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MASS SPECTROMETRY STUDIES OF FISSION PRODUCT BEHAVIOR
II. GAS PHASE SPECIES

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ABSTRACT

Revaporization of fission products from reactor system surfaces has become a complicating factor in source term definition. Critical to this phenomena is understanding the nature and behavior of the vapor phase species. This study characterizes the stability of the CsI•CsOH vapor phase complex. Vapor pressures were measured with a mass spectrometer. Thermodynamic data were obtained for CsOH(g), $Cs_2(OH)_2$(g), CsI(g), Cs_2I_2(g) and CsI•CsOH(g). Activity coefficients were derived for the CsI-CsOH system. The relative ionization cross section of CsOH is about ten times the cross section of CsI(g). CsI•CsOH fragments to Cs_2OH^+ and an iodine atom.

1. INTRODUCTION

The revolatilization of fission products from reactor system surfaces due to self-heating of the deposits by radioactive decay has become a complicating factor in the source term definition effort. Further, revaporization has had a major impact on calculations of fission product distribution during degraded core accidents. As currently modeled in PWR systems, this process will result in the delayed evolution of volatile fission products from the primary coolant system, thus increasing the containment airborne inventory at times when containment integrity may be less certain. In some BWR accidents, this process will cause eventual transport of most of the volatile fission products out of the drywell containment volume. In an experimental program focused on the characterization of vapor and aerosol transport, CsI and CsOH vapors were

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studied separately and together in flowing steam under a temperature gradient (from 1273 to 500 K). Analysis of the condensate revealed that the dew point of the iodine-carrying species was lower than expected when both CsI(g) and CsOH(g) were present in the gas mixture.[1] In order to explain this result it was postulated that CsI and CsOH formed a more volatile complex, i.e., CsI•CsOH(g), thereby, reducing the partial pressure of CsI(g) in the vapor.

In the current experimental effort, we investigated the iodide-hydroxide (CsI•CsOH) vapor species over a solution of CsI and CsOH. For these studies baseline data for CsI and CsOH were established separately and then the CsI-CsOH mixture was studied. A review of the literature showed fairly good agreement for the thermodynamic properties of CsI(g) and Cs_2I_2(g) in papers by Akishin,[2] Matsumoto,[3] Winchell,[4] Venugal,[5] and Barin.[6] The JANAF Tables showed a moderate uncertainty for the thermodynamic properties of the CsOH(g) monomer, and a large uncertainty for those of the $Cs_2(OH)_2$(g) dimer.[7] No data were found for CsI•CsOH(g).

2. EXPERIMENTAL

An Extranuclear quadrupole mass spectrometer was used to measure the partial pressures of vapor species over CsOH(l) held in a silver Knudsen cell. The Knudsen cell was heated in a tungsten resistance furnace. Temperatures were measured with a chromel alumel thermocouple inserted in a well in the Knudsen cell. The ion current for each of the positive ions was measured, multiplied by the absolute temperature, and plotted in Fig. 1. The top curve is for Cs^+, which is believed to be a fragment of the CsOH(g) monomer; the second curve is for $CsOH^+$; and the third curve is that for Cs_2OH^+, a fragment of $Cs_2(OH)_2$(g). CsOH(g) and $Cs_2(OH)_2$(g) pressures were calculated from the $CsOH^+$ and Cs_2OH^+ ion peaks. A silver Knudsen cell was also used in the mass spectrometric study of cesium iodide vapor where Cs^+, CsI^+ and Cs_2I^+ ion intensities were measured. Cs^+ is a fragment of the CsI(g) monomer and Cs_2I^+ is a fragment of $Cs_2I_2(g)$. The CsI^+ and Cs_2I^+ ions were used to calculate CsI(g) and $Cs_2I_2(g)$ pressures.

The partial pressures of the vapor species CsI(g), $Cs_2I_2(g)$, CsOH(g), and $Cs_2(OH)_2(g)$ over solutions of CsOH in CsI have been measured using the mass spectrometer. In these measurements, the ion intensities of the four gases, CsI, Cs_2I_2, CsOH, and $Cs_2(OH)_2$ were measured continuously with time and temperature. The ions detected were CsI^+, Cs_2I^+, $CsOH^+$, and Cs_2OH^+; the dimers lose either I or OH during the ionization process. When the samples were loaded into the silver Knudsen cell, the initial amount of CsI and CsOH was determined by weighing the cell before and after each addition. The CsOH used in our experiments contained about one mole of water per mole of CsOH. To remove the water of hydration, the loaded Knudsen cell was placed in a silver tube inside a quartz tube surrounded by a resistance furnace. Helium was flowed over the cell while slowly increasing the temperature to about 450°C. The temperature was held in this range for at least two hours. The Knudsen cell was cooled in flowing helium and then weighed to determine water loss; then it was immediately placed in the vacuum chamber of the mass spectrometer. This procedure allowed us to determine the initial composition of the CsI-CsOH sample. The final composition was determined by weighing the sample residue and chemical analysis of the residue after a series of pressure measurements.

