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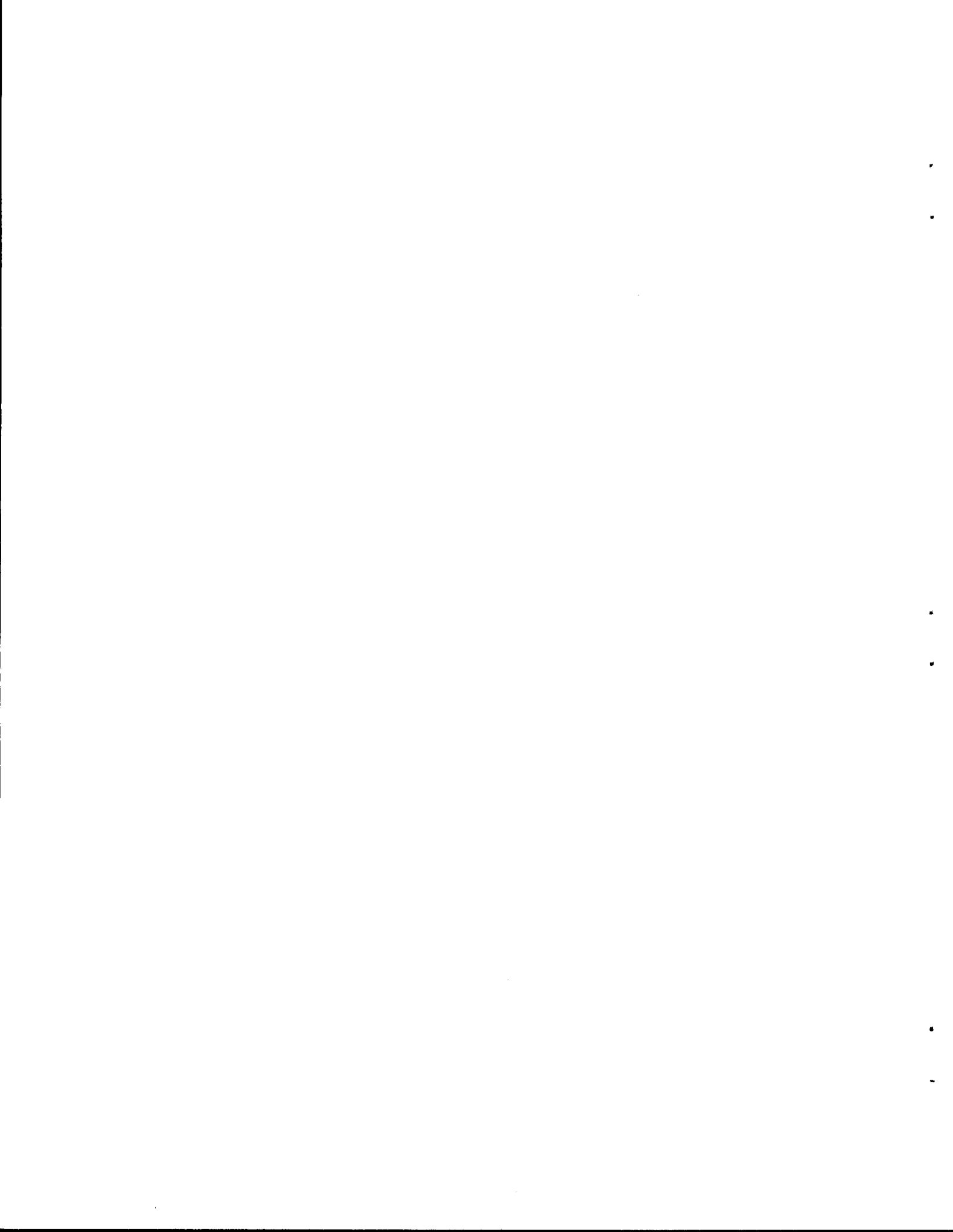
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## KNUDSEN CELL--MASS SPECTROMETER STUDIES OF CESIUM-URANIA INTERACTIONS

