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MASS SPECTROMETRIC KNUDSEN CELL STUDIES OF VAPORIZATION OF LANTHANUM AND SCANDIUM CARBIDES AND DISSOCIATION ENERGY OF LaC_2, LaC_3, LaC_4, ScC_2, AND ScC_4

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16. Abstract

The vaporization of the lanthanum-carbon and scandium-carbon systems was studied over the temperature ranges 2267 to 2600 K and 2165 to 2328 K, respectively. Experimentally determined reaction enthalpies were used to derive dissociation energies for the molecular metal dicarbides and tetracarbides: $D_0^0(\text{La-C}_2) = 668\pm8$ kJ mole^{-1}, $D_0^0(\text{C}_2\text{-La-C}_2) = 1320\pm16$ kJ mole^{-1}, $D_0^0(\text{Sc-C}_2) = 565\pm21$ kJ mole^{-1}, and $D_0^0(\text{C}_2\text{-Sc-C}_2) = 1217\pm24$ kJ mole^{-1}. The atomization energy of lanthanum tricarbide was determined to be 1759 ± 31 kJ mole^{-1}. The heat of formation of solid lanthanum dicarbide was calculated as $\Delta H^0_{298,f} = -89\pm24$ kJ mole^{-1}. For the lanthanum-carbon system, vapor pressures were determined (in N/m^2 and over the temperature range 1900 to 2600 K): $\log P_{La} = (-2.606\times10^4/T) + 10.162$, $\log P_{LaC_2} = (-3.327\times10^4/T) + 12.813$, $\log P_{LaC_3} = (-4.414\times10^4/T) + 14.557$, and $\log P_{LaC_4} = (-4.301\times10^4/T) + 15.067$.

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SUMMARY

The vaporization of the lanthanum-carbon and scandium-carbon systems was studied over the temperature ranges 2267 to 2600 K and 2165 to 2328 K, respectively. Experimentally determined reaction enthalpies were combined with published thermodynamic data to yield the following atomization energies in kilojoules per mole: $D^o_{0,atom}(LaC_2) = 1257\pm8$, $D^o_{0,atom}(LaC_3) = 1759\pm31$, $D^o_{0,atom}(LaC_4) = 2500\pm16$, $D^o_{0,atom}(ScC_2) = 1155\pm21$, and $D^o_{0,atom}(ScC_4) = 2397\pm24$. In addition, dissociation energies for the molecular metal dicarbides and tetracarbides were derived: $D^o_0(La\text{-}C_2) = 668\pm8$ kJmole^{-1}, $D^o_0(C_2\text{-}La\text{-}C_2) = 1320\pm16$ kJ mole^{-1}, $D^o_0(Sc\text{-}C_2) = 565\pm21$ kJ mole^{-1}, and $D^o_0(C_2\text{-}Sc\text{-}C_2) = 1217\pm24$ kJ mole^{-1}. Ion intensities of the parent molecular ions La^+, LaC_2^+, LaC_3^+, and LaC_4^+ were combined with absolute effusion measurements from the literature to obtain the vapor pressure equations (1900 to 2600 K): $\log_{10} P_{La} = (-2.606\times10^4/T) + 10.162$, $\log_{10} P_{LaC_2} = (-3.327\times10^4/T) + 12.813$, $\log_{10} P_{LaC_3} = (-4.414\times10^4/T) + 14.557$, and $\log_{10} P_{LaC_4} = (-4.301\times10^4/T) + 15.067$, where the units of pressure are newton per square meter. The heat of formation of solid lanthanum dicarbide was calculated as $\Delta H^o_{298,f} = -89\pm24$ kilojoules per mole.

INTRODUCTION

Vaporization studies of some group IIIB, IVB, VB, and VIB transition metal-carbon and rare-earth - carbon systems have shown that the dicarbide and tetracarbide species exist as stable molecules in the gas phase in thermodynamic equilibrium with the condensed phase system (refs. 1 to 4). These findings prompted us to investigate the vaporization of the carbon systems of two other group IIIB elements, lanthanum (La) and scandium (Sc). Previous studies of these two systems by other investigators have established the existence of the dicarbides but the tetracarbides were not reported (refs. 5 to 8). Chupka, Berkowitz, Giese, and Inghram reported the ratio of lanthanum dicarbide (LaC_2) to La to be equal to 0.6 at 2500 K from their mass spectrometric Knudsen cell experiments. They used both second- and third-law methods to obtain enthalpy values ΔH_0^o of 192±42 and 159±42 kilojoules per mole, respectively, for the reaction $La(g) + 2C(s) = LaC_2(g)$. Jackson, Bedford, and Barton (ref. 6) in a mass spectrometric free-vaporization experiment observed $LaC_2(g)$ and reported a ΔH_{2200}^o of 150±5 kilojoules per mole for the same reaction. Faircloth, Flowers, and Pummery (ref. 7) combined the gravimetric data they obtained from a target collection effusion experiment with the results of reference 5 to calculate La and LaC_2 vapor pressures and certain reaction enthalpies.

The scandium-carbon system has been studied in detail by Verhaegen, Smoes, and Drowart (ref. 8). They identified the gaseous ScC_2 molecule and in the temperature range from 2015 to 2111 K used the third-law method to calculate its dissociation energy $D_0^o(Sc\text{-}C_2)$ as 566±21 kilojoules per mole.

We speculated that by extending the temperature range to higher limits than used in previous investigations, the respective tetracarbide molecules could be identified and measured. The purpose of the research reported here was to observe all detectable carbide species of La and Sc and to evaluate some of the thermodynamic properties for the La-C and Sc-C systems.

EXPERIMENTAL

Samples

The mass spectrometer Knudsen cell apparatus used in this study was the same as that described previously (refs. 9 and 10). Tungsten Knudsen cells with graphite liners were used in all experiments. A mixture of metal filings and graphite powder made up the sample which was initially loaded into the liner. The graphite powder and liner were Ultra Carbon grade UFS material with a purity of 99.995 weight percent. The metal filings were obtained from La or Sc ingots purchased from Michigan Chemical Corporation and Alfa Inorganics, respectively. The ingots had a purity of 99.9 weight percent. Emission spectrographic analysis of the La filings showed iron to be the major metallic impurity with trace amounts of aluminum, calcium, copper, magnesium, manganese, nickel, silicon, tin, and titanium. The scandium filings had iron and tantalum as the major metallic impurities with traces of aluminum, calcium, magnesium, manganese, lead, and silicon.

Carbide samples were prepared in situ in the Knudsen cell vacuum chamber of the mass spectrometer. Verhaegen, Smoes, and Drowart (ref. 8) have shown that Sc reacts with graphite above 1650 K in successive steps to form the ScC phase. The metal-carbon mixtures were outgassed by heating them to 1500 K for 16 hours. When the pressure in the vacuum chamber decreased to the low 10^{-7} torr range, the cell temperature was raised to approximately 2300 K while the pressure was kept at or below 5×10^{-6} torr. The results of Spedding, Gschneidner, and Daane (ref. 11) indicate that this temperature was sufficient for lanthanum carbide ($LaC_2(s)$) formation.

For the lanthanum-carbon experiment the sample temperature was raised to 2651 K before systematic ion intensity measurements were begun. This temperature is above the dicarbide-graphite eutectic point (ref. 11). Upon cooling to the temperatures used in the experiment, the sample was assumed to be composed of a mixture of carbon saturated dicarbide phase and graphite which, according to the phase diagram, is a composition very close to $LaC_{2.0} + C$, that is, the ϵ-$LaC_2 + C$ phase boundary (ref. 11). At the conclusion of the experiment the sample residue was removed from the Knudsen cell for X-ray diffraction analysis which indicated a mixture of graphite and hydrated lanthanum oxide, $La(OH)_3$. The sample residue apparently reacted with atmospheric water vapor and oxygen. Hence the X-ray analysis confirmed only the presence of excess carbon.

