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# Atomistic modelling of tritium thermodynamics and kinetics in tungsten and its oxides

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ARTICLE INFO	A B S T R A C T		
Keywords: Tungsten oxides Tritium Thermodynamic Diffusion Ab initio	Atomistic simulations using <i>ab initio</i> density functional theory and machine-learned potentials have been employed to map the structural, thermodynamic, and kinetic properties of the $T$ -WO <sub>x</sub> system (x = 0 to 3). The simulations reveal that the T permeability is low in WO <sub>2</sub> , intermediate in W, and relatively high in WO <sub>3</sub> . Diffusion of T is slowest in WO <sub>2</sub> . Vacancies and self-interstitials are strong traps for T. Oxygen vacancies in WO <sub>2</sub> are very strong traps for a few T atoms, while vacancies in bulk W can trap up to ten T atoms. Segregation to WO <sub>2</sub> curfaces is appreciated by However, corresponding of T to WO <sub>3</sub> surfaces is appreciated by unforwardle at		
DFT	high surface coverage.		

#### 1. Introduction

Tungsten (W) is the prime candidate plasma-facing material for future fusion power reactors, owing to several favourable properties, including high thermal conductivity, low sputtering yield, and low intrinsic hydrogen isotope (HI) retention. The retention of radioactive tritium needs to be minimized, not only for avoiding the shortage of tritium resources but also for safety reasons. A large tritium inventory represents a potential safety hazard, for example in the case of a sudden loss of vacuum or during maintenance and decommissioning. For these reasons, a solid understanding of HI retention and transport in W is of vital importance.

HI retention is influenced by the specific processing and exposure history of the host material. For example, T retention is increased by trapping in lattice defects generated during neutron bombardment [1,2]. In *ex situ* situations where the material has been exposed to air under ambient conditions, W readily forms a natural oxide film on its surface due to its affinity for oxygen. An oxide film, which is not sustainable under reactor operating conditions, could influence HI retention and release by W *ex situ* [3,4]. Hence, a practical engineering understanding of HI retention in W requires a fuller understanding of the effects of both lattice damage and surface oxides on HI retention and release rates.

Many laboratory experiments have been conducted to increase the understanding of HI retention in W [5-8]. Most of these experiments

were performed ex situ, under conditions in which an oxide layer was present. Computational modelling has also been used to study HI retention and to interpret experimental results. The vast majority of the studies based on first-principles calculations relate to hydrogen absorbed within the W phase [9-14], though some studies also included the W surface [15-19]. From these studies, the thermodynamics and kinetics of H transport and trapping in vacancies are well established. The high affinity between HIs and free W surfaces has also been demonstrated. The influence of oxygen on hydrogen retention has been investigated both within bulk W, and at free W surfaces. Trapping of H in vacancyoxygen-hydrogen complexes in bulk W was studied by Kong et al. [20], showing that O can increase W vacancy stability. The effect of oxygen on hydrogen adsorption, absorption, and desorption at W surfaces was investigated by Ferro et al. [21]. This study found that adsorbed surface O reduces the H binding energy to W surfaces, and also reduces the activation barrier for H<sub>2</sub> molecular recombination on W surfaces.

There are fewer ab-initio studies of HI in tungsten oxide phases. Zhang et al. studied hydrogen adsorption on WO<sub>3</sub> surfaces [22]. Lin et al. investigated proton diffusion in WO<sub>3</sub> and its hydrates [23]. Interestingly, they found that there are pathways with small diffusion barriers in WO<sub>3</sub>, enabling fast diffusion.

The present study aims at providing a systematic investigation of T in each of the phases W, WO<sub>2</sub>, and WO<sub>3</sub>. To this end, atomistic simulations using *ab initio* density functional theory and machine-learned potentials

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have been employed to map the structural, thermodynamic, and kinetic properties of the T-WO<sub>x</sub> system (x = 0 to 3). The interactions between tritium and vacancies and self-interstitials in each of the phases are analysed. The computations of T energetics and diffusivity in each the phases enables an assessment of tritium retention and permeability, analogous to the analysis performed by Kremer et al. for the case of deuterium uptake in W [24]. The results reported herein, including diffusion barriers and trapping energies, are also well suited to be used as input data for macroscopic rate equation codes such as the Tritium Migration Analysis Program (TMAP) code [25] and the Migration of Hydrogen Isotopes in MaterialS (MHIMS) code [26].