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## ABSTRACT

Limited Knudsen cell--mass spectrometer studies have been made of the partial pressures of cesium-containing species [assumed to be primarily Cs(g)] over Cs<sub>2</sub>CO<sub>3</sub> and over phase equilibria involving UO<sub>2</sub> and probable Cs-U-O compounds formed from mixtures that initially contained either Cs<sub>2</sub>CO<sub>3</sub>-UO<sub>2</sub> or CsOH-UO<sub>2</sub>. Although additional work is required to further define the equilibria involved, the data demonstrate unambiguously a significant reduction in cesium partial pressures due to probable Cs-U-O compound formation and indicate essentially identical behavior with either CsOH or Cs<sub>2</sub>CO<sub>3</sub> as the starting material with UO<sub>2</sub>.

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1. INTRODUCTION

Studies of the chemistry of fission products in irradiated UO<sub>2</sub> are complicated by the large number of species involved, by changes in chemical composition which result from the fission process, and, particularly if fission product behavior during temperature transients is of interest, by chemical kinetics constraints. As a consequence, rather extensive experimental programs must be conducted in order to accurately describe the system response to the wide range of perturbations of practical interest. The associated experiments are best performed in-reactor with irradiated fuel, but this is generally impractical because of poor control of experimental conditions, cost, or inherent risks of radioactive release.

An alternative approach is to simulate the fuel in the desired irradiated condition by using appropriate stable chemical species for the corresponding radioactive nuclides and conducting the desired tests out-of-reactor. However, such an approach assumes knowledge of the chemical

forms of the various fission products that are present in the irradiated fuel. This restriction is not particularly severe for studies at elevated temperatures (e.g., investigations of fission product release during fuel meltdown) since the kinetics favor a rapid restoration to proper equilibrium conditions in the event that nonequilibrium states are introduced by the use of improper chemical species. At lower temperatures the chemical kinetics are not as favorable; this increases the likelihood that the behavior of the nuclides of interest is governed principally by the chemical forms selected for simulation. Thus, it is desirable to determine the limitations attending the use of simulants, especially for studies of fission product behavior at low temperatures.

For this reason a program of investigation was begun using a Knudsen cell--mass spectrometer apparatus as the research tool. In the initial tests, which are reported here, cesium partial pressures over  $\text{UO}_2$ --cesium compound mixtures were studied.

## 2. EXPERIMENTAL

The present investigations were made using an Associated Electrical Industries MS-702 double-focusing mass spectrometer having a Knudsen effusion cell attachment. As sketched in Fig. 1, the tungsten effusion cell contained a thin-edged 0.8-mm orifice and was fitted with a Zircaloy-2 liner to provide a more realistic light water reactor (LWR) fuel environment for the test specimen. Cell temperatures were determined with a calibrated Pt vs Pt--10% Rh thermocouple which was positioned in a well at the base of the cell.

Temperatures of less than  $1000^\circ\text{C}$  were maintained by radiation heating with a tantalum filament which surrounded the cell, whereas temperatures in excess of  $1000^\circ\text{C}$  required the use of an electron bombardment heating method. This method involved the application of a high negative potential to the heating filament while maintaining the cell and the thermocouple at ground potential. The heating filament was positioned between the gap and the first radiation shield in such a manner as to optimize uniform heating of the cell and minimize the likelihood of filament shorting either to the cell or to the radiation shield.