Unit activity for graphite ($C(s)$) was assumed in all the work reported here because excess carbon was assured by the graphite liner and carbon was found in the sample residue.

Measurements

Ion species were identified by their mass-to-charge ratio m/e and isotopic distribution. Shutter profile measurements were used to establish which species had neutral precursors originating in the Knudsen cell. All metal and carbide species were 100 percent shutterable. The resolution of the mass spectrometer, based on the 10-percent valley definition, was approximately 2000. Ionizing electrons with an energy of 30 or 35 electron volts were used and the electron current measured at the anode was 150 microamperes. Ionization efficiency curves were recorded for all species of interest except ScC_4^+ which was too low in intensity to obtain a meaningful curve. Appearance potentials were derived by the linear extrapolation method. A factor E_i was used to correct ion intensities measured at the working electron energy to the maximum of the ionization efficiency curve. This factor was determined for each species except ScC_4^+ by direct measurement from the respective curve. Electron multiplier gains γ_i for all species except ScC_4^+ were measured by ion counting using the equation

$$N = \frac{I_e}{\gamma e^-} \tag{1}$$

where N is the number of ions striking the first dynode of the multiplier, I_e is the current measured at the multiplier anode, γ is the multiplier gain, and e^- is the charge of the electron. Measured count rates Q were corrected for background count rate B and system dead time t_λ by the expression

$$\frac{dN}{dt} = \frac{Q}{1 - Qt_\lambda} - B \tag{2}$$

For our counting system, t_λ was experimentally determined to be 8×10^{-7} second. The background count rate B was measured for each Q by switching off the ion beam.

Temperatures were measured with a Micro Optical brightness pyrometer which was sighted into blackbody holes in the Knudsen cell. The holes were located opposite the effusion orifice, at heights near the top, middle, and bottom of the cell. The electron bombardment heating filaments were adjusted at each temperature until no perceptible temperature difference could be detected between the blackbody holes. This was taken to indicate that temperature gradients within the cell were negligible.

RESULTS AND CALCULATIONS

Vapor Species Identification

All detected La- and Sc-containing ions are listed in table I together with other parameters for the ions of particular interest. In addition to the dicarbides, the tetracarbides were readily identified as parent species by the appearance potential measurements. The LaC^+ ion was observed, but its high appearance potential indicated that it was a fragment, probably from the parent dicarbide. Unexpected was the observation of the tricarbide LaC_3^+ as a parent ion. This ion was believed to be a parent because its measured appearance potential of 6.8 electron volts was considerably below the value of about 11.5 electron volts, which was calculated to be the appearance potential of fragment LaC_3^+ from LaC_4. All La- and Sc-containing species other than the carbides were sufficiently low in intensity to be considered minor species and, for our purposes, were considered to be negligible. The various fluoride species were not unexpected because the metals were probably prepared by reduction of a fluoride.

TABLE I. - OBSERVED IONS WITH MEASURED AND DERIVED PARAMETERS

Ion	Parent	Relative intensity at T = 2651 K	Appearance potential, eV	Cross section, σ_i	Multiplier gain, γ_i	Ionization efficiency correction at 30 eV, E_i
$^{36}C_3^+$	C_3	7.1×10^{-2}	--------	-----	---------	----
$^{139}La^+$	La	8.2×10^{-1}	5.61^{a}	11.96	1.02×10^{7}	1.08
$^{151}LaC^+$	LaC_2	9.0×10^{-3}	14.9±0.5	-----	---------	----
$^{155}LaO^+$	LaO	1.1×10^{-3}	--------	-----	---------	----
$^{158}LaF^+$	LaF, LaF_2	1.3×10^{-2}	--------	-----	---------	----
$^{163}LaC_2^+$	LaC_2	1.0	5.4±0.3	15.42	1.09×10^{7}	1.00
$^{175}LaC_3^+$	LaC_3	3.5×10^{-3}	6.8±0.5	17.15	1.21×10^{7}	1.00
$^{177}LaF_2^+$	LaF_2, LaF_3	4.2×10^{-4}	--------	-----	---------	----
$^{187}LaC_4^+$	LaC_4	2.0×10^{-2}	4.7±0.5	18.88	1.16×10^{7}	1.07

Ion	Parent	Relative intensity at T = 2328 K	Appearance potential, eV	Cross section, σ_i	Multiplier gain, γ_i	Ionization efficiency correction, E_i, at -	
						30 eV	35 eV
$^{45}Sc^+$	Sc	1.8×10^{2}	6.54^{a}	6.56	1.01×10^{7}	1.25	1.16
$^{80}ScOF^+$	ScOF	--------	--------	-----	---------	----	----
$^{83}ScF_2^+$	ScF_2, ScF_3	--------	--------	-----	---------	----	----
$^{89}ScC_2^+$	ScC_2	1.0	7.7±0.2	10.02	1.24×10^{7}	1.0	1.0
$^{113}ScC_4^+$	ScC_4	4.2×10^{-3}	--------	13.48	$1.24\times10^{7\,b}$	1.0^{c}	1.0^{c}

[a] Standard, appendix IV of ref. 30.

[b] Assume $\gamma_{ScC_4^+} = \gamma_{ScC_2^+}$.

[c] Assume $E_{ScC_4^+} = E_{ScC_2^+}$.

Ion intensities for La^+, LaC_2^+, LaC_3^+, and LaC_4^+ were measured at 20 temperatures in the range from 2267 to 2600 K. In figures 1 to 4 the logarithm of the measured intensity - temperature product IT is plotted versus 1/T for La^+, LaC_2^+, LaC_3^+, and LaC_4^+. Measured intensities were corrected for E_i, γ_i, cross section σ_i, and isotopic abundance n_i. Cross sections for atoms were taken from Mann (ref. 12) and those for molecules were obtained by summing the values for the constituent atoms. The logarithms of corrected (c) ion intensity ratios $\log {}_cI_i/{}_cI_{La^+}$ are plotted versus 1/T in figure 5 for each carbide species containing La. The numbers shown with the data

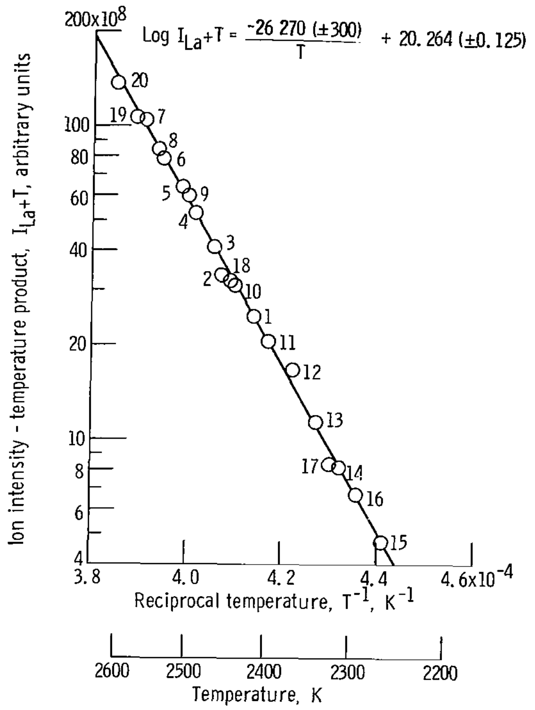

Figure 1. - Ion intensity - temperature product of La^+ as function of reciprocal temperature. Points are numbered chronologically.