To convert ion intensities to pressures it is necessary to determine the constant K in the formula,

$$P = K\,I\,T, \tag{1}$$

where P is the pressure in atmospheres, I is the ion intensity and T is the temperature in Kelvin. For this purpose the Langmuir equation is used,

$$P = \frac{wt \sqrt{T}}{44.33\ A\ t \sqrt{M}} \tag{2}$$

where wt is the weight lost, M is the molecular weight of the gas, A is the area of the Knudsen cell orifice corrected for the Clausing factor[8] and t is the time in seconds. The reciprocal of the constant K is calculated by combining the two equations,

$$\frac{1}{K} = \frac{44.33\ A \sqrt{M}\ \int I \sqrt{T}\, dt}{wt} \tag{3}$$

where wt is the weight of CsI or of CsOH vaporized. Equation (3) is numerically integrated over the total time, corresponding to the total weight loss, to obtain the constant K. Pressures were then calculated from Eqn. 1. The constant for the dimer is one-half that of the monomer assuming that the ionization cross section for the dimer is twice that for the monomer. The pressure is inversely proportional to the ionization cross section. The constant was determined for each set of measurements to minimize the effects of misalignment of the molecular beam from the Knudsen cell or other possible nonreproducible effects. For the conditions of our experiments, the values of the constants were approximately $K_{CsOH} = 10^8$ and $K_{CsI} = 10^9$ atm/amp/deg K. This means that the ionization cross section of CsOH(g) is about ten times higher than the cross section of CsI(g). The cesium iodide and hydroxide molecules were ionized with 30 ev electrons.

3. RESULTS AND DISCUSSION

3.1 Partial pressures over CsOH and over CsI

Equations 1, 2 and 3 were used to calculate pressures of CsOH, $Cs_2(OH)_2$, CsI, and Cs_2I_2 gas over liquid CsOH and CsI. It was assumed that the ionization cross section of the dimer is twice that of the monomer. The total weight loss for each measurement (i.e., over CsOH and over CsI) was apportioned to the monomer and dimer by √2 times the intensity ratio of monomer to dimer for each system. Third-law calculations were carried out using JANAF[9] free energy functions for CsOH(c), CsOH(l), CsOH(g), and $Cs_2(OH)_2$(g). Estimated[10] free energy functions for CsI(c), CsI(l), CsI(g), and Cs_2I_2(g) were used to calculate the heats of vaporization of CsI(g) and Cs_2I_2(g). These values were based on thermodynamic properties listed in NBS Technical Note 270-8[11] and heat content of solid and liquid data of Kaylor, Walden, and Smith.[12] Values for Cesium and iodine were taken from JANAF.[13] The free energy functions for gaseous CsI and Cs_2I_2 were also estimated[10] using the data of Welch et al.[14] and of Rusk and Gordy.[15]

Third-law calculations for the heat of vaporization ($\Delta H_{vap\ 298}$) yielded 36.330 ± 0.448 kcal/mol for CsOH(g), 37.199 ± 0.727 kcal/mol for $Cs_2(OH)_2$(g), 45.039 ± 0.315 kcal/mol for CsI(g), and 55.931 ± 0.519 kcal/mol for Cs_2I_2(g) where the uncertainty is one standard deviation. The experimental data are presented in Tables 1 through 4.

Figure 2 shows, as a function of temperature, the concentration of CsOH vapor species (monomer and dimer) over CsOH(l) that were determined from the JANAF tables and our mass spectrometric work. The JANAF tables predict that the dimer will be more abundant than the monomer below 800 K, and that the monomer will be the dominant species above 800 K. Our data show CsOH monomer pressures about one third of those calculated with JANAF values. The largest difference was found for the dimer, where the values are 100-fold lower than the JANAF values at 800 K. When both sets of CsOH species (monomer and dimer) are added, our CsOH concentrations are a factor of ten lower than the those calculated with JANAF data, but are in general agreement with the transpiration results of Cummings et al.[16]

TABLE 1

$CsOH(g)$ Pressure over Liquid $CsOH$

T, K	P_{CsOH} atm x 10^5	$-\left(\frac{G^o - H_{298}}{T}\right)_g$ cal/deg mol	$-\left(\frac{G^o - H_{298}}{T}\right)$ cal/deg mol	ΔH_{vap} kcal/mol
654	0.782	63.83	33.03	35.429
684	1.68	64.14	33.51	35.903
684	1.28	64.14	33.51	36.270
686	1.24	64.16	33.54	36.403
714	3.23	64.44	33.99	36.419
622	0.0560	63.50	32.50	37.074
672	0.553	64.02	33.32	36.797
736	5.70	64.67	34.33	36.621
759	11.6	64.90	34.69	36.592
702	3.19	64.32	33.80	35.875
681	1.49	64.11	33.46	35.914
743	8.04	64.74	34.44	36.431
772	17.1	65.03	34.89	36.573

Average $\Delta H^o_{vap\ 298}$ 36.330 ± 0.448 kcal/mol

TABLE 2

$Cs_2(OH)_2(g)$ Pressure over Liquid CsOH

T, K	$P_{Cs_2(OH)_2}$	$-\left(\frac{G^o - H_{298}}{T}\right)_g$	$-\left(\frac{G^o - H_{298}}{T}\right)_l$	ΔH_{vap}
	atm × 10^6	cal/deg mol	cal/deg mol	kcal/mol
759	1.88	93.25	34.69	38.003
702	1.53	92.21	33.80	35.958
681	0.394	91.82	33.46	36.916
743	1.81	92.90	34.39	37.289
768	2.81	93.41	34.83	37.747
772	4.21	93.48	34.89	37.283

Average $\Delta H^o_{vap\ 298}$ 37.199 ± 0.727 kcal/mol

TABLE 3

CsI(g) Pressure over Liquid CsI

T, K	P_{CsI}	$-\left(\frac{G^o - H_{298}}{T}\right)_g$	$-\left(\frac{G^o - H_{298}}{T}\right)_l$	ΔH_{vap}
	atm x 10^3	cal/deg mol	cal/deg mol	kcal/mol
917	0.634	69.72	35.39	44.894
942	0.935	69.88	35.81	45.146
949	1.78	69.92	35.93	45.202
955	1.77	69.95	36.03	44.435
977	1.96	70.09	36.38	45.043
993	2.46	70.19	36.64	45.180
1003	2.67	70.25	36.79	45.374
1017	3.74	70.34	37.01	45.191
1029	4.82	70.41	37.19	45.093
1035	5.08	70.45	37.28	45.191
1032	5.06	70.43	37.24	45.094
997	2.83	70.22	36.70	45.042
972	1.78	70.06	36.30	45.038
945	1.11	69.90	35.86	44.945
922	0 .771	69.75	35.48	44.732

