AECL EACL

AECL-12061

Calculations of Thermodynamic Data from Spectroscopic Data for Oxides of Cerium and Neodymium

Calculs des valeurs thermodynamiques provenant des données spectroscopiques relatives aux oxydes de cérium et de néodyme

S. Sunder, R.J. Lemire

January 2000 janvier

AECL

CALCULATIONS OF THERMODYNAMIC DATA FROM SPECTROSCOPIC DATA FOR OXIDES OF CERIUM AND NEODYMIUM

by

S. Sunder[1] and R.J. Lemire[2]

[1]Fuel Safety Branch
[2]Reactor Chemistry Branch
Chalk River Laboratories
Chalk River, Ontario K0J 1J0

2000 January

AECL-12061

EACL

CALCULS DES VALEURS THERMODYNAMIQUES PROVENANT DES DONNÉES SPECTROSCOPIQUES RELATIVES AUX OXYDES DE CÉRIUM ET DE NÉODYME

par

S. Sunder[1] et R.J. Lemire[2]

RÉSUMÉ

Un code pour calculer les fonctions thermodynamiques d'un gaz idéal (à une pression de 1 atm) à partir de ses données spectroscopiques en utilisant les méthodes de mécanique statistique a été mis en service, mis à l'essai et vérifié. Le code a été utilisé pour calculer les fonctions thermodynamiques de trois oxydes de produits de fission, CeO_2, Ce_2O_2 et NdO_2, avec des températures se situant entre 100 K et 3 000 K et une pression de 0,1 MPa. Les données thermodynamiques à haute température des produits de fission sont nécessaires pour calculer les termes-source dans les conditions d'accident en utilisant les codes de sûreté du combustible comme CHMWRK et F*A*C*T.

[1]Sûreté du combustible
[2]Chimie des réacteurs
Laboratoires de Chalk River
Chalk River (Ontario) K0J 1J0

Janvier 2000

AECL-12061

AECL

CALCULATIONS OF THERMODYNAMIC DATA FROM SPECTROSCOPIC DATA FOR OXIDES OF CERIUM AND NEODYMIUM

by

S. Sunder[1] and R.J. Lemire[2]

ABSTRACT

A code to calculate thermodynamic functions of an ideal gas (at 1 atm pressure) from its spectroscopic data using statistical mechanics methods was commissioned, tested and verified. The code was used to calculate the thermodynamic functions for three fission-product oxides, CeO_2, Ce_2O_2 and NdO_2, for temperatures between 100 K and 3000 K and 0.1 MPa. High-temperature thermodynamic data of fission products are needed to calculate the source terms under accident conditions using fuel safety codes such as CHMWRK and F*A*C*T.

[1]Fuel Safety Branch
[2]Reactor Chemistry Branch
Chalk River Laboratories
Chalk River, Ontario K0J 1J0

2000 January

AECL-12061

TABLE OF CONTENTS

List of Tables

1. INTRODUCTION

A knowledge of the nature of chemical species formed from fuel and fission products in the primary heat-transport system (PHTS) during a reactor accident is necessary to determine the source term for radionuclides entering containment. At high temperatures (i.e., above 1000 K) most chemical reactions, particularly those involving gas-phase species, are fast, and equilibration is achieved in a very short time (less than one second). Therefore, one can use chemical equilibrium calculations to obtain a description of fission-product speciation in fuel and defected fuel elements under high-temperature accident conditions. Several computer codes, such as CHMWRK [82GAR] and F*A*C*T [80THO/BAL, 84THO/BAL], have been developed to carry out such calculations.

The CHMWRK code was developed at AECL by Garisto [82GAR, 88GAR and 92GAR] to carry out chemical equilibrium calculations under postulated accident conditions. CHMWRK is a Gibbs function minimization program and the database associated with CHMWRK contains the Gibbs energy functions for species expected to occur at the equilibrium conditions. CHMWRK uses input in the form of $\Delta_f G^o$ at 298.15 K and a function:

$$\Delta_f G^o(T) = \Delta_f G^o(298.15\ K) - [T\ \Phi(T) - 298.15\ \Phi(298.15\ K)] \tag{1}$$

where $\Phi(T)$ is defined by:

$$\Phi(T) = -\ [G^o(T) - H^o(298.15\ K)]/T \tag{2}$$

that is, $\Phi(298.15\ K)$ is equal to $S^o(298.15\ K)$. Garisto [88GAR] fitted values of $\Phi(T)$ to an expression f(T) of the form:

$$f(T) = A_0 + A_{ln}\ln(X) + A_{-2}X^{-2} + A_{-1}X^{-1} + A_1X + A_2X^2 + A_3X^3 \tag{3}$$

where $X = 10^{-4}T$ (T in kelvin). The coefficients A_i are required for CHMWRK input.

Both cerium and neodymium are important fission products in calculations of the early and late consequences of radionuclides released from a nuclear reactor, as discussed in Appendix A. (Appendix A provides information about the yields, the radioactivity of the two elements in an irradiated fuel, and the health consequences of their release during a nuclear accident.) A review of the thermodynamic properties of oxides and hydroxides of fission products that are important in reactor safety calculations showed that there is insufficient thermodynamic information available for oxides of cerium ($CeO_2(g)$ and $Ce_2O_2(g)$) to derive functions $\Phi(T)$; i.e., to determine the coefficients A_i in Equation (1). There was also a need to confirm the literature values of $\Phi(T, NdO_2(g))$, quoted by Cordfunke and Konings [90COR/KON], because they suggest unexpectedly high stability for $NdO_2(g)$ relative to $NdO(g)$. Therefore, we have calculated relevant thermodynamic functions of gas-phase oxides of cerium and neodymium for temperatures between 100 K and 3000 K. This report documents those calculations.