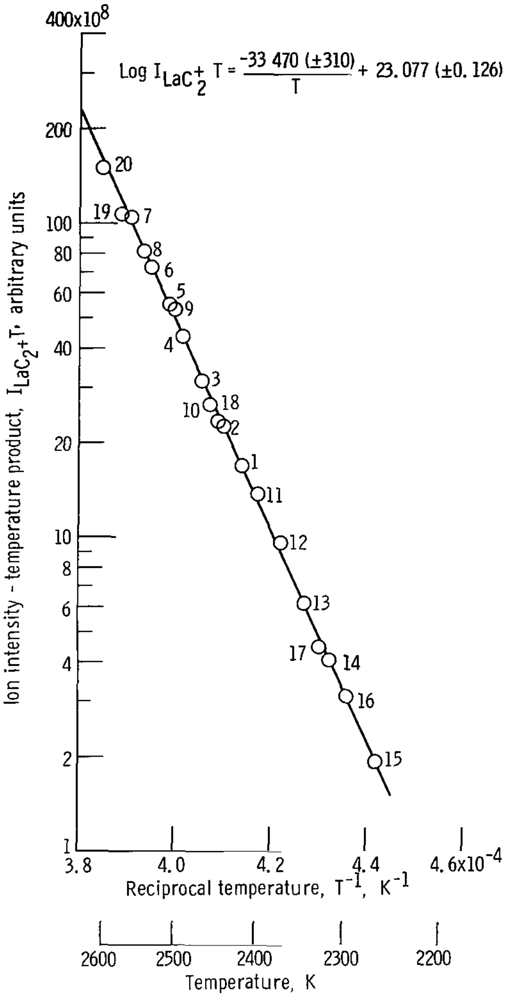

Figure 2. - Ion intensity - temperature product of LaC_2^+ as function of reciprocal temperature. Points are numbered chronologically.

points in figures 1 to 5 signify the sequence in which measurements were made, and the lines drawn were derived by the method of least squares.

Two separate experiments were performed in the case of Sc. For experiment I the electron energy was 35 electron volts, and for II it was 30 electron volts. The results of both experiments were combined and treated collectively. Ion intensities were measured at 17 temperatures for Sc^+ and ScC_2^+ and 10 temperatures for ScC_4^+ in the range from 2165 to 2328 K. The logarithms of corrected ion intensity ratios are plotted as functions of 1/T in figure 6. The lines drawn in this figure are least squares lines fitted to the data points.

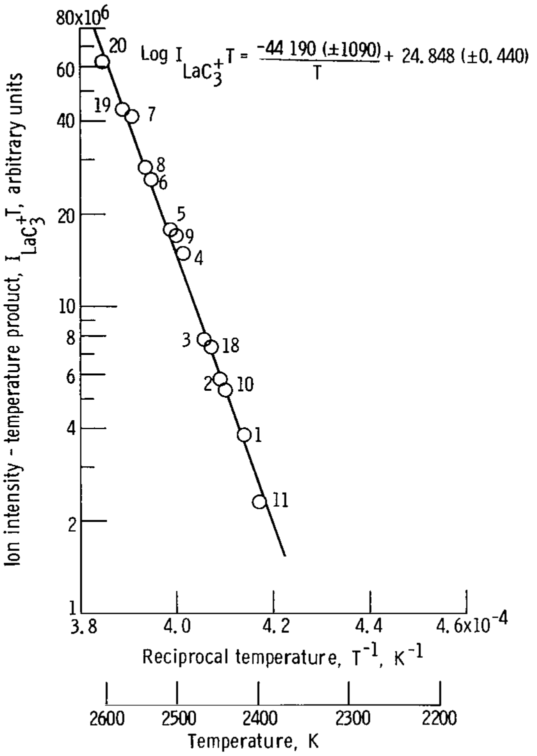

Figure 3. - Ion intensity - temperature product of LaC_3^+ as function of reciprocal temperature. Points are numbered chronologically.

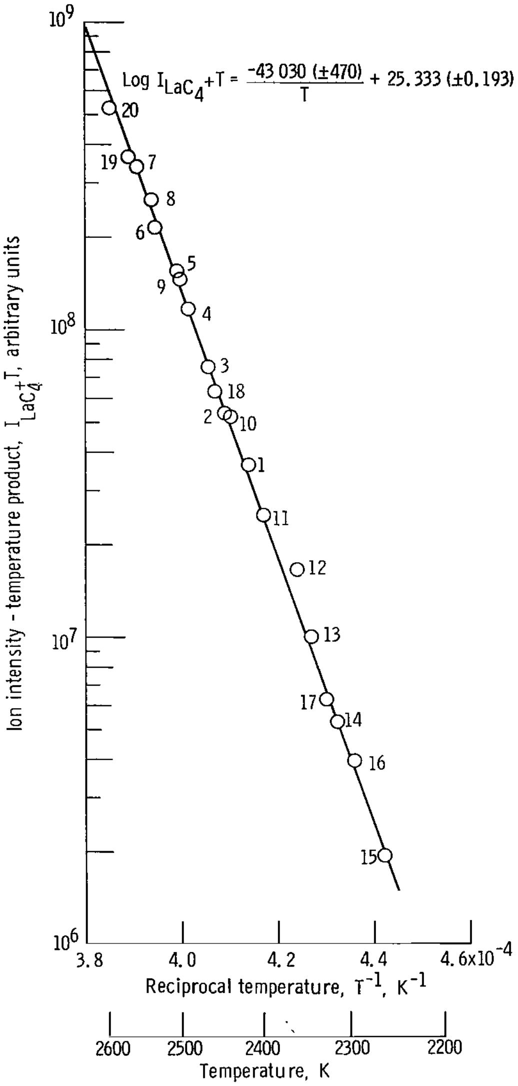

Figure 4. - Ion intensity - temperature products of LaC_4^+ as function of reciprocal temperature. Points are numbered chronologically.

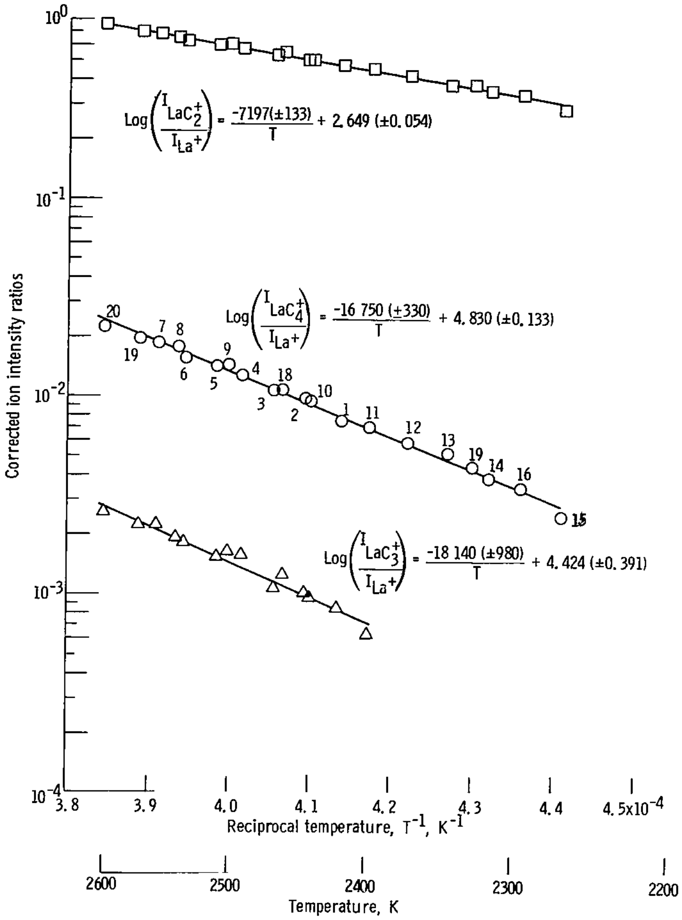

Figure 5. - Ion intensity ratios as functions of reciprocal temperature for lanthanum-carbon system ions. Points are numbered chronologically.

