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# Ab Initio Surface Thermodynamics in Multi Component Environments

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## Abstract

The methodology for the calculation of the phase stability of different surfaces in contact with a multi component environment of gases is presented. The evaluation of the surface free energy of a system is discussed in detail including the use of thermodynamic data tables.

## I. METHODOLOGY

The relative stability of surfaces with different stoichiometries is determined by the comparison of their surface free energy. The methodology used to calculate the surface free energy at a finite temperature and pressure has been developed for metal oxide systems<sup>1,2,3</sup> and extended to multicomponent environments<sup>4</sup>. Previously we have outlined a methodology to allow the evaluation of the surface free energy of  $\text{AlF}_3(01\bar{1}2)$  in the presence of HF and  $\text{H}_2\text{O}$ <sup>5</sup>. In the present work we present a full derivation and discussion of this methodology. Although expressed in terms of  $\text{AlF}_3$  the method is applicable to any multicomponent gas phase environment.

At a given temperature a solid is in equilibrium with its vapour when

$$\mu_{vapour}(T, P_{vap}) = \mu_{solid}(T, P_{tot}) \quad (1)$$

where  $P_{vap}$  is the vapour pressure of the material and  $P_{tot}$  is the total pressure of the system.  $P_{tot}$  enters equation 1 via the pressure dependence of the  $PV$  term in the Gibbs free energy of the solid. Consequently, the variation depends upon  $P_{tot}$  rather than any individual partial pressure. In the following derivation any terms which have a dependency on  $P_{tot}$  will be in the solid phase but could be rewritten in terms of the vapour pressure of that phase.

As an example we consider an  $\text{AlF}_3$  slab with adsorbed hydroxyl groups, water and HF exposed to an atmosphere containing gaseous  $\text{H}_2\text{O}$ ,  $\text{H}_2$  and HF. The methodology is trivially extended to other systems. Modelling the  $\text{AlF}_3$  surface including adsorbed HF, water and hydroxyl groups as a slab of material periodic in two dimensions and of finite thickness in the third, we define the surface free energy as<sup>6</sup>

$$\begin{aligned} \gamma(T, P_{F_2}, P_{O_2}, P_{H_2}, P_{tot}) = & \frac{1}{2A} [G_{slab}(T, P_{tot}) - N_{Al}\mu_{Al}(T, P_{tot}) \\ & - N_F \frac{1}{2} \mu_{F_2}(T, P_{F_2}) - N_O \frac{1}{2} \mu_{O_2}(T, P_{O_2}) - N_H \frac{1}{2} \mu_{H_2}(T, P_{H_2})] \quad (2) \end{aligned}$$

where  $A$  is the surface area of the unit cell (the factor of 2 accounts for both sides of the slab).  $G_{slab}$  is the Gibbs free energy per unit cell of the slab and  $N_{Al}$ ,  $N_F$ ,  $N_O$  and  $N_H$  are respectively the total number of aluminium, fluorine, oxygen and hydrogen ions within the slab.  $P_{F_2}$ ,  $P_{O_2}$  and  $P_{H_2}$  are the partial pressures of the  $\text{F}_2$ ,  $\text{O}_2$  and  $\text{H}_2$  molecules respectively and  $P_{tot}$  is the total pressure of the system. Note that for aluminium we could express the chemical potential as  $\mu_{Al}(P_{Al})$  where  $P_{Al}$  is the equilibrium vapour pressure of Al atoms

above a solid sample at the given temperature and total pressure.  $\mu_{Al}$ ,  $\mu_{F_2}$ ,  $\mu_{O_2}$  and  $\mu_{H_2}$  are the chemical potentials for aluminium, fluorine, oxygen and hydrogen respectively.

It is assumed that bulk aluminium fluoride is in equilibrium with aluminium and fluorine in their natural states, consequently

$$G_{bulk}(T, P_{tot}) = m\mu_{Al}(T, P_{tot}) + n\frac{1}{2}\mu_{F_2}(T, P_{F_2}) \quad (3)$$

where  $G_{bulk}$  is the Gibbs free energy per formula unit of the bulk crystal having stoichiometry  $Al_mF_n$ . Similarly, HF and H<sub>2</sub>O are in equilibrium with their constituent atoms, hence

$$\frac{1}{2}\mu_{H_2}(T, P_{H_2}) + \frac{1}{2}\mu_{F_2}(T, P_{F_2}) = \mu_{HF}(T, P_{HF}) \quad (4)$$

$$\mu_{H_2}(T, P_{H_2}) + \frac{1}{2}\mu_{O_2}(T, P_{O_2}) = \mu_{H_2O}(T, P_{H_2O}) \quad (5)$$

