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Vaporization of Several Rare Earth Oxides

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The lowering of the total energies of Li and Li_2 due to core polarization is shown in Table I. Numerical integrations were carried out on IBM 704. The value obtained for Li with the analytic[4] HF SCF $2s_R$ agrees with that of Callaway; he used[3] an earlier numerical HF orbital. The total energy of Li_2 is lowered by approx 0.25 ev. This should be compared to the "orbital average polarization" energy which should be less[6] than 0.019 ev as found by Ishiguro, *et al.*[2] The latter is not a correlation energy and arises as the difference between a complete SCF and a fixed core outer electron SCF calculation.[1,2]

TABLE I. Core polarization energies in electron volts.

	ev
Li atom	
(a) HF SCF $2s_R$	0.1018
(b) OAO (Eq. 1) $2s^0$	0.1066
Li_2 molecule ($R_e=5.051$ a.u.)	
(c) SCF MO [Eq. (2)] $(2\sigma_g)_R$	0.2473
(d) OMO [Eq. (3)] $(2\sigma_g)_{OMO}$	0.2520
Contribution to Li_2 binding energy	
(c) -2 (a)	0.0436
(d) -2 (b)	0.0387

Penetration effects are neglected in V_p. They were estimated previously[1] for Li to be less than 0.035 ev for the $1s_\beta 2s_\alpha$ interaction and 0.001 ev for $1s_\alpha 2s_\alpha$. The "exclusion effect"[1] of other electrons on the core-polarization energy of one, as well as three or more electron Coulomb correlations which may be small are also left out.

The contribution to the binding energy (1.03 ev) of Li_2 is also shown in Table I. We note that the energy is not very sensitive to the crudeness of the orbitals used. Thus where SCF MO's are not available, e.g., for Na_2, K_2, etc., it would suffice to use OMO's. Note also that though core polarization contributes quite appreciably to the total energies of Li and Li_2, the effects on the two almost cancel and yield a small contribution to the binding energy. Such a cancellation has often been assumed in semiempirical theories.

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[6] The value 0.019 ev is too high for "orbital average polarization" in Li_2, because it results from a very crude approximation[2] to outer MO's in the field of fixed cores.

Vaporization of Several Rare Earth Oxides*

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THE vaporization of two of the lightest rare earth oxides, La_2O_3 and Nd_2O_3 has been shown by several workers[1,2] to proceed principally by means of the reaction

$$M_2O_{3(s)}\rightarrow 2MO_{(g)}+O_{(g)}. \qquad (1)$$

The work of Chupka, Inghram, and Porter was a mass spectrometric study of the La–La_2O_3 system, and that of Walsh, Goldstein, and White was a simple effusion study of La_2O_3 and Nd_2O_3 vaporizing from tungsten effusion cells.

In this work, the vaporization of Pr_2O_3, Nd_2O_3, Sm_2O_3, and Eu_2O_3 has been studied at temperatures ranging from 1950°K to 2350°K by analyzing the species effusing from a Knudsen effusion cell with a Bendix time-of-flight mass spectrometer. Experimental details of the heating and temperature measuring techniques will be described elsewhere.[3]

The effusion cells were lined with either iridium or thoria. Studies in which iridium liners were used were principally to determine the relative amounts of the various species in equilibrium with the oxide with a minimum of chemical interference from the container. The ratio I_{M^+}/I_{MO^+} of ion currents due to the metal and monoxide when 20-ev electrons were used are given in the last column in Table I. For each of the compounds studied, a search for effusing species was made at several temperatures and electron bombardment energies.

If the ion current ratios in Table I represent the ratios of the equilibrium species with the effusion cell, it is obvious that among the oxides studied there is a change in the vaporization mode from that shown in Eq. (1) to that shown in Eq. (2), with increasing atomic number of the rare earth metal

$$M_2O_{3(s)}\rightarrow 2M_{(g)}+3O_{(g)}. \qquad (2)$$

Spurious results would be expected if the observed ions did not originate from simple ionization of neutral species, but from dissociative ionization of a parent molecule or by ion molecule combination in the ion source. In all the cases presented here, ion molecule combination is highly improbable because of the low concentration of ions and molecules in the ion source. If the MO^+ ions were due to dissociative ionization, ions of higher mass would be present in appreciable amounts. This is not the case.