## 2. Computational method

The ab initio results reported here were computed using the Generalized Gradient Approximation (GGA) level of density functional theory (DFT)[27,28], which describes electronic exchange–correlation effects in the manner given by Perdew et al. [29] The resulting effective singleparticle Schrödinger equations were solved using the Projector Augmented Wave (PAW) method [30] as implemented in the Vienna abinitio simulation package (VASP) Version 6 [31–33] within the *MedeA* materials modelling environment [34]. The Brillouin zone is sampled with a regular  $\Gamma$ -centred k-point mesh with a spacing of 0.15 Å<sup>-1</sup> for most computations. The plane-wave cutoff in the expansion of the wave functions is set to 400 eV. With these computational parameters, the energies of all phases (W, WO<sub>2</sub>, and WO<sub>3</sub>) are converged to less than 0.01 eV per formula unit. Geometry optimizations are converged to a maximum force of less than 0.02 eV Å<sup>-1</sup>.

The PBE-GGA functional was chosen after testing the performance of several functionals against experimental structural parameter values (lattice parameters and densities) and enthalpies of formation of W oxide phases. The phases were bcc-W, monoclinic WO<sub>2</sub>, tetragonal WO<sub>2</sub>, orthorhombic WO2, monoclinic W18O49, monoclinic WO3, and tetragonal WO3. The other tested functionals were rPBE [35], SCAN [36], and LDA [37]. In addition, PBE-D3 (with dispersion correction) functionals with zero damping [38] and with Becke-Johnson (BJ) damping [39] were tested with regard to vacancy formation energies. In the majority of computations, the GGA-PBE results are closer to experimental values than those of any other functional. This is the case also for the computed insertion energy of H in bcc-W, both in defect-free W as well as in vacancies. SCAN has severe convergence issues and is not a suitable choice for the W-O system. Based on these results it is judged that PBE is the most appropriate functional for the computational investigation of these phases.

While properties of defect-free bulk W can be modelled with conventional unit cells of the W-O phases, computations with defects have been modelled with supercells built from conventional unit cells. Interaction distances between periodic images extends up to 13 Å for W, 11 Å for WO<sub>2</sub>, and 15 Å for WO<sub>3</sub> (2 × 2 × 2 for WO<sub>2</sub> and WO<sub>3</sub>, and 4 × 4 × 4 for W).

Insertion free energies are computed with T in the gas phase (T<sub>2</sub>) as reference. The Helmholtz free energy of a crystal of N unit cells at a given volume is given by  $A_{tot} = N \bullet A$ , where A is the Helmholtz free energy of the unit cell. In the harmonic approximation this is

$$A = \sum A_{i,\mu} \tag{1}$$

$$A_{i,\mu} = dk_B T \int_0^\infty g_{i,\mu}(\omega) \ln(2\sinh\frac{h\omega}{4\pi k_B T}) d\omega$$
<sup>(2)</sup>

where  $A_{i_{b}\mu}$  is the contribution of atom  $\mu$  and vibrational direction *i* to the free energy.  $g_{i,\mu}$  ( $\omega$ ) is the partial phonon density of states, and *d* is the dimension of the dynamical matrix. The free energy of insertion  $E_{ins}$ , is computed by subtracting the sum of the free energies of pure bcc-W and T<sub>2</sub> (g) from the free energy of bcc-W with T. Free energies of the bulk phases, with and without T, can be accurately computed from respective

phonon computations. For improved accuracy, the values for the gas phases of  $T_2$  are taken from experiment, which are extremely well established [40].

Trapping energies are computed as the energy difference between a vacancy with N + 1 trapped atoms and a vacancy with N trapped atoms. The reference state for the trapped atom is as an interstitial in defect-free bulk. That is, the trapping energy is given by  $E_{trap} = E_{vac, N+1} + E_{W, bulk} - E_{vac, N} - E_{W,H}$  interst. Trapping energies for T at self-interstitials are computed in an analogous way.

