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THERMODYNAMIC PROPERTIES OF CESIUM UP TO 1500° K

by Sheldon Heimel

Lewis Research Center

Cleveland, Ohio

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THERMODYNAMIC PROPERTIES OF CESIUM UP TO 1500° K

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SUMMARY

Consistent tables of thermodynamic properties of elemental cesium were compiled for both the pure species and the equilibrium vapor on the saturation line using selected values of 10 500 calories per mole for the heat of dissociation of dimer and -18 920 calories per mole for the heat of condensation of monomer. The equilibrium vapor properties and properties of condensed cesium (Cs) are given to 1500° K, while properties of gaseous monomer and dimer are given to 2500° K.

The table of mixture properties on the saturation line gives the following thermodynamic functions: temperature T, total vapor pressure P, weight fraction of dimer in vapor x_2, molecular weight M_g, specific volume v, density ρ, enthalpy of condensed phase h_c, enthalpy of vaporization Δh_{vap}, enthalpy of vapor h_g, entropy of condensed phase s_c, entropy of vaporization Δs_{vap}, entropy of vapor s_g, and heat capacities (equilibrium and frozen) $(c_p)_{eq}$ and $(c_p)_{fr}$. Assigned enthalpies are relative to enthalpy of the crystal at 298.15° K, which is taken to be zero. The tables of properties for the pure species give the following thermodynamic functions for the standard state: heat capacity at constant pressure C_p^o, sensible enthalpy $H_T^o - H_O^o$, entropy S_T^o, sensible free energy $F_T^o - H_O^o$, the sum of sensible enthalpy at T° K and chemical energy at 0° K H_T^o, and values of enthalpy changes and logarithms of the equilibrium constants. The latter two functions are given for the reactions of formation of Cs(c), Cs_1(g), and Cs_2(g) from the assigned reference state Cs(c) ($(\Delta H_T^o)_f$ and $\log_{10} K_f$) and from Cs_1(g) (ΔH_T^o and $\log_{10}$ K).

Thermodynamic functions for the gases were generated from atomic and molecular data, whereas the functions of the condensed phase were based on selected experimental data that were smoothed and made self-consistent.

INTRODUCTION

Current work at the Lewis Research Center indicates the need for reliable vapor pressure data as well as other thermodynamic properties for cesium in the following areas:

(1) Rankine cycle engine. The thermodynamic properties of cesium are needed in order to make an analysis of a Rankine cycle system and its components.

(2) Thermionic plasma diode. Improved performance requires knowledge of the concentration of cesium in the gas phase and the rate of evaporation from a liquid surface. Such data can be derived with the help of an equation for pressure as a function of saturation temperature.

Accordingly, to meet these needs, the following tables have been generated:

(1) Boiling points corresponding to pressures of from 10^{-8} to 10 atmospheres

(2) Properties on the saturation line from 100° to 1500° K: temperature T, $^{\circ}$K; total vapor pressure P, atmospheres; partial pressure of monomer p_1, atmospheres; partial pressure of dimer p_2, atmospheres; weight fraction of dimer x_2, gram per gram mixture; molecular weight of vapor M_g, gram per mole; specific volume of vapor v, cubic centimeter per gram; density of vapor ρ, gram per 1000 cubic centimeters; enthalpy of condensed phase h_c, calories per gram; enthalpy of vaporization Δh_{vap}, calories per gram; enthalpy of vapor h_g, calories per gram; entropy of condensed phase s_c, calories per gram per $^{\circ}$K; entropy of vaporization Δs_{vap}, calories per gram per $^{\circ}$K; entropy of vapor s_g, calories per gram per $^{\circ}$K; equilibrium heat capacity of vapor $(c_p)_{eq}$, calories per gram per $^{\circ}$K; and frozen heat capacity of vapor $(c_p)_{fr}$, calories per gram per $^{\circ}$K

(3) Thermodynamic functions for each pure species: temperature T, $^{\circ}$K; heat capacity at constant pressure C_p°, calories per mole per $^{\circ}$K; sensible enthalpy $H_T^{\circ} - H_O^{\circ}$, calories per mole; entropy S_T°, calories per mole per $^{\circ}$K; sensible free energy $F_T^{\circ} - H_O^{\circ}$, calories per mole; sum of sensible enthalpy at T° K and chemical energy at 0° K H_T°, calories per mole; and values of enthalpy changes and logarithms of the equilibrium constants. The latter two functions are each given for two different reactions of formation. One set of functions, $(\Delta H_T^{\circ})_f$ and $\log_{10} K_f$ is for the reaction of formation of $Cs_1(g)$ and $Cs_2(g)$ from the assigned reference state $Cs(c)$. The other set of functions, ΔH_T° and $\log_{10} K$, is for the formation of $Cs(c)$ and $Cs_2(g)$ from $Cs_1(g)$. The symbols g and c refer to the gas and condensed phases (crystal and liquid), respectively. The thermodynamic functions for the gases were generated from atomic and molecular data, whereas the functions of the condensed phase were

based on selected experimental data that were smoothed and made self-consistent. The functions for the condensed phase are given up to 1500° K; those for the monomeric and dimeric gases are given up to 2500° K.

When vapor pressure data are available, they may be combined with sensible free energy data by use of the third law of thermodynamics to calculate an implied value of $(\Delta H_0^o)_c$ (heat of condensation of monomer at 0° K) for each available vapor pressure point. If the vapor pressure data are completely consistent with the thermodynamic data, the calculated values of $(\Delta H_0^o)_c$ will be constant. The usual result, however, is that there is variation in the calculated values of $(\Delta H_0^o)_c$. Depending on the extent and nature of this variation, some average $(\Delta H_0^o)_c$ may be selected. This selected value of $(\Delta H_0^o)_c$ together with the sensible free energy data may now be used to calculate vapor pressures. These calculated vapor pressures and the experimental vapor pressures will, of course, not agree. At this point either the experimental vapor pressures must be abandoned or the theoretical free energies must be modified.

In this report a similar procedure to that just outlined will be followed. There are several differences in the analysis, namely,

(1) The experimental vapor pressures are first smoothed.

(2) The gas is assumed to be a mixture of monomer and dimer. Therefore, the intermediate step of calculating equilibrium compositions is required.

(3) The procedure for selecting a value of $(\Delta H_0^o)_c$ is to find that value of $(\Delta H_0^o)_c$ which gives a minimum deviation of calculated and smoothed experimental vapor pressures over the entire range.

(4) The selected $(\Delta H_0^o)_c$ and thermodynamic data are used to calculate a recommended set of vapor pressures for the crystal and the liquid.

PRESENTATION OF TABLES

Table I contains the smoothed values of C_p^o for crystalline cesium up to 100° K together with consistent values of $H_T^o - H_0^o$, S_T^o, and $-(F_T^o - H_0^o)$. Generation of these data will be discussed in SELECTION OF INITIAL DATA.

Tables II to IV (pp. 5-7) give the thermodynamic properties of Cs (crystal, liquid) up to 1500° K; $Cs_1(g)$ up to 2500° K; and $Cs_2(g)$ up to 2500° K, respectively. The properties presented are C_p^o, $H_T^o - H_0^o$, S_T^o, $-(F_T^o - H_0^o)$, H_T^o, $(\Delta H_T^o)_f$, $\log_{10} K_f$, ΔH_T^o, and $\log_{10} K$. In table II, data for the crystal extend up to the melting point, 301.8° K. Data for the liquid are tabulated at 100° intervals from the melting point to 1500° K. In

TABLE I. - THERMODYNAMIC PROPERTIES OF CESIUM (CRYSTAL) UP TO 100° K

T, °K	C_p^o, cal/(mole)(°K)	$H_T^o - H_O^o$, cal/mole	S_T^o, cal/(mole)(°K)	$-(F_T^o - H_O^o)$, cal/mole
5	0.746	1.2	0.3342	0.5
10	2.379	9.0	1.3539	4.5
15	3.719	23.9	2.5835	14.9
20	4.680	44.5	3.7993	31.5
25	5.110	69.1	4.8935	53.3
30	5.385	95.3	5.8513	80.2
35	5.558	122.7	6.6955	111.6
40	5.668	150.8	7.4454	147.0
45	5.741	179.4	8.1174	185.9
50	5.795	208.2	8.7252	228.1
55	5.842	237.3	9.2798	273.1
60	5.888	266.6	9.7901	320.8
65	5.933	296.2	10.2631	370.9
70	5.977	325.9	10.7044	423.4
75	6.016	355.9	11.1182	477.9
80	6.049	386.1	11.5076	534.5
85	6.075	416.4	11.8751	593.0
90	6.097	446.8	12.2230	653.2
95	6.122	477.4	12.5533	715.2
100	6.160	508.1	12.8682	778.7

tables III (Cs_1) and IV (Cs_2), data are tabulated at 100° intervals from 0° to 2500° K for the ideal gases. Table V (p. 8) contains the molecular constants used to calculate thermodynamic functions for dimeric cesium.

