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OXYGEN TRANSPORT PROPERTIES OF RARE EARTH OXIDES

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ABSTRACT

The usefulness of the rare earth oxides as model systems for studies which include material transport is pointed out. The results so far obtained in kinetics studies of these systems are sketched and the whole placed against the emerging understanding of nonmetallic solids having extended defects.

INTRODUCTION

Whatever may be said of present understanding of material transport mechanisms in oxides with low concentrations of defects, (and this has recently been reviewed by Birchenall (1))


one must admit that next to nothing is known of these processes in oxides having extended defects. The beginnings of a foundation are being laid for such an understanding in several systems.
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The results on the rare earth oxides are to be summarized very briefly here.

There is much to recommend the rare earth oxides as the choice for such comprehensive studies. The higher oxides of cerium, praseodymium and terbium, especially praseodymium, exhibit complicated phase relationships including ordered intermediate compounds belonging to an homologous series having the formula $R_nO_{2n-2}$ $(n = 4, 7, 9, 10, 11, 12$ and $\infty$ for Pr) each of which has a small but measureable range of composition. In addition there are, in the praseodymium oxide system, two genuinely non-stoichiometric regions of wide composition range separated by a narrow miscibility gap. The structures of all these are related to fluorite and bixbyite. There exists also polymorphism in certain of the line phases. Furthermore the praseodymium oxide system and certain regions of the terbium oxide system can be studied at temperatures and oxygen pressures where unusual furnace and crucible materials and gas-buffer systems with their contamination possibilities are not required. Add to this the feasibility of subtle modifications of the system by the admixture of the chemically and structurally

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related other rare earths and actinide elements and one sees the practically unlimited possibilities of obtaining experimental information necessary for a comprehensive understanding of solid oxides. The actinide element oxides are analogous in a limited way yielding a set of oxides with related structures encompassing nearly one third of the known elements.

Startling advances into understanding grossly defective specimens have recently resulted from observations using the high resolution electron microscope. It is now clear that in the quenched samples which have been studied concentrations of random point defects are not high. It is likely that the same is true at moderately high temperatures as well. Grossly defective material restructures itself to economize on free energy and new structural features appear. The most studied so far are those oxides adjusting to oxygen deficiency by undergoing crystallographic shear in one dimension or forming block structure with crystallographic shear in two dimensions. In addition there are compounds where the clustering of defects occurs, such as in the Wüstite phase, FeO$_{1-x}$. As more is learned, other types of structural defects will appear and more suitable classifications will be made.

The premonitory effects of melting and hybrid crystal
formation described by Ubbelohde (4), microheterogeneity discussed by


discussed by Ariya (5), microdomains discussed by J. S. Anderson (6)
and microdomains and pseudo-phase formation discussed by Hyde et al, (2), are less direct manifestations of extended defects. It has become clear that the extension


of the treatment of materials with point defects to those with extended defects simply taking into account pairwise interactions will not suffice. Rather, new theories based on the new structural, thermodynamic and kinetic information must be devised and developed.

Studies of the kinetics of oxygen transport and phase reactions have been begun on the sesquioxides and other phases of narrow composition range for their own intrinsic interest and as a foundation for studies of nonstoichiometric and other non-classically behaving substances. It shall be the intent of this paper to sketch briefly what has been learned in recent years of the rate of oxygen transport and phase reactions in the rare earth oxides and to place this information against the larger study of the chemistry of materials having extended defects.
A SUMMARY OF RECENT TRANSPORT STUDIES

Some of the more important parameters describing the transport behavior of rare earth oxides together with references to the original experiments are given in Tables I and II.

Heterogeneous reactions have been studied and the reaction mechanism suggested by analysis of the rate of reaction. In these studies a model is assumed and the mathematical consequences determined. A satisfactory fit between the data and the calculated behavior suggests a plausible model.

