmonic motion. Under such circumstances, therefore, a relatively large, initial “puff” of HTO will be released from the monomolecular layers of water vapor, followed by a relatively long, much smaller trailing release. Because several curies of HTO can be released in a few seconds, and several tens of curies can be released in a few minutes, the speed of the “puff” portion of the release should not be underestimated. The duration of the trailing portion of the release should not be underestimated either. Depending on the concentration gradients involved and/or the time frames involved in the plate-out portion of the exposure, the trailing portion of the release can easily last from several days to several months, or even years.

As the trailing portion of the release asymptotically approaches zero, the outgassing part of the release becomes too small to measure on a real-time basis, and the tritium levels involved in any given release can only be measured by surface contamination measurement techniques. Under such circumstances, the situation reverts back to the circumstances described above in Section A.6.2. With no additional influx of tritium, tritium incorporated into all of the monomolecular layers of water vapor will eventually return to background levels, without human intervention, regardless of the method or level of contamination.

A.6.4 Bulk Contamination Modeling

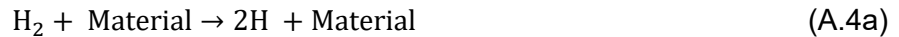
When an overpressure of tritium is added to the system (i.e., the surface of an idealized material), Le Châtelier's Principle indicates that the tritium levels in the monomolecular layers of water will be shifted to the right, as follows:



Tritium is incorporated first into the loosely bound, outer layers, then into the intermediate layers, and finally into the very-tightly-bound, near-surface layers. As the tritium loading in the near-surface layers builds, the disassociation processes that proceed normally as a result of the tritium decay make an overpressure of tritium available in the atomic form (i.e., as T). Relative to the normal amounts of elemental hydrogen that can be expected to be dissolved in the material, the availability of excess tritium in the atomic form represents a different type of perturbation on a system, and the available tritium begins to dissolve into the actual surface of the bulk material. As the local saturation sites in the actual surface of the bulk material begin to fill, the tritium dissolved in the surface begins to diffuse into the body of the bulk material. At that point, the behavior of the tritium in the body of the bulk material becomes totally dependent on the material in question.

A.7 Materials Compatibility Issues

Elemental hydrogen, regardless of its form (H_2 , D_2 , T_2 , and all combinations thereof), can be expected to dissolve to some extent in virtually all materials. For simple solubility reactions, such as Equations A.4a, A.4b, and A.4c, as follows:



Basic compatibility issues should be considered. As a general rule, the solubility of tritium in pure metals and/or ceramics should have a minimal effect, at normal room temperatures and pressures, except for the possibility of hydrogen embrittlement. For alloyed metals, such as stainless steel, similar considerations apply, again, at normal room temperatures and pressures. For alloyed metals, however, additional consideration must be given to the possible leaching of impurities from the alloyed metal, even at normal room temperatures and pressures. (In LP-50 containment vessels, for example, the formation of relatively large amounts of tritiated methane (i.e., up to 0.75 mole percent of CT_4) has been noted after containers of high-purity tritium have been left undisturbed for several years. The formation of the tritiated methane, in this case, has long been attributed to the leaching of carbon from the body of the stainless-steel containment vessel.)

A.7.1 Pressure Considerations

Under increased pressures (e.g., from a few tens to several hundred atmospheres), however, the general rules no longer apply because, in addition to the possibility of hydrogen embrittlement and possible leaching effects, helium embrittlement is also possible. Helium embrittlement tends to occur as a result of the dissolved tritium decaying within the body of the

material, the resultant migration of the helium-3 atoms to the grain boundaries of the material, the localized agglomerations of the helium-3 atoms at the grain boundaries, and the resultant high-pressure buildups at these localized agglomerations.

