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PART XIX

**VAPORIZATION OF COMPOUNDS AND ALLOYS AT HIGH
TEMPERATURES**

**PART XIX. MASS SPECTROMETRIC DETERMINATION OF THE DISSOCIATION
ENERGY OF THE MOLECULES Sc_2 , Y_2 , La_2 AND YLa**

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RESEARCH AND TECHNOLOGY DIVISION
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FOREWORD

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ABSTRACT ✓

The diatomic molecules Sc_2 , Y_2 , La_2 and YLa have been identified mass spectrometrically in the vapors above condensed scandium, yttrium, lanthanum and Y-La alloys respectively. Their dissociation energies are $D_0^\circ(\text{Sc}_2) = 25.9 \pm 5$, $D_0^\circ(\text{Y}_2) = 37.3 \pm 5$, $D_0^\circ(\text{La}_2) = 57.6 \pm 5$ and $D_0^\circ(\text{YLa}) = 47.3 \pm 5$ kcal/mole.

This technical documentary report has been reviewed and is approved.



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MASS SPECTROMETRIC DETERMINATION OF THE
DISSOCIATION ENERGY OF THE MOLECULES Sc_2 , Y_2 , La_2 and YLa^*

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Although classical chemistry, spectroscopy⁽¹⁾, and mass spectrometry⁽²⁾ have succeeded in identifying about 30 homonuclear diatomic molecules, those of the "true" transition elements, i.e. those with unfilled d shells, were as yet unidentified. A recent survey of heats of vaporization of elements and dissociation energies of known homonuclear diatomic molecules indicated that the transition elements of the molecules Sc_2 , Y_2 and La_2 should be the more easily detectable⁽³⁾ under usual experimental conditions in a mass spectrometer⁽²⁾.

Samples of metallic Sc, Y and La were therefore vaporized from Ta, Mo or W Knudsen cells. The effusing vapors were ionized by electron impact and subsequently mass analyzed^(2,4).

At temperatures where the effective pressure ranged from 10^{-5} to $5 \cdot 10^{-3}$ atm small peaks due to Sc_2^+ , Y_2^+ and La_2^+ ions were observed. Their intensity profile indicated the neutral precursor to originate from the Knudsen cell. Because of the low intensities, only qualitative ionization efficiency curves could be obtained, which indicate however that the approximate ionization potentials of these molecules are slightly lower than those of the

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corresponding atoms⁽⁵⁾. To avoid the possible interference of charge exchange $\text{Me}^{++} + \text{X} \rightarrow \text{Me}^+ + \text{X}^+$ which can give peaks at an apparent mass 2Me^+ ⁽⁶⁾, and fragmentation of Me_2O and Me_2O_2 molecules which were present in small concentration in the vapor the measurements were made with 12 eV electrons. It was further estimated that ion attachment reactions $\text{Me}^+ + \text{Me} \rightarrow \text{Me}_2^+$ possibly occurring in two or three body collisions in the source are unlikely to affect the measured Me_2^+ intensities.

Dissociation energies of Sc_2 , Y_2 , La_2 and YLa were calculated by the absolute entropy method. Pressure independent reactions $\text{Me}_2(\text{g}) \rightarrow \text{Me}(\text{g}) + \text{Me}(\text{s})$ were considered using $L_0^\circ(\text{Y}) = 97.6$ ⁽⁷⁾ and $L_0^\circ(\text{La}) = 104.1$ ⁽⁷⁾ kcal/mole. Since all crucible materials (Ta, Mo, W) gave rise to pronounced alloy formation with liquid Sc, pressure measurements based on the Hertz-Knudsen relation were made^(2,4) for this element. For gaseous Sc, Y and La, the free energy functions are those given by Stull and Sinke⁽⁸⁾. For consistency, those for condensed Y and La were taken from the same source as the heats of sublimation⁽⁷⁾. The free energy functions of Sc_2 , Y_2 and La_2 were calculated⁽⁸⁾ using an effective quantum weight of 5, a vibration frequency of 230 cm^{-1} (estimated by analogy with molecules of similar stability and molecular weight) and 2.70, 2.80 and 2.80 Å respectively as interatomic distance (obtained from Badger's rule⁽⁹⁾). For YLa the values of Y_2 and La_2 were

averaged and corrected for the absence of symmetry. The numerical values (in cal/deg.mole) for Sc_2 , Y_2 , La_2 and YLa are respectively 68.3, 72.3, 74.1 and 74.6 at 2000°K and 69.6, 73.6, 75.4 and 76.0 at 2300°K. Table 1 summarizes the data and results.

The dissociation energies of Sc_2 , Y_2 and La_2 are of the same magnitude as those of Cu_2 , Ag_2 and Au_2 : 45.5, 37.6 and 51.5 kcal/mole⁽⁴⁾ respectively, and seem as for the latter molecules⁽⁴⁾ to be related to the availability of low-lying excited states of the atoms.