For a surface with N adsorbed T atoms (with energy  $E_{surf, N \times T}$ ), the adsorption energy is computed as  $E_{ads} = E_{surf, N \times T} - E_{surf} - N/2 E_{T2}$ . Segregation energies  $E_{segr}$  are given by the energy difference between surface adsorption energies on, and bulk insertion energies for respective phases.

The mapping of preferred interstitial T adsorption sites. T diffusion pathways and the computation of their respective diffusion barriers, was accomplished by means of the recently implemented feature of on-thefly machine learning force fields (MLFF) [41] within VASP. This approach enables molecular dynamics simulations with DFT accuracy over sufficiently long times to capture the diffusion of T in the WO<sub>x</sub> systems. The MLFF simulations used atomic models with a frozen lattice and a single k-point, at  $\Gamma$ , in the Brillouin Zone. The precise locations of stable and meta-stable adsorption sites were obtained allowing complete relaxation of all atomic positions. Diffusion barrier energies were obtained using the nudged elastic band (NEB) algorithms [42,43] as implemented in MedeA. The NEB computations were performed using a **k**-point spacing of 0.3  $Å^{-1}$ . The temperature-dependent diffusion coefficients of interstitial T in W-O phases are computed using kinetic Monte Carlo and transition state theory [44]. The temperaturedependent diffusion barriers and free energies of insertion were derived from computations using the Phonon module of MedeA, which is based on the work of Parlinski [45]. Phonon computations use a k-point spacing of 0.5  ${\rm \AA}^{-1}.$ 

## 3. Results and discussion

# 3.1. Energy diagram of T in W, WO<sub>2</sub>, and WO<sub>3</sub>

An understanding of the detritiation process in W and its oxides can be informed by computing relevant fundamental material properties, such as T insertion energies and T diffusion constants in each of the separate phases W, WO<sub>2</sub>, and WO<sub>3</sub>. The current paper focuses on the monoclinic form of the oxides, which are the most stable phases at low temperatures. Thus, the results are most relevant to ex situ situations in which a W wall component has been exposed to air under ambient conditions. This focus maximises this study's relevance to ex situ experimental data and to reactor maintenance conditions. During sudden loss of containment accidents in a reactor, or if cooling of radioactive components fails during maintenance, W may be exposed to higher temperatures where other oxide phases may form instead. Future work will investigate the implications of the different phases on the diffusion behaviour of hydrogen isotopes as well as their interaction with defects; we have already confirmed that vibrational contributions to free energies of insertion can differ for the oxide phases by calculating the vibrational frequencies of hydrogen isotopes in the oxides (see below). On the other hand, experimental data confirm the presence of monoclinic oxide phases in W, even at elevated temperatures. With the aim to produce WO<sub>x</sub> coatings similar to the oxide layers in tokamaks, Pezzoli et. al. deposited oxide films via pulsed laser deposition [46]. During annealing at 870 K, monoclinic WO3 was found to be formed, while the Magneli phase  $(W_{18}O_{49})$  was observed at a higher temperature (1150 K). Addab et. al. produced thin WO3 layers on a W substrate to mimic possible oxidation of W plasma-facing components (PFCs). The temperature was set at 673 K in order to be relevant for PFCs. Raman microscopy and X-ray diffraction revealed that a nanocrystalline monoclinic oxide structure had formed.

The vibrational frequencies obtained from the phonon computations of HIs in W and the oxides are given in Table 3.1. This table also includes results for phases of the oxides other than monoclinic. Tritium preferentially binds to O atoms in the oxides, rather than to W atoms. The O-(H,D,T) vibrational modes have distinct frequencies in these phases, and thus may serve in the interpretation of experimental Raman spectra. All HI related frequencies are Raman active modes. The frequencies are similar in bcc-W and in orthorhombic WO<sub>2</sub>. These frequencies (highest modes) are about half the values of the frequencies in the other W-O phases. The frequencies are highest in hexagonal and triclinic WO<sub>3</sub>, but also the lowest frequencies are associated with O-(H,D,T) stretch modes. The low frequencies for these structures are bend modes where the HIs vibrates parallel to the channels in WO<sub>3</sub>.

