Die Werkstoffanstrengung im elastisch-plastischen Bereich kann beschrieben werden, indem man in den Lösungen (10) und (15) die elastische Querzahl ν durch die elastisch-plastische Querzahl ν_{ep} gemäß Gl. (22) ersetzt. Die Ergebnisse lauten dann:

$$\sigma^2 = \tfrac{3}{2}\left[1 - \tfrac{1}{3}(1-2\nu)\, T/E\right] \sigma'_{ij}\sigma'_{ij} + \tfrac{1}{3}(1-2\nu)(T/E)\,\sigma_{kk}{}^2 \quad (23\text{a})$$

bzw.

$$\sigma^2 = \tfrac{3}{2}\, \sigma'_{ij}\sigma'_{ij} - (1-2\nu)\,(J_2' - \tfrac{1}{3}J_1{}^2)\, T/E \quad (23\text{b})$$

und

$$\mathrm{d}\varepsilon^2 = \frac{\tfrac{2}{3}\mathrm{d}\varepsilon'_{ij}\mathrm{d}\varepsilon'_{ij}}{1 - \tfrac{1}{3}(1-2\nu)\, T/E} + \frac{\varepsilon_{kk}{}^2}{3(1-2\nu)\, T/E}\,, \quad (24)$$

die für $T = 0$ (idealplastischer Werkstoff) in die entsprechenden Beziehungen der Mises'schen Theorie übergehen und für $T = E$ (elastischer Bereich) mit den Ergebnissen gemäß Gl. (10) und Gl. (15) identisch sind.

In Gl. (23b) kann noch eine kürzere Schreibweise benutzt werden, wenn man berücksichtigt, daß

$$J_2' = \tfrac{1}{2}\sigma'_{ij}\sigma'_{ij} = \tfrac{1}{2}(\sigma_{ij}\sigma_{ij} - \tfrac{1}{3}\sigma_{kk}{}^2) \quad (25)$$

gilt, so daß damit

$$J_2' - \tfrac{1}{3}J_1{}^2 = \tfrac{1}{2}(\sigma_{ij}\sigma_{ij} - \sigma_{kk}{}^2) = J_2 \quad (26)$$

wird. Somit kann Gl. (23b) auch in der Form

$$\sigma^2 = 3\, J_2' - (1-2\nu)\,(T/E)\, J_2 \quad (27)$$

geschrieben werden. Darin ist J_2 die zweite Invariante des Spannungstensors σ_{ij}. Für den elastischen Bereich ($T = E$) geht Gl. (27) wegen des Zusammenhangs (26) über in:

$$\sigma^2 = J_1{}^2 + 2(1+\nu)\, J_2\,, \quad (28)$$

während für idealplastischen Werkstoff ($T = 0$) wieder der Mises'sche Ansatz anfällt.

Zusammenfassung

Im Gegensatz zur Mises'schen Theorie wird im vorliegenden Aufsatz zur Beurteilung der Werkstoffanstrengung das elastische Potential zu Grunde gelegt. Das führt auf die Hypothese von der elastischen Formänderungsarbeit, die auf Beltrami zurückzuführen ist und nur für den elastischen Bereich gültig ist. Für $\nu = \tfrac{1}{2}$ erfolgt ein zwangloser Übergang zur Mises'schen Theorie. Durch Einführung einer elastisch-plastischen Querzahl ν_{ep} kann die Hypothese von der elastischen Formänderungsarbeit auf den elastisch-plastischen Bereich erweitert werden, wie in der Untersuchung gezeigt wird.

Non-Congruent Vaporization of Some Rare Earth Oxides

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(Z. Naturforsch. **28a**, 37—45 [1973]; received 6 October 1972)

The vaporization of lanthanum and yttrium oxides has been studied at temperatures as high as 1 900 and 2 200 °C respectively, by means of high temperature mass spectrometry.

Emphasis has been placed on the study of the phenomenon on first heating (transient stage). Both monoxide and atomic oxygen partial pressures were recorded and found to be time dependent in the transient stage and in the case of the lanthanum oxide also dependent on the initial water content of the sample. Variations of the metal to oxygen ratio in the solid and the possible vaporization reactions are discussed.

1. Introduction

Extensive and systematic investigations of the vaporization processes of rare earth oxides have been carried out in the past years [1, 2, 3, 4].

From mass-spectrometric measurements, the com-

Reprint requests to Dr. G. TREVISAN, EURATOM, *Petten*, Niederlande.

[1] E. W. Westrum, Proc. Sci. Techn. Rare Earths, Pergamon Press **1**, 310 [1964].

[2] D. WHITE, P. WALSH, L. AMES, and H. GOLDSTEIN, Thermodynamic of nuclear materials, IAEA Vienna, p. 417 [1962].

[3] L. AMES, P. WALSH, and D. WHITE, J. Phys. Chem. **71**, 2707 [1967].

[4] R. ACKERMANN, E. RAUH, and R. THORN, J. Chem. Phys. **40**, 883 [1964].

ponents of the vapour phase over these oxides in the temperature range 2 000–2 400 °C have been found to be the monoxide, atomic oxygen and minor quantities of the metal, so that the vaporization process might be attributed to the simultaneous occurrence of the following reactions

$$Me_2O_3\,(c) \rightarrow 2\,MeO\,(g) + O\,(g)\ , \tag{1}$$

$$MeO\,(g) \rightarrow Me\,(g) + O\,(g)\ . \tag{2}$$

The relative weight of reaction (2) has been found to be nearly negligible in this temperature range and relevant only in the case of the heaviest rare earths.