A.7.2 Temperature Considerations

Under increased temperature situations, the matrix of solubility considerations becomes even more complicated because virtually all solubility reactions are exponentially dependent on temperature. In the case of diffusional flow through the walls of a containment vessel, for example, it can be assumed that steady-state permeation will have been reached when:

$$\left(\frac{Dt}{L^2}\right) \cong 0.45 \quad (\text{A.10})$$

where D is the diffusion rate in square centimeters per second, t is the time in seconds, and L is the thickness of the diffusion barrier. For Type 316 stainless steel, the value for the diffusion rate is as shown in Equation A.10a:

$$D = 4.7 \times 10^{-3} e^{-12,900/RT} \quad (\text{A.10a})$$

and the corresponding value for R , in the appropriate units, is 1.987 calorie per mole-Kelvin. With a nominal wall thickness of 0.125 inches [0.318 cm], Equation A.10 indicates that it will take about 875 years to reach steady-state permeation, at a temperature of 25 °C. At 100 °C, the time frame will be reduced to about 11 years, and at 500 °C, it only takes about 12 hours.

A.8 Organics

With the introduction of organic materials into any tritium-handling system, the matrix of solubility considerations becomes complicated to its maximum extent because the simple solubility reactions, such as those shown above as Equations A.4a, A.4b, and A.4c, are no longer working by themselves. With the availability of free tritium dissolved into the internal volume of the organic material, the molecular surroundings of the organic material see a local perturbation in their own internal systems, and Le Châtelier's Principle indicates that the system will adjust to the perturbation with the establishment of a new equilibrium. Under such circumstances, exchange reactions can be expected to dominate over simple solubility reactions, and the available tritium can be expected to replace the available protium in any and all available sites. Once the tritium has been incorporated into the structure of the organic material, the structure begins to break down from the inside out, primarily as a result of the tritium decay energy.

The specific activity of tritium gas at atmospheric pressure and 25 °C is 2.372 Ci/cm³. The expected range of the average energy tritium beta particle in unit density material is only 0.42 micrometer (μm). This means that all energy from the decay of the dissolved tritium is deposited directly into the surrounding material. At 2.372 Ci/cm³, this becomes equivalent to 2.88 × 10⁴ rads/hour.

The general rule for elastomers used for sealing is that total radiation levels of 10⁷ rads represent the warning point that elastomers may be losing their ability to maintain a seal. At 10⁸ rads, virtually all elastomers used for sealing lose their ability to maintain a seal. Typical failures occur as a result of compression set (i.e., the elastomer becomes brittle and loses its ability to spring back). At 10⁶ rads, on the other hand, the total damage is relatively minor, and most elastomers maintain their ability to maintain a seal. At 10⁷ rads, the ability of an elastomer

to maintain a seal becomes totally dependent on the chemical compounding of the elastomer in question. It only takes about 2 weeks for an elastomer to receive 10^7 rads at a dose rate of 2.88×10^4 rads/hour. Elastomers, therefore, cannot be used for sealing where they might be exposed to high concentrations of tritium.

Similar analogies can be drawn for all organic materials. The preferred rule of thumb is that the use of all organic materials should be discouraged wherever they might be exposed to tritium. Since this is neither possible nor practical, the relative radiation resistance for several elastomers, thermoplastic resins, thermosetting resins, and base oils is shown graphically in Figure A-3, Figure A-4, Figure A-5, and Figure A-6, respectively.

The damage done to organic materials by the presence of tritium in the internal structure of the material is not limited to the more obvious radiation damage effects. Tritium, particularly in the form of T^+ , has the insidious ability to leach impurities (and nonimpurities) out of the body of the parent material. In many cases, particularly where halogens are involved, the damage done by secondary effects, such as leaching, can be more destructive than the immediate effects caused by the radiation damage. In one such case, the tritium contamination normally present in heavy water up to several curies per liter was able to leach substantial amounts of chlorides out of the bodies of neoprene³ O-rings that were used for the seals. The chlorides leached out of the O-rings were subsequently deposited into the stainless-steel sealing surfaces above and below the trapped O-rings, which led directly to the introduction of chloride-induced, stress-corrosion cracking in the stainless steel.

The operational conditions that set up the introduction of the stress-corrosion cracking were moderately elevated temperatures (i.e., less than 100 °C), low pressures (i.e., less than 3 atmospheres), and exposure times of 3–5 years. Fortunately, the damage was discovered before any failures occurred. The neoprene O-rings were removed, and the seal design was changed to a non-O-ring type of seal.

