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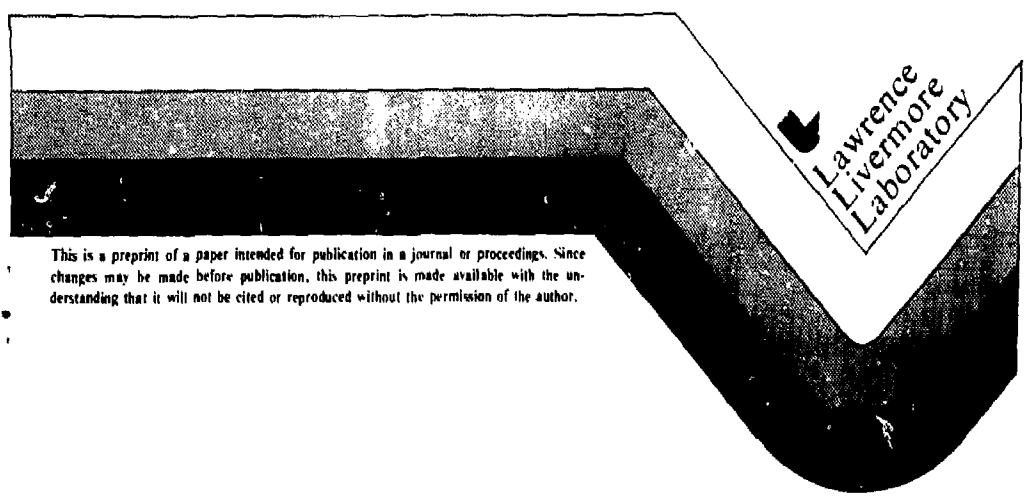
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Predictive Calculations of Volatilities
of Metals and Oxides
in Steam-Containing Environments

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Predictive calculations of volatilities of metals and oxides
in steam-containing environments*

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Abstract. Steam accelerated corrosion of metal alloys and
ceramics and steam volatilization of oxides in general,
presents serious problems in a number of energy applications,
especially as we strive to extend the conditions for use of
materials. Predictive methods are developed here for esti-
mating the bond energies and free energy functions of vola-
tile species having the general formula $MQ_x(OH)_y$, in order
to shed some light on the mechanisms and extent of steam

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accelerated volatilization processes. A specific example of applying the data is illustrated for the case of a proposed underground radioactive waste disposal process, where oxides of radionuclides are allowed to equilibrate with 100 atm steam and 10^{-2} atm oxygen at 1000-2000K. Vapor species found to have high volatilities include $\text{Cs}_2(\text{OH})_2$, CsOH , $\text{AmO}_2(\text{OH})_2$, $\text{AmO}(\text{OH})_3$, $\text{UO}_2(\text{OH})_2$, $\text{NbO}(\text{OH})_3$, $\text{PuO}_2(\text{OH})_2$, $\text{CeO}(\text{OH})_2$, $\text{Ba}(\text{OH})_2$, and $\text{Eu}(\text{OH})_3$. Thermodynamic data are tabulated for all possible monomeric species for this specific example.

1 Introduction

Corrosion by steam, and especially by steam that contains oxygen, has historically presented problems that have limited the use of many metals and ceramics in high temperature applications. Corrosion by steam continues to be of current and future concern as we strive to extend the conditions for use of materials in energy applications. Some of the important current and near-term applications areas where steam corrosion presents problems are coal combustion and coal gasification systems, oil shale retorting, geothermal, nuclear fission reactors, nuclear waste processing, steam turbine generators, and such components as compressors and heat exchangers in the chemical process industries. Among future applications are nuclear fusion reactors, solar central receivers, and more advanced forms of our current energy options.

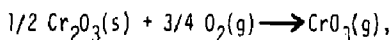
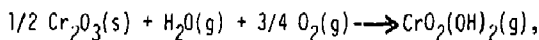
The carrying of salts and minerals by high temperature high pressure steam is well known to geologists and other

scientists, and experimental research has been conducted on a number of oxides to identify some of the important volatile hydroxide species carried by steam. As examples of recent articles that summarize a large number of references in this area: Jackson (1970) gives a summary of thermodynamic data on volatile hydroxides, Krikorian (1970) gives a detailed analysis of the volatility behavior of silica in steam, Krikorian (1973) also discusses the problems of steam corrosion and scaling in a proposed nuclear geothermal power plant, and Hastie (1975) discusses the spectroscopy and other aspects of volatile hydroxides in combustion processes.

