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Oxygen self-diffusion in ThO$_2$ under pressure: connecting point defect parameters with bulk properties

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Abstract

ThO$_2$ is a candidate material for use in nuclear fuel applications and as such it is important to investigate its materials properties over a range of temperatures and pressures. In the present study molecular dynamics calculations are used to calculate elastic and expansivity data. These are used in the framework of a thermodynamic model, the cBΩ model, to calculate the oxygen self-diffusion coefficient in ThO$_2$ over a range of pressures (−10 to 10 GPa) and temperatures (300 K to 1900 K). Increasing the hydrostatic pressure leads to a significant reduction in oxygen self-diffusion. Conversely, negative hydrostatic pressure significantly enhances oxygen self-diffusion.

1. Introduction

Nuclear energy production offers a way to address present and future energy demand without the generation of extensive amounts of greenhouse gases. The principal component of conventional nuclear fuel is UO_2 but it can be also blended with other actinide oxides such as ThO_2 and/or PuO_2 to form mixed oxide (MOX) fuel [1,2]. Additionally, the future sustainability of the nuclear industry requires considering or revisiting alternative nuclear fuel cycles. ThO_2 is a potentially important nuclear fuel owing to its high corrosion resistance, high melting point, higher thermal conductivity relative to UO_2-based fuels, and abundance [3]. Additionally, Th-U fuel cycles can offer lower concentrations of long-lived transuranic elements and are considered to be more proliferation-resistant [4,5], although this is still debatable.

The correlation of atomic defect properties with bulk properties is an efficient way to describe materials. In particular, the defect Gibbs energy (g^i) and bulk properties in solids has been the subject of thermodynamic models, as for example the cBΩ model proposed by Varotsos and Alexopoulos [6-8]. In the cBΩ model g^i is proportional to the isothermal bulk modulus B and the mean volume per atom [6-8]. The model adequately describes defect processes in solids and in particular self-diffusion in semiconductors, oxides, diamond and metals [9-17]. Recently, the cBΩ model was employed to describe oxygen self-diffusion in ThO_2 over a wide temperature range (2000-3000 K) [18].

Oxygen self-diffusion in ThO_2 is described by the vacancy mechanism in which the oxygen atoms exchange positions with oxygen vacancies. Consequently,

the cBΩ model is appropriate as it is applied to materials with a single diffusion mechanism operating over a range of temperatures. In the present study we use the cBΩ model to derive relations for oxygen self-diffusion coefficients in ThO_2 from 300 to 1900 K and −10 to 10 GPa.

2. Methodology

2.1 Molecular dynamics (MD)

Atomistic simulations can provide comprehensive data on the properties of energy and nuclear fuel materials that can be complementary to experimental results [19-23]. The Cooper-Rushton-Grimes (CRG) potential set [24] reproduces the thermomechanical and thermophysical properties of AmO_2, CeO_2, CmO_2, NpO_2, PuO_2 [25], ThO_2 and UO_2 for a wide temperature range (300-3000 K). In the CRG potential model many-body interactions are incorporated using the embedded atom method (EAM). The model describes the elastic constants of actinide oxides, the bulk moduli and importantly reproduces the Cauchy violation [24,25]. The applicability and furthermore the efficacy of this model has been demonstrated in the calculation of diffusion properties in CeO_2, $U_{1-x}Th_xO_2$ and $Pu_{1-x}U_xO_2$ [24-27]. Implementing this model, MD calculations were carried out using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) [28] to investigate the variation of bulk modulus as a function of pressure. Using a ThO_2 supercell of $10 \times 10 \times 10$ fluorite unit cells, calculations were carried out in the NPT ensemble with Nose-Hoover thermostat and barostat relaxation times of 0.1 ps and 0.5 ps and a timestep of 2 fs. For a given temperature the pressure was varied from −10 GPa to 10 GPa at 0.1 GPa intervals. At each interval the supercell was equilibrated for 10 ps with the volume and pressure averaged over the final 5 ps. As such, for a given temperature a P-V

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curve can be obtained (refer to Figure 1). A third order polynomial is then fitted to each P-V curve that describes P(V), the first derivative of which can be used in Eq. 1, to determine the bulk modulus:

$$B = -V\frac{dP}{dV} \tag{1}$$

where B is the bulk modulus, V is the volume and the first derivative of the P-V curve, $\frac{dP}{dV}$, can be determined by the analytical derivation of the polynomial descibing P(V). In the cBΩ model the bulk modulus as a function of pressure and temperature is required to calculate diffusivity and other defect properties. Note that due to the large pressure range examined here a third order polynomial was necessary for P(V), whereas just a second order polynomial was used previously for UO_2 between 0-10 GPa.