2. CALCULATION METHODS

The thermodynamic functions were calculated using statistical mechanics methods. Statistical mechanics allows one to calculate macroscopic properties, such as thermodynamic quantities, of an ensemble from a knowledge of the microscopic properties of molecules constituting the ensemble (such as molecular structure, energy levels, etc.). The theoretical basis of these calculations has been well established [49RUS, 61LEW/RAN, 62HER and 65MOO]. A few introductory notes on the theoretical basis of the calculations are given in Appendix B for the convenience of the reader interested but uninitiated in the subject.

The thermodynamic (ideal gas) functions were calculated assuming Maxwell-Boltzmann energy distribution for the molecules. It was assumed that the molecules behave as rigid rotators and harmonic oscillators [62HER]. The molecules were assumed to be in the ground electronic state and the contributions of the higher electronic energy levels were assumed to be negligible for the temperature range considered here.

3. COMPUTER CODES USED FOR CALCULATIONS

A code, called THERMO, was used to calculate the thermodynamic functions. The code calculates thermodynamic properties of an ideal gas as a function of temperature (K) and was previously used at the University of Alberta [72SUN, 72BER/SUN, 73BER/SUN] and the University of Heidelberg [79SUN/EYE]. THERMO is a FORTRAN code and input required by this code consists of:

- molecular mass (to calculate the contributions of translational energy levels);
- moments of inertia and the rotational symmetry number for the molecule (to calculate the contributions of rotational energy levels); and
- frequencies of normal vibrational modes, including degeneracy (to calculate the contributions of vibrational energy levels).

The moments of inertia values needed for the three oxides were calculated using a code called CART, a well-known code in molecular spectroscopy that was written by Schachtschneider [64SCH, 72SUN, 76SUN/BER, 77KOR/GIN]. The code calculates the moments of inertia and cartesian coordinates of a molecule from its structural parameters (bond lengths, bond angles, etc.) and the atomic weights of its atoms.

Both codes (THERMO and CART) were recompiled for use at the CRL computer center and the versions used in this work were verified by repeating calculations for several molecules with published results; i.e., methyl fluoride-h_3 and methyl fluoride-d_3 [64SCH], *t*-butyl bromide-h_9 and *t*-butyl bromide-d_9 [72SUN], and methylene-cyclopropane-h_6 and methylene-cyclopropane-d_6 [72BER/SUN] (Appendix C).

4. RESULTS

The structural parameters of the three oxides, CeO_2, Ce_2O_2 and NdO_2, are listed in Table 1. These parameters were calculated by Kordis and Gingerich [77KOR/GIN] from the electron diffraction data on lanthanide oxides and the Herschbach-Laurie relationship [61HER/LAU].

Table 1: Structural Data* for $CeO_2(g)$, $Ce_2O_2(g)$ and $NdO_2(g)$

Molecule	Structure	Molecular Symmetry	Rotational Symmetry Number	Bond Length/ nm	Bond Angle(s)/ degrees
$CeO_2(g)$	Symmetrical Bent	C_{2v}	2	0.188	146
$Ce_2O_2(g)$	Planar Square	D_{2h}	4	0.191	90
$NdO_2(g)$	Symmetrical Bent	C_{2v}	2	0.189	120

*Bond lengths and bond angles are from Kordis and Gingerich [77KOR/GIN]. Bond lengths are for metal oxygen bonds.

We used these parameters as input in CART to calculate the moments of inertia of the three oxides. The values of the moments of inertia (I_A, I_B, I_c) are listed in Table 2. The cartesian coordinates of the atoms in the molecules, calculated during the calculations of the moments of inertia, are listed in Appendix D. Note that the moments of inertia for cerium and neodymium oxides were calculated using cerium and neodymium atomic weights of 140.12 and 144.24, respectively [99LID].

Table 2: Principal Moments of Inertia of Three Oxides[a]

Oxide	10^{20} I_A	10^{20} I_B	10^{20} I_C
$CeO_2(g)$	103.399910	7.868519	111.268417
$Ce_2O_2(g)$	511.171875	58.351028	569.522888
$NdO_2(g)$	85.703140	23.382006	109.085136

[a] Units of moments of inertia are amu m^2.

The frequencies of the normal vibrational modes of three oxides are listed in Table 3. CeO_2 and NdO_2 have three normal vibrational modes each, denoted in Table 3 by the symbols ν_1, ν_2, and ν_3; Ce_2O_2 has five vibrational modes denoted in Table 3 by symbols ν_1, ν_2, ν_3, ν_4 and ν_5. The ν_2 vibration of Ce_2O_2 has a degeneracy equal to 2; all other vibrations are non-degenerate. The frequencies used in the present work were calculated by Kordis and Gingerich using normal coordinate analysis and are in good agreement with the available experimental data for these molecules [77KOR/GIN]. For example, the observed values for ν_1 and ν_3 in the infrared spectrum of matrix-isolated CeO_2 are 757.05 and 736.80 cm^{-1}, respectively; *cf.* the calculated values of 757 and 737 cm^{-1} [74GAB/REE]. (There are no experimental data available for the gas-phase spectra of these molecules.)

