Supplement of
Technical Note: Classical and statistical thermodynamic treatment of adsorption and desorption kinetics and rates

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S1 Definition of desorption and adsorption equilibrium constants

When defining the equilibrium constant and thermodynamic quantities, the subscripts describe the process direction in the order of (from left to right) process (adsorption or desorption), educt, and product. We are defining the equilibrium between the adsorbed 2D ideal gas and the 3D ideal gas as

$$X_{ads,2D} \leftrightarrow X_g, \text{ and } K^0_{des,2D,g} = \frac{a_g}{a_{ads,2D}} = \frac{\frac{(N_g/\mathcal{V})}{(N_g/\mathcal{V})^0}}{\frac{(N_{ads}/\mathcal{A})}{(N_{ads}/\mathcal{A})^0}} = \frac{\frac{(N_g/\mathcal{V})}{(N_A/\mathcal{V}^0_m)}}{\frac{(N_{ads})}{(N_A/\mathcal{A}^0_m)}}. \quad (1)$$

We define the equilibrium between the adsorbed 2D ideal lattice gas and the 3D ideal gas as

$$X_{ads,latt} \leftrightarrow X_g, \text{ and } K^0_{des,latt,g} = \frac{a_g}{a_{ads,latt}} = \frac{\frac{(N_g/\mathcal{V})}{(N_g/\mathcal{V})^0}}{\frac{(\theta/(1-\theta))}{(\theta^0/(1-\theta^0))}} = \frac{\frac{(N_g/\mathcal{V})}{(N_A/\mathcal{V}^0_m)}}{\frac{(\theta/(1-\theta))}{(\theta^0/(1-\theta^0))}}. \quad (2)$$

We define the equilibrium between the adsorbed 2D ideal gas and the TS for desorption as

$$X_{ads,2D} \leftrightarrow X_{TS}, \text{ and } K^0_{des,2D,TS} = \frac{a_{TS}}{a_{ads,2D}} = \frac{\frac{(N_{TS}/\mathcal{A})}{(N_{TS}/\mathcal{A})^0}}{\frac{(N_{ads}/\mathcal{A})}{(N_{ads}/\mathcal{A})^0}} = \frac{\frac{(N_{TS}/\mathcal{A})}{(N_A/\mathcal{A}^0_m)}}{\frac{(N_{ads})}{(N_A/\mathcal{A}^0_m)}}. \quad (3)$$

We define the equilibrium between the adsorbed 2D ideal lattice gas and the TS for desorption as

$$X_{ads,latt} \leftrightarrow X_{TS}, \text{ and } K^0_{des,latt,TS} = \frac{a_{TS}}{a_{ads,latt}} = \frac{\frac{(N_{TS}/\mathcal{A})}{(N_{TS}/\mathcal{A})^0}}{\frac{(\theta/(1-\theta))}{(\theta^0/(1-\theta^0))}} = \frac{\frac{(N_{TS}/\mathcal{A})}{(N_A/\mathcal{A}^0_m)}}{\frac{(\theta/(1-\theta))}{(\theta^0/(1-\theta^0))}}. \quad (4)$$

We define the equilibrium between the 3D ideal gas and the TS for adsorption as (note that the direction is different now, TS is the product)

$$X_g \leftrightarrow X_{TS}, \text{ and } K^0_{ads,g,TS} = \frac{a_{TS}}{a_g} = \frac{\frac{(N_{TS}/\mathcal{A})}{(N_{TS}/\mathcal{A})^0}}{\frac{(N_g/\mathcal{V})}{(N_g/\mathcal{V})^0}} = \frac{\frac{(N_{TS}/\mathcal{A})}{(N_A/\mathcal{A}^0_m)}}{\frac{(N_g/\mathcal{V})}{(N_A/\mathcal{V}^0_m)}}. \quad (5)$$

S2 Derivation of thermodynamic functions for desorption and adsorption

This section establishes the partition functions and their relationship to thermodynamic variables for desorption and adsorption considering the 3D ideal gas, 2D ideal gas, 2D ideal lattice gas, and transition state. The 3D gas case is reiterated here for reference and comparison to the other cases.

S2.1 Calculation of molecular and molar thermodynamic functions for the 3D ideal gas

With $= q^N/N!$, using Stirling's approximation, we can approximate:

$$\ln Q = N \ln q - \ln N! \approx N \ln q - N \ln N + N \, . \tag{6}$$

Considering translations in 3 dimensions only for a gas, $\frac{q_g}{\mathcal{V}} = (2\pi m k_B T/h^2)^{3/2}$, yields (Atkins et al., 2006)

$$q_g = \frac{\mathcal{V}}{\Lambda^3} = \mathcal{V}\left(\frac{2\pi m}{h^2 \beta}\right)^{3/2} = \mathcal{V}(2\pi m k_B T/h^2)^{3/2} \tag{7}$$

$$\text{with } \Lambda = h\left(\frac{\beta}{2\pi m}\right)^{1/2} = \frac{h}{(2\pi m k_B T)^{1/2}} \qquad \text{and } \beta = \frac{1}{k_B T} \, . \tag{8}$$

We can now derive the thermodynamic functions. The inner energy is

$$U_g - U_g(0) = -\left(\frac{\partial \ln Q_g}{\partial \beta}\right)_{\mathcal{V}} = -N_g \left(\frac{\partial \ln q_g}{\partial \beta}\right)_{\mathcal{V}} = -\frac{N_g}{q_g}\left(\frac{\partial q_g}{\partial \beta}\right)_V = -N_g \left(\frac{\Lambda^3}{\mathcal{V}}\right)\left(-\frac{3\mathcal{V}}{2\beta\Lambda^3}\right) = \frac{3}{2} N_g k_B T. \tag{9}$$

Note that the energy reference is set such that for $T = 0$, $U_g(0) = 0$, and thus

$$U_g = \frac{3}{2} N_g k_B T \text{ and } U_{g,m} = \frac{U_g}{n_g} = \frac{3}{2} RT \, . \tag{10}$$

For the enthalpy we derive

$$H_g - H_g(0) = -\left(\frac{\partial \ln Q_g}{\partial \beta}\right)_{\mathcal{V}} + k_B T \mathcal{V}\left(\frac{\partial \ln Q_g}{\partial \mathcal{V}}\right)_T = \frac{3}{2} N_g k_B T + \frac{N_g k_B T \mathcal{V}}{q_g}\left(\frac{\partial q_g}{\partial \mathcal{V}}\right)_T = \frac{3}{2} N_g k_B T + \frac{N_g k_B T V \Lambda^3}{\mathcal{V}} \frac{1}{\Lambda^3} = \frac{3}{2} N_g k_B T +$$

$$N_g k_B T = \frac{5}{2} N_g k_B T \, . \tag{11}$$

In this case, the reference conditions is in such a way that for $T = 0$, $H_g(0) = 0$, and thus $H_g = \frac{5}{2} N_g k_B T$ and $H_{g,m} = \frac{H_g}{n_g} =$

$$\frac{5}{2} RT \, . \tag{12}$$

For the Gibbs' free energy, we derive

$$G_g - G_g(0) = -k_B T \ln Q_g + k_B T \mathcal{V}\left(\frac{\partial \ln Q_g}{\partial \mathcal{V}}\right)_T = -k_B T N_g \ln q_g + k_B T\left(N_g \ln N_g - N_g\right) + N_g k_B T = -N_g k_B T \ln\left(\frac{q_g}{N_g}\right). \tag{13}$$

Note that the energy reference is set such that for $T = 0$, $G_g(0) = U_g(0) = 0$.

$$\text{Expressed in molar quantities: } G_{g,m} = -RT \ln\left(\frac{q_{g,m}}{N_A}\right). \tag{14}$$

Lastly, we derive the entropy for the 3D ideal gas as

$$S_g = \frac{U_g - U_g(0)}{T} + k_B \ln Q_g = \frac{3}{2} N_g k_B + N_g k_B \ln q_g - N_g k_B \ln N_g + N_g k_B = N_g k_B \left(\ln\left(e^{3/2}\right) + \ln q_g - \ln N_g + \ln e\right) =$$

$$N_g k_B \ln\left(\frac{e^{5/2} q_g}{N_g}\right) \tag{15}$$

Expressed in molar quantities, we can write

$$S_{g,m} = R \ln\left(\frac{e^{5/2} q_g}{N_g}\right) = R \ln\left(\frac{e^{5/2} q_{g,m}}{N_A}\right) = R \ln\left(\frac{e^{5/2}\left(2\pi m k_B T/h^2\right)^{3/2}}{(N_g/\mathcal{V})}\right) = R \ln\left(\frac{e^{5/2}\left(2\pi m k_B T/h^2\right)^{3/2}}{\left(\frac{p}{k_B T}\right)}\right). \tag{16}$$

The last expression is the Sackur-Tetrode equation (Atkins et al., 2006).

The chemical potential, μ_g, can be derived in the following way (Hill, 1986), accounting for the standard concentrations:

$$\mu_g(T) - \mu_g(0) = \frac{G_g - G_g(0)}{N_g} = -k_B T \left(\frac{\partial \ln Q_g}{\partial N_g}\right)_{T,\mathcal{V}} = -k_B T \ln \frac{q_g}{N_g} = -k_B T \ln\left[\left(\frac{2\pi m}{h^2 \beta}\right)^{3/2} \frac{1}{\mathcal{N}_g}\right] = -k_B T \ln\left[\left(\frac{2\pi m}{h^2 \beta}\right)^{3/2} \frac{1}{\mathcal{N}_g} \frac{\frac{N_A}{\mathcal{V}_m^0}}{\frac{N_A}{\mathcal{V}_m^0}}\right] =$$

$$-k_B T \ln\left[\left(\frac{2\pi m}{h^2 \beta}\right)^{3/2} \frac{1}{\frac{p}{k_B T}} \frac{\frac{p^0}{k_B T}}{\frac{p^0}{k_B T}}\right] = -k_B T \ln\left[\left(\frac{2\pi m}{h^2 \beta}\right)^{3/2} \frac{k_B T}{p^0} \frac{p^0}{p}\right] = -k_B T \ln\left[\left(\frac{2\pi m}{h^2 \beta}\right)^{3/2} \frac{kT}{p^0}\right] + k_B T \ln \frac{p}{p^0}. \tag{17}$$

The last term we identify with

$$\mu_g(T) - \mu_g(0) = \mu_g^0(T) + k_B T \ln \frac{p}{p^0}, \tag{18}$$

so that we can express the standard chemical potential of the ideal 3D gas as

$$\mu_g^0(T) = -k_B T \ln\left[\left(\frac{2\pi m}{h^2 \beta}\right)^{3/2} \frac{kT}{p^0}\right]. \tag{19}$$

Note that the energy reference is set such that for $T = 0$, $G_g(0) = U_g(0) = 0$, and thus also $\mu_g(0) = \mu_g^0(0) = 0$. With this we obtain the common general expression for the chemical potential of an ideal gas

$$\mu_g(T) = \mu_g^0(T) + k_B T \ln \frac{p}{p^0}.$$

S2.2 Calculation of molecular and molar thermodynamic functions for molecules adsorbed as 2D ideal gas

For the 2D ideal gas of adsorbates on a surface, the canonical ensemble still represents independent indistinguishable non-interacting molecules on the surface, as in the 3D ideal gas case. With $\frac{q_{trans,2D}}{\mathcal{A}} = (2\pi m k_B T/h^2)$, we can write

$$q_{trans,2D} = \frac{\mathcal{A}}{\Lambda^2} = \mathcal{A}\left(\frac{2\pi m}{h^2 \beta}\right)^{2/2} = \mathcal{A}(2\pi m k_B T/h^2)^{2/2}, \tag{20}$$

with

$$\Lambda = h\left(\frac{\beta}{2\pi m}\right)^{1/2} = \frac{h}{(2\pi m k_B T)^{1/2}} \text{ and } \beta = \frac{1}{k_B T}. \tag{21}$$

If the adsorbed molecule still has vibrations in the z-direction, this adds a factor $q_{z,vib}$. Then the overall partition function for the ideal 2D gas is

$$q_{ads,2D} = q_{trans,2D} q_{z,vib}. \tag{22}$$

Here, we just consider $q_{ads,2D} = q_{trans,2D}$ and obtain

$$U_{ads,2D} - U_{ads,2D}(0) = -N_{ads}\left(\frac{\partial \ln q_{ads,2D}}{\partial \beta}\right)_{\mathcal{A}} = -\frac{N_{ads}}{q_{ads,2D}}\left(\frac{\partial q_{ads,2D}}{\partial \beta}\right)_{\mathcal{A}} = -N_{ads}\left(\frac{\Lambda^2}{\mathcal{A}}\right)\left(-\frac{\mathcal{A}}{\beta\Lambda^2}\right) = N_{ads}k_BT\ . \quad (23)$$