In the specific cases of the lanthanum and yttrium oxides the absolute equilibrium partial pressures and the related thermodynamic data have been calculated by means of weight loss experiments [2, 4], assuming that only reaction (1) occurs.

Some authors [2, 3] have observed that an isothermal vaporization process can be subdivided into two stages characterized by varying values of the vaporization rate (transient stage) and constant values of this rate (steady state). Furthermore, at the end of the experiment the oxide is always darker in colour.

They tentatively explained these findings by supposing that during the transient stage the oxide vaporizes incongruently and oxygen is eliminated in excess of the stoichiometric rate, the sample thus turning to a slightly defective dark solid, which however, evaporates congruently in the steady state.

White [2] and Ackermann [4] report that after a typical experiment the formulas of the dark oxides were respectively $La_2\,O_{2,\,975\,\pm\,0{,}015}$ and $Y_2\,O_{2,\,996}$.

This paper represents a contribution to the study of the transient stage and deals with the results of isothermal vapour pressure measurements carried out with a high temperature mass-spectrometer.

2. Experimental

Materials

Lanthanum oxide

The lanthanum sesquioxide was obtained from Alfa Inorganics. The purity was reported to be 99,99 %. Two samples, A and B, were prepared, having respectively a high and a low hydroxide content at the time of their introduction into the furnace of the mass spectrometer. Both samples were first baked out at 1 000 °C in air to eliminate hydroxide and carbonate impurities. Sample A was then cooled in air during its loading into the Knudsen cell (10–15 minutes) which was introduced into the furnace of the spectrometer and outgassed overnight at 1 000 °C under vacuum. Sample B was cooled under vacuum, exposed to air during the loading of the cell and then treated as A.

Yttrium oxide

The yttrium sesquioxide was obtained from Alfa Inorganics. The samples were first heat-treated in air at 1 000 °C overnight and then outgassed at 1 200 °C under vacuum in the furnace of the spectrometer as in the case of the lanthanum oxide. The samples underwent a final outgassing at 1 700 °C for about two hours before the vaporization experiment was begun.

Apparatus and procedure

The Knudsen vaporization experiments were carried out at temperatures as high as 1 927 °C for the lanthanum oxide and 2 183 °C for the yttrium oxide in the high temperature furnace of a Nuclide Associates mass spectrometer type 90 HT following the technique described by Inghram and Drowart [5].

The Knudsen cells and liners which were made from tungsten, were first baked out at 2 200 °C in order to avoid any possible variation of the hole size as a consequence of recrystallization of the tungsten during the experiment. Knife edged holes of about 1 mm diameter and samples of about 0,5 g were used throughout. At the experimental temperature the samples sinter and take the form of small cylinders. The ratio of the area of the sample to that of the Knudsen hole was never lower than 100.

The temperature was measured by means of an automatic optical pyrometer (Pyro Photomatic) sighting a pyrometric hole of ⌀ 1 x 5 mm which was drilled in the Knudsen cell 1 mm below the bottom of the sample. The pyrometer was calibrated directly at the melting point of alumina, taken as 2 051 ± 6 °C [6].

The melting point of alumina was detected by monitoring the Al^+ ion current and recording the melting plateau.

The absolute pressures were obtained from the ion currents by means of a silver calibration, according to the relationship

$$P_x = \frac{I_x\,T_x\,P_{Ag}\,\gamma_{Ag}\,\sigma_{Ag}}{I_{Ag}\,T_{Ag}\,\gamma_x\,\sigma_x} \tag{3}$$

where I_i are the ion currents, γ_i the gains of the electron multiplier, σ_i the cross sections for the electron,

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[5] M. G. Inghram and J. Drowart, Proc. of an Int. Symp. on High Temp. Technology, Asilomar 1960.

[6] S. J. Schneider and C. L. McDaniell, J. Research of the N. B. S. **71 A**, 317 [1967]

T_i the temperatures in °K at which the species i is evaporated and P_i the partial pressures.

The electron multiplier gains were obtained by direct comparison of the Faraday cup and electron multiplier currents. The vaporization experiments were carried out at an electron energy of 25 eV for the lanthanum oxide and 45 eV for the yttrium oxide. The cross sections were obtained from published data [7] and experimental ionization efficiency curves according to:

$$\left(\frac{\sigma_i}{\sigma_j}\right)_E = \frac{(I_j)\ \max}{(I_j)_E} \cdot \frac{(I_i)_E}{(I_i)\ \max} \cdot \left(\frac{\sigma_i}{\sigma_j}\right)_{\max} \qquad (4)$$

where E = electron energy in eV.

The $(\sigma\mathrm{LaO}/\sigma\mathrm{La})_{\max}$ ratio has been taken as 0,60 and the $(\sigma\mathrm{YO}/\sigma\mathrm{Y})_{\max}$ one as 0,68 [8].

