Gibbs Energies of Formation of Rare Earth Oxysulfides

R. AKILA, K. T. JACOB, and A. K. SHUKLA

The standard Gibbs energy change accompanying the conversion of rare earth oxides to oxysulfides by reaction of rare earth oxides with diatomic sulfur gas has been measured in the temperature range 870 to 1300 K using the solid state cell: Pt/Cu + Cu_2S/R_2O_2S + $R_2O_3\|(CaO)ZrO_2\|$Ni + NiO, Pt where R = La, Nd, Sm, Gd, Tb, and Dy. The partial pressure of diatomic sulfur over a mixture of rare earth oxide (R_2O_3) and oxysulfide (R_2O_2S) is fixed by the dissociation of Cu_2S to Cu in a closed system. The buffer mixture of Cu + Cu_2S is physically separated from the rare earth oxide and oxysulfide to avoid complications arising from interaction between them. The corresponding equilibrium oxygen partial pressure is measured with an oxide solid electrolyte cell. Gibbs energy change for the conversion of oxide to the corresponding oxysulfide increases monotonically with atomic number of the rare earth element. Second law enthalpy of formation also shows a similar trend. Based on this empirical trend Gibbs energies of formation of oxysulfides of Pr, Eu, Ho, and Er are estimated as a function of temperature.

I. INTRODUCTION

THE use of rare earth elements at high temperatures in the treatment of iron and steel for purposes such as deoxidation, desulfurization, control of inclusion morphology in steel, and graphite morphology in cast iron necessitates the evaluation of the thermodynamic properties of rare earth compounds. Investigations in this field are, however, limited and often accompanied by large uncertainties in the thermodynamic properties. The present investigation is part of a larger study on thermodynamic properties of rare earth compounds.

Fruehan[1] determined the Gibbs energy of formation of Ce_2O_2S by equilibrating CeO_2 with $CO\text{-}CO_2\text{-}SO_2$ gas mixtures in the temperature range 1070 to 1750 K. For fixed CO/CO_2 ratios, the SO_2 concentration at which the sample was completely converted to Ce_2O_2S was determined. The equilibrium constant for the reaction,

$$2\,CeO_2 + 4\,CO + SO_2 \rightarrow Ce_2O_2S + 4\,CO_2 \qquad [1]$$

was calculated and combined with auxiliary thermodynamic data for CeO_2, CO, CO_2, and SO_2 in the literature to obtain the standard free energy of formation of Ce_2O_2S. The value was a sensitive function of the fourth power of the CO/CO_2 ratio. The value obtained was less negative by 13 kJ than the value of −1418 (±60) kJ mol^{-1} estimated by Gschneidner *et al.*[2] at 1100 K.

Dwivedi and Kay[3] used a galvanic cell technique with calcia stabilized zirconia as the solid electrolyte to measure the standard free energies of formation of Ce_2O_2S and Y_2O_2S. The sulfur potential corresponding to the equilibrium between the rare earth oxide and oxysulfide was fixed by the Cu/Cu_2S equilibrium. The experiments were performed in a limited temperature range, from 1040 to 1085 K. The Gibbs energies of formation reported by Dwivedi and Kay[3] are −1423 (±12.5) kJ mol^{-1} for Ce_2O_2S at 1072 K and −1482.4 (±12.5) kJ mol^{-1} for Y_2O_2S at 1068 K. The corresponding values from Gschneidner *et al.*[2] are −1426 (±60) kJ mol^{-1} and −1494 (±60) kJ mol^{-1}, respectively.

Other studies include the free energy determination of La_2O_2S by Kumar and Kay[4] and those of Fukatsu *et al.*[5] for the oxysulfides of Ce, Nd, Gd, and Y. Kumar and Kay[4] used an air-Pt reference electrode with a $(CaO)ZrO_2$ solid electrolyte tube. A Cu/Cu_2S mixture was employed to fix the sulfur pressure over the two phase oxide/oxysulfide electrode. The study was performed in the temperature range 1080 to 1350 K, with an accuracy of 1.6 kJ in the free energy change associated with the conversion of the oxide to the oxysulfide.