The effects of volatilization by steam of protective scales on metal alloys has not been so generally recognized as the steam carrying of minerals. Stewart and Stekebake (1971) mention the accelerated corrosion caused by small amounts of moisture in air and also by high pressure steam on 304 stainless steels. Zaplatynsky (1977) exposed several alloys to slowly convecting open air (containing normal moisture levels) at 1200°C for up to 32 hours and found very high volatilization rates for Cr, Mn, W, Mo, and Nb from alloys containing these elements, and enhanced loss rates were also observed for Ni, Fe, and Co. Elemental depletion was noted for the first listed metals above in both the surface scale and in a zone extending as deep as one mm into the alloy substrate. This author believes that the above enhanced volatilization behavior is primarily a result of a combined steam and oxygen reaction with the surface scale to

form gaseous oxyhydroxide molecules. In most of the alloys tested by Zaplatynsky, Cr_2O_3 was a dominant phase in the surface scale. Experimental studies by Caplan and Cohen (1961) and Graham and Davis (1971) clearly demonstrated the enhanced volatility effect for chromium from Cr_2O_3 as a result of trace amounts of steam; and further Graham and Davis found that the observed volatilities could not be explained on the basis of gaseous oxides such as CrO_3 , but rather that the formation of gaseous $\text{CrO}_2(\text{OH})$ would need to be invoked to explain the observed behavior. The more likely gaseous species is however $\text{CrO}_2(\text{OH})_2$, as indicated by mass spectrometric studies of Farber and Srivastava (1973), and by transpiration measurements by Glemser and Müller (1964).

Since the studies by Zaplatynsky (1977), Caplan and Cohen (1961), and Graham and Davis (1971) were all carried out at relatively high temperatures where corrosion is very rapid, it would be useful to examine and compare steam and oxygen induced volatilities of $\text{Cr}_2\text{O}_3(\text{s})$ scales on metals at more moderate temperatures. Using data summarized by Jackson (1970) for $\text{CrO}_2(\text{OH})_2(\text{g})$, and the balance of the data from JANAF (1971), we find according to the reactions



that when $\text{Cr}_2\text{O}_3(\text{s})$ is exposed to atmospheric air having 60% relative humidity at 298K ($p_{\text{H}_2\text{O}} = 0.0189 \text{ atm}$), that $\text{CrO}_2(\text{OH})_2(\text{g})$ dominates over $\text{CrO}_3(\text{g})$ as the major volatile

species at equilibrium as shown in Figure 1 (see Jackson (1970) and JANAF (1971 - 1975) for data references). Furthermore, depending upon kinetics, $\text{CrO}_2(\text{OH})_2(\text{g})$ should remain of significant importance to fairly low temperatures. For example, from the approach used by Graham and Davis (1971) for the kinetic hindrance due to slowly flowing air, we would expect about a 0.5 mm surface recession due to volatility loss of $\text{Cr}_2\text{O}_3(\text{s})$ in 10y at 1000K at the assumed humidity. More rapidly flowing air and additional moisture would of course accelerate the volatilization further. Nonetheless, the calculation gives a significant corrosion rate that cannot be ignored, particularly if the corrosion leads to localized attack along grain boundaries.

A better understanding of both the equilibrium thermodynamics and the kinetics of steam accelerated volatilization of not only chromium-containing species but alloy substrate and scale constituents in general is needed. This appears to be an area that has been seriously neglected in considering materials development for the future.

The objective of this paper is to suggest approximation methods that can be used to estimate bond energies and free energy functions for oxyhydroxide molecules, and to use the estimated data to calculate volatilities of oxyhydroxide molecules. Hopefully this is a start to alleviate the general lack of information.

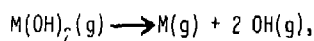
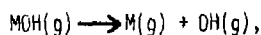
This approach is illustrated by means of an applied

example. The example chosen is that of identifying volatile radionuclide species in an underground environment. The environmental conditions result from a proposed method of radioactive waste disposal where aqueous high level radionuclide wastes which have been derived from a fission reactor and have been aged for more than a year would be introduced into a cavity located deep in a low permeability silicate rock formation (see Schwartz et al. (1976)). The radioactive solutions would be allowed to boil to dryness and over the period of several years would melt a region of rock due to the generated heat of decay. The molten region would then slowly harden and form a glassy matrix to entrap the radionuclides. It would be important to know how steam and oxygen pressures would affect the radionuclide volatilities over this period. We assume, for purposes of calculation, that the principal radionuclides include the elements Cs, Sr, Ba, Y, Zr, Nb, Ru, Rh, Ce, Pr, Eu, U, Pu, Am, and Cm, that steam is present at 100 atm, that oxygen is present at 10^{-2} atm, and that the temperatures of interest range from 1000-2000K. The volatilities of the oxyhydroxides are referred to the pure solid oxides of each of the elements. These are, of course, overly simplified assumptions, but suffice for purposes of illustrating which of the oxyhydroxide species are likely to be volatile in this type of application. (This particular example was chosen for illustration since the author already had calculational data available.)