The background does not interfere seriously at the mass numbers of the gaseous species coming from the vaporization reaction, except in the case of atomic oxygen.

In this case the oxygen ion current I_O was measured by making use of a movable shutter which can separate the ion source from the Knudsen cell furnace chamber, so that:

$$I_O = (I_O)\ \text{sh. on} - (I_O)\ \text{sh. off}\ . \qquad (5)$$

To make sure that I_O refers only to the oxygen evolved in the Knudsen cell, and not to oxygen present in the furnace, the cell was brought out of alignment with the ion source chamber by means of a micrometric device and the oxygen ion current $(I_O)'$ measured, keeping the shutter in its open position. $(I_O)'$ was found to be equal to (I_O) sh. off.

Possible interactions with the container have been also taken into account, monitoring the tungsten containing species in the vapour phase as well as analyzing the total tungsten content of the specimen after the vaporization experiment. The interaction has been found to be not negligible, and will be treated more extensively in the following chapter.

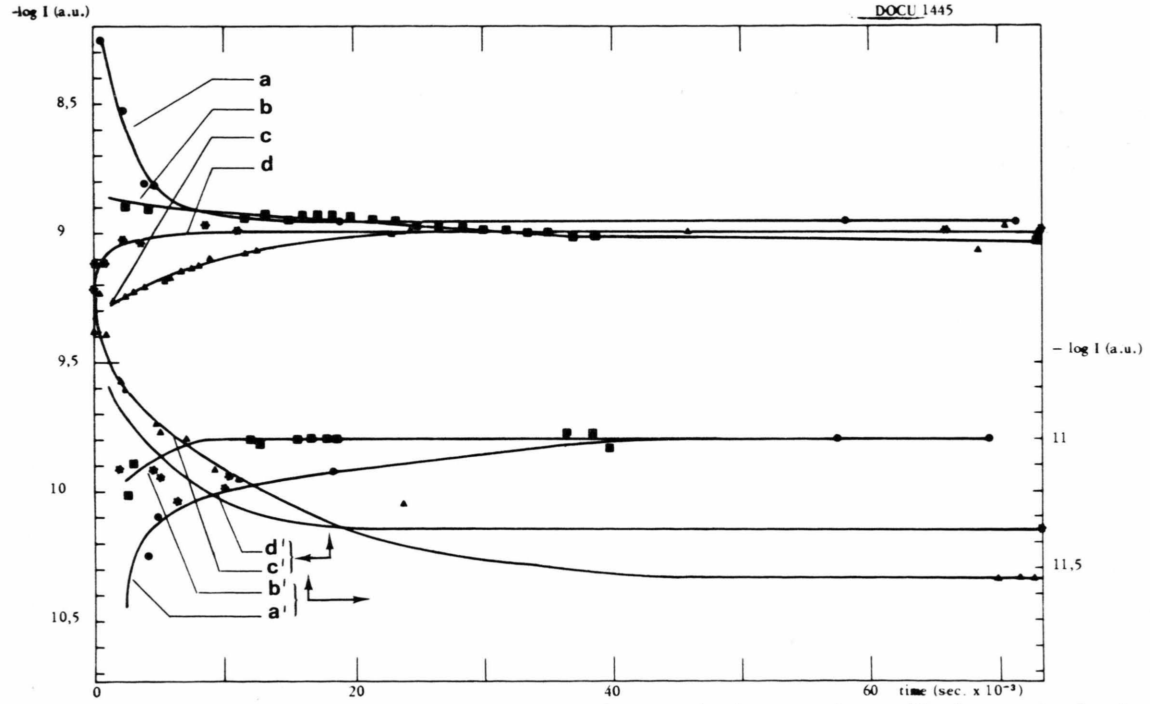

Fig. 1.
● {a I_{LaO}, a' I_{O}} vs. time sample A;
■ {b I_{LaO}, b' I_{O}} vs. time sample B;
▲ {c I_{YO}, c' I_{O}} vs. time sample C;
✦ {d I_{YO}, d' I_{O}} vs. time sample D.

Four isothermal vaporization experiments (A, B, C and D) were carried out with four different samples. A and B were lanthanum oxide samples and were vaporized at 1 927 °C. Sample A had a high initial hydroxide content and sample B a low one. Sample C was yttrium oxide pre-dryed as described before and sample D the sintered cylinder as obtained from the experiment C, heated in air at 1 500 °C until its white

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[7] J. Mann, J. Chem. Phys. **46**, 1646 [1967].

[8] J. Drowart and P. Goldfinger, Angew. Chem. **6**, 581 [1967] .

colour was restored. Both C and D were vaporized at 2 183 °C. The ion currents of monoxides and oxygen were plotted as functions of time (Figure 1).

The zero of the time scale was chosen as the time at which the samples reached the experimental temperature starting from the final outgassing temperature. The time needed for this step was of the order of 10 minutes.

All the physical parameters considered in this paper are derived from ion current vs. time curves (see Fig. 1), obtained from the experimental data by best fit treatment. From the ion currents the partial pressures were derived by means of the silver calibration (see above). From the partial pressures, the vaporization rates W and the fraction vaporized (defined as the ratio of the ~~vaporized~~ quantity to the initial weight of the sample) F_t were obtained by using Knudsen's equation.

$$Z_i = P_i\,(2\,\pi\,M_i\,R\,T)^{-\frac{1}{2}} \tag{6}$$

where

$$Z_i = \frac{1}{s} \cdot \frac{dN_i}{dt}\,, \tag{7}$$

s = area of the Knudsen hole, N_i = number of models evaporating at any instant and the other symbols have their usual meaning.