Fukatsu *et al.*[5] used an S-O gas mixture at a total pressure of one atmosphere to fix the sulfur pressures of the oxide/oxysulfide equilibria. The equilibrium oxygen potential was measured with a $(CaO)ZrO_2$ electrolyte having an air reference electrode. The gas composition was then numerically computed using thermodynamic data available in the literature for the various species coexisting at equilibrium. Since thermodynamic data for a large number of species are used in the computation, cumulative errors may be large.

In the present study, the Gibbs energy changes involved in the conversion of the rare earth oxides to oxysulfides have been measured. These data are combined with the standard Gibbs energies of formation of the rare earth oxides, available in the literature,[2] to obtain the Gibbs energies of formation of the rare earth oxysulfides from elements in their standard states.

II. EXPERIMENTAL ASPECTS

A. *Materials*

The rare earth oxysulfides were prepared by dissolving rare earth oxides of 99.9 pct purity in 60 pct sulfuric acid. The sulfate crystals so obtained were dehydrated by heating at 900 K. Further heating in air between 1073 and 1223 K produced the oxysulfate. The higher temperatures were used for the lighter rare earth elements. The oxysulfates were subjected to hydrogen reduction at 1000 K to produce the corresponding oxysulfides. The formation of oxysulfides

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was confirmed by X-ray diffraction. The copper sulfide was prepared from elements in evacuated quartz ampules.

B. *Cell Assembly*

The experimental arrangement is shown in Figure 1. An equimolar mixture of the rare earth oxide and the corresponding oxysulfide was packed into a $(CaO)ZrO_2$ crucible. An alumina crucible containing a $Cu + Cu_2S$ mixture in the molar ratio 1:2 was placed inside the $(CaO)ZrO_2$ crucible. The $Cu + Cu_2S$ buffer was chosen because it establishes a reasonably high sulfur pressure for gas transport. The $(CaO)ZrO_2$ crucible was covered with an alumina disk. The partial pressure of diatomic sulfur over the rare earth oxide/oxysulfide mixture was set by the dissociation of Cu_2S to Cu. A closed atmosphere for the dissociation reaction was provided by a gold O-ring placed between the $(CaO)ZrO_2$ crucible and the alumina lid as shown in Figure 1. A Pt lead contacting the R_2O_3/R_2O_2S mixture was taken out through an aperture on the alumina lid, the aperture being provided with a glass seal to ensure gas tightness. A special feature of the cell design was the physical separation of the sulfur buffer from the rare earth compounds, so that effects due to solid solubility or chemical reaction between the buffer components and electrode materials were avoided. The reference electrode was a mixture of $Ni + NiO$ in the molar ratio 1:1. A Pt wire served as the electrode lead for the reference electrode. The $Ni + NiO$ reference electrode was chosen as it results in a small cell emf, thus minimizing the electrochemical flux of oxygen through the electrolyte and the resulting polarization effects. The standard Gibbs energy of formation of NiO is also well established. The cell assembly was spring loaded by a set of alumina rods and slabs. The cell temperature was monitored by a Pt/Pt-13 pct Rh thermocouple enclosed in an alumina sheath.