2 Estimate of Bond Energies

In order to estimate bond energies for the gaseous $MO_x(OH)_y$ species, we assume as have others (e.g., Jackson (1970), Hastie (1975)), that the M-OH bond strength correlates with M-F and M-Cl bond strengths in similar gaseous molecules. For the M-O bonds, the bond strengths are taken to be identical to those in the corresponding metal oxide molecules (see Table 1).

The correlations of M-OH bond energies with M-F and M-Cl bond energies are illustrated in Figures 2 and 3. The bond energies are defined as ΔH_{298}° for reactions such as:



When more than one M-OH bond is broken, the M-OH bond energy is averaged for purposes of the plots. Bond energies (B.E.) are defined similarly for the corresponding molecules containing M-F and M-Cl bonds. The correlations give the following approximate expressions:

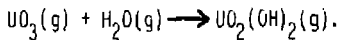
$$B.E.(M-OH) = 0.83 \times B.E.(M-F),$$

$$B.E.(M-OH) = 1.05 \times B.E.(M-Cl).$$

Thermodynamic data for the plots are taken from the JANAF Tables (1971 - 1975), except for the values for OCl and OF which are from Brewer and Rosenblatt (1969).

Table 1 summarizes the bond energy values that are needed to calculate the stabilities of the oxyhydroxide molecules

which result from the principal radionuclides involved in the nuclear waste disposal example. In general the M-OH bond energies are taken to be 0.83 times the analogous M-F bond energy. The estimate is least certain for cases where both M-O and M-OH bonds are present in the same molecule (i.e., column 9 of Table 1), and the author has taken considerable liberties in estimating these values. An approximate M-OH bond energy can be derived for the case of $UO_2(OH)_2(g)$. Alexander (1974), in unpublished work gives $\Delta G_{1773}^{\circ} = -50.1$ kJ/mol for the reaction



Dharwadkar et al. (1975) find

$$\Delta G_T^{\circ} = -186.1 \pm 15.6 + (93.0 \pm 10.5) \times 10^{-3} T \text{ kJ/mol}$$

at 1325 - 1575K for the same reaction.

Using estimated free energy functions for $UO_2(g)$ and $UO_3(g)$ given by Pattoret et al. (1968) and Schick (1966) and free energy functions for $UO_2(OH)_2(g)$ estimated here, together with free energies for $UO_2(g)$ and $UO_3(g)$ given by Ackermann and Chandrasekharaiah (1975), permits us to estimate a U-OH bond energy of about 486 kJ/mol based on Alexander's work and about 460 kJ/mol based on Dharwadkar's work. Alexander's value is selected here, since the work was conducted at a higher temperature and would be less subject to kinetics problems.

The molecular species selected for calculation were limited to a maximum of four oxygens surrounding each

central metal atom. Although valencies may allow for additional oxygens in some cases, such species would not appear to have a significant population under temperatures and pressures of interest here. Polymeric species that involve more than one metal atom may however be important, but have not been considered here.

In order to calculate $\Delta H_{f,298}^{\circ}$ for various $MO_x(OH)_y$ species, bond energy values from Table 1 are combined with sublimation enthalpies to the gaseous atoms (in Table 2) and with thermodynamic data on oxygen and hydrogen containing species given in the JANAF Tables (1971). Results of the $\Delta H_{f,298}^{\circ}$ calculations are summarized in column 2 of Table 3.

3 Estimate of Free Energy Functions

It is very difficult to apply the molecular constant approach to estimate free energy functions (refs) for the $MO_x(OH)_y$ species under consideration here, since experimental information on molecular structures, vibration frequencies, and electronic levels are completely lacking, and estimation of such information is subject to large uncertainties. An empirical method of estimating refs has therefore been selected for this study. Although this method is also subject to large uncertainties, it presents a simple and systematic approach that the author believes may give values that are comparable in accuracy to estimating molecular constants for these species. This method however does not bypass the problem of the unknown electronic levels.

The general expression for the room temperature fef (i.e., S_{298}°) is taken to be

$$S_{298}^{\circ} = a + b \ln A_M + cx + dy,$$

where a , b , c , and d are parametric constants, A_M is the atomic weight of the central metal atom and x and y refer to the coefficients in $MO_x(OH)_y$. Furthermore, $a + b \ln A_M$ represents the approximate translational contribution to the fef , while cx and dy represent the vibrational and rotational contributions due to oxygen and OH respectively. A first cut evaluation of the parameters based on the $MO_x(OH)_y$ species listed in the JANAF Tables (1971 - 1975) and on data estimated by Jackson (1970) for mono- and di-hydroxides using the molecular constant approach, gives the following expressions:

$$S_{298}^{\circ} = 108.8 + 25.1 \ln A_M + 20.9x + 41.8y \text{ (in J/mol-K),}$$

$$S_{298}^{\circ} = 26.0 + 6 \ln A_M + 5x + 10y \text{ (in cal/mol-K).}$$

These parameters allow for the fact that the OH contribution to the entropy is usually much larger than the oxygen contribution.

