Formation Energy Analysis

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1 Configurational thermodynamics of defects

1.1 What is formation energy?

Using the first law of thermodynamics the energy dE is defined through the generic intensive (Y_k), i.e., system size independent, and the corresponding conjugate extensive variable (X_k). The sum over k runs over all conjugate variable pairs available to the system such as:

$$dE = \sum_k Y_k dX_k = TdS - PdV + \sum_i \mu_i dN_i + \sum_d E_f^d dN_d + ... \tag{1}$$

- Temperature T and entropy S.

- Pressure P and volume V.

- Chemical potential μ_i and number of atoms N_i of species i.

- Defect formation energy E_f^d and number of such defects N_d.

Then the formation energy can be computed as:

$$E_f^d = \frac{dE}{dN_d} \tag{2}$$

In a typical DFT supercell approach, the derivative in replaced with a finite difference:

$$E_f^d = E_{defect}(n_i + \Delta n_i) - E_{pristine}(n_i) - \sum_i \Delta n_i \mu_i \tag{3}$$

Δn_i: refers to the number of atoms of type i that have been added to $(\Delta n_i > 0)$ or removed from $(\Delta n_i < 0)$ the supercell to form the defect. To determine the required size of the supercell convergence tests are required.

1.1.1 How to find the limits of μ_i?

let's talk about MoS_2, the thermodynamics equilibrium conditions is:

$$\mu_{Mo} + 2\mu_S = E_{MoS_2}^{Bulk} \tag{4}$$

$$\mu_S = \frac{1}{2}(E_{MoS_2}^{Bulk} - \mu_{Mo}) \tag{5}$$

The lower of μ_S is when $\mu_{Mo} = \mu_{Mo}^{Bulk}$, so:

$$\mu_S^{min} = \frac{1}{2}(E_{MoS_2}^{Bulk} - \mu_{Mo}^{Bulk}) \tag{6}$$

And the upper bound is the ring Sulfur:

$$\mu_S^{max} = \frac{1}{N}E_{S8} = \mu_{S8} \tag{7}$$

The higher of μ_{Mo} is when $\mu_S = \mu_{S8}$, so:

$$\mu_{Mo}^{min} = (E_{MoS_2}^{Bulk} - 2\mu_{S8}) \tag{8}$$

However the upper bound is the Mo bulk BCC:

$$\mu_{Mo}^{max} = E_{Mo}^{Bulk} \tag{9}$$

Therefore,
$$E_{MoS_2}^{Bulk} - 2\mu_{S8} \leq \mu_{Mo} \leq \mu_{Mo}^{Bulk} \tag{10}$$

Also,
$$\frac{1}{2}(E_{MoS2} - \mu_{Mo}^{Bulk}) \leq \mu_S \leq \mu_{S8} \tag{11}$$

P.S: E_{MoS2} is the total energy of the primitive unitcell monolayer

1.2 Full Temperature contribution

As the temperature increases the electronic excitations or atomic vibrations will be significant along the configurational contribution, so it is convenient to consider the Gibbs energy of formation as $G(P,T) = F(V,T) + PV = E - TS + PV$.

$$\Delta G = G_f^d(P,T) = G_{defect}(P,T) - G_{pristine}(P,T) - \sum_i \Delta n_i \mu_i \tag{12}$$

$$G_f^d(P,T) = F_{defect}(P,T) - F_{pristine}(P,T) + P\Delta V - \sum_i \Delta n_i \mu_i \tag{13}$$

The total free energy of the system, can be expressed as a sum of the different contributions:

$$F(V,T) = E_{DFT}(V) + F^{el}(V,T) + F^{qh}(V,T) + F^{ah}(V,T) + F^{mag}(V,T). \tag{14}$$

- E_{DFT}: The total energy of the system.

- F^{el} : Electronic free energy of the static lattice.

- F^{qh}: the harmonic free energy.

- F^{ah}: the anharmonic free energy.

- F^{mg}: contribution of free energy in magnetic materials.

In this work for neutral defects of 2D TMDC monolayes, we are including only the harmonic free energy contribution that is calculated via the vibrational partition function Z of the system using statistical.

$$F^{qh} = \sum_i^{3N} [\frac{\hbar w_i}{2} + kTln[1 - \exp\frac{\hbar w_i}{kT}] \tag{15}$$

Therefore,

$$G_f^d(P,T) = E_{defect} - E_{pristine} + \Delta F^{qh}(T) + P\Delta V - \sum_i \Delta n_i \mu_i(P,T) \tag{16}$$

The only term that need to be defined here is $\mu_i(P,T)$: The chemical potentials of the atoms involved depend on temperature and partial pressure. The chemical potential of S8 has to be taken into account, for a Sulfur vacancy, that can be approximately treated as an ideal gas composed of N indistinguishable.