The energy reference for the inner energy is the gas phase molecule at rest ($T = 0\ K$). The adsorbed molecule is at the bottom of a potential well, at $-q_{des}^0$ with q_{des}^0 being a positive number indicating the necessary heat for the molecule to desorb. At constant volume, the change in heat equals the change in inner energy. At $T = 0\ K$, $U_{ads,2D}(0) = -N_{ads}q_{des}^0 = -\varepsilon_{des}^0$, thus,

$$U_{ads,2D} = N_{ads}k_BT - \varepsilon_{des}^0 \quad (24)$$

and in molar quantities with $E_{des}^0 = N_A q_{des}^0$

$$U_{ads,2D,m} = RT - E_{des}^0\ . \quad (25)$$

As a reminder, E_{des}^0 represents the depth of the potential well in molar units and has a positive value. Similarly, for the enthalpy we can write

$$H_{ads,2D} - H_{ads,2D}(0) = -\left(\frac{\partial \ln Q_{ads,2D}}{\partial \beta}\right)_{\mathcal{A}} + k_BT\mathcal{A}\left(\frac{\partial \ln Q_{ads,2D}}{\partial \mathcal{A}}\right)_T = N_{ads}k_BT + \frac{N_{ads}k_BT\mathcal{A}}{q_{ads,2D}}\left(\frac{\partial q_{ads,2D}}{\partial \mathcal{A}}\right)_T = N_{ads}k_BT +$$

$$\frac{N_{ads}k_BT\mathcal{A}\Lambda^2}{\mathcal{A}}\frac{1}{\Lambda^2} = N_{ads}k_BT + N_{ads}k_BT = 2N_{ads}k_BT\quad . \quad (26)$$

Also, here at $T = 0\ K$:

$$H_{ads,2D}(0) = -N_{ads}q_{des}^0 = -\varepsilon_{des}^0, \text{ thus, } H_{ads,2D} = 2N_{ads}k_BT - \varepsilon_{des}^0 \quad (27)$$

and

$$H_{ads,2D,m} = 2RT - E_{des}^0\ . \quad (28)$$

Following with the derivation of Gibbs' free energy

$$G_{ads,2D} - G_{ads,2D}(0) = -k_BT\ln Q_{ads,2D} + k_BT\mathcal{A}\left(\frac{\partial \ln Q_{ads,2D}}{\partial \mathcal{A}}\right)_T = -k_BTN_{ads}\ln q_{ads,2D} + k_BT(N_{ads}\ln N_{ads} - N_{ads}) +$$

$$N_{ads}k_BT = -N_{ads}k_BT\ln\left(\frac{q_{ads,2D}}{N_{ads}}\right). \quad (29)$$

At T = 0 K, $G_{ads,2D}(0) = U_{ads,2D}(0) = -N_{ads}q_{des}^0 = -\varepsilon_{des}^0$, thus, we obtain

$$G_{ads,2D} = -N_{ads}k_BT\ln\left(\frac{q_{ads,2D}}{N_{ads}}\right) - \varepsilon_{des}^0\ . \quad (30)$$

In molar quantities, as above for the ideal 3D gas, we obtain

$$G_{ads,2D,m} = -RT\ln\left(\frac{q_{ads,2D,m}}{N_A}\right) - E_{des}^0 = -RT\ln\left(\frac{q_{ads,2D,m}}{N_A}e^{\frac{E_{des}^0}{RT}}\right), \quad (31)$$

while $q_{ads,2D,m}$ reflects only 2 translations and vibrations.

Lastly, for the entropy we can write

$$S_{ads,2D} = \frac{U_{ads,2D} - U_{ads,2D}(0)}{T} + k_B\ln Q_{ads,2D} = N_{ads}k_B + N_{ads}k_B\ln q_{ads,2D} - N_{ads}k_B\ln N_{ads} + N_{ads}k_B = N_{ads}k_B\big(\ln e +$$

$$\ln q_{ads,2D} - \ln N_{ads} + \ln e\big) = N_{ads}k_B\ln\left(\frac{e^2 q_{ads,2D}}{N_{ads}}\right), \quad (32)$$

with the molar quantities

$$S_{ads,2D,m} = R\ln\left(\frac{e^2 q_{ads,2D}}{N_{ads}}\right) = R\ln\left(\frac{e^2 q_{ads,2D,m}}{N_A}\right) = R\ln\left(\frac{e^2\mathcal{A}\left(2\pi m k_B T/h^2\right)^{2/2}}{N_{ads}}\right). \quad (33)$$

This is the equivalent of the Sackur-Tetrode equation in 2 dimensions.

The chemical potential for a mono-atomic 2D ideal gas can be derived in a similar way as shown above for the 3D ideal gas and considering that there are only 2 translational degrees of freedom (Hill, 1986)

$$\mu_{ads,2D}(T) - \mu_{ads,2D}(0) = \frac{G_{ads,2D} - G_{ads,2D}(0)}{N_{ads}} = -k_B T\left(\frac{\partial \ln Q_{ads,2D}}{\partial N_{ads}}\right)_{T,\mathcal{A}} = -k_B T\ln\frac{q_{ads,2D}}{N_{ads}} = -k_B T\ln\left[\left(\frac{2\pi m}{h^2\beta}\right)^{\frac{2}{2}}\frac{1}{\mathcal{N}_{ads}}\right] =$$

$$-k_B T\ln\left[\left(\frac{2\pi m}{h^2\beta}\right)^{\frac{2}{2}}\frac{\mathcal{A}}{N_{ads}}\frac{\frac{N_A}{\mathcal{A}_m^0}}{\frac{N_A}{\mathcal{A}_m^0}}\right] = -k_B T\ln\left[\left(\frac{2\pi m}{h^2\beta}\right)^{\frac{2}{2}}\frac{\mathcal{A}_m^0}{N_A}\frac{1}{a_{ads,2D}}\right] = -k_B T\ln\left[\left(\frac{2\pi m}{h^2\beta}\right)^{\frac{2}{2}}\frac{\mathcal{A}_m^0}{N_A}\right] + k_B T\ln a_{ads,2D}\,. \quad (34)$$

Since $\mu_{ads,2D}(0) = \frac{G_{ads,2D}(0)}{N_{ads}} = \frac{U_{ads,2D}(0)}{N_{ads}} = -q_{des}^0$, we obtain

$$\mu_{ads,2D}(T) = -k_B T\ln\left[\left(\frac{2\pi m}{h^2\beta}\right)^{\frac{2}{2}}\frac{\mathcal{A}_m^0}{N_A}\right] + k_B T\ln a_{ads,2D} - q_{des}^0 = -k_B T\ln\left[\left(\frac{2\pi m}{h^2\beta}\right)^{\frac{2}{2}}\frac{\mathcal{A}_m^0}{N_A}e^{\frac{q_{des}^0}{k_B T}}\right] + k_B T\ln a_{ads,2D} =$$

$$-k_B T\ln\left[\left(\frac{2\pi m}{h^2\beta}\right)^{\frac{2}{2}}\frac{\mathcal{A}_m^0}{N_A}e^{\frac{E_{des}^0}{RT}}\right] + k_B T\ln a_{ads,2D}\,. \quad (35)$$

Applying

$$\mu_{ads,2D}(T) = \mu_{ads,2D}^0(T) + k_B T\ln a_{ads,2D}\,, \quad (36)$$

we can express the standard chemical potential of the adsorbed ideal 2D gas as

$$\mu_{ads,2D}^0(T) = -k_B T\ln\left[\left(\frac{2\pi m}{h^2\beta}\right)\frac{\mathcal{A}_m^0}{N_A}e^{\frac{E_{des}^0}{RT}}\right]. \quad (37)$$

S2.3 Calculation of molecular and molar thermodynamic functions for molecules adsorbed as 2D ideal lattice gas

For the 2D ideal lattice gas, no translations are allowed, and the adsorbed molecules have three vibrational degrees of freedom, leading to (Hill, 1986)

$$q_{ads,latt} = q_{x,vib}q_{y,vib}q_{z,vib}\,. \quad (38)$$

For the vibrational partition function q_{vib}, we can write, setting the zero-point level ($\varepsilon_0 = \frac{1}{2}h\nu$) as 0 (Atkins et al., 2006),

$$q_{vib} = \frac{1}{1-e^{-\beta h\nu}}\,. \quad (39)$$

In the 2D lattice gas model, N adsorbed molecules distribute over M equivalent but distinguishable sites, leading to the canonical partition function being:

$$Q = \frac{M!q^N}{N!(M-N)!} \qquad \ln Q = M\ln M - N\ln N - (M-N)\ln(M-N) + N\ln q \quad (40)$$

It is worthwhile noting that this approach holds for a solid and liquid surface as long as the number of adsorption sites is given by M. In other words, the partition function does not consider how the M sites are distributed over the surface and time.

Using the definition of $\theta = \frac{N_{ads}}{M}$, this can also be written as:

$$\ln Q_{ads,latt} = \frac{N_{ads}}{\theta}\ln\frac{N_{ads}}{\theta} - N_{ads}\ln N_{ads} - \left(\frac{N_{ads}}{\theta} - N_{ads}\right)\ln\left(\frac{N_{ads}}{\theta} - N_{ads}\right) + N_{ads}\ln q_{ads,latt} = -\frac{N_{ads}}{\theta}\ln(1-\theta) +$$

$$N_{ads}\ln\left(\frac{1-\theta}{\theta}\right) + N_{ads}\ln q_{ads,latt} \quad . \tag{41}$$

For the thermodynamic functions, the number of sites M is the new variable that replaces the area (used in the 2D ideal gas) or the volume used in the 3D ideal gas as variables:

$$U_{ads,latt} - U_{ads,latt}(0) = -\left(\frac{\partial \ln Q_{ads,latt}}{\partial\beta}\right)_M = -N_{ads}\left(\frac{\partial \ln q_{ads,latt}}{\partial\beta}\right)_M = -\frac{N_{ads}}{q_{ads,latt}}\left(\frac{\partial q_{ads,latt}}{\partial\beta}\right)_M = \frac{N_{ads}\cdot h\nu}{e^{\beta h\nu}-1}. \tag{42}$$

Like the case of the 2D ideal gas, the adsorbed molecule resides in the bottom of the potential well:

$$U_{ads,latt}(0) = -N_{ads}q_{des}^0 = -\varepsilon_{des}^0, \tag{43}$$

and thus

$$U_{ads,latt} = \frac{N_{ads}\cdot h\nu}{e^{\beta h\nu}-1} - \varepsilon_{des}^0 \ . \tag{44}$$

In molar quantities, we derive

$$U_{ads,latt,m} = \frac{N_A\cdot h\nu}{e^{\beta h\nu}-1} - E_{des}^0 \ . \tag{45}$$

Note that the partition function of vibration does not depend on surface area and thus molecular partition functions are used here and for the remainder of the 2D ideal lattice gas discussion.

For the enthalpy of an adsorbed 2D ideal lattice gas, we obtain

$$H_{ads,latt} - H_{ads,latt}(0) = -\left(\frac{\partial \ln Q_{ads,latt}}{\partial\beta}\right)_M + k_BTM\left(\frac{\partial \ln Q_{ads,latt}}{\partial M}\right)_T = -\frac{N_{ads}}{q_{ads,latt}}\left(\frac{\partial q_{ads,latt}}{\partial\beta}\right) + k_BTM\ln\left(\frac{M}{M-N_{ads}}\right) =$$

$$-\frac{N_{ads}}{q_{ads,latt}}\left(\frac{\partial q_{ads,latt}}{\partial\beta}\right) + k_BT\frac{N_{ads}}{\theta}(-\ln(1-\theta)) = -\frac{N_{ads}}{q_{ads,latt}}\left(\frac{\partial q_{ads,latt}}{\partial\beta}\right) - k_BT\frac{N_{ads}}{\theta}\ln(1-\theta) = \frac{N_{ads}\cdot h\nu}{e^{\beta h\nu}-1} - k_BT\frac{N_{ads}}{\theta}\ln(1-$$

$$\theta) \ . \tag{46}$$

Also, here at $T = 0\ K$:

$$H_{ads,latt}(0) = -N_{ads}q_{des}^0 = -\varepsilon_{des}^0 \ . \tag{47}$$

We obtain

$$H_{ads,latt} = \frac{N_{ads}\cdot h\nu}{e^{\beta h\nu}-1} - k_BT\frac{N_{ads}}{\theta}\ln(1-\theta) - \varepsilon_{des}^0 \ . \tag{48}$$

In molar quantities, we can derive

$$H_{ads,latt,m} = \frac{N_A\cdot h\nu}{e^{\beta h\nu}-1} - RT\frac{\ln(1-\theta)}{\theta} - E_{des}^0 \ . \tag{49}$$