Further examining the JANAF Tables and Jackson's data indicates a nearly constant rate of increase of fef with temperature. This behavior can be expressed by:

$$-(G_T^{\circ} - H_{298}^{\circ})/T = S_{298}^{\circ} + 8.37 \times 10^{-4}(T-298)S_{298}^{\circ} \text{ (in J/mol-K),}$$

$$-(G_T^{\circ} - H_{298}^{\circ})/T = S_{298}^{\circ} + 2.2 \times 10^{-4}(T-298)S_{298}^{\circ} \text{ (in cal/mol-K).}$$

Values of S_{298}° and $-(G_T^{\circ} - H_{298}^{\circ})/T$ derived from the above relations are summarized in Table 3 for the $MO_x(OH)_y$ species of interest.

4. Results and Discussion

We are now in a position to calculate the volatilities of $MO_x(OH)_y$ for the radionuclides considered in the underground radioactive waste disposal example. In order to proceed, we assume that steam is present in the environment at 100 atm, oxygen at 10^{-2} atm, and that the radionuclides are present as the pure condensed-phase oxides. Thermodynamic data from the literature for the oxides is summarized in Table 4, and data for Cs, Sr, and Ba species are taken directly from the JANAF Tables (1971 - 1975). Using the above assumptions and the estimated data of Table 3, we obtain the volatilities shown on the right hand side of Figure 4. The species shown here are only the ones that are predicted to have the highest abundances under the assumed conditions. Other species also contribute and may even acquire a greater importance under a different set of conditions.

In order to put the calculated $MO_x(OH)_y$ volatilities into a proper frame of reference, it is useful to compare them with the volatilities of oxide species under the same conditions of oxygen pressure (i.e., 10^{-2} atm). This is illustrated on the left hand side of Figure 4. Data for Cs, Sr, and Ba species are from the JANAF Tables (1971 - 1975); for U and Pu species from Ackermann and Chandrasekharaiah (1975), Pattoret et al. (1968), Rand and Markin (1968), Ohse and Ciani (1968), and Schick (1966); for Ru species from Bell and Tagami (1963) and Schäfer et al. (1963); for Rh species

from Norman et al. (1964) and Alcock and Hooper (1960); for Nb species from Brewer and Rosenblatt (1969) and Schick (1966); for Ce, Pr, and Y species from Brewer and Resenblatt (1969), and for Zr species from Schick (1966). Volatilities of Eu, Am, and Cm oxides are not shown in Figure 4 due to lack of data. The author expects EuO(g) , $\text{AmU}_2\text{(g)}$, and CmU(g) to be the principal species, and that EuO(g) will be intermediate in volatility between SrO(g) and CeO(g) , $\text{AmO}_2\text{(g)}$ will be about 100 times more volatile than $\text{PuO}_2\text{(g)}$, and CmO(g) will be about 10 times more volatile than YO(g) .

In examining the role of steam on radionuclide volatilities in Figure 4, we can draw some general conclusions. Volatilities of Cs, Nb, Ce, U, Pu, and Am are extremely high, i.e., they are essentially permanent gases under the conditions chosen for the calculations. However, it is not a reasonable assumption to expect that the pure oxides of these elements will exist as condensed phases in a real situation, but that a significant lowering of the condensed phase activities will occur due to reaction with the silicate matrix. This in itself is a separate issue that would need to be resolved by experimental studies. Nonetheless, these radionuclides can be expected to have high volatilities in the presence of steam, as contrasted to the presence of oxygen alone. Steam also gives fairly high volatilities for Ba and Eu, and enhanced volatilities for Pr, Sr, Cm, Zr, and Y as compared to oxygen alone. The overall volatilities of Ru and

Rh generally show very little effects by steam compared to their behavior in oxygen.

Some conclusions that we can draw from this study are that (1) steam will markedly enhance the volatility of many metal oxides, (2) the presence of combined steam and oxygen in most cases will more strongly enhance metal oxide volatility than steam alone, (3) steam accelerated corrosion is a serious problem in many energy-related applications, and (4) a better understanding of the role of steam in the volatilization of metal oxides should allow us to develop better metal alloys, ceramics, and chemical processes for energy-related applications.