Average $\Delta H^o_{vap\ 298}$ 45.039 ± 0.315 kcal/mol

TABLE 4

$Cs_2I_2(g)$ Pressure over Liquid CsI

T, K	$P_{Cs_2I_2}$	$-\left(\frac{G^o - H_{298}}{T}\right)_g$	$-\left(\frac{G^o - H_{298}}{T}\right)_l$	ΔH_{vap}
	atm x 10^4	cal/deg mol	cal/deg mol	kcal/mol
924	0.515	111.57	35.51	55.594
944	0.789	111.85	35.84	55.632
950	1.28	111.93	35.94	54.980
968	1.35	112.18	36.24	55.582
984	1.70	112.40	36.49	55.760
997	1.87	112.58	36.70	56.079
1004	1.96	112.68	36.81	56.253
1022	2.59	112.92	37.09	56.368
1033	3.05	113.07	37.25	56.449
1041	3.25	113.18	37.38	56.615

Average $\Delta H^o_{vap\ 298}$ 55.931 ± 0.519 kcal/mol

A heat of formation at 298.15 K of -62.0 ± 3.0 kcal/mol was calculated for CsOH(g) based on atomic absorption spectroscopy of hydrogen-oxygen flames reacting with cesium gas[7]. Our heat of Formation is -60.7 ± 0.5 kcal/mol CsOH(g). The JANAF heat of formation for dimeric cesium hydroxide, $Cs_2(OH)_2(g)$, based on mass spectrometric measurements, is -164.4 ± 10.0 kcal/mol $Cs_2(OH)_2(g)$. A much smaller value of -156.9 ± 0.7 kcal/mol $Cs_2(OH)_2(g)$ was found here. The much lower pressure of dimeric cesium hydroxide gas accounts for the lower total concentration of cesium hydroxide measured in Cummings et al. transpiration measurements and our unpublished transpiration measurements.

Our data for the heats of formation of cesium iodide monomer and dimer gases are in reasonably good agreement with the NBS selected values of chemical thermodynamic properties[11]. We found heats of formation at 298.15 of -37.8 ± 0.7 and -109.8 ± 0.6 kcal/mol for CsI(g) and $Cs_2I_2(g)$ respectively. The NBS selected values are -36.3 and -109.6 kcal/mol respectively.

3.2 Gases over solutions of cesium iodide in cesium hydroxide

Liquid solutions of cesium iodide in cesium hydroxide were produced by adding weighed amounts of these two salts to the Knudsen cell, dehydrating at 450°C, and heating above the liquidus temperature in the mass spectrometer vacuum system. Reproducible partial pressures were taken as an indication of thorough mixing. This required heating above the CsI melting point, i.e., above 907 K. In the mass spectrometry measurements we attempted to measure the ion $CsI{\bullet}CsOH^+$ at mass 410 without success. Since the alkali halide polymers lose a halide atom and alkali hydroxide polymers lose OH during ionization to produce fragments of the parent molecules, the complex, CsI•CsOH(g) should lose either I or OH during ionization. The problem here is the two possible fragments are indistinguishable from those of $Cs_2I_2(g)$ or $Cs_2(OH)_2(g)$, i.e., Cs_2I^+ or Cs_2OH^+ respectively. Furthermore we do not know which fragment to look for.

By taking advantage of the relation between the CsOH or CsI concentration in liquid solution and its partial pressure, and the relation between the monomer and dimer pressures, it is possible to establish conditions where the concentration of the fragment of the complex (CsI•CsOH) may be larger than either fragments of the dimer [Cs_2I_2 or $Cs_2(OH)_2$] to be detected. Since the fragment of CsI•CsOH(g) has not been established, it is necessary to try both conditions (i.e., low concentrations of CsOH or low concentrations of CsI). The procedure outlined here will work only if the mixed anion complex (CsI•CsOH) is stable enough to produce an ion fragment that is large enough to be detected when added to the dimer fragment.

Figure 3 may help to explain the process we used to measure the partial pressure of CsI•CsOH(g). Figure 3 shows the partial pressures of $Cs_2I_2(g)$, $Cs_2(OH)_2(g)$, and CsI•CsOH(g) calculated from our measurements described above for $Cs_2I_2(g)$ and $Cs_2(OH)_2(g)$ and those described below for the complex CsI•CsOH(g). The calculated pressures at 925 K illustrate the effect of the activity changes of CsI and CsOH on the partial pressures. The ratio of CsI•CsOH(g) to $Cs_2(OH)_2(g)$ increases as the concentration of CsOH decreases changing from about 10 at 50% CsOH to 1000 at 1% CsOH. A similar effect is seen as the concentration of CsI decreases in the solution. It is apparent in Fig. 3 that if $Cs_2(OH)_2(g)$ and CsI•CsOH(g) species both produce Cs_2OH^+ fragments the majority of the fragment will represent the CsI•CsOH molecule for lower CsOH concentrations. If the complex were less stable, the curve representing CsI•CsOH would be lower and the fraction of ion fragment lower. Therefore, we investigated the lower CsOH concentrations to improve our chances of finding the complex.