In a second case, six failures out of six tests occurred when high-quality Type 316 stainless steel was exposed to tritium gas in the presence of Teflon™ shavings and 500 parts per million moisture. All the failures were catastrophic, and all were the result of massively induced stress-corrosion cracking. The conditions that set up the introduction of the massively induced stress-corrosion cracking in this case were moderately elevated temperatures (i.e., 104 °C), relatively high pressures (i.e., 10,000 to 20,000 psi), and exposure times that ranged from 11 to 36 hours. Since the time to failure for all the tests was directly proportional to the pressure (i.e., the higher pressure tests failed more quickly than the lower pressure tests), since identical control tests with deuterium produced no failures, and since comparable testing without the Teflon™ shavings indicated no failures after 3,200 hours, it was concluded that fluorides were being leached out of the Teflon™ and deposited directly into the bodies of the stainless steel test vessels. An interesting sideline to this test is that, after the tests, the Teflon™ shavings showed no obvious signs of radiation damage (i.e., no apparent discoloration or other change from the original condition).

³ The proper chemical name for neoprene is "chlorobutadiene."

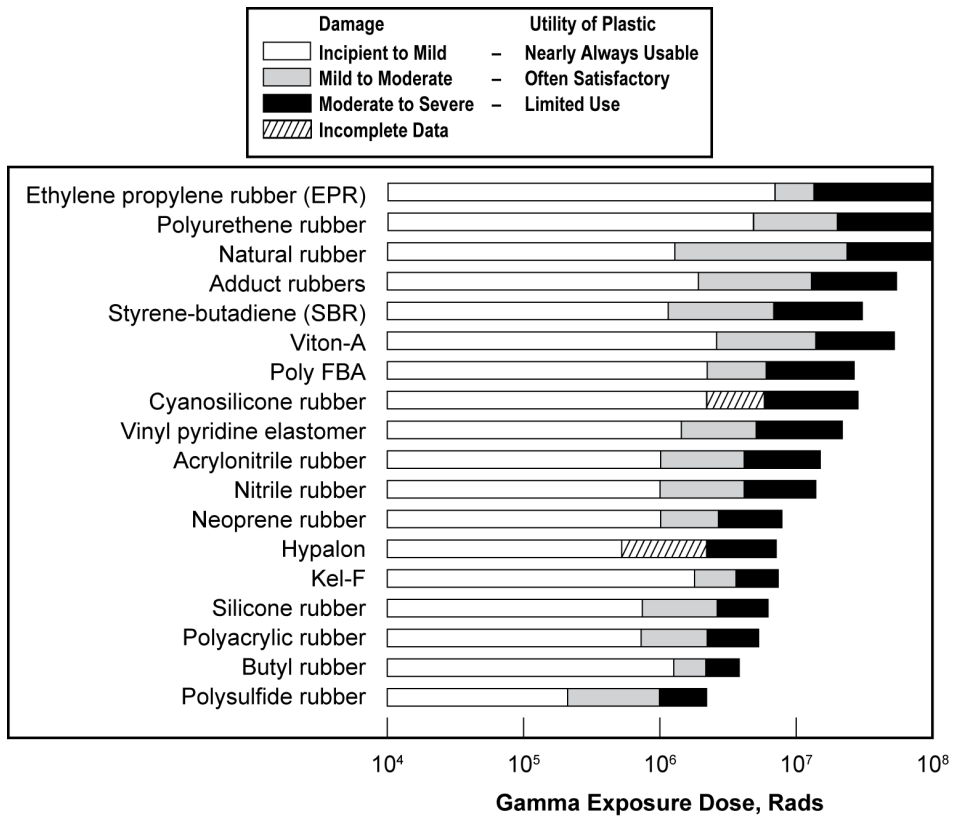


