GENERAL ATOMIC
DIVISION OF GENERAL DYNAMICS

GA-7058
OCD Work Unit # 3111A

HENRY'S LAW CONSTANTS FOR DISSOLUTION OF FISSION PRODUCTS IN A SILICATE FALLOUT PARTICLE MATRIX

by

J. H. Norman

Performed for
Office of Civil Defense
Secretary of the Army
Department of Defense, 20301
under
Contract N0022866CO403
through the
U.S. Naval Radiological Defense Laboratory
San Francisco, California 94135

December 29, 1966

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SUMMARY

Henry's Law constants for fission product elements and important activated elements are estimated for the system: dilute element, 1 atm oxygen pressure, and liquid silicate solvent. A lower oxygen pressure limit for use of these values is also presented. These constants may be used to calculate solubility of fission products in fallout as a function of temperature. In conjunction with diffusivities, half-lives, yields, and detonation parameters, these constants can be used to calculate fractionation effects in fallout. A simple estimating scheme is given for describing fission-product distribution and fractionation in fallout. ( )

INTRODUCTION

In order to describe fractionation of fission products in fallout, Miller(1) presented a phenomenological model describing the high temperature processes occuring during fallout formation. His model is based on the dissolution of gaseous fission-product oxides in the fallout particle matrix. Dissolution of volatile fission products from the gas phase into fallout particles is not generally as efficient a process as dissolution of a less volatile fission product. The efficiency difference is believed to be the cause of fractionation of fission products in fallout. Miller has employed ideal solution behavior for estimating the efficiency of dissolution (solubility) of gaseous fission products in fallout at a given temperature. He states, however, that employing Henry's Law constants (a thermodynamic representation of non-ideal solution behavior) would be preferable to using ideal solution behavior. His choice of ideal solution behavior was based on lack of information concerning non-ideal solution behavior.

Studies performed at General Atomic have been concerned with measuring the non-ideality of solutions of fission product oxides in a silicate matrix. Although these studies are not extensive enough at this time so that a complete experimental description of non-ideal behavior can be presented, enough has been learned so that a valuable interim estimation can be made. While this estimation, generally, can be considered only an order of magnitude-type description of solubility, it is believed that such a presentation represents a significant contribution to the description of the formation of silicate-type fallout. For these reasons, the thermodynamic tables representing the dissolution of fission products (and activated products) in a silicate-type matrix are presented.

BASIS FOR THE THERMODYNAMIC TABLES

The thermodynamic tables developed in this study to apply to fallout formation are derived from selected oxide vaporization thermodynamics and General Atomic's experimental CaO-Al_2O_3-SiO_2 fission-product absorption data.$^{(2,3)}$ Where oxide vaporization data were used, they were corrected for silicate interaction and oxide fusion, using data when they were available or by estimating necessary values. These two correction terms represent the philosophy adopted in attempting to estimate solution non-ideality in silicate systems.

In these tables the simplicity of the equations representing the Henry's Law constants is apparent. This simplicity is not only possible but would seem to be mandatory. Where uncertainties exist as great as must occur when applying oxide thermodynamics to silicate solutions, using reasonable correction terms, there is no necessity to present more complex equations. In fact, use of a heat capacity correction to these data generally is ignored in this presentation.

The ground rules employed for determining the values in these tables are listed as follows:

1. The system, condensed state—near atmospheric pressure oxygen—very dilute gaseous fission product (oxide), was chosen. The fission product was assumed to be so dilute that only one fission-product atom per gaseous molecule (or per dissolved ion) was considered possible. This assumption might be in error for Tc, As, and Sb, which form polymeric gaseous species very readily, but otherwise should be adequate.

2. Where appropriate, the dissolution process was considered to be pure liquid fission-product silicate in the molten silicate fallout particles. This solution process was considered to be ideal. In cases where liquid fission-product silicate was believed to be unstable, pure liquid fission-product oxide or liquid fission product was assumed to form an ideal solution with the silicate.

3. The valence of the condensed fission product, except in a few instances, was considered to be the same as for the oxide, which exists at 1500°C and 1 atm oxygen. Some problems were encountered, particularly in cases where oxides were unstable under this condition, i.e., Ag(l), Pd(l), and I(g). Exceptions were handled as indicated in the description of the behavior of individual fission products.

4. Often, no silicate thermodynamic data were availabe for the fission product elements. In this case, thermodynamics had to be estimated for silicate formation, which was done by using calculated general values for the reaction $O^{=}(\ell) + SiO_2(\ell) \rightarrow SiO_3^{=}(\ell)$. Silicate formation was then considered to occur by reacting oxide ions from the molten fission product oxide with $SiO_2(\ell)$.

Modification of the simple behavior was believed necessary, in many cases, in order to describe the different degrees of availability of the oxide ions in fission product oxide melts. Modification used in this report took several forms: some of the molten oxides were assumed to completely ionize and thus agree with the simple thermodynamic model; others were assumed to only partially ionize, freeing only a fraction of their oxides for reaction; others were assumed to have appreciable energy of association of the oxide ions with the metal ions that had to be overcome; and others were assumed not to dissociate.

5. Hydroxides and other species not classified as oxides, which may be important vapor species during fallout formation, have been ignored. An extension of Table 1 might include some of these species. Indeed, the problem of other species may be very severe for many elements and may greatly alter the behavior of these elements in fallout formation, as suggested by this study.

6. Elements considered included only those where the U^{238} thermonuclear yields and subsequent decay products represent in some manner, according to Crocker,(4) more than 1 atom per 10,000 fissions. Also included in these tables are thermodynamic representations of some arbitrarily selected activation products.

7. Results have been presented in terms of atmospheres of fission product per gram fission product per gram silicate. This form rather than a mole fraction form is used for simplicity and generally will result in a bias of no more than a factor of 2 in the vapor pressure--well within the uncertainties of the data in these tables.

8. The sources of the thermodynamic data used in preparing these tables were data from this laboratory(2, 3) and comparison of Miller's(1) Raoults Law constants with the Bedford and Jackson(5) volatilities of fission product oxides. Where appropriate, other sources were also employed. Sources used for a particular fission product are listed in the description of that fission product.

The following sections describe the determination of the reported thermodynamics for general and specific systems for calculating the values in these tables.

Development of the Silicate Correction Term

As previously mentioned, the non-ideality correction used in this report for the dissolution of oxides into silicates was based on the assumption that dissolution of molten silicate (where it is readily formed) into the fallout particle matrix is considered an ideal process ($\overline{\Delta F} = RT \ln C$). Data describing formation of liquid silicates are meager; therefore, it was necessary to construct a general situation and the following reactions were considered:

Reaction	ΔF	Ref.
$CaO(s) + SiO_2(s) \rightleftarrows CaSiO_3(s)$	-19,900 - 0.8 T	(6)
$CaO(s) \rightleftarrows CaO(l)$	12,200 - 4.1 T	(7,8)
$SiO_2(s) \rightleftarrows SiO_2(l)$	2,000 - 1.1 T	(9)
$CaSiO_3(s) \rightleftarrows CaSiO_3(l)$	13,400 - 7.5 T	(6,8)
$CaO(l) + SiO_2(l) \rightarrow CaSiO_3(l)$	-20,700 - 3.1 T	

or $O^{=}(l) + SiO_2(l) \rightleftarrows SiO_3^{=}(l)$,

since liquid oxides and silicates would appear to behave principally in an ionic fashion.

In this report the above correction is written in terms of a logarithmic equation;

$$\log \frac{C_{SiO_3^{=}}}{C_{O^{=}}\, C_{SiO_2}} = \frac{4520}{T} + 0.68 .$$

Replacing CaO with either Al_2O_3 or BaO(6) appears to give values similar to CaO per oxide ion, since the heats of formation of the barium and aluminum silicates from the oxides are similar to calcium silicate from the oxide. The oxides Na_2O and MgO,(6,7) provide some deviation from the above model; however, this formula will be used in this report. (The elements for which this correction is used in this presentation are in general more similar to the Ca, Ba, or Al than Na or Mg.) However, there does seem to be a tendency toward less energetic silicate formation as the electropositive character of a fission product decreases, so two methods of decreasing this silicate correction were applied: (1) certain polyvalent metals were allowed to form silicates with only a portion of their oxide ions and (2) the silicate correction, where employed, was halved for metals with filled or almost filled outer d electron shells. The actual silicate correction is discussed for each element.