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Table 1. Summary of M-O and M-OH bond energies (in kJ/mol at 298K) used to calculate binding energies for $MO_x(OH)_y$ molecules.^a

Metal M	Average M-O Bond Energy in				Average M-OH Bond Energy in			
	$MO(OH)_y$	$MO_2(OH)_y$	$MO_3(OH)_y$	MOH	$M(OH)_2$	$M(OH)_3$	$M(OH)_4$	$MO_x(OH)_y$
Y	678			498	515	523		(510)
Zr	757			527	573	544	536	(544)
Nb	791	715		515	556	519	494	(519)
Ru	481	(481)	481	364	352	335	326	(343)
Rh	418	427	(410)	339	331	305	301	(318)
Ce	787			(536)	(536)	536	(485)	(523)
Pr	753			(519)	(519)	519		(519)
Eu	544			(481)	481	456		(472)
U	761	736		(515)	(515)	515	498	486
Pu	682	(661)		(469)	(469)	469	444	(444)
Am	(649)	(594)		(477)	(477)	477	431	(452)
Cm	(669)			(519)	(519)	(519)	(469)	(490)

^a In general, the M-O bond energies have been taken to be identical to those given by Brewer and Rosenblatt (1969), and for M-OH bond energies to be 0.83 times the corresponding M-F bond energies given by Feber (1965). For two oxygens bonded to Nb, the data is from Schick (1966); for three oxygens on Ru, the data is from Bell and Tagami (1963); for one oxygen on Rh, the value is derived from the second law data of Norman et al. (1964) using estimated free energy functions, for two oxygens on Rh, the value is derived from Alcock and Hooper (1960) using estimated free energy functions; for two oxygens on U, the value is derived from experimental information given by Alexander (1974) as discussed in the text. All other values have been estimated by the author.

Table 2. Enthalpies of sublimation of various metals to gaseous atoms at 298K.^a

Metal M	$\Delta H_{s,298}^{\circ}$ (kJ/mol)	Metal M	$\Delta H_{s,298}^{\circ}$ (kJ/mol)
Y	425	Pr	356
Zr	609	Eu	175
Nb	721	U	523
Ru	651	Pu	352
Rh	553	Am	272
Ce	423	Cm	(418)

^a Data are taken from Hultgren et al. (1973), except for the value for Am, which has been extrapolated by the author from high temperature data summarized by Hultgren et al. (1973), and the value for Cm, which has been estimated by the author.

Table 3. Estimated thermodynamic data for gaseous $MO_x(OH)_y$ species

Species $MO_x(OH)_y$	$\Delta H_f^\circ, 298$ (kJ/mol) ^a	S_{298}° (J/mol-K) ^b	$-(G_T^\circ - H_{298}^\circ)/T$ (J/mol-K)		
			1000K	1500K	2000K
YOH	-33	263.3	300.2	326.6	352.9
Y(OH) ₂	-525	305.1	347.9	378.4	409.0
Y(OH) ₃	-1,025	347.0	395.7	430.4	465.1
YO(OH)	-475	284.2	324.1	352.5	381.0
ZrOH	121	263.9	301.0	327.4	353.8
Zr(OH) ₂	-458	305.8	348.7	379.3	409.8
Zr(OH) ₃	-904	347.6	396.4	431.2	465.9
Zr(OH) ₄	-1,374	389.4	444.1	483.0	522.0
ZrO(OH)	-404	284.8	324.8	353.3	381.8
ZrO(OH) ₂	-908	326.7	372.5	405.2	437.9
NbOH	246	264.4	301.5	327.9	354.4
Nb(OH) ₂	-312	306.2	349.2	379.8	410.5
Nb(OH) ₃	-716	348.1	396.9	431.7	466.5
Nb(OH) ₄	-1,095	389.9	444.6	483.6	522.6
NbO(OH)	-300	285.3	325.3	353.9	382.4
NbO(OH) ₂	-779	327.1	373.1	405.8	438.5
NbO(OH) ₃	-1,258	369.0	420.8	457.7	494.6
NbO ₂ (OH)	-690	306.2	349.2	379.8	410.5
RuOH	327	266.5	303.9	330.6	357.2
Ru(OH) ₂	28	308.3	351.6	382.5	413.3
Ru(OH) ₃	-233	350.2	399.3	434.3	469.4
Ru(OH) ₄	-495	392.0	447.1	486.3	525.5
RuO(OH)	116	287.4	327.8	356.5	385.3
RuO(OH) ₂	-187	329.2	375.5	408.4	441.3
RuO(OH) ₃	-491	371.1	423.2	460.3	497.4
RuO ₂ (OH)	-116	308.3	351.6	382.5	413.3
RuO ₂ (OH) ₂	-419	350.2	399.3	434.3	469.4
RuO ₃ (OH)	-348	329.2	375.5	408.4	441.3

Table 3. Estimated thermodynamic data for gaseous $\text{MO}_x(\text{OH})_y$ species