Figure A-3 Relative Radiation Resistance of Elastomers

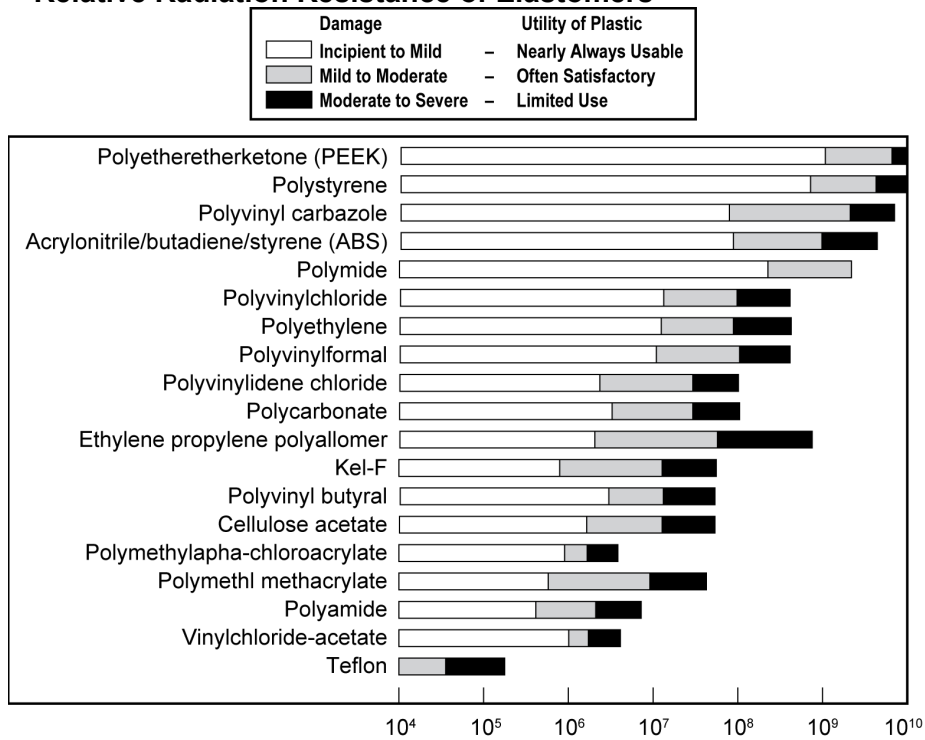


Figure A-4 Relative Radiation Resistance of Thermoplastic Resins

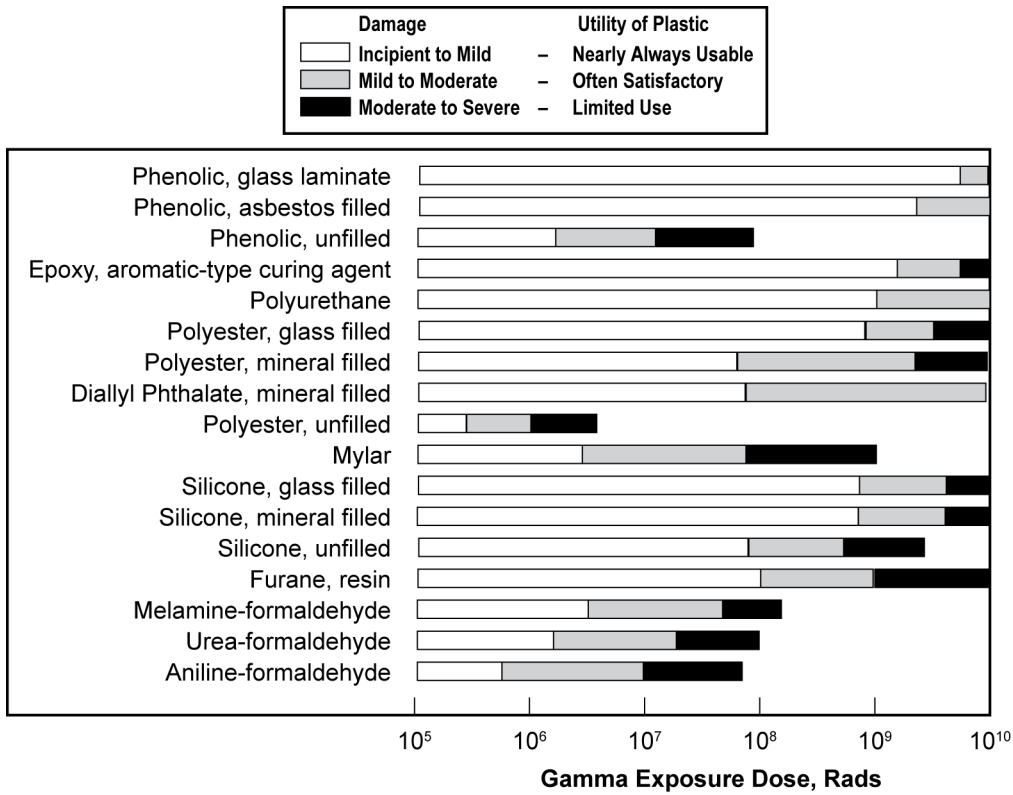


Figure A-5 Relative Radiation Resistance of Thermosetting Resins

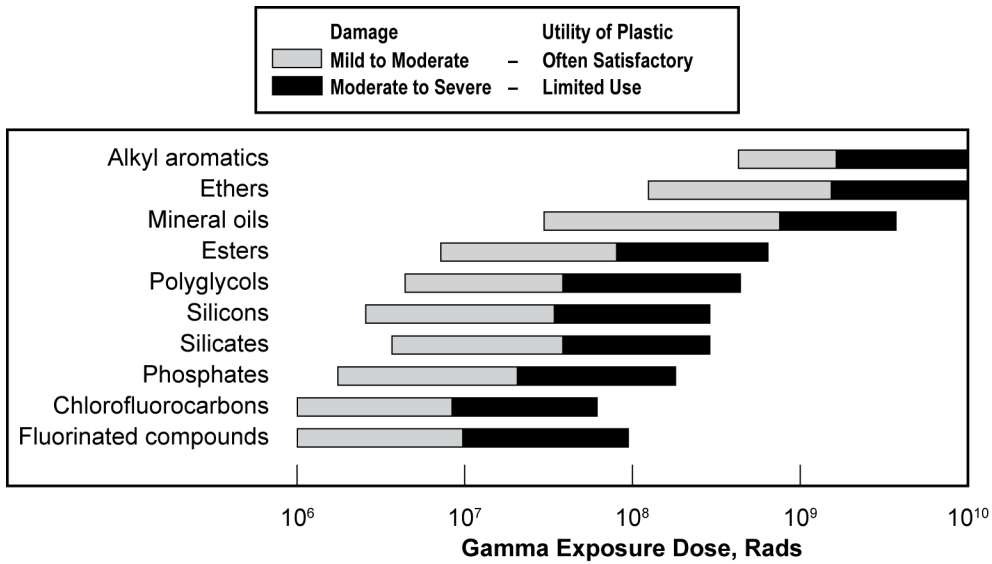


Figure A-6 Relative Radiation Resistance of Base Oils

A.9 Outgassing from Bulk Materials

Discussions on the outgassing from bulk materials can be subdivided into two parts: (i) outgassing from surfaces that have been wetted with tritium, and (ii) outgassing from surfaces that have not been wetted with tritium. For surfaces that have been wetted with tritium, the behavior of the outgassing should be virtually identical to that described above. For surfaces that have not been wetted with tritium, it should be assumed that the source of the outgassing is from tritium that has been dissolved in the body of the parent material.

As the saturation level in the body of the bulk material is reached, the dissolved tritium begins to emerge from the unexposed side of the material surface, where it then begins to move through the monomolecular layers of water vapor on that side. In the initial stages, the pattern of the tritium moving into these monomolecular layers tends to resemble the reverse of that described in the surface contamination model described above (i.e., the tritium is incorporated first into the very-tightly-bound, near-surface layers, then into the intermediate layers, and finally into the loosely bound, outer layers). As the tritium saturation levels in the body of the bulk material gradually reach steady-state, the tritium levels moving into the monomolecular layers gradually build over time, and the pattern slowly changes from one of a reverse surface-contamination model to one of a reverse outgassing model (i.e., the level of outgassing from any given surface can be expected to increase until it too reaches a steady-state, equilibrium level with its own local environment).

A.10 References

U.S. Department of Energy, "Design Considerations," DOE-HDBK-1132-99, U.S. Government Printing Office, Washington, D.C., April 1999. (Note: The bulk of the material presented in this attachment has been adapted from this reference. See, in particular, Sections 2.10.1 through 2.10.6, pp. 1-86 through 1-109.)

A.11 Suggested Additional Reading

U.S. Department of Energy, "Primer on Tritium Safe Handling Practices," DOE-HDBK-1079-94, December 1994.

U.S. Department of Energy, "Radiological Training for Tritium Facilities," DOE-HDBK-1105—2002 Chg Notice 2, May 2007.

U.S. Department of Energy, "Tritium Handling and Safe Storage," DOE-HDBK-1129-2015, September 2015.