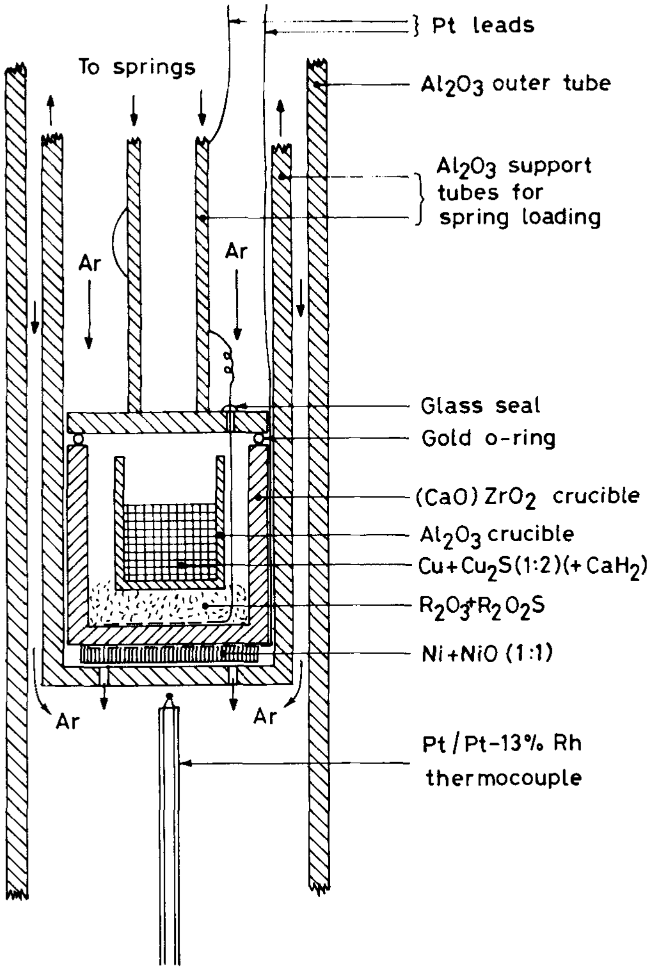

Fig. 1—A schematic diagram of the arrangement of the cell.

C. *Experimental Procedure*

The cell assembly was placed in a vertical furnace having an alumina tube heated by resistance winding. The temperature in the even zone was controlled to ±1 K by a Thyristor temperature controller. The reference electrode side of the $(CaO)ZrO_2$ crucible was flushed with purified argon gas for 2 hours before the furnace was switched on. The flow rate was then adjusted to about 100 ml min^{-1}. The emfs of the cells

$$Pt/Cu + Cu_2S/R_2O_2S + R_2O_3 \| (CaO)ZrO_2 \| Ni + NiO, Pt$$

where R = La, Nd, Sm, Gd, Tb, and Dy were measured in the temperature range 870 to 1300 K with a Princeton Applied Research (model 136) high impedance electrometer.

In preliminary experiments, it was found that the emf attained constant values in 2 hours near 1300 K, whereas periods in excess of 12 hours were required near 870 K, probably due to the low partial pressure of sulfur established by the $Cu + Cu_2S$ buffer. It was found that the addition of approximately 0.02 g of CaH_2 to the buffer resulted in quicker response of the cell. Reversible emfs were obtained in approximately 3 hours at 870 K and 0.5 hour at 1300 K. The CaH_2 is expected to react completely with Cu_2S to form CaS, releasing H_2 to the gas phase. Part of this H_2 would be converted to H_2S until the equilibrium ratio of P_{H_2S}/P_{H_2} corresponding to the $Cu + Cu_2S$ buffer is established in the closed crucible. Since the partial pressure of H_2S in the crucible would be higher than that of S_2, H_2S would be the primary species responsible for the transfer of sulfur potential established by the $Cu + Cu_2S$ buffer to the $R_2O_3 + R_2O_2S$ electrode *via* the gas phase. The presence of a small amount of CaS would not alter the sulfur potential of the buffer. Even if compound formation occurred in the pseudo-binary system CaS-Cu_2S, there would still be a large excess of Cu_2S at unit activity in the buffer. It should be noted that the buffer action of the $Cu + Cu_2S$ electrode will be maintained only if the oxygen potential established does not alter the composition of the buffer electrode mixture. The equilibrium oxygen potentials in the present study are too low for the formation of Cu_2O. All experimental data reported in this paper were obtained with the addition of 0.02 g of CaH_2 to the buffer which weighed approximately 4 g.