Heats of Reaction

For the thermodynamic analysis of the vaporization of the La-C system, the five equilibrium reactions, listed in table II, were considered. Only the two reactions listed in table III were used for the Sc-C system. In both table II and III the second-law heats ΔH_T^0 were obtained from the slopes of the respective least squares lines log ${}_cI_i/{}_cI_j$ or log I_iT versus $1/T$. The ΔH_T^0 values were corrected to 0 K to obtain the second-law heats ΔH_0^0. The errors associated with the ΔH_0^0 values are overall estimated errors and were obtained by combining standard deviations with the uncertainty produced by a maximum temperature error of ±10 K and an uncertainty in the sum of the heat content functions. The uncertainty in the sum of the heat content function was estimated to be ±4 kilojoules per mole for reactions (1), (2), (3), (6), and (7) and ±8 kilojoules per mole for reactions (4) and (5).

Third-law heats were calculated by the standard relation

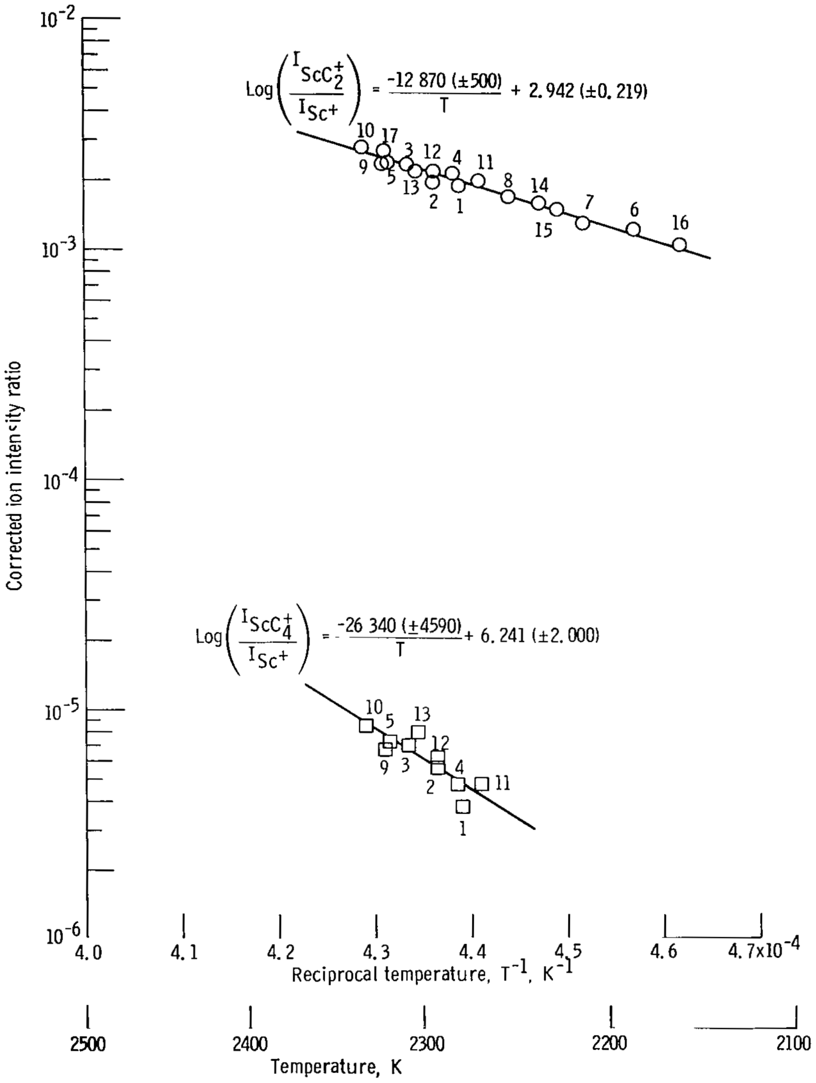

Figure 6. - Ion intensity ratios as functions of reciprocal temperature for scandium-carbon system ions. Points are numbered chronologically.

TABLE II. - REACTIONS AND ENTHALPIES FOR THE LANTHANUM-CARBON SYSTEM

Reaction	Temperature range, K	Enthalpy, kJ mole^{-1}		
		Second-law		Third-law
		ΔH_T^{o} [a]	ΔH_0^{o} [b]	ΔH_0^{o} [b]
(1) $La(g) + 2C(s) = LaC_2(g)$	2267 - 2600	137.8±2.5 (2438 K)	161.8±7.5	162.9±22.1
(2) $La(g) + 3C(s) = LaC_3(g)$	2397 - 2600	347.2±18.7 (2493 K)	369.2±30.9	(c)
(3) $La(g) + 4C(s) = LaC_4(g)$	2267 - 2600	320.7±6.2 (2438 K)	338.5±15.5	318.4±22.1
(4) $LaC_2(s) = La(g) + 2C(s)$	2267 - 2600	503.0±5.8 (2438 K)	523.4±23.5	489.5±22.2
(5) $LaC_2(s) = LaC_2(g)$	2267 - 2600	640.8±5.9 (2438 K)	685.2±28.9	652.3±22.3

[a] Errors are standard deviations of the slopes.

[b] Errors are overall estimated uncertanties (see text).

[c] No free energy functions were estimated for $LaC_3(g)$.

TABLE III. - ENTHALPIES FOR REACTIONS IN THE SCANDIUM-CARBON SYSTEM

Reaction	Temperature range, K	Enthalpy, kJ mole^{-1}		
		Second-law		Third-law
		ΔH_T^{o} [a]	ΔH_0^{o} [b]	ΔH_0^{o} [b]
(6) $Sc(g) + 2C(s) = ScC_2(g)$	2165 - 2328	246.4±9.5 (T = 2269 K)	256.7±23.7	264.3±20.5 [c] 257.7±20.9
(7) $Sc(g) + 4C(s) = ScC_4(g)$	2267 - 2328	504.2±87.9 (T = 2298 K)	----------	441.3±21.0

[a] Data from experiments I and II combined. Errors are standard deviations of slopes.

[b] Errors are estimated overall uncertainties.

[c] Ref. 8.

$$\Delta H^o_0 = -2.303\ RT \log K_p - T\Delta \left[\frac{G^o_T - H^o_0}{T} \right] \tag{3}$$

where K_p is the equilibrium constant for the reaction, R is the gas constant, and $\Delta\left[\left(G^o_T - H^o_0\right)/T\right]$ is the change of the Gibbs free-energy function. Third-law heats for the reactions considered are tabulated for each data point in tables IV to IX. The third-law ΔH^o_0 values summarized in tables II and III are the average of all data points, and the estimated errors listed with these values were obtained by combining the standard

TABLE IV. - THIRD-LAW ENTHALPIES FOR THE REACTION

$La(g) + 2C(s) = LaC_2(g)$

Temperature, T, K	Logarithm of equilibrium constant, $-\log K_p$	Change of Gibbs free-energy function, $-\Delta\left[\left(G^o_T - H^o_0\right)/T\right]$, J deg^{-1} $mole^{-1}$	Third-law enthalpy, ΔH^o_0, kJ $mole^{-1}$
2417	0.3307	61.11	163.0
2442	.3025	61.02	163.1
2466	.2750	60.92	163.2
2490	.2437	60.83	163.1
2509	.2290	60.75	163.4
2534	.2022	60.64	163.5
2557	.1629	60.54	162.8
2539	.1789	60.62	162.6
2501	.2168	60.79	162.4
2439	.3006	61.03	162.9
2397	.3466	61.19	162.6
2369	.3826	61.31	162.6
2342	.4315	61.43	163.2
2314	.4577	61.55	162.7
2267	.5495	61.74	163.8
2295	.4807	61.63	162.6
2326	.4314	61.50	162.3
2458	.2598	60.95	162.1
2572	.1577	60.48	163.3
2600	.1218	60.36	163.0
		Average[a]	162.9±0.4

[a] The error is the standard deviation of the points. See text for overall estimated uncertainty.