Species $\text{MO}_x(\text{OH})_y$	$\Delta H_f^\circ, 298$ (kJ/mol) ^a	S_{298}° (J/mol-K) ^b	$-(G_T^\circ - H_{298}^\circ)/T$ (J/mol-K)		
			1000K	1500K	2000K
RhOH	254	266.9	304.4	331.1	357.8
Rh(OH) ₂	-28	308.8	352.1	383.0	413.9
Rh(OH) ₃	-244	350.6	399.9	434.9	470.0
Rh(OH) ₄	-493	392.5	447.6	486.8	526.1
RhO(OH)	105	287.9	328.3	357.1	385.8
RhO(OH) ₂	-173	329.7	376.0	408.9	441.9
RhO(OH) ₃	-451	371.5	423.7	460.9	498.0
RhO ₂ (OH)	-80	308.8	352.1	383.0	413.9
RhO ₂ (OH) ₂	-359	350.6	399.9	434.9	470.0
RhO ₃ (OH)	-208	329.7	376.0	408.9	441.9
CeOH	-73	274.7	313.3	340.7	368.2
Ce(OH) ₂	-569	316.5	361.0	392.6	424.3
Ce(OH) ₃	-1,065	358.4	408.7	444.5	480.4
Ce(OH) ₄	-1,360	400.2	456.4	496.4	536.4
CeO(OH)	-598	295.6	337.1	366.7	396.2
CeO(OH) ₂	-1,082	337.4	384.8	418.6	452.3
PrOH	-123	274.8	313.4	340.9	368.4
Pr(OH) ₂	-602	316.7	361.1	392.8	424.5
Pr(OH) ₃	-1,082	358.5	408.9	444.7	480.5
PrO(OH)	-628	295.8	337.3	366.9	396.4
EuOH	-266	276.7	315.6	343.3	370.9
Eu(OH) ₂	-708	318.6	363.3	395.1	427.0
Eu(OH) ₃	-1,074	360.4	411.0	447.1	483.1
EuO(OH)	-553	297.6	339.4	369.2	399.0
UOH	48	288.0	328.4	357.2	386.0
U(OH) ₂	-427	329.8	376.1	409.1	442.1
U(OH) ₂	-902	371.7	423.8	461.0	498.2
U(OH) ₄	-1,310	413.5	471.6	512.9	554.3

Table 3. Estimated thermodynamic data for gaseous $MO_x(OH)_y$ species

Species $MO_x(OH)_y$	$\Delta H_f^\circ, 298$ (kJ/mol) ^a	S°_{298} (J/mol-K) ^b	$-(G_T^\circ - H_{298}^\circ)/T$ (J/mol-K)		
			1000K	1500K	2000K
UO(OH)	-435	308.9	352.3	383.2	414.1
UO(OH) ₂	-881	350.7	400.0	435.1	470.2
UO(OH) ₃	-1,326	392.6	447.7	487.0	526.2
UO ₂ (OH)	-897	329.8	376.1	409.1	442.1
UO ₂ (OH) ₂	-1,343	371.7	423.8	461.0	498.2
PuOH	-77	288.4	328.9	357.7	386.6
Pu(OH) ₂	-506	330.2	376.6	409.7	442.7
Pu(OH) ₃	-935	372.1	424.3	461.5	498.7
Pu(OH) ₄	-1,263	413.9	472.0	513.4	554.8
PuO(OH)	-485	309.3	352.8	383.7	414.6
PuO(OH) ₂	-889	351.2	400.5	435.6	470.7
PuO(OH) ₃	-1,292	393.0	448.2	487.5	526.8
PuO ₂ (OH)	-876	330.2	376.6	409.7	442.7
PuO ₂ (OH) ₂	-1,279	372.1	424.3	461.5	498.7
AmOH	-165	288.5	329.0	357.9	386.7
Am(OH) ₂	-602	330.4	376.7	409.8	442.8
Am(OH) ₃	-1,040	372.2	424.5	461.7	498.9
Am(OH) ₄	-1,293	414.0	472.2	513.5	555.0
AmO(OH)	-540	309.4	352.9	383.8	414.8
AmO(OH) ₂	-952	351.3	400.6	435.7	470.8
AmO(OH) ₃	-1,364	393.1	448.3	487.6	526.9
AmO ₂ (OH)	-830	330.4	376.7	409.8	442.8
AmO ₂ (OH) ₂	-1,242	372.2	424.5	461.7	498.9
CmOH	-61	288.9	329.5	358.4	387.3
Cm(OH) ₂	-540	330.8	377.2	410.3	443.3
Cm(OH) ₃	-1,019	372.6	424.9	462.2	499.4
Cm(OH) ₄	-1,297	414.5	472.6	514.1	555.5
CmO(OH)	-452	309.9	353.3	384.3	415.3
CmO(OH) ₂	-902	351.7	401.1	436.2	471.4

Table 3. Estimated thermodynamic data for gaseous $MO_x(OH)_y$ species

a The enthalpies of formation of $MO_x(OH)_y$ species in this table are based upon the enthalpies of formation of gaseous atoms given in Table 2 combined with the bond energy estimates given in Table 1 together with thermodynamic data for oxygen and hydrogen containing species given in the JANAF Tables (1971).

b The following expressions:

$$S_{298}^{\circ} = 108.8 + 25.1 \ln A_M + 20.9x + 41.8y,$$
$$-(G_T^{\circ} - H_{298}^{\circ})/T = S_{298}^{\circ} + 8.37 \times 10^{-4}(T-298) S_{298}^{\circ},$$

are used to estimate the values listed in columns 3-6 of this table. Units are in J/mol-K, A_M is the atomic weight of the metal M in species $MO_x(OH)_y$, and x and y are the numbers of M-O and M-OH bonds respectively for each molecule.