1.3 How to calculate chemical potential as function of temperature and pressure?

1.3.1 What is the partition function Z of S8 ring?

Using the born Oppenheimer approximation:

$$Z(V,T) = Z_{trans}(V,T)Z_{rot}(T)Z_{vib}(T)Z_{elec}(T) \tag{17}$$

Translational Part:

The partition function is obtained from a gas of N diatomic molecules, that have three translational degrees of freedom and inclosed in a rectangular box. The energy is defined as:

$$E = \frac{h^2}{8mL^2}(n_x^2 + n_y^2 + n_z^2) \tag{18}$$

Therefore,

$$Z = \sum_{n_x,n_y,n_z=1}^{\infty} exp(-\frac{\beta h^2}{8mL^2}n_x^2)exp(-\frac{\beta h^2}{8mL^2}n_y^2)exp(-\frac{\beta h^2}{8mL^2}n_z^2) \tag{19}$$

$$Z = [\sum_{n=1}^{\infty} exp(-\frac{\beta h^2}{8mL^2} n^2)]^3 \tag{20}$$

However, translational energy levels are spaced very dense then:

$$Z = (\int_{1}^{\infty} exp(-\frac{\beta h^2}{8mL^2} n^2))^3 dn \approx (\int_{0}^{\infty} exp(-\frac{\beta h^2}{8mL^2} n^2))^3 dn \tag{21}$$

Knowing that,

$$\int_{0}^{\infty} exp(-\alpha n^2) dn = \sqrt{\frac{\pi}{4\alpha}} \tag{22}$$

Thus,

$$Z = (\frac{2\pi m k T L^2}{h^2})^{\frac{3}{2}} = (\frac{2\pi m k T}{h^2})^{\frac{3}{2}} V \tag{23}$$

Rotational Part:

The rotational energy levels of a polyatomic molecule is obtained from the rigid rotor model, for asymmetrical top with three degrees of freedom in non-linear molecules. The partition function is defined as:

$$Z_{rot} = \frac{\pi^{\frac{1}{2}}}{\sigma} (\frac{8\pi I_A k T}{h^2})^{\frac{1}{2}} (\frac{8\pi I_B k T}{h^2})^{\frac{1}{2}} (\frac{8\pi I_C k T}{h^2})^{\frac{1}{2}} \tag{24}$$

Suchthat, $I's$ represents the moment of inertia along the principle axis of rotation of the molecule.

Vibrational Part:

For nonlinear molecule 3N-6, the vibrational energy is that of an independent harmonic oscillators as:

$$E_{vib} = \sum_{i}^{3N-6} (n_i + \frac{1}{2}) \hbar \omega_i \tag{25}$$

The vibrational partition function is given by the product of vibrational functions for each frequency.

$$Z_{vib} = \prod_{i}^{3N-6} \sum_{n=0}^{\infty} exp(-\beta E_{vib}) \tag{26}$$

$$Z_{vib} = \prod_{i}^{3N-6} \sum_{n=0}^{\infty} exp(-\beta (n_i + \frac{1}{2}) \hbar \omega_i) \tag{27}$$

$$Z_{vib} = \prod_{i}^{3N-6} exp(-\frac{\beta \hbar \omega_i}{2}) (\sum_{n=0}^{\infty} exp(-\beta \hbar \omega_i))^n \tag{28}$$

$$(\sum_{n=0}^{\infty} exp(-x))^n = \frac{1}{1-x} \tag{29}$$

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$$Z_{vib} = \prod_i^{3N-6} \frac{exp(-\frac{\beta\hbar\omega_i}{2})}{1 - exp(-\beta\hbar\omega_i)} \tag{30}$$

$$Z_{vib} = exp(-\frac{\sum_i \beta\hbar\omega_i}{2}) \prod_i^{3N-6} \frac{1}{1 - exp(-\beta\hbar\omega_i)} \tag{31}$$

Electronic Part:
Molecules can exist with electrons excited to states higher than the ground state. At ordinary temperatures, most of the molecules are usually in their ground state whose energy can be taken as zero. Therefore,

$$Z_e = g_1 exp(-\beta E_1) \tag{32}$$

The ground-state degeneracy, g_1, is one for most molecules.