TABLE V. - THIRD-LAW ENTHALPIES FOR THE REACTION

$La(g) + 4C(s) = LaC_4(g)$

Temperature, T, K	Logarithm of equilibrium constant, $-\log K_p$	Change of Gibbs free-energy function, $-\Delta\left[\left(G^o_T - H^o_0\right)/T\right]$, J deg^{-1} $mole^{-1}$	Third-law enthalpy, ΔH^o_0, kJ $mole^{-1}$
2417	2.0755	91.57	317.4
2442	2.0156	91.50	317.7
2466	1.9757	91.44	318.8
2490	1.8930	91.37	317.7
2509	1.8529	91.31	318.1
2534	1.8035	91.23	318.7
2557	1.7310	91.15	318.8
2539	1.7429	91.21	316.3
2501	1.8518	91.34	317.1
2439	2.0142	91.51	317.2
2397	2.1612	91.63	318.8
2369	2.2262	91.72	318.3
2342	2.2955	91.81	317.9
2314	2.4211	91.90	319.9
2267	2.6253	92.03	322.6
2295	2.4696	91.96	319.6
2326	2.3537	91.86	318.9
2458	1.9625	91.46	317.2
2572	1.7023	91.10	318.4
2600	1.6541	91.01	319.0
		Average[a]	318.4±1.3

[a] The error is the standard deviation of the points. See text for overall estimated uncertainty.

TABLE VI. - THIRD-LAW ENTHALPIES FOR THE REACTION

$LaC_2(s) = La(g) + 2C(s)$

Temperature, T, K	Logarithm of equilibrium constant, $-\log K_p$	Change of Gibbs free-energy function, $-\Delta\left[(G^o_T - H^o_0)/T\right]$, J deg^{-1} mole^{-1}	Third-law enthalpy, ΔH^o_0, kJ mole^{-1}
2417	5.6308	94.74	489.5
2442	5.5214	94.70	489.4
2466	5.4123	94.67	489.0
2490	5.3045	94.63	488.5
2509	5.2211	94.60	488.2
2534	5.1290	94.56	488.4
2557	5.0061	94.51	486.7
2539	5.1013	94.55	488.0
2501	5.2487	94.62	488.0
2439	5.5361	94.71	489.5
2397	5.7077	94.77	489.1
2369	5.8210	94.85	488.7
2342	5.9666	94.93	489.9
2314	6.1221	95.02	491.1
2267	6.3556	95.11	491.5
2295	6.2020	95.07	490.7
2326	6.1068	94.98	492.9
2458	5.5058	94.68	491.8
2572	5.0039	94.48	489.4
2600	4.8928	94.43	489.1
		Average[a]	489.5±1.5

[a] The error is the standard deviation of the points. See text for overall estimated uncertainty.

TABLE VII. - THIRD-LAW ENTHALPIES FOR THE REACTION

$LaC_2(s) = LaC_2(g)$

Temperature, T, K	Logarithm of equilibrium constant, $-\log K_p$	Change of Gibbs free-energy function, $-\Delta\left[\left(G^o_T - H^o_0\right)/T\right]$, J deg^{-1} $mole^{-1}$	Third-law enthalpy, ΔH^o_0, kJ $mole^{-1}$
2417	5.9626	155.85	652.6
2442	5.8239	155.72	652.5
2466	5.6861	155.59	652.1
2490	5.5482	155.46	651.6
2509	5.4498	155.35	651.6
2534	5.3307	155.20	651.9
2557	5.1694	155.06	649.5
2539	5.2798	155.17	650.6
2501	5.4647	155.40	650.3
2439	5.8356	155.73	652.3
2397	6.0540	155.96	651.7
2369	6.2020	156.17	651.2
2342	6.3990	156.36	653.1
2314	6.5800	156.57	653.8
2267	6.9031	156.85	655.2
2295	6.6819	156.70	653.2
2326	6.5346	156.48	655.0
2458	5.7645	155.63	653.8
2572	5.1612	154.96	652.7
2600	5.0150	154.79	652.1
		Average[a]	652.3±1.4

[a] The error is the standard deviation of the points. See text for overall estimated uncertainty.

TABLE VIII. - THIRD-LAW ENTHALPIES FOR THE REACTION

$Sc(g) + 2C(s) = ScC_2(g)$

Experiment number	Temperature, T, K	Logarithm of equilibrium constant, $-\log K_p$	Change of Gibbs free-energy function, $-\Delta\left[\left(G^o_T - H^o_0\right)/T\right]$, J deg^{-1} $mole^{-1}$	Third-law enthalpy, ΔH^o_0, kJ $mole^{-1}$
I	2276	2.7378	64.21	265.4
	2291	2.7142	64.18	266.1
	2306	2.6354	64.15	264.3
	2282	2.6798	64.20	263.6
	2316	2.6321	64.13	265.2
	2197	2.9211	64.38	264.3
	2225	2.8374	64.32	264.0
	2251	2.7820	64.26	264.5
	2318	2.6326	64.12	265.5
II	2328	2.5674	64.10	263.7
	2267	2.7073	64.23	263.1
	2292	2.6689	64.18	264.2
	2301	2.6588	64.16	264.8
	2235	2.8049	64.30	263.7
	2213	2.8906	64.34	264.9
	2165	2.9955	64.44	263.7
	2319	2.5763	64.12	263.1
			Average[a]	264.3±0.9

[a] The error is the standard deviation of the points. See the text for overall estimated uncertainty.

TABLE IX. - THIRD-LAW ENTHALPIES FOR THE REACTION

$Sc(g) + 4C(s) = ScC_4(g)$

Experiment number	Temperature, T, K	Logarithm of equilibrium constant, $-\log K_p$	Change of Gibbs free-energy function, $-\Delta\left[(G_T^o - H_0^o)/T\right]$, J deg^{-1} $mole^{-1}$	Third-law enthalpy, ΔH_0^o, kJ $mole^{-1}$
I	2276	5.4259	92.11	446.1
	2291	5.2522	92.09	441.3
	2306	5.1579	92.07	440.0
	2282	5.3242	92.10	442.8
	2316	5.1522	92.06	441.7
	2318	5.1772	92.06	443.1
II	2328	5.0753	92.04	440.5
	2267	5.3402	92.12	440.6
	2292	5.2145	92.09	439.9
	2301	5.1048	92.08	436.8
			Average[a]	441.3±2.4

[a] The error is the standard deviation of the points. See the text for overall estimated uncertainty.

deviations from the mean of all respective data points with estimated uncertainties in the values of K_p (±50 percent), T (±10 K), and $\Delta\left[(G_T^o - H_0^o)/T\right]$ (±8.2 J deg^{-1} $mole^{-1}$).

Thermodynamic Functions

The values of the heat content and free-energy functions for La(g) and Sc(g) were taken from Hultgren, Orr, Anderson, and Kelley (ref. 13) and those for C(s) were taken from the JANAF tables (ref. 14). The free-energy functions for $LaC_2(g)$ were estimated in a manner identical to that used by Faircloth, Flowers, and Pummery (ref. 7) but are included here for completeness.