REFERENCES.

1. G. Herzberg, "Spectra of Diatomic Molecules" (D. Van Nostrand Company. Inc. Princeton, New Jersey, 1950) 2nd Ed.
2. J. Drowart and M.G. Inghram, "Mass Spectrometry Applied to High temperature Chemistry" in "High Temperature Technology" (McGraw-Hill Book Co., New York, 1960).
3. G. Verhaegen, F.E. Stafford, P. Goldfinger and M. Ackerman, Trans. Faraday Soc., 58, 1926 (1962).
4. M. Ackerman, F.E. Stafford and J. Drowart, J. Chem. Phys., 33, 1784 (1960).
5. C.E. Moore, "Atomic Energy Levels", Circ. 467 (Nat. Bur. Standards, 1949).
6. F.H. Fields and J.L. Franklin "Electron Impact Phenomena", (Academic Press Inc. Publishers, New York, 1957).
7. R.J. Ackermann and E.G. Rauh, J. Chem. Phys., 36, 448 (1962).
8. D.R. Stull and G.C. Sinke, "Thermodynamic Properties of the Elements", Advances in Chemistry Series (American Chemical Society, Washington D.C., 1956) Vol. 18.
9. K.S. Pitzer, "Quantum Chemistry", (Prentice Hall Inc., Englewood Cliffs., New York, 1953).
10. R.M. Badger, J. Chem. Phys., 3, 710 (1935).

TABLE 1

Mole- cule	Equilibrium	T°K	$\log I_1/I_2^{(a)}$	$\log K$	ΔH_0° kcal/mole	D_0° kcal/mole
Sc ₂	Sc ₂ (g) → 2Sc(g)	2097	4.94	2.66	25.8	25.9±5
		2152	5.04	2.90	24.1	
		2165	4.92	2.67	26.6	
		2000	4.67	2.39	27.0	
		2001	4.68	2.50	26.0	
		1999	4.56	2.25	28.2	
				mean:	25.9	
Y ₂	Y ₂ (g) → Y(g) + Y(s, 1)	2300	4.82	4.82	-60.9	37.3±5
		2286	4.69	4.69	-59.3	
		2304	4.58	4.58	-58.5	
		2315	4.80	4.80	-61.0	
		2248	4.99	4.99	-61.6	
		2271	4.84	4.84	-60.5	
				mean:	-60.3	
La ₂	La ₂ (g) → La(g) + La(1)	1998	4.14	4.19	-47.3	57.6±5
		2003	4.23	4.28	-48.2	
		1945	3.85	3.90	-43.8	
		1998	3.87	3.92	-44.8	
		2065	3.80	3.85	-45.3	
		2161	3.46	3.51	-43.3	
		2154	3.42	3.47	-43.9	
		2185	3.64	3.69	-45.3	
		2091	3.79	3.84	-45.5	
		2102	4.08	4.13	-48.5	
		2117	3.92	3.97	-47.3	
		2070	3.83	3.88	-45.7	
		2055	4.11	4.16	-48.1	
		2190	3.86	3.91	-47.8	
		2180	3.79	3.84	-47.0	
		2159	3.78	3.83	-46.5	
		2128	3.82	3.87	-46.5	
		2304	3.74	3.79	-48.2	
		2274	3.66	3.71	-47.1	
		2274	3.84	3.89	-48.9	
		2307	3.66	3.71	-47.4	
		2316	3.73	3.78	-48.3	
		2295	3.63	3.68	-46.7	
		2311	3.24	3.29	-43.1	
				mean:	-46.5	

TABLE 1 (cont.)

Mole- cule	Equilibrium	T°K	logK	ΔH_0° kcal/mole	D_0° kcal/mole
YLa	$YLa(g) + La(g) \rightarrow Y(g) + La_2(g)$	2307	0.46	-10.2	48.0
		2316	0.51	-10.8	
		2295	0.50	-10.6	
		2311	0.30	- 8.5	
		2299	0.31	- 8.6	
		2220	0.49	-10.1	
		2211	0.35	- 8.5	
		mean:		- 9.6	
YLa(g)+Y(g)->La(g)+Y ₂ (g)	2262	-0.91	8.6	45.6	
	2248	-0.85	8.1		
	2290	-0.89	8.2		
	mean:		8.3		
2YLa(g)->Y ₂ (g)+La ₂ (g)	2186	-0.47	- 0.9	47.0	
	mean:		47.3±5		

(a) $\log P_1/P_2 = \log(I_1/I_2) (\eta_2/\eta_1)$; η_2/η_1 = ratio of ionization cross sections = 1.6 ; γ_2/γ_1 = ratio of secondary electron multiplier yields.