

# Bibliography

## Self-diffusion and impurity diffusion in oxides

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An updated bibliography of diffusion data in oxides is provided for the materials scientist who requires a convenient source of published results. The scope of the review has been enlarged to include data for the diffusion of the host and impurity species in both binary and multiple oxides. Brief descriptions of terminology, diffusional behaviour and new measurement techniques are followed by tables of selected results and associated experimental details.

### 1. Introduction

Diffusion is believed to be the rate determining step in many processes of interest to the materials scientist. These include creep, sintering, annealing of radiation damage [1, 2], and the formation and ageing of protective oxide coatings on metals [3, 4]. The movement of impurity species from the surface into the body of ceramics and machine components is of great industrial importance since the diffusion results in their degradation, e.g. sulphur in turbine blades, chloride in metals [2] and various ions in furnace elements [5].

Although the transport properties of the alkali halides are thought to be reasonably well understood [6], the same cannot be said of oxides, where there is as yet only limited data for crystals of the highest quality and purity, and the agreement with theory is comparatively poor, e.g. MgO [7]. In order to provide the materials scientist with a source of self-diffusion data for simple oxides, Harrop [1] produced a bibliography which covered studies up to 1967. Since that time a considerable number of good-quality data have become available and this review is an attempt to update the earlier publication [1]. The scope of the present work has been extended to include results for the diffusion of impurity species.

The bibliography of diffusion data for binary and multiple oxides is preceded by brief details of terminology, diffusional behaviour and new measurement techniques.

### 2. Diffusion in oxides

Diffusion in a crystalline solid proceeds as ions (or atoms, or molecules) migrate via lattice defects which may be generated either thermally or by the presence of impurities [8]. There are a variety of possible diffusion mechanisms [9] of which vacancy and interstitial are the most common. Identification of the individual process is, however, not easy. Isotope mass effect studies are one approach and these have been performed on several oxides [10]. Such work is beyond the scope of the present review and the detailed mechanisms will not be considered further.

A number of diffusion coefficients ( $D$ ) are encountered in the literature for oxides, and it is helpful to differentiate between them: self-diffusion is the movement of the host (metal or oxygen) ions; whilst impurity diffusion is the transport of any species other than the host in the crystal. In these cases the moving ions may be at any concentration. Tracer diffusion refers to either self- or impurity diffusion when the species of interest is at infinitely small dilution. At any temperature the tracer diffusion coefficient ( $D^*$ ) is assumed to be constant, and independent of tracer composition (although this is not always the case [11]).

Interdiffusion is the process by which two adjacent solids (lamellae or single crystals) of differing compositions homogenize by the mutual diffusion of species across the common boundary.

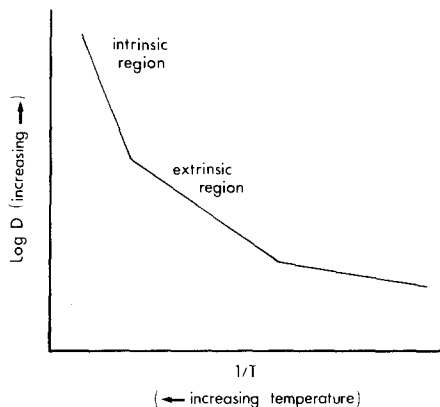


Figure 1 Temperature dependence of diffusion coefficients, showing a series of diffusion regimes with different activation energies.

The interdiffusion coefficient ( $\tilde{D}$ ) is composition-dependent.

Tracer ( $D^*$ ) and interdiffusion coefficients ( $\tilde{D}$ ) for a binary pair (A, B) are related by Darken's equation [12]

$$\tilde{D}_{AB} = (D^*_A x_B + D^*_B x_A)S \quad (1)$$

where  $S$  is a complex term involving the chemical activities of  $x_i$ , the mole fractions of the components.

The term "chemical diffusion coefficient" (also denoted by  $\tilde{D}$ ) is employed to describe the homogenization process as a binary crystal changes from one non-stoichiometric composition to another, e.g. CoO [13]. For the remainder of this section no distinction will be made between the diffusion coefficients, and the following arguments apply to all forms of  $D$ .

The diffusion of any species is characterized by its diffusion coefficient  $D(\text{m}^2\text{sec}^{-1})$ , and its temperature dependence (Fig. 1) is best described by an Arrhenius equation of the form

$$D = D_0 \exp(-Q/RT), \quad (2)$$

where  $D_0$  is the pre-exponential factor ( $\text{m}^2\text{sec}^{-1}$ ),  $Q$  the activation energy ( $\text{kJ mol}^{-1}$ ) and  $R$  the gas constant. Unfortunately, much of the data cited in this work was originally reported in different units, namely  $\text{cm}^2\text{sec}^{-1}$  for  $D$  and  $D_0$ , and  $\text{kcal mol}^{-1}$  for  $Q$ . Occasionally, electron volts (eV)\* were used for the latter quantity, in which case it is necessary to replace  $R$  in Equation 2 by  $k$ , Boltzmann's constant.

\* 1eV = 23.06 kcal mol<sup>-1</sup> = 96.39 kJ mol<sup>-1</sup>.

Plots of  $\log_e D$  against  $1/T$  may be linear over much of the measured range (Fig. 1), but at the higher temperatures, the slope and hence  $Q$  may increase as different diffusion regimes are reached. It is, therefore, dangerous to extrapolate data to temperatures outside the range of measurement.

An intrinsic regime operates at the highest temperatures where the defect concentrations are thermally controlled. The presence of impurities tends to generate additional defects, and when these dominate ones which have been thermally activated, there is an effective lowering of  $Q$  and enhancement of  $D$ , signifying the onset of extrinsic diffusion. This "knee", or change in slope of the Arrhenius plot is sensitive to the impurity content of the crystal, and if it is too high, the intrinsic region may not be reached before the melting temperature [7]. The presence of grain boundaries and dislocations will also cause enhanced diffusion rates. Conversely, at the lowest temperatures other processes may become important [14]. For oxides Harrop [1] has summarized the properties of the two main regions of interest, intrinsic and extrinsic, and suggested that activation energies for these are typically  $625 \pm 210$ , and  $250 \pm 160 \text{ kJ mol}^{-1}$ , respectively.

Evaluating and interpreting the diffusional properties of highly pure oxides may be difficult, but with non-stoichiometric compounds further problems are encountered. Diffusion rates in the "binary" oxides of the transition metal ions Fe, Co and Mn are a function of the ambient  $p\text{O}_2$  and hence composition. In  $\text{Fe}_{1-x}\text{O}$ , for example [15], tracer self-diffusion coefficients at a given temperature may vary by an order of magnitude depending upon the  $p\text{O}_2$  (Fig. 2), and it is necessary

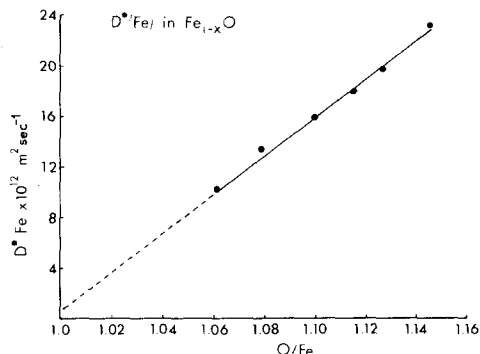


Figure 2 Tracer diffusion coefficient of Fe in wustite as a function of oxygen to metal ratio (O/Fe) at 1373K. (After Hembree and Wagner [15].)

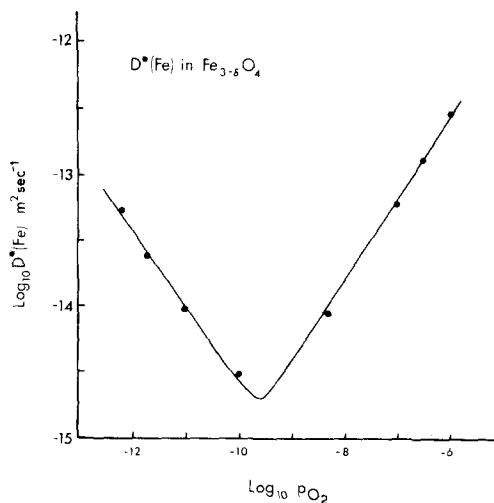


Figure 3 Tracer diffusion coefficient of Fe in Magnetite as a function of oxygen partial pressure ( $pO_2$ ) at 1273 K. (After Dieckmann and Schmalzried [16].)

to distinguish between results at constant composition and constant  $pO_2$ . Some of the ternary oxides, for example  $Fe_3O_4$  [16], present even more hazards since  $D$  will be a function of chemical activity, and may vary in a complicated way (Fig. 3). Under these circumstances it is not strictly valid to talk about an activation energy, but it may be useful to employ the concept for order-of-magnitude estimates at constant composition.