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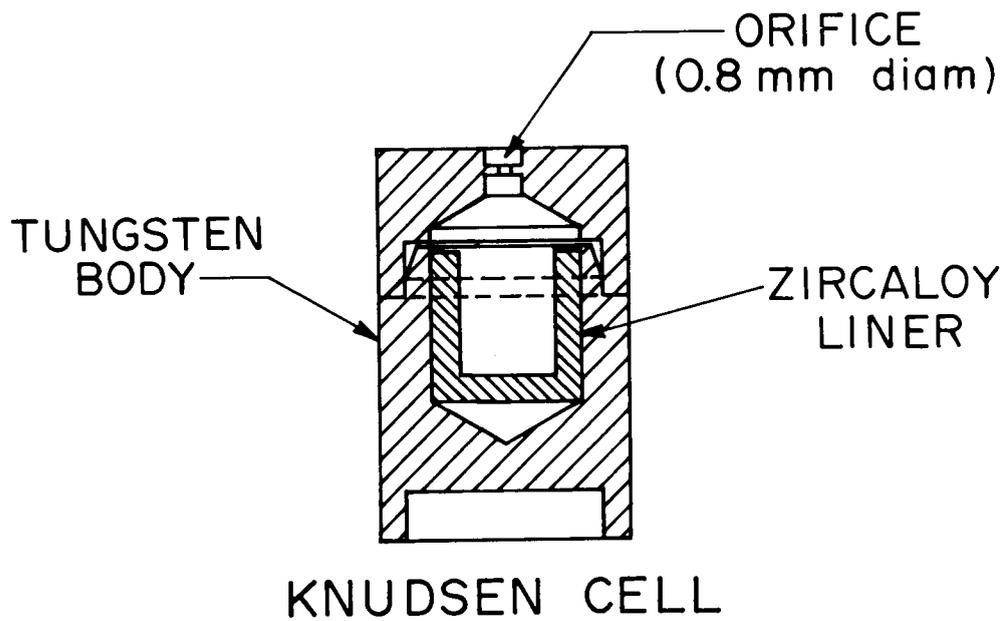


Fig. 1. Zircaloy-lined Knudsen effusion cell.

The MS-702 ion detection system contains a 20-stage multiplier with a gain in excess of  $10^8$  and a rise time of about 5 nsec for a single ion pulse. The mass scanner has an upper limit of about mass 500. The vacuum pumping system provides vacuum conditions of about  $10^{-6}$  torr in the region of the effusion cell and the ionization chambers, and about  $10^{-8}$  torr in the analyzer region.

Preparation of the cesium carbonate which was employed in the experiments involved the reaction of cesium nitrate with excess oxalic acid and subsequent pyrolysis of the cesium oxalate to the carbonate. The cesium hydroxide was obtained by hydrolysis of a cesium oxide sample which had been prepared by controlled oxidation of elemental cesium in a flowing argon-oxygen stream. The mixtures with  $\text{UO}_2$  were made by adding powdered  $\text{UO}_2$  ( $\text{O/U} = 2.072$ ) to an aqueous solution of the cesium compound and taking the resulting slurry to dryness at about  $150^\circ\text{C}$  in air. The mixtures were formulated with the objective of simulating fission product/fuel ratios that might be found in high-burnup fuel. Thus, the Cs/U weight ratio was  $3.2 \times 10^{-3}$  in the carbonate sample and  $4.5 \times 10^{-3}$  in the hydroxide sample.

Mass identification was made using xenon; this species is particularly appropriate since the xenon isotopic mass distribution is easy to identify and, moreover, brackets the  $^{133}\text{Cs}^+$  channel. Prior to each scan, a shutter which is located between the effusion cell chamber and the ionization chamber was closed, and the background of the system was determined.

### 3. RESULTS

Table 1 presents the mass spectra of the vaporization products of the three types of specimens which were employed in this study, along with similar data obtained by Gorokhov<sup>1</sup> with  $\text{Cs}_2\text{CO}_3$ . Most of the minor species observed in the present work were just above the background signal; therefore, the relative intensities probably represent upper limit values. A surprisingly low  $\text{Cs}_2\text{O}^+$  intensity was observed over  $\text{Cs}_2\text{CO}_3$  in this work. Although we are unable to account for the anomaly, the result is clearly at variance with the observation of Gorokhov<sup>1</sup> and with our own data for the  $\text{UO}_2$ -containing mixtures. In agreement with the observations by Johnson and Johnson<sup>2</sup> of vapor species over  $\text{Cs}_2\text{UO}_4$ , no uranium-containing species were detected in the vapor phase over the