For the Gibbs free energy, we derive

$$G_{ads,latt} - G_{ads,latt}(0) = -k_BT\ln Q_{ads,latt} + k_BTM\left(\frac{\partial \ln Q_{ads,latt}}{\partial M}\right)_T = -k_BT\left(-\frac{N_{ads}}{\theta}\ln(1-\theta) + N_{ads}\ln\left(\frac{(1-\theta)}{\theta}\right) +\right.$$

$$\left. N_{ads}\ln q_{ads,latt}\right) - k_BT\frac{N_{ads}}{\theta}\ln(1-\theta) = -N_{ads}k_BT\ln q_{ads,latt} - N_{ads}k_BT\ln\left(\frac{(1-\theta)}{\theta}\right) = N_{ads}k_BT\ln\left(1-e^{-\beta h\nu}\right) -$$

$$N_{ads}k_BT\ln\left(\frac{(1-\theta)}{\theta}\right). \tag{50}$$

At $T = 0\ K$, $G_{ads,latt}(0) = U_{ads,latt}(0) = -N_{ads}q_{des}^{0} = -\varepsilon_{des}^{0}$, thus, we obtain

$$G_{ads,latt} = N_{ads}k_BT\ln\left(1 - e^{-\beta h\nu}\right) - N_{ads}k_BT\ln\left(\frac{(1-\theta)}{\theta}\right) - \varepsilon_{des}^{0}\ . \quad (51)$$

Expressed in molar quantities:

$$G_{ads,latt,m} = -RT\ln q_{ads,latt} - RT\ln\left(\frac{(1-\theta)}{\theta}\right) - E_{des}^{0} = RT\ln\left(1 - e^{-\beta h\nu}\right) - RT\ln\left(\frac{(1-\theta)}{\theta}\right) - E_{des}^{0}\ . \quad (52)$$

Lastly, we derive the entropy of the adsorbed 2D ideal lattice gas:

$$S_{ads,latt} = \frac{U_{ads,latt} - U_{ads,latt}(0)}{T} + k_B\ln Q_{ads,latt} =$$

$$\frac{-\frac{N_{ads}}{q_{ads,latt}}\left(\frac{\partial q_{ads,latt}}{\partial\beta}\right)}{T} + k_B\left(-\frac{N_{ads}}{\theta}\ln(1-\theta) + N_{ads}\ln\left(\frac{(1-\theta)}{\theta}\right) + N_{ads}\ln q_{ads,latt}\right) = \frac{-\frac{N_{ads}k_B}{q_{ads,latt}}\left(\frac{\partial q_{ads,latt}}{\partial\beta}\right)}{k_BT} +$$

$$k_BN_{ads}\ln q_{ads,latt} + k_BN_{ads}\ln\left(\frac{(1-\theta)}{\theta}\right) - k_B\frac{N_{ads}}{\theta}\ln(1-\theta) = N_{ads}k_B\left(\ln q_{ads,latt} - \beta\left(\frac{\partial\ln q_{ads,latt}}{\partial\beta}\right)\right) +$$

$$N_{ads}k_B\left(\ln\left(\frac{(1-\theta)}{\theta}\right) - \frac{\ln(1-\theta)}{\theta}\right) = S_{ads,latt,vib} + S_{ads,latt,config}. \quad (53)$$

In molar quantities:

$$S_{ads,latt,m} = R\left(\ln q_{ads,latt} - \beta\left(\frac{\partial\ln q_{ads,latt}}{\partial\beta}\right)\right) + R\left(\ln\left(\frac{(1-\theta)}{\theta}\right) - \frac{\ln(1-\theta)}{\theta}\right). \quad (54)$$

The chemical potential of the adsorbed 2D ideal lattice gas can be derived in the following way:

$$\mu_{ads,latt}(T) - \mu_{ads,latt}(0) = \frac{G_{ads,latt} - G_{ads,latt}(0)}{N_{ads}} = -k_BT\left(\frac{\partial\ln Q_{ads,latt}}{\partial N_{ads}}\right)_{T,M} = k_BT\left(-\ln N_{ads} + \ln N_{ads} + \ln\left(\frac{M}{N_{ads}} - 1\right) +\right.$$

$$\left.\ln q_{ads,latt} = \ln\theta - \ln(1-\theta) - \ln q_{ads,latt}\right) = k_BT\ln\left(\frac{\theta}{(1-\theta)q_{ads,latt}}\right). \quad (55)$$

Accounting for the standard surface coverage, keeping the same dependence as θ, we can write (Hill, 1986;Campbell et al., 2016)

$$\mu_{ads,latt}(T) - \mu_{ads,latt}(0) = k_BT\ln\left(\frac{\theta}{(1-\theta)q_{ads,latt}}\right) = k_BT\ln\left[\frac{1}{q_{ads,latt}}\frac{\theta}{(1-\theta)}\frac{\frac{\theta^0}{1-\theta^0}}{\frac{\theta^0}{1-\theta^0}}\right] = -k_BT\ln\left[q_{ads,latt}\frac{1-\theta^0}{\theta^0}\right] +$$

$$k_BT\ln\left[\frac{\frac{\theta}{(1-\theta)}}{\frac{\theta^0}{1-\theta^0}}\right] = -k_BT\ln\left[q_{ads,latt}\frac{1-\theta^0}{\theta^0}\right] + k_BT\ln a_{ads,latt}\ . \quad (56)$$

Since $\mu_{ads,latt}(0) = \frac{G_{ads,latt}(0)}{N_{ads}} = \frac{U_{ads,latt}(0)}{N_{ads}} = -q_{des}^{0}$, we obtain

$$\mu_{ads,latt}(T) = -k_BT\ln\left[q_{ads,latt}\frac{1-\theta^0}{\theta^0}\right] + k_BT\ln a_{ads,latt} - q_{des}^{0} = -k_BT\ln\left[q_{ads,latt}\frac{1-\theta^0}{\theta^0}e^{\frac{q_{des}^{0}}{k_BT}}\right] + k_BT\ln a_{ads,latt} =$$

$$-k_BT\ln\left[q_{ads,latt}\frac{1-\theta^0}{\theta^0}e^{\frac{E_{des}^{0}}{RT}}\right] + k_BT\ln a_{ads,latt}\ . \quad (57)$$

Applying

$$\mu_{ads,latt}(T) = \mu_{ads,latt}^{0}(T) + k_BT\ln a_{ads,latt}\ , \quad (58)$$

we can express the standard chemical potential of the adsorbed 2D ideal lattice gas as

$$\mu^0_{ads,latt}(T) = -k_B T \ln\left[q_{ads,latt}\frac{1-\theta^0}{\theta^0}e^{\frac{E^0_{des}}{RT}}\right]. \quad (59)$$

S2.4 Calculation of molecular and molar thermodynamic functions for molecules in the transition state for desorption or adsorption

The TS for desorption is assumed to exist at some fixed distance from the surface but within a very thin layer of thickness d. The molecules do not have any interactions with the surface, but it is activated to an energy level according to the barrier height above the gas phase reference. According to TS theory, the molecules are moving in the direction of the reaction coordinate (thus desorption or adsorption) with the mean thermal velocity. They are treated as a 2D ideal gas in the plane parallel to the surface, but they feature translation in the direction orthogonal to it, which is confined to d. Therefore, when omitting vibrations, the total partition function is

$$q_{TS} = q_{TS,2D}q_{TS,des} = \frac{\mathcal{A}}{\Lambda^2}\frac{d}{\Lambda} = \mathcal{A}\left(\frac{2\pi m}{h^2\beta}\right)^{2/2} d\left(\frac{2\pi m}{h^2\beta}\right)^{1/2} = \mathcal{A}d\left(\frac{2\pi m}{h^2\beta}\right)^{3/2} = \mathcal{A}d\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} = \frac{\mathcal{A}d}{\Lambda^3}, \quad (60)$$

$$\text{with } \Lambda = h\left(\frac{\beta}{2\pi m}\right)^{1/2} = \frac{h}{(2\pi m k_B T)^{1/2}} \text{ and } \beta = \frac{1}{k_B T}. \quad (61)$$

The partition function of the TS is made up of the partition function of the TS confined to two dimensions similar to a 2D ideal gas ($q_{TS,2D}$) and the one dimensional translation ($q_{TS,des}$). Thus, overall, the partition function of the TS is similar to that of a 3D ideal gas, confined, however, to a thin layer.

The energy reference for the inner energy is the gas phase molecule at rest ($T = 0\ K$). The molecule in the TS does not have any interactions with the surface, but is activated to the level of the energy barrier for desorption or adsorption. Hence, for the inner energy, we obtain

$$U_{TS} - U_{TS}(0) = -\left(\frac{\partial \ln Q_{TS}}{\partial\beta}\right)_{\mathcal{A}} = -N_{TS}\left(\frac{\partial \ln q_{TS}}{\partial\beta}\right)_{\mathcal{A}} = -\frac{N_{TS}}{q_{TS}}\left(\frac{\partial q_{TS}}{\partial\beta}\right)_{\mathcal{A}} = -N_{TS}\left(\frac{\Lambda^3}{\mathcal{A}d}\right)\left(-\frac{3\mathcal{A}d}{2\beta\Lambda^3}\right) = \frac{3}{2}N_{TS}k_B T \quad (62)$$

Since the molecule in the TS does not have any interactions with the surface but sits on top of the energy barrier, q^0_b, thus, we obtain at $T = 0\ K$, $U_{TS}(0) = N_{TS}q^0_b = \varepsilon^0_b$, so that:

$$U_{TS} = \frac{3}{2}N_{TS}k_B T + \varepsilon^0_b \quad (63)$$

and in molar quantities

$$U_{TS,m} = \frac{3}{2}RT + E^0_b. \quad (64)$$

The inner energy of the TS includes the two translations in the horizontal and the orthogonal translation along the reaction axis. In contrast, the activation inner energy associated with the TS corresponds to the TS with the translational motion along the desorption or adsorption direction omitted, and thus, is similar to a 2D gas. Here, the activation process can be conceptionally envisioned by bringing the molecules in the 2D ideal gas from the zero-point energy to the actual energy level that allows for the formation of the TS. In other words, without bringing up the adsorbed molecules to the actual energy level,

desorption cannot progress. For the remainder of the manuscript the subscript "*act*" refers to the TS described as a 2D ideal gas. Therefore, we obtain the corresponding inner energy of activation, neglecting vibrations:

$$U_{act} - U_{act}(0) = -N_{TS}\left(\frac{\partial \ln q_{TS,2D}}{\partial \beta}\right)_{\mathcal{A}} = -\frac{N_{ads}}{q_{ads,2D}}\left(\frac{\partial q_{TS,2D}}{\partial \beta}\right)_{\mathcal{A}} = -N_{TS}\left(\frac{\Lambda^2}{\mathcal{A}}\right)\left(-\frac{\mathcal{A}}{\beta\Lambda^2}\right) = N_{TS}k_BT\ , \quad (65)$$

with $U_{act}(0) = \varepsilon_b^0$ and in molar quantities

$$U_{act,m} = RT + E_b^0\ . \quad (66)$$

For the enthalpy, we proceed analogously:

$$H_{TS} - H_{TS}(0) = -\left(\frac{\partial \ln Q_{TS}}{\partial \beta}\right)_{\mathcal{A}} + k_BT\mathcal{A}\left(\frac{\partial \ln Q_{TS}}{\partial \mathcal{A}}\right)_T = \frac{3}{2}N_{TS}k_BT + \frac{N_{TS}k_BT\mathcal{A}}{q_{TS}}\left(\frac{\partial q_{TS}}{\partial \mathcal{A}}\right)_T = \frac{3}{2}N_{TS}k_BT + \frac{N_{TS}k_BT\mathcal{A}\Lambda^3}{d\mathcal{A}}\frac{d}{\Lambda^3} =$$

$$\frac{3}{2}N_{TS}k_BT + N_{TS}k_BT = \frac{5}{2}N_{TS}k_BT. \quad (67)$$

For the same reasons as above, the reference conditions are in such a way that for $T = 0$, $H_{TS}(0) = \varepsilon_b^0$, and thus

$$H_{TS} = \frac{5}{2}N_{TS}k_BT + \varepsilon_b^0 \text{ and } H_{TS,m} = \frac{H_{TS}}{n_{TS}} = \frac{5}{2}RT + E_b^0\ . \quad (68)$$

Correspondingly, for the enthalpy of activation (assuming 2D ideal gas only), we obtain

$$H_{act} = 2N_{TS}k_BT + \varepsilon_b^0 \text{ and } H_{act,m} = 2RT + E_b^0 \quad (69)$$

Following with the derivation of Gibbs' free energy

$$G_{TS} - G_{TS}(0) = -k_BT\ln Q_{TS} + k_BT\mathcal{A}\left(\frac{\partial \ln Q_{TS}}{\partial \mathcal{A}}\right)_T = -k_BTN_{TS}\ln q_{TS} + k_BT(N_{TS}\ln N_{TS} - N_{TS}) + N_{TS}k_BT =$$

$$-N_{TS}k_BT\ln\left(\frac{q_{TS}}{N_{TS}}\right). \quad (70)$$

At T = 0 K, $G_{TS}(0) = U_{TS}(0) = \varepsilon_b^0$, thus, we obtain

$$G_{TS} = -N_{TS}k_BT\ln\left(\frac{q_{TS}}{N_{TS}}\right) + \varepsilon_b^0\ . \quad (71)$$