By making measurements with solutions poor in CsOH or poor in CsI we can lower the activity and partial pressure of CsOH or CsI respectively. Since the dimer pressures are proportional to the the square of the monomer pressures, the partial pressures of the dimers of the low activity species will be substantially reduced, while those for the complex will be reduced much less (see Fig. 3). The complex pressures are proportional to the product of CsI and CsOH pressures; the low activity species will have a low partial pressure, whereas the other species will have a high partial pressure. From our measurements of CsI(g) and Cs_2I_2(g) pressures over CsI(l) in section 3.1 we calculated the relation between the two gases for dimerization,

$$2\ \mathrm{CsI(g)} = \mathrm{Cs_2I_2(g)},$$

where the dimer pressure may be calculated from,

$$P_{Cs_2I_2} = P^2_{CsI}\ \exp(17915/T - 13.34) \qquad (4)$$

For dimerization of CsOH,

$$2\ \mathrm{CsOH(g)} = \mathrm{Cs_2(OH)_2(g)},$$

where the dimer pressure is calculated from,

$$P_{Cs_2(OH)_2} = P^2_{CsOH}\ \exp(18574/T - 19.08) \qquad (5)$$

using our measurements in section 3.1.

Measurements of the Cs_2I^+ ion over CsI-CsOH solutions with low CsI concentrations produced intensities expected for fragments of $Cs_2I_2(g)$. This eliminated Cs_2I^+ as a fragment of CsI•CsOH. Calculations using measurements of CsI-CsOH solutions with an initial mole fraction of 0.135 CsOH showed that the fragmentation of the CsI•CsOH produces Cs_2OH^+ rather than Cs_2I^+. The ion intensity of the Cs_2OH^+ was more than 18-fold higher than calculations suggested it should be if it were only a fragment of $Cs_2(OH)_2(g)$. The results of analysis of this set of experiments are given in Table 5.

In Table 5, the first column gives the time of the experiment in minutes. Earlier measurements in this series did not include measurements of Cs_2OH^+ because temperatures were too low for its detection. The mole fraction of CsOH in the Knudsen cell was computed from initial and final analysis and numerical integration of the pressures of CsOH and CsI with time. The CsOH mole fraction is tabulated in the second column. The temperature (column 3) was also changing as the composition changed. The pressure of the Cs_2OH^+, calculated as $Cs_2(OH)_2(g)$, is given in the next column. [The Cs_2OH^+ ion intensity is the sum of the ion fragments from $Cs_2(OH)_2(g)$ and CsI•CsOH(g)]. Pressures of CsOH and CsI, given in the next two columns, were interpolated from their ion intensities at intermediate times and temperatures. Equation 5 was used to calculate the expected Cs_2OH^+ ion intensity for a fragment of $Cs_2(OH)_2(g)$ for the corresponding CsOH pressure in the column headed Calc Cs_2OH. The ratio of the measured Cs_2OH^+ to the calculated Cs_2OH^+ ion intensity is given in the next column. The total Cs_2OH^+ ion intensity varies from 17 to 378 times the fragment concentration expected if only $Cs_2(OH)_2(g)$ were present. The partial pressure of the CsI•CsOH complex is calculated from the total ion fragment intensity minus that calculated from the calculated pressure of $Cs_2(OH)_2(g)$. The ion fragment intensity attributed to the complex

(CsI•CsOH) is converted to pressure with the constants in Eqn. 2 and the relative ionization cross sections. The ionization cross section for the complex is assumed to be the sum of the cross sections for CsI(g) and CsOH(g). The last column gives the equilibrium constant Keq for the reaction of CsI(g) and CsOH(g) to form the complex. For the reaction,

$$\mathrm{CsI(g) + CsOH(g) = CsI{\bullet}CsOH(g)},$$

$$\mathrm{Keq} = \exp(17713/T - 14.47), \tag{6}$$

where Eqn. 6 was calculated from a least squares fit to the data. Eqn. 6 can also be derived with the measured free energy change and an estimated entropy for the complex. The entropy of the complex was estimated from the entropies of $Cs_2I_2(g)$ and of $Cs_2(OH)_2(g)$. From the entropy change (31.4 e.u.) and the free energy at 900 K (-10350 cal) we calculate an enthalpy change of -38590 cal for the reaction to form the complex CsI•CsOH(g). This gives an equation for the equilibrium constant,

$$\mathrm{Keq} = \exp(19420/T - 15.79). \tag{7}$$

Pressures of CsI and CsOH over the mixture were measured to establish activities of CsI and CsOH in the solution. The mixture with an initial composition of 0.135 CsOH - 0.865 CsI was heated to a maximum temperature of 927 K while measuring the ion intensities of $CsOH^+$, $Cs2OH^+$, CsI^+, and Cs_2I^+. During the measurements almost all of the CsOH was vaporized and over half of the CsI was lost. The final composition of the sample was found to be 0.018 CsOH - 0.982 CsI. The data were numerically integrated to obtain the constants to use in equation (1) for pressure calculation. The pressures were used with those for pure CsI and for CsOH to calculate activities of CsI and CsOH. The pressures were also used to calculate the change in composition between the initial and final values. From these activities and compositions we calculated the formula for the activity coefficient for CsOH,[17]

$$R\ T\ \ln \gamma_{CsOH} = -\ 2600 \pm 280\ N_{CsI}^{2}, \qquad (8)$$

where R is the gas constant, T is the absolute temperature, γ_{CsOH} is the CsOH activity coefficient and N_{CsI} is the mole fraction of CsI. The activity coefficient in Eqn. 8 was calculated from the last 7 experimental points in Table 5. Lumsden[17] reported a value of -2600 cal for the activity coefficient for a similar system, KI-KOH.