Table 4. Thermodynamic data for solid oxides

Oxide	$\Delta H_{f,298}^{\circ}$ (kJ/mol) ^a	S_{298}° (J/mol-K)	$-(G_T^{\circ} - H_{298}^{\circ})/T$ (J/mol-K)			References
			1000K	1500K	2000K	
Cs ₂ O	-339	(133.89)	(189.18)	(229.89)	(260.99)	est. by author ^b
Y ₂ O ₃	-1,906	98.74	157.23	194.81	224.85	Pankratz et al. (1962), Kelley and King (1961)
ZrO ₂	-1,100	50.71	84.06	106.02	124.47	Schick (1966)
Nb ₂ O ₅	-1,902	137.24	213.93	264.05	311.33	Schick (1966)
RuO ₂	-301	(51.46)	(95.06)	(119.66)	(142.59)	est. by author
Rh ₂ O ₃	-297	(98.32)	(159.41)	(199.33)	(232.46)	est. by author
Ce ₂ O ₃	-1,796	150.62	217.32	(261.50)	(298.40)	Weller and King (1963), Pankratz and Kelley (1963) ^c
Pr ₂ O ₃	-1,828	(152.72)	(218.07)	(260.50)	(295.22)	Pankratz (1966) ^d
Eu ₂ O ₃	-1,649	(150.62)	(217.90)	(261.21)	(296.14)	Pankratz et al. (1962) ^d
UO ₂	-1,084	77.95	115.85	140.67	160.62	Schick (1966)
PuO ₂	-1,058	68.37	109.58	136.48	158.07	Kruger and Savage (1968), Ogard (1970)
AmO ₂	-1,004	(68.37)	109.58)	(136.48)	(158.07)	est. by author
Cm ₂ O ₃	(-1,841)	(150.62)	(217.32)	(261.50)	(298.40)	est. by author

^a $\Delta H_{f,298}^{\circ}$ values are from Brewer and Rosenblatt (1969), except for the value for Rh₂O₃ which is from Brewer (1953), and for Cm₂O₃ which has been estimated by the author.

^b Cs₂O melts at 924K according to Brewer (1953).

^c The transition enthalpy for Ce₂O₃ at 1050K is estimated to be 920J/mol.

^d S_{298}° has been estimated by the author.

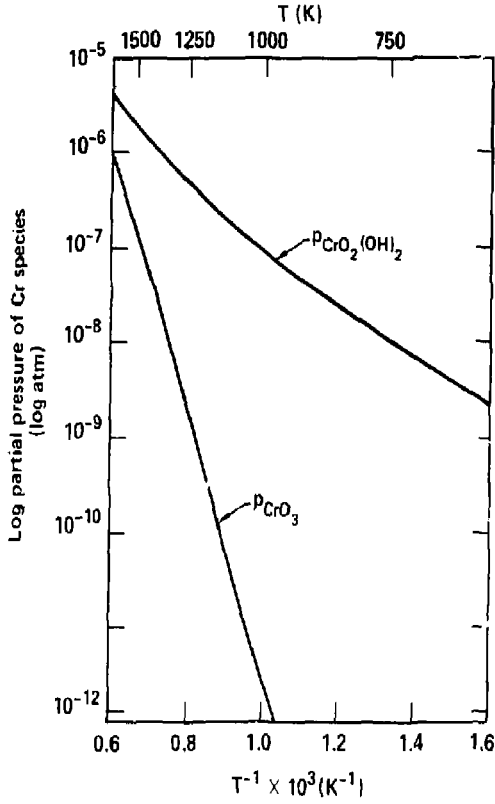


Figure 1. The volatility of $\text{CrO}_2(\text{OH})_2(\text{g})$ clearly dominates over $\text{CrO}_3(\text{g})$ at equilibrium for $\text{Cr}_2\text{O}_3(\text{s})$ exposed to air with a relative humidity of 60% at 25°C. This illustrates the importance of even traces of steam in enhancing volatilization of $\text{Cr}_2\text{O}_3(\text{s})$, which normally forms a protective scale that prevents corrosion in many metallic alloy systems.