By combining (6) and (7) and integrating to obtain the total number of moles evaporated at the time t:

$$(N_i)_t = \frac{s}{(2\pi\,M_i\,R\,T)^{\frac{1}{2}}} \int_{t_0}^{t_1} \cdot\ P_i\,dt \tag{8}$$

both the total effusion rate (W) and the fraction vaporized (F_t) can in principle be calculated at any time according to:

$$W = \Sigma\,W_i = \Sigma\,Z_i M_i = (2\,\pi R T)^{-\frac{1}{2}}\,\Sigma\,\sqrt{M_i\,P_i}\,, \tag{9}$$

$$F_t = \frac{\Sigma_i\,(N_i)_t\,M_i}{g_{M_2O_3}} \tag{10}$$

where $g_{M_2O_3}$ is the initial weight of the sample in grams.

In order to give a quantitative description of the vaporization during the transient stage we write formally the following reactions

$$\xi La_2O_3\,(c) + \zeta La_i \rightarrow (2\xi + \zeta) LaO\,(g) + (\xi - \zeta)\,O\,(g), \tag{11}$$

$$\xi Y_2O_3\,(c) \rightarrow (2\xi - \zeta)\,YO\,(g) + \zeta Y_i + (\xi + \zeta)\,O\,(g) \tag{12}$$

where La_i and Y_i mean interstitial atoms in the oxide lattice and ξ and ζ are the stoichiometric coefficients. We define a parameter R as the ratio of the stoichiometric coefficients of MO to O in reactions (11) or (12)

$$R = Z_{MO}/Z_O = (2\,\xi \pm \zeta)\,/\,(\xi \pm \zeta) = P_{MO}/P_O\,\sqrt{M_O/M_{MO}}\,. \tag{13}$$

The parameter R thus describes the tendency of the oxide to deviate from stoichiometry during the transient stage: if R approaches its steady state value from lower values, the solid will become oxygen deficient, and if R approaches the steady state starting from higher values, the solid will become metal deficient.

Experimental results and discussion

In agreement with published data [2, 3] we found that the gaseous phases in equilibrium with lanthanum and yttrium oxides were composed of the respective monoxides, atomic oxygen and minor quantities of atomic metal.

The P_{LaO}/P_{La} ratio at 1 927 °C and the P_{YO}/P_Y one at 2 183 °C were found to be about 13 and 26 respectively throughout the whole isothermal vaporization experiment. In agreement with published data [2, 3, 4] we also found that the white lanthanum and yttrium sesquioxides turn darkgrey under vacuum at temperatures of the order of 1 900 °C.

Possible reactions of the lanthanum and yttrium oxides with the tungsten container were carefully checked, by monitoring the tungsten containing vapour species in the gaseous phase and analyzing the samples after the experiments.

The only tungsten containing vapour species observed were WO_2, WO and WO_3 in order of abundance. It was observed that the pressure of these species is directly proportional to the atomic oxygen partial pressures. In the case of the lanthanum oxide at 1 927 °C at the steady state, a pressure of $3.8\ 10^{-9}$ at. was measured for the species WO_2, the ratio being $P_{WO} : P_{WO} : P_{WO_3} = 1 : 0{,}46 : 0{,}13$.

For the yttrium oxide at 2 183 °C it was observed that these species are only detectable during the initial phase of the vaporization and become undetectable at the steady state.

The chemical analysis of the samples after a typical vaporization experiment are given in Table I.

Table 1. Tungsten content of the oxide samples after the vaporization experiment.

Sample	Tungsten content weight %
lanthanum oxide	0.116
yttrium oxide	6.8

It must be pointed out here that at the end of the experiment the sintered cylinders both of lanthanum and yttrium oxide look black, but that in the case of the yttrium oxide the lateral wall of the liner appeared to be covered by a layer of a red compound. Both red compound and black cylinder were separately analyzed: the cylinder was found to contain some less tungsten than the red compound (5.96 weight %). For our purposes however we have neglected this small difference and have considered that the composition of the black cylinder and of the red compound be approximately the same.

The red compound has been also analyzed by means of X-ray diffraction: the X-ray data could not be referred to any structure reported by the ASTM system; even though similarities were found with the patterns of certain $Y_2O_3 - WO_3$ solid solutions.

The samples of lanthanum and yttrium oxide resulting from the vaporization experiments were reheated in air or oxygen at 1 200–1 500 °C for periods of the order of days until a constant weight had been achieved and checked for colour and weight variations. The lanthanum oxide on being held at 1 500 °C for 7 days did not change its colour nor showed any tendency to increase its weight. On the other hand the yttrium oxide after a heating at 1 200 °C lasting 64 hrs became white in colour and increased its weight by 0.62 ± 0.1 %, which in terms of stoichiometric coefficients corresponds to a variation between Y_2O_3 and $Y_2O_{2.915 \pm 0.15}$.