For the dicarbides a linear asymmetric structure of the type M-C-C was assumed by analogy to other metal dicarbides, and the parameters used for this structure are listed in table X for both $LaC_2(g)$ and $ScC_2(g)$. The fundamental vibrational frequencies

TABLE X. - ESTIMATED MOLECULAR PARAMETERS FOR

ScC_2, LaC_2, ScC_4, AND LaC_4

	Molecule			
	ScC_2	LaC_2	ScC_4	LaC_4
Internuclear separation, pm				
Sc-C*	165	---	165	---
La-C*	---	183	---	183
C-C**	131	131	131	131
Moment of inertia, g cm^2	15.52×10^{-39}	22.71×10^{-39}	45.81×10^{-39}	52.69×10^{-39}
Force constants, N/m				
k_{Sc-C}†	6.56×10^2	-----------	6.56×10^2	-----------
k_{La-C}†	----------	5.57×10^2	-----------	5.57×10^2
k_{C-C}**	9.25×10^2	9.25×10^2	9.25×10^2	9.25×10^2
k_δ, Nm/rad‡	6.70×10^{-19}	6.70×10^{-19}	-----------	-----------
$f_{13,22}$§	----------	-----------	1.30×10^2	1.30×10^2
Frequencies (degeneracy), cm^{-1}				
ω_1	761 (1)	626 (1)	791 (1)	763 (1)
ω_2	492 (2)	469 (2)	1862 (1)	1836 (1)
ω_3	1792 (1)	1754 (1)	1008 (1)	777 (1)
ω_4	-------	-------	1817 (1)	1775 (1)
ω_5	-------	-------	139 (2)	108 (2)
ω_6	-------	-------	576 (2)	509 (2)
ω_7	-------	-------	468 (2)	445 (2)
Symmetry number	1	1	2	2
Electronic contribution‖	From Sc^{+2}	From La^{+2}	From Sc^{+2}	From La^{+2}

*Calculated by use of modified Badger's rule (ref. 28).

**From C_2(g) (ref. 29).

†Stretching force constants for La-C and Sc-C were assumed to be the same as those of the corresponding oxides (ref. 29).

‡See ref. 15 for bending force constant.

§See ref. 16.

‖See ref. 18.

for these molecules were calculated according to the valence force formulation given by Herzberg (ref. 15).

For $LaC_4(g)$ and $ScC_4(g)$ the linear symmetric structure C-C-M-C-C was assumed. The parameters for this structure are also listed in table X. The method of Engler and Kohlrausch (ref. 16) was used to calculate the fundamental vibrational frequencies for these molecules.

Electronic ground states and excited states are not known for the MC_2 and MC_4 molecules. Therefore, we estimated the electronic contributions to the partition functions according to the method of Brewer and Chandrasekharaiah (ref. 17). For $LaC_2(g)$ and $ScC_2(g)$ we assumed that the energy levels of the molecules could be approximated by the levels of La^{+2} and Sc^{+2} ions, respectively. This treatment is based on an ionic model of the type $M^{+2}C_2^{-2}$ and assumes that the C_2^{-2} ion neither makes a contribution to the electronic partition function nor perturbs the energy levels of M^{+2}. For La^{+2}, the levels to 6s ^2S, 13 590.76 reciprocal centimeters, were used; for Sc^{+2} the levels to 4p ^2P, 62 475.9 reciprocal centimeters, were used (ref. 18). An alternate method of computing the electronic partition function could have been to choose a ground-state statistical weight of two and exclude any low lying excited states as had previously been done for $YC_2(g)$[1]. The basis for this procedure is the postulate (ref. 5) that the bonding of the C_2^{-2} group is isoelectronic to 0^{-2} and the experimental electronic ground states of ScO, YO, and LaO are $^2\Sigma^+$ (statistical weight = 2). However, for LaC_2, this alternate procedure yielded free-energy functions with significantly lower values. This resulted in poor agreement between second- and third-law heats for reactions involving $LaC_2(g)$ and a significant trend in the values of ΔH_0^o as a function of temperature. Thus, we concluded that the use of the La^{+2} energy levels was the more appropriate procedure. For the tetracarbides the same electronic contributions were used as for the respective dicarbides.

Thermodynamic functions were calculated with a computer program (ref. 19) using the rigid-rotator harmonic-oscillator approximation. Heat content and free-energy functions for the various molecules are listed in tables XI and XII.

No molecular configuration was assumed for $LaC_3(g)$, and no free-energy functions were calculated. The heat content $H_{2493}^o - H_0^o = 196.7$ kilojoules per mole of $LaC_3(g)$ was estimated by taking the average of the heat contents of $LaC_2(g)$ and $LaC_4(g)$. This is a reasonable estimate since the molecular weight term predominates in the heat content function.

The estimated free-energy functions for $LaC_2(s)$ were taken from reference 7. The heat content functions were estimated in a similar manner by assuming that $H_T^o - H_0^o$ was equal to that of $CaC_2(s)$ plus the difference between the heat contents of La(s) and Ca(s). Heats contents and free-energy functions for $LaC_2(s)$ are listed in table XI.

TABLE XI. - ESTIMATED HEAT CONTENTS AND FREE-ENERGY FUNCTIONS FOR $LaC_2(g)$, $LaC_4(g)$, AND $LaC_2(s)$

Temperature, T, K	$LaC_2(g)$		$LaC_4(g)$		$LaC_2(s)$	
	Heat content, $H^o_T - H^o_0$, kJ $mole^{-1}$	Free-energy function, $-(G^o_T - H^o_0)/T$, J deg^{-1} $mole^{-1}$	Heat content, $H^o_T - H^o_0$, kJ $mole^{-1}$	Free-energy function, $-(G^o_T - H^o_0)/T$, J deg^{-1} $mole^{-1}$	Heat content, $H^o_T - H^o_0$, kJ $mole^{-1}$	Free-energy function, $-(G^o_T - H^o_0)/T$, J deg^{-1} $mole^{-1}$
298.15	10.38	227.01	15.48	246.66	12.2	-----
1800	101.07	309.41	170.87	380.06	-----	149.8
1900	107.43	312.45	182.03	385.21	-----	153.3
2000	113.78	315.36	193.20	390.15	135.1	156.9
2100	120.12	318.15	204.38	394.88	143.8	160.2
2200	126.46	320.81	215.57	399.42	152.5	163.6
2300	132.79	323.37	226.77	403.79	161.4	166.7
2400	139.12	325.84	237.96	408.00	170.3	169.9
2500	145.44	328.21	249.17	412.06	179.3	172.8
2600	151.76	330.49	260.38	415.98	188.4	175.7
2700	158.08	332.70	271.59	419.77	-----	-----
2800	164.39	334.83	282.80	423.43	-----	-----

TABLE XII. - ESTIMATED HEAT CONTENTS AND FREE-ENERGY FUNCTIONS FOR $ScC_2(g)$ AND $ScC_4(g)$

Temperature, T, K	$ScC_2(g)$		$ScC_4(g)$	
	Heat content, $H^o_T - H^o_0$, kJ $mole^{-1}$	Free-energy function, $-(G^o_T - H^o_0)/T$, J deg^{-1} $mole^{-1}$	Heat content, $H^o_T - H^o_0$, kJ $mole^{-1}$	Free-energy function, $-(G^o_T - H^o_0)/T$, J deg^{-1} $mole^{-1}$
298.15	10.99	216.51	15.55	236.69
2000	107.90	303.18	185.61	375.66
2100	114.00	305.82	196.53	380.21
2200	120.11	308.35	207.48	384.58
2300	126.24	310.78	218.45	388.78
2400	132.37	313.12	229.44	392.84
2500	138.51	315.38	240.45	396.76

Dissociation Energies

The quality of the second-law data for the system containing La makes the second-law reaction enthalpies preferred over the third-law values. Although the agreement between the two sets of heat values are acceptable for all reactions of this system, the second-law value has a smaller error associated with it and thus is considered the more reliable. For the system containing Sc, third-law values of reaction enthalpies are preferred because they have the smaller error. Fewer data points and scatter in measured intensities make the second-law values less reliable in this case. Thus in subsequent thermodynamic calculations, second-law heats were used for La reactions and third-law heats were used for Sc reactions.

