# Redetermination of the Dissociation Energy of Europium Monoxide and Its Bearing on Atmospheric Release Experiments

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The dissociation energy, $D_0{}^0$, of EuO has been redetermined and found to be 4.80 ± 0.11 eV. This value is substantially lower than previous data indicated. The results of recent atmospheric release of europium metal are discussed in light of this finding.

Recent atmospheric metal release experiments involving strontium, barium and europium by Drapatz et al.[1] have raised some questions about the interpretation of the results. In particular, it was expected on thermochemical grounds that barium and europium would have similar reaction cross sections for the process

$$M + O_2 \rightarrow MO + O \qquad (1)$$

and that molecular EuO would be observed as a result of metal releases at 150 – 200 km, just as BaO had been observed[2]. However, no EuO was observed in the release experiments, and the authors could offer no reasonable explanation for this negative result[1]. We became aware of the anomalous results on europium in the course of some new thermochemical measurements of the dissociation energy, $D_0{}^0$, of EuO, and it seemed worthwhile to report our findings here.

The earlier thermochemical data for EuO, on which the predictions of atmospheric behavior were based, were obtained from effusion studies of the vaporization of solid $Eu_2O_3$, and from mass spectrometric measurements of a gaseous exchange reaction with SmO[3]. However, a reexamination reveals that the interpretation of the effusion measurements is open to question, as Ames et al.[3] themselves stated, and the exchange reaction measurements involved only a few scattered points. It seemed valuable, therefore, to undertake new thermochemical measurements on EuO, and the results of such measurements are reported here.

In the present work, the two gaseous exchange equilibria

$$Eu + BaO = EuO + Ba \qquad (2)$$

and

$$Eu + AlO = EuO + Al \qquad (3)$$

were studied by high temperature mass spectrometry and the results were used to derive the reaction enthalpy changes. By this means, $D_0{}^0(EuO)$ could be measured by reference to both $D_0{}^0(BaO)$ and $D_0{}^0(AlO)$, since the reaction enthalpy yields directly the difference between the corresponding molecular dissociation energies. The apparatus, experimental technique, and data evaluation methods have been described previously[4]. The data were obtained in two separate sets of experiments in which molybdenum effusion cells containing mixtures of the solid oxides served as equilibrium effusion beam sources.

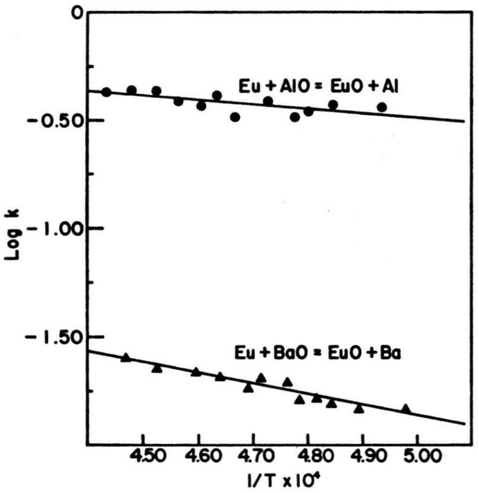

Fig. 1. Temperature Dependence of Equilibrium Constants.

Figure 1 is a plot of the measured equilibrium constant, $K_{eq}$, of reactions (2) and (3) as a function of temperature over the approximate range 2000 – 2250 K. From these data, the desired reaction enthalpies were derived from the magnitude (third-law method) and from the temperature dependence (second-law method) of $K_{eq}$. The third-law method (III) is sensitive to the choice of spectroscopic constants of the gaseous species involved, while the second-law method (II) is not; thus a comparison of the two methods tends to serve as an internal check.

In this fashion, the results $[D_0{}^0(BaO) - D_0{}^0(EuO)] = 0.80 \pm 0.11$ eV (III) and $0.95 \pm 0.10$ eV (II),

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together with $[D_0^0(\mathrm{AlO}) - D_0^0(\mathrm{EuO})] = 0.52 \pm 0.11$ eV (III) and $0.45 \pm 0.12$ eV (II) were obtained. Combining an average of the second- and third-law values with the established dissociation energies of BaO ($5.68 \pm 0.09$ eV)[5] and AlO ($5.29 \pm 0.03$ eV)[6], one obtains $D_0^0(\mathrm{EuO}) = 4.80 \pm 0.11$ eV and 4.81 $\pm 0.11$ eV from the Eu-Ba-O and Eu-Al-O studies, respectively. Our new value for $D_0^0(\mathrm{EuO})$ is substantially lower than the previous thermochemical result[3] of $5.80 \pm 0.20$ eV, but, as noted above, there are several reasons for questioning the earlier study. A complete description of our work and a comparison with other measurements will be presented in another publication.

The newly-obtained result for $D_0^0(\mathrm{EuO})$ indicates that the gaseous reaction

$$\mathrm{Eu} + \mathrm{O}_2 \rightarrow \mathrm{EuO} + \mathrm{O}$$

is endothermic by $5.12 - 4.80 = 0.32$ eV at thermal energies, and is in accord with the failure of Drapatz et al.[1] to observe EuO in the artificial metal cloud experiments at altitudes of about 150 km. The corresponding reaction for Ba is exothermic by 0.56 eV, and did, indeed, lead to spectroscopic observation of BaO in the experiments with barium clouds[2]. Thus there appears to be no conflict between the thermochemical data and the metal release experiments.

Contrary to the foregoing, recent studies of chemiluminescent processes involving europium oxidation were interpreted by Dickson and Zare[7] to yield $D_0^0(\mathrm{EuO}) \geqq 5.70 \pm 0.03$ eV. At this stage, there is no readily apparent explanation for the discrepancy. However, a detailed analysis of the earlier thermochemical measurements[3] leads to a revision which strongly supports the mass spectrometric value for $D_0^0(\mathrm{EuO})$ reported here.

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