Table 3: Vibrational Frequencies* of $CeO_2(g)$, $Ce_2O_2(g)$ and $NdO_2(g)$

Vibrational Mode	$CeO_2(g)$	$Ce_2O_2(g)$	$NdO_2(g)$
ν_1	757	917	754
ν_2	264	772	256
ν_3	737	588	716
ν_4		71	
ν_5		53	

*Vibrational frequencies are in units of cm^{-1}, data from Kordis and Gingerich [77KOR/GIN].

The code THERMO calculates thermodynamic functions for molecules in the electronic ground state with a degeneracy of 1. It does not take into account the contributions to the thermodynamic functions resulting from the multiple degeneracy of the electronic ground state. The degeneracy of the electronic ground state, denoted by *g*, contributes an amount R ln(*g*) to the entropy and Gibbs energy, but does not contribute to the heat capacity of the molecules [49RUS]. The contributions of electronic degeneracy to the Gibbs function and entropy for molecules with multiple electronic degeneracy (e.g., $Ce_2O_2(g)$ and $NdO_2(g)$) were calculated separately and added to the results obtained from the THERMO code. We assumed, following Kordis and Gingerich [77KOR/GIN], that the electronic ground state degeneracy, *g*, is equal to 1, 6, and 3, for $CeO_2(g)$, $Ce_2O_2(g)$ and NdO_2 (g), respectively. Thus, the correction applied to the entropy and Gibbs energy function results obtained from THERMO were 14.8976 and 9.1344 $J{\cdot}K^{-1}{\cdot}mol^{-1}$ for $Ce_2O_2(g)$ and $NdO_2(g)$, respectively.

The calculated thermodynamic functions for $CeO_2(g)$, $Ce_2O_2(g)$ and $NdO_2(g)$ are listed in Tables 4, 5 and 6, respectively. Following the practice in thermodynamic literature, extra (non-significant) figures are shown in Tables 4 to 6 to preclude rounding errors and to help maintain consistency when differences in thermodynamic quantities are known to much greater accuracy than the quantities themselves. Tables 4 to 6 also contain the values of Gibbs energy functions for five temperatures for these oxides as reported by Kordis and Gingerich [77KOR/GIN]. A comparison of the values reported by Kordis and Gingerich [77KOR/GIN] with those calculated here shows good agreement, and gives confidence in the present calculations. The predicted high relative stability of $NdO_2(g)$ seems to be the result of the negative enthalpy of formation reported from the analysis of Kordis and Gingerich [77KOR/GIN], rather than to any specific error related to calculations based on the spectroscopic data.

Table 4: Thermodynamic Functions of CeO_2 in Ideal Gaseous State at 1 Bar Pressure[a]

T	$(H-H^o_0)/T$	$-(G^o_T-H^o_0)/T$		S^o	C^o_p
		calculated	literature[b]		
100.00	33.970	193.716		227.687	36.095
200.00	36.438	217.991		254.429	41.695
298.15	39.030	233.039		272.069	46.719
300.00	39.078	233.280		272.358	46.800
400.00	41.487	244.859		286.346	50.361
500.00	43.507	254.339		297.846	52.627
600.00	45.158	262.421		307.579	54.085
700.00	46.507	269.486		315.994	55.055
800.00	47.621	275.770		323.391	55.725
900.00	48.550	281.434		329.984	56.205
1000.00	49.335	286.590		335.925	56.558
1100.00	50.005	291.324		341.329	56.826
1200.00	50.583	295.700		346.282	57.032
1300.00	51.086	299.768		350.854	57.195
1400.00	51.527	303.570		355.097	57.326
1500.00	51.918	307.138		359.056	57.432
1600.00	52.266	310.500		362.766	57.519
1700.00	52.577	313.677		366.255	57.592
1800.00	52.858	316.690	316.88	369.548	57.653
1900.00	53.112	319.555		372.667	57.705
2000.00	53.343	322.285	322.49	375.628	57.750
2100.00	53.554	324.892		378.447	57.788
2200.00	53.748	327.388	327.59	381.136	57.822
2300.00	53.926	329.781		383.707	57.851
2400.00	54.090	332.079	333.32	386.169	57.877
2500.00	54.243	334.290		388.532	57.900
2600.00	54.384	336.420	336.63	390.804	57.920
2700.00	54.515	338.474		392.990	57.938
2800.00	54.638	340.459		395.097	57.954
2900.00	54.753	342.378		397.131	57.968
3000.00	54.861	344.236		399.097	57.981

---

[a] Temperature in K, all other functions are in units of $J \cdot mol^{-1} \cdot K^{-1}$.

[b] Literature values from Kordis and Gingerich [77KOR/GIN].