This approach is arbitrary, but it appears to be in the right direction and because of lack of data is necessary in estimating the fallout behavior.

Liquid Correction Term

Since, in the temperature range of interest, roughly 2500° to 1000°K, most oxide thermodynamics are presented for a crystalline condensed state and since the philosophy accepted here is that a liquid silicate (or oxide) will dissolve ideally in the fallout particle matrix, it is necessary to consider the thermodynamics of fusion. In the previous section, an outline for correction due to liquid silicate formation from liquid oxides is presented. To be consistent with this correction, it is necessary to use vaporization thermodynamic values of the liquid oxides; these are normally available by converting sublimation thermodynamics to vaporization thermodynamics, using the thermodynamics of fusion.

The thermodynamics of fusion of some fission-product oxides, however, have not been measured. To estimate fusion thermodynamic values, Brewer(10) suggests using an entropy of fusion of 2.5 to 3.5 e.u. per ion formed during melting. Selecting entropies of fusion from Wicks,(7) Kubaschewski,(11) and Kelley,(8) where the three compilations are in reasonable agreement and where the oxides would be expected to be ionic, one finds an entropy of melting of 2.5 ±0.7 e.u./gram atom for fourteen selected oxides. Twenty-two oxides, both of ionic and non-ionic nature, gave 2.2 ±0.9 e.u./gram atom. This value of 2.5 e.u. per ion for highly ionic oxides and 2.2 e.u./gram atom for other types was employed. The scatter and small quantity of data on non-ionic types seemed to be good justification for not employing the non-ionic average separately. Values so estimated were used only where there are insufficient data.

Using measured or estimated fusion temperatures (occasionally, it was necessary to estimate a fusion temperature for an oxide), enthalpies of fusion can be calculated from entropies of fusion. The entropy and enthalpy of fusion were then combined giving the fusion correction in Table 2. This fusion correction generally has a relatively small but non-negligible influence on the reported pressure data.

TABLE DESCRIPTION (TABLES 1 AND 2)

In Table 1, vaporization thermodynamics are reported for fission products listed according to atomic number. The equation governing the thermodynamics is presented in equilibrium constant form. For example, log $P_{GeO}P_{O_2}^{1/2}/C_{GeO_3^=}$ suggests that germanate ions are evaporated from the silicate solution by decomposition to GeO(g), 1/2 O_2, and $O^=(\ell)$, the activity of $O^=$ being set by the silicate system. The numerical equilibrium constant expression (logarithm of the Henry's Law constant) follows this term. The next column gives the oxygen pressure below which another known gaseous species of the fission product in question is of similar pressure to the species described in the table when the pure oxide pressure is 10^{-4} atm. If this does not occur between 1000° and 2000°K, then the value is calculated at the appropriate temperature limit of these two temperatures. For a land surface detonation it would not appear that oxide species other than those listed in the table are important.

The following three columns describe, respectively, the source of the data used for the melting correction, the basis for the silicate correction, and the references used in the vapor pressure estimation. The silicate correction basis is given as, for instance, full (ZrO^{+2}). This means that dissolution of $ZrO_2(1)$ was taken as equivalent to dissolution of one $O^=(1)$ from CaO(1). This was done assuming that ZrO^{+2} could be considered the solute ion in the silicate.

Table 2 describes melting thermodynamics of the appropriate fission product oxides. In succeeding columns, the oxide, its melting point, heat of fusion, entropy of fusion, and a thermodynamic equation representing the melting of one gram atom of the fission product element in oxide form are given. The last column indicates references for the data. Values in parentheses have been estimated.

The data of Table 1 are presented graphically in Fig. 1 at 1 atm O_2 pressure in order that a comparison of fission product volatilities might readily be made.

Table 1

SUGGESTED HENRY'S LAW CONSTANTS FOR FALLOUT FORMATION CALCULATIONS

Element	Estimated or Measured Thermodynamic Equations for Fallout Formation	Lower P_{O_2} Limit (atm)	Melting Correction References	Silicate Correction	Vapor Pressure References
Ga	$\log P_{GaO}\, P_{O_2}^{1/4}/C_{Ga^{+3}} = 9.7 - \frac{35,200}{T}$		15	1/2 (Ga^{+3})	12, 13, 14
	$\log P_{Ga} P_{O_2}^{3/4}/C_{Ga^{+3}} = 13.0 - \frac{43,300}{T}$				
Ge	$\log P_{GeO} P_{O_2}^{1/2}/C_{GeO_3^=} = 12.5 - \frac{23,600}{T}$	10^{-16}	15	0	5
As	$\log P_{AsO} P_{O_2}^{1/2}/C_{AsO_3^=} = 10.4 - \frac{17,800}{T}$	10^{-8}	15	0	5
	$\log P_{AsO_2}/C_{AsO_3^=} = 6.9 - \frac{6,000}{T}$		15		16, 17, Est.
Se	$\log P_{SeO_2}/C_{SeO_3^=} = 7.0 - \frac{4,200}{T}$	10^{-16}		0	5, 13
Br	$\log P_{Br}/P_{O_2}^{1/4} C_{Br^-} = 4.0 - \frac{5,200}{T}$	10^{-10}	7, 8, 11	Full (Br^-)	7, 18
Kr	$\log P_{Kr}/C_{Kr} = 4.0 - \frac{500}{T}$				18

Table 1--continued

Element	Estimated or Measured Thermodynamic Equations for Fallout Formation	Lower P_{O_2} Limit (atm)	Melting Correction References	Silicate Correction	Vapor Pressure References
Rb	$\log P_{Rb(?)}/C_{Rb^+} = 7.0 - \frac{18,100}{T}$	$<10^{-4}$	Exp.	Exp.	2, 3
Sr	$\log P_{SrO}/C_{Sr^{++}} = 4.4 - \frac{26,700}{T}$	10^{-6}	11	Full (Sr^{++})	2, 5
Y	$\log P_{YO}P_{O_2}^{1/4}/C_{Y^{+3}} = 7.7 - \frac{49,100}{T}$	10^{-20}	7	Full (Y^{+3})	19, 5, 1
Zr	$\log P_{ZrO_2}/C_{ZrO^{+2}} = 6.7 - \frac{38,200}{T}$	10^{-10}	7, 8	Full (ZrO^{+2})	5
Nb	$\log P_{NbO_2}P_{O_2}^{1/4}/C_{NbO^{+3}} = 8.5 - \frac{44,800}{T}$	10^{-11}	7, 13	Full (NbO^{+3})	22, 5
Mo	$\log P_{MoO_3}/C_{MoO_4^{=}} = 7.6 - \frac{20,400}{T}$	10^{-10}	Exp.	Exp.	2, 23, 24
Tc	$\log P_{TcO_3}/C_{TcO_3^{=}}P_{O_2}^{1/2} = 4.1 - \frac{7,100}{T}$	10^{-10}	15	0	5, Est.
Ru	$\log P_{RuO_4}/P_{O_2}C_{RuO_3^{=}} = 1.2 - \frac{2,600}{T}$		Exp.	Exp.	2, 25
	$\log P_{RuO_3}/P_{O_2}^{1/2}C_{RuO_3^{=}} = 6.2 - \frac{9,000}{T}$	10^{-9}	Exp.	Exp.	2, 25