2.2 cBΩ model

In stoichiometric ThO_2, oxygen self-diffusion is vacancy-mediated. Formally, the oxygen diffusion process is described by the Gibbs activation energy (g^{act}), which is the sum of the Gibbs formation (g^f) energy and the Gibbs migration (g^m) energy. The activation entropy s^{act} and the activation enthalpy h^{act} are described by [9,10]:

$$s^{act} = -\frac{dg^{act}}{dT}\bigg|_P \tag{2}$$

$$h^{act} = g^{act} + Ts^{act} \tag{3}$$

The diffusion coefficient D is defined via the following relation:

$$D = fa_0^2 v e^{-\frac{g^{act}}{k_B T}} \tag{4}$$

Where f is the diffusion correlation factor, a_0 is the lattice constant, v is the attempt frequency and k_B is Boltzmann's constant.

In the framework of the cBΩ model the Gibbs defect energy g^i is related to the bulk properties of the material through [6-8]:

$$g^i = c^i B\Omega \qquad (5)$$

Combining Eqs. (4) and (5) we obtain:

$$D = f a_0^2 v e^{-\frac{c^{act} B\Omega}{k_B T}} \qquad (6)$$

Where c^{act} is a constant that is assumed to be temperature- and pressure-independent [9,10]. This relation implies that with an experimentally-determined diffusivity (D_1) at a temperature (T_1), c^{act} can be calculated provided that the pre-exponential factor $f a_0^2 v$ can also be estimated. The latter term is basically dependent upon the diffusion correlation factor (related in turn upon the diffusion mechanism and the crystal structure) and the attempt frequency. Thereafter, given that the elastic data and expansivity are known for any temperature T_i, the diffusivity D_i at T_i can be calculated using Eq. 6. This is known as the single experimental measurement method of the cBΩ model [9,10]. It is important to note that the cBΩ model encapsulates anharmonic effects exhibited by the temperature decrease in B and by the thermal expansivity, and therefore is appropriate when considering pressure and temperature variations. In a recent study Zhang and Wu [29] provided an example of the applicability of the cBΩ model to reproduce experimental self-diffusion values in diamond for a range of temperatures (1000–2800 K) and pressures (0–80 GPa).

3. Results and discussion

The pre-exponential factor and c parameter of ThO$_2$ has been recently derived [18] using the "mean value" method [30,31]. In the framework of the cBΩ model the following relation links the oxygen diffusion coefficients to the isothermal bulk modulus and the mean volume per atom:

$$D_{cB\Omega}^{ThO_2} = 3.442e^{-\frac{0.3388B\Omega}{k_BT}} \cdot 10^{-4}m^2s^{-1} \qquad (7)$$

Here both the expansivity and the isothermal bulk modulus data were calculated using MD for a range of temperatures and pressures. The mean volume per atom is approximated at every temperature and pressure by dividing the total volume of the unit cell by the number of atoms in the unit cell.

Figure 2 shows the variation of bulk modulus, calculated from the PV curves shown in Figure 1, reported a) as a function of pressure for a set of temperatures and b) as a function of temperature for a set of pressures. Although each curve in Figure 2, be it B(T) or B(P), could be represented by a second order polynomial, it is useful to provide a single expression for B(T,P) that matches the full set of MD data:

$$B(T,P) = a + b \cdot T + c \cdot T^2 + d \cdot P + e \cdot P^2 + f \cdot P \cdot T + g(PT)^2 + h(PT)^3 \qquad (8)$$

where a is the bulk modulus at (T = 0, P = 0), b and c represent temperature-dependent terms, d and e are dependent on pressure and f accounts for a degree of interdependency between pressure and temperature. Using CurveExpert, which enables multivariable fitting, all parameters (a, b, c, d, e, f, g and h) were fitted simultaneously to the modelling bulk modulus data with a very strong agreement ($r^2 =$ 0.997). The resultant parameters are reported in Table 1 and the functional form of equation 8 is plotted alongside the MD data in Figure 2, further demonstrating the strong correlation. As well as being used here to investigate diffusivity, a single equation that describes the UO_2 bulk modulus over a wide range of temperatures and pressures is useful to inform higher-level models, such as those developed from finite element analysis.