Using equations 3, 4 and 5 we can eliminate  $\mu_{Al}$ ,  $\mu_{F_2}$  and  $\mu_{O_2}$  from equation 2.

$$\begin{aligned} \gamma(T, P_{HF}, P_{H_2O}, P_{H_2}) = \frac{1}{2A} \left\{ G_{slab}(T, P_{tot}) - \frac{N_{Al}}{m}G_{bulk}(T, P_{tot}) \right. \\ \left. - \left( N_F - \frac{n}{m}N_{Al} \right) \left[ \mu_{HF}(T, P_{HF}) - \frac{1}{2}\mu_{H_2}(T, P_{H_2}) \right] \right. \\ \left. - N_O \left[ \mu_{H_2O}(T, P_{H_2O}) - \mu_{H_2}(T, P_{H_2}) \right] \right. \\ \left. - N_H \frac{1}{2} \left[ \mu_{H_2}(T, P_{H_2}) \right] \right\} \quad (6) \end{aligned}$$

Re-arranging this equation we obtain

$$\begin{aligned} \gamma(T, P_{HF}, P_{H_2O}, P_{H_2}) = \frac{1}{2A} \left\{ G_{slab}(T, P_{tot}) - \frac{N_{Al}}{m}G_{bulk}(T, P_{tot}) \right. \\ \left. - \left( N_F - \frac{n}{m}N_{Al} \right) \mu_{HF}(T, P_{HF}) - N_O \mu_{H_2O}(T, P_{H_2O}) \right. \\ \left. - \frac{1}{2} \left( \frac{n}{m}N_{Al} - N_F - 2N_O + N_H \right) \mu_{H_2}(T, P_{H_2}) \right\} \quad (7) \end{aligned}$$

Alternatively we could express the surface free energy as a function of  $\mu_{O_2}(T, P_{O_2})$  by substituting for  $\mu_{H_2}(T, P_{H_2})$  from equation 5.

$$\begin{aligned} \gamma(T, P_{HF}, P_{H_2O}, P_{O_2}, P_{tot}) = \frac{1}{2A} \left\{ G_{slab}(T, P_{tot}) - \frac{N_{Al}}{m}G_{bulk}(T, P_{tot}) - \left( N_F - \frac{n}{m}N_{Al} \right) \mu_{HF}(T, P_{HF}) \right. \\ \left. - \frac{1}{2} \left( \frac{n}{m}N_{Al} - N_F + N_H \right) \mu_{H_2O}(T, P_{H_2O}) \right. \\ \left. - \frac{1}{4} \left( N_F - \frac{n}{m}N_{Al} + 2N_O - N_H \right) \mu_{O_2}(T, P_{O_2}) \right\} \quad (8) \end{aligned}$$

The chemical potential of an ideal gas can be written as

$$\mu_X(T, P_X) = \mu_X(T, P_X^\circ) + kT \ln \left( \frac{P_X}{P_X^\circ} \right) \quad (9)$$

We can therefore calculate the chemical potential at any pressure if we know the value of  $\mu_X(T, P_X)$  at a given pressure  $P_X^\circ$ .

The above derivation is relative to the energy zero of classical thermodynamics where the energy of formation of an element in its standard state at standard temperature and pressure is zero. However, we need to convert to the energy zero of the DFT calculations so that  $G_{bulk}$  and  $G_{slab}$  are simply the DFT total energies of the system. To do this we write equation 9 as

$$\mu_X(T, P_X) = \mu_X(0, P_X^\circ) + [\mu_X(T, P_X^\circ) - \mu_X(0, P_X^\circ)] + kT \ln \left( \frac{P_X}{P_X^\circ} \right) \quad (10)$$

where the term in square brackets is now the change in the chemical potential in moving from  $T = 0$  to  $T = T$  at constant pressure  $P_X^\circ$ .

$$\mu_X(T, P_X) = \mu_X(0, P_X^\circ) + \Delta\mu_X(P_X^\circ) \Big|_{T=0}^{T=T} + kT \ln \left( \frac{P_X}{P_X^\circ} \right) \quad (11)$$

we can define the chemical potential on the DFT energy scale as

$$\mu'_X(T, P_X) = \mu_X(T, P_X) - \mu_X(0, P_X^\circ) + E_{DFT}(T = 0) \quad (12)$$

Traditionally, phase diagrams in the literature<sup>2,3</sup> have been plotted as a function of

$$\mu_X^*(T, P_X) = \Delta\mu_X(P_X^\circ) \Big|_{T=0}^{T=T} + kT \ln \left( \frac{P_X}{P_X^\circ} \right) \quad (13)$$

which does not include the term  $\mu_X(0, P_X^\circ)$  which is the enthalpy of the compound at  $T=0$ K.