Table 1--continued

Element	Estimated or Measured Thermodynamic Equations for Fallout Formation	Lower P_{O_2} Limit (atm)	Melting Correction References	Silicate Correction	Vapor Pressure References
Rh	$\log P_{RhO_2}/P_{O_2}^{1/4}C_{RhO_2^-} = 7.2 - \frac{18,400}{T}$	10^{-4}	Est.	0	26, 27, 28
Pd	$\log P_{Pd}P_{O_2}^{1/2}/C_{Pd^{++}} = 8.7 - \frac{24,700}{T}$		Est.	1/2 (Pd^{+2})	13, 29
Ag	$\log P_{Ag}P_{O_2}^{1/4}/C_{Ag^+} = 6.2 - \frac{14,300}{T}$		Est.	1/2 (Ag^+)	13, 14, 30
Cd	$\log P_{Cd}P_{O_2}^{1/2}/C_{Cd^{++}} = 9.0 - \frac{19,200}{T}$		Est.	1/2 (Cd^{++})	13, 5
In	$\log P_{InO}P_{O_2}^{1/4}/C_{In^{+3}} = 9.1 - \frac{30,600}{T}$		15	1/2 (In^{+3})	5, 32 13, 14
	$\log P_{In}P_{O_2}^{3/4}/C_{In^{+3}} = 12.2 - \frac{37,500}{T}$				
Sn	$\log P_{SnO}P_{O_2}^{1/2}/C_{SnO^{++}} = 13.1 - \frac{32,100}{T}$	10^{-10}	13	1/2 (SnO^{+2})	13, 33, 34, 35
Sb	$\log P_{Sb}P_{O_2}^{3/4}/C_{SbO_3^{-3}} = 11.1 - \frac{29,500}{T}$			0	5, 2, 33
	$\log P_{SbO}P_{O_2}^{1/4}/C_{SbO_3^{-3}} = 8.6 - \frac{25,900}{T}$				

Table 1--continued

Element	Estimated or Measured Thermodynamic Equations for Fallout Formation	Lower P_{O_2} Limit (atm)	Melting Correction References	Silicate Correction	Vapor Pressure References
Te	$\log P_{TeO_2}/C_{TeO_3^{=}} = 9.2 - \frac{11,800}{T}$	10^{-18}		Exp.	5
I	$\log P_I/C_{I^-}P_{O_2}^{1/4} = 3.8 - \frac{1000}{T}$	10^{-15}	7	Full (I^-)	7, 18, 3
Xe	$\log P_{Xe}/C_{Xe} = 4.1 - \frac{700}{T}$				18
Cs	$\log P_{Cs}/C_{Cs^+} = 6.6 - \frac{17,300}{T}$	$<10^{-4}$	Exp.	Exp.	2, 3
Ba	$\log P_{BaO}/C_{Ba^{++}} = 4.8 - \frac{22,500}{T}$	10^{-12}	7, 11	Full (Ba^{++})	2, 5, 1
La	$\log P_{LaO}P_{O_2}^{1/4}/C_{La^{+3}} = 7.3 - \frac{41,800}{T}$	10^{-22}	15	Full (La^{+3})	21, 13, 5, 1
Ce	$\log P_{CeO_2}/C_{CeO^{+2}} = 7.5 - \frac{31,300}{T}$	10^{-12}	15	Full (CeO^{+2})	36, 37, 17
Pr	$\log P_{PrO_2}/P_{O_2}^{1/4}C_{Pr^{+3}} = 4.2 - \frac{24,900}{T}$	10^{-10}	15	Full (Pr^{+3})	36, 37, 17
Nd	$\log P_{NdO}P_{O_2}^{1/4}/C_{Nd^{+3}} = 9.4 - \frac{43,200}{T}$	10^{-20}	15	Full (Nd^{+3})	5

Table 1--continued

Element	Estimated or Measured Thermodynamic Equations for Fallout Formation	Lower P_{O_2} Limit (atm)	Melting Correction References	Silicate Correction	Vapor Pressure References
Pm	$\log P_{PmO} P_{O_2}^{1/4} / C_{Pm^{+3}} = 8.9 - \frac{42,900}{T}$	10^{-18}	1	Full (Pm^{+3})	5
Sm	$\log P_{SmO} P_{O_2}^{1/4} / C_{Sm^{+3}} = 6.7 - \frac{41,400}{T}$	10^{-14}	15	Full (Sm^{+3})	5
Mn	$\log P_{MnO} / C_{Mn^{++}} = 6.8 - \frac{26,400}{T}$	10^{-3}	15	1/2 (Mn^{++})	33, 16, 17, 18, 7
Fe	$\log P_{FeO} P_{O_2}^{1/4} / C_{Fe^{+3}} = 7.5 - \frac{34,100}{T}$	($>10^{-4}$)		1/2 (Fe^{+3})	7, 39, 14, 16, 33, 18
Co	$\log P_{Co} P_{O_2}^{1/2} / C_{Co^{++}} = 9.2 - \frac{33,500}{T}$		15	1/2 (Co^{+2})	7, 14, 33
Ta	$\log P_{TaO_2} P_{O_2}^{1/4} / C_{TaO^{+3}} = 9.3 - \frac{47,600}{T}$			Full (TaO^{+3})	41, 7, 17
W	$\log P_{WO_3} / C_{WO_4^{=}} = 7.8 - \frac{22,200}{T}$	10^{-7}	15	None	42, 23
Pb	$\log P_{PbO} / C_{Pb^{+2}} = 8.4 - \frac{16,700}{T}$	10^{-7}	9	1/2 (Pb^{+2})	43
U	$\log P_{UO_3} / C_{UO_2^{++}} = 5.7 - \frac{21,000}{T}$	10^{-6}	15	Full (UO_2^{++})	46, 7

Table 1--continued

Element	Estimated or Measured Thermodynamic Equations for Fallout Formation	Lower P_{O_2} Limit (atm)	Melting Correction References	Silicate Correction	Vapor Pressure References
Np	$\log P_{NpO_2}/C_{NpO^{++}} = 6.2 - \frac{32,100}{T}$	$>10^{-12}$	15	Full (NpO^{++})	48
Na	$\log P_{Na}/C_{Na^+} = 7.0 - \frac{18,100}{T}$				