Table VI (p. 8) contains recommended boiling points of liquid cesium calculated from the final set of thermodynamic properties. These boiling points correspond to pressures from 10^{-8} to 10 atmospheres at every power of 10. For comparison, boiling points obtained from equation (33) are also given.

Table VII (p. 9) gives the following thermodynamic properties of the equilibrium gaseous mixture on the saturation line: T, P, p_1, p_2, x_2, M_g, v, ρ, h_c, Δh_{vap}, h_g, s_c, Δs_{vap}, s_g, $(c_p)_{eq}$, and $(c_p)_{fr}$. The values of P, p_1, p_2, v, and ρ are given in floating-point notation, where the decimal number is to be multiplied by 10 raised to the power of the sign and the two digits following the letter E; for example, 0.100000E-03 is $0.100000 \times 10^{-3} = 0.0001$.

Assigned Reference State

The assigned reference state is Cs (crystal, liquid). The crystal is the reference state up to the melting point, and the liquid phase is the reference state above the melting point.

Assigned Enthalpy Values H_T^o

For some applications (ref. 1), it is convenient to combine sensible enthalpy $H_T^o - H_O^o$ and chemical energy H_O^o into one numerical value, H_T^o. The arbitrary base

TABLE II. - THERMODYNAMIC PROPERTIES OF CESIUM (CRYSTAL, LIQUID)

T, ^{o}K	C_p^o, cal/(mole)(^{o}K)	$H_T^o - H_O^o$, cal/mole	S_T^o, cal/(mole)(^{o}K)	$-(F_T^o - H_O^o)$, cal/mole	H_T^o, cal/mole	Formation from assigned reference state		Formation from gaseous atoms	
						$(\Delta H_T^o)_f$, cal/mole	$\log_{10} K_f$	ΔH_T^o, cal/mole	$\log_{10} K$
0	-----	0	0	0	-1807.2	0	----	-18920.0	-------
100	6.160	508.1	12.8662	778.7	-1299.1	0	0	-18906.7	36.1548
200	6.560	1144.1	17.2607	2308.0	-663.1	0	0	-18757.5	15.5456
298.15	6.953	1807.2	19.9532	4141.8	0.0	0	0	-18594.0	8.8232
300	6.960	1820.1	19.9962	4178.8	12.9	0	0	-18590.4	8.7302
a301.8	6.967	1832.6	20.0379	4214.8	25.4	0	0	-18586.8	8.6584
a301.8	7.455	2352.7	21.7612	4214.8	545.5	0	0	-18066.7	8.5544
400	7.455	3084.8	23.8613	6459.7	1277.6	0	0	-17622.4	5.4664
500	7.455	3830.3	25.5246	8932.1	2023.1	0	0	-17573.8	3.5315
600	7.455	4575.8	26.8840	11554.6	2768.6	0	0	-17325.1	2.2588
700	7.455	5321.3	28.0332	14301.9	3514.1	0	0	-17076.4	1.3445
800	7.455	6066.8	29.0287	17156.1	4259.6	0	0	-16827.7	0.7027
900	7.455	6812.3	29.9067	20103.3	5005.1	0	0	-16579.0	0.1956
b937.71	7.455	7093.4	30.2127	21237.4	5286.2	0	0	-16485.2	0.0341
1000	7.455	7557.8	30.6922	23134.4	5750.6	0	0	-16330.3	-0.2041
1100	7.455	8303.3	31.4027	26239.7	6496.1	0	0	-16081.7	-0.5241
1200	7.455	9048.8	32.0514	29412.9	7241.6	0	0	-15833.1	-0.7434
1300	7.455	9794.3	32.6481	32648.3	7987.1	0	0	-15584.6	-1.0105
1400	7.455	10539.8	33.2006	35941.0	8732.6	0	0	-15336.4	-1.1962
1500	7.455	11285.3	33.7150	39287.1	9478.1	0	0	-15088.7	-1.3545

[a]Melting point.

[b]Normal boiling point to equilibrium mixture.

TABLE III. - THERMODYNAMIC PROPERTIES OF Cs_1 (GAS)

T, ^oK	C_p^o, $\frac{cal}{(mole)(^oK)}$	$H_T^o - H_O^o$, cal/mole	S_T^o, $\frac{cal}{(mole)(^oK)}$	$-(F_T^o - H_O^o)$, cal/mole	H_T^o, cal/mole	Formation from assigned reference state		Formation from gaseous atoms	
						$(\Delta H_T^o)_f$, cal/mole	$\log_{10} K_f$	ΔH_T^o, cal/mole	$\log_{10} K$
0	------	0	-------	0	17112.8	18920.0	-------	0	-----
100	4.9681	496.8	36.5168	3154.9	17609.6	18908.7	-37.1548	0	0
200	4.9681	993.6	39.9605	6998.5	18105.4	18769.5	-15.5486	0	0
298.15	4.9681	1481.3	41.9442	11024.4	18594.0	18594.0	-8.8232	0	0
300	4.9681	1490.4	41.9749	11102.0	18603.2	18590.3	-8.7392	0	0
301.8	4.9681	1499.4	42.0046	11177.6	18612.2	18066.7	-8.6584	0	0
a400	4.9681	1987.3	43.4042	15374.4	19100.0	17822.4	-5.4064	0	0
500	4.9681	2484.1	44.5128	19772.3	19596.8	17573.8	-3.5315	0	0
600	4.9681	2980.9	45.4186	24270.2	20093.7	17325.1	-2.2593	0	0
700	4.9682	3477.7	46.1844	28851.4	20590.5	17076.4	-1.3645	0	0
800	4.9682	3974.5	46.8478	33503.7	21087.3	16827.7	-0.7027	0	0
900	4.9682	4471.3	47.4330	38218.3	21584.1	16579.0	-0.1956	0	0
937.71	4.9682	4658.7	47.6369	40010.9	21771.5	16485.2	-0.0341	0	0
1000	4.9683	4968.2	47.9564	42938.3	22080.4	16330.3	0.2041	0	0
1100	4.9686	5465.0	48.4300	47808.0	22577.8	16081.7	0.5261	0	0
1200	4.9694	5961.9	48.8623	52672.9	23074.7	15833.1	0.7904	0	0
1300	4.9712	6458.9	49.2601	57579.3	23571.7	15584.6	1.0105	0	0
1400	4.9749	6956.2	49.6287	62524.0	24069.0	15336.4	1.1952	0	0
1500	4.9814	7454.0	49.9721	67504.2	24566.7	15088.7	1.3545	0	0
1600	4.9919	7952.6	50.2939	72517.7	25065.4			0	0
1700	5.0079	8452.6	50.5970	77562.3	25565.3			0	0
1800	5.0307	8954.4	50.8839	82636.5	26067.2			0	0
1900	5.0618	9459.0	51.1566	87738.6	26571.7			0	0
2000	5.1025	9967.1	51.4173	92867.4	27079.9			0	0
2100	5.1541	10479.8	51.6674	98021.8	27592.6			0	0
2200	5.2175	10998.3	51.9086	103200.6	28111.1			0	0
2300	5.2936	11523.8	52.1422	108403.2	28636.5			0	0
2400	5.3832	12057.5	52.3693	113628.8	29170.3			0	0
2500	5.4867	12600.9	52.5911	118876.9	29713.6			0	0

[a]The reference element is crystal cesium up to 301.8° K and liquid cesium above 301.8° K.