Table 5: Thermodynamic Functions of Ce_2O_2 in Ideal Gaseous State at 1 Bar Pressure[a]

T	$(H-H^\circ_0)/T$	$-(G^\circ_T-H^\circ_0)/T$		S°	C°_p
		calculated	literature[b]		
100.00	43.578	240.786		284.364	48.942
200.00	47.391	272.252		319.643	54.305
298.15	50.947	291.825		342.772	61.987
300.00	51.015	292.141		343.156	62.122
400.00	54.607	307.314		361.921	68.257
500.00	57.780	319.848		377.628	72.379
600.00	60.458	330.625		391.083	75.112
700.00	62.694	340.117		402.810	76.965
800.00	64.565	348.613		413.178	78.262
900.00	66.143	356.310		422.453	79.197
1000.00	67.486	363.350		430.835	79.891
1100.00	68.639	369.837		438.476	80.417
1200.00	69.640	375.852		445.492	80.826
1300.00	70.514	381.461		451.975	81.149
1400.00	71.284	386.715		457.999	81.408
1500.00	71.967	391.656		463.623	81.619
1600.00	72.577	396.320		468.897	81.793
1700.00	73.124	400.736		473.860	81.939
1800.00	73.618	404.930	405.16	478.548	82.061
1900.00	74.066	408.922		482.988	82.165
2000.00	74.474	412.731	412.94	487.205	82.254
2100.00	74.847	416.373		491.220	82.331
2200.00	75.189	419.863	420.10	495.052	82.398
2300.00	75.505	423.212		498.716	82.457
2400.00	75.796	426.431	426.67	502.227	82.508
2500.00	76.066	429.531		505.596	82.554
2600.00	76.317	432.519	432.78	508.835	82.594
2700.00	76.550	435.403		511.953	82.631
2800.00	76.769	438.191		514.959	82.663
2900.00	76.973	440.888		517.861	82.692
3000.00	77.164	443.500		520.665	82.718

[a] Temperature in K, all other functions are in units of $J \cdot mol^{-1} \cdot K^{-1}$.

[b] Literature values from Kordis and Gingerich [77KOR/GIN].

Table 6: Thermodynamic Functions of NdO_2 in Ideal Gaseous State at 1 Bar Pressure[a]

T	$(H-H^o_0)/T$	$-(G^o_T-H^o_0)/T$		S^o	C^o_p
		calculated	literature[b]		
100.00	34.037	206.848		240.885	36.273
200.00	36.576	231.194		267.770	41.933
298.15	39.204	246.288		285.491	46.961
300.00	39.252	246.530		285.782	47.042
400.00	41.673	258.161		299.834	50.559
500.00	43.690	267.683		311.373	52.781
600.00	45.333	275.798		321.131	54.204
700.00	46.673	282.889		329.562	55.149
800.00	47.777	289.195		336.971	55.801
900.00	48.696	294.876		343.572	56.266
1000.00	49.472	300.047		349.519	56.609
1100.00	50.133	304.793		354.927	56.868
1200.00	50.704	309.180		359.884	57.069
1300.00	51.200	313.258		364.458	57.226
1400.00	51.636	317.068		368.704	57.353
1500.00	52.021	320.644		372.665	57.456
1600.00	52.364	324.012		376.375	57.540
1700.00	52.671	327.195		379.866	57.611
1800.00	52.947	330.213	330.44	383.160	57.670
1900.00	53.198	333.082		386.280	57.720
2000.00	53.425	335.817	336.04	389.242	57.764
2100.00	53.633	338.428		392.061	57.801
2200.00	53.823	340.927	341.15	394.751	57.833
2300.00	53.999	343.323		397.322	57.862
2400.00	54.160	345.625	345.83	399.785	57.886
2500.00	54.310	347.838		402.148	57.908
2600.00	54.449	349.971	350.18	404.420	57.928
2700.00	54.579	352.028		406.607	57.945
2800.00	54.699	354.015		408.714	57.961
2900.00	54.812	355.936		410.748	57.975
3000.00	54.918	357.796		412.714	57.988

---

[a] Temperature in K, all other functions are in units of $J \cdot mol^{-1} \cdot K^{-1}$.

[b] Literature values from Kordis and Gingerich [77KOR/GIN].

5. SUMMARY AND CONCLUSIONS

High-temperature thermodynamic data of fission products are needed to calculate the source terms under accident conditions using thermodynamic codes such as CHMWRK and F*A*C*T. Direct experimental measurements of high-temperature thermodynamic properties are usually difficult and sometimes impossible to obtain. Frequently, the values calculated from the spectroscopic data are more accurate than those determined by direct thermal measurements [62HER]. A code to calculate thermodynamic functions of an ideal gas, at 1 atmospheric pressure, from its spectroscopic data using statistical mechanics methods was commissioned (modified and recompiled); it was tested and verified by comparing of results of calculations for several molecules to results published previously.

The code was used to calculate the thermodynamic functions for three fission-product oxides, $CeO_2(g)$, $Ce_2O_2(g)$ and $NdO_2(g)$, for temperatures between 100 K and 3000 K at 1 bar. These calculations illustrate that one can obtain high-temperature thermodynamic data for gaseous molecules from a knowledge of their spectroscopic properties determined experimentally at more readily accessible temperatures.

We show in Appendix A that fission-product cerium and neodymium make a significant contribution to the health consequences of any nuclear accident. The thermodynamic results obtained on their oxides in this work can be used in the database of a thermodynamic code (such as CHMWRK) that is used to calculate the source term for a nuclear reactor accident condition. As stated earlier (Section 1), the CHMWRK code has been developed by AECL for that purpose, and has a well-documented database. The results obtained from CHMWRK can be used to test and verify other commercial codes, such as SOURCE, SOPHAROES, etc., which are presently being used for safety analyses in the nuclear industry, but may have less transparent database.