Figure 3 is the Arrhenius plot for oxygen self-diffusion coefficients in ThO_2 for a range of pressures, derived by the $cB\Omega$ model using Eq. (7). Figure 4 shows the pressure dependence for oxygen self-diffusion coefficients in ThO_2 over the

temperature range considered. Hydrostatic pressure decreases oxygen self-diffusion coefficients in ThO_2 and negative pressures enhance the diffusivity. The trend in the diffusivities is analogous to what has been previously observed using the cBΩ model to investigate diffusion properties under pressure [29, 32]. As can be inferred by the change in the slope of Fig. 3 with respect to pressure, there is also an impact on the activation energies (E_a) of oxygen diffusion. This pressure dependence of E_a is illustrated in Fig. 5 and can be described by:

$$E_a = 5.95 + 0.115 \cdot P - 0.000495 \cdot P^2 \tag{9}$$

The lower coefficients in Eq. 9 compared to the same equation for UO_2 [32] indicates a reduced dependence of activation energy on pressure for ThO_2.

The activation volume can be defined by $v^{act} = -\left(\frac{\partial g^{act}}{\partial P}\right)_T$. Therefore, by differentiating Eq. 4 the activation volume is given by:

$$v^{act}(P,T) = -k_B T \left(\frac{\partial lnD}{\partial P}\right)_T \tag{10}$$

where $\left(\frac{\partial lnD}{\partial P}\right)_T$ is effectively the slope of Figure 4. v^{act} is calculated to be 11.61-12.75 10^{-6} $m^3 mol^{-1}$ over the T range 700-1500 K and is as expected comparable with the isostructural UO_2 (8.75-10.66 10^{-6} $m^3 mol^{-1}$), but higher than materials such as diamond (3.26-3.37 10^{-6} $m^3 mol^{-1}$ over the temperature range 1800-2600 K) [29].

Figure 6 represents the cBΩ model results for the pressure dependence of the ratio of oxygen self-diffusion coefficients at a temperature over the self-diffusion coefficients at P = 0 for T = 300-1900 K. The enhancement (or suppression) of oxygen self-diffusion spans many orders of magnitude, being more significant at low temperature. These lower temperatures are difficult to investigate using MD or experimental work in these materials owing to the high activation energies. Whilst in reality a ceramic is unlikely to withstand such high pressures, the present study

demonstrates that the cBΩ model can be employed to investigate and predict microscopic properties at adverse conditions.

4. Conclusions

In the present study MD is used to examine and express the variation of the ThO_2 bulk modulus with respect to temperature and pressure in a single equation. The cBΩ model is used to model oxygen self-diffusion in ThO_2 over a range of pressures and temperatures. It is calculated that positive hydrostatic pressure drastically decreases the oxygen diffusivities in ThO_2, and *vice versa* negative hydrostatic pressure enhances diffusivity. It is calculated that the activation energies for oxygen self-diffusion increase with increasing pressure. The enhancement or suppression of oxygen self-diffusion spans many orders of magnitude, being particularly marked for the lower temperatures. We have therefore demonstrated that the cBΩ model can be employed in conjunction with MD calculations to derive point defect properties in ThO_2 and related materials for a range of pressures and temperatures.

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Table 1. The derived coefficients of Eq. 8, that describe the bulk modulus of ThO_2.