TABLE IV. - THERMODYNAMIC PROPERTIES OF Cs_2 (GAS)

T, ^oK	C_p^o, cal/(mole)(^oK)	$H_T^o - H_O^o$, cal/mole	S_T^o, cal/(mole)(^oK)	$-(F_T^o - H_O^o)$, cal/mole	H_T^o, cal/mole	Formation from assigned reference state		Formation from gaseous atoms	
						$(\Delta H_T^o)_f$, cal/mole	$\log_{10} K_f$	ΔH_T^o, cal/mole	$\log_{10} K$
0	------	0	-------	0	23725.6	27340.1	-------	-10500.0	-------
100	8.9436	843.2	57.9961	4956.4	24565.8	27157.1	-52.3203	-10655.3	19.9869
200	9.0457	1743.6	64.2330	11103.0	25469.2	26795.5	-22.7462	-10743.6	8.3110
298.15	9.1202	2635.4	67.8598	17597.0	26361.0	26361.0	-13.2133	-10827.1	4.4332
300	9.1215	2652.3	67.9162	17722.6	26377.9	26352.1	-13.0041	-10828.6	4.3842
301.8	9.1227	2668.7	67.9707	17844.9	26394.3	25303.3	-12.9797	-10830.0	4.3372
[a]400	9.1893	3567.8	70.5456	24652.0	27293.4	24738.2	-8.5271	-10906.7	2.4057
500	9.2572	4490.1	72.6074	31813.6	28215.7	24169.6	-5.8528	-10978.0	1.2102
600	9.3259	5419.3	74.3012	39161.5	29144.9	23607.7	-4.1114	-11042.4	0.4983
700	9.3959	6355.4	75.7441	46665.5	30081.0	23052.8	-2.8967	-11100.0	-0.1578
800	9.4674	7298.5	77.0034	54304.2	31024.1	22504.9	-2.0073	-11150.5	-0.6919
900	9.5402	8248.9	78.1227	62061.5	31974.5	21964.3	-1.3321	-11193.7	-0.9410
937.71	9.5681	8609.2	78.5148	65015.0	32334.8	21762.3	-1.1186	-11208.1	-1.0504
1000	9.6146	9206.6	79.1317	69925.1	32937.2	21431.0	-0.8051	-11229.6	-1.2132
1100	9.6905	10171.8	80.0516	77884.9	33897.4	20995.3	-0.3843	-11258.1	-1.4366
1200	9.7679	11144.7	80.8981	85932.9	34870.3	20387.2	-0.0424	-11279.0	-1.6232
1300	9.8468	12125.5	81.6830	94062.5	35851.1	19876.9	0.2397	-11292.3	-1.7313
1400	9.9273	13114.2	82.4157	102267.8	36839.8	19374.6	0.4754	-11298.2	-1.9169
1500	10.0093	14111.0	83.1034	110544.1	37836.6	18880.4	0.6745	-11296.9	-2.0345
1600	10.0928	15116.1	83.7520	118887.2	38841.7			-11289.1	-2.1373
1700	10.1779	16129.6	84.3664	127293.4	39855.2			-11275.4	-2.2780
1800	10.2646	17151.7	84.9506	135759.4	40877.3			-11257.1	-2.3085
1900	10.3527	18182.6	85.5080	144282.6	41908.2			-11235.3	-2.3803
2000	10.4425	19222.3	86.0413	152860.2	42947.9			-11211.8	-2.4449
2100	10.5337	20271.1	86.5530	161490.1	43996.7			-11188.5	-2.5032
2200	10.6266	21329.1	87.0451	170170.2	45054.7			-11167.5	-2.5560
2300	10.7209	22396.5	87.5196	178898.6	46122.1			-11151.0	-2.6042
2400	10.8168	23473.3	87.9779	187673.6	47198.9			-11141.6	-2.6483
2500	10.9143	24559.9	88.4214	196493.6	48285.5			-11141.8	-2.6889

[a]The reference element is crystal cesium up to 301.8^o K and liquid cesium above 301.8^o K.

TABLE V. - MOLECULAR CONSTANTS FOR DIATOMIC CESIUM

Molecular weight	265.82
Symmetry number	2
Electronic state[a]	$^1\Sigma$
Statistical weight	1
ω_e, cm^{-1} [a]	41.990
$\omega_e x_e$, cm^{-1} [a]	0.08005
$\omega_e y_e$, cm^{-1} [a]	-0.0001643
B_e, cm^{-1} [b]	0.01272
α_e, cm^{-1} [b]	0.000035
D_e, cm^{-1} [b]	0.467×10^{-8}

[a]Constant from ref. 10.
[b]Constant from ref. 11.

TABLE VI. - BOILING POINTS OF LIQUID CESIUM FROM 10^{-8} TO 10 ATMOSPHERES

$\log_{10} P_{atm}$	Boiling points, $^{\circ}$K	
	Recommended	From equation (33)[a]
-8	317.8	317.8
-7	345.8	345.8
-6	379.2	379.4
-5	420.1	420.3
-4	471.2	471.4
-3	537.0	537.2
-2	625.0	625.0
-1	749.1	748.7
0	937.7	937.3
1	1264.0	1264.5

[a]$\log_{10} P_{atm} = \frac{-4053.30}{T} + 7.04453 - 0.915282 \log_{10} T$.

for assigning values to the enthalpy of Cs(c) was a value of zero at 298.15° K. Since table II gives $(H^{\circ}_{298.15} - H^{\circ}_{O})_{Cs(c)} = 1807.2$ calories per mole, then $(H^{\circ}_{O})_{Cs(c)} =$ -1807.2 calories per mole. From table II, $(\Delta H^{\circ}_{O})_{c} = (H^{\circ}_{O})_{Cs(c)} - (H^{\circ}_{O})_{Cs_1(g)} =$ -18 920.0 calories per mole. Therefore, $(H^{\circ}_{O})_{Cs_1(g)} = -1807.2 - (-18\,920.0) =$ 17 112.8 calories per mole. From table IV, $(\Delta H^{\circ}_{O})_{2} = -D^{\circ}_{O} = (H^{\circ}_{O})_{Cs_2(g)} - 2(H^{\circ}_{O})_{Cs_1(g)} =$ -10 500 calories per mole. Therefore,

$$(H^{\circ}_{O})_{Cs_2(g)} = -10\,500.0 + 2(17\,112.8) = 23\,725.6 \qquad \text{cal/mole}$$

Heats of Formation

Two sets of values for heats of formation are given in tables II to IV. The first set (col. 7) is for the formation of the given species from Cs(c), $(\Delta H^{\circ}_{T})_{f}$; the second set (col. 9) is for the formation from $Cs_1(g)$, (ΔH°_{T}). For $Cs_2(g)$ at 298.15° K, for example,

$$(\Delta H^{\circ}_{298.15})_{f,2} = (H^{\circ}_{298.15})_{Cs_2(g)} - 2(H^{\circ}_{298.15})_{Cs(c)} \tag{1}$$