6. ACKNOWLEDGMENTS

We thank G.A. Bickel and S.P. Mezyk for reviews of a draft of this report.

7. REFERENCES

[49RUS]
Rushbrooke, G.S. 1949. "Introduction to Statistical Mechanics". Oxford University Press, Oxford, UK.

[61HER/LAU]
Herschbach, D.R. and V.W. Laurie. 1961. "Anharmonic Potential Constants and their Dependence Upon Bond Lengths". J. Chem. Phys. 35, 458-463.

[61LEW/RAN]
Lewis, G. and M. Randall. 1961. "Thermodynamics". 2^{nd} ed. Revised by K.S. Pitzer and L. Brewer. McGraw-Hill, New York, NY.

[62HER]
Herzberg, G. 1962. "Molecular Spectra and Structure. II Infrared and Raman Spectra of Polyatomic Molecules". D. van Nostrand Company Inc. New York, N.Y., USA.

[64SCH]
Schachtschneider, J.H. 1964. "Vibrational Analysis of Polyatomic Molecules". Technical Report 57-65 and 231-64, Shell Development Co. Emeryville, Calif. USA.

[65MOO]
Moore, W.J. 1965. "Physical Chemistry". Prentice-Hall Inc. Englewood Cliffs, N.J., USA.

[72BER/SUN]
Bertie, J.E. and S. Sunder. 1972. "Normal Coordinate Calculations of the Vibrations of Methylene Cyclopropane h_6 and d_6: Erratum". Can. J. Chem. 50, 765.

[72SUN]
Sunder, S. 1972. The Vibrational Spectra of *t*-Butyl Bromide". Ph.D. Thesis. Chemistry Department, University of Alberta, Edmonton, Canada.

[73BER/SUN]
Bertie, J.E. and S. Sunder. 1973. "The Infrared and Raman Spectra and Vibrational Assignment of *t*-Butyl Bromide h_9 and d_9". Can. J. Chem. 51, 3344-3353.

[74GAB/REE]
Gabeinick, S.D., G.T. Reedy and M.G. Chasanov. 1974. "Infrared Spectra and Structure of Some Matrix-isolated Lanthanide and Actinide Oxides". J. Chem. Phys. 60, 1167-1171.

[76SUN/BER]
Sunder, S. and H.J. Bernstein. 1976. "The Vibrational Spectra of the Metalloporphins: A Normal Coordinate Analysis of the Planar Vibrations in the Cu-chelates of Porphin, Porphin-d_4 (*meso*), 1:3:5:7-Tetramethyl Porphin and 1:2:3:4:5:6:7:8-Octamethyl Porphin". J. Raman Spectrosc. 5, 351-371.

[77KOR/GIN]
Kordis, J. and K.A. Gingerich. 1977. "Mass Spectroscopic Observations of Some Polyatomic Gaseous Rare Earth Oxides and their Atomization Energies". J. Chem. Phys. 65, 483-491.

[79SUN/EYE]

Sunder, S., H.H. Eysel, A. Kleeman and K. Seppelt. 1979. "Raman and Infrared Spectra, Normal Coordinate Analysis and Thermodynamic Properties of (methylene-h_2) Sulfur Tetrafluoride and (methylene-d_2) Sulfur Tetrafluoride". Inorg. Chem. 18, 3208-3213.

[80THO/BAL]

Thompson, W.T., C.W. Bale and A.D. Pelton, 1980. "Interactive Computer Tabulation of Thermodynamic Properties with the F*A*C*T System". J. of Metals 33 (12), 18-22.

[82GAR]

Garisto, F. 1982. "Thermodynamics of Iodine, Cesium and Tellurium in the Primary Heat-Transport System Under Accident Conditions". Atomic Energy of Canada Limited Report, AECL-7782.

[84THO/BAL]

Thompson, W.T., C.W. Bale and A.D. Pelton. 1984. "Facility for the Analysis of Chemical Thermodynamics". A.I.Ch.E. Symposium Series, 80 (237), 50-63.

[86ALP/CHA]

Alpert, D.J., D.I.Chanin and L.T. Ritchie. 1986. "Relative Importance of Individual Elements to Reactor Accident Consequences Assuming Equal Release Fractions", Sandia National Laboratories Report, NUREG/CR-4467, SAND85-2575.

[86COH/TAY]

Cohen, E.R. and B.N. Taylor. 1986. "The 1986 Adjustment of the Fundamental Physical Constants". CODATA Bulletin Number 63. Pergamon Press, Oxford.

[88GAR]

Garisto, F. 1988. "Thermodynamic Behaviour of Ruthenium at High Temperatures". Atomic Energy of Canada Limited Report, AECL-9552.

[89TAI/GAU]

Tait, J.C., I.C. Gauld and G.B. Wilkin. 1989. "Derivation of Initial Radionuclide Inventories for the Safety Assessment of the Disposal of Used CANDU Fuel". Atomic Energy of Canada Limited Report, AECL-9881.

[90COR/KON]

Cordfunke, E.H.P. and R.J.M. Konings (Editors). 1990. "Thermochemical Data for Reactor Materials and Fission Products". Elsevier Science Publishers, Amsterdam.

[92GAR]

Garisto, F. 1992. "Thermodynamic Behaviour of Tellurium at High Temperatures". Atomic Energy of Canada Limited Report, AECL-10691, COG-92-248.