Diffusion rates in oxides are therefore sensitive to a number of factors, which may be broadly divided into (1) environmental, and (2) properties of the crystal. The former includes temperature total pressure and oxygen activity. The latter includes chemical purity, defect concentration, chemical activity of specific components, and, depending upon the nature of the sample, crystal orientation (for single crystals) or density and porosity (for polycrystalline material). Harrop [1] noted that diffusion rates measured in the intrinsic region at "high temperatures" were usually reproducible under the same conditions by other workers, but at "low temperatures" where there were varying extrinsic factors, discrepancies in the data were to be expected despite careful experiments.

### 3. Measurement techniques

An extensive critical review of techniques for measuring diffusion rates in solids, liquids and gasses has been provided by the Diffusion Information Center [17] and this is updated period-

ically. The most common methods for studying diffusion in oxides are those employing radioactive tracers, where the geometry of the experiment may be varied to suit the crystal and the tracer concerned. The results of such experiments usually refer unambiguously to the transport of the ion of interest. A number of indirect procedures are also available, but these suffer from varying degrees of inaccuracy and difficulty of interpretation, e.g. creep, shrinkage in sintering, kinetics of necking of spheres, ionic electrical conductivity and the study of oxidation kinetics by thermogravimetry or optical absorption [1].

In the last decade several new techniques and instruments have been introduced, and one of the most promising is the ion microprobe [18]. Following a tracer diffusion experiment the diffusion profile is deduced by sputtering a hole in the surface of the crystal, and analysing the sputtered material by mass spectrometer. As the depth of the hole need be only a few thousand Angstroms, high resolution may be obtained for very slowly diffusing species [18]. An alternative to this approach, employing radio-frequency sputtering as a microsectioning technique, has been described by Atkinson and Taylor [19]. The lowest measurable limit of diffusion coefficient by the latter procedure was estimated to be  $10^{-24} \text{ m}^2 \text{ sec}^{-1}$ .

Mössbauer spectroscopy, where diffusion leads to a broadening of the  $\gamma$ -ray emission or absorption peak, appeared to be a powerful tool for the study of oxide diffusion. However, in order to avoid excessive counting periods (possibly several weeks) diffusion rates must be typically  $10^{-12} \text{ m}^2 \text{ sec}^{-1}$  at temperatures of approximately 1000 K. One of the few materials which meets this requirement is  $Fe_{1-x}O$  [20].

A useful application of an existing technique is to maximize the available data from an interdiffusion experiment. Equation 1 shows the relation between  $\tilde{D}$  and  $D^*$  for a binary pair of solids. If  $S$  is assumed to be equal to unity, then to a first approximation  $\tilde{D}$  may be extrapolated to the limit of composition to yield successively  $D^*_A$  in material B, and  $D^*_B$  in material A. When tracers of a particular species are not readily available (e.g. Al) it may be possible to obtain the required information from a suitably designed interdiffusion experiment: the interdiffusion of  $Fe_3O_4$  and  $FeAl_2O_4$  yields data  $D^*(Al)$  in  $Fe_3O_4$  [21].

TABLE I Self- and impurity diffusion in "binary" oxides ( $A_xO_y$ )\*

Substance	Ref.	Diffusing element	$D_0$ ( $m^2 s^{-1}$ )	$Q$ ( $kJ mol^{-1}$ )	Temperature range (K)	Comments	Year
Aluminium oxide ( $Al_2O_3$ )	[1]	$^{242}Am$	$4.94 \times 10^2$	$564 \pm 29$	1473–1703	(P) $\alpha$ energy absorption	1968
	[2]	$^{45}Ca$	—	—	1670	(P) $D = 3.1 \times 10^{-13}$ , R.A.	1971
	[3]	$^{59}Fe$	$9.18 \times 10^{-12}$	112	1173–1373	(P) S.S., and absorption methods	1959
	[2]	$^{22}Na$	$2 \times 10^{-6}$	$209 \pm 8$	1496–2023	(P)	
		$^{22}Na$	—	—	1841	(S) $\parallel c D = 2.3 \times 10^{-11}$ R.A.	1971
		$^{27}Na$	—	—	1841	(S) $\perp c D = 1.2 \times 10^{-11}$ R.A.	1971
	[4]	O	$4.6 \times 10^3$	598	1245–1348	(S) From sintering of powder	1971
	[5]	$^{18}O$	—	$\approx 241$	1503–1923	(S) Gas-solid isotope exchange.	1977
Boron Oxide ( $B_2O_3$ )	[6]	$^{18}O$	$1.56 \times 10^{-10}$	$788 \pm 29$	1903–2023	(S) mas spec.	1978
	[7]	$^{147}Pm$	$1.18 \times 10^4$	656	1853–2113	(S) Ion microprobe	1965
	[1]	$^{239}Pu$	$1.54 \times 10^4$	$594 \pm 25$	1623–1813	(P) $\beta$ absorption	1968
	[8]	$^{35}S$	—	—	1473–1723	(P) $\alpha$ absorption	1974
			$\approx 9.5 \times 10^{-9}$	189	1573	(S) $D \approx 10^{-19}$ R.A.	
			$\approx 4.8 \times 10^{-11}$	194	1273–1473	(P) 94% density	
			$3 \times 10^{-9}$	36.4	1273–1473	(P) 97.2% density	
	[9]	O	$3 \times 10^{-9}$	—	983–1473	Thermogravimetry	1973
Barium Oxide (BaO)	[10]	$^{133}Ba$	$7.52 \times 10^{-12}$	101	1173–1223	(S), Gruzin	1971
			$1.2 \times 10^{-4}$	$271 \pm 20$	1223–1373		
			1.35	$368 \pm 7$	1473–1673		
Beryllium oxide (BeO)	[11]	Be	—	477	1436–1853	(P) Creep	1967
	[12]	$^7Be$	—	339	1633–1873	(P) Ionic conductivity	1969
	[13]	Li	$2.9 \times 10^{-5}$	$564 \pm 84$	1573–1826	(P) Radiotracer experiments	1969
		$1.5 \times 10^{-9}$	230	1634–1972	(P) Neutron activation Calculation of $D$ based on macroscopic dimensions	1967	
		$1.61 \times 10^{-10}$	206 $\pm$ 9	1634–1972	method calculation of $D$ based on grain size	1967	
Calcium oxide CaO	[14]	$^{18}O$	$1.61 \times 10^{-10}$	206 $\pm$ 9	1673–2173	(P) $^{18}O$ reaction ( $p, n$ ) <sup>18</sup> F	1969
Cerium oxide CeO <sub>2</sub>	[15]	$^{45}Ca$	$1.13 \times 10^{-8}$	269 $\pm$ 6	1738–2033	(S), R.A.	1969
	[16]	O	$5.34 \times 10^{-2}$	306 $\pm$ 25	1423–1823	(S) Pure	1970
	[17]	$^{18}O$	$9.55 \times 10^{-9}$	91 $\pm$ 27	1373–1573	(S) 0.3% Gd during oxidation	1971
			$1.9 \times 10^{-8}$	104 $\pm$ 15	1123–1423	(S) $pO_2 = 0.21$ atm	
			$1.4 \times 10^{-8}$	89 $\pm$ 3	1123–1423	(P) $pO_2 = 0.21$ atm	
			$1.8 \times 10^{-9}$	73 $\pm$ 8	1123–1423	(S) $pO_2 = 0.02$ atm	
	[18]	$^{60}Co$	$4.8 \times 10^{-7}$	150	1373–1673	(S), R.A.	1969
	[19]	$^{60}Co$	$5.0 \times 10^{-4}$	161 $\pm$ 1	1236–1911	Serial sectioning	1969

TABLE I (continued)