The heat of reaction (1), 161.8±7.5 kilojoules per mole, was combined with the $C_2(g)$ heat of formation of $\Delta H^o_{0,f} = 829.3 \pm 3.8$ kJ mole^{-1} (ref. 14) to give the dissociation energy of $LaC_2(g)$

$$LaC_2(g) = La(g) + C_2(g) \qquad D^o_0 = 668 \pm 8 \text{ kJ mole}^{-1}$$

The following dissociation energies were obtained by similar thermodynamic analyses using the reactions and data tables II and III:

$$LaC_4(g) = La(g) + 2C_2(g) \qquad D^o_0 = 1320 \pm 16 \text{ kJ mole}^{-1}$$

$$ScC_2(g) = Sc(g) + C_2(g) \qquad D^o_0 = 565 \pm 21 \text{ kJ mole}^{-1}$$

$$ScC_4(g) = Sc(g) + 2C_2(g) \qquad D^o_0 = 1217 \pm 24 \text{ kJ mole}^{-1}$$

Atomization energies $D^o_{0,\text{atom}}$ were obtained by combining appropriate reaction enthalpies with the heat of formation of $C(g)$, $\Delta H^o_{0,f} = 709.5 \pm 1.9$ kilojoules per mole, (ref. 14) to obtain

$$LaC_2(g) = La(g) + 2C(g) \qquad D^o_{0,\text{atom}} = 1257 \pm 8 \text{ kJ mole}^{-1}$$

$$LaC_3(g) = La(g) + 3C(g) \qquad D^o_{0,\text{atom}} = 1759 \pm 31 \text{ kJ mole}^{-1}$$

$$LaC_4(g) = La(g) + 4C(g) \qquad D^o_{0,\text{atom}} = 2500 \pm 16 \text{ kJ mole}^{-1}$$

$$ScC_2(g) = Sc(g) + 2C(g) \qquad D^o_{0,\text{atom}} = 1155 \pm 21 \text{ kJ mole}^{-1}$$

$$ScC_4(g) = Sc(g) + 4C(g) \qquad D^o_{0,\text{atom}} = 2397 \pm 24 \text{ kJ mole}^{-1}$$

Heat of Formation of $LaC_2(s)$

The heat of formation of the condensed phase of LaC_2 was obtained by combining the heat of reaction (4) (table II) with the heat of vaporization of La, $\Delta H^{o}_{298,\mathrm{vap}}$ = 519.6±23.5 kilojoules per mole (ref. 13):

$$\mathrm{La(s) + 2C(s) = LaC_2(s)} \qquad \Delta H^{o}_{298,f} = -89\pm24\ \mathrm{kJ\ mole^{-1}}$$

Rigorously, the condensed phase in this reaction should be written as LaC_{2-x} since the exact composition of this phase is not known. Spedding, Gschneidner, and Daane (ref. 11) have concluded that the carbide saturated LaC_2 phase is probably substoichometric.

Vapor Pressures of La, LaC_2, LaC_3, and LaC_4

By suitably combining our ion intensity data with the gravimetric data of reference 7, pressures for La, LaC_2, LaC_3, and LaC_4 can be derived. Also, the data of reference 7 can be recalculated using our results to obtain improved vapor pressures and more reliable values of reaction enthalpies.

Faircloth, Flowers, and Pummery (ref. 7) used the equation

$$p = W_{La}\left(\frac{2\pi RT}{M_{La}}\right)^{1/2} \tag{4}$$

to calculate effective pressures p from measured values of W_{La}, the weight of La metal effused per unit area per second. Here, M_{La} is the molecular weight of La, and in what follows, M_i represents the molecular weight of species i. Actually W_{La} is the sum of the weight of La in each effusing species. Letting w_i be the weight of La in species i and ${}_{T}W_i$ the total weight of species i, we can write

$$W_{La} = \sum w_i \tag{5}$$

$$w_i = {}_{T}W_i\left(\frac{M_{La}}{M_i}\right) \tag{6}$$

$$W_{La} = \sum {}_{T}W_i\left(\frac{M_{La}}{M_i}\right) \tag{7}$$

Because the effusion equation for each species i is

$$P_i = {}_TW_iM_i^{-1/2}\,(2\pi RT)^{1/2} \tag{8}$$

we can derive by substitution the following equation

$$p = \sum P_i\left(\frac{M_{La}}{M_i}\right)^{1/2} \tag{9}$$

Our mass spectrometric results show that pressures of La and LaC_2 are orders of magnitude greater than all other La containing species. Therefore, a good approximation is to let all P_i except P_{La} and P_{LaC_2} be zero. This approximation is correct to within 2 percent. With this approximation the working equation becomes

$$p = P_{La} + P_{LaC_2}\left(\frac{M_{La}}{M_{LaC_2}}\right)^{1/2} \tag{10}$$

From the empirical equation of reference 7,

$$\log p\left(\frac{N}{m^2}\right) = \frac{-27\,300}{T} + 10.81$$

we calculate at a temperature of 2300 K, $p_{2300} = 8.63\times10^{-2}$ newtons per square meter. Although this temperature is 27 K above the maximum temperature of reference 7, we believe the slight extrapolation used here is valid. Our experiment gave the equation

$$\left(\frac{P_{LaC_2}}{P_{La}}\right) = \frac{-7197}{T} + 2.649$$

from which we obtain $\left(P_{LaC_2}/P_{La}\right)_{2300} = 0.331$. By using these values together with $\left(M_{La}/M_{LaC_2}\right)^{1/2} = 0.9233$ in equation (10), we calculate $\left(P_{La}\right)_{2300} = 6.612\times10^{-2}$ newtons per square meter and $\left(P_{LaC_2}\right)_{2300} = 2.189\times10^{-2}$ newtons per square meter. Knowing these values of pressure, the pressure-relating sensitivity constant k for the Knudsen cell mass spectrometer system can readily be determined from the equation

$$P_i = \frac{kI_iTE_i}{\sigma_i n_i \gamma_i} \tag{11}$$

Using the average computed value $k = 1.344\times10^{11}$ newtons per square meter per ampere per Kelvin, we converted our intensities for La^+, LaC_2^+, LaC_3^+, and LaC_4^+ to pressures which are plotted versus 1/T in figure 7. The recalculated values of P_{La} and P_{LaC_2} from the data of reference 7 using our P_{LaC_2}/P_{La} ratios are also plotted in this figure. Each group of results were fitted to a straight line by the method of least