In molar quantities, we obtain

$$G_{TS,m} = -RT\ln\left(\frac{q_{TS,m}}{N_A}\right) + E_b^0. \quad (72)$$

The Gibbs' free energy of activation, which does not include the motion along the desorption coordinate, is derived as, with $G_{act}(0) = U_{act}(0) = \varepsilon_b^0$,

$$G_{act} = -N_{TS}k_BT\ln\left(\frac{q_{TS}}{q_{TS,des}N_{TS}}\right) + \varepsilon_b^0 = -N_{TS}k_BT\ln\left(\frac{q_{TS,2D}}{N_{TS}}\right) + \varepsilon_b^0 \quad (73)$$

and

$$G_{act,m} = -RT\ln\left(\frac{q_{TS,m}}{q_{TS,des}N_A}\right) + E_b^0 = -RT\ln\left(\frac{q_{TS,2D,m}}{N_A}\right) + E_b^0. \quad (74)$$

Lastly, for the entropy we write

$$S_{TS} = \frac{U_{TS} - U_{TS}(0)}{T} + k_B\ln Q_{TS} = \frac{3}{2}N_{TS}k_B + N_{TS}k_B\ln q_{TS} - N_{TS}k_B\ln N_{TS} + N_{TS}k_B = N_{TS}k_B\big(\ln e + \ln q_{TS} - \ln N_{TS} +$$

$$\ln e^{3/2}\big) = Nk_B\ln\left(\frac{e^{5/2}q_{TS}}{N_{TS}}\right), \quad (75)$$

with the corresponding molar quantities

$$S_{TS,m} = R\ln\left(\frac{e^{5/2}q_{TS}}{N_{TS}}\right) = R\ln\left(\frac{e^{5/2}q_{TS,m}}{N_A}\right) = R\ln\left(\frac{e^{5/2}\mathcal{A}d\left(2\pi m k_B T/h^2\right)^{3/2}}{N_{TS}}\right). \quad (76)$$

For the activation entropy, we obtain

$$S_{act,m} = R\ln\left(\frac{e^{2}q_{TS,2D}}{N_{TS}}\right) = R\ln\left(\frac{e^{2}q_{TS,2D,m}}{N_A}\right) = R\ln\left(\frac{e^{2}\mathcal{A}\left(2\pi m k_B T/h^2\right)^{2/2}}{N_{TS}}\right). \quad (77)$$

The chemical potential for the TS can be derived the following way

$$\mu_{TS}(T) - \mu_{TS}(0) = \frac{G_{TS}-G_{TS}(0)}{N_{TS}} = -k_B T\left(\frac{\partial \ln Q_{TS}}{\partial N_{TS}}\right)_{T,\mathcal{A}} = -k_B T\ln\frac{q_{TS}}{N_{TS}} = -k_B T\ln\left[\left(\frac{2\pi m}{h^2\beta}\right)^{\frac{3}{2}}\frac{d}{\mathcal{N}_{TS}}\right] =$$

$$-k_B T\ln\left[\left(\frac{2\pi m}{h^2\beta}\right)^{\frac{3}{2}}\frac{d\mathcal{A}}{N_{TS}}\frac{\frac{N_A}{\mathcal{A}_m^0}}{\frac{N_A}{\mathcal{A}_m^0}}\right] = -k_B T\ln\left[\left(\frac{2\pi m}{h^2\beta}\right)^{\frac{3}{2}} d\frac{\mathcal{A}_m^0}{N_A}\frac{1}{a_{TS}}\right] = -k_B T\ln\left[\left(\frac{2\pi m}{h^2\beta}\right)^{\frac{3}{2}} d\frac{\mathcal{A}_m^0}{N_A}\right] + k_B T\ln a_{TS}\,. \quad (78)$$

Since $\mu_{TS}(0) = \frac{G_{TS}(0)}{N_{TS}} = \frac{U_{TS}(0)}{N_{TS}} = q_b^0$, we obtain

$$\mu_{TS}(T) = -k_B T\ln\left[\left(\frac{2\pi m}{h^2\beta}\right)^{\frac{3}{2}} d\frac{\mathcal{A}_m^0}{N_A}\right] + k_B T\ln a_{TS} + q_b^0. \quad (79)$$

Applying

$$\mu_{TS}(T) = \mu_{TS}^0(T) + k_B T\ln a_{TS}\,, \quad (80)$$

we can express the standard chemical potential of the TS as

$$\mu_{TS}^0(T) = -k_B T\ln\left[\left(\frac{2\pi m}{h^2\beta}\right)^{\frac{3}{2}} d\frac{\mathcal{A}_m^0}{N_A}\right] + q_b^0\,. \quad (81)$$

The chemical potential for the activated state can be derived the following way

$$\mu_{act}(T) - \mu_{act}(0) = \frac{G_{act}-G_{act}(0)}{N_{TS}} = -N_{TS}k_B T\ln\left(\frac{q_{TS}}{q_{TS,des}N_{TS}}\right) = -N_{TS}k_B T\ln\left(\frac{q_{TS,2D}}{N_{TS}}\right) = -k_B T\ln\left[\left(\frac{2\pi m}{h^2\beta}\right)^{\frac{2}{2}}\frac{1}{\mathcal{N}_{TS}}\right] =$$

$$-k_B T\ln\left[\left(\frac{2\pi m}{h^2\beta}\right)^{\frac{2}{2}}\frac{\mathcal{A}}{N_{TS}}\frac{\frac{N_A}{\mathcal{A}_m^0}}{\frac{N_A}{\mathcal{A}_m^0}}\right] = -k_B T\ln\left[\left(\frac{2\pi m}{h^2\beta}\right)\frac{\mathcal{A}_m^0}{N_A}\frac{1}{a_{TS}}\right] = -k_B T\ln\left[\left(\frac{2\pi m}{h^2\beta}\right)\frac{\mathcal{A}_m^0}{N_A}\right] + k_B T\ln a_{TS}\,. \quad (82)$$

Since $\mu_{act}(0) = \frac{G_{act}(0)}{N_{TS}} = \frac{U_{act}(0)}{N_{TS}} = q_b^0$, we obtain

$$\mu_{act}(T) = -k_B T\ln\left[\left(\frac{2\pi m}{h^2\beta}\right)\frac{\mathcal{A}_m^0}{N_A}\right] + k_B T\ln a_{TS} + q_b^0\,. \quad (83)$$

Applying

$$\mu_{act}(T) = \mu_{act}^0(T) + k_B T\ln a_{TS}\,, \quad (84)$$

we can express the standard chemical potential of activation as

$$\mu_{act}^0(T) = -k_B T\ln\left[\left(\frac{2\pi m}{h^2\beta}\right)\frac{\mathcal{A}_m^0}{N_A}\right] + q_b^0\,. \quad (85)$$

S3 Standard molar enthalpies, entropies, and Gibbs free energies

For the relationship to the equilibrium constant, we need the standard molar Gibbs free energies. Those are derived in the following subsections for the 3D ideal gas, 2D ideal gas, 2D ideal lattice gas, and TS.

S3.1 3D ideal gas

$$H_{g,m} = -\left(\frac{\partial \ln Q_{g,m}}{\partial \beta}\right)_{\mathcal{V}} + k_B T\mathcal{V}\left(\frac{\partial \ln Q_{g,m}}{\partial \mathcal{V}}\right)_T = \frac{3}{2}RT + \frac{RT\mathcal{V}}{q_{g,m}}\left(\frac{\partial q_{g,m}}{\partial \mathcal{V}}\right)_T = \frac{3}{2}RT + RT = \frac{5}{2}RT \quad (86)$$

and

$$H^0_{g,m} = -\left(\frac{\partial \ln Q^0_{g,m}}{\partial \beta}\right)_{\mathcal{V}} + k_B T\mathcal{V}\left(\frac{\partial \ln Q^0_{g,m}}{\partial \mathcal{V}}\right)_T = \frac{3}{2}RT + \frac{RT\mathcal{V}^0_m}{q^0_{g,m}}\left(\frac{\partial q^0_{g,m}}{\partial \mathcal{V}^0_m}\right)_T = \frac{3}{2}RT + RT = \frac{5}{2}RT. \quad (87)$$

$$S_{g,m} = R\ln\left(\frac{e^{5/2}q_{g,m}}{N_A}\right) = R\ln\left(\frac{e^{5/2}\left(2\pi m k_B T/h^2\right)^{3/2}}{\left(N_g/\mathcal{V}\right)}\right) \quad (88)$$

and

$$S^0_{g,m} = R\ln\left(\frac{e^{5/2}q^0_{g,m}}{N_A}\right) = R\ln\left(\frac{e^{5/2}\left(2\pi m k_B T/h^2\right)^{3/2}}{\left(N_g/\mathcal{V}\right)^0}\right). \quad (89)$$

$$G_{g,m} = -RT\ln\left(\frac{q_{g,m}}{N_A}\right) \quad (90)$$

and

$$G^0_{g,m} = -RT\ln\left(\frac{q^0_{g,m}}{N_A}\right), \quad (91)$$

with $q^0_{g,m} = \mathcal{V}^0_m(2\pi m k_B T/h^2)^{3/2}$, (92)

where the standard molar partition function $q^0_{g,m}$ is the molar partition function evaluated using the standard molar volume $\mathcal{V}^0_m$.

S3.2 Adsorbed 2D ideal gas

$$H_{ads,2D,m} - H_{ads,2D,m}(0) = 2RT - E^0_{des} \quad (93)$$

and

$$H^0_{ads,2D,m} - H^0_{ads,2D,m}(0) = -\left(\frac{\partial \ln Q^0_{ads,2D,m}}{\partial \beta}\right)_{\mathcal{A}^0_m} + k_B T\mathcal{A}^0_m\left(\frac{\partial \ln Q^0_{ads,2D,m}}{\partial \mathcal{A}^0_m}\right)_T - E^0_{des} = RT + \frac{RT\mathcal{A}^0_m}{q_{ads,2D,m}}\left(\frac{\partial q_{ads,2D,m}}{\partial \mathcal{A}^0_m}\right)_T - E^0_{des} = 2RT - E^0_{des}. \quad (94)$$

$$S_{ads,2D,m} = R\ln\left(\frac{e^2 q_{ads,2D,m}}{N_A}\right) = R\ln\left(\frac{e^2\left(2\pi m k_B T/h^2\right)^{2/2}}{\left(N_{ads}/\mathcal{A}\right)}\right) \quad (95)$$

and

$$S^0_{ads,2D,m} = R\ln\left(\frac{e^2 q^0_{ads,2D,m}}{N_A}\right) = R\ln\left(\frac{e^2\left(2\pi m k_B T/h^2\right)^{2/2}}{(N_{ads}/\mathcal{A})^0}\right). \quad (96)$$

$$G_{ads,2D,m} = -RT\ln\left(\frac{q_{ads,2D,m}}{N_A}\right) - E^0_{des} \quad (97)$$

and

$$G^0_{ads,2D,m} = -RT\ln\left(\frac{q^0_{ads,2D,m}}{N_A}\right) - E^0_{des}, \quad (98)$$

$$\text{with } q^0_{ads,2D,m} = \mathcal{A}^0_m(2\pi m k_B T/h^2)\,, \quad (99)$$

where the standard molar partition function $q^0_{ads,2D,m}$ is the molar partition function evaluated using the standard molar area $\mathcal{A}^0_m$.