Table 2

THERMODYNAMICS OF FUSION OF SELECTED OXIDES

Oxide	Melting Point (°K)	ΔH (kcal/mole)	ΔS (cal/deg-mole)	Equation	Reference	Oxide	Melting Point (°K)	ΔH (kcal/mole)	ΔS (cal/deg-mole)	Equation	Reference
Ga_2O_3	2013	22.	11.	$= \frac{4800}{T} - 2.4$	15	TeO_2	1006	3.2	3.2	$= \frac{700}{T} - 0.7$	15
GeO_2	1389	10.5	7.56	$= \frac{2300}{T} - 1.65$	15	CaI_2	1013	5.0	5.1	$= \frac{1090}{T} - 1.11$	7
As_2O_4	1200	18.0	15.0	$= \frac{3900}{T} - 3.3$	15	BaO	2196	13.8	6.3	$= \frac{3000}{T} - 1.4$	7, 11
SeO_2	613	2.0	3.2	$= \frac{430}{T} - 0.7$		La_2O_3	2590	18.0	7.0	$= \frac{3900}{T} - 1.5$	15
$CaBr_2$	1033	4.2	4.1	$= \frac{900}{T} - 0.9$	7, 8, 11	CeO_2	3000	19.	6.3	$= \frac{2900}{T} - 1.4$	15
CaO	2873	12.2	4.1	$= \frac{2670}{T} - 0.89$	7, 8	Pr_2O_3	2200	22.	10.	$= \frac{4800}{T} - 2.2$	15
SrO	2733	16.7	6.1	$= \frac{3600}{T} - 1.5$	11	Nd_2O_3	2545	22.	8.8	$= \frac{4800}{T} - 1.9$	15
Y_2O_3	2500	25.0	10.	$= \frac{5500}{T} - 2.2$	7	Pm_2O_3	2300	21.	9.0	$= \frac{4600}{T} - 2.0$	15
ZrO_2	2950	20.8	7.0	$= \frac{4550}{T} - 1.52$	7, 8	Sm_2O_3	2150	20.	9.3	$= \frac{4400}{T} - 2.0$	15
Nb_2O_5	1785	24.2	13.56	$= \frac{5280}{T} - 2.96$	7	MnO	2058	13.0	6.32	$= \frac{2840}{T} - 1.38$	15
TcO_2	(2400)	(18.0)	(7.5)	$= \frac{3900}{T} - 1.6$	15	Fe_2O_3	(2000)	(25.)	(12.5)	$= \frac{2700}{T} - 1.4$	Est.
Rh_2O_3	(1500)	(16.5)	(11.)	$= \frac{1800}{T} - 1.2$	Est.	CoO	2078	12	5.8	$= \frac{2600}{T} - 1.3$	15
PdO	(1500)	(7.5)	(5.0)	$= \frac{1650}{T} - 1.1$	Est.	Ta_2O_5	2150	16	7.4	$= \frac{1750}{T} - 0.8$	15
Ag_2O	(1502)	(13.4)	(8.9)	$= \frac{2900}{T} - 1.9$		WO_3	1743	17	9.3	$= \frac{3700}{T} - 2.1$	15
CdO	(1700)	(8.5)	(5.0)	$= \frac{1900}{T} - 1.1$	Est.	PbO	1170	6.1	5.2	$= \frac{1330}{T} - 1.14$	9
In_2O_3	(2000)	(20.)	(10.0)	$= \frac{4400}{T} - 2.2$	15	UO_3	(1500)	(13.2)	(8.8)	$= \frac{2900}{T} - 1.9$	Est.
SnO_2	1898	11.39	5.95	$= \frac{2500}{T} - 1.3$	13	NpO_2	2600	15	5.7	$= \frac{3300}{T} - 1.3$	15

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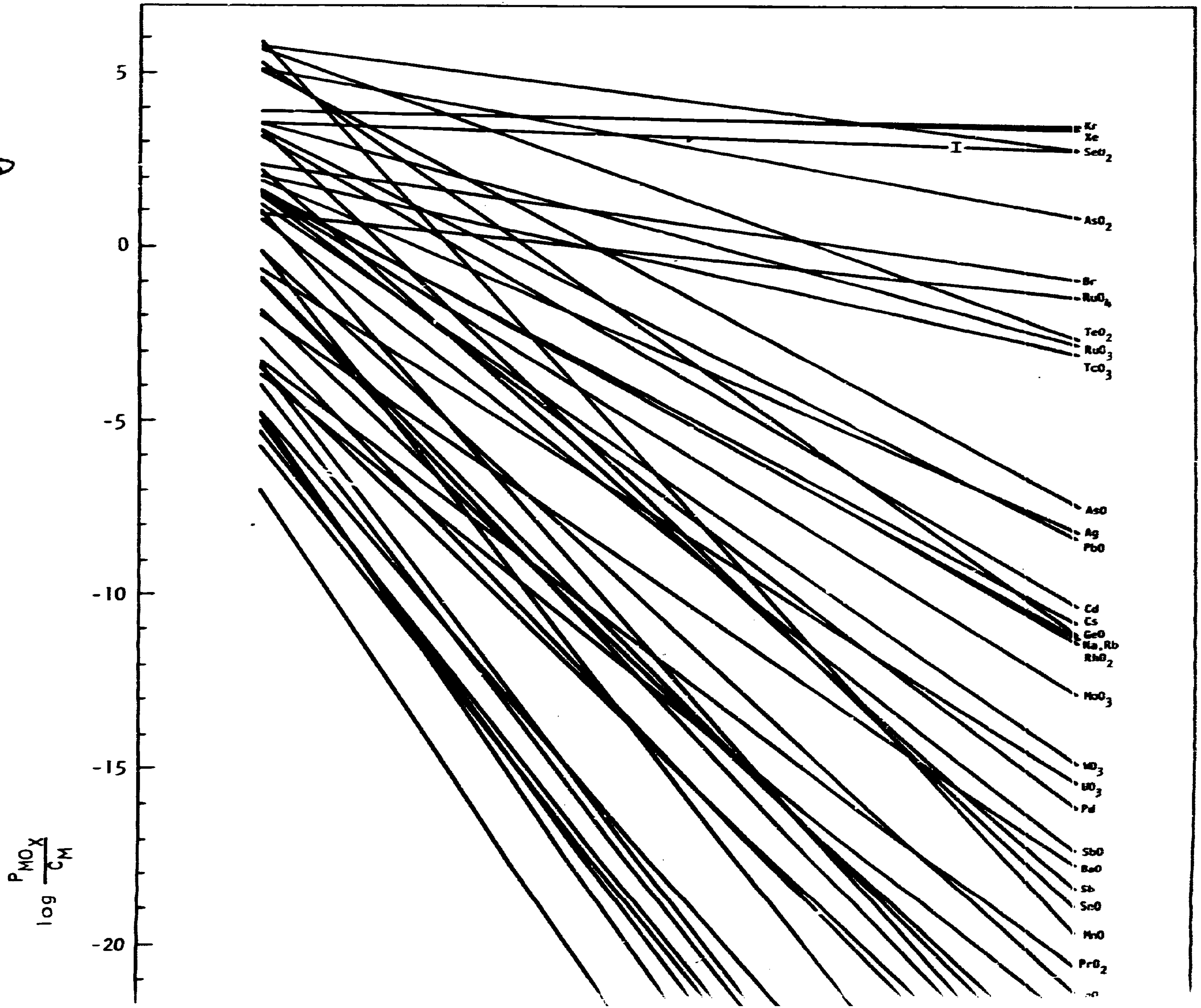
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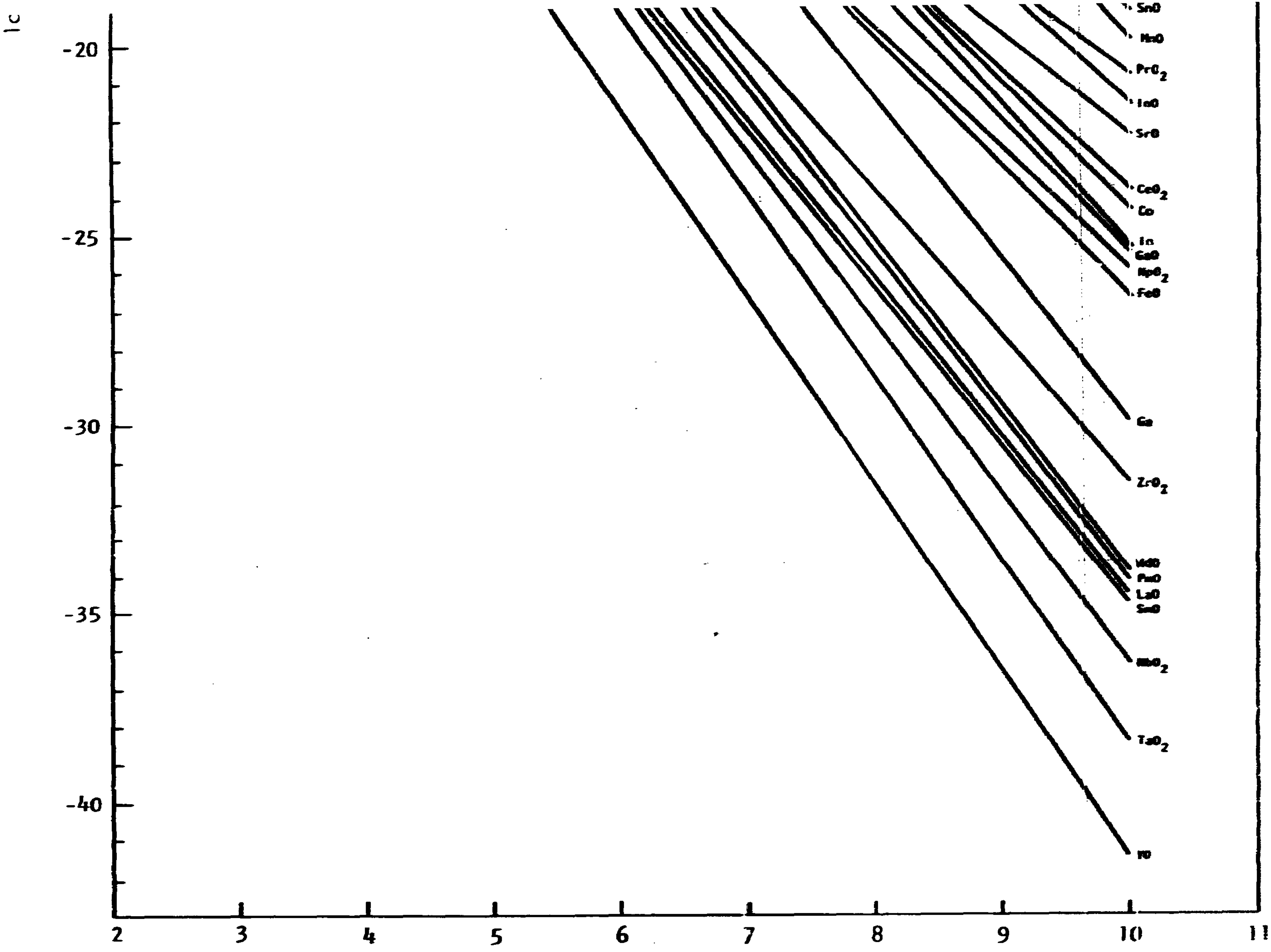