**Phase boundary controlled reactions.**—If the sample consists of spheres whose reaction rate is controlled by a phase boundary retreating into the sphere at a uniform rate a plot of the cube root of the unreacted remainder against time will be a straight line. In such a reaction nucleation of the new phase must be rapid over the entire surface yielding a spherical phase boundary. Excellent agreement between this model and the reduction rate of PrO₂, PrO₁.₇₈ and the oxidation rate of PrO₁.₈₃ has been observed (Table I).(7, 8)

**Diffusion controlled reactions.**—A diffusion mechanism including phase boundary movement has been proposed (9) for the oxidation


of substoichiometric rare earth sesquioxides although rather than the phase boundary formation itself being rate controlling it is chemical diffusion through the reaction product. If on the other hand the rate controlling step is simply diffusion into the sphere along a radial concentration gradient a plot of the logarithm of the amount of unreacted sample against time gives a curve which falls off rapidly at first while a uniform gradient is being established then becomes linear. Such a mechanism apparently obtains in the reduction of PrO$_1.71$. In the case of the reduction of TbO$_1.82$ and TbO$_1.71$ only the linear behavior at longer times is observed. (Table I). (7) The chemical diffusion coefficient may be calculated from these experiments if one knows the radius of the particles being studied. In a few cases the rate of oxidation of the solid (10) or liquid (11) rare earth metals have yielded chemical diffusion information from the Wagner equation.


Self diffusion studies.--More recently studies of self-diffusion
of oxygen in rare earth oxides has been undertaken (Table II) employing heterogeneous isotope exchange. (12, 13)


The results are treated to yield surface and diffusion parameters. A sectioning technique was used to obtain diffusion and surface parameters for calcia stabilized zirconia. (14)


These results are included in Table II for comparison with the data from the rare earth oxides.

DISCUSSION

The superficial results of the experiments performed so far confirm that oxygen diffusion is relatively rapid being only one or two orders of magnitude smaller than in calcia stabilized zirconia. This is to be contrasted with the cation diffusion which is negligible at the temperatures of these experiments.

The absence of a pressure dependance of the self-diffusion rate in the sesquioxides was surprising and the unusual pressure
dependance of self-diffusion for the Pr$_7$O$_{12+\delta}$ may ultimately be understood in terms of a complex diffusion mechanism.

It comes as no surprise that results obtained from chemical and self-diffusion measurements are not the same. At present there are insufficient data to make any attempt at correlation meaningful.

Although all the data are for compounds which are said to be line phases they all have a measureable range of composition hence their behavior must be considered in terms of complex defect interaction and are therefore the foundation for studies of grossly nonstoichiometric oxides. When rationalized in these terms they shall make their peculiar contribution to full understanding.

The mechanism of formation of transition metal oxides and oxide fluorides which have regularly spaced crystallographic shear planes as structural features have received some attention. B. G. Hyde (15) discusses three mechanisms in the light of recent


high resolution electron microscopic studies on the NbO$_2$F, V$_2$O$_5$, MoO$_3$ and TiO$_2$ systems. It is apparent from these studies that the nucleation of partial dislocation loops is well advanced at very low levels of nonstoichiometry and that these loops grow
longitudinally as they serve as a sink for the low concentration of random vacancies formed in the host lattice as oxygen is removed. However, this mechanism, proposed by Anderson and Hyde,(16, 17) cannot provide for the lateral motion of the planes of crystallographic shear needed to secure their order in the final structures. In at least one case this mechanism is seen to operate in conjunction with a cooperative mechanism of cation diffusion by which an entire shear plane may move laterally (perhaps by means of steps or screw dislocations) as had been proposed by Andersson and Wadsley.(18)


O'Keeffe (19) has recently reviewed the problems associated with attempting a mechanistic description of diffusion or phase reaction in materials having extended defects. Some simple

models are discussed including diffusion of vacancies with nearest neighbor repulsion on a single cubic lattice. The fluorite-related oxides are given as an example.

The consequences of the simple cubic treatment is that the conductivity is drastically reduced when certain restrictions on vacancy environments are taken into account. In the case of no nearest neighbors, a maximum conductivity is reached at a concentration of vacancies of 0.10 (compared to 0.50 for random vacancies, or corresponding higher values at higher temperatures).