1.4   How to connect to experimental data from tables?

Using ideal gas law at constant T:

$$dG = V dp \tag{33}$$

$$G - G^0 = \int_{p_0}^p V dp = \int_{p_0}^p \frac{NKT}{p} dp = NKT \ln \frac{p}{p_0} \tag{34}$$

If N is 1 mole then,

$$\Delta\mu = \mu - \mu^0 = RT \ln \frac{p}{p_0} \tag{35}$$

At equilibrium $\Delta\mu$=0, then

$$\mu = \mu^0 + kT \ln \frac{p}{p_0} \tag{36}$$

On the other hand, for an ideal gas the chemical potential is related to the partition function.

$$\mu = -kT \ln \frac{Z}{V} kT + kT \ln p \tag{37}$$

$$\mu = -kT \ln \frac{Z}{V} kT + kT \ln p + kT \ln \frac{p_0}{p_0} \tag{38}$$

$$\mu = -kT \ln \frac{Z}{V} \frac{kT}{p_0} + kT \ln \frac{p}{p_0} \tag{39}$$

Compare eq. (37) in (39):

$$\mu^0(T) = -kT \ln \frac{Z}{V} \frac{kT}{p_0} \tag{40}$$

Suchthat, p_0 is 1 atm.
The partition function Z can be written as:

$$Z(V,T) = Z_{trans}(V,T) Z_{rot}(T) Z_{vib}(T) Z_{elec}(T) \tag{41}$$

1.4.1 what about zero energy reference?

Concerning the Z_{elec}, the zero of energy convention is used, then:

$$Z_{elec}(T) = g_1 exp(-\frac{E_1}{kT}) + g_2 exp(-\frac{E_2}{kT}) + ... \tag{42}$$

We can choose the energy to be the ground state energy:

$$Z_{elec}(T) = g_1 exp(-\frac{E_1}{kT}) \tag{43}$$

Then,

$$Z_{elec}(T) = Z_{elec}^0(T)exp(E_{gs}) \tag{44}$$

Suchthat, $Z_{elec}^0(T)$ is the electronic partition function of a molecule with its ground state taken to be zero.

However, $Z_{trans}(V,T)$ and $Z_{rot}(T)$ are calculated on the basis that the lowest translational state is zero, so we can write them as $Z_{trans}^0(V,T)$ and $Z_{rot}^0(T)$. For $Z_{vib}(T)$ has a ground state vibration energy that is equal to $exp(-\sum_i \frac{\hbar\omega_i}{2})$. By convention this can be added to the electric exponential terms, thus, we get:

$$Z(V,T) = Z_{trans}^0(V,T)Z_{rot}^0(T)Z_{vib}^0(T)Z_{elec}^0(T)exp - (\beta E_1 + \sum_i \frac{\beta\hbar\omega_i}{2}) \tag{45}$$

Therefore, now,

$$Z(V,T) = Z^0 exp - (\beta E_1 + \sum_i \frac{\beta\hbar\omega_i}{2}) \tag{46}$$

Substituting it in eq.(23), we get:

$$\mu - \epsilon^0 = -kT \ln \frac{Z^0}{V} \frac{kT}{p_0} + kT \ln \frac{p}{p_0} \tag{47}$$

Suchthat,

$$\epsilon^0 = E_1 + \sum_i \frac{\beta\hbar\omega_i}{2} \tag{48}$$

Such that, E1 can be DFT calculated energy.

1.4.2 What is calculated from Thermodynamics tables?

As defined previously,

$$\mu^0(T) = \epsilon^0 - kT \ln \frac{Z^0}{V} \frac{kT}{p_0} \tag{49}$$

Then,

$$\frac{\mu^0(T) - \epsilon^0}{T} = -k \ln \frac{Z^0}{V} \frac{kT}{p_0} \tag{50}$$

Now multiplying by Avogadro's number,

$$-(\frac{G^0(T) - E^0}{T}) = R \ln \frac{Z^0}{V} \frac{kT}{p_0} \tag{51}$$

The factor in the right is what is calculated in the thermodynamics tables.

1.5 What is then μ for S8 ring?

$$\ln \frac{Z^0}{V} \frac{kT}{p_0} = \ln \frac{Z^0_{trans} kT}{V p_0} + \ln Z^0_{vib} + \ln Z^0_{rot} \tag{52}$$

$$\ln(\frac{Z^0_{trans} kT}{V}) = \ln[(\frac{2\pi m}{h^2})^{\frac{3}{2}} \frac{(kT)^{\frac{5}{2}}}{p_0}] \tag{53}$$

$$\ln Z^0_{vib} = -\sum_i^{3N-6} \ln(1 - exp(-\beta\hbar\omega_i)) \tag{54}$$

$$\ln Z^0_{rot} = \ln(\frac{\pi^{\frac{1}{2}}}{\sigma}(\frac{8\pi I_A kT}{h^2})^{\frac{1}{2}}(\frac{8\pi I_B kT}{h^2})^{\frac{1}{2}}(\frac{8\pi I_C kT}{h^2})^{\frac{1}{2}}) \tag{55}$$