From the above data, we see that in the case of both lanthanum and yttrium oxides on first heating a non-congruent vaporazition takes place.

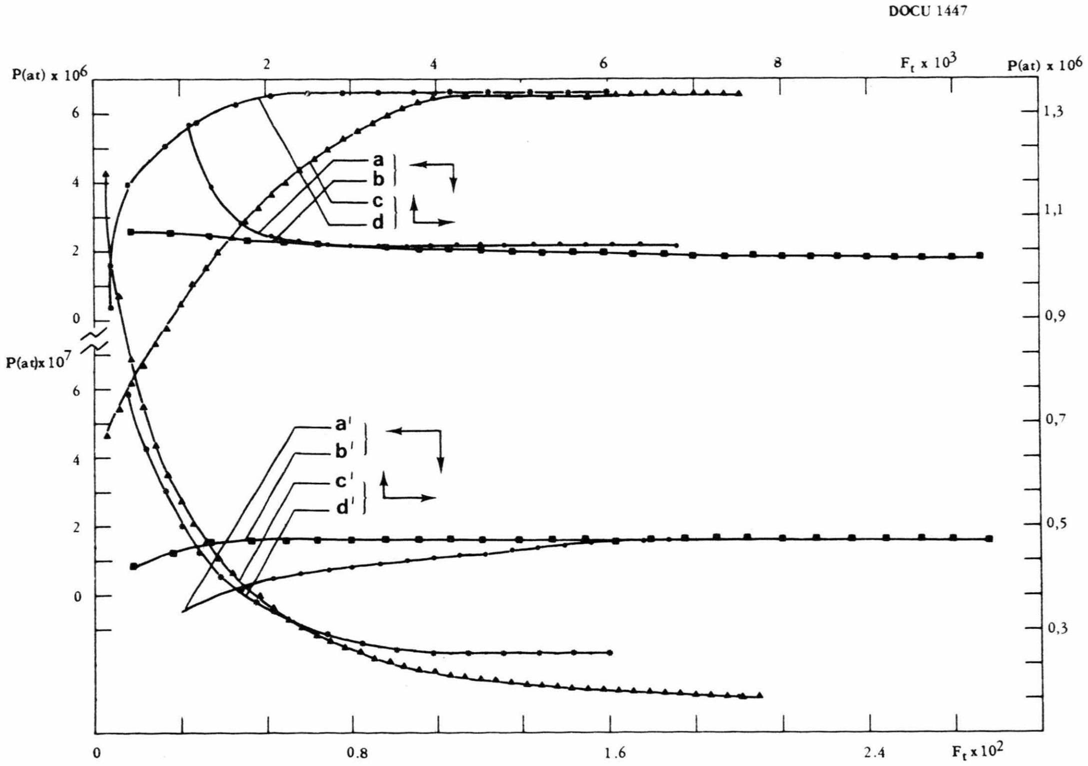

Fig. 2.
● {a P_{LaO} / a' P_O} vs. fraction vaporized (F_t) sample A;
■ {b P_{LaO} / 'b P_O} vs. fraction vaporized (F_t) sample B;
▲ {c P_{YO} / c' P_O} vs. fraction vaporized (F_t) sample C;
✦ {d P_{YO} / d' P_O} vs. fraction vaporized (F_t) sample D;

Figure 2 presents the partial pressures of the monoxides and of the atomic oxygens as functions of the fraction vaporized for the samples A, B, C and D. It is evident from these plots that, in agreement with the cited data [2, 3], the partial pressures of the involved species are time dependent on the first heating. It appears also that the partial pressures of the monoxides (and atomic metals) on one side and those of the atomic oxygen on the other, approach their steady states following opposite paths. In agreement with the equilibrium constants for the reaction (11) and (12)

$$K = P_{MO}^{2\xi \pm \zeta} P_{O}^{\xi \pm \zeta} / a_{M_2O_3}^{\zeta} \tag{14}$$

where $a_{M_2O_3} \cong 1$ is assumed.

After the transient period the partial pressures do not show any tendency to further changes in the time considered.

As far as the P_{MO}/P_M ratios are concerned, it must be pointed out here that in the case of the lanthanum oxide, it is much lower and in the case of the yttrium oxide somewhat higher than those reported by WHITE[2] and AMES[3]. The high value of P_{La} cannot be explained however in terms of fragmentation of the LaO molecule. Indeed experimental ionization efficiency curves as well as the cited sources[3] show that the ion La$^+$ does not originate from the fragmentation of the LaO molecule.

From the plots in Fig. 2 the influence of the hydroxide content on the form of the pressure isotherm for the case of the lanthanum oxide is also apparent.

In particular, we see that the isotherms of lanthanum monoxide become smoother and reach their steady state value more slowly as the initial content of hydroxide is reduced. On the other hand, the isotherm of the atomic oxygen shows the opposite trend, i. e. when the initial content of hydroxide is reduced, the curve is steeper and the equilibrium value is reached faster.

A more comprehensive picture of the phenomenon of the transient stage of vaporization can be drawn in terms of parameter R.

As also demonstrated in separate experiments, the parameter R (see Fig. 3) approaches the steady state value in a time, which is inversely proportional to the temperature, directly to the initial weight of the sample and in the case of the lanthanum oxide depends on the initial state of hydration of the sample.

