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MASTER

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))

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(1) C. E. Birchenall in "Mass Transport in Oxides," J. B. Wachtman, Jr. and A. D. Franklin, Eds., N.B.S. Special Publication, 296 (1968) p. 119.

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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 ∞ 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.(2) The structures of all these are related to fluorite and bixbyite.(3) There

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(2) B. G. Hyde, D. J. M. Bevan and L. Eyring, Trans. Roy. Soc., London, Ser. A No 1106, 259, 583 (1966).

(3) J. O. Sawyer, B. G. Hyde and L. Eyring, Bull. Soc. Chim. Fr., 1190 (1965).

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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

related other rare earths and actinide elements and one sees
the practically unlimited possibilities of obtaining
experimental information necessary for a comprehensive under-
standing 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 under-
going 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 dis-

(4) A. R. Ubbelohde, J. Chim. Phys., 62, 33 (1966).

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

(5) S. M. Ariya and Yu. G. Popov, J. Gen. Chem., Moscow, 32,
2077, (1962).

(6) J. S. Anderson, Proc. Chem. Soc., 166 (1964).

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 PrO_2, $PrO_{1.78}$ and the oxidation rate of $PrO_{1.83}$ has been observed (Table I).(7, 8)

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

(7) U. E. Kuntz and L. Eyring, "Kinetics of High Temperature Processes," W. D. Kingery, Ed., John Wiley and Sons, Inc., New York, (1965) p. 50.

(8) B. G. Hyde, E. E. Garver, U. E. Kuntz and L. Eyring, J. Phys. Chem., 69, 1667 (1965).

(9) M. F. Berard, C. D. Wirkus, and D. R. Wilder, J. Am.

     Ceram. Soc., 51, 643 (1968).

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 $TbO_{1.83}$ 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.

(10) H. J. Borchardt, J. Inorg. Nucl. Chem., 26, 711 (1964).

(11) J. Brett and L. Seigle, J. Less-Common Metals, 10, 22 (1966).

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)

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(12) G. D. Stone, G. R. Weber and L. Eyring, "Mass Transport in
Oxides," J. B. Wachtman, Jr., and A. D. Franklin, Eds.,
N.B.S. Special Publication 296 (1968) p. 179.

(13) G. R. Weber and L. Eyring, Proceedings, International
Colloquy of the C.N.R.S. on the Rare Earth Elements, Paris-
Grenoble, May 5-10, 1969, in press.

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)

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(14) L. A. Simpson and R. E. Carter, J. Am. Ceram. Soc., 49,
139 (1966).

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 $Pr_7O_{12+\delta}$ 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

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(15) B. G. Hyde and L. A. Bursill, "Chemistry of Extended Defects in Non-Metallic Solids," L. Eyring and M. O'Keeffe, Eds., North-Holland, Amsterdam, 1969, in press.

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high resolution electron microscopic studies on the NbO_2F, V_2O_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

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(16) J. S. Anderson and B. G. Hyde, Bull. Soc. Chim. Fr., 1215 (1965).

(17) J. S. Anderson and B. G. Hyde, J. Phys. Chem. Solids, 28,
       1393 (1967).

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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)

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(18) S. Andersson and A. D. Wadsley, Nature, 211, 581 (1966).

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

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(19) M. O'Keeffe, "Chemistry of Extended Defects in Non-Metallic
       Solids," L. Eyring and M. O'Keeffe, Eds., North-Holland,
       Amsterdam, 1969, in press.

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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 $Zr_{1-x}Ca_xO_{2-x}$ the conductivity
goes through a maximum at $x \simeq 0.12$ at $1000^\circ C$ and at higher x at
higher temperatures. The activation energy for conductivity
also increases with x.[20] Also discussed are some problems

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(20) R. E. Carter and W. L. Roth, in "Electromotive Force
Measurements in High Temperature Systems," C. B. Alcock, Ed.,
American Elsevier, New York.

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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

(21) B. G. Hyde and L. Eyring, "Rare Earth Research III,"
L. Eyring, Ed., Gordon and Breach, New York, (1965) p. 623.
(22) B. G. Hyde, D. J. M. Bevan and L. Eyring, "International
Conference on Electron Diffraction and Crystal Defects,"
Melbourne, II C-4, (1965), published and distributed for
the Australian Academy of Science by Pergamon Press (1966).

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 consistant with the structural and
thermodynamic properties.

