substance: titanium oxide (TiO_2)
property: point defect thermodynamics in pure n-type TiO_{2-x} (rutile)

Theoretical reviews: [72K, 73D]. High-temperature studies of stoichiometry: Figs. 1, 2. Lines in the figures are derived from a model [67K] that assumes the concentration of conduction band electrons n arising from point defects only

$n = 3[Ti_i^{3\cdot}] + 4[Ti_i^{4\cdot}] + 2[V_0^{\cdot\cdot}]$ with $[V_0^{\cdot\cdot}]\, n^2 = k_1\, p_{O_2}^{-1/2}$, $[Ti_i^{3\cdot}]\, n^3 = k_2\, p_{O_2}^{-1}$, $[Ti_i^{4\cdot}]\, n = k_i\, [Ti_i^{3\cdot}]$

with

k_1	$4\cdot10^2 \exp(-105(\text{kcal/mol})/RT)$ [$\text{atm}^{1/2}$]
k_2	$9.3\cdot10^9 \exp(210(\text{kcal/mo1})/RT)$ [atm]
k_i	$3\cdot10^2 \exp(-35(\text{kcal/mol})/RT)$

where the defect concentration in number of moles per mol of oxide is

$x = (2([Ti_i^{3\cdot}] + [Ti_i^{4\cdot}]) + [V_0^{\cdot\cdot}])/(1 + [Ti_i^{3\cdot}] + [Ti_i^{4\cdot}])$

If oxygen vacancies are the dominant defect, $n \propto 2[V_0^{\cdot\cdot}]$ and $n \propto p_{O_2}^{-1/6}$. If $Ti_i^{4\cdot}$ is the dominant defect, $[Ti_i^{3\cdot}] \propto n[Ti_i^{4\cdot}] \propto n^2$, so that $n \propto p_{O_2}^{-1/5}$. If $Ti_i^{3\cdot}$ is dominant, $[Ti_i^{3\cdot}] \propto n$ and $n \propto p_{O_2}^{-1/4}$. For the application of this model to transport data, see documents on transport properties. For impurities in doped TiO_2, see other documents of this substance.

References:

62K Kofstad, P.: J. Phys. Chem. Solids 23 (1962) 1579.

64F Forland, K. S.: Acta Chem. Scand. 18 (1964) 1267.

65M Moser, J. B., Blumenthal, R. N., Whitmore, D. H.: J. Am. Ceram. Soc. 48 (1965) 384.

67A Alcock, C. B., Zadov, S., Steele, B. C. H.: Proc. Br. Ceram. Soc. 8 (1967) 231.

67K Kofstad, P.: J. Less-Common Met. 13 (1967) 635.

72K Kofstad, P.: Nonstoichiometry, Diffusion and Electrical Conductivity in Binary Metal Oxides, New York: Wiley, 1972.

73D DeFord, J. W., Johnson, O. W.: J. Appl. Phys. 44 (1973) 3001.

Fig. 1.

TiO_{2-x}.Composition parameter x vs. oxygen partial pressure in the temperature range 1000...1350ºC. Full circles [67A], squares [64F], upwards triangles [65M], open circles [62K], downwards triangles [65M]. 1 atm = 101 325 Pa.

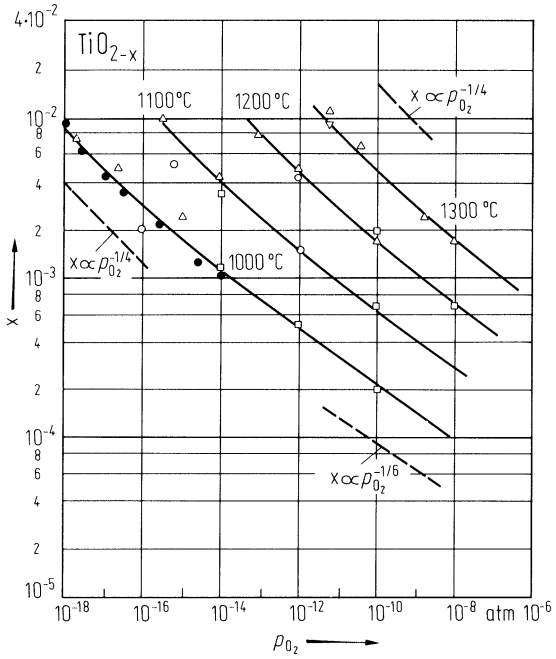

Fig. 2.

TiO_{2-x}. Composition parameter x vs. (reciprocal) temperature at various oxygen partial pressures. Symbols as in Fig. 1.