UNITED STATES DEPARTMENT OF COMMERCE
National Bureau of Standards
Washington, D.C. 20234

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MEMORANDUM FOR M. Silberberg, Chief
Experimental Advanced Safety Technology Branch
U.S. Nuclear Regulatory Commission

From: D. Garvin, Acting Deputy Director D.G.
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Subject: Comments on draft of NUREG 0772

These comments are limited to the thermodynamic data and calculations in
NUREG 0772 "Technical Bases for Estimating Fission Product Behavior during LWR Accidents"
March 6, 1981. I reference only the main text. But the commentary covers the Appendix.

1. Data Base . Approximations have been necessary at various stages. Alternative
sources of data may provide additional insight. The tables attached here show the
selected values of chemical thermodynamic properties being published in NBS Technical
Note 270-8 (1981), for Cs and U compounds, and those published earlier for iodine
species in TN 270-3 (1968). Some comments are included. More detailed documentation
can be provided by the Chemical Thermodynamics Data Center, NBS, Washington, D.C. 20234.

2. Table 4.2 pg. 4.6. "Characteristics of some key materials". This table
contains Gibbs Energies of formation at 1000K. These appear to have been calculated
from Table 1 in Besmann and Lindmer, Nuclear Technology (1978) 40 297, using the
approximate formula:

$$\Delta G(T) = \Delta H(298) - T \cdot \Delta S(298).$$

Better values can be calculated from the sources cited in NUREG 0772 for use in the
modelling. In any event, the values for Cs(g) and Iz(g) are not correct. The JANAF
Thermochemical Tables take these species as the reference state at 1000K. Thus $\Delta_f G = 0$
for both. Nor does the value for Cs(g) match the assumption that Cs(c,298) is the
reference state. For these two the approximation is poor. If an analogous procedure
was used in the modelling, there may be trouble.

Pg. 5.3 et. seq. Equilibrium calculations. It is not easy to check what has
been done without redoing the calculations independently. But for this to be easy more
data should be provided. There are many traps, hopefully avoided here that could be
checked if the data and algorithms for property values were provided. For example: (1)
the problem of reference states mentioned earlier, and, (2) the conversion of Barin
and Knacke's data to the same basis as used by the JANAF tables.

It would help if there was a more explicit statement of the conditions used in the models. For example, for the oxidizing atmospheres, is there air present? Have gas imperfections been ignored (and is this practical) at 150 bars? These are points that are obvious when doing the work but that are not obvious to the general reader.

Also, this study considers only vapor phase equilibria. Besmann and Lindmer (loc. cit.) considered solids and liquids. These persist into the temperature range of interest. Why are they left out? How does the present study agree or disagree with that of Bessmann and Lindmer?

Related to the previous paragraph, but more general, is the question of whether or not there are other species that should be considered. These might remove Cs species, allowing more I and HI to form, or remove I from the vapor. The justification of the limitations of this study is, in my opinion, insufficient (or hidden in a mountain of text!)

Pg. 5.14 Solution Chemistry. The equilibrium constants calculated here and in the Appendix appear to be good.

The text suggests that the oxidation of HOI is very slow. I wonder. This may be due to depletion of oxygen in the solution. Adachi, Equchi and Fujido, CA 77-16926 seen to have been able to get some information on the rate. (I have not seen their paper.)

Pg. 5-21 Organic Iodides. This may be the crucial aspect of the post-accident (potential) release of iodine. A conclusion from the report is that the mechanism of formation of methyl iodide is unknown, thus its steady-state value cannot be established. (I gather from the text that TMI showed a continuing source of organic iodide. Methyl iodide is known to hydrodyze. Hence the steady-state).

Methyl iodide has been omitted from figures 5.4 and 5.5, although it is present in eq. 5.7, pg. 5.23. This is consistent with the caution stated above. However, since the figures are optimistic, another set is needed that includes the MeI. Figure captions should summarize major data and assumptions.

The references to Kabat, pg. 5.23 should be to 5.50, 5.51.

Attachments

Selected Values of Chemical Thermodynamic Properties
at 298.15K from NBS TN. 270-8 (1981)

	$\Delta_f H^O$ kcal/mol	$\Delta_f G^O$ kcal/mol	S^O cal/mol•K	C_p cal/mol•K
$UO_2(c)$	-259.3	-246.6	18.41	15.20
$UO_2(g)$	-111.3	-112.7	65.6	12.28
$UO(g)$	5.			
$UO_3(c)$	-292.5	-273.9	22.97	19.52
$UI_4(c)$	-122.4	-121.1	63.0	32.1
$UI_4(g)$	-72.1	-87.2	11.8	
$Cs_2O(c)$	-82.64	-73.65	35.10	18.16
$Cs_2O(g)$	-37.			
$CsOH(c)$	-99.72			
$CsOH(g)$	-59.	-59.1	60.88	11.88
$Cs_2UO_4(c)$	-461.0	-431.7	52.50	36.51
$CsI(c)$	-82.84	-81.40	29.41	12.62
$CsI(g)$	-36.3	-45.7	65.77	8.95
$Cs_2I_2(g)$	-209.6	-119.8	102.6	19.7