The reproducibility of the cell emfs was checked by temperature cycling. To ensure cell reversibility, small currents were passed in either direction for short intervals of time and it was verified that the cell emfs returned to their original values before the titration. The electrode pellets were examined before and after the experiment by X-ray diffraction. No changes were detected in the diffraction pattern, suggesting the absence of significant solid solubility or chemical reaction during the experiments.

III. RESULTS AND DISCUSSION

The measured cell emfs are plotted as a function of temperature for the different rare earth systems in Figure 2. The variation of emf with temperature is linear over the temperautre range investigated. The equations relating cell emf to temperature obtained by least mean square analysis are shown in Table I for the different rare earth systems investigated.

The overall cell reaction may be written as the sum of the reactions occurring at the cathode and the anode. The cathodic reaction is

$$\langle NiO\rangle + 2e^- \rightarrow \langle Ni\rangle + O^{2-} \qquad [2]$$

while the anodic reaction is

$$\langle R_2O_2S\rangle + 2\langle Cu\rangle + O^{2-} \rightarrow \langle R_2O_3\rangle + \langle Cu_2S\rangle + 2e^- \qquad [3]$$

Thus the cell reaction is given by

$$\langle R_2O_2S\rangle + 2\langle Cu\rangle + \langle NiO\rangle \rightarrow \langle R_2O_3\rangle + \langle Cu_2S\rangle + \langle Ni\rangle \qquad [4]$$

where ⟨ ⟩ represents the solid state. The standard states for the solids involved in the reactions are the saturated coexisting phases. The solubility of the two phase electrode mixtures was found to be negligible by X-ray diffraction and from available phase diagrams. Consequently, no appreciable error is introduced in the Gibbs energies by assuming unit activity for reactants and products involved in the cell reaction.

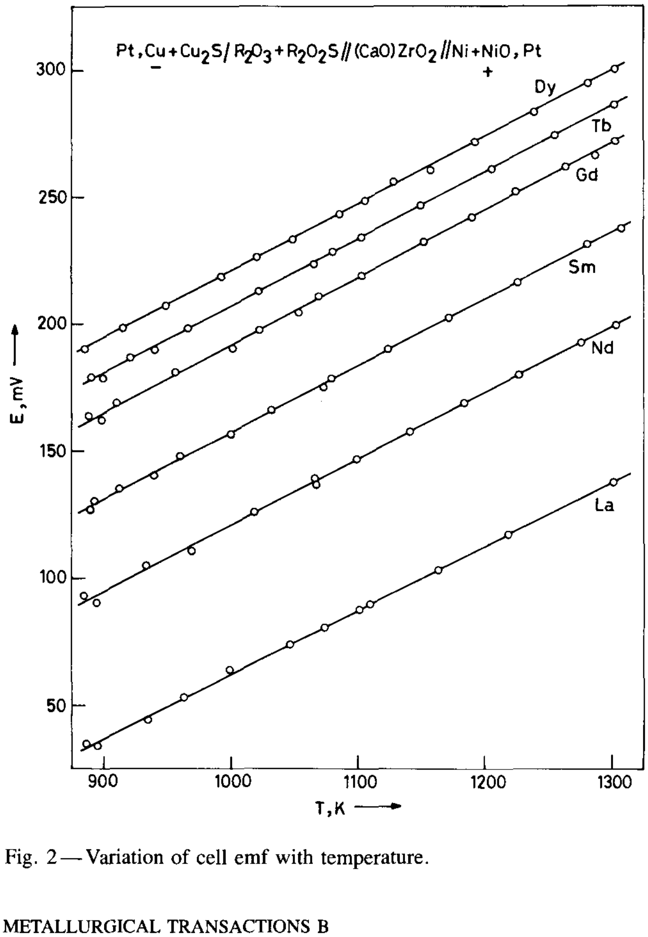

Fig. 2 — Variation of cell emf with temperature.