The energy landscape is first mapped in the defect-free phases by computations of T binding energies in interstitial sites. Then the interaction between T and point defects (vacancies and self-interstitials) is computed, in order to refine the understanding of the relative propensity for T to reside in each phase. A similar analysis was performed by Kremer et al. for the case of deuterium uptake in W [24]. Kremer's analysis considered only the W and WO<sub>3</sub> phases.

The main results obtained in the present study are summarised in the energy diagram shown in Fig. 3-1. The energy diagram shows free energies of insertion as a function of temperature (displayed as colour spectra), diffusion barriers  $E_A$ , vacancy formation energies  $E_{vac}^f$ , interstitial formation energies  $E_{int}^f$ , and vacancy and interstitial trapping energies  $E_{trap}$ . Free energies of insertion are discussed in this section, while diffusion and trapping are discussed in the following sections.

The computed free energies of insertion show that the WO<sub>3</sub> phase has the highest affinity for T. T insertion into WO<sub>3</sub> is even exoergic at low temperature. In contrast, the WO2 phase has the highest (i.e., least favourable) free energy of insertion. This means that a monoclinic WO<sub>2</sub> oxide layer on W would act as a barrier layer for T. At low temperature, the energy difference between T in WO<sub>2</sub> and in WO<sub>3</sub> is 1.58 eV (a barrier for T moving from  $WO_3$  to  $WO_2$ ), and the energy difference between WO<sub>2</sub> and W is 0.44 eV (a barrier for T moving from W to WO<sub>2</sub>). The insertion energy of T into W ranges from 0.97 eV at T = 0 K to 1.93 eV at T = 1000 K. Insertion energies are very similar for H, 1.03 eV at T = 0 K to 1.90 eV at T = 1000 K. This computed value can be compared to an experimental value for H of 1.04  $\pm$  0.17 eV, measured by Lassner et al. [47]. A comparison can be made between the energy diagram given by Fig. 3-1, and the energy diagram for D provided by Kremer et al. [48]. Kremer et al. considered only the phases WO<sub>3</sub> and W. The enthalpy of solution of D in W is taken to be slightly above 1 eV (from [49]). This is equivalent to the value for T in W in Fig. 3-1. The enthalpy of solution for D in WO3 is assumed to be slightly above zero based on observations of absorption in WO<sub>3</sub> from an HI-rich atmosphere at temperatures above 394 K. Hence, Kremer at al. assign an energy barrier of about 1 eV

#### Table 3-1

Characteristic O–H, O-D and O-T frequencies. All frequencies are Raman active modes.

	O–H (THz)	O-D (THz)	O-T (THz)
bcc-W	35.2, 45.8	24.9 32.4	20.5, 26.5
WO <sub>2</sub> (monoclinic)	22.8, 30.4, 98.4	17.3, 21.8,	11.1, 15.6, 19.2,
		71.4	59.9
WO2 (orthorhombic)	34.5, 40.6, 42.6	24.8, 29.5,	20.9, 24.6, 28.6
		32.1	
W18O49	16.3, 29.6, 99.5	14.0, 19.7,	10.5, 17.1, 60.5
(monoclinic)		72.3	
WO <sub>3</sub> (monoclinic)	20.9, 37.1, 88.9	16.1, 27.1,	14.3, 22.0, 54.5
		64.2	
WO3 (orthorhombic)	23.0, 38.9, 84.2	16.3, 27.5,	14.4, 23.7, 51.8
		59.6	
WO <sub>3</sub> (hexagonal)	6.4, 29.6, 110.8	4.5, 20.9, 78.4	3.7, 17.2, 64.3
WO <sub>3</sub> (triclinic)	12.7, 31.5,	9.0, 22.3, 76.3	7.4, 18.3, 62.5
	107.8		