a (GPa)	b (GPa·K^{-1})	c (GPa·K^{-2})	D	e (GPa^{-1})	f (K^{-1})	G (K^{-2}GPa^1)	h (K^{-3}GPa^2)
1.93×10^2	-2.93×10^{-2}	-1.18×10^{-6}	4.81	-2.60×10^2	8.47×10^{-4}	-3.44×10^{-8}	9.15×10^{-13}
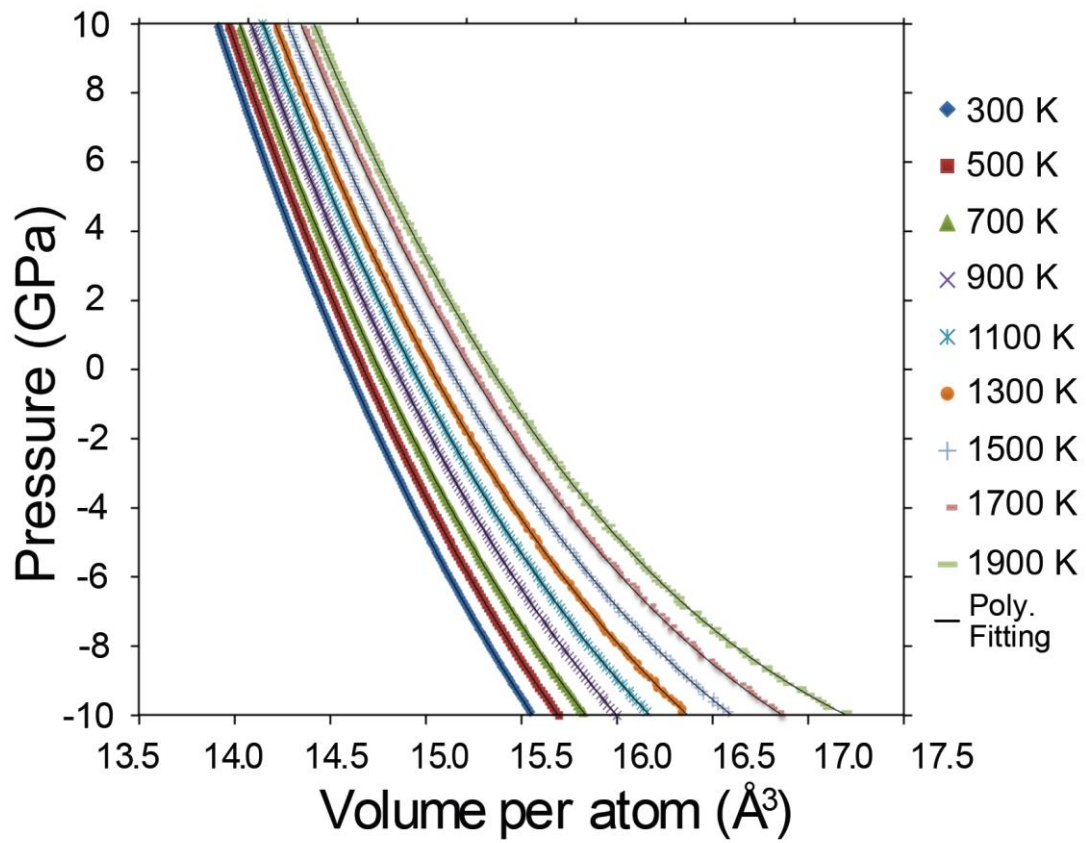
Figure 1. The variation of pressure as a