[94POW/KME]

Powers, D.A., L.N. Kmetyk and R.C. Schmidt. 1994. "A Review of the Technical Issues of Air Ingression During Severe Reactor Accidents". NUREG/CR-6218, SAND94-0731.

[98BUR]

Bureau International des Poids et Mesures. 1998. "Le Système International d'Unités". 7e Édition. Organisation Intergouvernementale de la Convention du Mètre.

[99LID]

Lide, D.R. (Editor). 1999. "CRC Handbook of Chemistry and Physics". 80th Edition.

APPENDIX A

CERIUM AND NEODYMIUM FISSION PRODUCTS: YIELDS AND CONSEQUENCES

The amounts of different cerium and neodymium isotopes present in typical used CANDU fuel are listed in Table A1. The isotope yields are for UO_2 fuel used in the Bruce "A" reactor, at a burnup of 685 GJ/kg initial U [89TAI/GAU]. The yields are for freshly discharged fuel – a condition relevant for the calculation of the source term for an accident in an operating reactor. The half-lives and the decay modes of cerium and neodymium isotopes present in the irradiated nuclear fuel are also listed in this table. The results listed in Table A1 show that irradiated fuel contains significant quantities of radioactive isotopes of cerium and neodymium (Ce 141, Ce 144, Nd 147 and Nd 148).

Table A1: Cerium and Neodymium Isotopes in Used CANDU Fuel

Nuclide	Yield[a] (mol/kg initial U)	Half-Life[b]	Decay Mode/Energy[b] (/MeV)
Ce 140	1.99E-03		
Ce 141	3.85E-04	32.5 d	β^-/0.581
Ce 142	1.91E-03		
Ce 144	1.24E-03	284.6 d	β^-/0.391
Nd 142	1.52E-05		
Nd 143	1.28E-03		
Nd 144	8.15E-04		
Nd 145	1.17E-03		
Nd 146	1.03E-03		
Nd 147	5.16E-05	10.98 d	β^-/0.896
Nd 148	5.90E-04	1.73 h	β^-/1.691
Nd 150	2.83E-04		

[a] Yields calculated using the ORIGIN-S code by Tait et al. [89TAI/GAU].
[b] From [99LID].

Various workers have combined the information about the radioactivity of the isotopes of the elements present in the irradiated fuel with their biological effects, to determine the relative consequences of their release during a nuclear accident [86ALP/CHA, 94POW/KME]. Table A2 lists the results of Powers et al. [94POW/KME] for cerium and neodymium for a nuclear reactor accident accompanied by air ingress. Their results for iodine and cesium are also shown in this table for comparison purposes.

Table A2: Relative Consequences of Release of Selected Fission Products*

Fission-product Element	Early Exposure[a]			Long-term Exposure[b]	
	Normalized 4 h Bone-Marrow Dose	Normalized 24 h Bone-Marrow Dose	Lung Dose	Bone-Marrow Dose	Total Lung Dose
Ce	0.1	0.2	8.1	0.05	210
Nd	0.03	0.04	0.3	0.002	0.9
I	1.0	1.0	1.0	0.005	0.35
Cs	0.2	0.1	0.09	1.0	1.0

* Results from [94POW/KME].
[a] Normalized with respect to iodine.
[b] Normalized with respect to cesium.

It is clear from the results shown in Table A2 that cerium and neodymium fission products can make significant contributions to the health consequences from any nuclear accident. Hence, it is essential to have reliable data for their relevant compounds (particularly their oxides and hydroxides) in the thermodynamic database used to calculate the source term for a nuclear accident.

APPENDIX B

CALCULATIONS OF THERMODYNAMIC PROPERTIES USING STATISTICAL MECHANICS: INTRODUCTORY NOTES

As stated in Section 2, the theoretical basis for calculating thermodynamic properties from molecular properties using statistical mechanics is well established. This appendix introduces the basic concepts underlying these calculations.

The primary concept in statistical mechanics for calculation of the value of a macroscopic property (such as a thermodynamic property) of a system (called an *ensemble* in statistical mechanics) is a term called "partition function", Q. The partition function of a system is defined as:

$$Q = \Sigma g_i \, e^{-\varepsilon_i/kT} \qquad \text{(B.1)}$$

where ε_I is an energy state (with degeneracies g_i) of its constituent particles, T is the temperature (K) and k is the Boltzmann constant. The partition function is also known as the *sum-over-states*, from the German word *Zustandsumme* [49RUS].

The partition function (Q) of the system is used to calculate its macroscopic properties from the microscopic properties of its constituents; i.e., molecular weight, molecular structure and energy states etc. (Spectroscopic techniques are used to obtain the values of the microscopic properties.) Thus, for example, the entropy (S^0) and the Gibbs energy (G^0) of one mole of a perfect gas are described in terms of its total partition function (Q) by equations [62HER]:

$$S^0 = R(1 - \ln N) + RT\,(d\,(\ln Q)/dT) + R\ln Q \qquad \text{(B.2)}$$

and

$$G^0 = H_0{}^0 + RT \ln N - RT \ln Q \qquad \text{(B.3)}$$

where R is the gas constant, N is the Avogadro number, and $H_0{}^0$ is the zero-point energy.