The M^+ ions observed when vaporizing Sm_2O_3 and Eu_2O_3 could have derived from dissociative ionization. In order to determine which process led to the formation of these ions, Sm_2O_3 and Eu_2O_3 were vaporized from ThO_2 effusion cells containing a small amount of SiO_2. The vaporization thus occurred in an oxidizing atmosphere. Under these conditions, the MO^+ ions, rather than M^+ ions, were the major species observed. It follows that the M^+ ions observed as the major, or as an important species under neutral conditions, were due principally to simple ionization of the parent M atoms in the effusion beam.

TABLE I. Equilibrium vaporization data at 2000°K.

Oxide	P_M (atm)	P_{MO} (atm)	P_{MO_2} (atm)	I_M^+/I_{MO}^+
Pr_2O_3	$<1\times10^{-8}$	1×10^{-7}	$<5\times10^{-9}$	<0.1
Nd_2O_3	$<5\times10^{-9}$	5×10^{-8}	...	<0.1
Sm_2O_3	$\approx3\times10^{-9}$	$\approx3\times10^{-9}$	...	0.5–1.0
Eu_2O_3	7×10^{-8}	9×10^{-9}	...	8.0 ± 2

The vaporization of the oxides under neutral conditions appeared to be stoichiometric. X-ray analyses of the oxides after heating indicated that only M_2O_3 was present at the end of the run.

In order to determine the approximate equilibrium pressures of the vaporizing species, mixtures of the oxide and rhodium powder were effused from thoria-lined cells. The rhodium provided an internal calibration by which the pressure of the species could be calculated from

$$P_X=(I_X^+\sigma_{Rh}/I_{Rh}^+\sigma_X)\,P_{Rh}, \tag{3}$$

where P, σ, and I^+ are the vapor pressures, electron cross sections, and ion currents of the species X and rhodium. Iridium vaporizing from the liner in the first experiments could not be used for calibration because of its low vapor pressure.[3] The vapor pressures of rhodium estimated by Stull and Sinke,[4] and confirmed in this laboratory,[3] were used.

The electron cross sections of rhodium, the rare earth metals, and oxygen were taken as 40.6, 73, and 3.3, respectively, on the basis of the work of Otvos and Stevenson.[5] It was assumed that the electron cross sections of the oxides were equal to the sums of the cross sections for the metals and oxygen. The uncertainties included in the extrapolation of the data of Otvos and Stevenson and in the assumption that electron cross sections are additive could, of course, have led to errors as large as a factor of 2 or 3 in the absolute pressure data. The values reported in Table I can, therefore, only be considered to be approximate.

It is assumed that the predegassed thoria liners did not interfere with these measurements. No condensed phase interaction was noted and the equilibrium vapor pressure of $ThO_{(g)}$ and $ThO_{2(g)}$ with $ThO_{2(s)}$ was several orders of magnitude lower than that of the gaseous species of the least volatile of the compounds studied.[6] The ratios of the various species effusing from the thoria lined cells were not markedly different from those obtained with the iridium cells.

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Density Measurements in Reflected Shock Waves

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THE state of experimental gas behind reflected shock waves is usually calculated from the velocity of the incident wave using the simple theory of plane shock wave reflection. Recent results have indicated, however, that the reflected waves may actually be substantially weaker than calculated, even in a pure monatomic gas.[1–3] We have carried out a number of experiments using the technique of soft x-ray absorption to see if the density behind reflected shock waves in pure xenon would be significantly lower than calculated.

The apparatus described previously[4] was rebuilt to enable shock wave experiments to be done under clean vacuum conditions. The shock tube is of 3-in. i.d. steel tubing, with a 10-ft driver section and an 11-ft expansion section. It can be evacuated to less than 10^{-5} mm Hg and has an outgassing rate of about 1–3 μ/hr. Shock velocities were measured using platinum resistance gauges and a raster-sweep oscilloscope. Attenuation was less than 0.2% in 50 cm. Beryllium slits 1.5 mm wide define the x-ray beam. The intensity of the