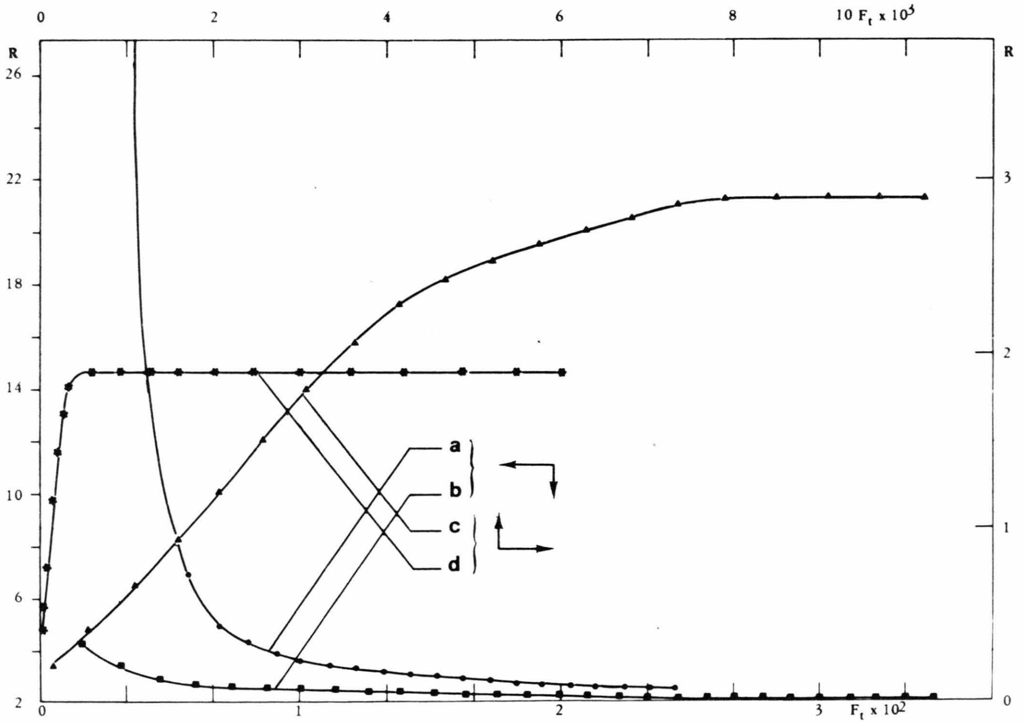

Fig. 3. R vs. fraction vaporized (F_t) sample

● ■ ▲ ✦
a b c d
A B C D

From plots in Fig. 3 it appears that at the steady state the parameter R has a value of about 2.3 for the lanthanum oxide and 2.8 for the yttrium oxide. Taking into account the uncertainty relevant to the procedures adopted, these values appear as very near to 2, which is the value of R in the stoichiometric reaction (1). The problem of the determination of the accuracy and reliability of the partial pressures obtained employing the theoretical cross sections is still a matter of discussion [8]. We have kept a pragmatic attitude to this problem and have approached it as follows. In Table 2 the vaporized weight loss measured by weighing the sample before and after the vaporization experiment (*G*) is compared with the weight loss (*G′*) obtained from the equation:

$$G' = F_t \, g_{M_2O_3} \tag{15}$$

where *t* is the total time of the experiment, and the experimental vaporization rates (*W*) are compared with the ones reported in the literature (*W′*).

Table 2. Comparison of the weighed (*G*) and calculated (*G′*) weight losses on vaporization and of the experimental (*W*) and literature vaporization rates (*W′*). Sample B is lanthanum oxide and sample C is yttrium oxide

Sample	Temp. °C	*G* g	*G′* g	*W* $\mathrm{gcm^{-2}sec^{-1}} \times 10^5$	*W′* $\mathrm{gcm^{-2}sec^{-1}} \times 10^5$
B	1927	0,035	0,017	2,1	3,9
C	2183	0,013	0,008	1,3	1,3

Therefore we have taken the satisfactory agreement between *G* and *G′* on one side and between *W* and *W′* on the other as an overall proof on the reliability of the methods adopted.

From these plots it is also evident that, in the case of lanthanum oxide the parameter *R* approaches its steady state value from higher values and that the higher the initial hydroxide content of the lanthanum oxide is, the higher is the starting value of *R*.

Therefore in the case of the lanthanum oxide during the transient stage the non-congruent vaporization results in a monoxide overloss and its extent is directly proportional to the initial hydroxide content of the sample.

Thus, if the starting composition of the oxide were stoichiometric, the overloss of monoxide should give rise, after the vaporization experiment, to a hyperstoichiometric solid of the type La_2O_{3+x}.

In the case of the yttrium oxide we observe that the parameter *R* approaches its steady state value from lower values, therefore indicating that the transient stage produces an oxygen deficient oxide. The exploitation of Eq. (8), assuming that the starting composition be stoichiometric leads to the fomula $Y_2O_{2.998}$. On the other hand the reoxidation of the black sample (see above) indicates that the composition of the yttrium oxide after a typical vaporization experiment at 2 183 °C is $Y_2O_{2.915 \pm 0.15}$. The average value for the oxygen coefficient is 2.9565 ± 0.0415. This expresses a composition which is more oxygen deficient than that reported by Ackermann [4] for the same oxide at 2 300 ± 200 °C, but still within the stability limits given by the same author elsewhere [9] for the $Y_2O_3 + Y$ solid solution in the same temperature range.