Table 1. Mass spectra of vaporization products of cesium-containing species

	Condensed phase			
	$\text{Cs}_2\text{CO}_3^{\text{a}}$	$\text{Cs}_2\text{CO}_3$	$\text{Cs}_2\text{CO}_3\text{-UO}_2$	$\text{CsOH-UO}_2$
Temperature, °C	834	890	1045	1032
Electron energy, eV	75	80	80	80
Species <sup>b</sup>				
$\text{O}_2^+$	0.7	-	-	-
$\text{CO}_2^+$	8	-	-	-
$\text{Cs}^+$	100	100	100	100
$\text{Cs}_2^+$	1.9	2	-	4
$\text{CsO}^+$	-	2	4	4
$\text{Cs}_2\text{O}^+$	31	4	16	13
$\text{Cs}_2\text{O}_2^+$	0.04	-	-	-
$\text{Cs}_2\text{CO}_3^+$	4.8	-	-	-

<sup>a</sup>Data obtained from ref. 1.

<sup>b</sup>Values are given as relative intensities, using  $\text{Cs}^+$  as the reference point (100).

mixtures that initially contained either  $\text{Cs}_2\text{CO}_3\text{-UO}_2$  or  $\text{CsOH-UO}_2$ .

The product of ion intensity (peak height) of a species effusing from the Knudsen cell and the absolute temperature of the cell is directly proportional to the partial pressure of the effusing species inside the cell.<sup>3,4</sup> Figure 2 presents the experimental results in this form as a function of reciprocal temperature for the  $^{133}\text{Cs}^+$  ion intensity. Although absolute partial pressure values require extensive calibration of the system, it is nonetheless possible to determine apparent heats of reaction,  $\Delta H_{\text{app}}$ , for the unspecified equilibria from the relationship

$$\Delta H_{\text{app}} = - R \frac{d \ln (IT)}{d(1/T)}, \quad (1)$$

in which R is the gas constant, T is the absolute temperature, and I is the ion intensity at the cell temperature T. Given the particular equilibrium, it is then generally possible to relate  $\Delta H_{\text{app}}$  to the heat of reaction that is characteristic of the equilibrium condition.

Application of Eq. (1) to the case involving pure  $\text{Cs}_2\text{CO}_3$  yields a  $\Delta H_{\text{app}}$  of 25.0 kcal/mole, whereas the values derived from studies on the  $\text{Cs}_2\text{CO}_3\text{-UO}_2$  and  $\text{CsOH-UO}_2$  mixtures are 53.0 and 60.4 kcal/mole, respectively. It is clear from the results presented in Fig. 2 that the partial pressures of cesium-containing species over the two uranium-containing mixtures are indistinguishable within the uncertainty of the data.

It is also of interest to note that a detectable cesium ion current was first observed at about 650°C in the experiments with pure  $\text{Cs}_2\text{CO}_3$ , whereas the corresponding temperature for detection in the tests with  $\text{Cs}_2\text{CO}_3\text{-UO}_2$  and  $\text{CsOH-UO}_2$  mixtures was approximately 925°C. Furthermore, at the experimental temperatures employed, simple vaporization of cesium metal cannot be involved since this would have resulted in pressures sufficiently large to remove the effusion cell cover.

#### 4. DISCUSSION

High background signals prevented determinations of  $\text{O}_2$  and  $\text{CO}_2$  partial pressures, and this lack of information limits a thermodynamic interpretation of the data. Hence it is not possible to relate the  $\Delta H_{\text{app}}$  value which was derived from the cesium partial pressures over  $\text{Cs}_2\text{CO}_3$  to the appropriate heat of reaction.