The total partition function (Q) of the system can be written as a product of the partition functions of the different degrees of freedom of its constituents; i.e.,

$$Q = Q_{tr} \bullet Q_r \bullet Q_v \bullet Q_e \qquad \text{(B.4)}$$

where the subscripts tr, r, v, and e represent the translation, rotational, vibrational and electronic degrees of freedom, respectively. Equation (B.4) implies that there is no coupling between the various degrees of freedom. Also, the *extensive* thermodynamic functions, such as entropy and

Gibbs energy, can be written as the sum of the functions derived from the different degrees of freedom; i.e.,

$$S^0 = S_{tr}^0 + S_r^0 + S_v^0 + S_e^0 \tag{B.5}$$

$$G^0 = G_{tr}^0 + G_r^0 + G_v^0 + G_e^0 \tag{B.6}$$

Thus, one can obtain the entropy of a system by using Equations (B.2), (B.4) and (B.5), and its Gibbs energy by using Equations (B.3), (B.4) and (B.6).

Several authors have derived mathematical formulations to simplify the calculations of the thermodynamic functions by statistical mechanics (e.g., see texts by Rushbrooke [49RUS], Lewis and Randall [61LEW/RAN] and Herzberg [62HER]). The computer code THERMO, the code used in the present work, follows the formulations given by Herzberg. Also, the values of the physical constants used in this code are the same as those used by Herzberg, Table B1. The values of the physical constants given by Herzberg are slightly different from those accepted in the present-day literature [86COH/TAY, 98BUR]. We believe that the errors in the values of the thermodynamic functions, caused by the use of the values for the physical constants listed in Table A1, are much less than the errors from other sources — such as the errors in the values of the structural parameters (used to calculate the rotational parameters), errors in the values of the vibrational frequencies (see Section 4), and errors caused by the assumption of the harmonic behaviour for the vibrations, etc. [62HER].

The code THERMO calculates the thermodynamic functions in units of cal·mole^{-1}·K^{-1}, the units used by Herzberg. The results obtained from THERMO are for an ideal gas at a pressure of 1 atmosphere. These results were converted(1) into J·mole^{-1}·K^{-1}, and for a pressure of 1 bar (Tables 4 to 6) to conform with current thermodynamic conventions and for their use in present-day reactor safety codes, such as CHMWRK.

---

(1) The conversions used were 1 standard atmosphere = 101 325 Pa, and 1 calorie = 4.184 J. The latter conversion may not correspond exactly to the definition for the calorie as used in the original publication [62HER], but it is adequate for our present purposes [98BUR].

Table B1: Physical Constants*

Constant	Symbol	Value
Avogadro number	N	6.0224 E+23
Boltzmann constant	k	1.3807 E-16 erg $\cdot K^{-1}$
Planck constant	h	6.6260 E-27 erg $\cdot$s
Gas constant	R	1.9863 cal$\cdot$mole$^{-1}\cdot K^{-1}$
1/16 mass of the O^{16} atom	amu	1.6600 E-24 g
Velocity of light	c	2.99776E+10 cm$\cdot s^{-1}$
1 atm	P	1.0132E+06 dynes$\cdot cm^{-2}$

*Physical constants used in the code THERMO, from Herzberg, page 538 [62HER].

APPENDIX C

VERIFICATION OF THE CODES

The codes CART and THERMO used in this work were verified by repeating the calculations for several molecules with published results. The code CART was tested by repeating calculations for methyl fluoride-h_3 and methyl fluoride-d_3 [64SCH], *t*-butyl bromide-h_9 and *t*-butyl bromide-d_9 [72SUN], and methylene-cyclopropane-h_6 and methylene-cyclopropane-d_6 [72BER/SUN]. Comparison of the results calculated here with those in the literature showed excellent agreement. The moments of inertia values for *t*-butyl bromide-h_9, *t*-butyl bromide-d_9, methylene-cyclopropane-h_6, and methylene-cyclopropane-d_6 were used, as part of the input for THERMO, to calculate their thermodynamic functions (*vide-infra*).

Thermodynamic functions for several molecules, with published values of the thermodynamic properties, were calculated to verify the computer codes used in the present work. The results of these calculations are listed in Tables C1 to C4. These tables show the values as obtained in the computer output, without rounding them to the appropriate significant figures. (The significant figures in these results are only to the second decimal place, as indicated in the publications of Bertie and Sunder [72BER/SUN], [72SUN] and [73BER/SUN].) A comparison of the results shown in Tables C1 to C4 with those given in the literature for these molecules shows good agreement between the results obtained here and those in the published literature. This provides confidence in the results obtained in the present work.

Table C1: Thermodynamic Functions of Methylene Cyclopropane-*h*$_6$

T	$(H_0-E_0)/T$	$-(G_0-H_0)/T$	S_0	C_p
150	8.619070	46.885630	55.504700	10.274474
200	9.255796	49.447821	58.703617	12.152920
250	10.068722	51.596946	61.665669	14.555906
300	11.038698	53.516069	64.554767	17.240579
350	12.119766	55.297527	67.417293	19.954723
400	13.262982	56.989857	70.252838	22.539393
450	14.428549	58.619043	73.047592	24.922071
500	15.588361	60.199228	75.787589	27.085537

Temperature in K, all other functions are in units of cal·mol^{-1}·K^{-1}.

The expressions $(H_0-E_0)/T$ and $-(G_0-H_0)/T$ from the original references correspond to $(H-H^o_0)/T$ and $-(G^o_T-H^o_0)/T$ as used elsewhere in the present report.