O'Keeffe observes that in $\text{Zr}_{1-x}\text{Ca}_x\text{O}_{2-x}$ the conductivity goes through a maximum at $x \approx 0.12$ at $1000^\circ\text{C}$ and at higher $x$ at higher temperatures. The activation energy for conductivity also increases with $x$.\(^{(20)}\) Also discussed are some problems


in the interpretation of atom transport measurements in Wüstite where the extended defects are known to be clusters of rather large size.

Of course the nonstoichiometric rare earth oxides are not shear structures or clusters of the type discussed above. The structural feature which has been proposed to account for the homologous series and range of composition is a string of
oxygen vacancies in characteristic crystallographic directions. (21, 22) The detailed mechanism of the formation of this


structural feature or the movement of oxygen in structures containing it have not yet been seriously proposed.

It is clear that a satisfactory atomic mechanism of diffusion in such materials as the rare earth oxides must take into account the nature of the defects and especially their interaction. These may or may not correlate with the structural entity considered as the extended defect but the final results must be consistent with the structural and thermodynamic properties.

Acknowledgement. The United States Atomic Energy Commission has supported much of the work reported here; we are grateful to them.
TABLE I  HETEROGENEOUS REACTIONS

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Controlling Mechanism</th>
<th>Activation Energy (kcal)</th>
<th>Temperature Range</th>
<th>Oxygen Pressure</th>
<th>( D_p ) (cm²/sec x 10⁶)</th>
<th>( D ) (1000⁰K) (x 10¹⁰)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>PrO₂.00 (a)</td>
<td>Phase Boundary</td>
<td>50</td>
<td>289-347</td>
<td>vac</td>
<td></td>
<td></td>
<td>8</td>
</tr>
<tr>
<td>PrO₁.₈₃ (b)</td>
<td>&quot;</td>
<td>26.9</td>
<td>265-305</td>
<td>1 atm</td>
<td></td>
<td></td>
<td>8</td>
</tr>
<tr>
<td>PrO₁.₇₈ (c)</td>
<td>&quot;</td>
<td>49.6</td>
<td>407-493</td>
<td>vac</td>
<td></td>
<td></td>
<td>7</td>
</tr>
<tr>
<td>PrO₁.₇₁ (d)</td>
<td>Diffusion</td>
<td>42</td>
<td>700-970</td>
<td>vac</td>
<td></td>
<td></td>
<td>7</td>
</tr>
<tr>
<td>*TbO₁.₈₂ (e)</td>
<td>&quot;</td>
<td>41.5</td>
<td>383-471</td>
<td>vac</td>
<td></td>
<td></td>
<td>7</td>
</tr>
<tr>
<td>*TbO₁.₇₁ (f)</td>
<td>&quot;</td>
<td>~ 40</td>
<td>570-643</td>
<td>vac</td>
<td></td>
<td></td>
<td>7</td>
</tr>
<tr>
<td>Sc₂O₃ (g)</td>
<td>Diffusion with a moving boundary</td>
<td>38.30</td>
<td>1106-1298</td>
<td>air</td>
<td>7.72</td>
<td>2.27</td>
<td>9</td>
</tr>
<tr>
<td>Y₂O₃ (g)</td>
<td>&quot;</td>
<td>19.58</td>
<td>1064-1241</td>
<td>air</td>
<td>0.0606</td>
<td>27.6</td>
<td>9</td>
</tr>
<tr>
<td>Dy₂O₃ (g)</td>
<td>&quot;</td>
<td>26.24</td>
<td>1087-1235</td>
<td>air</td>
<td>0.163</td>
<td>5.27</td>
<td>9</td>
</tr>
<tr>
<td>Ho₂O₃ (g)</td>
<td>&quot;</td>
<td>40.53</td>
<td>1050-1274</td>
<td>air</td>
<td>71.8</td>
<td>8.26</td>
<td>9</td>
</tr>
<tr>
<td>Er₂O₃ (g)</td>
<td>&quot;</td>
<td>30.12</td>
<td>1060-1292</td>
<td>air</td>
<td>1.31</td>
<td>0.958</td>
<td>9</td>
</tr>
<tr>
<td>Tm₂O₃ (g)</td>
<td>&quot;</td>
<td>45.56</td>
<td>1015-1235</td>
<td>air</td>
<td>114.1</td>
<td>1.97</td>
<td>9</td>
</tr>
<tr>
<td>Lu₂O₃ (g)</td>
<td>&quot;</td>
<td>29.76</td>
<td>1020-1297</td>
<td>air</td>
<td>1.88</td>
<td>1.58</td>
<td>9</td>
</tr>
<tr>
<td>Y₂O₃ (h)</td>
<td>Metal Tarnishing</td>
<td>44.50</td>
<td>900-1400</td>
<td>air</td>
<td>14.3</td>
<td>0.37</td>
<td>10</td>
</tr>
<tr>
<td>Ra₂O₃ (h)</td>
<td>&quot;</td>
<td>~100(1600⁰C)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Behavior deviates from diffusion-like mechanism in the early stages of reaction (modified diffusion behavior).

