Exercise 6 Hydrogen on graphite

a) The reference value should be two atoms at infinite separation (left image) at 2.51 eV. The dimers A and B has hence a binding energy of -2.51 eV (0.0 eV in Figure 1). Dimer I has binding energy of -2.51+1.17 = -1.34 eV.

b) Assuming that the desorption rate is purely determined by the binding energy loss, $R_{\text{des}} = \nu \exp(-E_{\text{bind}}/(kT)) = 10^{12} \cdot \exp(-(2.51-0.6)/(k_{\text{B}}T))$ for dimers A and B using $k_{\text{B}} = 8.617 \cdot 10^{-5}$ eV K^{-1}.

c) For A to I: $R_{\text{diff}} = \nu \exp(-E_{\text{diff}}/(kT)) = 10^{12} \cdot \exp(-1.63/(k_{\text{B}}T))$
For B to I: $R_{\text{diff}} = \nu \exp(-E_{\text{diff}}/(kT)) = 10^{12} \cdot \exp(-1.67/(k_{\text{B}}T))$
For I to A: $R_{\text{diff}} = \nu \exp(-E_{\text{diff}}/(kT)) = 10^{12} \cdot \exp(-0.46/(k_{\text{B}}T))$
For I to B: $R_{\text{diff}} = \nu \exp(-E_{\text{diff}}/(kT)) = 10^{12} \cdot \exp(-0.5/(k_{\text{B}}T))$

d) $\frac{R_{\text{diff}}^{A\to I}}{R_{\text{diff}}^{I\to A}} = \exp(-(1.63-0.46)/(k_{\text{B}}T)) = \exp(-\Delta E//(k_{\text{B}}T))$
$\frac{R_{\text{diff}}^{A\to I}}{R_{\text{diff}}^{I\to A}} = \exp(-(1.67-0.5)/(k_{\text{B}}T)) = \exp(-\Delta E//(k_{\text{B}}T))$

e) The figure includes diffusion pairs where one diffusion leads to a energy lowering by ΔE and the reverse by an energy increase of ΔE.

$$\frac{R_{\text{diff}}^{forwards}}{R_{\text{diff}}^{backwards}} = \frac{\exp(-(A+B\Delta E)/(k_{\text{B}}T))}{\exp(-(A-B\Delta E)/(k_{\text{B}}T))} = \exp(-2B\Delta E/(k_{\text{B}}T))$$

Detailed balance is fulfilled if $B = 0.5$, which is in accordance with the results.

f) Normally the new time is determined using

$$\ln(X) = -\int_{t_{\text{start}}}^{t_{\text{end}}} R_{\text{tot}} \mathrm{d}t'$$

which leads to

$$t_{\text{end}} = t_{start} - \frac{\ln(X)}{R_{\text{tot}}}.$$

Now we have

$$\ln(X) = -\int_{t_{\text{start}}}^{t_{\text{current}}} R_{\text{tot}}^{\text{old}} \mathrm{d}t' - \int_{t_{\text{current}}}^{t_{\text{end}}} R_{\text{tot}}^{\text{new}} \mathrm{d}t' = R_{\text{tot}}^{\text{old}}(t_{\text{current}} - t_{\text{start}}) - R_{\text{tot}}^{\text{new}}(t_{\text{end}} - t_{\text{current}})$$

$$t_{\text{end}} = -\frac{\ln(X) + R_{\text{tot}}^{\text{old}}(t_{\text{current}} - t_{\text{start}})}{R_{\text{tot}}^{\text{new}}} + t_{\text{current}}$$

Hence we will need to store the original $\ln(X)$, the old total rate and the time at which the original time was set.