Substance	Ref.	Diffusing element	$D_0$ ( $\text{m}^2 \text{s}^{-1}$ )	$Q$ ( $\text{kJ mol}^{-1}$ )	Temperature range (K)	Comments	Year
	[20]	$^{60}\text{Co}$	$7.1 \times 10^{-7}$	190	1293–1723	(S) Serial sectioning	1973
	[21]	$^{60}\text{Co}$	—	—	1273	$D = (5.4-9.0) 10^{-11}$ , Gruzin	1975
	[22]	Co	—	$(\Delta H_m = 96-125)$	1223–1573	Oxidation of Co ( $p\text{O}_2 = 6.6 \times 10^{-4} - 0.33$ atm)	
	[23]	Co	—	—	1273–1673	Radiotracer experiments, various $p\text{O}_2$	1977
	[24]	$^{60}\text{Co}$	$3.89 \times 10^{-8}$	132	1310–1573	(S) $\text{Co}_{0.995}\text{O}$	1977
			—	—	1423	(S) $D = 9.7 \times 10^{-13}$ ( $p\text{O}_2^{0.279}$ ) } S.S.	
	[18]	$^{55}\text{Fe}$	$2.4 \times 10^{-7}$	150	1371–1673	(S), R.A.	1969
		$^{63}\text{Ni}$	$3.9 \times 10^{-7}$	164	1373–1673	(S), R.A.	1969
	[25]	$^{57}\text{Ni}$	$3.3 \times 10^{-6}$	197	1293–1723	(S) Serial sectioning	1973
	[26]	$^{18}\text{O}$	$5 \times 10^{-3}$	$397 \pm 21$	1448–1833	(S), Gas-solid exchange ( $p\text{O}_2 = 0.21$ )	1969
[27]	$^{35}\text{S}$	$5 \times 10^{-7}$	244	1273–1363	(S), R.A.	1972	
[28]	$\bar{D}$	$4.8 \times 10^{-7}$	94.1	1173–1573	Thermogravimetry	1975	
[29]	$^{51}\text{Cr}$	—	—	1473	(S) $D = 3 \times 10^{-26}$	1970	
[30]	Cr	$5 \times 10^{-5}$	468.2	1533–1673	Ar–H <sub>2</sub> atm. } (P) from sintering	1971	
		$4.8 \times 10^{-8}$	468.2	1533–1673	Air		
[31]	$^{59}\text{Fe}$	$4.95 \times 10^{-10}$	184	1173–1373	(P) Radiotracer experiments	1958	
[29]	$^{55}\text{Fe}$	—	—	1473	(S) $D = 5 \times 10^{-19}$	1970	
[32]	O	$\approx 1.59 \times 10^{-3}$	$\approx 419$	1350–1675	(P) Creep	1978	
[33]	$^{35}\text{S}$	—	—	1273	$D = 1.5 \times 10^{-14}$ , Gruzin	1968	
[34]	$^{35}\text{S}$	$\approx 3.8 \times 10^{-11}$	74.4	973–1323	(P), R.A.	1974	
[35]	$^{110}\text{Ag}$	$6 \times 10^{-7}$	116	1073–1323	(S) Radiotracer experiments	1960	
		$3.8 \times 10^{-7}$	59	973–1073	(P) Radiotracer experiments	1960	
[36]	Cu	—	100	1173–1323	Kinetics of Cu oxidation	1970	
[37]	Cu	$6 \times 10^{-6}$	$141 \pm 17$	1263–1318	Oxidation kinetics	1974	
[38]	Cu	$\approx 3.5 \times 10^{-5}$	154	1073–1273	Oxidation kinetics	1977	
[39]	$^{114}\text{In}$	$1.6 \times 10^{-2}$	140	1073–1323	(S) Serial sectioning	1962	
		$2.4 \times 10^{-12}$	51.8	973–1053	(P) Radiotracer experiments	1960	
[40]	S	$8.9 \times 10^{-10}$	104	1053–1323	(P) Serial sectioning	1962	
[41]	$^{65}\text{Zn}$	—	—	1273	$D = 8.9 \times 10^{-13}$	1956	
		$1.7 \times 10^{-12}$	37.6	873–1173	(P) Radiotracer experiments	1960	
[42]	O	$5.2 \times 10^{-8}$	129	1173–1323	(S) Oxidation kinetics (thermogravimetry)	1960	
		$1.63 \times 10^{-9}$	110	1360–1508	(S) Oxidation kinetics (thermogravimetry)	1968	
Dysprosium oxide ( $\text{Dy}_2\text{O}_3$ )	[43]	$^{169}\text{Er}$	$1.48 \times 10^{-4}$	427	1673–1973	(P) Serial sectioning	1969
Erbium oxide ( $\text{Er}_2\text{O}_3$ )	[44]	Hf	$3.28 \times 10^6$	$874 \pm 188$	1837–2173	(P) Extrapolated from interdiffusion data	1976
	[45]	$^{175}\text{Hf}$	$1.15 \times 10^{-10}$	248.3	1874–2103	(Impurities < 617 ppm) Extrinsic diffusion (P)	1978
			$1.48 \times 10^{10}$	295	1874–2013	(Impurities < 319 ppm) Extrinsic diffusion } serial	
			$2.91 \times 10^8$	985	2103–2243	Intrinsic diffusion } sectioning	
	[46]	O	$1.31 \times 10^{-8}$	126	1333–1565	(S) Oxidation kinetics (thermogravimetry)	1968

TABLE I (continued)

Substance	Ref.	Diffusing element	$D_0$ ( $\text{m}^2 \text{s}^{-1}$ )	$Q$ ( $\text{kJ mol}^{-1}$ )	Temperature range (K)	Comments	Year
Iron oxides (FeO)	[47]	$^{55}\text{Fe}$	—	—	1373	$D = 1.03 \times 10^{-11}$ in $\text{Fe}_{0.94}\text{O}$ $D = 1.31 \times 10^{-11}$ in $\text{Fe}_{0.93}\text{O}$ Surface $D = 1.99 \times 10^{-11}$ in $\text{Fe}_{0.89}\text{O}$ decrease $D = 2.35 \times 10^{-11}$ in $\text{Fe}_{0.87}\text{O}$ method	1969
	[48]	Fe	$6 \times 10^{-9}$	$105 \pm 13$	873–1183	Mössbauer broadening	1970
	[49]	Fe	—	$140 \pm 20$	1073	$D = (4.6-6.8) \times 10^{-11}$ in $\text{Fe}_{0.94}\text{O}$ Mössbauer $D = (2-2.3) \times 10^{-12}$ in $\text{Fe}_{0.91}\text{O}$ broadening	1972
	[50]	$^{52,55}\text{Fe}$	—	$135 \pm 20$	1173	$\text{Fe}_{0.94}\text{O}$ , S.S.	1973
	[51]	$^{57}\text{Fe}$	—	133	973–1613	$(P_{\text{CO}_2}/P_{\text{O}_2} = 1.6)$ Mössbauer $(P_{\text{CO}_2}/P_{\text{O}_2} = 0.9)$ broadening $(P_{\text{CO}_2}/P_{\text{O}_2} = 0.5)$ broadening	1973
	[52]	O	—	$113 \pm 3$	1073–1323	$D = 3.5 \times 10^{-11}$ in $\text{Fe}_{0.93}\text{O}$ oxidation $D = 1.6 \times 10^{-11}$ in $\text{Fe}_{0.88}\text{O}$ kinetics	1969
	[53]	O	—	$113 \pm 3$	1328		1972
	[54]	S	—	—	1090–1328	Oxidation kinetics of Fe–S alloys	1972
	[54]	$\bar{D}$	—	83.6	1323–1523	$D = 1.1 \times 10^{-11}$ in $\text{Fe}_{0.857}\text{O}$ oxidation $D = 9.0 \times 10^{-12}$ in $\text{Fe}_{0.93}\text{O}$ kinetics $D = 7.0 \times 10^{-12}$ in $\text{Fe}_{0.909}\text{O}$ kinetics	1967
	[55]	$^{55}\text{Fe}$	—	—	1273	$D = 1.1 \times 10^{-16}$ , $P_{\text{O}_2} = 1.0$ (S)    c $D = 5.9 \times 10^{-16}$ , $P_{\text{O}_2} = 0.1$ (S)    c $D = 2.19 \times 10^{-15}$ , $P_{\text{O}_2} = 0.01$ Gruzin $D = 6.9 \times 10^{-16}$ , $P_{\text{O}_2} = 1.0$ $D = 3.14 \times 10^{-15}$ , $P_{\text{O}_2} = 0.1$ $D = 21. \times 10^{-17}$ , $P_{\text{O}_2} = 1$ , R.A.	1972
(Fe <sub>3</sub> O <sub>4</sub> )	[56]	$^{35}\text{S}$	—	—	1573	Extrapolated from $\text{Fe}_3\text{O}_4$ – $\text{FeAl}_2\text{O}_4$ interdiffusion data	1974
	[57]	Al	—	—	1473		1978
	[57]	$^{60}\text{Co}$	—	—	1553–1773		1978
	[57]	$^{51}\text{Cr}$	—	—	1179–1483	(S) (d log $D^*/d \log P_{\text{O}_2}$ ) = $\pm \frac{2}{3}$ , R.A.	1978
	[58]	$^{59}\text{Fe}$	—	—	1483–1683	(S) (d log $D^*/d \log P_{\text{O}_2}$ ) = $\pm \frac{2}{3}$ , R.A.	1978
	[59]	Ni	—	—	1173–1673	(S) (d log $D^*/d \log P_{\text{O}_2}$ ) = $\pm \frac{2}{3}$ , R.A.	1977
	[60]	O	—	260	1173–1373	Microprobe analysis	1978
	[61]	O	—	$71 \pm 7$	575–823	Isotope exchange, mass spec.	1967
	[61]	O	—	$1.8 \times 10^{-22} (P_{\text{H}_2}/P_{\text{H}_2\text{O}})^{0.27}$	723–823	Isotope exchange, mass spec.	1969
	[62]	Ti	—	$1.5 \times 10^{-7}$	1161–1673	(S) Extrapolated from $\text{Fe}_3\text{O}_4$ – $\text{Fe}_{2.8}\text{Ti}_{0.2}\text{O}_4$ interdiffusion data	1978
Gadolinium oxide (Gd <sub>2</sub> O <sub>3</sub> )	[63]	O	—	—	1010–1277	Thermogravimetry	1969
Holmium oxide (Ho <sub>2</sub> O <sub>3</sub> )	[64]	O	—	—	1323–1541	(S) Thermogravimetry	1968