\( \text{PrO}_2.00 \rightarrow \text{PrO}_1.₈₃ + 0.085 \text{O}_2 \)
\( \text{PrO}_1.₈₃ + 0.085 \text{O}_2 \rightarrow \text{PrO}_2.₀₀ \)
\( \text{PrO}_1.₇₈ \rightarrow \text{PrO}_1.₇₁ + 0.035 \text{O}_2 \)
\( \text{PrO}_1.₇₁ \rightarrow \text{PrO}_1.₅₀ + 0.105 \text{O}_2 \)
\( \text{TbO}_1.₈₂ \rightarrow \text{TbO}_1.₇₁ + 0.055 \text{O}_2 \)
\( \text{TbO}_1.₇₁ \rightarrow \text{TbO}_1.₅₀ + 0.105 \text{O}_2 \)
\( \text{RO}_1.₅₀ - \delta + \delta \text{O}_₂ = \text{RO}_1.₅₀ \)
\( \text{R} + 3/2 \text{O}_₂ = \text{RO}_1.₅₀ \)
TABLE II

<table>
<thead>
<tr>
<th>Oxygen Self-diffusion</th>
<th>Activation Energy (kcal)</th>
<th>Temperature Range</th>
<th>$D_b$ (cm$^2$/sec)</th>
<th>$D_{1000}$ (1000°K)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr$<em>{0.85}$Ca$</em>{0.15}$O$_{1.85}$</td>
<td>31.20</td>
<td>781-1097</td>
<td>1.8x10$^{-2}$</td>
<td>8.1 x10$^{-6}$</td>
<td>14</td>
</tr>
<tr>
<td>Nd$_2$O$_3$ (99.999%) (a)</td>
<td>31</td>
<td>700-1000</td>
<td>1.3x10$^{-6}$</td>
<td>7.7 x10$^{-10}$</td>
<td>12</td>
</tr>
<tr>
<td>Sm$_2$O$_3$ (99.9%) (b)</td>
<td>23.5</td>
<td>700-950</td>
<td>9.2x10$^{-6}$</td>
<td>8.96x10$^{-10}$</td>
<td>12</td>
</tr>
<tr>
<td>Sm$_2$O$_3$ (99.998%) (b)</td>
<td>21.3</td>
<td>700-1000</td>
<td>6.0x10$^{-6}$</td>
<td>1.39x10$^{-9}$</td>
<td>12</td>
</tr>
<tr>
<td>Er$_2$O$_3$ (99.999%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>12</td>
</tr>
</tbody>
</table>

$t$-Pr$_7$O$_{12}$ (low temp) (c) | 8.21                     | 725-930           | 9 x10$^{-8}$       | 3.58x10$^{-9}$    | 13  |

$t$-Pr$_7$O$_{12}$ (high temp) (d) | 19.05                    | 725-930           | 2.9x10$^{-8}$      | 1.65x10$^{-9}$    | 13  |

(a) Very small oxygen pressure dependence.
(b) Virtually no oxygen pressure dependence.
(c) $D = 1.6 \times 10^{-2}$ exp ($-27,000/RT$)$f_{II}^{3/2}$. $f$ equals the atom fraction of excess oxygen.
(d) $D = 1.3 \times 10^{-3}$ exp ($-24,000/RT$)$f_{I}^{3/2}$. 