The free energy change associated with the virtual cell reaction can be calculated using the relationship,

$$\Delta G^\circ = -n\mathrm{F}E \qquad [5]$$

where $n = 2$, the number of electrochemical equivalents in the cell reaction, F is the Faraday constant, and E is the measured cell emf.

In order to obtain the free energy change associated with the reaction

$$\langle R_2O_3\rangle + \frac{1}{2}(S_2) \rightarrow \langle R_2O_2S\rangle + \frac{1}{2}(O_2) \qquad [6]$$

where ( ) represents the gaseous state, it is necessary to combine the ΔG° values given by expression [5] with the standard free energies of formation of NiO and Cu_2S. For NiO, the value given by Steele[8] is used.

$$\Delta G^\circ_{NiO} = -234{,}160 + 84.89T\ (\pm 545)\ \mathrm{J\ mol^{-1}} \qquad [7]$$

The Gibbs energies of Cu_2S in the temperature range 900 to 1300 K reported by Ferrante *et al.*[9] were fitted to a linear equation of the form,

$$\Delta G^\circ_{Cu_2S} = -128{,}540 + 30.38T\ (\pm 800)\ \mathrm{J\ mol^{-1}} \qquad [8]$$

These values are slightly more positive (by ~3.6 kJ) than the free energies given by Barin and Knacke[6] and Mills.[7] The difference may arise from the different values of the standard entropy at 298 K. The value given by Barin and Knacke and Mills is $S^\circ_{298} = 120.92$ J K^{-1} mol^{-1}. This is based on the low temperature heat capacity data of Anderson[10] for Cu_2S, in which the values below 56 K were estimated. Ferrante *et al.*[9] report a value of $S^\circ_{298} = 116.15$ J K^{-1} mol^{-1} based on their experimental investigations down to 5 K, and their values have been used in the calculations.

The standard free energy changes associated with reaction [6] are expressed as a function of temperature for the various rare earth systems in Table II. The values at 1100 K, plotted as a function of rare earth atomic number in Figure 3, show a smooth increase with increasing atomic number. The ionic radii of trivalent rare earth ions decrease continuously with atomic number. The consequent increase in their polarizing power with atomic number is a probable factor in the decreasing stability of the oxysulfides relative to the corresponding oxides. The oxides have more closely packed structures than the oxysulfides, which are composed of R-O sheets between which is a plane hexagonal lattice of

Table I. Temperature Dependence of Cell Emf Corresponding to the R_2O_2S/R_2O_3 Equilibrium in the Temperature Range 870 to 1300 K

R	E, mV
La	−191.3 + 0.2532T (±1.1)
Nd	−138.7 + 0.260T (±1.9)
Sm	−105.0 + 0.2627T (±1.8)
Gd	− 74.19 + 0.266T (±1.2)
Tb	− 56.73 + 0.264T (±1.3)
Dy	− 44.21 + 0.2654T (±0.6)

Table II. Standard Gibbs Energy Change for the Reaction $\langle R_2O_3\rangle + 1/2(S_2) \rightarrow \langle R_2O_2S\rangle + 1/2(O_2)$ in the Temperature Range 870 to 1300 K

R	$\Delta G°$, J mol^{-1}
La	$68{,}700 - 5.65T$ ($\pm$ 990)
Nd	$78{,}850 - 4.34T$ ($\pm$1035)
Sm	$85{,}355 - 3.81T$ ($\pm$1025)
Gd	$91{,}300 - 3.17T$ ($\pm$ 995)
Tb	$94{,}670 - 3.56T$ ($\pm$1000)
Dy	$97{,}085 - 3.30T$ ($\pm$ 975)

sulfur atoms. The value obtained by Kumar and Kay[4] for La is in good agreement with the present study. The sulfur potential of their auxiliary Cu + Cu_2S electrode, taken from Kubaschewski and Alcock,[11] is less positive (by ~2.6 kJ) than the values given by Eq. [8]. The close agreement shown in Figure 3 with our value is therefore fortuitous. The values reported by Fukatsu *et al.*[5] for Nd and Gd agree within 2.1 kJ. The agreement among the three investigations is remarkable. The curve can be extrapolated to higher atomic numbers and the free energies for reaction [6] of the heavier rare earth elements estimated.