Fig. 1--Henry's Law constants (P_{O_2} = 1 atm)

THERMODYNAMIC BEHAVIOR OF FISSION PRODUCT ELEMENTS

Gallium

Burns'[(12)] representation of the volatility of $GaO(g)$ over Ga_2O_3 was accepted, but it seems apparent that Ga vaporization from $Ga_2O_3(s)$ must be considered as well. Coughlin's[(13)] data on $Ga_2O_3(s)$ formation and Hultgren's[(14)] Ga vaporization data were used for the gallium pressure equation. Glassner's[(15)] melting thermodynamics and one-half the normal silicate correction were applied to these data to describe the behavior of this element in fallout formation.

Germanium

Bedord's[(5)] representation of GeO vapor pressures over GeO_2 and Glassner's[(15)] GeO_2 melting thermodynamics were used. These data give a little lower vapor pressure than Miller's[(1)] representation. No silicate correction was made as it is expected that silicates and germanates will have about the same formation thermodynamics. The species $GeO_2(g)$ may predominate over $GeO(g)$ in one atmosphere of oxygen. This predomination factor, however, is likely to be small, and without further data it seems reasonable to consider $GeO(g)$ as the only gaseous germanium species important in fallout formation.

Arsenic

The Bedord[(5)] presentation was used to represent the vaporization of AsO from As_2O_4. Melting data on $As_2O_4(s)$ was taken from Glassner.[(15)] The condensed species $As_2O_4(s)$ was chosen as a compromise between As_2O_5 and As_2O_3.

An additional equation is also presented in which the dissociation energy of $AsO_2(g)$ was taken as equal to twice the D_0AsO (actually $D_0PO_2 = 2.25\ D_0PO$, $D_0SO_2 = 2.20\ D_0SO$, $D_0SeO_2 = 2.45\ D_0SeO$, and $D_0TeO_2 = 2.75\ D_0TeO$).[(16)] A standard entropy of the reaction $MO(g) + 1/2O_2 \rightarrow MO_2(g)$, according to Searcy[(17)] (-17.1 e.u.), was accepted.

Selenium

Coughlin(13) gives the sublimation point of SeO_2 as 595°K and the heat of sublimation at this temperature as 21.0 kcal/mole. Since an entropy of melting of $SeO_2(s)$ is not available, it has been assumed to be equal to the entropy of melting of TeO_2, according to Glassner.(15) Kubaschewski(11) suggests a melting temperature of 613°K.

At 2000°K and 1 atm O_2, SeO and Se will be almost as important gaseous species as SeO_2, and at 1500°K and 1 atm O_2, SeO_2 is 1000 times more important than SeO, according to Bedford.(5) Incorporation of Se into fallout particles should occur at very low temperatures, where SeO_2 strongly predominates. Thus, the data on SeO_2 alone would seem to suffice for fallout formation calculations.

Bromine

An appropriate reaction to describe either bromine or iodine behavior in fallout is not readily apparent. Certainly both of these elements form volatile salts, and Miller(1) has chosen the volatility of the sodium halides to describe these systems. It is believed now, however, that displacement of the atomic halogen by oxygen would give a better description of the volatilities. The suggested fallout reaction is

$$1/2\ SiO_2(l) + X^- + 1/4\ O_2 \rightarrow 1/2\ SiO_3^=(l) + X(g)\ .$$

Although X^- might be bound to silica, it will be assumed that this interaction is negligible. In any case, data for evaluating this interaction are meager.

Available thermodynamics for this reaction would, indeed, indicate that both bromine and iodine behave as extremely volatile elements during fallout formation. The oxidation of $CaBr_2(l)$ to CaO(l) was taken to represent this system. Wicks'(7) values for the heats of formation of CaO and $CaBr_2$ were used with $CaBr_2(c)$ fusion data.(7, 8, 11) The silicate correction described earlier and the bromine dissociaton data from Stull and Sinke(18) were used.

Krypton

The boiling point and the heat of vaporization of krypton were taken from Stull and Sinke.(18) Volatility is obviously high in fallout formation using the equation in Table 1, but the main question would be whether the volatility is underestimated with these data. This question, however, does not appear to be very important, since this element will be only slightly condensed at working temperatures.

Rubidium

The recommended equation for rubidium is a central value of our experimentally measured rubidium absorption in $CaO \cdot Al_2\text{-}SiO_2$ samples.(3) This value is several orders of magnitude below the expected Rb(g) pressures over rubidium oxide. The variation may be attributed to non-ideality of the silicate solution, and, since it is highly questionable whether Rb(g) is the volatile species in our experiments, the rubidium oxide-silicate system solutions may be more non-ideal than those data would indicate.

Strontium

The basis for this estimation is the strontium oxide vaporization studies made under an OCD contract.(2) The vapor pressures of strontium oxide presented in this report are in reasonable agreement with Bedford(5) but are somewhat different from those presented by Miller.(1) A full silicate correction for $O^{=}$ from strontium oxide going to $SiO_3^{=}$ was made, as outlined earlier. Melting thermodynamics as given by Kubaschewski(11) were used. His heat of fusion of 16.7 kcal/mole, however, seems somewhat high when compared with 12.2 and 13.8 kcal/mole, respectively, for CaO and BaO. Kubaschewski gives 19.0 kcal/mole for the heat of fusion of CaO, instead of the 12.2 kcal/mole used in this report. If ΔH_f of CaO is 19.0 kcal/mole, then 16.7 kcal/mole is reasonable for ΔH_f of SrO. This problem, however, cannot be considered a major difficulty.

Yttrium

Bedford(5) and Miller(1) present data on YO vapor pressure which do not differe appreciably; Miller's value is about an order of magnitude higher than Bedford's value at 1800°K. Ackermann, Rauh, and Thorn(19) give values which when extrapolated to 2000°K are about an order of magnitude lower than Bedford's values. The values given by Ackermann have been accepted here, and the values given by Wicks(7) for the melting temperature and heat of fusion of Y_2O_3 have been used, although Schneider(20) would indicate a higher melting temperature.