function of volume per atom for ThO$_2$ calculated using MD. The data are fitted using second order polynomials and these are used to calculate the bulk modulus as a function of pressure.
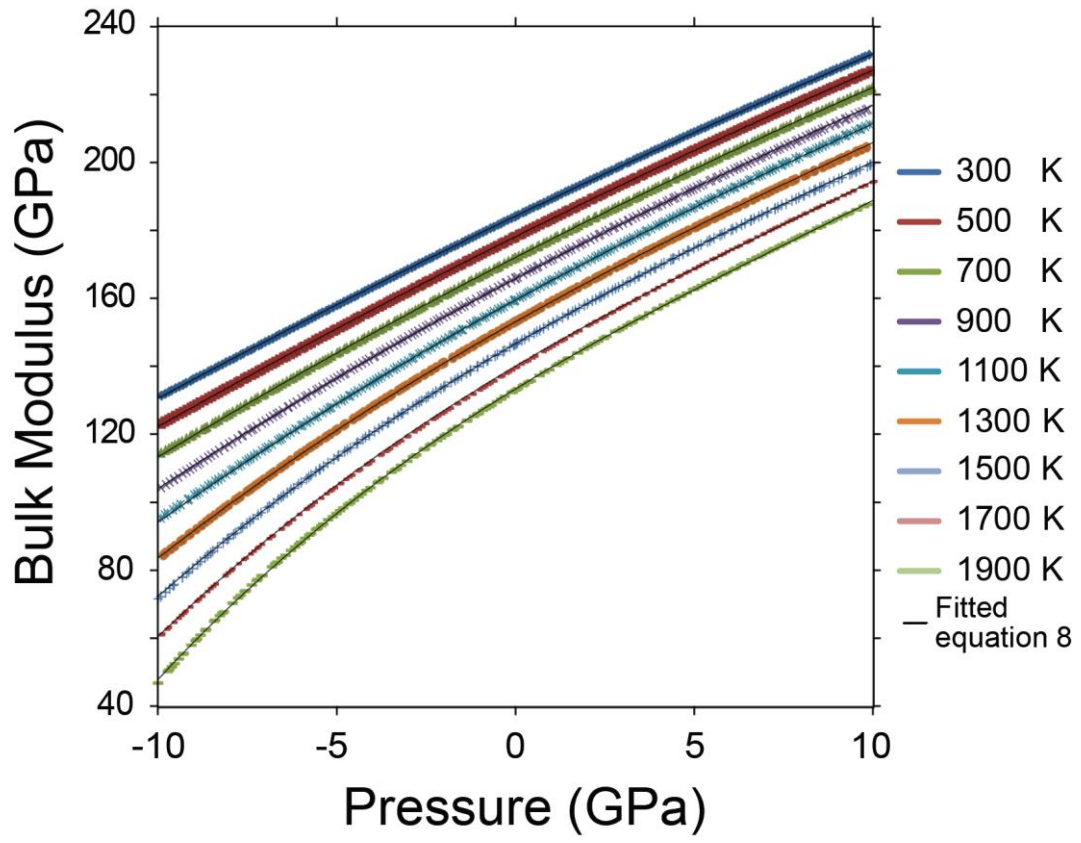
(a)
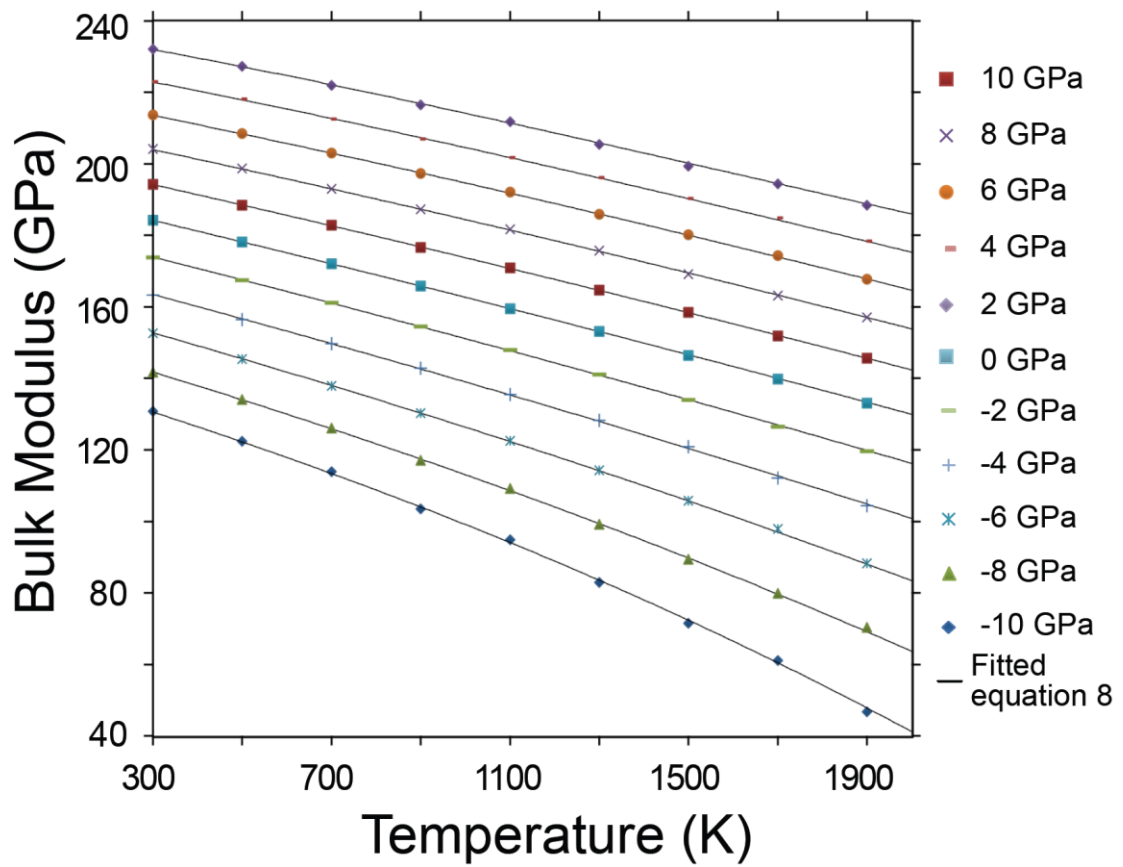
(b)