between the phases WO<sub>3</sub> and W for D. They argue that this energy barrier is controlling the limited uptake of D in W from the WO<sub>3</sub> phase. Their estimate of a small positive heat of solution in WO<sub>3</sub> agrees with the computed value for T in WO<sub>3</sub> in Fig. 3-1. Although insertion of T in WO<sub>3</sub> is exogenic at very low temperature, the insertion energy becomes positive for temperatures above 285 K. The main difference between Fig. 3-1 and Kremer's energy diagram is that Fig. 3-1 includes the WO<sub>2</sub> phase. The WO<sub>2</sub> phase acts as a transport barrier layer, increasing the barrier from WO<sub>3</sub> to W to 1.58 eV. Furthermore, the presence of a WO<sub>2</sub> phase would also introduce a transport barrier in the opposite direction, from W to WO<sub>3</sub> of 0.44 eV.

## 3.2. Diffusion of T in W, WO<sub>2</sub>, and WO<sub>3</sub>

Free energies of insertion represent the minima on an energy hypersurface in defect-free bulk material. Insertion sites are tetrahedral sites in W and positions close to O atoms in the oxides. These sites are illustrated in Fig. 3-2, which shows an MLFF trajectory used to map preferred interstitial adsorption sites and diffusion pathways in WO<sub>3</sub>.

Diffusing T atoms will experience the energy barriers  $E_A$  given in Fig. 3-1. Diffusion of T in WO<sub>2</sub>, which is by interstitial pathways, is slow. Diffusion pathways in WO<sub>2</sub>, consisting of a sequence of jumps between neighbouring O atoms, are shown in Fig. 3-3. The most frequent jump (between site 1 and sites 2, 4, 5, and 6 in Fig. 3-3) has an energy barrier of 0.81 eV. This barrier is rate limiting for T diffusion. The other barriers are higher in energy, 1.06 eV for jumps between sites 1 and 3, and 1.03 eV for jumps between sites 1 and 7.

The T diffusion barrier in WO<sub>2</sub> is much higher than that in bulk W or in bulk WO<sub>3</sub>. In fact, for the faster diffusion in W and WO<sub>3</sub>, two models of diffusion are used. In one approach the host lattice is kept in a frozen state, and in the other approach all atoms in the host lattice are allowed to relax when the diffusing atom moves through the lattice. The rationale behind the frozen lattice approach is the large mass difference between T and the atoms in the host lattice, with a corresponding large difference in the time scales of their motion. For the much slower diffusion in WO<sub>2</sub>, only full relaxation was considered. The frozen lattice approximation would make diffusion in WO<sub>2</sub> even slower. Diffusion barriers for T in W are 0.21 eV allowing for atomic relaxation, or 0.33 eV in the frozen lattice model. The barriers in WO<sub>3</sub> are 0.03 eV allowing for atomic relaxation, or 0.36 eV in the frozen lattice model. We find the same diffusion mechanism for the diffusion in WO<sub>3</sub> as described by Lin et al. [23]. The rate-limiting diffusion mechanism is a two-step process with a rotation step at the corner of a WO<sub>6</sub> octahedra followed by a jump to the next corner site. The obtained diffusion barriers are used as input to kinetic Monte Carlo simulations to compute the diffusion coefficients. The resulting computed diffusion coefficients are shown in Fig. 3-4.

HI diffusion is clearly much slower in WO<sub>2</sub> than in W and WO<sub>3</sub>. The computed H diffusivity in W agrees well with experimental data for H in W from Frauenfelder [49] and Holtzner [50] (experimental data included in Fig. 3-4). Holtzner finds that protium and deuterium have the same activation energy of 0.28  $\pm$  0.06 eV, and slightly different prefactors of  $D_0 = 2.06 \times 10^{-3} cm^2/s$  for protium and  $D_0 = 1.60 \times 10^{-3} cm^2/s$ s for deuterium, respectively. The experimental data in Fig. 3-4 refers to protium. Diffusion of tritium is slightly slower than diffusion of the lighter isotopes. Although we only present data for tritium, we can mention that our computed diffusion coefficients for protium are shifted up to even closer agreement with the experimental data. The isotope difference in diffusion coefficients obtained by explicit Monte Carlo simulations are found to be well described by a simple mass relation given by  $D_T/D_H = \sqrt{m_H/m_T}$ . Tritium diffusion rates in WO<sub>3</sub> are comparable to those in W, but T diffusion in WO3 is faster than that in W at temperatures above 700 K. The simulations show that T diffusion is isotropic in W and WO2 and anisotropic in WO3.