S3.3 Adsorbed ideal 2D lattice gas

$$H_{ads,latt,m} = \frac{N_A\cdot h\nu}{e^{\beta h\nu}-1} - RT\frac{\ln(1-\theta)}{\theta} - E^0_{des} \quad (100)$$

and

$$H^0_{ads,latt,m} = \frac{N_A\cdot h\nu}{e^{\beta h\nu}-1} - RT\frac{\ln\left(1-\theta^0\right)}{\theta^0} - E^0_{des}\,. \quad (101)$$

$$S_{ads,latt,m} = R\left(\ln q_{ads,latt} - \beta\left(\frac{\partial \ln q_{ads,latt}}{\partial\beta}\right)\right) + R\left(\ln\left(\frac{(1-\theta)}{\theta}\right) - \frac{\ln(1-\theta)}{\theta}\right) \quad (102)$$

and

$$S^0_{ads,latt,m} = R\left(\ln q_{ads,latt} - \beta\left(\frac{\partial \ln q_{ads,latt}}{\partial\beta}\right)\right) + R\left(\ln\left(\frac{(1-\theta^0)}{\theta^0}\right) - \frac{\ln(1-\theta^0)}{\theta^0}\right). \quad (103)$$

$$G_{ads,latt,m} = -RT\ln q_{ads,latt} - RT\ln\left(\frac{(1-\theta)}{\theta}\right) - E^0_{des} \quad (104)$$

and

$$G^0_{ads,latt,m} = -RT\ln q^0_{ads,latt} - RT\ln\left(\frac{(1-\theta^0)}{\theta^0}\right) - E^0_{des}\,. \quad (105)$$

Note that in the first term, the molecular partition function is used (not the molar). Because the vibrational q_{vib} are independent of the surface coverage,

$$q_{ads,latt} = q_{x,vib}q_{y,vib}q_{z,vib} = \frac{1}{1-e^{-\beta h\nu}}\,. \quad (106)$$

S3.4 Transition state for desorption or adsorption

$$H_{TS,m} = H^0_{TS,m} = \frac{H_{TS}}{n_{TS}} = \frac{5}{2}RT + E^0_b \quad (107)$$

and

$$H_{act,m} = H^0_{act,m} = 2RT + E^0_b \quad (108)$$

$$S_{TS,m} = R \ln\left(\frac{e^{5/2} q_{TS,m}}{N_A}\right) = R \ln\left(\frac{e^{5/2} \mathcal{A} d \left(2\pi m k_B T/h^2\right)^{3/2}}{N_{TS}}\right) \quad (109)$$

and

$$S^0_{TS,m} = R \ln\left(\frac{e^{5/2} q^0_{TS,m}}{N_A}\right) = R \ln\left(\frac{e^{5/2} d \left(2\pi m k_B T/h^2\right)^{3/2}}{(N_{TS}/\mathcal{A})^0}\right). \quad (110)$$

$$S_{act,m} = R \ln\left(\frac{e^{2} q_{TS,2D,m}}{N_A}\right) = R \ln\left(\frac{e^{2} \mathcal{A} \left(2\pi m k_B T/h^2\right)^{2/2}}{N_{TS}}\right) \quad (111)$$

and

$$S^0_{act,m} = R \ln\left(\frac{e^{2} q^0_{TS,2D,m}}{N_A}\right) = R \ln\left(\frac{e^{2} \left(2\pi m k_B T/h^2\right)^{2/2}}{(N_{TS}/\mathcal{A})^0}\right). \quad (112)$$

$$G_{TS,m} = -RT \ln\left(\frac{q_{TS,m}}{N_A}\right) + E^0_b \quad (113)$$

and

$$G^0_{TS,m} = -RT \ln\left(\frac{q^0_{TS,m}}{N_A}\right) + E^0_b. \quad (114)$$

$$G_{act,m} = -RT \ln\left(\frac{q_{TS,2D,m}}{N_A}\right) + E^0_b \quad (115)$$

and

$$G^0_{act,m} = -RT \ln\left(\frac{q^0_{TS,2D,m}}{N_A}\right) + E^0_b\,, \quad (116)$$

with $q^0_{TS,m} = q^0_{TS,2D,m} q_{TS,des} = \mathcal{A}^0_m d (2\pi m k_B T/h^2)^{3/2}$ (117)

and $q^0_{TS,2D,m} = \mathcal{A}^0_m (2\pi m k_B T/h^2)$, (118)

where the standard molar partition function $q^0_{TS,m}$ is the molar partition function evaluated using the standard molar area $\mathcal{A}^0_m$. Note that the thickness d as part of $q_{TS,des}$ remains as is and is not normalized to a standard length. $q_{TS,des}$ acts as a multiplicator to the standard molecular partition function of the 2D ideal gas and remains specified by the thickness of the layer assumed.

S4 Derivation of Equilibrium Constants

Here, we derive the thermodynamic functions that describe the equilibrium constants between the gas phase and the adsorbed state for the different adsorbate models and TS.

4.1 Standard molar thermodynamic functions and equilibrium constant between 2D ideal gas and 3D ideal gas

The standard molar change in Gibbs free energy for desorption from a 2D ideal gas is given by:

$$\Delta G^0_{des,2D,g,m} = G^0_{g,m} - G^0_{ads,2D,m} = -RT\ln\left(\frac{q^0_{g,m}}{N_A}\right) - \left[-RT\ln\left(\frac{q^0_{ads,2D,m}}{N_A}\right) - E^0_{des}\right] = E^0_{des} - RT\ln\left[\frac{\left(\frac{q^0_{g,m}}{N_A}\right)}{\left(\frac{q^0_{ads,2D,m}}{N_A}\right)}\right] =$$

$$-RT\left[\frac{-E^0_{des}}{RT} + \ln\left[\frac{\left(\frac{q^0_{g,m}}{N_A}\right)}{\left(\frac{q^0_{ads,2D,m}}{N_A}\right)}\right]\right]. \quad (119)$$

For the change in enthalpy, we can write

$$\Delta H^0_{des,2D,g,m} = H_{g,m} - H_{ads,2D,m} = \frac{5}{2}RT - 2RT + E^0_{des} = \frac{1}{2}RT + E^0_{des}\,. \quad (120)$$

For the change in entropy, we derive

$$\Delta S^0_{des,2D,g,m} = S^0_{g,m} - S^0_{ads,2D,m} = R\ln\left(\frac{e^{5/2}q^0_{g,m}}{N_A}\right) - R\ln\left(\frac{e^2 q^0_{ads,2D,m}}{N_A}\right) = R\ln\left(\frac{e^{1/2}q^0_{g,m}}{q^0_{ads,2D,m}}\right). \quad (121)$$

The equilibrium constant, $K^0_{ads,2D,g}$, is also related to the free energy change, $\Delta G^0_{ads,2D,g,m}$, via

$$K^0_{des,2D,g} = e^{-\Delta G^0_{des,2D,g,m}/RT}\,. \quad (122)$$

We can, thus, express the equilibrium constant as

$$K^0_{des,2D,g} = \frac{\left(\frac{q^0_{g,m}}{N_A}\right)}{\left(\frac{q^0_{ads,2D,m}}{N_A}\right)} e^{-\frac{E^0_{des}}{RT}} = \frac{q^0_{g,m}}{q^0_{ads,2D,m}} e^{-\frac{E^0_{des}}{RT}}\,. \quad (123)$$

When setting in the expressions for the standard molar partition functions:

$$K^0_{des,2D,g} = \frac{\mathcal{V}^0_m(2\pi m k_B T/h^2)^{3/2}}{\mathcal{A}^0_m(2\pi m k_B T/h^2)} e^{-\frac{E^0_{des}}{RT}} = \frac{\mathcal{V}^0_m}{\mathcal{A}^0_m}(2\pi m k_B T/h^2)^{1/2} e^{-\frac{E^0_{des}}{RT}} = \frac{(N_{ads}/\mathcal{A})^0}{(N_g/\mathcal{V})^0}(2\pi m k_B T/h^2)^{1/2} e^{-\frac{E^0_{des}}{RT}}\,. \quad (124)$$

We should obtain the same result, when assuming equilibrium and using the chemical potential of the gas and the adsorbed 2D ideal gas:

$$\mu_g(T) = \mu^0_g(T) + k_B T\ln\frac{p}{p^0} = \mu_{ads,2D}(T) = \mu^0_{ads,2D}(T) + k_B T\ln a_{ads,2D}\,. \quad (125)$$

We use above derivations to write

$$-k_B T\ln\left[\left(\frac{2\pi m}{h^2\beta}\right)^{\frac{3}{2}}\frac{kT}{p^0}\right] + k_B T\ln\frac{p}{p^0} = -k_B T\ln\left[\left(\frac{2\pi m}{h^2\beta}\right)^{\frac{2}{2}}\frac{\mathcal{A}^0_m}{N_A}e^{\frac{E^0_{des}}{RT}}\right] + k_B T\ln a_{ads,2D}\,, \quad (126)$$

$$-k_B T\ln\left[\frac{q_g}{\mathcal{V}}\frac{\mathcal{V}^0_m}{N_A}\right] + k_B T\ln\frac{\mathcal{N}_g}{\frac{N_A}{\mathcal{V}^0_m}} = -k_B T\ln\left[\frac{q_{ads,2D}}{\mathcal{A}}\frac{\mathcal{A}^0_m}{N_A}e^{\frac{E^0_{des}}{RT}}\right] + k_B T\ln\left[\frac{\mathcal{N}_{ads}}{\frac{N_A}{A^0_m}}\right]. \quad (127)$$

Rearranging terms yields

$$k_B T\ln\frac{\mathcal{N}_g}{\frac{N_A}{\mathcal{V}^0_m}} - k_B T\ln\left[\frac{\mathcal{N}_{ads}}{\frac{N_A}{A^0_m}}\right] = k_B T\ln\left[\frac{q_g}{\mathcal{V}}\frac{\mathcal{V}^0_m}{N_A}\right] - k_B T\ln\left[\frac{q_{ads,2D}}{\mathcal{A}}\frac{\mathcal{A}^0_m}{N_A}e^{\frac{E^0_{des}}{RT}}\right], \quad (128)$$

$$k_B T\ln\left[\frac{a_g}{a_{ads,2D}}\right] = k_B T\ln K^0_{des,2D,g} = k_B T\ln\left[\frac{q_g}{q_{ads,2D}}\frac{\mathcal{A}}{\mathcal{V}}\frac{\mathcal{V}^0_m}{\mathcal{A}^0_m}e^{-\frac{E^0_{des}}{RT}}\right], \quad (129)$$

$$K^0_{des,2D,g} = \frac{q_g}{q_{ads,2D}}\frac{\mathcal{A}}{\mathcal{V}}\frac{\mathcal{V}^0_m}{\mathcal{A}^0_m}e^{-\frac{E^0_{des}}{RT}} = \frac{\left(2\pi m k_B T/h^2\right)^{3/2}}{\left(2\pi m k_B T/h^2\right)}\frac{\mathcal{V}^0_m}{\mathcal{A}^0_m}e^{-\frac{E^0_{des}}{RT}} = \frac{\mathcal{V}^0_m}{\mathcal{A}^0_m}\left(2\pi m k_B T/h^2\right)^{1/2}e^{-\frac{E^0_{des}}{RT}}. \quad (130)$$

This is the same result for $K^0_{des,2D,g}$ we obtained when solving for the Gibbs free energy.

4.2 Standard molar thermodynamic functions and equilibrium constant between 2D ideal lattice gas and 3D ideal gas

The standard molar change in Gibbs free energy for desorption from a 2D ideal lattice gas is given by:

$$\Delta G^0_{des,latt,g,m} = G^0_{g,m} - G^0_{ads,latt,m} = \left[-RT\ln\left(\frac{q^0_{g,m}}{N_A}\right)\right] - \left[-RT\ln q^0_{ads,latt} - RT\ln\left(\frac{(1-\theta^0)}{\theta^0}\right) - E^0_{des}\right] = E^0_{des} -$$

$$RT\ln\left[\frac{\left(\frac{q^0_{g,m}}{N_A}\right)}{q^0_{ads,latt}\frac{(1-\theta^0)}{\theta^0}}\right] = -RT\left[\frac{-E^0_{des}}{RT} + \ln\left[\frac{\left(\frac{q^0_{g,m}}{N_A}\right)}{q^0_{ads,latt}\frac{(1-\theta^0)}{\theta^0}}\right]\right]. \quad (131)$$

For the change in enthalpy, we can write

$$\Delta H^0_{des,latt,g,m} = H_{g,m} - H_{ads,latt,m} = \frac{5}{2}RT - \frac{N_A\cdot h\nu}{e^{\beta h\nu}-1} + RT\frac{\ln(1-\theta)}{\theta} + E^0_{des}, \quad (132)$$

when neglecting the vibrational term:

$$\Delta H^0_{des,latt,g,m} = H_{g,m} - H_{ads,latt,m} = \frac{5}{2}RT + RT\frac{\ln(1-\theta)}{\theta} + E^0_{des}. \quad (133)$$

For the change in entropy, we derive

$$\Delta S^0_{des,latt,g,m} = S^0_{g,m} - S^0_{ads,latt,m} = R\ln\left(\frac{e^{5/2}q^0_{g,m}}{N_A}\right) - R\left(\ln q_{ads,latt} - \beta\left(\frac{\partial \ln q_{ads,latt}}{\partial\beta}\right)\right) - R\left(\ln\left(\frac{(1-\theta^0)}{\theta^0}\right) - \frac{\ln(1-\theta^0)}{\theta^0}\right). \quad (134)$$

Note that $q_{ads,latt}$ only consists of vibrations and as such does not refer to a standard state. When neglecting the contribution of vibrations, we obtain

$$\Delta S^0_{des,latt,g,m} = S^0_{g,m} - S^0_{ads,latt,m} = R\ln\left(\frac{e^{5/2}q^0_{g,m}}{N_A}\right) - R\left(\ln\left(\frac{(1-\theta^0)}{\theta^0}\right) - \frac{\ln(1-\theta^0)}{\theta^0}\right). \quad (135)$$