TABLE VII. - THERMODYNAMIC PROPERTIES OF CESIUM ON SATURATION LINE

T, ^{o}K	P, atm	Partial pressure, atm		x_2, g/g mixture	M_g, g/mole	v, cc/g	ρ, g/1000 cc
		p_1	p_2				
100	0.700238E-36	0.700238E-36	0	0	132.9100	0.881712E 38	0.113416E-34
200	0.282767E-15	0.282767E-15	0.163606E-22	0.000000	132.9100	0.436690E 18	0.228995E-14
298.15	0.150230E-08	0.150223E-08	0.611635E-13	0.000081	132.9154	0.122528E 12	0.816142E-08
300	0.182308E-08	0.182300E-08	0.804806E-13	0.000088	132.9159	0.101594E 12	0.984309E-08
[a]301.8	0.219558E-08	0.219547E-08	0.104789E-12	0.000095	132.9163	0.848638E 11	0.117836E-07
[a]301.8	0.219561E-08	0.219550E-08	0.104792E-12	0.000095	132.9163	0.848626E 11	0.117837E-07
400	0.341969E-05	0.341672E-05	0.296875E-08	0.001735	133.0254	0.721553E 08	0.138590E-04
500	0.295484E-03	0.294083E-03	0.140152E-05	0.009441	133.5404	0.103981E 07	0.961717E-03
600	0.557482E-02	0.549759E-02	0.772344E-04	0.027330	134.7514	0.655416E 05	0.152575E-01
700	0.444664E-01	0.432016E-01	0.126485E-02	0.055316	136.6906	0.945055E 04	0.105814E-00
800	0.208062E-00	0.198266E-00	0.979553E-02	0.089926	139.1674	0.226720E 04	0.441072E-00
900	0.683671E 00	0.637354E 00	0.463169E-01	0.126898	141.9143	0.761201E 03	0.131371E 01
[b]937.71	0.100008E 01	0.924375E 00	0.757002E-01	0.140736	142.9706	0.538170E 03	0.185815E 01
1000	0.175554E 01	0.159982E 01	0.155720E-00	0.162950	144.6994	0.323037E 03	0.309562E 01
1100	0.376807E 01	0.335835E 01	0.409726E-00	0.196145	147.3621	0.162561E 03	0.615152E 01
1200	0.707012E 01	0.617109E 01	0.899025E 00	0.225626	149.8106	0.929698E 02	0.107562E 02
1300	0.119630E 02	0.102442E 02	0.171877E 01	0.251251	152.0058	0.586644E 02	0.170461E 02
1400	0.186618E 02	0.157093E 02	0.295255E 01	0.273202	153.9381	0.399906E 02	0.250059E 02
1500	0.272819E 02	0.226204E 02	0.466151E 01	0.291861	155.6196	0.289923E 02	0.344919E 02

T, ^{o}K	h_c, cal/g	Δh_{vap}, cal/g	h_g, cal/g	s_c, cal/(g)(^{o}K)	Δs_{vap}, cal/(g)(^{o}K)	s_g, cal/(g)(^{o}K)	$(c_p)_{eq}$, cal/(g)(^{o}K)	$(c_p)_{fr}$, cal/(g)(^{o}K)
100	-9.7743	142.2668	132.4925	0.0968139	1.4226679	1.5194868	0.0373794	0.0373794
200	-4.9891	141.2196	136.2305	0.1298676	0.7060981	0.8359656	0.0373801	0.0373794
298.15	0	139.8963	139.8963	0.1501256	0.4692146	0.6193402	0.0375824	0.0373792
300	0.0971	139.8683	139.9653	0.1504492	0.4662276	0.6166767	0.0375969	0.0373792
[a]301.8	0.1911	139.8410	140.0321	0.1507629	0.4633566	0.6141195	0.0376118	0.0373791
[a]301.8	4.1043	135.9279	140.0321	0.1637288	0.4503905	0.6141193	0.0376118	0.0373791
400	9.6125	134.0232	143.6357	0.1795298	0.3350579	0.5145876	0.0398111	0.0373752
500	15.2216	131.8333	147.0549	0.1920465	0.2636666	0.4557130	0.0458544	0.0373554
600	20.8306	129.2160	150.0466	0.2022730	0.2153599	0.4176329	0.0541423	0.0373147
700	26.4397	126.1692	152.6089	0.2109194	0.1802417	0.3911611	0.0614825	0.0372601
800	32.0488	122.8336	154.8824	0.2184094	0.1535420	0.3719515	0.0660140	0.0372054
900	37.6578	119.3871	157.0449	0.2250162	0.1326523	0.3576685	0.0676452	0.0371621
[b]937.71	39.7735	118.0880	157.8615	0.2273185	0.1259323	0.3532508	0.0676643	0.0371503
1000	43.2676	115.9676	159.2352	0.2309262	0.1159676	0.3468938	0.0671774	0.0371375
1100	48.8767	112.6646	161.5413	0.2362719	0.1024224	0.3386943	0.0654981	0.0371339
1200	54.4857	109.5154	164.0011	0.2411527	0.0912628	0.3324155	0.0632733	0.0371519
1300	60.0948	106.5303	166.6251	0.2456422	0.0819464	0.3275866	0.0609153	0.0371916
1400	65.7039	103.7060	169.4098	0.2497991	0.0740757	0.3238748	0.0586486	0.0372548
1500	71.3129	101.0281	172.3410	0.2536686	0.0673521	0.3210207	0.0565811	0.0373430

[a]Melting point.

[b]Normal boiling point to equilibrium mixture.

$$(\Delta H^{o}_{298.15})_2 = (H^{o}_{298.15})_{Cs_2(g)} - 2(H^{o}_{298.15})_{Cs_1(g)} \tag{2}$$

Equilibrium Constants

Two sets of logarithms of the equilibrium constants for the two formation reactions discussed previously are also listed in tables II to IV. The equilibrium constant K_f for formation from the assigned reference element (col. 8) is obtained from the standard free energy change $(\Delta F^{o}_{T})_f$ by means of the equation

$$\log_{10} K_f = -\frac{(\Delta F^{o}_{T})_f}{2.3025851\ RT} \tag{3}$$

The equilibrium constant K for formation from the atomic gas is obtained from a similar equation

$$\log_{10} K = -\frac{\Delta F^{o}_{T}}{2.3025851\ RT} \tag{4}$$

Atomic weights, the universal gas constant and the constants used in the evaluation of the entropy constant were the same as those used in reference 1.

SELECTION OF INITIAL DATA

Crystal

Heat capacities of the crystal (table I, p. 4) were derived by smoothing the experimental data from the sources given in table VIII.

The following procedure was used to obtain smooth data from 0^{o} to 100^{o} K. A least-squares fit of the data of reference 2 was used in the temperature range from 0^{o} to 4^{o} K. Data from 4^{o} to 20^{o} K were obtained from a curve drawn through the data of reference 2 at 4^{o} K and through the data of references 3 and 4 at 20^{o} K. Data from 20^{o} to 100^{o} K were obtained from a least-squares fit of the data of reference 4 in that temperature range.

Between 100^{o} and 210^{o} K, the data of reference 4 are approximately linear in tem-

TABLE VIII. - REFERENCES FOR HEAT CAPACITIES OF CRYSTAL

Temperature range, $^{\circ}K$	Source
0.3 to 4	Ref. 2
8 to 12	Private communication from Professor D. C. McCollum of University of California in Riverside, California and ref. 3
20 to 210	Ref. 4

perature. The heat capacities at 100° and 210° K yield the equation

$$C_p^o = 5.76 + 0.004\ T \tag{5}$$

Above 210° K, thermal effects associated with the cesium-oxygen system cause anomalous increases in heat capacity and therefore these data were not used. Equation (5) was used to extrapolate heat capacities up to the melting point. The melting point of 301.8° K and the heat of fusion of 520.1 calories per mole were taken from reference 5.

Reference 4 gives a melting point of 300.5° K and the total heat absorption between the crystal at 262.5° K and the liquid at 300.5° K. If this heat is compared with the sensible enthalpy change of the crystal between these two temperatures, as calculated from equation (5), the implied heat of melting is 514 calories per mole. This value is in reasonable agreement with the value adopted.

The enthalpy from the linear equation for C_p^o, when combined with the heat of fusion, gave

$$\left(H^o_{301.8}\right)_{Cs(liquid)} - \left(H^o_{298.15}\right)_{Cs(crystal)} = 545.5 \quad \text{cal/mole} \tag{6}$$

Liquid

A number of empirical equations have been used to satisfactorily fit enthalpy data as a function of temperature for various substances; however, heat capacity data derived from differentiation of the enthalpy equations are often very unreliable. For any particular species, various empirical enthalpy equations that might be chosen yield considerably different sets of heat capacities.