Figure 2. The bulk modulus of ThO$_2$ derived using MD and the CRG model as a function of (a) pressure and (b) temperature. The fit from equation 8 is shown alongside the modeling data using the parameters reported in Table 1.
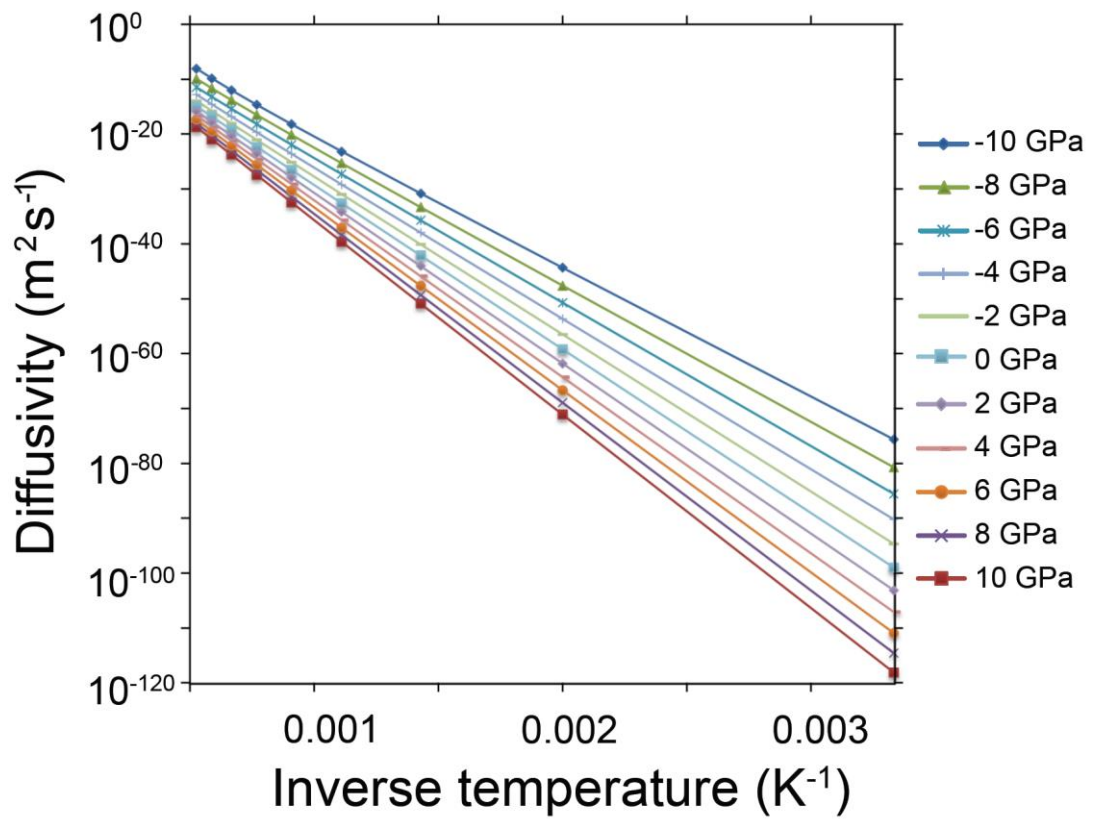
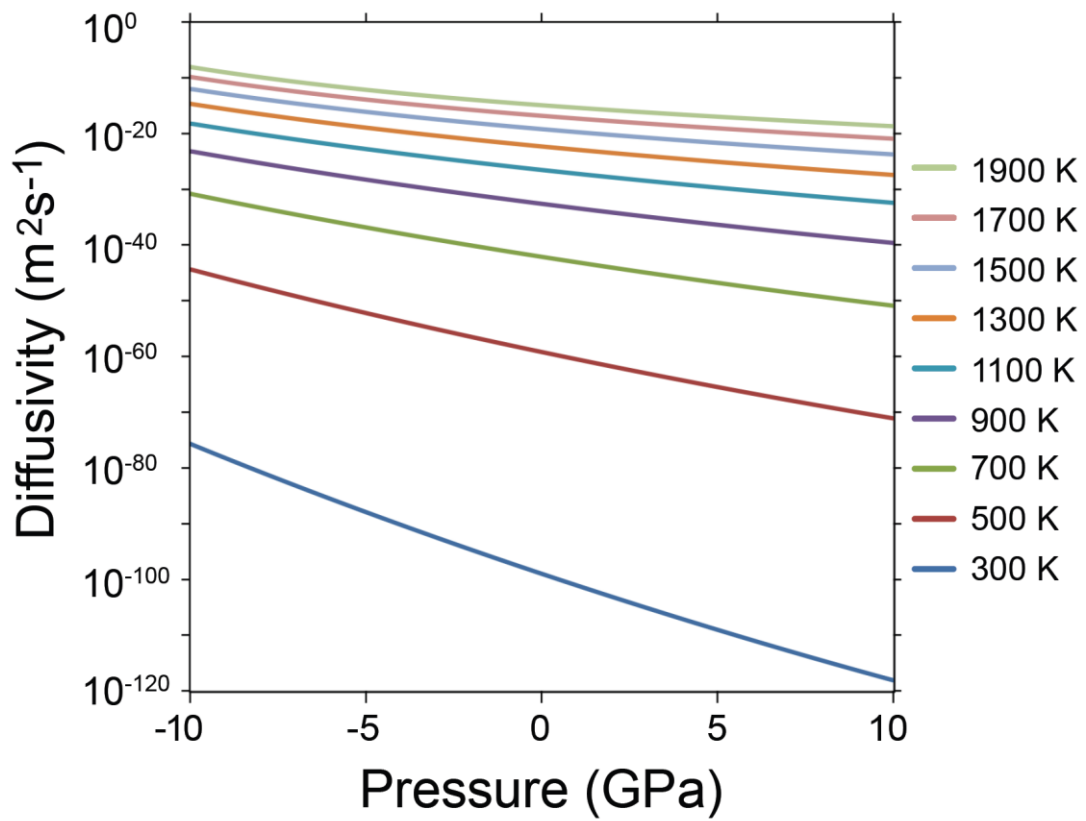**Figure 3.** Arrhenius plot for oxygen diffusivities in ThO_2 derived using the cBΩ model for a range of pressures.