Therefore, we can express the equilibrium constant as

$$\ln K^0_{des,latt,g} = \frac{-E^0_{des}}{RT} + \ln\left[\frac{\left(\frac{q^0_{g,m}}{N_A}\right)}{q_{ads,latt}\frac{(1-\theta^0)}{\theta^0}}\right] \quad (136)$$

and

$$K^0_{des,latt,g} = \frac{\left(\frac{q^0_{g,m}}{N_A}\right)}{q_{ads,latt}\frac{(1-\theta^0)}{\theta^0}}e^{-\frac{E^0_{des}}{RT}}. \quad (137)$$

When setting in the expressions for the standard molar partition functions:

$$K^0_{des,latt,g} = \frac{\left(\frac{\mathcal{V}^0_m\left(2\pi m k_B T/h^2\right)^{3/2}}{N_A}\right)}{q_{ads,latt}\frac{(1-\theta^0)}{\theta^0}}e^{-\frac{E^0_{des}}{RT}} = \frac{\left(2\pi m k_B T/h^2\right)^{3/2}}{\left(N_g/\mathcal{V}\right)^0 q_{ads,latt}\frac{(1-\theta^0)}{\theta^0}}e^{-\frac{E^0_{des}}{RT}}. \quad (138)$$

We should obtain the same result, when assuming equilibrium and using the chemical potential of the gas and the adsorbed 2D ideal lattice gas:

$$\mu_g(T) = \mu_g^0(T) + k_B T \ln \frac{p}{p^0} = \mu_{ads,latt}(T) = \mu_{ads,latt}^0(T) + k_B T \ln a_{ads,latt} \,. \tag{139}$$

We use above derivations to write

$$-k_B T \ln \left[\left(\frac{2\pi m}{h^2 \beta} \right)^{\frac{3}{2}} \frac{kT}{p^0} \right] + k_B T \ln \frac{p}{p^0} = -k_B T \ln \left[q_{ads,latt} \frac{1-\theta^0}{\theta^0} e^{\frac{E_{des}^0}{RT}} \right] + k_B T \ln a_{ads,latt} \,, \tag{140}$$

$$-k_B T \ln \left[\frac{q_g}{\mathcal{V}} \frac{\mathcal{V}_m^0}{N_A} \right] + k_B T \ln \frac{\frac{\mathcal{N}_g}{N_A}}{\mathcal{V}_m^0} = -k_B T \ln \left[q_{ads,latt} \frac{1-\theta^0}{\theta^0} e^{\frac{E_{des}^0}{RT}} \right] + k_B T \ln \left[\frac{\frac{\theta}{(1-\theta)}}{\frac{\theta^0}{1-\theta^0}} \right]. \tag{141}$$

Rearranging terms yields

$$k_B T \ln \frac{\frac{\mathcal{N}_g}{N_A}}{\mathcal{V}_m^0} - k_B T \ln \left[\frac{\frac{\theta}{(1-\theta)}}{\frac{\theta^0}{1-\theta^0}} \right] = k_B T \ln \left[\frac{q_g}{\mathcal{V}} \frac{\mathcal{V}_m^0}{N_A} \right] - k_B T \ln \left[q_{ads,latt} \frac{1-\theta^0}{\theta^0} e^{\frac{E_{des}^0}{RT}} \right], \tag{142}$$

$$k_B T \ln \left[\frac{a_g}{a_{ads,latt}} \right] = k_B T \ln K_{des,latt,g}^0 = k_B T \ln \left[\frac{q_g}{q_{ads,latt} \frac{1-\theta^0}{\theta^0}} \frac{1}{\mathcal{V}} \frac{\mathcal{V}_m^0}{N_A} e^{-\frac{E_{des}^0}{RT}} \right], \tag{143}$$

$$K_{des,latt,g}^0 = \frac{q_g}{q_{ads,latt} \frac{1-\theta^0}{\theta^0}} \frac{1}{\mathcal{V}} \frac{\mathcal{V}_m^0}{N_A} e^{-\frac{E_{des}^0}{RT}} = \frac{(2\pi m k_B T/h^2)^{3/2}}{q_{ads,latt} \frac{1-\theta^0}{\theta^0}} \frac{\mathcal{V}_m^0}{N_A} e^{-\frac{E_{des}^0}{RT}} = \frac{(2\pi m k_B T/h^2)^{3/2}}{(N_g/\mathcal{V})^0 q_{ads,latt} \frac{(1-\theta^0)}{\theta^0}} e^{-\frac{E_{des}^0}{RT}}. \tag{144}$$

This is the same result for $K_{des,latt,g}^0$ we obtained when solving for the Gibbs free energy.

4.3 Standard molar thermodynamic functions and equilibrium constant between the 2D ideal gas and the transition state for desorption

The standard molar change in Gibbs free energy between the TS for desorption and the adsorbed 2D ideal gas is given by:

$$\Delta G_{des,2D,TS,m}^0 = G_{TS,m}^0 - G_{ads,2D,m}^0 = -RT \ln \left(\frac{q_{TS,m}^0}{N_A} \right) + E_b^0 - \left[-RT \ln \left(\frac{q_{ads,2D,m}^0}{N_A} \right) - E_{des}^0 \right] = E_{des}^0 + E_b^0 - RT \ln \left[\frac{\left(\frac{q_{TS,m}^0}{N_A} \right)}{\left(\frac{q_{ads,2D,m}^0}{N_A} \right)} \right] =$$

$$-RT \left[\frac{-(E_{des}^0 + E_b^0)}{RT} + \ln \left[\frac{\left(\frac{q_{TS,m}^0}{N_A} \right)}{\left(\frac{q_{ads,2D,m}^0}{N_A} \right)} \right] \right]. \tag{145}$$

In the CTST, the free energy of activation is similar to that of the TS, but with the contribution of the motion along the desorption coordinate omitted:

$$\Delta G_{des,2D,act,m}^0 = G_{act,m}^0 - G_{ads,2D,m}^0 = -RT \ln \left(\frac{q_{TS,2D,m}^0}{N_A} \right) + E_b^0 - \left[-RT \ln \left(\frac{q_{ads,2D,m}^0}{N_A} \right) - E_{des}^0 \right] = E_{des}^0 + E_b^0 -$$

$$RT \ln \left[\frac{\left(\frac{q_{TS,2D,m}^0}{N_A} \right)}{\left(\frac{q_{ads,2D,m}^0}{N_A} \right)} \right] = -RT \left[\frac{-E_{des}^0}{RT} + \ln \left[\frac{\left(\frac{q_{TS,2D,m}^0}{N_A} \right)}{\left(\frac{q_{ads,2D,m}^0}{N_A} \right)} \right] \right] = -RT \left[\frac{-(E_{des}^0 + E_b^0)}{RT} + \ln \left(\frac{q_{TS,2D,m}^0}{q_{ads,2D,m}^0} \right) \right]. \tag{146}$$

For the change in enthalpy we can write for the TS and activated state

$$\Delta H^0_{des,2D,TS,m} = H_{TS,m} - H_{ads,2D,m} = \frac{1}{2}RT + E^0_b + E^0_{des} \tag{147}$$

and

$$\Delta H^0_{des,2D,act,m} = H_{act,m} - H_{ads,2D,m} = E^0_b + E^0_{des}\,. \tag{148}$$

For the change in entropy we can write for the TS and activated state

$$\Delta S^0_{des,2D,TS,m} = S^0_{TS,m} - S^0_{ads,2D,m} = R\ln\left(\frac{e^{1/2}q^0_{TS,m}}{q^0_{ads,2D,m}}\right) = R\ln\left(\frac{e^{1/2}q^0_{TS,2D,m}q_{TS,des}}{q^0_{ads,2D,m}}\right) \tag{149}$$

and

$$\Delta S^0_{des,2D,act,m} = S^0_{act,m} - S^0_{ads,2D,m} = R\ln\left(\frac{q^0_{TS,2D,m}}{q^0_{ads,2D,m}}\right). \tag{150}$$

Therefore, we can express the equilibrium constant with respect to the TS as

$$\ln K^0_{des,2D,TS} = \frac{-\left(E^0_{des}+E^0_b\right)}{RT} + \ln\left[\frac{\left(\frac{q^0_{TS,m}}{N_A}\right)}{\left(\frac{q^0_{ads,2D,m}}{N_A}\right)}\right] \tag{151}$$

and

$$K^0_{des,2D,TS} = \frac{\left(\frac{q^0_{TS,m}}{N_A}\right)}{\left(\frac{q^0_{ads,2D,m}}{N_A}\right)} e^{-\frac{\left(E^0_{des}+E^0_b\right)}{RT}} = \frac{q^0_{TS,m}}{q^0_{ads,2D,m}} e^{-\frac{\left(E^0_{des}+E^0_b\right)}{RT}}\,. \tag{152}$$

When setting in the expressions for the standard molar partition functions:

$$K^0_{des,2D,TS} = \frac{\mathcal{A}^0_m d\left(2\pi m k_B T/h^2\right)^{3/2}}{\mathcal{A}^0_m (2\pi m k_B T/h^2)} e^{-\frac{\left(E^0_{des}+E^0_b\right)}{RT}} = \frac{(N_{ads}/\mathcal{A})^0}{(N_{TS}/\mathcal{A})^0} d(2\pi m k_B T/h^2)^{1/2} e^{-\frac{\left(E^0_{des}+E^0_b\right)}{RT}} = d(2\pi m k_B T/h^2)^{1/2} e^{-\frac{\left(E^0_{des}+E^0_b\right)}{RT}}\,. \tag{153}$$

We should obtain the same result, when assuming equilibrium and using the chemical potential of the TS and adsorbed 2D ideal gas:

$$\mu_{TS}(T) = \mu^0_{TS}(T) + k_B T\ln a_{TS} = \mu_{ads,2D}(T) = \mu^0_{ads,2D}(T) + k_B T\ln a_{ads,2D}\,. \tag{154}$$

We use above derivations to write

$$-k_B T\ln\left[\left(\frac{2\pi m}{h^2\beta}\right)^{\frac{3}{2}} d\,\frac{\mathcal{A}^0_m}{N_A}\right] + k_B T\ln a_{TS} + q^0_b = -k_B T\ln\left[\left(\frac{2\pi m}{h^2\beta}\right)^{\frac{2}{2}}\frac{\mathcal{A}^0_m}{N_A} e^{\frac{E^0_{des}}{RT}}\right] + k_B T\ln a_{ads,2D}\,, \tag{155}$$

$$-k_B T\ln\left[\frac{q_{TS}}{\mathcal{A}d}\,d\,\frac{\mathcal{A}^0_m}{N_A}\right] + k_B T\ln\left[\frac{\mathcal{N}_{TS}}{\frac{N_A}{A^0_m}}\right] + q^0_b = -k_B T\ln\left[\frac{q_{ads,2D}}{\mathcal{A}}\frac{\mathcal{A}^0_m}{N_A} e^{\frac{E^0_{des}}{RT}}\right] + k_B T\ln\left[\frac{\mathcal{N}_{ads}}{\frac{N_A}{A^0_m}}\right]. \tag{156}$$

Rearranging terms yields

$$k_B T\ln\left[\frac{\mathcal{N}_{TS}}{\frac{N_A}{A^0_m}}\right] - k_B T\ln\left[\frac{\mathcal{N}_{ads}}{\frac{N_A}{A^0_m}}\right] + q^0_b = k_B T\ln\left[\frac{q_{TS}}{\mathcal{A}d}\,d\,\frac{\mathcal{A}^0_m}{N_A}\right] - k_B T\ln\left[\frac{q_{ads,2D}}{\mathcal{A}}\frac{\mathcal{A}^0_m}{N_A} e^{\frac{E^0_{des}}{RT}}\right], \tag{157}$$

$$k_B T \ln\left[\frac{a_{TS}}{a_{ads,2D}}\right] = k_B T \ln K^0_{des,2D,TS} = k_B T \ln\left[\frac{q_{TS}}{q_{ads,2D}} e^{-\frac{E^0_{des}}{RT}}\right] - q^0_b = k_B T \ln\left[\frac{q_{TS}}{q_{ads,2D}} e^{-\frac{E^0_{des}}{RT}}\right] - k_B T \ln\left[e^{\frac{q^0_b}{k_B T}}\right] =$$

$$k_B T \ln\left[\frac{q_{TS}}{q_{ads,2D}} e^{-\frac{E^0_{des}}{RT}}\right] - k_B T \ln\left[e^{\frac{E^0_{des}}{RT}}\right] = k_B T \ln\left[\frac{q_{TS}}{q_{ads,2D}} e^{-\frac{\left(E^0_{des}+E^0_b\right)}{RT}}\right], \quad (158)$$

$$K^0_{des,2D,TS} = \frac{q_{TS}}{q_{ads,2D}} e^{-\frac{\left(E^0_{des}+E^0_b\right)}{RT}} = \frac{\left(2\pi m k_B T/h^2\right)^{3/2}}{\left(2\pi m k_B T/h^2\right)} \frac{\mathcal{A}d}{\mathcal{A}} e^{-\frac{\left(E^0_{des}+E^0_b\right)}{RT}} = d\left(2\pi m k_B T/h^2\right)^{1/2} e^{-\frac{\left(E^0_{des}+E^0_b\right)}{RT}}. \quad (159)$$

This is the same result for $K^0_{des,2D,TS}$ we obtained when solving for the Gibbs free energy.