Fig. 3-1. Computed energy diagram of T in a stack of W-WO<sub>2</sub>-WO<sub>3</sub>.d.



**Fig. 3–2.** A T diffusion path between O atoms in  $WO_3$ , as obtained from an MLFF simulation of T in  $WO_3$ .

# 3.3. Trapping of T

Tungsten metal components subject to high energy neutron fluxes, especially in the presence of T, are very likely to develop very high concentrations of W vacancies. The vacancies are strong traps capable of holding multiple T atoms to high temperatures. A single W vacancy can trap up to 10 T atoms. The first six T atoms in the vacancy are more strongly bound, where the T atoms occupy the five-fold coordinated sites. These results agree well with other computational data from the literature [13,14,51]. Tungsten vacancy T traps in W metal are sufficiently strong that it may be necessary to anneal most of them out in order to extract all the T trapped within. Self-interstitials ( $\langle 111 \rangle$  crowdions) have large trapping capacity, but the traps are relatively shallow. Thus, T may be relatively easily evacuated from interstitial traps. The maximum interstitial trapping energy is -0.38 eV. In simulations with



Fig. 3–3. Diffusion paths in  $WO_2$  indicated by connected O atoms. O-O distances less than 3 Å are taken into account. The labels indicate symmetry independent O atoms.

30 trapped atoms, it is found that the average trapping energy for atoms 25 to 30 is -0.04 eV. Tungsten SIA's likely can be annealed out as well, as SIA recombination is very favourable thermodynamically. The maximum values of the computed T trapping energies, in W, WO<sub>2</sub>, and WO<sub>3</sub>, are given in Fig. 3-1. These values represent those for a single T atom in the trap. The trapping energies decrease with increasing concentration of trapped T. Fig. 3-1 shows that point defects in WO<sub>2</sub> and WO<sub>3</sub> also can be strong traps for T. Oxygen vacancies are particularly strong T traps in WO<sub>2</sub>, where a single vacancy can trap three T atoms. A W vacancy in WO<sub>2</sub> has a lower maximum trapping energy than an oxygen vacancy but can trap up to six T atoms (Fig. 3-5 (a)). Interstitials in WO<sub>2</sub> bind one T atom. Oxygen interstitials are especially strong traps for



Fig. 3-4. Diffusion of T in W, m-WO<sub>2</sub>, and m-WO<sub>3</sub>. For diffusion in W and in WO<sub>3</sub>, results are also shown for a frozen lattice model (dashed lines). Experimental measurements for H in W from Holtzner [50] and Frauenfelder [49] are included for comparison.



**Fig. 3–5.** (a) Trapping of six T atoms at an W vacancy in  $WO_2$  (the position of the vacancy is indicated by the dotted circle). (b) Trapping of two T atoms at an O self-interstitial in  $WO_3$ , forming  $T_2O$ .

T in WO<sub>3</sub>, with a capacity to trap three atoms. The maximum trapping energy is obtained for trapping a second T atom, leading to formation of T<sub>2</sub>O (Fig. 3-5 (b)). An O vacancy in WO<sub>3</sub> can trap one T atom. Thus, there is a trend towards trapping fewer atoms going from W to WO<sub>2</sub> and then to WO<sub>3</sub>.

# 3.4. Surface segregation of T

Fig. 3-6 shows the computed binding energy diagram of T in bulk and surface W, WO<sub>2</sub>, and WO<sub>3</sub>. The energy levels for T at the surface represent adsorption energies per T atom. Fig. 3-6 shows energy levels of T at the surface both at low surface coverage (dilute limit) and at full surface coverage.