Figure 4. The pressure dependence for oxygen self-diffusion coefficients in ThO_2 calculated using the cBΩ model for T = 300-1900 K.
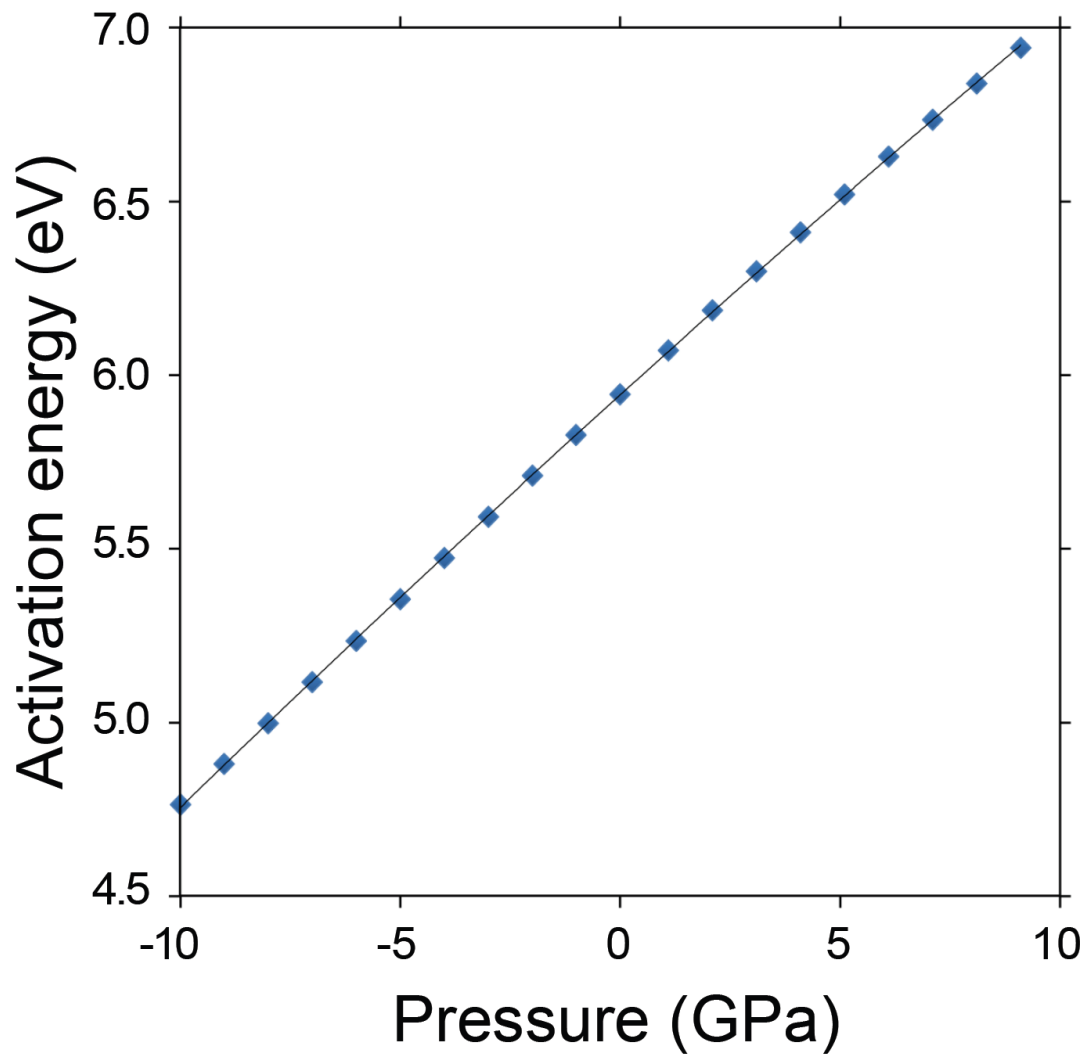
Figure 5. The pressure dependence of activation energies of oxygen diffusion in ThO$_2$.