We can express the equilibrium constant with respect to the activated state as

$$\ln K^0_{des,2D,act} = \frac{-\left(E^0_{des}+E^0_b\right)}{RT} + \ln\left[\frac{\left(\frac{q^0_{TS,2D,m}}{N_A}\right)}{\left(\frac{q^0_{ads,2D,m}}{N_A}\right)}\right] \quad (160)$$

and

$$K^0_{des,2D,act} = \frac{\left(\frac{q^0_{TS,2D,m}}{N_A}\right)}{\left(\frac{q^0_{ads,2D,m}}{N_A}\right)} e^{-\frac{\left(E^0_{des}+E^0_b\right)}{RT}} = \frac{q^0_{TS,2D,m}}{q^0_{ads,2D,m}} e^{-\frac{\left(E^0_{des}+E^0_b\right)}{RT}}. \quad (161)$$

When setting in the expressions for the standard molar partition functions:

$$K^0_{des,2D,act} = \frac{\mathcal{A}^0_m\left(2\pi m k_B T/h^2\right)}{\mathcal{A}^0_m\left(2\pi m k_B T/h^2\right)} e^{-\frac{\left(E^0_{des}+E^0_b\right)}{RT}} = \frac{\left(N_{ads}/\mathcal{A}\right)^0}{\left(N_{TS}/\mathcal{A}\right)^0} e^{-\frac{\left(E^0_{des}+E^0_b\right)}{RT}} = e^{-\frac{\left(E^0_{des}+E^0_b\right)}{RT}}. \quad (162)$$

We should obtain the same result, when assuming equilibrium and using the chemical potential of the activated state and adsorbed 2D ideal gas:

$$\mu_{act}(T) = \mu^0_{act}(T) + k_B T \ln a_{TS} = \mu_{ads,2D}(T) = \mu^0_{ads,2D}(T) + k_B T \ln a_{ads,2D}. \quad (163)$$

We use above derivations to write

$$-k_B T \ln\left[\left(\frac{2\pi m}{h^2\beta}\right)\frac{\mathcal{A}^0_m}{N_A}\right] + k_B T \ln a_{TS} + q^0_b = -k_B T \ln\left[\left(\frac{2\pi m}{h^2\beta}\right)\frac{\mathcal{A}^0_m}{N_A} e^{\frac{E^0_{des}}{RT}}\right] + k_B T \ln a_{ads,2D}, \quad (164)$$

$$-k_B T \ln\left[\frac{q_{TS,2D}}{\mathcal{A}}\frac{\mathcal{A}^0_m}{N_A}\right] + k_B T \ln\left[\frac{\mathcal{N}_{TS}}{\frac{N_A}{A^0_m}}\right] + q^0_b = -k_B T \ln\left[\frac{q_{ads,2D}}{\mathcal{A}}\frac{\mathcal{A}^0_m}{N_A} e^{\frac{E^0_{des}}{RT}}\right] + k_B T \ln\left[\frac{\mathcal{N}_{ads}}{\frac{N_A}{A^0_m}}\right]. \quad (165)$$

Rearranging terms yields

$$k_B T \ln\left[\frac{\mathcal{N}_{TS}}{\frac{N_A}{A^0_m}}\right] - k_B T \ln\left[\frac{\mathcal{N}_{ads}}{\frac{N_A}{A^0_m}}\right] + q^0_b = k_B T \ln\left[\frac{q_{TS,2D}}{\mathcal{A}}\frac{\mathcal{A}^0_m}{N_A}\right] - k_B T \ln\left[\frac{q_{ads,2D}}{\mathcal{A}}\frac{\mathcal{A}^0_m}{N_A} e^{\frac{E^0_{des}}{RT}}\right], \quad (166)$$

$$k_B T \ln\left[\frac{a_{TS}}{a_{ads,2D}}\right] = k_B T \ln K^0_{ads,2D,act} = k_B T \ln\left[\frac{q_{TS,2D}}{q_{ads,2D}} e^{-\frac{E^0_{des}}{RT}}\right] - q^0_b = k_B T \ln\left[\frac{q_{TS,2D}}{q_{ads,2D}} e^{-\frac{\left(E^0_{des}+E^0_b\right)}{RT}}\right], \quad (167)$$

$$K^0_{des,2D,act} = \frac{q_{TS,2D}}{q_{ads,2D}} e^{-\frac{\left(E^0_{des}+E^0_b\right)}{RT}} = \frac{\left(2\pi m k_B T/h^2\right)}{\left(2\pi m k_B T/h^2\right)}\frac{\mathcal{A}}{\mathcal{A}} e^{-\frac{\left(E^0_{des}+E^0_b\right)}{RT}} = e^{-\frac{\left(E^0_{des}+E^0_b\right)}{RT}}. \quad (168)$$

This is the same result for $K^0_{des,2D,act}$ we obtained when solving for the Gibbs free energy.

4.4 Standard molar thermodynamic functions and equilibrium constant between the 2D ideal lattice gas and the transition state for desorption

The standard molar change in Gibbs free energy between the transition state for desorption and the adsorbed 2D ideal lattice gas is given by:

$$\Delta G^0_{des,latt,TS,m} = G^0_{TS,m} - G^0_{ads,latt,m} = \left[-RT\ln\left(\frac{q^0_{TS,m}}{N_A}\right)+E^0_b\right] - \left[-RT\ln q_{ads,latt} - RT\ln\left(\frac{(1-\theta^0)}{\theta^0}\right) - E^0_{des}\right] = E^0_{des}+E^0_b - RT\ln\left[\frac{\left(\frac{q^0_{TS,m}}{N_A}\right)}{q_{ads,latt}\frac{(1-\theta^0)}{\theta^0}}\right] = -RT\left[\frac{-\left(E^0_{des}+E^0_b\right)}{RT} + \ln\left[\frac{\left(\frac{q^0_{TS,m}}{N_A}\right)}{q_{ads,latt}\frac{(1-\theta^0)}{\theta^0}}\right]\right]. \quad (169)$$

For the change in enthalpy, we can write for the TS and activated state

$$\Delta H^0_{des,latt,TS,m} = H^0_{TS,m} - H^0_{ads,latt,m} = \frac{5}{2}RT - \frac{N_A\cdot h\nu}{e^{\beta h\nu}-1} + RT\frac{\ln(1-\theta)}{\theta} + E^0_{des}+E^0_b \quad (170)$$

and

$$\Delta H^0_{des,latt,act,m} = H^0_{act,m} - H^0_{ads,latt,m} = 2RT - \frac{N_A\cdot h\nu}{e^{\beta h\nu}-1} + RT\frac{\ln\left(1-\theta^0\right)}{\theta^0} + E^0_{des}+E^0_b\,. \quad (171)$$

For the change in entropy, we can write for the TS and activated state

$$\Delta S^0_{des,latt,TS,m} = S^0_{TS,m} - S^0_{ads,latt,m} = R\ln\left(\frac{e^{5/2}q^0_{TS,m}}{N_A}\right) - R\left(\ln q_{ads,latt} - \beta\left(\frac{\partial \ln q_{ads,latt}}{\partial\beta}\right)\right) - R\left(\ln\left(\frac{(1-\theta^0)}{\theta^0}\right) - \frac{\ln(1-\theta^0)}{\theta^0}\right). \quad (172)$$

and

$$\Delta S^0_{des,latt,act,m} = S^0_{act,m} - S^0_{ads,latt,m} = R\ln\left(\frac{e^2q^0_{TS,2D,m}}{N_A}\right) - R\left(\ln q_{ads,latt} - \beta\left(\frac{\partial \ln q_{ads,latt}}{\partial\beta}\right)\right) - R\left(\ln\left(\frac{(1-\theta^0)}{\theta^0}\right) - \frac{\ln(1-\theta^0)}{\theta^0}\right). \quad (173)$$

We can express the equilibrium constant as

$$\ln K^0_{des,latt,TS} = \frac{-\left(E^0_{des}+E^0_b\right)}{RT} + \ln\left[\frac{\left(\frac{q^0_{TS,m}}{N_A}\right)}{q_{ads,latt}\frac{(1-\theta^0)}{\theta^0}}\right] \quad (174)$$

and

$$K^0_{des,latt,TS} = \frac{\left(\frac{q^0_{TS,m}}{N_A}\right)}{q_{ads,latt}\frac{(1-\theta^0)}{\theta^0}}e^{-\frac{\left(E^0_{des}+E^0_b\right)}{RT}}\,. \quad (175)$$

When setting in the expressions for the standard molar partition functions:

$$K^0_{des,latt,TS} = \frac{\left(\frac{\mathcal{A}^0_m d\left(2\pi m k_B T/h^2\right)^{3/2}}{N_A}\right)}{q_{ads,latt}\frac{(1-\theta^0)}{\theta^0}} e^{-\frac{\left(E^0_{des}+E^0_b\right)}{RT}} = \frac{d\left(2\pi m k_B T/h^2\right)^{3/2}}{(N_{TS}/\mathcal{A})^0 q_{ads,latt}\frac{(1-\theta^0)}{\theta^0}} e^{-\frac{\left(E^0_{des}+E^0_b\right)}{RT}}. \quad (176)$$

We should obtain the same result, when assuming equilibrium and using the chemical potential of the TS and adsorbed ideal 2D lattice gas:

$$\mu_{TS}(T) = \mu^0_{TS}(T) + k_B T \ln a_{TS} = \mu_{ads,latt}(T) = \mu^0_{ads,latt}(T) + k_B T \ln a_{ads,latt}\,. \quad (177)$$

We use above derivations to write

$$-k_B T \ln\left[\left(\frac{2\pi m}{h^2\beta}\right)^{\frac{3}{2}} d\,\frac{\mathcal{A}^0_m}{N_A}\right] + k_B T \ln a_{TS} + q^0_b = -k_B T \ln\left[q_{ads,latt}\frac{1-\theta^0}{\theta^0} e^{\frac{E^0_{des}}{RT}}\right] + k_B T \ln a_{ads,latt} \quad (178)$$

$$-k_B T \ln\left[\frac{q_{TS}}{\mathcal{A}d}\,d\,\frac{\mathcal{A}^0_m}{N_A}\right] + k_B T \ln\left[\frac{\frac{\mathcal{N}_{TS}}{N_A}}{\frac{A^0_m}{}}\right] + q^0_b = -k_B T \ln\left[q_{ads,latt}\frac{1-\theta^0}{\theta^0} e^{\frac{E^0_{des}}{RT}}\right] + k_B T \ln\left[\frac{\frac{\theta}{(1-\theta)}}{\frac{\theta^0}{1-\theta^0}}\right]. \quad (179)$$

Rearranging terms yields

$$k_B T \ln\left[\frac{\frac{\mathcal{N}_{TS}}{N_A}}{\frac{A^0_m}{}}\right] - k_B T \ln\left[\frac{\frac{\theta}{(1-\theta)}}{\frac{\theta^0}{1-\theta^0}}\right] = k_B T \ln\left[\frac{q_{TS}}{\mathcal{A}d}\,d\,\frac{\mathcal{A}^0_m}{N_A}\right] - k_B T \ln\left[q_{ads,latt}\frac{1-\theta^0}{\theta^0} e^{\frac{E^0_{des}}{RT}}\right] - q^0_b\,, \quad (180)$$

$$k_B T \ln\left[\frac{a_{TS}}{a_{ads,latt}}\right] = k_B T \ln K^0_{des,latt,TS} = k_B T \ln\left[\frac{q_{TS}}{q_{ads,latt}\frac{1-\theta^0}{\theta^0}}\frac{1}{\mathcal{A}}\frac{\mathcal{A}^0_m}{N_A} e^{-\frac{E^0_{des}}{RT}}\right] - q^0_b\,, \quad (181)$$

$$K^0_{des,latt,TS} = \frac{q_{TS}}{q_{ads,latt}\frac{1-\theta^0}{\theta^0}}\frac{1}{\mathcal{A}}\frac{\mathcal{A}^0_m}{N_A} e^{-\frac{\left(E^0_{des}+E^0_b\right)}{RT}} = \frac{\left(2\pi m k_B T/h^2\right)^{3/2}}{q_{ads,latt}\frac{1-\theta^0}{\theta^0}}\frac{d\mathcal{A}^0_m}{N_A} e^{-\frac{\left(E^0_{des}+E^0_b\right)}{RT}} = \frac{d\left(2\pi m k_B T/h^2\right)^{3/2}}{(N_{TS}/\mathcal{A})^0 q_{ads,latt}\frac{(1-\theta^0)}{\theta^0}} e^{-\frac{\left(E^0_{des}+E^0_b\right)}{RT}}. \quad (182)$$

This is the same result for $K^0_{des,latt,TS}$ we obtained when solving for the Gibbs free energy.