In this case the presence of tungsten in the residual solid after the vaporization experiment should be taken into account (assuming that the oxygen to metal ratio be theoretical, the composition could be tentatively described as $10\ Y_2O_3 \cdot WO_3$), which could be responsible for the discrepancy between the composition calculated via Eq. (8) and that obtained by means of reoxidation. From the plots in Fig. 2 it is also evident that the doping of the yttrium oxide with tungsten does not seriously affect its steady state vapour pressure nor prevent the transient stage from occurring. In fact the steady state vapour pressures of the sample D (doped with tungsten during experiment C) are the same (within the experimental errors) as those of the sample C.

A difference however can be observed in the form of the isotherm of the monoxide partial pressure (insufficient experimental points are available for the oxygen partial pressure): in case D the equilibration time is about one half of that experiment C. As far as the vaporization rate is concerned it is evident from the plots in Fig. 4 that the vaporization rates of lanthanum and yttrium oxides during the transient stage have different trends. The vaporization rate of the former indeed behaves like the White's [2] pattern, i. e. decreasing until reaching a steady state value, whilst that of the second after reaching a minimum, increases until the steady state value is attained, thus showing the opposite trend.

The time necessary to establish steady state conditions is a function of the temperature, which obviously determines the kinetics of the process but at constant temperature also depends on the initial weight of the sample. These facts suggest that the factor determining arrival at steady state conditions is a concentration factor.

The picture is therefore the following. During the transient stage a compositional shift takes place that causes the solid to reach a metal to oxygen ratio dif-

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[9] R. Ackermann and E. Rauh, J. Chem. Thermodynamics **3**, 445 [1971]; and R. Ackermann, E. Rauh, and R. Walters, ibid. **2**, 139 [1970].

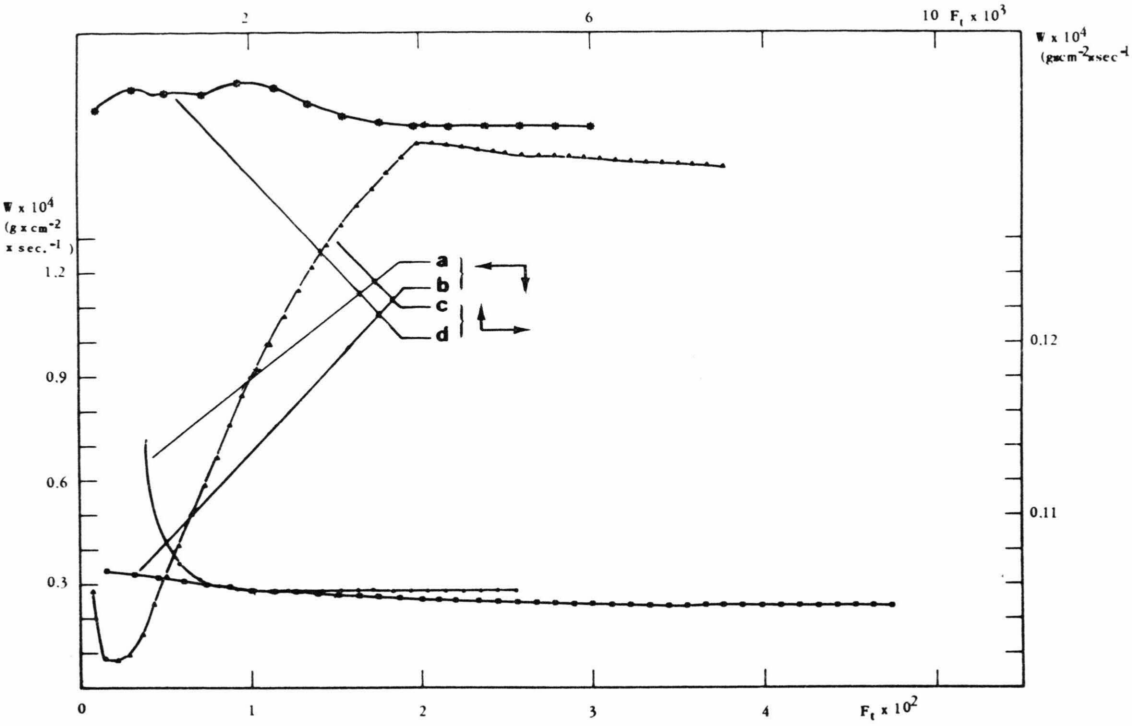

Fig. 4. Vaporization rate (*W*) vs. fraction vaporized (F_t) sample

	■	●	▲	✦
	a	b	c	d
sample	A	B	C	D

ferent from the stoichiometric one. The term $(M/O)_{exp} - (M/O)_{theor.}$ is usually positive and directly proportional to the temperature. As required by the different exponents of the P_{MO} and P_O terms in the equilibrium constant (15), the curves P_{MO} vs. F_t and P_O vs. F_t are not symmetric. After the transient stage however, the vaporization occurs congruently, or at least according to a reaction of the type (11) or (12) where ξ is very near to one and ζ very near to zero. An analysis of the published data [10, 11] shows that also the thorium and zirconium oxides undergo the transient stage of vaporization. Reportedly their monoxide partial pressures increase during a time interval that is inversely proportional to the temperature. No data are reported on the oxygen partial pressures. We therefore suggest here that the majority of the refractory oxides might behave during the transient according to the yttrium oxide pattern.