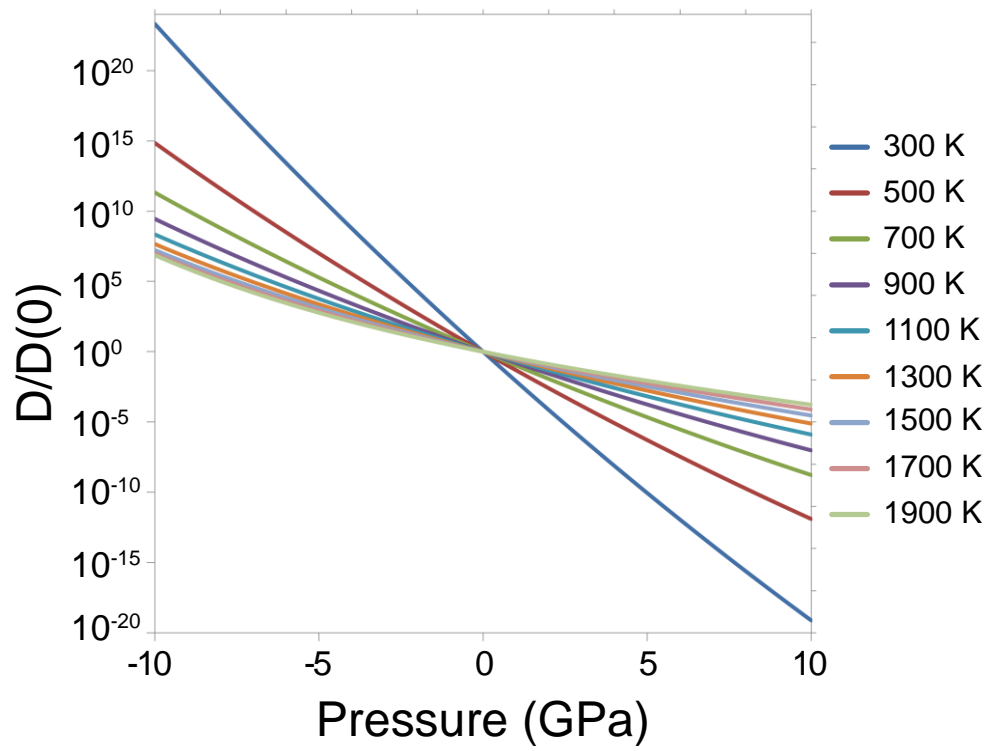
Figure 6. The pressure dependence for the ratio of oxygen self-diffusion coefficients at a temperature over the self-diffusion coefficients at $P = 0$ in ThO_2 calculated using the cBΩ model for T = 300-1900 K.