Equation 8 was used to calculate the activities of CsOH and CsI at 925 K. The CsOH(g) and CsI(g) pressures were calculated with these activities and the pressures of pure CsOH(l) and CsI(l) described in section 3.1. The pressures are the product of the activity and pressure of the pure substance. The pressures of Cs_2I_2(g), $Cs_2(OH)_2$(g) and CsI•CsOH(g) were calculated with Eqns. 4, 5 and 6. These pressures (at 925 K) are plotted as a function of the mole fraction of CsOH in the CsOH-CsI solution in Fig. 3.

Calculated pressures of CsOH(g), CsI(g) and CsI•CsOH(g) as a function of the CsI mole fraction at 800 K are presented in Table 6. The percentage of iodine present as CsI•CsOH(g) is given in the last column. CsI•CsOH(g) accounts for almost half of the gaseous iodine when the condensed CsI constitutes on tenth of the CsI-CsOH solution in agreement with the work of Johnson et al.[1] Since the fission yield of ^{235}U produces about 16 times as much CsOH as CsI, the presence of CsI•CsOH(g) will nearly double the concentration of iodine in the gas during revaporization. Table 6 also

Table 5

Pressures of the Complex CsI•CsOH in Equilibrium with CsI and CsOH Gas

Pressures in atmospheres

TIME Min	N_{CsOH}	T, K	P Cs_2OH^+ $\times 10^6$	P CsOH $\times 10^5$	P CsI $\times 10^5$	Calc $Cs_2O_2H_2$ $\times 10^8$	Ratio Col 4 / Col 7	P CsI·CsOH $\times 10^6$	Keq
142	0.122	809	4.05	7.52	2.97	23.1	17.5	7.15	3198
151	0.114	839	6.47	9.43	11.8	16.0	40.3	11.8	1063
162	0.105	876	5.06	9.70	23.2	6.67	76.	9.33	414
166	0.102	888	6.16	11.2	29.9	6.64	92.7	11.4	341
173	0.093	918	7.78	16.0	42.7	6.89	113.	14.4	291
179	0.085	925	9.63	15.9	59.8	5.81	166.	17.9	188
189	0.071	926	9.99	14.6	77.9	4.83	207.	18.6	163
196	0.062	927	7.86	12.2	81.7	3.25	242.	14.6	147
205	0.053	927	6.08	8.54	68.8	1.60	378.	11.3	193

Table 6. Calculation of CsI•CsOH Pressure Over CsI-CsOH Liquid Solutions

x,CsI	CsI•CsOH	CsI	CsOH	%CsI•CsOH
	Pressures in Atm. at 800 K			
0.00	0.00E0	0.00E0	4.24E-4	0.00
0.10	4.53E-7	5.63E-7	3.75E-4	44.6
0.20	1.01e-6	1.49E-6	3.17E-4	40.4
0.30	1.56E-6	2.85E-6	2.56E-4	35.4
0.40	1.97E-6	4.70E-6	1.96E-4	29.5
0.50	2.12E-6	7.03E-6	1.41E-4	23.2
0.60	1.97E-6	9.78E-6	9.40E-5	16.8
0.70	1.56E-6	1.28E-5	5.70E-5	10.9
0.80	1.01E-6	1.59E-5	2.98E-5	5.97
0.90	4.53E-7	1.87E-5	1.13E-5	2.36
1.00	0.00E0	2.12E-5	0.00E0	0.00

2.12E-5	Partial pressure of CsI over pure CsI
4.24E-4	Partial pressure CsOH over pure CsOH
2.15E+3	Equilibrium constant, formation of CsI•CsOH (Blackburn data)

compares the pressures of CsI(g), CsOH(g), and CsI•CsOH(g) as a function of CsI concentration dissolved in liquid CsOH. The fifth column gives the percentage of iodine in the vapor as CsI•CsOH(g); the rest of the iodine is present as CsI(g).

Figure 4 compares the pressures of CsOH(g), CsI(g) and CsI•CsOH(g) over a solution containing 0.1 CsI - 0.9 CsOH at temperatures from 600 to 1300 K. The composition of this solution is near that expected if cesium and iodine are released in ratios proportional to the fission product yield. The ratio of CsI•CsOH(g) to CsI(g) is close to one at low temperatures and decreases slightly with increasing temperature. The presence of the complex nearly doubles the amount of volatile iodine in the gas compared to that as CsI(g) and could double the amount of iodine released from the containment building.

4. Conclusions

Gas pressures over cesium iodide, cesium hydroxide and solutions of cesium iodide and cesium hydroxide were measured with a quadrupole mass spectrometer. CsI(g) and Cs_2I_2(g) pressures agreed with those reported in the literature. The heats of formation at 298.15 K found here were -37.8 ± 0.7 kcal/mol CsI(g) and -109.8 ± 6 kcal/mol Cs_2I_2(g). CsOH(g) pressures, in fair agreement with literature data, yielded a heat of formation of -60.7 ± 0.5 kcal/mol CsOH(g). The heat of formation of cesium hydroxide dimer, calculated from our pressure measurements, is -156.9 ± 0.7 kcal/mol $Cs_2(OH)_2$(g). Our value for $Cs_2(OH)_2$(g) is substantially lower than the JANAF data, but values for the CsOH monomer and dimer are consistent with transpiration measurements of CsOH from literature data and our own unpublished results. The relative ionization cross section of CsOH(g) was found to be about ten times the cross section of CsI(g).