Two sets of experimental enthalpy data were considered: that of references 6 and 7. The curve of reference 6 exhibits an anomalous bump from 351° to 620° K, followed by a straight line to 1238° K. It is recommended in reference 6 that just the straight-line portion be used, which has a standard deviation $\sigma = 1.5$ percent. For the cubic equation (from 340° to 1176° K) of reference 7, $\sigma = 1.1$ percent.

The implied $C_p^o = 7.25$ calories per mole per $^{\circ}K$ of reference 6 differs greatly from the heat capacities derived from the enthalpy curve of reference 7 and listed in table IX.

According to reference 7, the curves of heat capacity against temperature of liquid

TABLE IX. - HEAT CAPACITIES DERIVED FROM ENTHALPY CURVE OF REFERENCE 7

Absolute temperature, T, $^{\circ}K$	Heat capacity at constant pressure for standard state, C_p^o, cal/(mole)($^{\circ}K$)
301.8	10.35
500	7.28
700	6.23
1000	8.53
1200	12.64
1500	22.67

cesium and other alkali metals have a parabolic shape; that is, heat capacity initially decreases with increasing temperature, reaches a minimum, and then increases continuously. However, a parabolic shape for heat capacity of these species is only the result of selecting a cubic to represent experimental enthalpy data.

It was thought advisable to use a straight line for enthalpy because (1) the straight line, in the standard deviation sense, represents cesium enthalpies about as well as the cubic does and (2) the cubic has the disadvantage of implying very large heat capacities for even a few hundred degrees extrapolation.

The actual straight line used in this report was based on the straight-line data of reference 6 but was constrained to go through the previously calculated relative heat content of 545.5 calories per mole at the melting point (eq. (6)). This gives the following equation:

$$(H_T^o)_{Cs(liquid)} - (H_{298.15}^o)_{Cs(crystal)} = -1704.5 + 7.455\ T \qquad (7)$$

Equation (7) implies a constant value of $C_p^o = 7.455$ calories per mole per $^{\circ}K$.

Had the data of reference 7 been fitted to a straight line and similarly constrained to go through the heat content of 545.5 calories per mole, a constant value of $C_p^o = 7.595$ calories per mole per $^{\circ}K$ would have resulted. The enthalpies would be, on the average, only about 1 percent higher than those derived from the data of reference 6.

The enthalpy data of reference 8 are about 6 to 7 percent lower than the data of both references 6 and 7 over the range from about 600° to 1300° K; therefore, they were not used.

Monomer (Gas)

The partition function used to compute the thermodynamic properties of Cs_1 was truncated by the temperature-dependent cutoff technique used in reference 1. The results of these computations are exactly the same up to 2200° K as would be obtained by simply using all levels given in reference 9 with no cutoff. Above 2200° K enthalpy and entropy differ only in the last place computed and heat capacity in the last or second last place.

Dimer (Gas)

The method used to compute the thermodynamic properties of Cs_2 is the method for diatomic molecules described in reference 1. The constants for the dimer are shown in table V (p. 8). They were taken from references 10 and 11.

Vapor Pressures

During the period 1913 to 1937, the investigations reported in references 12 to 18 obtained vapor pressure data for cesium in the temperature range from 238° to 670° K. This early work was evaluated in reference 19 where it was concluded that, except for the results of references 17 and 18, the early work is not too reliable.

The vapor pressures in the 455° to 589° K range (ref. 17) were used in reference 19 to generate a vapor pressure equation. Inasmuch as the data of reference 17 are only relative pressure data (obtained by the magneto-optical method) and are converted to absolute pressure data by relating them to the unreliable data of reference 13, it seems prudent to disregard the data of reference 17.

Recently, the first experimental measurements in the temperature range that included the boiling point (742° to 1199° K) were reported in reference 20. These data check reasonably well with the later data of reference 6 (727° to 1334° K).

In view of the previous observations, the data of references 18 (vapor pressures in the liquid range), 20, and 6 were combined and fitted by the least-squares technique. All the data were given the same weight. The results of several empirical equations were compared. The following equation, which is in the form of the Kirchhoff equation, was accepted because it gave as satisfactory results as the other forms considered:

$$\log_{10} P = -\frac{3920.38}{T} + 5.71342 - 0.519781 \log_{10} T \tag{8}$$

If only vapor pressures were considered in this report, then the smoothed experimental vapor pressures obtained from equation (8) would be accepted. As pointed out in the INTRODUCTION, however, these smoothed data, when combined with other thermodynamic data, lead to inconsistencies in the heat of condensation of the monomer at 0° K $(\Delta H_0^{\circ})_c$. Therefore, the data from equation (8) are used only for preliminary analysis, whereas the final recommended vapor pressures are calculated as explained in detail in the section Pressures and Weight Fractions of Gaseous Species.

Heat of Dissociation at 0^{o} K

An upper bound (4020 cm^{-1}) for the heat of dissociation at 0^{o} K(D_O^o) is estimated in reference 21 by analytical extrapolation of the ground state vibrational intervals. A lower bound (3318 cm^{-1}) is estimated in reference 21 by making certain assumptions as to the final states of the excited atoms produced. The average of these two values, which is equivalent to 10 500±1000 calories per mole of dimer, is recommended in this reference.

The estimate of 0.453 eV or 10 450 calories per mole from the correlation of force constants, equilibrium internuclear distances, and heats of dissociation of the alkali metals is obtained in reference 22. A technique for deducing a value of D_O^o where D_O^o was not well known is suggested in reference 23. This technique gave an optimum D_O^o = 10 000 calories per mole which is in fairly close agreement with the spectroscopic value of 10 500 calories per mole.

The calculation of $(\Delta H_O^o)_c$, which is discussed in the next section, depends in part on the value of D_O^o. While no value of D_O^o that was tried gave a constant value of $(\Delta H_O^o)_c$ over the entire temperature range of 301.8° to 1500° K, values of D_O^o from about 10 000 to 11 500 calories per mole gave the most nearly constant value of $(\Delta H_O^o)_c$.

Based on this analysis, the conclusion was that the spectroscopic value was approximately correct, and the value D_O^o = 10 500 calories per mole was selected.

Heat of Condensation of Monomer at 0^{o} K

The values of $(\Delta H_O^o)_c$ in calories per mole are given in a number of publications as follows: -19 048 (ref. 24), -18 790 (ref. 19), -19 050 (ref. 25), and -19 035 (ref. 26).

The aforementioned values of $(\Delta H_O^o)_c$ are based on the pre-1962 vapor pressures. Therefore, this report will recommend a "best" (ΔH_O^o) of -18 920 on the basis of the newer vapor pressures, as discussed in the following section.

THERMODYNAMIC ANALYSIS

As discussed in the INTRODUCTION, the procedure for the selection of a value for $(\Delta H_O^o)_c$ is to find that $(\Delta H_O^o)_c$ for which the difference between the calculated and smoothed experimental vapor pressures is a minimum. As a first step, it is necessary to compute $(\Delta H_O^o)_c$ for each temperature in the range of interest.