Zirconium

Zirconium dioxide vapor pressures given by Bedord(5) and Miller(1) are close, but differ by about an order of magnitude. Although for zirconium it probably makes little difference to fallout formation, Bedord's values were used. In addition, Ackermann and Thorn(21) give values about an order of magnitude higher than Bedford's and two orders of magnitude higher than Miller's. Melting data used for $ZrO_2(s)$ were those reported by Kelley.(8) Since ZrO^{++} ions are kno [illegible] felt that it would be reasonable to consider the silicate co [illegible] the basis of

$$ZrO_2 + SiO_2 \rightarrow Zr \text{ [illegible] } SiO_3^{=} .$$

Niobium

Experimental data for this element are essentially negligible. Vapor pressures presented by Miller(1) and Beford(5) differ by quite a few orders of magnitude. Using the estimations of $NbO_2(g)$ formation values given by Brewer and Rosenblatt,(22) $Nb_2O_5(c)$ data from Wicks,(7) O data from Stull and Sinke,(18) and Nb(g) data from Hultgren,(14) thermodynamic values for the reaction

$$1/2\ Nb_2O_5(s) \rightleftarrows NbO_2(g) + 1/4\ O_2$$

are very close to the values presented by Bedord;(5) therefore, his values are accepted in lieu of experimental data. Melting data for $Nb_2O_5(c)$ were presented by Coughlin(13) and Wicks.(7) The silicate correction was applied for the formation of an NbO^{+3} ion.

Molybdenum

Work performed at General Atomic has led to an estimation of the volatility of molybdenum from silicate matrices.(2) The estimate for CaO-Al_2O_3-SiO_2 eutectic would appear to be somewhat high for fallout considerations because calculations show that polymeric gaseous molybdenum oxides were present in the experimental study. We have corrected the data for polymers according to data given by Norman(23) and Burns.(24) The resulting data for $MoO_3(g)$ vaporizing from the silicate are presented in Table 1.

Technetium

The reported technetium oxide species probably will have little to do with the history of this element in fallout formation. It would seem more reasonable to consider a $TcO_3(g)$ species as the dominant oxide species in fallout formation situations. For this report, this was done by using Bedord's(5) presentation on $Tc(g)$, $TcO(g)$, $TcO_2(g)$, $Tc_2O_7(g)$, and appropriate vapor pressures over $TcO_2(s)$ in an oxygen atmosphere. From Bedord's presentation, bond energies at 1500°K for Tc-O bonds in TcO and TcO_2 were calculated as 129 kcal/mole. For Tc_2O_7, the bond energy is 121 kcal/mole, if Tc_2O_7 has eight Tc-O bonds (10 TcO bonds are probable). However, it seems reasonable to use 129 kcal/mole for the third Tc-O bond in $TcO_3(g)$, according to an additivity rule. The entropy difference between the formation of $MoO_2(g)$ and $MoO_3(g)$(5) was used as the entropy difference between the formation of $TcO_2(g)$ and $TcO_3(g)$. These calculations suggest that $TcO_3(g)$ is important and lead to the formula used to describe technetium absorption in Table 1, using the melting correction of Glassner.(15) The species $Tc_2O_7(g)$ has been discounted here because of its polymeric nature.

Ruthenium

Ruthenium vaporization from silicates has been measured in a cursory manner.(2) These measurements would indicate a somewhat higher volatility than would be estimated by Bell's(25) data on RuO_4 and RuO_3 vaporization. The silicate measurements, in addition to not being very accurate, were made at only one temperature. For this reason, an equation was derived from Bell's data and the experimental silicate data, by altering Bell's pressure data at 1400°C so that the higher experimental pressure was obtained half through enthalpy changes and half through entropy changes.

Rhodium

There has been quite a bit of confusion about the oxides of this element in both the gas and condensed phases. We are accepting Bell's(26) statement that Rh_2O_3 is the only stable, condensed, high-temperature oxide of rhodium. Norman(27) has observed the gaseous oxides RhO and RhO_2 but does not give complete thermodynamic data. Alcock(28) does give values for the thermodynamics of formation of $RhO_2(g)$. These latter data are the basis for the description of rhodium in this report. The melting temperature of Rh_2O_3 was taken as 1500°K and the entropy of fusion as 11 e.u. (Bedford(5) reported $Rh_2O_3(l)$ at 1500°K without further discussion. This temperature has not been properly evaluated, but will be used here in lieu of better information.)

Palladium

Palladium vapor pressures as given by Norman(29) and PdO(s) formation data as given by Coughlin(13) have been used. At temperatures of interest, gaseous palladium oxide is almost as volatile as palladium metal in an atmosphere of oxygen; at lower oxygen pressures PdO(g) becomes less important, as shown by Norman, and it is believed that PdO(g) need not be considered. The fusion thermodyanmics for PdO were only assumed.

Silver

The behavior of silver in fallout formation is based on the fact that (1) silver has been found in silicates only in ionic form(30) and (2) that gaseous silver oxides have not been observed. Therefore, Coughlin's(13) $Ag_2O(s)$ data and Hultgren's(14) silver vapor pressures have been used in estimating the silver values in this report. The Cu_2O melting data given by Wicks(7) were used for Ag_2O and one-half the normal silicate correction term was used.

Cadmium

Cadmium oxide is assumed to behave similar to silver. Coughlin(13) gives sufficient data to estimate cadmium pressures above CdO(s). Bedford's(5) pressure values for CdO are quite small; so, this species can be neglected. Melting data are unavailable. The melting point was assumed to be 1700°K and the entropy of melting to be 5.0 e.u. In addition to the melting correction, one-half the normal silicate correction was applied. Zinc silicate has a low heat of formation(31) from the oxides, suggesting that the use of a reduced silicate correction term (one-half normal), as used for CdO, is reasonable.

Indium

Calculations of the vapor pressure of InO over $In_2O_3(s)$ were made according to Bedord,(5) Hultgren,(14) and Coughlin.(13) These data were corrected for melting at 2000°K according to Glassner,(15) (Miller(1) claims 1500°K and Schneider(20) gives 2183°K), and one-half the normal silicate correction was applied. The InO data are uncertain as it is apparent that Burns'(32) dissociation energy of InO(g), on which one of the equations developed here is based, is somewhat doubtful.

Tin

Johnston(33) indicates Sn^{+4} to be the important valence state in certain glasses in a highly oxidizing atmosphere. Colin(34) has presented a new value for the dissociation energy of SnO(g) and Koenig(35) gives a value similar to Colin's D_o. From Colin's vapor pressure data for SnO(g) over SnO_2(c), the melting data of Coughlin,(13) and one-half the silicate correction for SnO^{++}, the formula reported here is obtained. These data, although somewhat different from those of either Miller(1) or Bedford,(5) do not result in very different vapor pressure values. In the case of this element, there is a question as to whether SnO_2(g) might be important.

Antimony

Both experimental silicate data(2) and oxide information are available to formulate a description of this element in fallout formation. The experimental information is really very meager as it consists of data at only a single temperature and is questionable because of antimony absorption by platinum.(2) In addition, it seems probable that the principal gaseous species present when these data were measured was Sb_4O_6(g). If this is the case, these data (pressure over concentration) would be too high, by three orders of magnitude, for use in fallout calculation; in this report, it is assumed that this is the case. Antimony behavior in fallout formation will be used as described by Bedford's(5) Sb(g) and SbO(g) pressures over Sb_2O_3(1) with no corrections. Johnston(33) points out that Sb^{+3} and Sb^{+5} each have a range of importance in glasses. One further question would be the possible importance of SbO_2(g). If this species has a dissociation energy >150 kcal/mole, its role in fallout formation should become dominant. This question is not resolved at present.

Tellurium

An apparently reliable experimental pressure for tellurium has been reported;(2) however, no temperature dependence associated with this value was given. It seems certain that TeO_2(g) is the species that should be considered here. Bedford's(5) data on TeO_2(s) vaporization to TeO_2(g), corrected to the experimental Te pressure from the silicate by making half the total adjustment in the entropy term, have been used to describe tellurium behavior in fallout formation. It should be noted that Bedford's data give a vapor pressure only one order of magnitude smaller than the experimental silicate numbers. A melting correction for $TeO_2(s)$ was made from Glassner's(15) data.