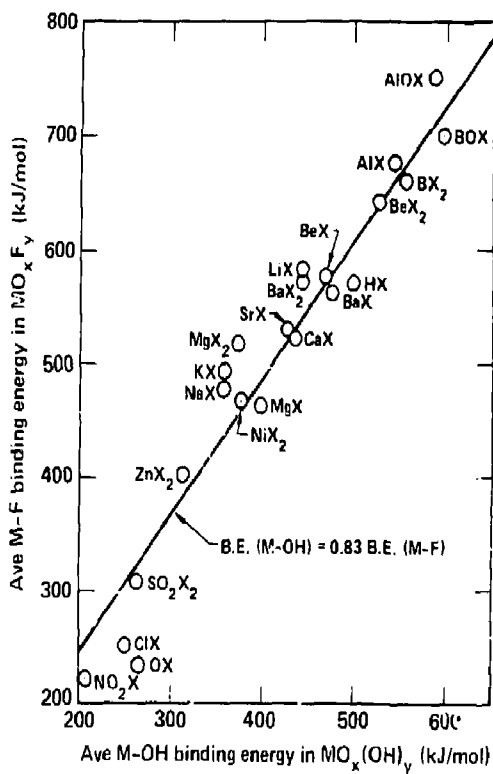


Figure 2. A comparison is made between M-OH and M-F bond energies in similar gaseous molecules, where X represents either F or OH. The bond energies are found to be correlated by the expression $\text{B.E. (M-OH)} = 0.83 \text{ B.E. (M-F)}$.

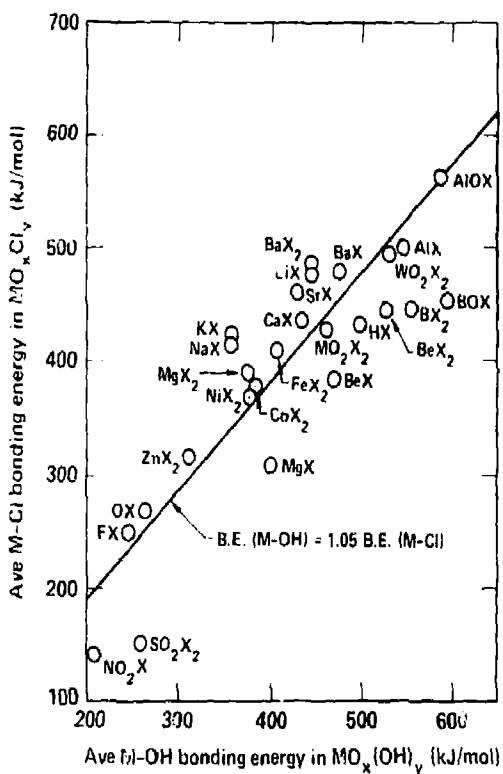


Figure 3. A comparison is made between M-OH and M-Cl bond energies in similar gaseous molecules, where X represents either Cl or OH. The bond energies are found to be correlated by the expression $B.E.(M-OH) = 1.05 B.E.(M-Cl)$.

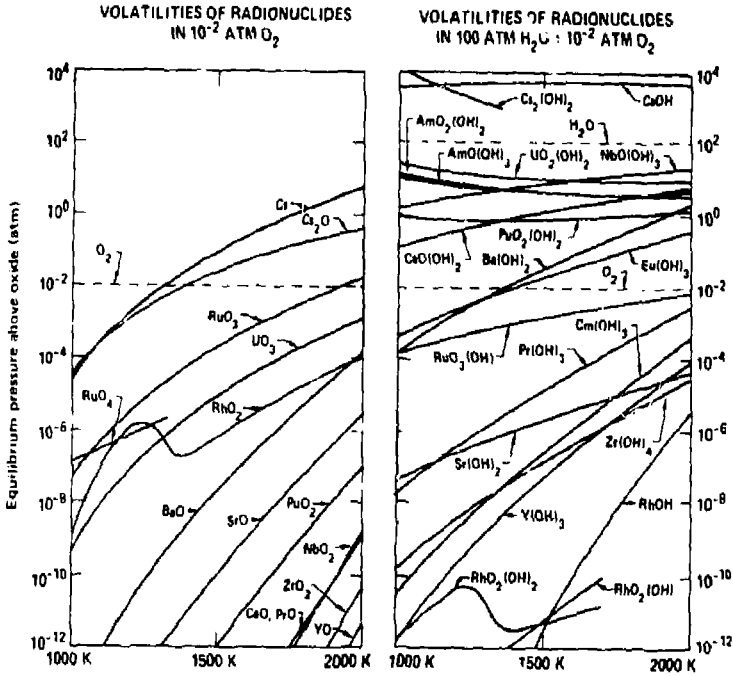


Figure 4. Partial pressures of the principal equilibrium species are compared for two environments at 1500-2000 K for radionuclides from the pure solid oxides in an idealized underground waste disposal application. A steam-free environment with 10^{-2} atm oxygen is shown at the left, and an environment with 100 atm steam and 10^{-2} atm oxygen at the right. Metal oxide species are omitted from the graph on the right for purposes of clarity. Steam is predicted to significantly promote the volatilization of Cs, Am, U, Nb, Pu, Ce, Ba, and Eu.