TABLE I (continued)

Substance	Ref.	Diffusing element	$D_0$ ( $\text{m}^2 \text{s}^{-1}$ )	$Q$ ( $\text{kJ mol}^{-1}$ )	Temperature range (K)	Comments	Year
Lutetium oxide ( $\text{Lu}_2\text{O}_3$ )	[65]	O	$1.88 \times 10^{-8}$	124	1293–1570	(S) Thermogravimetry	1968
Magnesium oxide ( $\text{MgO}$ )	[66]	$^{133}\text{Ba}$	$2.8 \times 10^{-6}$	$337 \pm 29$	2173–2723	Intrinsic diffusion } (S) serial sectioning Extrinsic diffusion }	1972
	[67]	$^7\text{Be}$	$4.2 \times 10^{-6}$	$318 \pm 10$	1501–1695		1973
	[68]	$^{45}\text{Ca}$	$1.99 \times 10^{-9}$	$162 \pm 2$	907–2614	(S) Air and Argon atmos, S.S.	1966
	[69]	$^{45}\text{Ca}$	$2.9 \times 10^{-9}$	$205 \pm 1$	1173–1973	(S) Thin film tracer, autoradiography	1968
	[70]	Ca	$8.9 \times 10^{-8}$	266	1063–2123	(S) Microprobe analysis	1973
	[71]	$^{45}\text{Ca}$	$3.43 \times 10^{-7}$	$309 \pm 19$	2123–2673	(S) Gruzin	1971
	[72]	$^{45}\text{Cd}$	$1.7 \times 10^{-6}$	$328 \pm 29$	2053–2543	(S) Serial sectioning	1962
	[73]	Co	$5.78 \times 10^{-9}$	199	1278–2123	(S) Chloride solution "tracer", microprobe analysis	1965
	[74]	Cr	$9.8 \times 10^{-8}$	284	1573–1973	(S) Chloride solution "tracer", microprobe analysis	1977
	[75]	$^{51}\text{Cr}$	$1.02 \times 10^{-7}$	294	1626–1826	(S) Serial sectioning	1969
	[76]	Ga	—	—	1773	$D = 7.53 \times 10^{-14}$ (P)	1973
	[77]	$^{68}\text{Ge}$	$3.4 \times 10^{-5}$	$386 \pm 19$	2123–2673	(S) Gruzin	1962
[78]	Fe	$8.83 \times 10^{-9}$	174.5	1273–2123	(S) Chloride solution "tracer", microprobe analysis	1965	
[79]	Fe	$3.2 \times 10^{-8}$	176	1573–1973	(S) Chloride solution "tracer" } microprobe (S) Fe metal "tracer" } analysis	1972	
[80]	$^{28}\text{Mg}$	$7.43 \times 10^{-6}$	$334 \pm 18$	2178–2615	Intrinsic diffusion } serial Extrinsic diffusion } (S) sectioning	1973	
[81]	$^{28}\text{Mg}$	$7.48 \times 10^{-10}$	151	1723–2173	Precipitation region	1965	
[82]	Mn	$5.4 \times 10^{-5}$	309	1538–1813	(S) Solid–vapour exchange, mass spec.	1973	
[83]	Mn	$4.19 \times 10^{-8}$	$266 \pm 8$	1273–2673	(S) Chloride solution "tracer", microprobe analysis	1978	
[84]	Mn	$4.1 \times 10^{-11}$	117	1573–1973	E.P.R. spectroscopy	1962	
[85]	Ni	$9.4 \times 10^{-10}$	$202 \pm 24$	1473–1793	(S) Chloride solution "tracer", microprobe analysis	1971	
[86]	Ni	$1.8 \times 10^{-9}$	202	1373–2083	(S) Solid–vapour exchange, microprobe analysis	1971	
[87]	$^{63}\text{Ni}$	$6 \times 10^{-10}$	174	1473–1573	(S) MgO wafers, radiotracer experiments	1972	
[88]	Ni	$1.8 \times 10^{-9}$	202	2173–2733	(S) Solid–vapour exchange, microprobe analysis	1972	
[89]	$^{63}\text{Ni}$	$1.4 \times 10^{-6}$	$318 \pm 30$	2173–2723	Intrinsic diffusion } (S) serial Extrinsic diffusion } sectioning	1972	
[90]	$^{63}\text{Ni}$	$1.3 \times 10^{-10}$	154	1773–1973	Mesh 80–115 $\mu\text{m}$ } (P) gas–solid Mesh 170–200 $\mu\text{m}$ } (P) exchange	1972	
[91]	$^{18}\text{O}$	$4.5 \times 10^{-9}$	252	1373–1673	Well sintered } (P) Loosely sintered } gas–solid isotope exchange	1973	
[92]	$^{18}\text{O}$	$1.3 \times 10^{-9}$	233 $\pm$ 21	1293–1723			
[93]	$^{18}\text{O}$	$2.4 \times 10^{-11}$	252 $\pm$ 25	1293–1553			
[94]	$^{18}\text{O}$	$1.6 \times 10^{-11}$	426 $\pm$ 42	1553–1723			

Substance	Ref.	Diffusing element	$D_0$ ( $\text{m}^2 \text{s}^{-1}$ )	$Q$ ( $\text{kJ mol}^{-1}$ )	Temperature range (K)	Comments	Year
	[84]	$^{46}\text{Sc}$	—	—	1773	$D = 3 \times 10^{-14} - 7.4 \times 10^{-16}$ (S), S.S. $D = (0.51 - 1.8) \times 10^{-15}$ (S)	1970
	[85]	$^{46}\text{Sc}$	—	—	1773		R.A.
	[86]	$^{85}\text{Sr}$	$6 \times 10^{-8}$	212.1	1273–1873	(S) Serial sectioning	1973
	[87]	$^{91}\text{Y}$	$2.11 \times 10^{-6}$	$299 \pm 7$	1678–2033	(S) Serial sectioning	1971
Manganese oxide (MnO)	[88]	$^{54}\text{Mn}$	—	—	1305	$D = 2.57 \times 10^{-13}$ ; $\log_{10} P_{\text{O}_2} = -8$ $D = 1.10 \times 10^{-13}$ ; $\log_{10} P_{\text{O}_2} = -10$ $D = 5.02 \times 10^{-15}$ ; $\log_{10} P_{\text{O}_2} = -17$ $D = 3.16 \times 10^{-15}$ ; $\log_{10} P_{\text{O}_2} = -18$	1970
	[89]	$^{18}\text{O}$	$9.1 \times 10^{-12}$	131 84.9		1123–1413 683–773	$P_{\text{O}_2} = 0.21 - 1.0$ , isotope exchange and ionic conductivity (Nernst equation)
Molybdenum oxide ( $\text{MoO}_3$ )	[90]	$^{18}\text{O}$	$5.4 \times 10^{-2}$	255	593–1023	(P) Isotope exchange	1975
	[91]	O	—	—	1173 1123	$\parallel c D = 8.3 \times 10^{-15}$ } $P_{\text{O}_2} = 10^{-1.7}$ atm (S) $\perp c D = 1.4 \times 10^{-16}$ } $^{18}\text{O}(p, n)^{16}\text{F}$ $\parallel c D = 2.1 \times 10^{-14}$ } reaction $\perp c D = 1.1 \times 10^{-16}$ } $P_{\text{O}_2} = 10^{-2}$ atm } and then auto-radiography	1968
Neodymium oxide ( $\text{Nd}_2\text{O}_3$ )	[92]	O	—	212	953–1238	$P = 10^{-5} - 1$ atm (S) electrical conductivity	1968
	[93]	O	$1.07 \times 10^{-6}$	179	1143–1273	$P_{\text{O}_2} = 0.21 - 1.0$ , isotope exchange and ionic conductivity	1971
	[94]	$^{18}\text{O}$	$1.85 \times 10^{-6}$	$203 \pm 13$	1173–1473	$P_{\text{O}_2} = 0.18$ atm, gas–solid exchange	1976
	[95]	$^{18}\text{O}$	—	—	1373	$D = 3.2 \times 10^{-14}$ } $P_{\text{O}_2} = 0.08$ atm } gas– $D = 2.6 \times 10^{-14}$ } $P_{\text{O}_2} = 0.12$ atm } solid $D = 3.0 \times 10^{-14}$ } $P_{\text{O}_2} = 0.18$ atm } exchange	1978
Nickel oxide (NiO)	[96]	$^{18}\text{O}$	$1.3 \times 10^{-8}$	$128 \pm 6$	979–1275	(S) Isotope exchange	1968
	[97]	$^{60}\text{Co}$	$4.6 \times 10^{-6}$	222	1373–1673	(S), R.A.	1969
Nickel oxide (NiO)	[98]	$^{60}\text{Co}$	$9.12 \times 10^{-7}$	227	1358–1922	(S) Serial sectioning	1971
	[99]	$^{36}\text{Cl}$	$1.8 \times 10^{-11}$	160	1473–1703	R.A.	1974
	[100]	$^{51}\text{Cr}$	$9.36 \times 10^{-9}$	197	1373–1523	(S) Serial sectioning	1971
	[101]	$^{51}\text{Cr}$	$8.6 \times 10^{-7}$	282	1465–1915	(S) Serial sectioning	1973
	[102]	$^{51}\text{Cr}$	—	—	1273 1573	$D = 2 \times 10^{-16}$ } (S) serial sectioning $D = 2 \times 10^{-14}$ }	1973
	[97]	$^{55}\text{Fe}$	$2.2 \times 10^{-7}$	193	1373–1673	(S) R.A.	1969
Iron (Fe)	[103]	Fe	$1.6 \times 10^{-12}$	76.2	1334–1514	$P_{\text{O}_2} = 0.011$ atm (S) electron microprobe analysis	1975
			$5.9 \times 10^{-11}$	108		$P_{\text{O}_2} = 0.21$ atm	
			$6.7 \times 10^{-11}$	108		$P_{\text{O}_2} = 1$ atm	