The term  $\Delta\mu_X(P_X^\circ) \Big|_{T=0}^{T=T}$  in equations 11 and 13 and implicitly in equation 12 can be obtained from thermodynamical reference tables<sup>7</sup>, as described in section III. The values that we have used in this paper are displayed in table I. Formally  $\mu$  is a Gibb's free energy while  $E_{DFT}$  is an enthalpy,  $H$ . These are related via

$$G(T, P) = H(T, P) - TS(T, P) \quad (14)$$

where  $S$  is the entropy of the system, but at  $T = 0$ ,  $G$  and  $H$  become identical.

The Gibbs free energies of the slab and bulk crystal are computed at the athermal limit and their temperature dependence is ignored as it is negligible compared to that of the gas. Correction to finite temperature is possible by either molecular dynamics simulation or the calculation of the lattice dynamics and the use of the quasiharmonic approximation. However, as the current article is concerned with the qualitative behaviour of the surface

TABLE I: Calculated values  $\Delta\mu$  at 1 atm obtained from thermochemical tables<sup>7</sup>.

Temp (K)	$\Delta\mu_{H_2O} \big _{T=0}^{T=T}$ (eV)	$\Delta\mu_{HF} \big _{T=0}^{T=T}$ (eV)
300	-0.48	-0.45
600	-1.11	-1.03

stability rather than a quantitative determination of the absolute surface formation energy these small corrections have not been computed. The small PV term due to the change in volume of the surface and bulk phases is also neglected. This approximation is in line with previous studies<sup>1,2,3</sup>.

Substituting equation 11 into equation 12 allows us to express the variation of  $\mu'_X(T, P_X)$  with pressure at fixed  $T$  as

$$\mu'_X(T, P_X) = E_{DFE}(T=0) + \Delta\mu_X(P_X^\circ) \big|_{T=0}^{T=T} + kT \ln \left( \frac{P_X}{P_X^\circ} \right) \quad (15)$$

Equation 7 can be used along with equation 15 for HF and H<sub>2</sub>O allows us to evaluate the surface energies of different clean and hydroxylated AlF<sub>3</sub> surfaces as a function of HF and H<sub>2</sub>O partial pressure at fixed temperature and at a fixed value of  $\mu_{H_2}$ . The lowest energy surfaces can then be plotted as a function of  $\mu_{HF}$  and  $\mu_{H_2O}$ .

## II. LIMITING VALUES

In principle the limiting values of  $\mu_X(T, P_X)$  can be estimated or calculated. The lower limit is the value at which the compound decomposes into its constituent elements. At this point

$$\mu_{XY}(T, P_{XY}) = \mu_X(T, P_X) + \mu_Y(T, P_Y) \quad (16)$$

this limit can be obtained either from thermodynamic tables or via calculation of the energy of the components of the system in their standard states.

For example, considering the lower limit of F<sub>2</sub>, below which AlF<sub>3</sub> decomposes into Al<sub>(s)</sub> and F<sub>2</sub>, we obtain

$$\Delta G_{reaction} = G_{bulk}^{AlF_3} - G_{bulk}^{Al} - \frac{3}{2}G_{F_2} \quad (17)$$

$$= kT \ln\left(\frac{P_{F_2}}{P_{F_2}^\circ}\right) \quad (18)$$

$$\min[\mu_{F_2}] = \frac{2}{3}[G_{bulk}^{AlF_3} - G_{bulk}^{Al}] \quad (19)$$

This value can be obtained via the calculation of the energy of bulk Al and AlF<sub>3</sub>. However, often it is not possible within the given calculational scheme to obtain accurate results for both a metallic and ionic solid. It may therefore be preferable to obtain values from thermodynamical tables. The free energy of formation of crystalline AlF<sub>3</sub> is -14.8eV at standard temperature and pressure. This is equivalent to a partial pressure of F<sub>2</sub> of 10<sup>-170</sup> atm at 300K. Thus in this case the lower limit would be determined by the quality of the vacuum in the experiment.