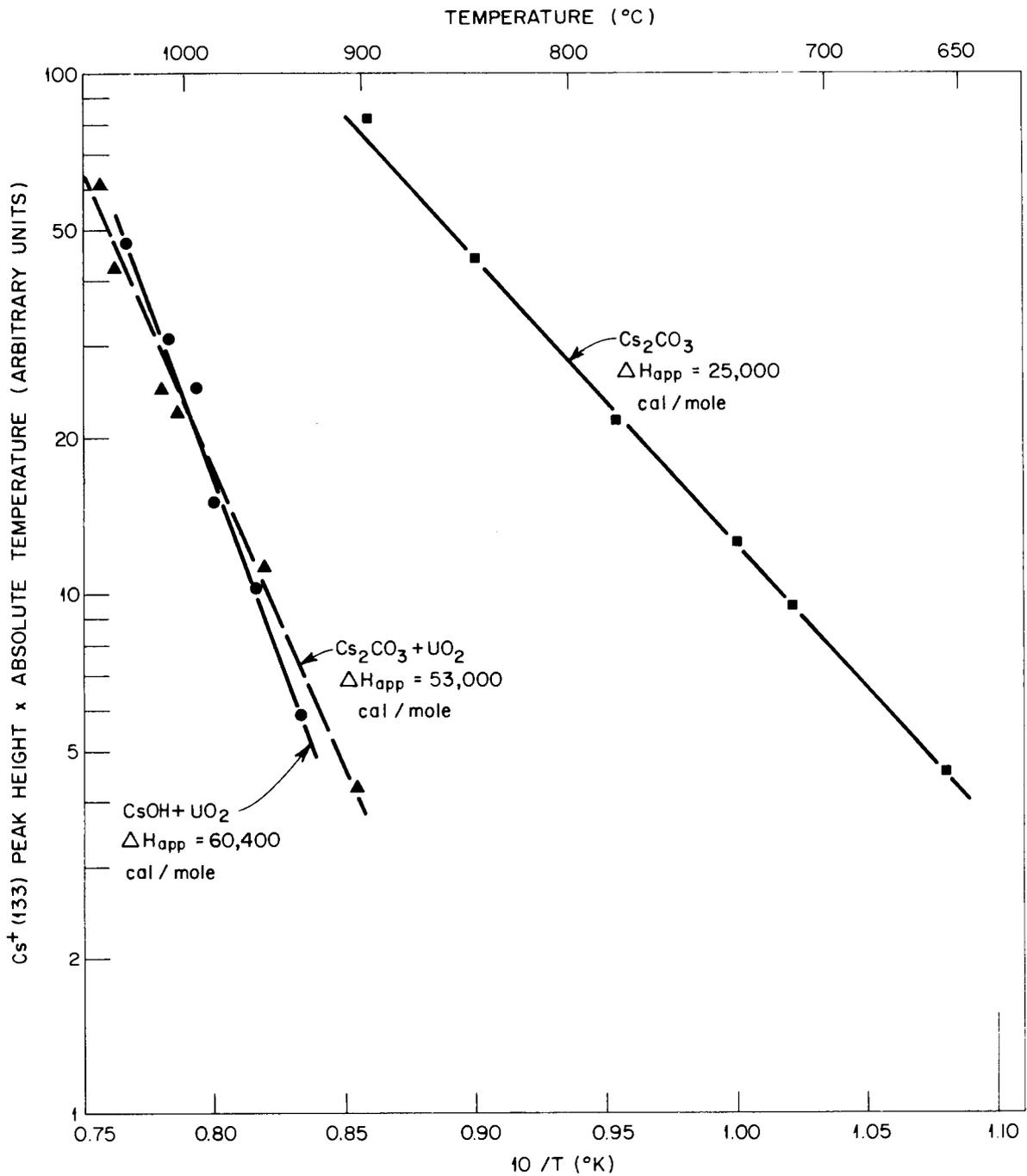


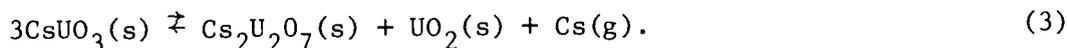
Fig. 2. Relative vapor pressures of cesium-containing species as determined by Knudsen cell--mass spectrometer measurements.