Surface segregation is energetically favourable for all phases at low surface coverage but differs significantly between the phases. Tritium has the largest propensity to segregate to a WO<sub>2</sub> surface, with a computed segregation energy of -2.57 eV. The segregation energy is -1.72 eV for the W(100) surface and -1.09 eV for the WO<sub>3</sub>(001) surface. For WO<sub>2</sub>, the (012) surface [52] is used in the simulations. At low temperature, a surface reconstruction occurs for the W(100) surface with a  $(\sqrt{2} \times \sqrt{2})$ R45 unit cell, but it is known that the reconstruction disappears above 370 K [53-55]. The WO<sub>3</sub>(001) surface is used in the modelling of the WO3 surface since this surface has the lowest surface energy at room temperature. The segregation energies have a weak temperature dependence, below 0.1 eV in the temperature range up to T = 1000 K. The dependence of segregation energies on the surface coverage  $\theta$  is stronger. Surface segregation is no longer energetically favourable above  $\theta = 0.5$  on the WO<sub>3</sub> surface. For higher coverages, the T atoms will combine with surface O atoms to form T<sub>2</sub>O. This effect is evident in the simulations for coverages above  $\theta = 0.7$ . This effect could have significant implications for oxide volatility. The enhanced volatility of tungsten oxides in the presence of water was first reported by Millner and Neugebauer (at 1 atm and 1000 °C) [56].

HI segregation to the WO<sub>2</sub> surface is energetically favourable up to full HI coverage. On the other hand, HI surface adsorption from the gas phase is energetically favourable up to a coverage of  $\theta = 0.5$ . T<sub>2</sub> forms on the WO<sub>2</sub> surface above this coverage value.

## 4. Summary and conclusion

In summary, T thermodynamics and diffusion processes in the W-O system have been analysed based on DFT calculations. The quantitative results obtained within the present study could improve the ability to manage the capture and release of T from W fusion reactor components.



Fig. 3–6. Computed energy diagram of T in bulk and surface W, WO<sub>2</sub>, WO<sub>3</sub>. The energy levels (adsorption energies per T atom) for T at the surface are given at both low surface coverage (dilute limit) and at full surface coverage.

A primary result from the calculations herein reported is that the permeability of T in  $WO_2$  is significantly lower than that in both bulk W and  $WO_3$ . A pre-existing  $WO_2$  surface phase on a W reactor component would therefore act as a barrier layer for T uptake, whereas a  $WO_2$  surface phase that formed after T already has been absorbed into the component would be likely to complicate efficient T extraction from the W substrate. HI permeability in  $WO_3$  is expected to by high, based on the very favourable free energy of HI insertion and high HI diffusivity.

The results presented here can be seen as an expansion of the analysis provided by Kremer et al. [24], which considered HI energetics and transport in W and WO<sub>3</sub>. There is good agreement between their analysis and the results presented in the current work. The main difference is that the present work also considers a potential WO<sub>2</sub> phase. The possible presence of a WO<sub>2</sub> surface layer on a W component could have significant consequences for detritiation, as it could be expected to act as a transport barrier both for T ingress to and T egress from the W substrate.

Large fluences of high-energy neutrons likely will produce high W and O vacancy and interstitial concentrations within the W first wall fusion reactor components. Subsequent oxidation of a heavily neutrondamaged W substrate might produce heavily defected surface oxides as well. Such point defects are both capacious and tenacious T traps. The strongly trapped T atoms may be considered immobile, and unable to diffuse. The impact of such traps on T mobility is dictated directly by the strength, capacity, and concentration of traps. At sufficient T concentrations to saturate all traps, diffusion accelerates. Tritium within bulk oxide phases likely will migrate to free surfaces and other defects. However, the energetic driving force for T surface segregation is lower in WO<sub>3</sub> than in WO<sub>2</sub>. In fact, the driving force for T surface coverages.

# CRediT authorship contribution statement

M. Christensen: Formal analysis, Investigation, Writing – original draft. E. Wimmer: Conceptualization, Supervision, Writing – review & editing. M.R. Gilbert: Project administration, Conceptualization, Supervision. C. Geller: Writing – original draft, Writing – review & editing. B. Dron: Project administration. D. Nguyen-Manh: Project administration, Supervision, Writing – review & editing.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

# Data availability

Data will be made available on request.

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