TABLE I (continued)

Substance	Ref.	Diffusing element	$D_0$ ( $\text{m}^2 \text{s}^{-1}$ )	$Q$ ( $\text{kJ mol}^{-1}$ )	Temperature range (K)	Comments	Year
	[104]	Ni	$6.5 \times 10^{-6}$	204	1073–1273	(P) Electrical conductivity	1969
	[97]	$^{63}\text{Ni}$	$8.9 \times 10^{-7}$	229	1373–1673	(S) R.A.	1969
	[105]	$^{63}, ^{57}\text{Ni}$	$4.77 \times 10^{-6}$	$254 \pm 3$	1453–2033	$\text{O}_2$ atmos } (S) R.A. and S.S. $\text{CO}_2$ atmos }	1970
	[106]	Ni	$2.06 \times 10^{-6}$	$262 \pm 1$	1173–1543	Oxidation kinetics of Ni	1972
	[107]	$^{63}\text{Ni}$	—	226	1073	$D = 6.0 \times 10^{-18}$ (P), R.A.	1972
	[108]	Ni	$1.85 \times 10^{-7}$	201	1123–1443	in $\text{O}_2$ } (P) Gruzin in air } in $\text{N}_2$ }	1974
	[109]	Ni	$1.01 \times 10^{-8}$	197	1333–1523	Oxidation kinetics of Ni	1975
	[110]	$^{63}\text{Ni}$	$2.91 \times 10^{-8}$	187	973–1673	(S) Gruzin	1978
	[111]	$^{18}\text{O}$	$1.5 \times 10^{-6}$	$113 \pm 33$	1373	$D = 5 \times 10^{-19}$ } gas–solid exchange, $D = 2 \times 10^{-17}$ } $D = 4 \times 10^{-16}$ }	1976
	[112]	$^{35}\text{S}$	—	—	1873	(S), R.A.	1972
	[113]	$^{35}\text{S}$	$3.87 \times 10^{-7}$	238	1273–1363	(S), R.A.	1976
	[114]	$^{35}\text{S}$	$1.89 \times 10^{-9}$	185	1093–1473	(S), R.A.	1978
	[115]	$\bar{D}$	$2.9 \times 10^{-4}$	370	1273–1523	Diffusion via Ni vacancies } (S), R.A. Diffusion via oxygen vacancies }	1971
	[116]	$\bar{D}$	$1.08 \times 10^{-13}$	137	1373–1573	(S) Electrical conductivity	1973
	[117]	$\bar{D}$	$6.45 \times 10^{-6}$	141	1273–1443	(S) Electrical conductivity	1979
	[118]	$^{18}\text{O}$	$2.9 \times 10^{-7}$	91	1273–1473	(S) Conductivity (during oxidation)	1972
Lead oxide ( $\text{PbO}$ )	[119]	$^{18}\text{O}$	$1.64 \times 10^{-6}$	94	787	Conductivity (during reduction)	1971
	[120]	$^{18}\text{O}$	$9.68 \times 10^{-7}$	86	1008–1138	$D \approx 4 \times 10^{-15}$ (S) gas–solid isotope exchange, mass spec.	1971
Praeseodymium oxide ( $\text{Pr}_2\text{O}_3$ )	[121]	$^{18}\text{O}$	$5.5 \times 10^{-10}$	$77 \pm 1$	1103–1203	$P_{\text{O}_2} = 0.04$ atm } isotope exchange $P_{\text{O}_2} = 0.28$ atm }	1973
	[122]	$^{18}\text{O}$	$1.3 \times 10^{-9}$	$80 \pm 2$	1003–1073	$P_{\text{O}_2} = 0.28$ atm }	1973
	[123]	$^{18}\text{O}$	$9. \times 10^{-12}$	$34 \pm 3$	1286–1426	$P_{\text{O}_2} = 0.09$ atm }	1976
	[124]	$^{18}\text{O}$	$7.34 \times 10^{-11}$	$64.5 \pm 2$	1286–1446	$P_{\text{O}_2} = 0.14$ atm } (S), isotope exchange $P_{\text{O}_2} = 0.26$ atm }	1973
	[125]	$^{18}\text{O}$	$6.28 \times 10^{-11}$	62.6	1013–1173	$P_{\text{O}_2} = 0.14$ atm (P) (S) isotope exchange	1976
Plutonium oxide ( $\text{PuO}_2$ )	[126]	$^{18}\text{O}$	$9.65 \times 10^{-11}$	176.4	1273–1573	Gas–solid isotope exchange	1973
Scandium oxide ( $\text{Sc}_2\text{O}_3$ )	[127]	O	$6.29 \times 10^{-11}$	60.1	1379–1571	(S) Thermogravimetry	1968
Silicon oxide ( $\text{SiO}_2$ )	[128]	Au	$7.72 \times 10^{-8}$	81.9	473–873	(S) Rutherford scattering	1976
	[129]	$^{45}\text{Ca}$	$5 \times 10^{-14}$	284.2	873–1093	(S)    c, R.A.	1970