Derivation of $(\Delta H_0^o)_c$

The zero-degree heat of condensation of monomer was computed by means of the relation

$$(\Delta H_O^o)_c = (\Delta F_T^o)_c - \Delta(F_T^o - H_O^o)_c \tag{9}$$

where

$$(\Delta F_T^o)_c = (F_T^o)_{Cs(c)} - (F_T^o)_{Cs_1(g)} = RT \ln p_1 \tag{10}$$

and

$$\Delta(F_T^o - H_O^o)_c = (F_T^o - H_O^o)_{Cs(c)} - (F_T^o - H_O^o)_{Cs_1(g)} \tag{11}$$

Partial Pressure of Monomer

The partial pressure of monomer p_1 in atmospheres is obtained from the simultaneous solution of Dalton's Law and the equilibrium-constant equation for the dimerization reaction

$$2\,Cs_1 = Cs_2$$

The equations are

$$P = p_1 + p_2 \tag{12}$$

and

$$K_2 = \frac{p_2}{p_1^2} \tag{13}$$

where P is the total pressure, p_2 is the partial pressure of dimer, and K_2 is the equilibrium constant of dimerization. Values of K_2 are obtained from table IV (p. 7). The solution of equations (12) and (13) is

$$p_1 = \frac{-1 + \sqrt{4PK_2 + 1}}{2K_2} \tag{14}$$

Therefore, apparent values of $(\Delta H_O^o)_c$ can be computed at every temperature of interest by starting with given values of D_O^o, values of $F_T^o - H_O^o$ for monomer, dimer, and condensed phase, and smoothed experimental vapor pressures P_{FIT}. This procedure can be summarized as follows:

$$\begin{array}{cccc}
(F_T^o - H_O^o)_{Cs(c)} & (F_T^o - H_O^o)_{Cs_1(g)} & K_2 & P_{FIT} \\
\text{(Table II)} & \text{(Table III)} & \text{(Table IV)} & \text{(Eq. (8))}
\end{array}$$

$$\begin{array}{ccc}
(F_T^o - H_O^o)_{Cs(c)},\ (F_T^o - H_O^o)_{Cs_1(g)} \xrightarrow{\text{Equation (11)}} \Delta(F_T^o - H_O^o)_c & & K_2,\ P_{FIT} \xrightarrow{\text{Equation (14)}} p_1
\end{array}$$

$$\Delta(F_T^o - H_O^o)_c,\ p_1 \xrightarrow{\text{Equation (9)}} (\Delta H_O^o)_c$$

RESULTS OF CALCULATING $(\Delta H_O^o)_c$

The apparent $(\Delta H_O^o)_c$ values computed by means of this procedure from equation (9) are given in table X. The maximum difference is about 1 percent.

If some single arbitrary value of $(\Delta H_O^o)_c$ is selected, then for each of the previous temperatures there will be a difference between the smoothed experimental vapor pressure P_{FIT} and the vapor pressure P_{CALC} calculated with this arbitrary $(\Delta H_O^o)_c$ value.

For this analysis, an error function may be defined as $|P_{FIT} - P_{CALC}|/P_{FIT}$ averaged over the previous number of temperatures. The procedure for selecting a value of $(\Delta H_O^o)_c$ is to find that value of $(\Delta H_O^o)_c$ which gives the minimum error function.

The results of calculating the error function for various values of $(\Delta H_O^o)_c$ are given in table XI. The optimum $(\Delta H_O^o)_c$ was taken to be -18 920 calories per mole to the nearest 5 calories.

The fact that there is still about 4 percent error between the smoothed experimental vapor pressure and vapor pressure calculated with the optimum $(\Delta H_O^o)_c$, indicates that

TABLE X. - APPARENT VALUES OF $-(\Delta H^0_0)_c$

AS A FUNCTION OF TEMPERATURE

Temperature, T, ^{o}K	$-(\Delta H^0_0)_c$, cal/mole	Temperature, T, ^{o}K	$-(\Delta H^0_0)_c$, cal/mole
301.8	18 791.6	1000	18 965.1
400	18 872.5	1100	18 954.3
500	18 921.7	1200	18 937.0
600	18 949.3	1300	18 913.1
700	18 963.6	1400	18 881.9
800	18 969.7	1500	18 843.4
900	18 970.0		

TABLE XI. - ERROR FUNCTION

FOR VARIOUS VALUES

OF $-(\Delta H^0_0)_c$

$-(\Delta H^0_0)_c$, cal/mole	Error function, $\lvert\Delta P\rvert/P$
18 850	0.0538
18 900	.0397
18 910	.0381
18 920	.0370
18 925	.0370
18 930	.0372
18 950	.0389
18 970	.0458

discrepancies still remain which may be in any of the following data:

(a) Experimental vapor pressures

(b) D^0_0

(c) Molecular constants of dimer (and, consequently, its thermodynamic properties)

(d) Heat content (and other derived thermodynamic properties) of the condensed phase

(e) $(\Delta H^0_0)_c$

The 4 percent error may also be due, in part, to the presence of a higher polymer, for example, trimer or tetramer; however, this possibility has not been considered in this report.

CALCULATION OF EQUILIBRIUM MIXTURE PROPERTIES ON SATURATION LINE

As explained in the INTRODUCTION, selection of an optimum value of $(\Delta H^0_0)_c$ makes it possible to compute a set of vapor pressures consistent with the sensible free energies of the pertinent species. These vapor pressures and other equilibrium properties on the saturation line (e.g., enthalpy, specific heat, and entropy) are given in table VII (p. 9). The equations used to obtain these properties are given in the following sections.

Pressures and Weight Fractions of Gaseous Species

By starting with the optimized $(\Delta H^0_0)_c$ and the sensible free energies of monomer and condensed phase, monomer pressure was computed with equations (9) to (11).

Dimer pressure was computed from equation (13). The total pressure P_{CALC} was obtained from the sum of p_1 and p_2.

The weight fraction of monomer x_1 was obtained from the mole fraction of monomer N_1; thus,

$$N_1 = \frac{p_1}{P} \tag{15}$$

$$x_1 = \frac{N_1}{2 - N_1} \tag{16}$$

The weight fraction of the dimer x_2 was obtained from the defining equation

$$x_1 + x_2 = 1 \tag{17}$$

Enthalpy of Vaporization and Entropy of Vaporization

The heat of vaporization in calories per gram from the condensed state to the equilibrium mixture on the saturation line was obtained from

$$\Delta h_{vap} = \frac{2x_1(\Delta H_T^O)_{f,1} + x_2(\Delta H_T^O)_{f,2}}{M_2} \tag{18}$$

where M_2 is the molecular weight of dimer (265.82 g/mole). The heats of formation are obtained from tables III and IV (pp. 6 and 7).

The entropy of vaporization in calories per gram is obtained from equation (18) by means of

$$\Delta s_{vap} = \frac{\Delta h_{vap}}{T} \tag{19}$$

Enthalpy, Specific Heat, and Entropy of Cesium Vapor

The enthalpy h_g in calories per gram of an equilibrium mixture can be defined by

$$h_g = \sum_{i=1}^{2} \frac{x_i (H_T^o)_i}{M_i} = \sum_{i=1}^{2} x_i h_i \tag{20}$$

Equation (20) for saturation conditions gives the same results as the usual equation for the enthalpy of a mixture

$$h_g = h_{vap} + h_c$$

where h_c is the enthalpy of the condensed phase in calories per gram (table VII, p. 9).

The equilibrium specific heat at constant pressure in calories per gram per ^oK is defined by

$$(c_p)_{eq} = \left(\frac{\partial h}{\partial T}\right)_p \tag{21}$$

Using equation (20) results in equation (21) becoming

$$(c_p)_{eq} = \sum_{i=1}^{2} x_i (c_p)_i + \sum_{i=1}^{2} h_i \left(\frac{\partial x_i}{\partial T}\right)_p \tag{22}$$

or

$$(c_p)_{eq} = (c_p)_{fr} + (c_p)_r \tag{23}$$

From equation (17), it follows that

$$\left(\frac{\partial x_1}{\partial T}\right)_p = -\left(\frac{\partial x_2}{\partial T}\right)_p \tag{24}$$

Therefore,

$$(c_p)_r = \left(\frac{\partial x_2}{\partial T}\right)_p (h_2 - h_1) = \left(\frac{\partial x_2}{\partial T}\right)_p \frac{(\Delta H_T^o)_2}{M_2} \tag{25}$$

Values of $(\Delta H_T^o)_2$ are tabulated in table IV (p. 7). Values of $(\partial x_2/\partial T)_p$ may be calculated from the following equation:

$$\left(\frac{\partial x_2}{\partial T}\right)_p = \frac{(\Delta H_T^o)_2}{RT^2} \frac{x_2(2 - x_2)(1 - x_2)}{2} \tag{26}$$

Equation (26) may be derived from the following expression, which is equivalent to equation (13):

$$K_2 = \frac{x_2(2 - x_2)}{4P(1 - x_2)^2} \tag{27}$$

and from the van't Hoff isobar, namely,

$$\left(\frac{\partial \ln K_2}{\partial T}\right)_p = \frac{(\Delta H_T^o)_2}{RT^2} \tag{28}$$

The entropy of the gas mixture may be obtained from

$$s_g = \Delta s_{vap} + s_c \tag{29}$$

where s_c is the entropy of the condensed phase in calories per gram per ^oK (table VII, p. 9) and Δs_{vap} is obtained from equation (19). Equation (29) gives the identical results as the usual equation for the entropy of a mixture.