The enthalpy change associated with reaction [6] is plotted as a function of rare earth atomic number in Figure 4. The behavior is similar to that exhibited by the free energy values. The value given by Kumar and Kay[4] is about 5 kJ more positive for the lanthanum oxide/oxysulfide equilibrium. The values of Fukatsu *et al.*[5] are smaller by 17 kJ and 22 kJ for the Nd and Gd systems, respectively.

The standard entropy change accompanying the conversion of the rare earth oxide to the oxysulfide is shown as a function of rare earth atomic number in Figure 5. The entropy decreases slightly with increase in atomic number. The values obtained by Kumar and Kay[4] and Fukatsu *et al.*[5] again show significant deviations from the values obtained in this study.

The Gibbs energy changes associated with reaction [6] obtained in this study have been combined with the standard free energies of formation of the rare earth oxides compiled by Gschneidner *et al.*[2] to obtain the standard free energies of formation of the rare earth oxysulfides from the elements in their standard states. The values are tabulated in Table III as linear functions of temperature in the range 900 to 1300 K. The values for Pr, Eu, Ho, Er, and Tm are estimated from the empirical trends obtained in this study. Because of the large uncertainties in the free energy values for the rare earth oxides (8 to 15 kJ), the free energies of formation of the oxysulfides also have large error bars. As more accurate data on free energies of formation of the rare earth oxides become available, the data obtained in this study may be used to obtain more accurate values for the free energies of formation of the corresponding oxysulfides.

The Gibbs energies of formation of rare earth oxysulfides at 1100 K are plotted in Figure 6 as a function of the rare

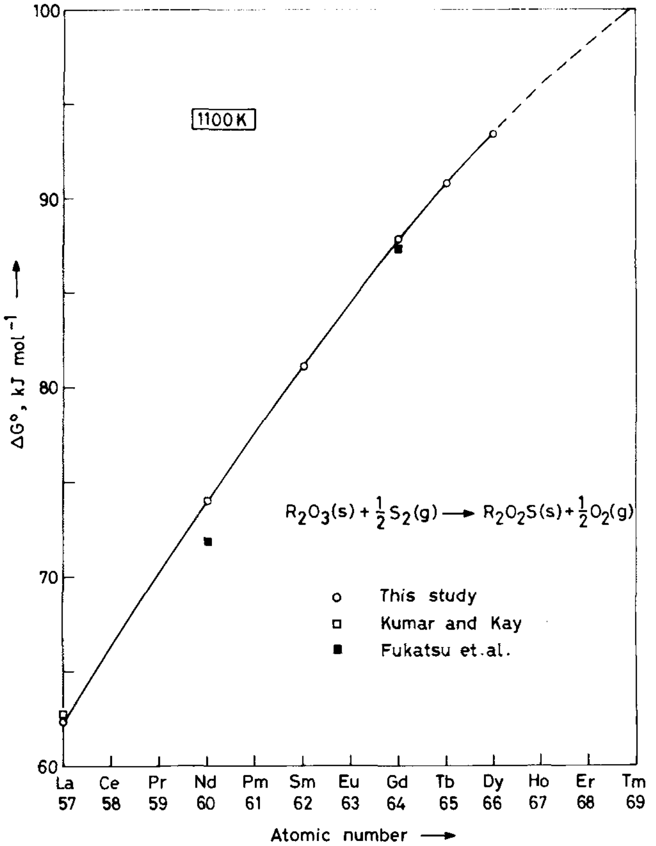

Fig. 3—The standard Gibbs energy change for the reaction $R_2O_3(s) + 1/2S_2(g) \rightarrow R_2O_2S(s) + 1/2O_2(g)$ plotted as a function of rare earth atomic number at 1100 K.