CsI•CsOH(g) has been postulated as a stable molecule, but has not been positively identified. To investigate this molecule we measured pressures over CsI-CsOH solutions. We discovered that CsI•CsOH(g) fragments when ionized with 30 ev electrons to Cs_2OH^+ and an iodine atom. We were able to establish the part of the Cs_2OH^+ ion fragment due to fragmentation of $Cs_2(OH)_2(g)$ and to fragmentation of CsI•CsOH(g) with a thermodynamic argument. From our pressures and an estimated entropy we calculate a heat of formation from CsI(g) and CsOH(g) of -38.6 kcal/mol CsI•CsOH(g) at 900K. Activity coefficients were derived from CsOH pressures and liquid phase compositions in CsI-CsOH solutions.

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Fig. 1

Product of CsOH Vapor Ion Currents and Temperatures Measured with a Mass Spectrometer

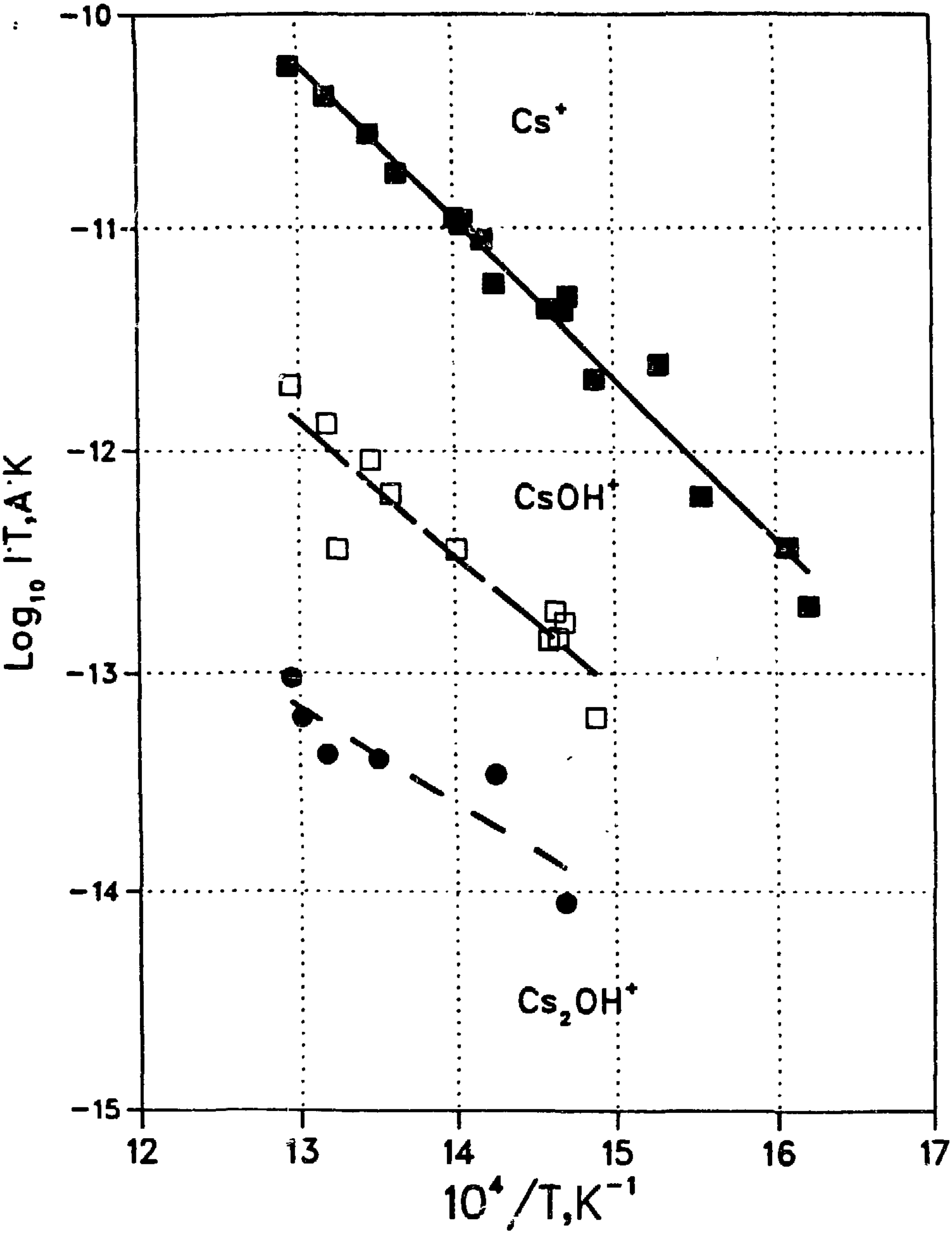


Fig. 2

Comparison of Measured CsOH Gas Concentration With CsOH Concentration Calculated from JANAF

