Non-stoichiometric surface phase diagrams: methodology

Part1: surface energy vs chemical potentials

We consider an oxide of chemical formula A_mO_n, in chemical equilibrium with an atmosphere containing O_2, H_2 or H_2O, the oxide slab contains N_A metal atoms at chemical potential μ_A, N_O oxygen atoms at chemical potential μ_O and N_H hydrogen atoms at chemical potential μ_H.

$$\Gamma_O = \left[N_O \middle/ N_A \right] = \frac{1}{2S}\left(N_O - \frac{n}{m} N_A \right)$$ oxygen excess

$$\Gamma_H = \left[N_H \middle/ N_A \right] = \frac{1}{2S}\left(N_H \right)$$ hydrogen excess

$$\gamma_{AO} = \frac{1}{2S}\left(G_{AO}^{slab} - N_A\mu_A - N_O\mu_O - N_H\mu_H \right),$$ Definition for Surface Energy

$$g_{AO} = m\mu_A + n\mu_O .$$ Equilibrium in the bulk

$$\gamma_{AO} = \frac{1}{2S}\left(G_{AO}^{slab} - \frac{N_A}{m} g_{AO} \right) - \Gamma_O\mu_O - \Gamma_H\mu_H$$ various manipulation of above

$$\gamma_{AO} = \frac{1}{2S}\left(E_{AO}^{slab} - \frac{N_A}{m} e_{AO} \right) - \Gamma_O\mu_O - \Gamma_H\mu_H ,$$

Note that the change from G to E (which is what is calculated), i.e. neglecting the entropy from slab and bulk. The method is not affected really, and it would be possible to introduce corrections based on the harmonic approximation for instance.

At this stage, it is possible to produce a phase diagram, as a function of the chemical potentials, which already maps the relative stability of the various slabs. One has to some more efforts though to replace these chemical potentials by 'real' variables (P,T) (the chemical potentials have no absolute value here, as they depend on the pseudopotentials for instance)

Part2: chemical potentials as functions of P,T

$$\mu_O = \mu_O^\circ(T) + \frac{1}{2} kT \log\left(\frac{P_{O_2}}{P^\circ} \right)$$ Ideal gas, O2 case

Case 1

Is when it is possible to compute the energy of a molecule accurately enough (not always so easy with plane waves). P° and T° are the standard pressure and temperature (1bar and 298.15K). When a quantity is so superscripted, it usually implies standard pressure and temperature, except in the case when the temperature is also given as a variable, in which case it corresponds to standard pressure only. g° and μ° are essentially used interchangeably.

$$g_{molecule}^\circ(T) = H_{molecule}(T,P^\circ) - T \cdot S_{molecule}(T,P^\circ)$$

$$g_{molecule}^\circ(T) = H_{molecule}(0,P^\circ) + \left(H_{molecule}(T,P^\circ) - H_{molecule}(0,P^\circ) \right) - T \cdot S_{molecule}(T,P^\circ)$$

$$g^{\circ}_{molecule}(T) = E_{molecule} + \Delta H^{\circ}_{molecule}(T,0) - T \cdot S^{\circ}_{molecule}(T)$$

One can obtain $\Delta H^{\circ}_{molecule}(T,0)$ and $S^{\circ}_{molecule}(T)$ from tables [1, 2] (had to faff between 0 and 298.15 because of the way tables are set up)
$E_{molecule}$, as we calculate it, does not include the ZPE, but it is possible to get it very easily from tabulated frequencies for instance

Case 2, for O2

(there are good arguments that any gas should be treated this way, to be investigated !)
The problem is that it is difficult with DFT, to compute an accurate energy for O2, therefore, one uses a cycle:

$mA^S + \frac{n}{2} O_2^G \rightarrow A_m O_n^S$

$\Delta G^{\circ}_f(A_m O_n) = g^{\circ}_{AO} - m\mu^{\circ}_A - n\mu^{\circ}_O$. This is at 298.15K !!!

This gives us $\mu^{\circ}_O(T^{\circ})$, which is also expressed as

$\mu^{\circ}_O(T^{\circ}) = H_O(T^{\circ},P^{\circ}) - T^{\circ} \cdot S_O(T^{\circ},P^{\circ})$

What we really want is:

$$\mu^{\circ}_O(T) = H_O(T,P^{\circ}) - T \cdot S_O(T,P^{\circ})$$

So

$$\mu^{\circ}_O(T) = \frac{g^{\circ}_{AO}(T^{\circ}) - m\mu^{\circ}_A(T^{\circ}) - \Delta G^{\circ}_f(A_m O_n)}{n} + \Delta H^{\circ}_O(T,T^{\circ}) - \left(T \cdot S^{\circ}_O(T) - T^{\circ} \cdot S^{\circ}_O(T^{\circ})\right)$$

In which there is no need to compute any molecular vibrational entropy (but we get the metal instead :0/)

$\Delta G^{\circ}_f(A_m O_n)$, $\Delta H^{\circ}_O(T,T^{\circ})$, $S^{\circ}_O(T)$ and $S^{\circ}_O(T^{\circ})$ are obtained from the tables.

As an aside, there are no reasons to use the same oxide/metal in this cycle as the one under study ! (just requires les calculations)

All this malarkey can be strongly simplified by using a spreadsheet containing the tabulated values.

Tables of Thermodynamical quantities

[1] H. Y. Afeefy, J. F. Liebman, and S. E. Stein "Neutral Thermochemical Data", in NIST Chemistry WebBook, NIST Standard Reference Database Number 69, P. J. Linstrom and W. G. Mallard, eds. National Institute of Standards and Technology, Gaithersburg MD, March 2003.

[2] "CRC Handbook of Chemistry and Physics", CRC Press, Boca Raton FL, 1981.