$$\ln Z^0_{rot} = \ln(\frac{\pi^{\frac{1}{2}}}{\sigma}) + \ln((\frac{8\pi kT}{h^2})^{\frac{3}{2}} I_A^{\frac{1}{2}} I_B^{\frac{1}{2}} I_C^{\frac{1}{2}}) \tag{56}$$

$$\mu^0 = -kT \ln \frac{Z^0}{V} \frac{kT}{p_0} = -kT \ln[(\frac{2\pi m}{h^2})^{\frac{3}{2}} \frac{(kT)^{\frac{5}{2}}}{p_0}] - kT \ln(\frac{\pi^{\frac{1}{2}}}{\sigma}) -$$
$$kT \ln((\frac{8\pi kT}{h^2})^{\frac{3}{2}} I_A^{\frac{1}{2}} I_B^{\frac{1}{2}} I_C^{\frac{1}{2}}) + kT \sum_i^{3N-6} \ln(1 - exp(-\beta h\omega_i)) \tag{57}$$

The full temperature and pressure chemical potential is then:

$$\mu = -kT \ln[(\frac{2\pi m}{h^2})^{\frac{3}{2}} \frac{(kT)^{\frac{5}{2}}}{p_0}] - kT \ln(\frac{\pi^{\frac{1}{2}}}{\sigma}) -$$
$$kT \ln((\frac{8\pi kT}{h^2})^{\frac{3}{2}} I_A^{\frac{1}{2}} I_B^{\frac{1}{2}} I_C^{\frac{1}{2}}) + kT \sum_i^{3N-6} \ln(1 - exp(-\beta h\omega_i))$$
$$+ kT \ln \frac{p}{p_0} + E_{DFT} + \sum_i \frac{\hbar\omega_i}{2kT} \tag{58}$$

1.6 Calculating μ^0 from thermodynamics tables

From thermodynamics at 500 k, $-(\frac{G^0(T) - E^0}{T})$ is equal 34.78 $J.k^{-1}.mol^{-1}$

- $I_A = I_B =$ 791.35901439 amuA^2=$1.314051643394595 \times 10^{-37}$ g.cm^2

- $I_C =$ 1461.37283288 amuA^2=$2.42660958899724 \times 10^{-37}$ g.cm^2

- $\sigma =$8

- R=8.31446261815324 $J.k^{-1}.mol^{-1}$

- k= 1.380649×10^{-16} g.$cm^2/(s^2.K)$

- h=$6.62607015 \times 10^{-27} g.cm^2/s$
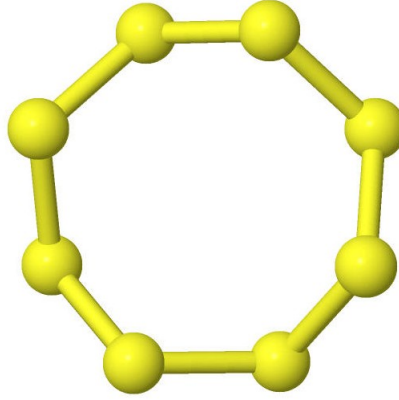
- $\hbar =$1.054571817$\times 10^{-27} g.cm^2/s$

Figure 1: S8 ring

- $m = \sum_i m_{i,S}$=32.06*6= 192.36 amu=$3.1941378 \times 10^{-22}$ g
- p_0=1 atm= 1013250 $g/(cm.s^2)$

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1.7 What is the chemical potential of bulk Mo?

2 What is point defect concentration?

3 Appendix

Another form of writing the chemical potential of an ideal gas is:

$$\mu = \frac{1}{N}(-kT \ln Z + PV) \tag{59}$$

$$\mu = \frac{1}{N}(-kT \ln \frac{z^N}{N!} + PV) \tag{60}$$

$$\mu = \frac{-kT}{N} \ln z^N + \frac{kT}{N}(N \ln N - N) + kT \tag{61}$$

$$\mu = -kT \ln z + kT \ln N \tag{62}$$

$$\mu = -kT \ln z + kT \ln \frac{PV}{kT} \tag{63}$$

$$\mu = -kT \ln \frac{zKT}{V} + kT \ln p + kT \ln \frac{p_0}{p_0} \tag{64}$$

$$\mu = -kT \ln \frac{zKT}{p_0 V} + kT \ln \frac{p}{p_0} \qquad (65)$$

That is the same as eq. (23).

4   References

[1] [2] [3] [4] [5] [6]

References

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