Similarly, an upper limit can be defined as the point at which the constituent gases condense onto the surface of the material.

$$\mu_X^{\text{gaseous}}(T, P_X) = \mu_X^{\text{Condensed Phase}}(T, P_{tot}) \quad (20)$$

This value can again be obtained from thermodynamic tables provided data for a condensed phase exists for the given temperature and pressure. If not, it can be approximated as the point at which

$$\mu_X^*(T, P_X) = 0 \quad (21)$$

For example, the vapour pressure of H<sub>2</sub>O at 300K is 3.6x10<sup>-2</sup> atm, this corresponds to  $\mu^* = -0.57\text{eV}$ . However, in the temperature range that we are typically interested in data for the condensed phase of F<sub>2</sub> is not apparently available. We therefore take the maximum value of  $\mu_{F_2}$  to be the total energy of a isolated F<sub>2</sub> molecule at T=0K. The vapour pressure of HF at 300K is 1.3 atm, corresponding to  $\mu^* = -0.44\text{eV}$ . At 600K the condensed phase of both HF and H<sub>2</sub>O are not apparently available hence we set the maximum value of  $\mu^*$  to zero.

### III. OBTAINING $\Delta\mu(P^\circ)$ FROM THERMODYNAMIC TABLES

It is important that the values in equation 15 are evaluated correctly. In particular, care should be taken in calculating the term  $\Delta\mu_X(P_X^\circ)|_{T=0}^{T=T}$ . Values in tables are often given with respect to T = 298.15 K hence it is important to make a correction to T = 0 K.



As an example, we will consider obtaining  $\Delta\mu(P^\circ)|_{T=0}^{T=T}$  for HF using data from the NIST website<sup>8</sup>. The quantities  $C_p^\circ$ ,  $H^\circ - H_{298.15}^\circ$  and  $S^\circ$  are given as a function of temperature. For instance, at 600K  $C_p^\circ = 29.23 \text{ J mol}^{-1} \text{ K}^{-1}$ ,  $H^\circ - H_{298.15}^\circ = 8.80 \text{ kJ mol}^{-1}$  and  $S^\circ = 194.2 \text{ J mol}^{-1} \text{ K}^{-1}$ .

We can write

$$\Delta\mu_X(P_X^\circ)|_{T=0}^{T=T} = H^\circ - H_0^\circ - TS^\circ \quad (22)$$

Hence we also require the value of  $H_{298.15}^\circ - H_0^\circ$ . This has to be obtained separately, for instance from the CODATA tables<sup>9</sup>. Values for many molecules are also given on their website<sup>10</sup>. For instance,  $H_{298.15}^\circ - H_0^\circ = 8.599 \text{ kJ mol}^{-1}$  for HF. Hence,

$$\begin{aligned} \Delta\mu_{HF}(P_{HF}^\circ)|_{T=0}^{T=600K} &= (H^\circ - H_{298}^\circ) + (H_{298}^\circ - H_0^\circ) - TS^\circ \\ &= 8.80 \text{ kJ mol}^{-1} + 8.599 \text{ kJ mol}^{-1} - 600 \text{ K} \times 0.1942 \text{ kJ mol}^{-1} \text{ K}^{-1} \\ &= 99.121 \text{ kJ mol}^{-1} = -1.03 \text{ eV} \end{aligned} \quad (23)$$

#### IV. ENTROPY OF MIXING

In reality, however, the transition from one phase to another will not be immediate, consequently, mixing of two or more phases will occur. Entropy associated with the mixing of phases will reduce the energy of the surface. Calculating this entropy allows us to estimate the extent of mixing that will occur at these phase boundaries. Following the methodology developed by Reuter and Scheffler<sup>4</sup> we have calculated the configurational entropy,  $S^{config}$ , per unit surface area as

$$\frac{TS^{config}}{NA_{site}} = \frac{k_B T}{A_{site}} \left[ \ln \left( 1 + \frac{n}{N} \right) + \left( \frac{n}{N} \right) \ln \left( 1 + \frac{N}{n} \right) \right] \quad (24)$$

where  $A_{site}$  is the surface area per defect site,  $N$  is the number of surface sites and  $n$  is the number of defect sites in the limit of  $n/N \ll 1$ . If we set  $n/N = 0.1$ , then,

$$\frac{TS^{config}}{NA_{site}} = 0.335 \frac{k_B T}{A_{site}} \quad (25)$$

This is used to determine regions on our phase diagram where more than 10% mixing between adjacent phases is expected.