Methylene cyclopropane-*h*$_6$, a_2 frequencies values used are 30816, 1013.4, 860.6, 751.1 cm^{-1} [72BER/SUN].

Table C2: Thermodynamic Functions of Methylene Cyclopropane-d_6

T	$(H_0-E_0)/T$	$-(G_0-H_0)/T$	S_0	C_p
150	9.015	48.165	57.180	11.634
200	10.034	50.891	60.925	14.645
250	11.291	53.261	64.552	18.006
300	12.688	55.441	68.130	21.303
350	14.140	57.506	71.646	24.336
400	15.588	59.489	75.077	27.054
450	17.000	61.406	78.406	29.478
500	18.359	63.268	81.627	31.645

Temperature in K, all other functions are in units of cal·mol^{-1}·K^{-1}.
The expressions $(H_0-E_0)/T$ and $-(G_0-H_0)/T$ from the original references correspond to $(H-H^\circ_0)/T$ and $-(G^\circ_T-H^\circ_0)/T$ as used elsewhere in the present report.
Methylene cyclopropane-d_6, a_2 frequencies values are used 2307.0, 785.0, 631.3 and 534.7 cm^{-1} [72BER/SUN].

Table C3: Thermodynamic Functions of *t*-Butyl Bromide-h_9

T	$(H_0-E_0)/T$	$-(G_0-H_0)/T$	S_0	C_p
50	7.975433	43.533861	51.509294	8.190258
100	8.883293	49.260198	58.143491	11.957543
150	10.683334	53.189230	63.872564	16.447683
200	12.588028	56.524532	69.112561	20.042890
250	14.406083	59.530032	73.936115	23.288695
300	16.155966	62.311673	78.467638	26.518261
350	17.868561	64.930822	82.799383	29.754198
400	19.553725	67.426901	86.980626	32.912839
450	21.207446	69.825594	91.033040	35.917373
500	22.821418	72.143725	94.965143	38.727393

Temperature in K, all other functions are in units of cal·mol^{-1}·K^{-1}.
t-Butyl bromide-h_9, a_2 frequencies values used are 2982, 1457, 1005 and 276 cm^{-1} [72SUN and 73BER/SUN].

Table C4: Thermodynamic Functions of *t*-Butyl Bromide-d_9

T	$(H_0-E_0)/T$	$-(G_0-H_0)/T$	S_0	C_p
50	8.083185	44.329491	52.412676	8.803061
100	9.717860	50.346208	60.064067	14.129193
150	12.011932	54.717461	66.729393	18.871890
200	14.247953	58.481151	72.729105	23.015094
250	16.419144	61.893988	78.313132	27.198644
300	18.566792	65.077342	83.644134	31.383501
350	20.687412	68.098850	88.786262	35.382016
400	22.759973	70.996951	93.756923	39.084746
450	24.765498	73.793962	98.559460	42.463587
500	26.692136	76.503478	103.195614	45.531157

Temperature in K, all other functions are in units of $cal \cdot mol^{-1} \cdot K^{-1}$.

t-Butyl bromide-d_9, a_2 frequencies values used are 2223, 1046, 759 and 196 cm^{-1} [72SUN and 73BER/SUN].

APPENDIX D

CALCULATIONS OF MOMENTS OF INERTIA AND CARTESIAN COORDINATES USING CART

The code CART calculates the moments of inertia and cartesian coordinates of a molecule from its molecular parameters and the atomic weights of the different atoms in the molecule [64SCH]. The moments of inertia for the three oxides (CeO_2(g), Ce_2O_2(g) and NdO_2(g)) are listed in Table 2 of the main text. Here we list the cartesian coordinates of the atoms in the molecules calculated using CART. The atomic coordinates are in units of nm.

CeO_2(g)

Atom	Atom No.	X	Y	Z	Mass
Ce	1	0.0	0.0	0.0	140.12
O	2	0.188	0.0	0.0	15.99491
O	3	-0.1558591	0.1051283	0.0	15.99491

Ce_2O_2(g)

Atom	Atom No.	X	Y	Z	Mass
Ce	1	0.0	0.0	0.0	140.12
O	2	0.191	0.0	0.0	15.99491
O	3	0.0	0.191	0.0	15.99491
Ce	4	0.191	0.191	0.0	140.12

NdO_2(g)

Atom	Atom No.	X	Y	Z	Mass
Nd	1	0.0	0.0	0.0	144.24
O	2	0.189	0.0	0.0	15.99491
O	3	-0.0945	0.1636788	0.0	15.99491

ISSN 0067-0367

To identify individual documents in the series, we have assigned an AECL-number to each.

Please refer to the AECL-number when requesting additional copies of this document from:

Information Centre, Information Management Branch
AECL
Chalk River, Ontario
Canada K0J 1J0

Fax: (613) 584-8144 Tel.: (613) 584-3311 ext. 4623

Pour identifier les rapports individuels faisant partie de cette series, nous avons affecté un numéro AECL-à chacun d'eux.

Veuillex indiquer le numéro AECL-lorsque vous demandez d'autres exemplaires de ce rapport au:

Service de Distribuition des Documents Officiels
EACL
Chalk River (Ontario)
Canada K0J 1J0

Fax: (613) 584-8144 Tel.: (613) 584-3311 poste 4623