Selected Values of Chemical Thermodynamic Properties
at 298.15K from NBS TN. 270-3 (1968)

	$\Delta_f H^\circ$ kcal/mol	$\Delta_f G^\circ$ kcal/mol	S° cal/mol·K	C_p° cal/mol K
H^+ (aq, std. st.)	0	0	0	0
$H_2O(\ell)$	-68.315	-56.687	16.71	17.995
OH^- (aq, std. st.)	-54.970	-37.594	-2.57	-35.5
I^- (aq, std. st.)	-13.19	-12.33	26.6	-34.0
I_2 (aq, std. st.)	5.4	39.2	32.8	
I_3^- (aq, std. st.)	-12.3	-12.3	57.2	
IO^- (aq, std. st.)	-25.7	-9.2	-1.3	
HOI (aq, undissoc.)	-33.0	-23.7	22.8	
IO_3^- (aq, st. state)	-52.9	-30.6	28.3	
$I_2(c) = I_2$(aq, std. st.)	$\Delta G^\circ = 3.92$			

$$K_S = 1.34 \times 10^{-3} \text{ mol/kg of } H_2O$$

Thermal Functions Used in NBS TN 270-8 (1981)

$CsI(cl)$

T	$S^° - S(298)$	$H^° - H(298)$
K	cal/mol. K	kcal/mol
Crystal		
298.15	0	0
400	3.58	1.24
500	6.45	2.53
600	8.93	3.89
700	11.12	5.31
800	13.12	6.81
899	14.95	8.36
Liquid		
899	21.81	14.53
900	21.83	14.55
1000	23.42	16.06
1100	25.06	17.79
1200	26.74	19.73
S(298)=	29.41	

$UO_2(g)$

T	$S^°(T)$	$[H^° - H^°(0)]/T$
K	cal/mol. K	
Gas		
298.15	65.582	10.571
400	69.310	11.113
500	72.287	11.561
600	74.797	11.929
700	76.962	12.232
800	78.864	12.484
Gas		
900	80.557	12.694
1000	82.082	12.872
1100	83.469	13.025
1200	84.740	13.156
1300	85.912	13.271
1400	87.000	13.372
1500	88.015	13.461
1600	88.967	13.591

$CsI(g)$

T	$S^°$	$(H^° - H^°(0))/T$
	cal/mol · K	
298.15	65.767	8.457
600	72.068	8.738
800	74.684	8.828
1000	76.728	8.894
1200	78.407	8.947
1400	79.831	8.989
1600	81.066	9.020

Comments on Tables of Selected Values

    <u>Iodine species in solution</u>. These selected values were based on more data than was available for Latimer (who used NBS Circular 500 extensively). They are now being superseded by the CODATA Key Values for Thermodynamics which include I_2, I^- but not IO^- or IO_3^-.

    Examination of recent studies suggests that ΔG^o for the various equilibria of interest in the NUREG 0772 study <u>will not change appreciably</u> * although ΔH and S may, to be consistent with the CODATA selections.

    <u>$Cs_2UO_4(c)$</u>. The new IAEA Series has thermal function for $Cs_2UO_4(c)$. Cordfunke, E. H. P., and O'Hare, P. A. G., "Part 3. Miscellaneous Actinide Compounds" in "The Chemical Thermodynamics of Actinide Elements and Compounds", Medvedev, Rand and Westrum, Editors, IAEA, Vienna, 1978.

    $UO_2(c)$. The IAEA volume on the oxides has not been published. NBS Tech. Note 270-8 used the thermal functions of Godfrey, Wooley and Leitmaker, ORNL-TM 1596 (1966).

    $UO_2(g)$. Thermal functions were calculated for UO_2 as a linear, harmonic oscillator-rigid rotor with frequencies from Gabelnick et al, J. Chem. Phys. (1973), <u>58</u>, 4468.

    $CsI(c,\ell)$. Thermal functions based on Smith, Kaylor, Walder, Taylor and Gate. U.S. Bur. Mines Rept. of Investigation 5832 (1961). This is essentially the same set of data as that used by Kubaschewski, Evans and Alcock and reported by Barin and Knacke. NUREG 0772 quotes the last. The NBS analysis, however, get ΔH(melting, 899K) 6.17 kcal as opposed to 5.7 used by KE and A. This changes all values for the liquid. The accuracy of the data is not very high. Note that S(298) = 29.41, while KE and A estimated 30.0± 2.5.

    $CsI(g)$. Thermal function based on frequencies in Brumer and Karplus, J. Chem. Phys. (1973) <u>58</u>, 3902. They yield S(1600K) = 8.06 compared to B and K's S = 85.8 cal/mol K.

*Later note: $\Delta_f G (IO_3^-, aq)$ and ΔG for the equilibria will change, but how much cannot be identified accurately without a major reassessment of the data network for iodine species in solution. It is my <u>guess</u> that the changes will be small.