The behaviour of the lanthanum oxide however is clearly in contradiction with this picture. In fact the trend of the parameter *R* and the vaporization rate during the transient appear to be opposed to those of the yttrium oxide.

Thus, applying to the lanthanum oxide the adopted reasoning, we should be forced to the absurd conclusion that the lanthanum oxide becomes hyperstoichiometric as a consequence of the initial non-congruent vaporization.

To tentatively explain our findings, we have related this deviation from the general trend to the hygroscopicity which is a property which makes lanthanum differ from the cited oxides.

We would guess that the solid, at time zero on our scale, contains lanthanum interstitials in excess of the equilibrium concentration at 1 927 °C and would relate this initial excess to a reaction of the type

$$x\,\mathrm{La(OH)_3} + \mathrm{La_2O_3} \rightarrow \mathrm{La}_{2+x}\mathrm{O_3} + 1{\cdot}5\,x\,\mathrm{H_2O} + 1{,}5\,x\,\mathrm{O} \qquad (16)$$

which might occur during the outgassing of the sample in the mass spectrometer furnace at 1 000 °C.

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[10] R. J. Ackermann, E. G. Rauh, and R. J. Thorn, J. Phys. Chem. **67**, 762 [1963].

[11] S. A. Schukarev and G. A. Semenov, Issledovanija v oblasti khimii silicatov i okislov. Moskva; Izdat Nauka 208—214, 1965.

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Verzögerte Fluoreszenz von Mischkristallen aus Benzophenon und aromatischen Kohlenwasserstoffen

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Delayed Fluorescence of Benzophenone-Aromatic Hydrocarbon Mixed Crystals

The earlier observation of delayed fluorescence in mixed crystals of aromatic hydrocarbons in benzophenone is studiedby time-resolved spectroscopy using methyl-coronene, pentaphene, anthanthrene and 1.8.9-peri-naphto-xanthene besides naphthalene as guests. Host-guest triplet annihilation is identified as the mechanism of delayed fluorescence. Naphthalene as an additional guest component acts as trap for the triplet excitation of the host and further increases the delay of fluorescence emission.

Einleitung

Die verzögerte Fluoreszenz von Mischkristallen, bei denen sowohl die Wirts- wie die Gastkomponente aromatische Kohlenstoffe sind, ist gut untersucht [1-3]. Dagegen wurde in Mischkristallen mit Benzophenon als Wirt und aromatischen Kohlenwasserstoffen als Gast-Komponenten eine verzögerte Fluoreszenz erst kürzlich beobachtet [4]. Die beiden Typen von Mischkristall-Systemen unterscheiden sich in spektroskopischer Hinsicht charakteristisch durch die erheblich größere Triplett-Excitonen-Leitfähigkeit des Wirts im Falle der reinen Kohlenwasserstoff-Systeme. Da der Anregungsmechanismus der verzögerten Fluoreszenz bei den Kohlenwasserstoff-Systemen wesentlich an die große Triplett-Excitonen-Leitfähigkeit des Wirts gebunden ist, mußte für die Benzophenon-Aromat-Systeme ein anderer Anregungsmechanismus der verzögerten Fluoreszenz erwartet werden.

Der niedrigste Triplettzustand von Benzophenon ist vom n, π^*-Typ. Die hiermit verbundene, für einen Phosphoreszenzübergang große Oszillatorenstärke ist die wesentliche Ursache dafür, daß Benzophenon auch im Kristallzustand im Gegensatz zu reinen aromatischen Kohlenwasserstoff-Kristallen eine deutliche Phosphoreszenz zeigt [5]. Diese Festkörperphosphoreszenz des Benzophenons wird bei genügend tiefer Temperatur durch aromatische Kohlenwasserstoffe als Gast-Komponenten gelöscht, wobei die sensibilisierte Phosphoreszenz des Gastes auftritt [6]. Bei geeigneter Trip-

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[1] M. ZANDER, Ber. Bunsenges. phys. Chem. **68**, 301 [1964].

[2] L. AZARRAGA, T. N. MISRA u. S. P. MCGLYNN, J. Chem. Phys. **42**, 3720 [1965].

[3] S. P. MCGLYNN, B. N. SRINIVASAN u. H. J. MARIA in „Spectrochemical Methods of Analysis“, ed. J. D. WINEFORDNER, Wiley-Interscience, John Wiley u. Sons, Inc., New-York 1971, S. 295 ff.

[4] M. ZANDER, Z. Naturforsch. **27a**, 172 [1972].

[5] H. STERNLICHT, G. C. NIEMAN u. G. W. ROBINSON, J. Chem. Phys. **38**, 1326 [1963].

[6] R. M. HOCHSTRASSER, J. Chem. Phys. **39**, 3153 [1963]; **40**, 1038 [1964].