Measurements of  $\text{CO}_2$  partial pressures over molten cesium carbonate have been described throughout the temperature range 883 to 1453°K by the relation<sup>5</sup>

$$\log_{10} p_{\text{CO}_2} = 3.532 - (6080/T), \quad (2)$$

in which  $p_{\text{CO}_2}$  is the  $\text{CO}_2$  partial pressure in atmospheres. The apparent heat of reaction as determined from Eq. (2) is 27.8 kcal/mole; while this result is in excellent agreement with the value (25.0 kcal/mole) determined from the temperature dependence of  $\text{Cs}^+$  ion current in the present studies, the agreement may be fortuitous.

The situation involving the  $\text{Cs}_2\text{CO}_3\text{-UO}_2$  and  $\text{CsOH-UO}_2$  mixtures is somewhat more favorable. Although information on the  $\text{Cs-U-O}$  system is lacking, features of the equilibrium diagram can be deduced from analogous sodium systems. The data presented by Battles et al.<sup>6</sup> and Blackburn,<sup>7</sup> as well as the  $\text{Cs/U}$  mole ratios which were employed in the present studies, indicate that only two equilibria are likely. One of these involves the components  $\text{UO}_2\text{-CsUO}_3\text{-Cs}_2\text{U}_2\text{O}_7$ ; for this system,  $\Delta H_{\text{app}}$  as derived from the  $\text{Cs}^+$  ion current can be related to the heat of reaction characteristic of the equilibrium



Consideration of this reaction yields the result

$$\begin{aligned} \Delta H_{\text{app}} &= -R \frac{d \ln (I_{\text{Cs}} T)}{d (1/T)} \\ &= \Delta H_{\text{f}}^{\circ}[\text{Cs}_2\text{U}_2\text{O}_7(\text{s})] + \Delta H_{\text{f}}^{\circ}[\text{UO}_2(\text{s})] + \Delta H_{\text{f}}^{\circ}[\text{Cs}(\text{g})] \\ &\quad - 3\Delta H_{\text{f}}^{\circ}[\text{CsUO}_3(\text{s})]. \end{aligned} \quad (4)$$

All of the heat of formation values,  $\Delta H_{\text{f}}^{\circ}$ , have been determined at 298°K except that for  $\text{CsUO}_3$ . This quantity can be estimated by noting (see the data in Table 2) that the heats of formation of the cesium uranates are about 4 kcal/mole more negative per cesium atom than the corresponding sodium compounds. Moreover, more extensive comparisons between the oxides, carbonates, halides, sulfides, and sulfates support this observation.<sup>8</sup> (We will also use the reasonably accurate approximation that  $\Delta H_{\text{T}}^{\circ}$  is assumed to be equivalent to  $\Delta H_{\text{f}}^{\circ}_{298}$  in the following discussions.)

Table 2. Heats of formation (298°K)

Species	$\Delta H_f^\circ$ (kcal/mole)	Reference
Cs(g)	18	9
UO <sub>2</sub> (s)	-259	10
NaUO <sub>3</sub> (s)	-350; -358	10; 11
CsUO <sub>3</sub> (s)	(-354); <sup>a</sup> (-362) <sup>b</sup>	
Na <sub>2</sub> UO <sub>4</sub> (s)	-446	12
Cs <sub>2</sub> UO <sub>4</sub> (s)	-454	13
Na <sub>2</sub> U <sub>2</sub> O <sub>7</sub> (s)	-745	6
Cs <sub>2</sub> U <sub>2</sub> O <sub>7</sub> (s)	-754	14
Na <sub>3</sub> UO <sub>4</sub> (s)	-474	6
Cs <sub>3</sub> UO <sub>4</sub> (s)	(-486) <sup>c</sup>	

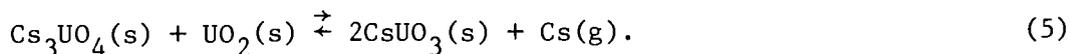
<sup>a</sup>Estimated from  $\Delta H_f^\circ(\text{NaUO}_3) = -350$  kcal/mole.