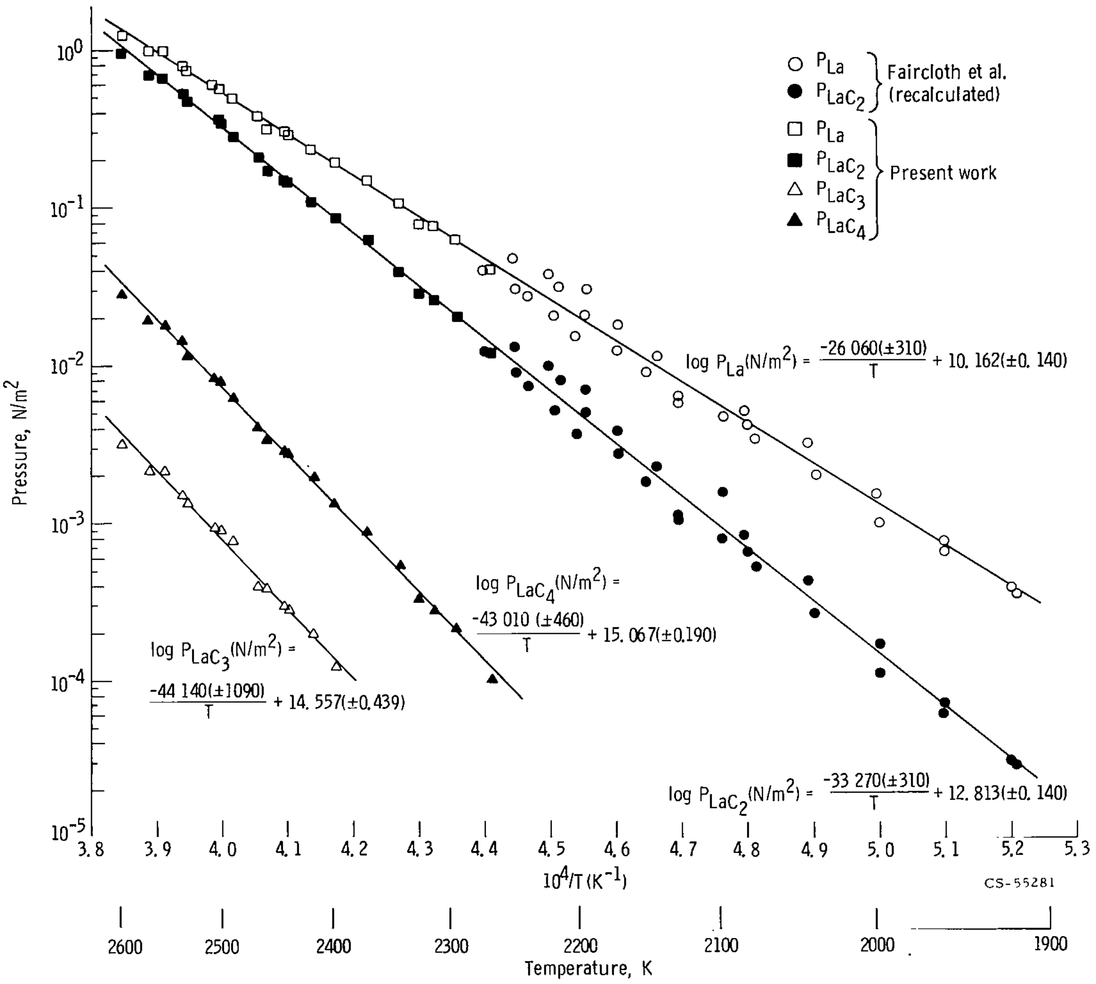

Figure 7. - Equilibrium vapor pressures of La, LaC_2, LaC_3, and LaC_4 over LaC_2-C(s) as functions of reciprocal temperature.

squares. The resulting lines matched, so all the data points for each species were finally combined and fit to single lines as shown in figure 7 together with the equations for these lines.

As a check of the pressure calibration procedure and an additional check of the assumption of unit activity for C(s), the pressure of $C_3(g)$ at 2651 K was calculated from the measured intensity of C_3^+. The calculated value $P_{C_3} = 3.9\times10^{-1}$ newton per square meter compares favorably with the value of 2.5×10^{-1} interpolated from the tables of reference 13 for the case of pure graphite.

DISCUSSION

The mode of vaporization of the lanthanum-carbon and scandium-carbon systems has been found to be generally as expected on the basis of considerations of other metal-carbon systems (refs. 1 to 4). The major vaporization products for both systems are the metal atoms, dicarbides and tetracarbides. Beyond this similarity the individual systems are sufficiently different to warrant separate discussion.

The excellent agreement between our second-law and third-law enthalpies for reaction (1) (table II) indicates that the results for the lanthanum-carbon system are reliable. This degree of agreement could not have been obtained had any large systematic errors been present in the experiment or had the assumptions concerning ionization cross sections and estimated thermodynamic functions not been adequate.

Although the results for reaction (1) are in general agreement with the third-law value reported by Chupka, Berkowitz, Giese, and Inghram (ref. 5), we consider our results to be more reliable because of the smaller probable errors and excellent second-law and third-law agreement. The results reported by Jackson, Bedford, and Barton (ref. 6) do not compare well with our results. For example, for reaction (1), Jackson, Bedford, and Barton obtained a ΔH_T^o value that, when corrected to 0 K, gave $\Delta H_0^o =$ 128.9±5.0 kilojoules per mole, which is about 43 kilojoules per mole lower than our value. Better agreement is not really expected because theirs was not an equilibrium vaporization experiment.

The agreement between our reaction enthalpy values and those of Faircloth, Flowers, and Pummery (ref. 7) for reactions (4) and (5) is suitable, but again, we prefer our values. For the recalculated pressures of reference 7, agreement is improved. For reactions (4) and (5) the recalculated second-law heats are 522.6 and 678.4 kilojoules per mole, respectively. Also, using the recalculated heat of reaction (4) the data of reference 7 yield the same heat of formation for $LaC_2(s)$ as obtained in the present experiment.

The agreement between our second- and third-law heats for reactions (4) and (5) is well within the overlapping estimated uncertainties. However, a difference of about 33 kilojoules per mole does exist between these values. This is probably due to the uncertainty in the estimated free-energy functions for $LaC_2(s)$. The direction of this difference indicates that the estimated values of $-\Delta\left[\left(G^o_T - H^o_0\right)/T\right]$ for $LaC_2(s)$ are too high.

The three experimental points at the highest temperatures of our experiment were above the LaC_2-C eutectic temperature of 2544±15 K. This fact was apparently inconsequential because these points did not deviate significantly from the vapor pressure lines fitted to the remaining lower temperature data points. This indicates that the activity of La in the condensed phase did not change appreciably in going over the eutectic point temperature into the liquid phase.

It is interesting to note that the heat of formation of $LaC_2(s)$, $\Delta H^o_{298,f} = -89\pm24$ kilojoules per mole, is almost identical to that of $YC_2(s)$, which is -91±17 kilojoules per mole (ref. 1). These values are in turn similar to those for HoC_2 (ref. 4), ErC_2 (ref. 20), SmC_2 (ref. 21), GdC_2 (ref. 22), and YbC_2 (ref. 23), but are lower by some 30 to 50 kilojoules per mole than those for DyC_2 (ref. 4), EuC_2 (ref. 24), NdC_2 (ref. 7), and CeC_2 (ref. 25). The relatively large uncertainties associated with all of these values preclude any speculative interpretations of individual differences.

For the scandium-carbon system third-law reaction enthalpies are preferred over the second-law values. The second-law data showed considerable scatter in individual data points and the relatively small number of experimental points contributed to the larger uncertainties. The atomization energy of $ScC_2(g)$ determined in this study, 1155±21 kilojoules per mole, is in excellent agreement with the value of 1162±23 kilojoules per mole reported in reference 8.

Both the dicarbides and tetracarbides of La and Sc follow the general trend of the M-C_2 bond strength, which decreases going from La to Y to Sc. This is analogous to the trend observed for the oxides LaO, YO, and ScO. The dissociation energies of LaC_2 and ScC_2 follow the postulated rule (ref. 26) that the M-C_2 bond energy is 40 to 130 kilojoules less than that of the corresponding M-O bond. Similar bond strength comparison analogies cannot be extended to the tetracarbide LaC_4 and ScC_4 because the corresponding isoelectronic dioxide molecules have not been observed. Following the estimation procedure of Balducci, Capalbi, DeMaria, and Guido (ref. 27), we are led to predict that LaO_2 and ScO_2 can exist as stable molecules with dissociation energies of 1570 and 1450 kilojoules per mole, respectively.

Our observation of the tricarbide species $LaC_3(g)$ is unique in that no other tricarbides have been reported in the many studies of transition-metal - carbon and rare-earth - carbon systems. LaC_3 is most likely a chain-like structure (C-La-C-C or La-C-C-C), being either linear or bent. Because of the paucity of analogous molecules, no molecular parameters or free-energy functions were estimated for this molecule. For all the metal carbide molecules, more sophisticated theoretical and experimental work is needed before sound structural arguments can be presented. Because of the high P_{LaC_2}/P_{La} ratio for the vaporization of the La-C system, LaC_2 appears to be an ideal candidate for infrared spectroscopic examination by the matrix isolation technique.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, September 10, 1970,
129-03.

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