Iodine

Calculations assuming I^- as the dissolved species and I as the gaseous species were made in a similar manner to those for bromine. Using Wicks'(7) formation thermodynamics for $CaI_2(s)$ and CaO(s) and also his melting thermodynamics and Stull's(18) values for I(g), an estimating formula was derived. This formula was corrected for silicate formation of the CaO, but CaI_2 was assumed not to interact. A rough experimental point has also been obtained at 1470°K. This point indicates that the estimating formula for pressures is too low by about three orders of magnitude. The formula, however, does seem to be giving pressures high enough so that any higher value will not appreciably change the calculated behavior of I in fallout formation.

Xenon

Stull's(18) values for the thermodynamics of vaporization of Xe were used to represent the Henry's Law constants from a molten silicate. It is probable that Xe volatility is underestimated by this equation, but this probably is not a severe problem to fallout simulation calculations. The belief that underestimation exists stems from the feeling that activity coefficients of Xe (or Kr) in these solutions would be expected to be higher than ideal. That is, one should not be surprised if the ionic silicate matrix strongly "salted out" non-polar atoms, as it seems to do for metal atoms such as silver.(30)

Cesium

Cesium behavior is reported according to the averaged experimental results of Norman.(2, 3) These data give considerably smaller vapor pressures for cesium at temperatures of interest in fallout formation than Miller(1) or Bedford(5) would suggest, using the normal silicate correction term.

Barium

Norman,(2) Bedford,(5) and Miller(1) are all in reasonable agreement on the vapor pressure of BaO over BaO(g). Norman's data were used together with melting data by Kubaschewski(11) and Wicks.(7) The normal silicate formation correction term was applied.

Lanthanum

The data on free energy of formation of gaseous LaO by Ackermann and Thorn(21) were used with Coughlin's(13) data on La_2O_3(s). These data are comparable to those given by both Bedford(5) and Miller.(1) Melting data on La_2O_3(s) reported by Glassner(15) were used, together with the full silicate correction.

Cerium

Recently, White(36) has observed CeO_2(g) over CeO_2(s), but he has only semiquantitative data on the dissociation energy of CeO_2(g). He has suggested(37) that this energy might be considered as 180% of the dissociation energy of CeO(g) and gives the dissociation energy of CeO(g) as 140 kcal/mole. Pressures of CeO(g) and CeO_2(g) can be compared by using the above dissociation energies, the dissociation energy of oxygen, and Searcy's average entropy(17) for the reaction $MO(g) + 1/2\ O_2 \rightleftarrows MO_2(g)$ of -17.1 e.u. Heat capacity data for the above reaction for Zr were assumed to apply to Ce in order to develop the equilibrium constant equation. These data were applied to Bedford's(5) CeO(g) vapor pressures over CeO_2(s). The obtained CeO_2 pressures were corrected for CeO_2 melting, according to Glassner,(15) and silicate formation to CeO^{++}.

Praseodymium

Similar to the case of Ce, White(36) has observed the gaseous species $PrO_2(g)$. Using the same estimating system for PrO_2 pressures (D_0 PrO_2 = 1.80 D_0 PrO) and Bedford's(5) PrO pressures over $Pr_2O_3(s)$, pressures of $PrO_2(g)$ over $Pr_2O_3(s)$ can be calculated. These data were corrected for Pr_2O_3 melting, according to Glassner,(15) and for silicate formation.

Neodymium

Pressures of this element over $Nd_2O_3(s)$ were taken from Bedford's(5) representation. The $Nd_2O_3(s)$ melting data by Glassner(15) and the full silicate correction were used.

Promethium

Bedford's(5) data on the volatility of $Pm_2O_3(s)$ served as a basis for the estimation. Glassner's(15) presentation of Nd_2O_3 and Sm_2O_3 melting data were averaged to obtain melting thermodynamics. The resulting melting point is in good agreement with Miller's(1) value. A full silicate correction was applied to this system.

Samarium

Bedford's(5) representation was used for Sm. Although Schneider(20) would indicate higher melting temperature, correction for melting of $Sm_2O_3(c)$ was made according to Glassner,(15) and a full silicate correction was employed.

THERMODYNAMIC BEHAVIOR OF IMPORTANT ACTIVATED ELEMENTS

In estimating the total activities associated with a nuclear event, activation of certain elements which may be associated with the device or its surrounding should be considered. The histories of these activated elements should be traced in a manner consistent with their formation.

Elements that are associated closely with the nuclear device are probably best handled by considering them in a manner similar to fission products. There is, however, some question of how to handle activated elements from the detonation site. It has been suggested(2,3) that condensed-state diffusion limitation of fission-product absorption by fallout should be important. Accordingly, evaporation of activated products from soil particles, which do not experience very high temperatures, should be rate controlling, and even with highly volatile activation products there may be considerably less fractionation of volatile activation products, formed in the fallout particle matrix, than of volatile fission products. Also, an activated product may be more than a trace element; therefore interaction may occur in the gas state leading to polymerization. With these points in mind, only important activated products that might reasonably be associated with the nuclear device need be considered here. The list developed with the aid of P. LaRiviere(38) includes Mn, Fe, Co, Ta, W, Po, U, and Np. The thermodynamic behavior of the Na is listed, but it is suggested that the data may not be applicable in the same manner as the rest of the data since it should be present mainly from the activation of fallout particle matrix or saltwater.

Manganese

Johnston(33) suggests that Mn^{+2} predominates over Mn^{+3} in a high-temperature glass at 1 atm O_2 pressure. Wicks'(7) values for MnO(c) formation, Stull's(16) O values, and Brewer's(16) estimate of MnO bond energy, together with Searcy's(17) entropy for $M(c) + 1/2\ O_2 \rightleftarrows MO(g)$ were used to describe Mn behavior. Glassner(15) gives the melting data for MnO(c), which was used. One-half the normal silicate correction for Mn^{++} formation was used.

Iron

Trivalent iron predominates in a soda-silica glass at 1 atm air up to about 2500°K.(33) For this reason dissolution of Fe_2O_3 in glass was used to describe iron behavior. Data for $Fe_2O_3(c)$ were taken from Wicks' report(7) and data for FeO(g) were taken from Washburn's paper,(39) using Brewer's(16) estimate of the dissociation energy of this molecule. Hultgren's(14) compilation was used for iron vapor pressure and Stull's(18) thermodynamic values for O dimerization were used. Fe_2O_3 was assumed to melt at 2000°K and have an entropy of melting of 12.5 e.u. The melting correction was made according to these estimates and the silicate correction was made on the basis of one-half the normal correction for Fe^{+3} formation.

Cobalt

Johnston(33) indicates that Co^{+2} is the stable cobalt valence in a high-temperature glass at 1 atm oxygen. Estimates made from Brewer's(16) gaseous monoxide dissociation energy estimates and Norman's(40) studies on noble metal oxides suggest that CoO(g) will not be important. Therefore Wicks'(7) data on CoO(c) formation and Hultgren's(14) cobalt vapor pressure data were used. Glassner's(15) melting data were used for CoO(c). One-half the normal silicate correction was used.

Tantalum

Krikorian's(41) description of $TaO_2(g)$ and TaO(g) thermodynamics and Wicks'(7) $Ta_2O_5(c)$ values were used in conjunction with Searcy's(17) average entropy of formation of $MO_2(g)$ molecules to describe Ta behavior in fallout formation. The ΔCp for the formation reaction of $TaO_2(g)$ was assumed to be zero. Glassner's(15) melting data for Ta_2O_5 were used and a silicate correction for the formation of a TaO^{+3} ion was applied.

Tungsten

Ackermann and Rauh(42) presented some rather detailed data on the vaporization of tungsten oxides. The formation thermodynamics used here for $WO_3(c)$ and $W_3O_9(g)$ have been extracted from their article. Norman(23) has presented trimerization thermodynamics for $WO_3(g)$. These data, together with Glassner's melting thermodynamics data,(15) were used to calculate the values of Table 1. No silicate correction was used.