## V. THE ROLE OF $\mu_{H_2}$

The only source of fluorine and of hydroxyl groups in our formulism is HF and H<sub>2</sub>O respectively. The addition and subtraction of such groups introduces an explicit dependence of the surface energy on  $\mu_{H_2}$ . Consequently we need to assign a value to  $\mu_{H_2}$  in order to plot phase diagrams, although in practice this would be controlled via the gas phase equilibrium established within the experimental chamber. A first reference point is obtained by setting the chemical potential of H<sub>2</sub> to its saturation limit ( $\mu_{H_2}=0$ ). This corresponds to an extremely H<sub>2</sub> rich environment. At a fixed chemical potential of HF or H<sub>2</sub>O, lowering the value of  $\mu_{H_2}$  is equivalent to increasing the values of  $\mu_F$  and  $\mu_{OH}$  which stabilises F and OH rich surfaces respectively.

In order to assign a realistic value to  $\mu_{H_2}$  we note that the partial pressure of H<sub>2</sub> in air at 300K and 1 atm is typically  $5 \times 10^{-7}$  atm<sup>11</sup>. This can be converted to a chemical potential using the data from thermochemical tables<sup>7</sup>. This results in a classical chemical potential for H<sub>2</sub> of  $\mu_{H_2} = -0.5025$  eV.

## VI. AN EXAMPLE PHASE DIAGRAM

Figure 1 shows the phase diagram for the clean and hydroxylated  $\alpha$ -AlF<sub>3</sub> (0001) (1×2) surface as a function of H<sub>2</sub>O and HF chemical potentials and partial pressures at 300K and 600K. Only the stoichiometric surface and surfaces obtained from this surface via the substitution of F ions for OH ions are stable. As a consequence the phase diagram is independent of  $\mu_{H_2}$ . The highlighted areas on the diagram are regions where at least 10% of the neighbouring phase is expected to co-exist at 300K. It can be seen that under normal atmospheric conditions, assuming a partial pressure of HF of  $10^{-10}$  atm and H<sub>2</sub>O of  $1.8 \times 10^{-2}$  atm (50% humidity) the 2F 1OH and 1F 2OH are predicted to co-exist. Under reaction conditions (600K) assuming a partial pressure of HF of 1.0 atm and H<sub>2</sub>O of  $10^{-2}$  atm the 3F surface is predicted to be stable. A more detailed discussion of this diagram will be given elsewhere<sup>12</sup>. Within this phase diagram the adsorption of H<sub>2</sub>O and HF molecules to the surface has not been considered. However, this is a situation that is likely to occur. We are currently in the process of calculating the effect on the surface stability of such adsorbed species. Detailed discussion of the resultant phase diagrams will be presented elsewhere<sup>12</sup>.

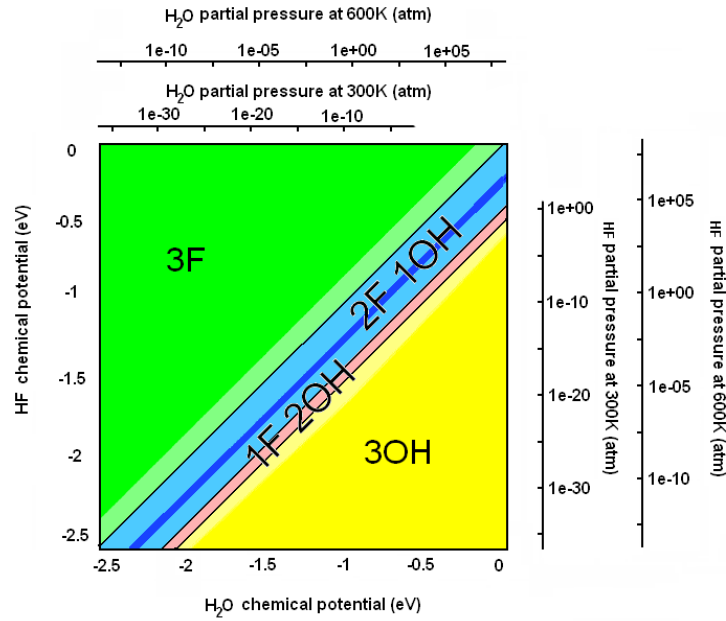


FIG. 1: The stability of clean and hydroxylated  $\alpha$ -AlF<sub>3</sub> (0001) (1×2) surfaces as a function of HF and H<sub>2</sub>O partial pressures. The pressure scale bars extend across the accessible range of partial pressures and terminate at -0.57eV for H<sub>2</sub>O and -0.44eV for HF at 300K as discussed in section II. Calculations for the  $\alpha$ -AlF<sub>3</sub>(01 $\bar{1}$ 2)(1×1) surface result in a very similar phase diagram<sup>12</sup>.

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