Substance	Ref.	Diffusing element	$D_0$ ( $\text{m}^2 \text{s}^{-1}$ )	$Q$ ( $\text{kJ mol}^{-1}$ )	Temperature range (K)	Comments	Year
	[126]	Na	$3.8 \times 10^{-6}$	102.4	673–1273	Infrared spectroscopy and neutron activation analysis	1967
	[127]	$^{22}\text{Na}$	$7.09 \times 10^{-7}$	$48.1 \pm 8$	873–1073	$\parallel c$	1970
	[125]	$^{22}\text{Na}$	$6.8 \times 10^{-5}$	$84 \pm 1$	573–843	$\parallel c$ (S), R.A.	1970
	[128]	$^{22}\text{Na}$	$4 \times 10^{-6}$	$113 \pm 4$	873–1063	$\perp c$	1970
			$2 \times 10^{-2}$	$171 \pm 4$	713–843	$\perp c$	
Samarium oxide ( $\text{Sm}_2\text{O}_3$ )	[129]	$^{18}\text{O}$	$9.2 \times 10^{-10}$	$98 \pm 8$	969–1223	99.9% $\text{Sm}_2\text{O}_3$ } isotope exchange	1968
			$6.0 \times 10^{-10}$	$89 \pm 2$	975–1272	99.99% $\text{Sm}_2\text{O}_3$ }	
Strontium oxide ( $\text{SrO}$ )	[130]	$^{85}\text{Sr}$	$2.52 \times 10^{-2}$	$444 \pm 6$	1723–1873	(S) Gruzin	1971
			$4.48 \times 10^{-8}$	$266 \pm 4$	1473–1673	Isotope exchange and ionic conductivity (Nernst equation)	1971
Tantalum oxide ( $\text{Ta}_2\text{O}_5$ )	[131]	O	$4.26 \times 10^{-6}$	179.3	1173–1273	Gas–solid isotope exchange	1976
			$5.73 \times 10^{-6}$	73.6	1118–1919		1976
Thorium oxide ( $\text{ThO}_2$ )	[132]	$^{18}\text{O}$	—	$\approx 238$	2373–3073		1976
	[133]	O	$2.91 \times 10^{-9}$	$315 \pm 21$	2073–2273	Lattice diffusion } (P) serial	1968
	[134]	$^{233}\text{Pa}$	$6.66 \times 10^{-15}$	$128 \pm 13$		Grain-boundary diffusion } sectioning	
	[135]	$^{230}\text{Th}$	$1.25 \times 10^{-11}$	245.8	1873–2373	(P) $\alpha$ -energy spectrometry	1968
	[136]	Th	$3.5 \times 10^{-5}$	625	2119–2318	(S) Serial sectioning	1971
	[137]	$^{232}\text{Th}$	$1.1 \times 10^{-8}$	319.4	2073–2273	(P) S.S. and $\gamma$ -ray spectrometry	1968
	[138]	$^{233}\text{U}$	$5 \times 10^{-5}$	627	1923–2373	(S) $\alpha$ -energy spectrometry	1976
	[139]	$^{44}\text{Ti}$	$3 \times 10^{-5}$	268		$\text{TiO}_{0.807}$ } serial sectioning	1976
Titanium oxide ( $\text{TiO}_2$ )			$1 \times 10^{-4}$	272	1523–1823	$\text{TiO}_{1.006}$ }	1973
			$6 \times 10^{-5}$	263		$\text{TiO}_{1.06}$ }	
			$4 \times 10^{-5}$	238		$\text{TiO}_{1.259}$ }	
	[140]	$^{110}\text{Ag}$	—	—	$1083 \pm 10$	$D = (1.9 - 9.4) \times 10^{-13}$ (P) Gruzin	1967
	[141]	$^{59}\text{Fe}$	$1.92 \times 10^{-5}$	231.6	1043–1273	(P)	1958
			$1.98 \times 10^{-6}$	229.9		$p\text{O}_2 = 0.92$ atm, (S) $^{18}\text{O}(p, \alpha)^{15}\text{N}$	1971
	[142]	O	$1.7 \times 10^{-6}$	276	1223–1673	Isotope exchange and ionic conductivity (Nernst equation)	1971
	[143]	O	$2.88 \times 10^{-5}$	222.4	1173–1273	$\left\{ \begin{array}{l} D = 1.7 \times 10^{-19}, \perp c \text{ (S) isotope} \\ D = 3.2 \times 10^{-20}, \parallel c \text{ } \\ D = 2.15 \times 10^{-16}; 75\text{--}150 \mu\text{m isotope} \\ D = 6.78 \times 10^{-17}; 150\text{--}300 \mu\text{m isotope} \end{array} \right.$	1976
	[144]	$^{18}\text{O}$	—	—	1079	(S) Electrical conductivity	1971
	[145]	$^{18}\text{O}$	—	—	1273	(S) Serial sectioning	1976
			—	—	1269	$\parallel c$ (S)	1970
	[146]	O	$2.61 \times 10^{-7}$	886.9	1453–1793	$\perp c$ } serial sectioning	1973
	[147]	$^{44}\text{Ti}$	$6.4 \times 10^{-6}$	257	1173–1573		1977
	[148]	$^{44}\text{Ti}$	$4.6 \times 10^{-6}$	250.4	1470–1783		
			$2.4 \times 10^{-7}$	202.7			

TABLE I (continued)

Substance	Ref.	Diffusing element	$D_0$ ( $\text{m}^2 \text{s}^{-1}$ )	$Q$ ( $\text{kJ mol}^{-1}$ )	Temperature range (K)	Comments	Year
Thulium oxide ( $\text{Tm}_2\text{O}_3$ )	[149]	Ti	$6.8 \times 10^{-7}$	$191 \pm 13$	1773–1973	(S)	1978
	[150]	$^{44}\text{Ti}$	—	$(\Delta H_m \approx 238)$	1273–1373	(S) Thermogravimetry and S.S.	1968
	[151]	O	$1.14 \times 10^{-6}$	190.4	1288–1508	(S) Thermogravimetry	
Uranium oxide ( $\text{UO}_{2+x}$ )	[152]	$^{241}\text{Am}$	$3 \times 10^{-6}$	384.6	1473–1773	(P) $\alpha$ energy degradation	1965
	[152]	$^{237}\text{Np}$	$2.9 \times 10^{-4}$	455.6	1473–1773	(P) $\alpha$ energy degradation	1965
	[153]	O	$3.8 \times 10^{-4}$	271.7	1173–1373	diffusion in an electric field	1967
	[154]	$^{18}\text{O}$	—	—	$1273 \pm 1$	$D = (1.3-3.4) \times 10^{-14}$ ; spark source spectrometry analysis	1967
	[155]	O	—	—	1293	$D = 1.04(\pm 0.05)10^{-14}$ ; analysis of secondary ionic emission for $^{18}\text{O}/^{16}\text{O}$ ratio	1968
	[156]	O	$9.9 \times 10^{-3}$	$238 \pm 8$	1158–2108	(P) Thermogravimetry	1969
	[157]	$^{18}\text{O}$	$2.6 \times 10^{-5}$	248	1053–1523	(P) $\alpha$ energy degradation	1969
	[158]	O	$5 \times 10^{-5}$	$191 \pm 15$	873–1373	Electrical conductivity	1970
	[159]	O	—	—	$1198 \pm 5$	$D = 1.8 \times 10^{-16}$	
					$1298 \pm 5$	$D = 2.4 \times 10^{-16}$ (P) nuclear reaction	1971
					$1498 \pm 5$	$D = 3.7 \times 10^{-14}$ ( $^{18}\text{O}(p, \gamma)^{19}\text{F}$ )	
					$1698 \pm 5$	$D = 6.9 \times 10^{-14}$	
	[160]	$^{18}\text{O}$	$5 \times 10^{-9}$	87.8	673–1173	$\text{UO}_{2.006}$ mass spectroscopy of	1972
			$10 \times 10^{-9}$	87.8	673–1073	$\text{UO}_{2.020}$ ( $^{18}\text{O}(p, \gamma)^{19}\text{F}$ )	
			$2.7 \times 10^{-8}$	89.9	773–1073	$\text{UO}_{2.100}$	
			$\approx 6 \times 10^{-8}$	$\approx 92$	1073–1183	$\text{UO}_{2.16}$ nuclear reaction	
			—	190.9	473–723	$\text{UO}_{2.01}$ Thermogravimetry	1974
	[161]	O	$6.25 \times 10^{-8}$	$97 \pm 16$	833–1073	$\text{UO}_{2.08}$ ( $^{18}\text{O}(p, n)^{18}\text{F}$ and $^{17}\text{O}(\alpha, n)^{18}\text{F}$ reactions)	1975
	[162]	O	—	—	—	—	
	[152]	Pa	$2.5 \times 10^{-4}$	449.8	1473–1773	(P) $\alpha$ energy degradation	1965
	[163]	$^{147}\text{Pm}$	$3.5 \times 10^{-10}$	237.4	1393–1683	(P) Radiotracer experiments	1961
	[152]	$^{239}\text{Pu}$	$3.4 \times 10^{-5}$	406.7	1473–1773	(P) $\alpha$ energy degradation	1965
	[152]	Th	$1.6 \times 10^{-5}$	409.6	1473–1773	(P) $\alpha$ energy degradation	1965
[164]	$^{235}\text{U}$	—	—	1773	$\log_{10} D = (-14.8 + 1.9 \log x)$ for $(0.007 \leq x < 0.17)$	1967	
[165]	$^{233}\text{U}$	$2.04 \times 10^{-7}$	371.6	1673–1923	$\text{UO}_{2.01}$ (P), (S)	1968	
		$2.79 \times 10^{-6}$	396.7	1673–1873	$\alpha$ energy degradation		
		$1.09 \times 10^{-4}$	438.9	1673–1923	$\text{UO}_{2.08}$ $\alpha$ energy degradation		
		$6.79 \times 10^{-7}$	338.2	1623–1723	$\text{UO}_{2.15}$		
[166]	$^{233}\text{U}$	—	—	1673	$D < 10^{-21}$ , $\text{UO}_{2.025}$ (S) $\alpha$ energy degradation	1968	
[167]	U	—	$463 \pm 29$	1473–1873	$\log_{10} D = (-14.85 + 1.5 \log x)$	1969	
			—	1773	—		