Lead

Wicks'(7) representation of the formation of solid oxides of lead is such as to suggest that PbO is the stable oxide at temperatures above 1000°C and at 1 atm oxygen pressure. The JANAF(9) tables give thermodynamics for yellow lead oxide. Also, Drowart(43) has presented the thermodynamics of sublimation of PbO(g) and gaseous polymers of PbO. The polymer data are unimportant in this presentation. Melting data were taken from the JANAF(9) tables and one-half the normal silicate correction was made. This correction assumes an activity coefficient PbO of $\sim$0.01 at 1200°K. An activity coefficient of $\sim$0.1 at this temperature in acidic silicates is reported by Richardson.(44)

Uranium

Stevels(45) discusses U^{+6} as either a network former or a network modifier in glasses. In acidic glasses it should be a network modifier, and it is so treated here. The thermodynamics of UO_3(c) as described by Wicks(7) and the thermodynamics of gaseous species UO_3 (and UO_2) described by Ackermann(46) are considered to govern this system. The melting point of UO_3(c) was estimated to be 1500°K, and the entropy of fusion was estimated as 8.8 e.u. The silicate correction was made as though UO_2^{++} was the important ion in solution, although $UO_4^{=}$ might be as good a choice. The thermodynamics used are closer to Bedford's(5) estimates than to Miller's.(1)

Neptunium

According to Katz and Seaborg,(47) condensed neptunium oxides are less stable than the equivalent uranium oxides; so much so that the stability of NpO_2 is compared with that of U_3O_8. Although Np^{+6} compounds are known, it will be assumed that hexavalent neptunium is not stable enough to be considered the existing species in glass under fallout conditions. Pentavalent neptunium might be considered if proper data were available.

Ackermann's(48) paper describing the partial pressures of NpO and NpO_2 over $NpO_2(c)$ was used in describing this element. Glassner's(15) NpO_2 fusion thermodynamics were used with a full silicate correction for NpO^{++}.

Sodium

Studies(49) of the gaseous molecules Cs_2O, Rb_2O, and Na_2O have led to the fact that there is not much difference in the bond energies of any of these metals with oxygen in these species. Other studies(2, 3) suggest that Cs and Rb are evaporating from silicates as some molecular species. Thermodynamic data on this process with sodium are nonexistent. For these reasons, the Henry's Law constant formulation for Rb was used for Na.

GENERALIZED BEHAVIOR OF FISSION PRODUCT CHAINS DURING FALLOUT FORMATION

Fallout formation is considered to be governed basically by a two-step process: (1) absorption of fission product oxide from the gas phase into the surface layers of a fallout particle and (2) diffusion of this fission product into the bulk of the fallout particle.(2, 3) Using diffusivities that we have measured for fission products in a $CaO{-}Al_2O_3{-}SiO_2$ glass matrix(2, 3) and the thermodynamics reported here, the behavior of a particular nuclide during fallout can be calculated. A cursory estimate can be made of the nature of the absorption process. Such an estimation has been made in Tables 3 and 4 for a megaton-yield detonation, about as many moles of condensed soil as gas in the fireball as Miller(50) has employed, and 100μ particles. The description in these tables depends to only a slight degree on these parameters (the parameter to which fallout absorption is the most sensitive is particle size). Table 3 suggests which elements will govern each nuclide chain behavior. Table 4 describes the character of the absorbing nuclides. The character of any particular fission-product chain in collected fallout can be estimated by using Table 3 to decide which elements govern the fate of the fission-product chain, and using Table 4 to suggest the type of absorption expected for the determining elements.

Table 3

ELEMENTS WHOSE CHEMICAL BEHAVIOR CHARACTERIZES DISTRIBUTION OF GIVEN NUCLIDE CHAINS IN FALLOUT

Nuclide Chain	Element*	Nuclide Chain	Element*	Nuclide Chain	Element*
77	Ga, Ge	105	Nb, Mo,(Tc)	133	(Sn), Sb, (Te)
78	Ga, Ge	106	(Nb), Mo, Tc,(Ru)	134	Sb, Te, (I)
79	(Ga), Ge,(As)	107	(Nb, Mo), Tc,(Ru)	135	Te, (I)
80	(Ga), Ge,(As)	108	Tc,(Ru)	137	I, Xe
83	(Ge, As),Se	109	Ru, Rh	138	Xe, (Cs)
84	(Ge),Se,(Br)	111	(Ru),Rh	139	Xe, (Cs)
87	Se, Br,(Kr)	112	Rh, Pd	140	Xe, Cs
88	(Br),Kr	113	Rh, Pd	141	Cs, (Ba)
89	Kr,(Rb)	114	Rh, Pd	142	Cs, Ba
90	Kr, Rb	115	(Rh), Pd	143	Ba,(La)
91	(Kr), Rb	116	(Rh), Pd, Ag	144	Ba, La
92	Rb, (Sr)	117	Pd, Ag	145	(Ba), La
93	Rb, Sr	118	Pd, Ag	146	(Ba), La, Ce
94	(Rb), Sr	119	Pd, Ag	147	(La), Ce
95	(Rb),Sr	120	(Pd, Ag), Cd	148	(La), Ce
96	Sr,(Y)	121	(Pd, Ag), Cd	149	Ce, Pr
97	Sr, (Y)	123	Cd, In	151	Pr, Nd
98	(Sr), Y,(Zr)	125	Cd, In	152	Pr, Nd
99	(Sr), Y, Zr,(Nb)	126	(Cd), In, (Sn)	153	(Pr), Nd
100	(Y), Zr,(Nb)	127	In, Sn	154	Nd, (Pm)
101	(Y), Zr, Nb	128	In, Sn	155	Nd, Pm
102	Zr, Nb, (Mo)	129	(In), Sn, (Sb)	156	(Nd), Pm
103	(Zr), Nb, Mo, (Tc)	130	(In), Sn, (Sb)	157	(Nd), Pm, (Sm)
104	Nb, Mo,(Tc)	131	Sn, (Sb)	158	Pm, Sm
		132	Sn, Sb,(Te)		

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*Elements in parentheses have between an ~5% and ~25% role in the chemistry of the particular chain during formation of fallout. The elements mainly determining

Table 4

GENERAL BEHAVIOR OF ELEMENT IN FALLOUT FORMATION

Element	Designation	Element	Designation
Ga	U	Ag	G
Ge	M	Cd	M
As	G	In	U
Se	V	Sn	M
Br	S	Sb	M
Kr	V	Te	S
Rb	M	I	V
Sr	U	Xe	V
Y	U	Cs	M
Zr	U	Ba	U
Nb	U	Ce	U
Mo	M	Pr	U
Tc	S	Nd	U
Ru	S	Pm	U
Rh	G	Sm	U
Pd	M		

T°K	P/C	Designation	Explanation
2000	$<10^{-3}$	U (uniform loading)	Little gradient
1500	$<10^{-3}$	M (mixed behavior)	Appreciable gradient, some bulk loading
1000	$<10^{-3}$	G (gradient)	Well-established gradient
500	$<10^{-3}$	S (surface concentrated)	Near surface gradient
500	$>10^{-3}$	V (vapor)	Little penetration

This estimation of the type of fission-product distribution in fallout can be used for simulation purposes. That is, fallout simulants for fission-product chains, whose behavior-determining elements are listed as M, G, and S in Table 4, should be prepared by some incomplete diffusion process. For systems described by U, preparing a uniform distribution would be better but for V a surface-deposited element would be preferred. Mixtures should be considered where these tables suggest this to be proper. This method of using the data in this report certainly is not intended to be the primary purpose, but may represent an additional value.

With this report and a planned similar report presenting diffusion constants and a method for using these values, the calculation of distribution of fission products in a silicate-type fallout should be greatly improved.

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