TABLE I HETEROGENEOUS REACTIONS

Reaction	Rate Controlling Mechanism	Activation Energy (kcal)	Temperature Range	Oxygen Pressure	D_0 (cm^2/sec x 10^6)	D (1000°K) (x 10^{10})	Ref.
$PrO_{2.00}$ (a)	Phase Boundary	50	289-347	vac			8
$PrO_{1.83}$ (b)	" "	26.9	265-305	1 atm			8
$PrO_{1.78}$ (c)	" "	49.6	407-493	vac			7
$PrO_{1.71}$ (d)	Diffusion	42	700-970	vac			7
*$TbO_{1.82}$ (e)	"	41.5	383-471	vac			7
*$TbO_{1.71}$ (f)	"	~40	570-643	vac			7
Sc_2O_3 (g)	Diffusion with a moving boundary	38.30	1106-1298	air	7.72	2.27	9
Y_2O_3 (g)	" "	19.58	1064-1241	air	0.0606	27.6	9
Dy_2O_3 (g)	" "	26.24	1087-1235	air	0.163	5.27	9
Ho_2O_3 (g)	" "	40.53	1050-1274	air	71.8	8.26	9
Er_2O_3 (g)	" "	30.12	1060-1292	air	1.31	0.958	9
Tm_2O_3 (g)	" "	45.56	1015-1235	air	114.	1.97	9
Lu_2O_3 (g)	" "	29.76	1020-1297	air	1.88	1.58	9
Y_2O_3 (h)	Metal Tarnishing	44.50	900-1400	air	14.3	0.37	10
R_2O_3 (h)	" "					~100(1600°C)	11

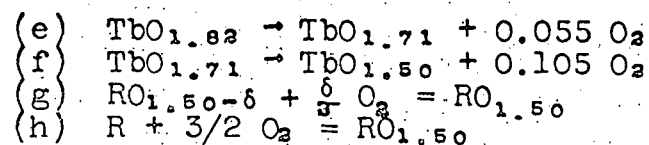*Behavior deviates from diffusion-like mechanism in the early stages of reaction (modified diffusion behavior).

(a) $PrO_{2.00} \rightarrow PrO_{1.83} + 0.085\ O_2$

(b) $PrO_{1.83} + 0.085\ O_2 \rightarrow PrO_{2.00}$

(c) $PrO_{1.78} \rightarrow PrO_{1.71} + 0.035\ O_2$

(d) $PrO_{1.71} \rightarrow PrO_{1.50} + 0.105\ O_2$

(e) $TbO_{1.82} \rightarrow TbO_{1.71} + 0.055\ O_2$

(f) $TbO_{1.71} \rightarrow TbO_{1.50} + 0.105\ O_2$

(g) $RO_{1.50-\delta} + \frac{\delta}{2} O_2 = RO_{1.50}$

(h) $R + 3/2\ O_2 = RO_{1.50}$

12
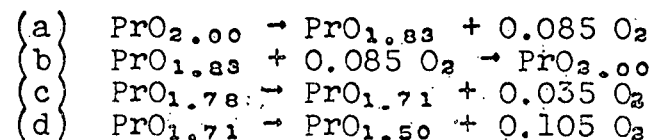
TABLE II

Oxygen Self-diffusion	Activation Energy (kcal)	Temperature Range	D_o (cm^2/sec)	D $(1000°K)$	Ref.
$Zr_{0.858}Ca_{0.142}O_{1.858}$	31.20	781-1097	1.8×10^{-2}	8.1×10^{-8}	14
Nd_2O_3 (99.999%) (a)	31	700-1000	1.3×10^{-4}	7.7×10^{-10}	12
Sm_2O_3 (99.9%) (b)	23.5	700-950	9.2×10^{-6}	8.96×10^{-10}	12
Sm_2O_3 (99.998%) (b)	21.3	700-1000	6.0×10^{-6}	1.39×10^{-9}	12
Er_2O_3 (99.999%)				$\sim 10^{-14}$	12
$\iota-Pr_7O_{12}$ (low temp) (c)	8.21	725-930	9×10^{-8}	3.58×10^{-9}	13
$\iota-Pr_7O_{12}$ (high temp) (d)	19.05	725-930	2.9×10^{-8}	1.65×10^{-9}	13

(a) Very small oxygen pressure dependence.

(b) Virtually no oxygen pressure dependence.

(c) $D = 1.6 \times 10^{-2} \exp(-27,000/RT) f_{II}^{\frac{1}{2}}$. f equals the atom fraction of excess oxygen.

(d) $D = 1.3 \times 10^{-3} \exp(-24,000/RT) f_I^{\frac{1}{2}}$.