Substance	Ref.	Diffusing element	$D_0$ ( $\text{m}^2 \text{s}^{-1}$ )	$Q$ ( $\text{kJ mol}^{-1}$ )	Temperature range (K)	Comment	Year	
Vanadium oxide ( $\text{V}_2\text{O}_5$ )	[168]	$^{233}\text{U}$	$6.8 \times 10^{-9}$	$411 \pm 41$	1893–2283	(S) $\alpha$ energy degradation	1969	
	[169]	$^{91}\text{Y}$	$6.8 \times 10^{-12}$	194	1423–1723	(P) Radiotracer experiments	1961	
	[169]	$^{95}\text{Zr}$	$1.6 \times 10^{-10}$	248	1393–1692	(P) Radiotracer experiments	1961	
	[170]	O	2	255	833–923	$p\text{O}_2 = 0.16$ atm, gas–solid isotope exchange	1972	
Yttrium oxide ( $\text{Y}_2\text{O}_3$ )	[171]	O	$6.06 \times 10^{-10}$	81.8	1337–1514	(S) Thermogravimetry	1968	
	[172]	$^{91}\text{Y}$	$1.65 \times 10^{-6}$	289.3	1637–1943	(P) Serial sectioning	1969	
	[173]	Al	$5.3 \times 10^{-7}$	264.1	1053–1163	(P) Photometric method	1969	
	[174]	Co	$1.1 \times 10^{-4}$	383.7	1381–1556	(S) Atomic absorption analysis	1974	
	[175]	Cu	$2 \times 10^3$	$463 \pm 10$	1373–1523	(S) Atomic absorption analysis	1971	
	[173]	Ga	$3.6 \times 10^{-7}$	361.5	1003–1073	(P) Photometric method	1969	
	[174]	Mn	$3.2 \times 10^{-7}$	276.7	1377–1563	(S) Atomic absorption analysis	1974	
	[176]	O	0.105	394.6	1423–1673	(S) gas–solid isotope exchange	1970	
	[177]	$^{18}\text{O}$	$1.2 \times 10^{-14}$	$124 \pm 7$	1213–1413	(S) Proton activation analysis	1973	
	[178]	Zn	–	$197 \pm 17$	573–1073	Mass spectroscopic study of the evaporation of Zn from ZnO	1967	
	Zirconium oxide ( $\text{ZrO}_2$ )	[179]	O	$1.05 \times 10^{-7}$	122.5	673–1123	Calculated from oxidation data	1967
		[180]	O	$7.11 \times 10^{-6}$	140.5	1323–1473		
[181]		O	$2.88 \times 10^{-8}$	118.7	873–1123	(S) $p\text{O}_2 = 0.4$ atm, gas–solid isotope exchange	1968	
[182]		O	$1.36 \times 10^{-8}$	118.7	1148–1323	$p\text{O}_2 = 0.53$ atm, growth kinetics	1968	
[183]	$^{18}\text{O}$	–	–	1263	Growth kinetics	1970		
[184]	$^{18}\text{O}$	$2.34 \times 10^{-6}$	189.4	873–1273	$D = 1.9 \times 10^{-16}$ (S) isotope exchange	1971		
					$p\text{O}_2 = 0.92$ atm, gas–solid isotope exchange	1971		

TABLE II Self- and impurity diffusion in "multiple oxides" ( $A_xB_yO_z$ )\*

Substance	Ref.	Diffusing element	$D_0$ ( $m^2 \text{ sec}^{-1}$ )	$Q$ ( $\text{kJ mol}^{-1}$ )	Temperature range (K)	Comments	Year
BaTiO <sub>3</sub>	[185]	<sup>131</sup> Ba	$8 \times 10^{-5}$	372	1157-1453	(P)	1953
	[186]	<sup>18</sup> O	—	—	1073	$D = 2.6 \times 10^{-14}$	
CaFe <sub>2</sub> O <sub>4</sub>	[185]	<sup>51</sup> Ti	—	≈ 293	—	technical } gas-solid isotope } exchange, } mass spec. }	1953
	[187]	<sup>45</sup> Ca	$3 \times 10^{-3}$	360	1163-1313	(P) Radiotracer experiments	1952
	[187]	<sup>59</sup> Fe	$3.2 \times 10^{-4}$	301	1108-1365	(P) Radiotracer experiments	1952
	[188]	W	$5 \times 10^{-3}$	$209 \pm 13$	1173-1373	Estimated from the reaction of CaO and WO <sub>3</sub>	1975
	[189]	<sup>185</sup> W	$2.9 \times 10^{-9}$	$208.2$ $227.5$	1523-1723	l.c (S) }    c Gruzin }	1975
CoAl <sub>2</sub> O <sub>4</sub>	[190]	<sup>60</sup> Co	$8 \times 10^{-4}$	355.3	1812-2043	(P) Radiotracer experiments	1962
	[191]	<sup>60</sup> Co	$1 \times 10^{-7}$	214	1673-1873	(P) Serial sectioning	1958
CoCr <sub>2</sub> O <sub>4</sub>	[192]	<sup>60</sup> Co	$8 \times 10^{-3}$	376.2	1755-1968	(P) Radiotracer experiments	1962
	[191]	<sup>51</sup> Cr	$2 \times 10^{-4}$	293	1673-1873	(P) Serial sectioning	1958
CoFe <sub>2</sub> O <sub>4</sub>	[192]	<sup>51</sup> Cr	$3 \times 10^{-2}$	355.3	1755-1968	(P) Radiotracer experiments	1962
	[193]	<sup>60</sup> Co	—	—	1453	(P) ( $d \log D^*/d \log P_{O_2}$ ) = -0.61, +0.85	1964
	[194]	<sup>60</sup> Co	$4.55 \times 10^{-3}$	$271 \pm 10$	1504-1663	Co <sub>1-x</sub> Fe <sub>2+x</sub> O <sub>4</sub> (x = 0.003)	1976
	[194]	<sup>59</sup> Fe	$7 \times 10^{-2}$	$385 \pm 16$	1526-1668	(S) Radiotracer experiments	1976
	[195]	<sup>60</sup> Co	5	397.1	1539-1766	(P) Radiotracer experiments	1962
Co <sub>2</sub> TiO <sub>4</sub>	[196]	<sup>59</sup> Fe	$3.16 \times 10^{-6}$	$198 \pm 16$	873-1023	(P) Absorption	1975
	[196]	<sup>185</sup> W	$2 \times 10^{-11}$	$100 \pm 50$	873-973	Gruzin } Absorption }	1969
LaFe <sub>2</sub> O <sub>3</sub>	[197]	<sup>59</sup> Fe	$1.6 \times 10^{-4}$	355.3	1513-1693	Gruzin } Absorption }	1969
	[197]	<sup>140</sup> La	$1.7 \times 10^{-5}$	271.7	—	Gruzin } absorption }	1969
LiNbO <sub>3</sub>	[198]	Co	$1.55 \times 10^{-7}$	225.7	1243-1353	Based on measurements of refractive index	1977
	[198]	Cu	$3.89 \times 10^{-10}$	129.2	1113-1333	(S)	1976
	[199]	Cs	$1.33 \times 10^{-6}$	173.5	1073-1373	(S)    c	1976
	[199]	Na	$3.2 \times 10^{-12}$	76.1	873-1373	(S)    c	1976
	[199]	Na	$4.6 \times 10^{-14}$	34.3	—	(S)    c	1976
LiNbO <sub>3</sub>	[199]	Nb	$2.5 \times 10^{-13}$	51.8	1073-1273	(S)	1977
	[199]	Nb	$2.0 \times 10^{-11}$	102.8	1243-1423	Based on measurements of refractive index	1977
	[198]	Ni	$3.11 \times 10^{-7}$	198.6	1000-1200	$P_{O_2} = 0.08 \text{ atm}$ , (S) isotope exchange	1969
	[200]	O	$3.03 \times 10^{-10}$	122.9	—	(S)    c	1969
	[199]	Rb	$2 \times 10^{-13}$	59.4	973-1273	(S)    c	1976
	[199]	Rb	$6.3 \times 10^{-13}$	70.2	—	(S)    c	1976