<sup>b</sup>Estimated from  $\Delta H_f^\circ(\text{NaUO}_3) = -358$  kcal/mole.

<sup>c</sup>Estimated from  $\Delta H_f^\circ(\text{Na}_3\text{UO}_4) = -474$  kcal/mole.

Unfortunately,  $\Delta H_{\text{app}}$  is quite sensitive to the value selected for  $\Delta H_f^\circ[\text{CsUO}_3(\text{s})]$ , and two estimates can be made from literature values for  $\Delta H_f^\circ[\text{NaUO}_3(\text{s})]$ . These estimates plus the other pertinent data given in Table 2 yield, through application of Eq. (4),  $\Delta H_{\text{app}}$  values of 67 and 91 kcal/mole. The former value is in reasonably good agreement with the  $\Delta H_{\text{app}}$  values of 53 and 60 kcal/mole that were determined for the  $\text{Cs}_2\text{CO}_3\text{-UO}_2$  mixture and the  $\text{CsOH-UO}_2$  mixture, respectively. The value of 91 kcal/mole, which is derived from  $\Delta H_f^\circ[\text{CsUO}_3(\text{s})] = -362$  kcal/mole, is not in satisfactory agreement with our experimental data.

The second likely equilibrium involves the system  $\text{UO}_2\text{-CsUO}_3\text{-Cs}_3\text{UO}_4$ ; in this case, an expression for  $\Delta H_{\text{app}}$  can be deduced by considering the reaction



The relationship sought is given by

$$\begin{aligned} \Delta H_{\text{app}} = & 2\Delta H_f^\circ[\text{CsUO}_3(\text{s})] + \Delta H_f^\circ[\text{Cs}(\text{g})] - \Delta H_f^\circ[\text{Cs}_3\text{UO}_4(\text{s})] \\ & - \Delta H_f^\circ[\text{UO}_2(\text{s})]. \end{aligned} \quad (6)$$

In this case, values must be estimated for both  $\text{CsUO}_3$  and  $\text{Cs}_3\text{UO}_4$ . Use of the two estimates for  $\text{CsUO}_3$  yields  $\Delta H_{\text{app}}$  values of 55 and 39 kcal/mole. Once again, the former value, which corresponds to  $\Delta H_f^\circ[\text{CsUO}_3(\text{s})] = -354$  kcal/mole, is in good agreement with the experimental data, whereas the second is not.

In summary, it is evident that more extensive studies are required to better define the equilibria that were involved in these investigations; nonetheless, at temperatures of interest to LWR safety studies, compound formation between cesium and  $\text{UO}_2$  is indicated. Two likely equilibria were investigated; regrettably, it was not possible to eliminate one or the other by comparison with experiment. Furthermore, if  $\Delta H_f^\circ[\text{CsUO}_3(\text{s})] = -362$  kcal/mole and all other pertinent heat of formation values are assumed to be correct, then neither equilibrium describes the experimental data.

Presumed formation of Cs-U-O compounds from the  $\text{Cs}_2\text{CO}_3\text{-UO}_2$  and the  $\text{CsOH-UO}_2$  mixtures results in a marked decrease in the partial pressure of cesium-containing species over the condensed phase as compared with

that over  $\text{Cs}_2\text{CO}_3$  (and probably over the cesium oxides as well). Moreover, it appears likely that cesium fission product simulant may be introduced with  $\text{UO}_2$  as either  $\text{Cs}_2\text{CO}_3$  or  $\text{CsOH}$ , not only for the purpose of investigating behavior during fuel meltdown conditions, but also under the more moderate temperature conditions which are involved in successfully terminated loss-of-coolant accidents and spent fuel transportation accidents.

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