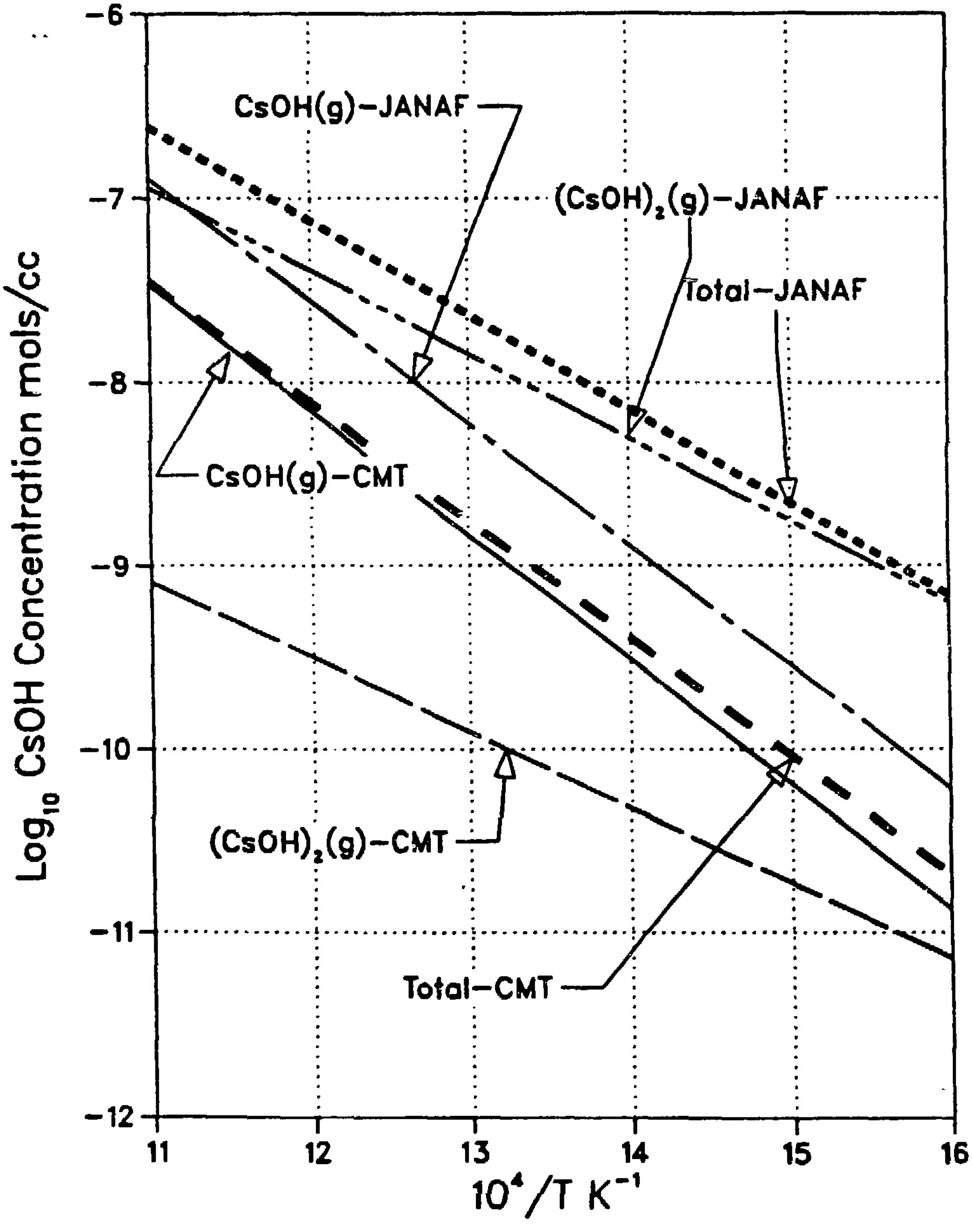
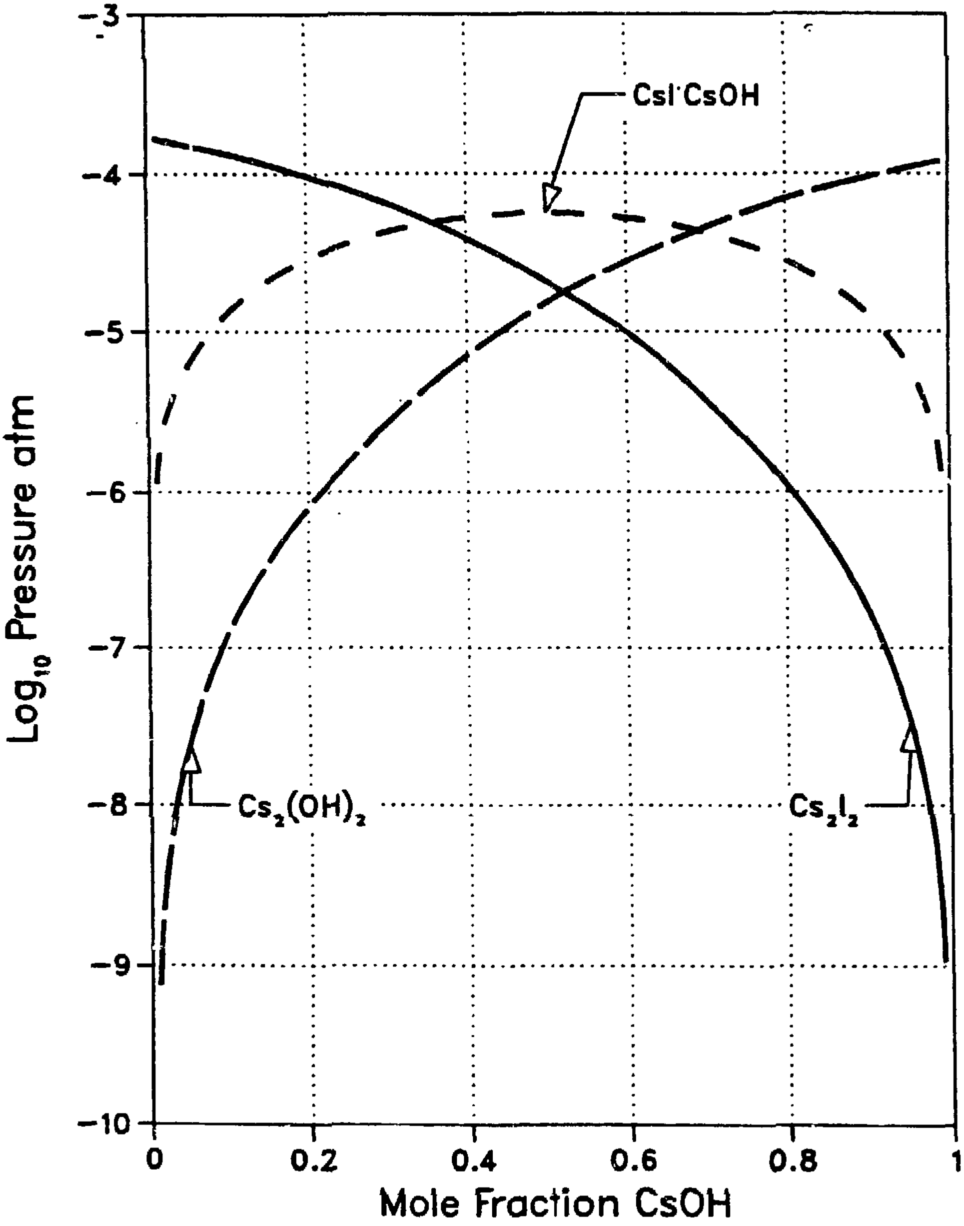
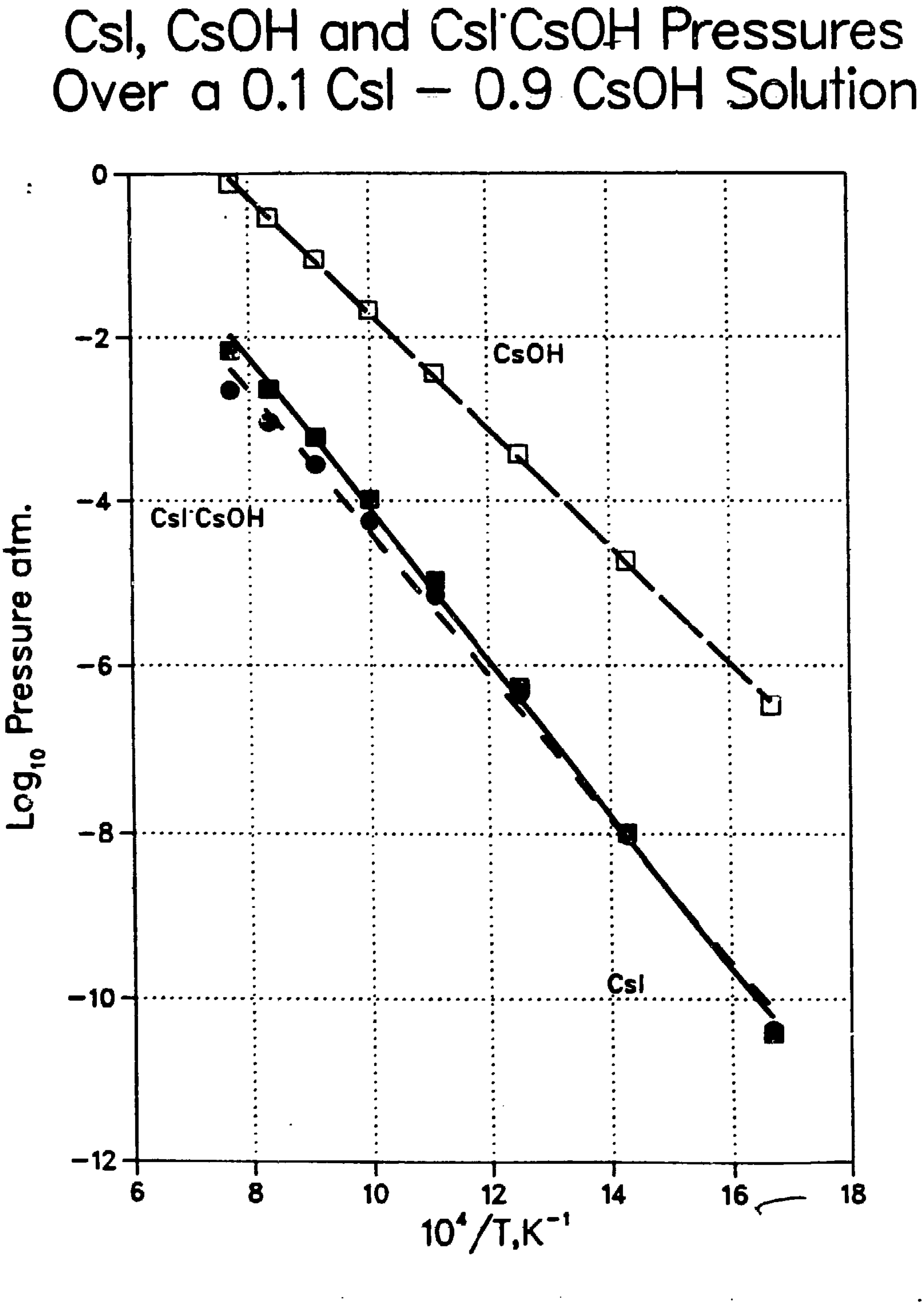


Fig. 3



Pressure Variation of Cs_2I_2, $Cs_2(OH)_2$ and CsI·CsOH at 925 K

Fig. 4


CsI, CsOH and CsI·CsOH Pressures
Over a 0.1 CsI – 0.9 CsOH Solution
CsOH
CsI·CsOH
CsI
0
−2
−4
−6
−8
−10
−12
6
8
10
12
14
16
18
Log$_{10}$ Pressure atm.
10^4/T,K^{-1}