Substance	Ref.	Diffusing element	$D_0$ ( $\text{m}^2 \text{sec}^{-1}$ )	$Q$ ( $\text{kJ mol}^{-1}$ )	Temperature range (K)	Comments	Year
	[201]	Ti	—	210.2	1273 1323 1373	$D = 5.06 \times 10^{-17}$ electron $D = 1.06 \times 10^{-16}$ (S) microprobe analysis $D = 2.13 \times 10^{-16}$ (S) microprobe analysis	1978
MgAl <sub>2</sub> O <sub>4</sub>	[198]	Zn	$2.26 \times 10^{-9}$	154.2	1303–1493	Based on measurements of refractive index	1977
	[202]	Al	$8.9 \times 10^{-5}$	439	1703–2013	Electron microprobe analysis	1972
	[203]	<sup>26</sup> Mg	$2 \times 10^{-2}$	360.5	1173–1673	(P) Radiotracer experiments	1958
	[204]	<sup>18</sup> O	0.15	568.5	1623–1873	(S) Gas–solid isotope exchange	1972
	[205]	<sup>18</sup> O	$8.9 \times 10^{-3}$	438.5	1705–2013	(S) Gas–solid isotope exchange	1974
	[206]	<sup>18</sup> O	$3.8 \times 10^{-2}$	384.1	1583–1967	(P) Gas–solid isotope exchange	1975
Mg <sub>2</sub> TiO <sub>4</sub>	[207]	O	$2.3 \times 10^{-3}$	$393 \pm 21$	1353–1723	(S) Gas–solid isotope exchange	1977
MnFe <sub>2</sub> O <sub>4</sub>	[208]	$\bar{D}$	—	241.0	573–693	Electrical conductivity	1974
Na <sub>2</sub> WO <sub>4</sub>	[209]	Ag	0.13	$154 \pm 19$	862–967	Electrochemical cell method	1976
NdFeO <sub>3</sub>	[210]	<sup>59</sup> Fe	$2 \times 10^{-6}$	280.1		Absorption	
			$6.3 \times 10^{-5}$	334.4		Sectioning	1970
			$1.2 \times 10^{-4}$	342.8		Absorption	
			$1.6 \times 10^{-3}$	388.7		Sectioning	
		<sup>147</sup> Nd	$1.17 \times 10^{-7}$	209		Sectioning	
NiAl <sub>2</sub> O <sub>4</sub>	[211]	<sup>51</sup> Cr	$3.4 \times 10^{-8}$	229.9	1173–1373	Sectioning	1958
	[212]	<sup>65</sup> Ni	$3 \times 10^{-9}$	227.7	1273–1673	(P) Sinter, radiotracer experiments	1956
	[213]	<sup>63</sup> Ni	$7.4 \times 10^{-3}$	303.7	1153–1661	(P) Sinter, radiotracer experiments	1958
	[214]	<sup>51</sup> Cr	$2.03 \times 10^{-9}$	187.3	1223–1673	(P) Sinter, radiotracer experiments	1956
	[215]	<sup>51</sup> Cr	$2 \times 10^{-4}$	418	1173–1373	Serial sectioning	1958
	[216]	<sup>51</sup> Cr	$1.35 \times 10^{-7}$	255	1795–1940	(P) Radiotracer experiments	1962
	[215]	<sup>59</sup> Fe	$8.5 \times 10^{-3}$	312.3	1273–1473	Serial sectioning	1958
	[214]	<sup>65</sup> Ni	$1.5 \times 10^{-7}$	256.4	1423–1773	(P) Sinter, radiotracer experiments	1956
	[217]	<sup>63</sup> Ni	$1.7 \times 10^{-6}$	273.8	1133–1550	(P) Sinter, radiotracer experiments	1958
	[218]	<sup>18</sup> O	$\approx 1.7 \times 10^{-3}$	343.2	1473–1823	(P) Gas–solid isotope exchange, mass spec.	1960
	[219]	<sup>55</sup> Fe	$8.2 \times 10^{-4}$	$324 \pm 22$	1123–1473	R.A.	1960
	[220]	<sup>59</sup> Fe	$5.5 \times 10^2$	$510 \pm 25$	1473–1673	(P) R.A.	1977
	[221]	<sup>65</sup> Ni	$5.0 \times 10^{-7}$	255.5	1573–1723	(S) Gas–solid isotope exchange	1970
PbTiO <sub>3</sub>	[222]	Pb	$7.2 \times 10^{-8}$	181.8	1413–1613	Mass spec. Study of vapourization of PbTiO <sub>3</sub>	1972
SnZn <sub>3</sub> O <sub>4</sub>	[223]	Sn	23	455.6	1273–1348	(P) (Sn isotopes: 119, 121, 123, 125)	1956
		<sup>65</sup> Zn	$3.7 \times 10^{-3}$	318.9	1273–1573	(P)	
		<sup>18</sup> O	$1.6 \times 10^{-11}$	64.8	1098–1473	Dislocation density $1.4 \times 10^6 \text{ cm}^{-2}$ (S) Gas–	1965
SrTiO <sub>3</sub>	[224]		$1.2 \times 10^{-9}$	122.5	1123–1798	Dislocation density $6.6 \times 10^5 \text{ cm}^{-2}$ solid	
	[225]	O	$6 \times 10^{-3}$	$238 \pm 67$	973–1248	(S) Capacitance manometry method	1975

TABLE II (continued)

Substance	Ref.	Diffusing element	$D_0$ ( $m^2 \text{ sec}^{-1}$ )	$Q$ ( $\text{kJ mol}^{-1}$ )	Temperature range (K)	Comments	Year
$\text{Y}_3\text{Fe}_5\text{O}_{12}$	[226]	$^{18}\text{O}$	$3.3 \times 10^{-10}$	95.3	1333–1673	(S) Isotope exchange	1975
	[227]	$^{89}\text{Sr}$	$3.6 \times 10^{-11}$	66.9	1333–1573	(P) Radiotracer experiments	1960
$\text{ZnAl}_2\text{O}_4$	[228]	$^{18}\text{O}$	$4 \times 10^{-4}$	292.3	1273–1573	(P) Radiotracer experiments	1964
	[229]	$^{90,91}\text{Y}$	$4 \times 10^{-5}$	273.4	1373–1673	(S), (P) Gas–solid isotope exchange	1977
$\text{ZnCr}_2\text{O}_4$	[230]	$^{65}\text{Zn}$	34	$499.9 \pm 51$	1573–1773	(S) Radiotracer experiments	1956
	[231]	$^{51}\text{Cr}$	$2.5 \times 10^{-2}$	326.8	1273–1673	(P) Radiotracer experiments	1956
$\text{ZnFe}_2\text{O}_4$	[232]	$^{65}\text{Zn}$	$8.9 \times 10^{-4}$	339.3	1273–1573	(P) Sinter, radiotracer experiments	1956
	[233]	$^{59}\text{Fe}$	$6 \times 10^{-3}$	358.6	1273–1673	(P) Sinter, radiotracer experiments	1952
	[233]	$^{65}\text{Zn}$	$8.5 \times 10^{-2}$	343.2	1023–1573	(P) Radiotracer experiments	1952
			$8.8 \times 10^{-2}$	360.5	1173–1623	(P) Radiotracer experiments	1952

\* Abbreviations used in Tables I and II

(S) Single crystal material

(P) Polycrystalline material

S.S analysis by serial sectioning technique

R.A. analysis by residual activity technique

 $\parallel c$  diffusion coefficient measured parallel to  $c$ -axis $\perp c$  diffusion coefficient measured perpendicular to  $c$ -axis $\tilde{D}$  Chemical diffusion coefficient

#### 4. General diffusional trends

For self-diffusion in oxides it is generally found that the smaller species (in most cases the metal ion) diffuses faster than the larger species. Exceptions to this rule are mainly those materials which can easily become oxygen deficient [1]. In the "low temperature" region some oxides have metal and oxygen diffusion rates within a few orders of magnitude of each other, and in some cases there may be a cross-over point below which the oxygen diffuses faster than the metal ion. These include  $\alpha\text{-Al}_2\text{O}_3$ ,  $\alpha\text{-Fe}_2\text{O}_3$ ,  $\text{Nb}_2\text{O}_5$ ,  $\text{Ta}_2\text{O}_5$  and  $\text{WO}_3$  [1, 2], but there is some contradictory evidence [2].

There have been numerous studies of impurity diffusion in oxides, but few systematic examinations, so it is difficult to extract trends with any reliability. Wuensch and Vasilos [22] measured the diffusion of Fe, Ni and Co in MgO and noted a linear relation between the quotient of the ionic radius ( $r$ ) and the polarizability ( $\alpha$ ) of the diffusing ion, and  $Q$ . The diffusion of Ca and Mg in MgO also follow this behaviour [23], but the trend is not universal as the agreement with the results for Be are very poor [24]. Mortlock and Price [25] analysed the data for the transport of several species in MgO, and found that  $D$  could be expressed in terms of a rapidly varying function of  $r$  and temperature for a limited range of  $r$ . Crow [26] measured the diffusion rates of Fe, Co and Ni in CoO and NiO, and found that, in general, the lower the atomic number of the diffusing species, the faster the diffusing rate and the lower the activation energy. The relations between the various parameters are not simple, and more studies of this type would obviously be helpful.

#### 5. Use of the bibliography

The format of the bibliography is essentially the same as that of its predecessor [1], and is intended as a guide to the best available self-diffusion data since 1967, and impurity diffusion data since 1950. Whilst it incorporates one earlier bibliography [27] it does not contain any of the data given by Harrop [1], and seeks to complement the latter publication. The present work represents an attempt to cover the literature up to May 1979. For convenience the data have been subdivided into "binary oxides" (Table I), and "multiple oxides" (Table II). References are given in the Appendix.

The data contained in the bibliography are limited to those which can conveniently be presented in tables. Where possible this comprises the

specification of: diffusing species,  $D_0$ ,  $Q$ , temperature range of measurement, nature of sample (single crystal or polycrystalline), experimental conditions and techniques of measurement. Experimental details are contained in the comments column. The absence of information does not necessarily imply that it cannot be obtained from the appropriate reference, and in some cases (where  $D$  is a function of  $p\text{O}_2$ , etc.) it is essential to consult the original publication.

Using values of  $D_0$  and  $Q$  from the tables, diffusion coefficients may be readily calculated by Equation 2 for the temperature range where the original measurements were made. Care should be taken to ensure that the reported experimental conditions are compatible with the situation of interest as far as possible, and that the data do refer to the movement of the ion, and not the defect which enables it to move. The notes of caution detailed by Harrop [1] are also appropriate to the present bibliography.

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## Appendix

The references are numbered consecutively, but subdivided into individual oxides. Experimental details and results of the diffusion studies are given in Tables I and II.

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