Molecular Weight of Mixture

An expression for the molecular weight of the mixture M_g (in g/mole) in terms of the molecular weight and weight fraction of the dimer may be obtained as follows:

$$M_g = \frac{1}{n} = \frac{1}{n_1 + n_2} = \frac{1}{\frac{x_1}{M_1} + \frac{x_2}{M_2}} = \frac{M_2}{2 - x_2} \tag{30}$$

where n, n_1, and n_2 are the number of moles of mixture, monomer, and dimer per gram of mixture, respectively.

Specific Volume and Density of Mixture

The specific volume v in cubic centimeters per gram may be obtained from the ideal gas law

$$v = \frac{RT}{PM_g} = \frac{82.05971\ T}{PM_g} \tag{31}$$

The density ρ in grams per 1000 cubic centimeters is, therefore,

$$\rho = \frac{1000}{v} \tag{32}$$

DISCUSSION OF VAPOR PRESSURES

Vapor Pressures Above Liquid

Table VI contains boiling points of liquid cesium at saturation pressures from 10^{-8} to 10 atmospheres at every power of 10. These data were calculated in two ways:

(1) From the recommended thermodynamic data, as explained in the section THERMODYNAMIC ANALYSIS

(2) By a least-squares equation fitted to the recommended P_{CALC} values with a standard deviation of 0.5 percent

$$\log_{10} P_{atm} = \frac{-4053.30}{T} + 7.04453 - 0.915282 \log_{10} T \tag{33}$$

On the average the two sets of boiling points differ by about 0.2° K. It should be emphasized that the vapor pressure equation (eq. (33)) is recommended rather than equation (8).

Figures 1 and 2 compare the experimental vapor pressures of liquid cesium with a curve drawn through the recommended vapor pressures. The agreement of the two sets is seen to be very good. Figure 1 covers the temperature range from 303° to 1334° K. Figure 2 covers only the range from 729° to 1334° K to facilitate detailed comparison.

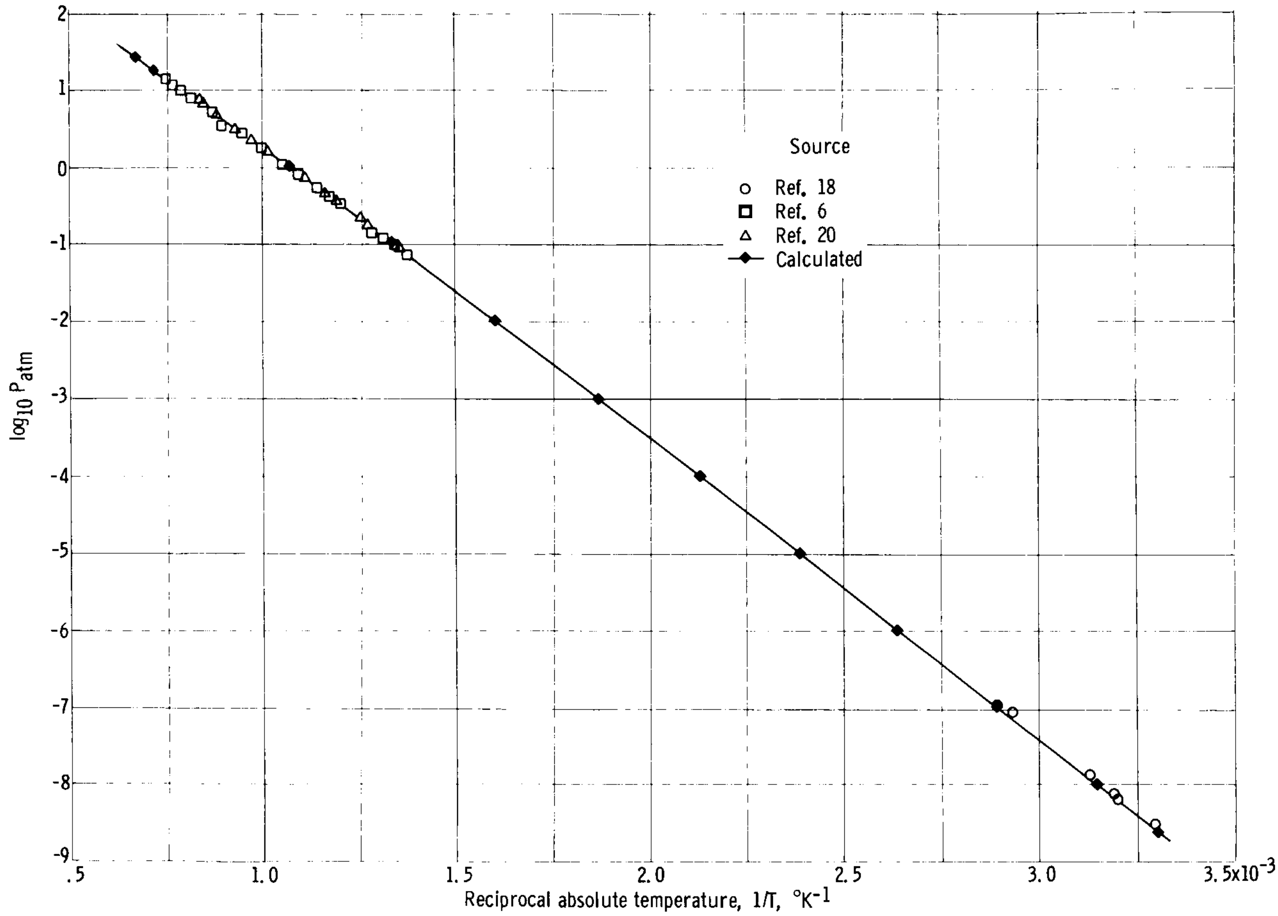

Figure 1. - Comparison of experimental and calculated vapor pressures above liquid cesium (303° to 1334° K).