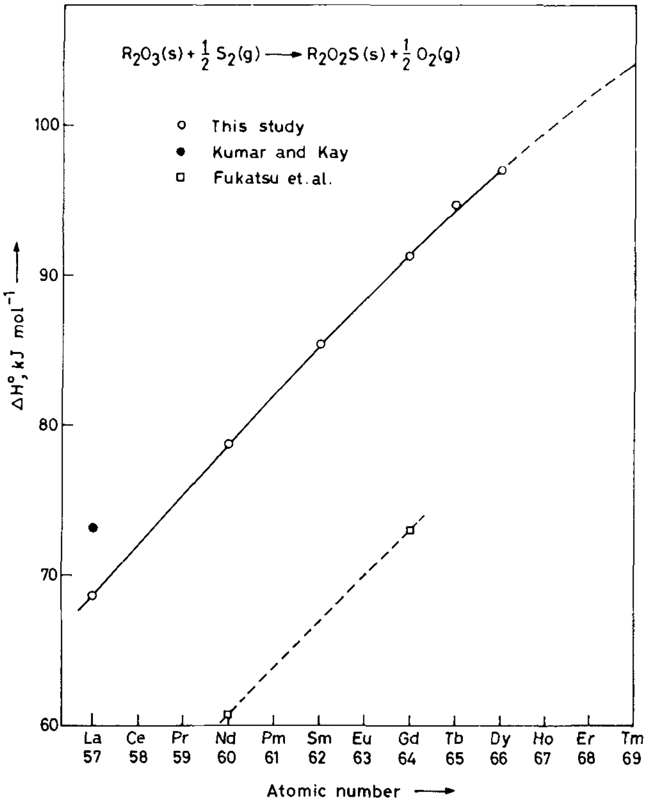

Fig. 4—Variation of the standard enthalpy change associated with the conversion of oxides to their corresponding oxysulfides with atomic number of the rare earth element.

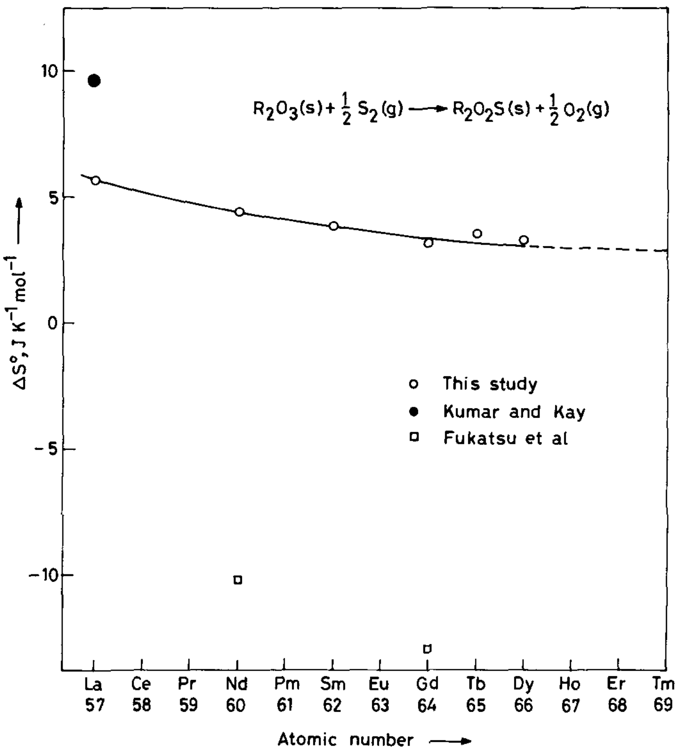

Fig. 5 — Dependence of the standard entropy change for the conversion of rare earth oxides to oxysulfides on the atomic number of the rare earth element.