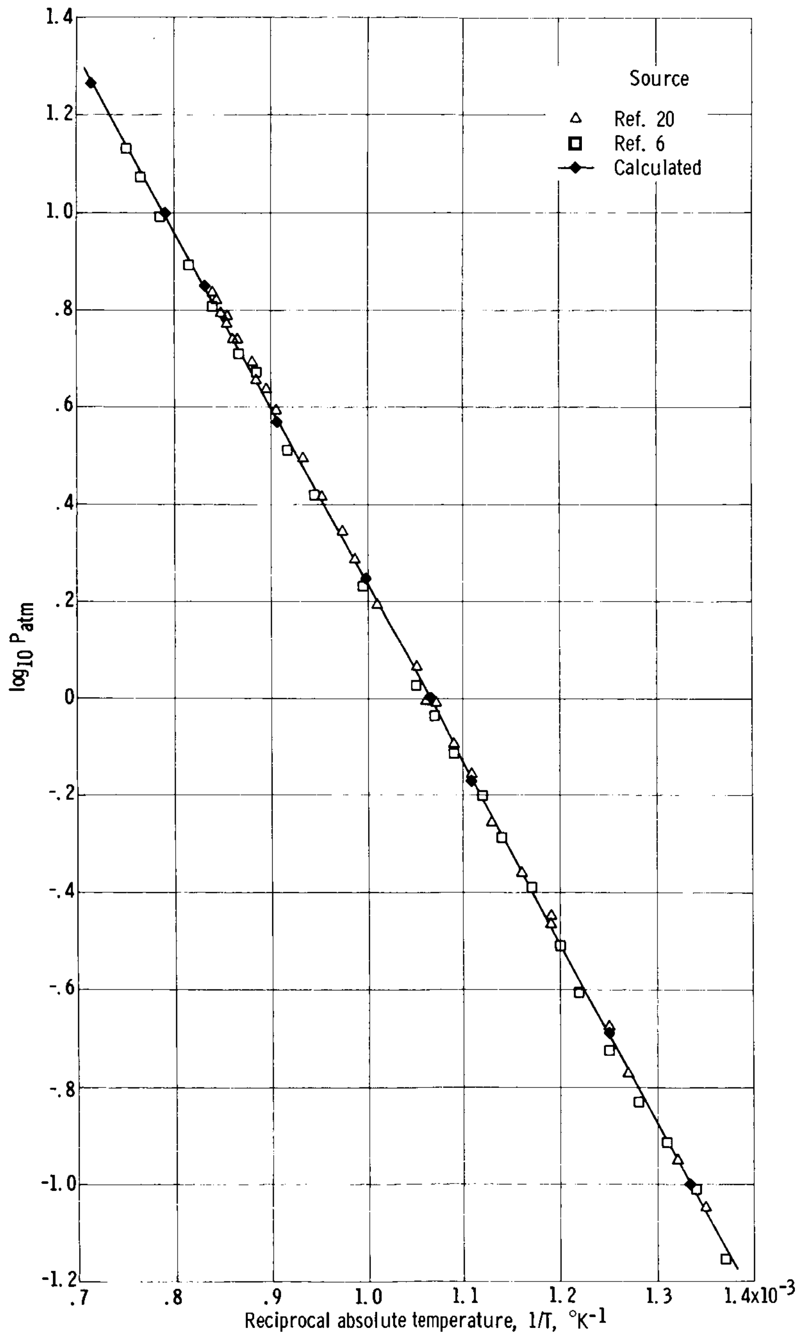

Figure 2. - Comparison of experimental and calculated vapor pressures above liquid cesium (729° to 1334° K).

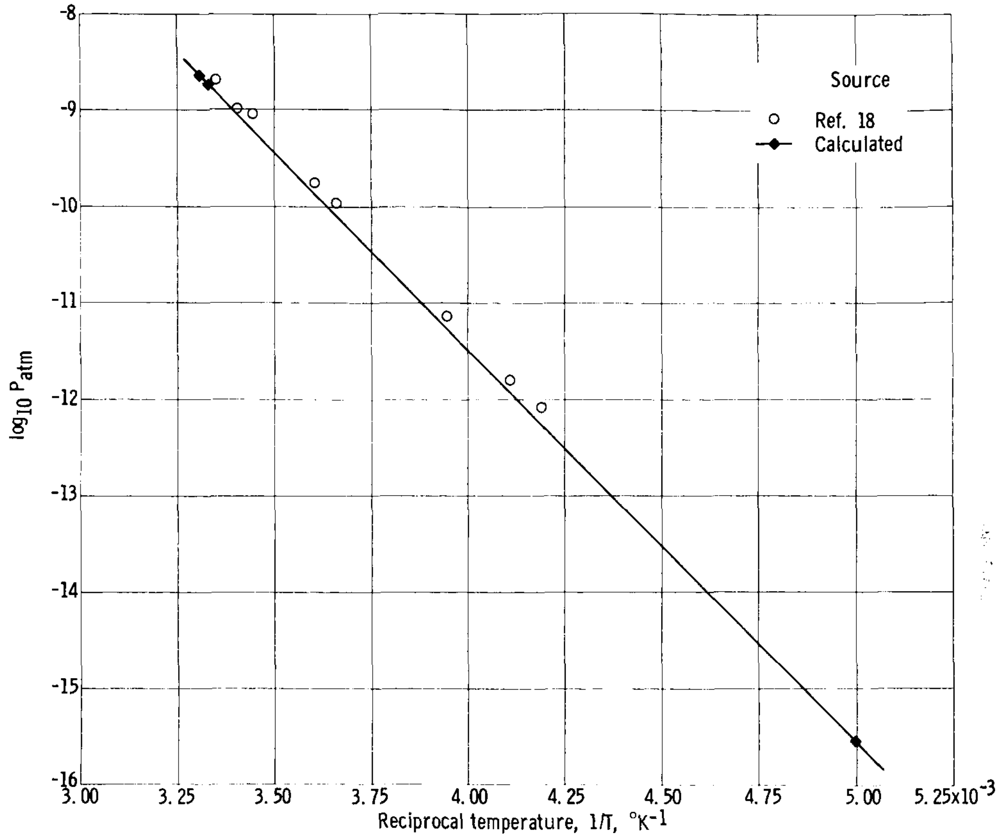

Figure 3. - Comparison of experimental and calculated vapor pressures above crystalline cesium.

Subsequent to the completion of the analysis, a vapor pressure equation in the temperature range 928° to 1558° K was presented in reference 27. On the average, these vapor pressures are about 2 percent lower than those recommended in this report.

Vapor Pressures Above Crystal

Experimental vapor pressures above the crystal are available from reference 18 at temperatures from 238° to 298° K. In order to be consistent with the thermodynamic data adopted for this report, however, vapor pressures from 100° to 301.8° K were calculated in the same manner as were the vapor pressures above the liquid.

On the average, the calculated vapor pressures between 238° and 298° K were 30 percent lower than the experimental ones (fig. 3). This difference is not significant, however, inasmuch as at the low pressure levels involved, the average difference is only in the order of 10^{-9} atmosphere. Furthermore, the lower calculated vapor pressures are consistent with the assumption of reference 26 that the experimental vapor pressures are too high.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, April 26, 1965.

APPENDIX - SYMBOLS

B_e rotational constant, cm^{-1}

C_p^o heat capacity at constant pressure for standard state, cal/(mole)(^oK)

$(c_p)_{eq}$ equilibrium specific heat at constant pressure of mixture, cal/g

$(c_p)_{fr}$ frozen specific heat at constant pressure of mixture, cal/g

$(c_p)_r$ reactive specific heat at constant pressure of mixture, cal/g

D_e spectroscopic constant for rotational stretching, cm^{-1}

D_O^o dissociation energy at 0^o K, cal/mole

F_T^o Gibbs free energy for standard state, cal/mole

$F_T^o - H_O^o$ sensible free energy for standard state, cal/mole

H_T^o sum of sensible enthalpy at T^o K and chemical energy at 0^o K for standard state, cal/mole

$H_T^o - H_O^o$ sensible enthalpy for standard state, cal/mole

ΔH_T^o enthalpy change for formation of substance from element in atomic gas state, cal/mole

$(\Delta H_T^o)_f$ enthalpy change for formation of substance from assigned reference element, cal/mole

H_O^o chemical energy at 0^o K for standard state, cal/mole

h enthalpy, cal/g

Δh_{vap} heat of vaporization to 1 gram of equilibrium vapor

K equilibrium constant for reaction of formation from element in atomic gas state

K_f equilibrium constant for reaction of formation from assigned reference element

M molecular weight based on chemical scale of natural oxygen, g/mole

N_i mole fraction of i^{th} species, moles of i^{th} species per mole of mixture

n number of moles per gram of equilibrium mixture

P total vapor pressure, atm

p_i partial pressure of i^{th} species, atm

R universal gas constant, 1.98726 cal/(mole)(^oK) or 82.05971 (cc)(atm)/(mole)(^oK)

S_T^o entropy for standard state, cal/(mole)(^oK)

s	entropy, $cal/(g)(^{o}K)$
Δs_{vap}	entropy of vaporization to 1 gram of equilibrium vapor
T	absolute temperature, ^{o}K
v	specific volume of vapor, cc/g
x_i	weight fraction of i^{th} species, g of i^{th} species per g of mixture
α_e	vibration-rotation interaction constant for diatomic molecule, cm^{-1}
ρ	density of vapor, g/1000 cc
σ	standard deviation
ω_e	zero-order vibrational frequency for diatomic molecule, cm^{-1}
$\omega_e x_e, \omega_e y_e$	anharmonicity constants for diatomic molecule, cm^{-1}

Subscripts:

c	condensed phase property
f	formation from assigned reference element
g	property of equilibrium vapor mixture
1	monomer property
2	dimer property

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