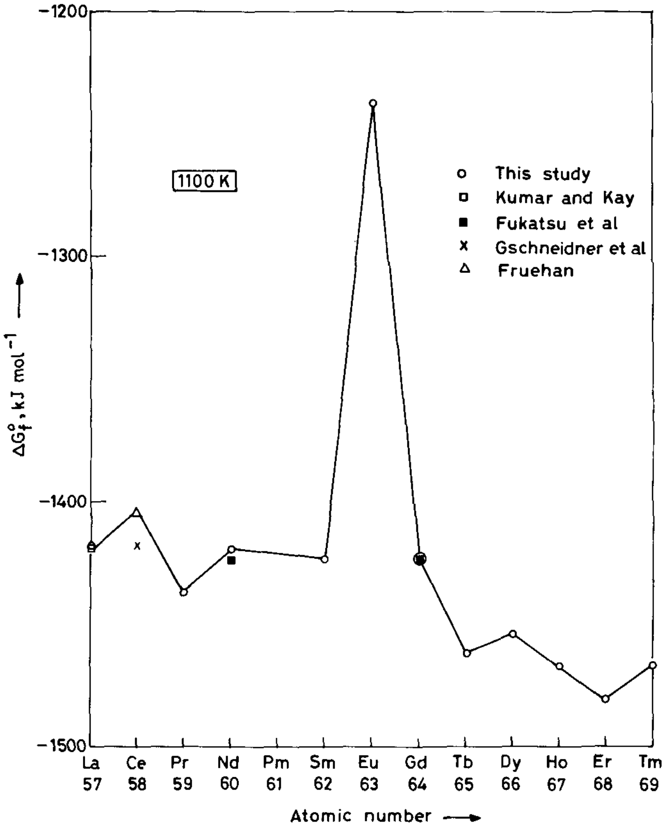

Fig. 6 — The standard free energies of formation of rare earth oxysulfides, R_2O_2S, as a function of rare earth atomic number.

earth atomic number. The trend observed is a reflection of that seen for the oxides. The value given by Kumar and Kay[4] for La_2O_2S and that of Fukatsu *et al.*[5] for Nd_2O_2S and Gd_2O_2S show excellent agreement with the corresponding values obtained in our study. The free energy values also are in reasonable agreement (±7.5 to 24.5 kJ) with the estimated values of Gschneidner *et al.*[2] despite the large uncertainty limits (±60 kJ) quoted by them. The standard free energy of formation of Eu_2O_2S is more positive (by more than 190 kJ mol^{-1}) than that of Sm_2O_2S or Gd_2O_2S. The Eu^{2+} ion has [Xe] $4f^7$ and the Yb^{2+} ion has [Xe] $4f^{14}$ electronic configuration. The half filled and completely filled f-shell configurations are chemically stable, and extra energy has to be supplied to convert the Eu^{2+} and Yb^{2+} ions to the trivalent state. As pointed out by Gschneidner,[12] the promotion energies from divalent to trivalent state are 98 kJ mol^{-1} for Eu and 36 kJ mol^{-1} for Yb. The free energies of formation of the oxides, oxysulfides, and oxysulfates of these rare earth metals are therefore less negative than those of their neighboring elements.

Table III. Standard Free Energies of Formation of Rare Earth Oxysulfides (R_2O_2S) in the Temperature Range 900 to 1300 K

R	$\Delta G°$, J mol^{-1}
La	$-1717220 + 272.19T$ (±10,900)
Pr	$-1737580 + 273.61T$ (±15,000)*
Nd	$-1720190 + 273.72T$ (± 9,200)
Sm	$-1734300 + 282.81T$ (±10,100)
Eu	$-1564180 + 297.70T$ (±12,100)*
Gd	$-1724455 + 273.91T$ (±12,200)
Tb	$-1753305 + 265.01T$ (±12,200)
Dy	$-1748355 + 268.00T$ (±11,700)
Ho	$-1767415 + 273.02T$ (±13,400)*
Er	$-1784220 + 276.19T$ (±10,000)*
Tm	$-1770360 + 277.24T$ (±14,200)*

*Estimated values

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