For the free energy of activation (with the translation along the desorption coordinate omitted), we obtain:

$$\Delta G^0_{des,latt,act,m} = G^0_{act,m} - G^0_{ads,latt,m} = \left[-RT \ln\left(\frac{q^0_{TS,2D,m}}{N_A}\right) + E^0_b\right] - \left[-RT \ln q_{ads,latt} - RT \ln\left(\frac{(1-\theta^0)}{\theta^0}\right) - E^0_{des}\right] =$$

$$E^0_{des} + E^0_b - RT \ln\left[\frac{\left(\frac{q^0_{TS,2D,m}}{N_A}\right)}{q_{ads,latt}\frac{(1-\theta^0)}{\theta^0}}\right] = -RT\left[\frac{-\left(E^0_{des}+E^0_b\right)}{RT} + \ln\left[\frac{\left(\frac{q^0_{TS,2D,m}}{N_A}\right)}{q_{ads,latt}\frac{(1-\theta^0)}{\theta^0}}\right]\right]. \quad (183)$$

Therefore, we can express the equilibrium constant as

$$\ln K^0_{des,latt,act} = \frac{-\left(E^0_{des}+E^0_b\right)}{RT} + \ln\left[\frac{\left(\frac{q^0_{TS,2D,m}}{N_A}\right)}{q_{ads,latt}\frac{(1-\theta^0)}{\theta^0}}\right] \quad (184)$$

and

$$K^0_{des,latt,act} = \frac{\left(\frac{q^0_{TS,2D,m}}{N_A}\right)}{q_{ads,latt}\frac{(1-\theta^0)}{\theta^0}} e^{-\frac{\left(E^0_{des}+E^0_b\right)}{RT}}. \quad (185)$$

When setting in the expressions for the standard molar partition functions:

$$K^0_{des,latt,act} = \frac{\left(\frac{\mathcal{A}^0_m(2\pi m k_B T/h^2)}{N_A}\right)}{q_{ads,latt}\frac{(1-\theta^0)}{\theta^0}} e^{-\frac{\left(E^0_{des}+E^0_b\right)}{RT}} = \frac{(2\pi m k_B T/h^2)}{(N_{TS}/\mathcal{A})^0 q_{ads,latt}\frac{(1-\theta^0)}{\theta^0}} e^{-\frac{\left(E^0_{des}+E^0_b\right)}{RT}}. \quad (186)$$

We should obtain the same result, when assuming equilibrium and using the chemical potential of the activated state and adsorbed 2D ideal lattice gas:

$$\mu_{act}(T) = \mu^0_{act}(T) + k_B T \ln a_{TS} = \mu_{ads,latt}(T) = \mu^0_{ads,latt}(T) + k_B T \ln a_{ads,latt}\,. \quad (187)$$

We use above derivations to write

$$-k_B T \ln\left[\left(\frac{2\pi m}{h^2\beta}\right)\frac{\mathcal{A}^0_m}{N_A}\right] + k_B T \ln a_{TS} + q^0_b = -k_B T \ln\left[q_{ads,latt}\frac{1-\theta^0}{\theta^0} e^{\frac{E^0_{des}}{RT}}\right] + k_B T \ln a_{ads,latt}\,, \quad (188)$$

$$-k_B T \ln\left[\frac{q_{TS,2D}}{\mathcal{A}}\frac{\mathcal{A}^0_m}{N_A}\right] + k_B T \ln\left[\frac{\mathcal{N}_{TS}}{\frac{N_A}{A^0_m}}\right] = -k_B T \ln\left[q_{ads,latt}\frac{1-\theta^0}{\theta^0} e^{\frac{E^0_{des}}{RT}}\right] + k_B T \ln\left[\frac{(\theta/(1-\theta))}{(\theta^0/(1-\theta^0))}\right] - q^0_b\,. \quad (189)$$

Rearranging terms yields

$$k_B T \ln\left[\frac{\mathcal{N}_{TS}}{\frac{N_A}{A^0_m}}\right] - k_B T \ln\left[\frac{(\theta/(1-\theta))}{(\theta^0/(1-\theta^0))}\right] = k_B T \ln\left[\frac{q_{TS,2D}}{\mathcal{A}}\frac{\mathcal{A}^0_m}{N_A}\right] - k_B T \ln\left[q_{ads,latt}\frac{1-\theta^0}{\theta^0} e^{\frac{E^0_{des}}{RT}}\right] - q^0_b, \quad (190)$$

$$k_B T \ln\left[\frac{a_{TS}}{a_{ads,latt}}\right] = k_B T \ln K^0_{des,latt,act} = k_B T \ln\left[\frac{q_{TS,2D}\frac{\mathcal{A}^0_m}{N_A}}{\mathcal{A} q_{ads,latt}\frac{(1-\theta^0)}{\theta^0}} e^{-\frac{\left(E^0_{des}+E^0_b\right)}{RT}}\right], \quad (191)$$

$$K^0_{des,latt,act} = \frac{q_{TS,2D}\frac{\mathcal{A}^0_m}{N_A}}{\mathcal{A} q_{ads,latt}\frac{(1-\theta^0)}{\theta^0}} e^{-\frac{\left(E^0_{des}+E^0_b\right)}{RT}} = \frac{(2\pi m k_B T/h^2)}{q_{ads,latt}\frac{(1-\theta^0)}{\theta^0}}\frac{\mathcal{A}\frac{\mathcal{A}^0_m}{N_A}}{\mathcal{A}} e^{-\frac{\left(E^0_{des}+E^0_b\right)}{RT}} = \frac{(2\pi m k_B T/h^2)}{(N_{TS}/\mathcal{A})^0 q_{ads,latt}\frac{(1-\theta^0)}{\theta^0}} e^{-\frac{\left(E^0_{des}+E^0_b\right)}{RT}}. \quad (192)$$

This is the same result for $K^0_{des,latt,act}$ we obtained when solving for the Gibbs free energy.

S5. Standard molar Gibbs free energy change and equilibrium constant between the 3D ideal gas and the transition state for adsorption

Here, we derive the thermodynamic functions that describe the interactions between the gas phase and transition state for adsorption.

The standard molar change in Gibbs free energy between the transition state for adsorption and the 3D ideal gas is given by:

$$\Delta G^0_{ads,g,TS,m} = G^0_{TS,m} - G^0_{g,m} = \left[-RT\ln\left(\frac{q^0_{TS,m}}{N_A}\right) + E^0_b\right] - \left[-RT\ln\left(\frac{q^0_{g,m}}{N_A}\right)\right] = -RT\ln\left[\frac{q^0_{TS,m}}{q^0_{g,m}}\right] + E^0_b = -RT\ln\left[\frac{q^0_{TS,m}}{q^0_{g,m}}\right] + RT\ln\left[e^{\frac{E^0_b}{RT}}\right] = -RT\ln\left[\frac{q^0_{TS,m}}{q^0_{g,m}} e^{-\frac{E^0_b}{RT}}\right]. \quad (193)$$

For the change in enthalpy, we can write for the TS and activated state

$$\Delta H^0_{ads,g,TS,m} = H^0_{TS,m} - H^0_{g,m} = \frac{5}{2}RT + E^0_b - \frac{5}{2}RT = E^0_b \quad (194)$$

and

$$\Delta H^0_{ads,g,act,m} = H^0_{act,m} - H^0_{g,m} = 2RT + E^0_b - \frac{5}{2}RT = -\frac{1}{2}RT + E^0_b \,. \tag{195}$$

For the change in entropy, we can write for the TS and activated state

$$\Delta S^0_{ads,g,TS,m} = S^0_{TS,m} - S^0_{g,m} = R\ln\left(\frac{e^{5/2}q^0_{TS,m}}{N_A}\right) - R\ln\left(\frac{e^{5/2}q^0_{g,m}}{N_A}\right) = R\ln\left(\frac{q^0_{TS,m}}{q^0_{g,m}}\right) = R\ln\left(\frac{q^0_{TS,2D,m}q_{TS,des}}{q^0_{g,m}}\right) \tag{196}$$

and

$$\Delta S^0_{ads,g,act,m} = S^0_{act,m} - S^0_{g,m} = R\ln\left(\frac{e^{2}q^0_{TS,2D,m}}{N_A}\right) - R\ln\left(\frac{e^{5/2}q^0_{g,m}}{N_A}\right) = R\ln\left(\frac{q^0_{TS,2D,m}}{e^{1/2}q^0_{g,m}}\right) . \tag{197}$$

We can express the equilibrium constant as

$$\ln K^0_{ads,g,TS} = \ln\left[\frac{q^0_{TS,m}}{q^0_{g,m}}e^{-\frac{E^0_b}{RT}}\right] \tag{198}$$

and

$$K^0_{ads,g,TS} = \frac{q^0_{TS,m}}{q^0_{g,m}}e^{-\frac{E^0_b}{RT}} \,. \tag{199}$$

When setting in the expressions for the standard molar partition functions:

$$K^0_{ads,g,TS} = \frac{\mathcal{A}^0_m d\left(2\pi m k_B T/h^2\right)^{3/2}}{\mathcal{V}^0_m (2\pi m k_B T/h^2)^{3/2}}e^{-\frac{E^0_b}{RT}} = \frac{\mathcal{A}^0_m d}{\mathcal{V}^0_m}e^{-\frac{E^0_b}{RT}}. \tag{200}$$

We should obtain the same result, when assuming equilibrium and using the chemical potential of the TS and adsorbed 2D ideal lattice gas:

$$\mu_{TS}(T) = \mu^0_{TS}(T) + k_B T\ln a_{TS} = \mu_g(T) = \mu^0_g(T) + k_B T\ln\frac{p}{p^0} \,. \tag{201}$$

We use above derivations to write

$$-k_B T\ln\left[\left(\frac{2\pi m}{h^2\beta}\right)^{\frac{3}{2}} d\,\frac{\mathcal{A}^0_m}{N_A}\right] + k_B T\ln a_{TS} + q^0_b = -k_B T\ln\left[\left(\frac{2\pi m}{h^2\beta}\right)^{\frac{3}{2}}\frac{kT}{p^0}\right] + k_B T\ln\frac{p}{p^0} \tag{202}$$

$$-k_B T\ln\left[\frac{q_{TS}}{\mathcal{A}d}\,d\,\frac{\mathcal{A}^0_m}{N_A}\right] + k_B T\ln\left[\frac{\mathcal{N}_{TS}}{\frac{N_A}{A^0_m}}\right] = -k_B T\ln\left[\frac{q_g}{\mathcal{V}}\frac{\mathcal{V}^0_m}{N_A}\right] + k_B T\ln\frac{\mathcal{N}_g}{\frac{N_A}{\mathcal{V}^0_m}} - q^0_b \,. \tag{203}$$

Rearranging terms yields

$$k_B T\ln\left[\frac{\mathcal{N}_{TS}}{\frac{N_A}{A^0_m}}\right] - k_B T\ln\frac{\mathcal{N}_g}{\frac{N_A}{\mathcal{V}^0_m}} = k_B T\ln\left[\frac{q_{TS}}{\mathcal{A}d}\,d\,\frac{\mathcal{A}^0_m}{N_A}\right] - k_B T\ln\left[\frac{q_g}{\mathcal{V}}\frac{\mathcal{V}^0_m}{N_A}\right] - k_B T\ln\left[e^{\frac{q^0_b}{k_B T}}\right] \tag{204}$$

$$k_B T\ln\left[\frac{a_{TS}}{a_g}\right] = k_B T\ln K^0_{g,TS} = k_B T\ln\left[\frac{q_{TS}}{q_g}\frac{\mathcal{V}}{\mathcal{A}}\frac{\mathcal{A}^0_m}{\mathcal{V}^0_m}e^{-\frac{E^0_b}{RT}}\right] . \tag{205}$$

Thus, we obtain

$$K^0_{ads,g,TS} = \frac{q_{TS}}{q_g}\frac{\mathcal{V}}{\mathcal{A}}\frac{\mathcal{A}^0_m}{\mathcal{V}^0_m}e^{-\frac{E^0_b}{RT}} = \frac{(2\pi m k_B T/h^2)^{3/2}}{(2\pi m k_B T/h^2)^{3/2}}\frac{d\mathcal{A}^0_m}{\mathcal{V}^0_m}e^{-\frac{E^0_b}{RT}} = \frac{d\mathcal{A}^0_m}{\mathcal{V}^0_m}e^{-\frac{E^0_b}{RT}}. \quad (206)$$

This is the same result for $K^0_{ads,g,TS}$ we obtained when solving for the Gibbs free energy.

For the free energy of activation (with the translation along the adsorption coordinate omitted), we obtain:

$$\Delta G^0_{ads,g,act,m} = G^0_{act,m} - G^0_{g,m} = \left[-RT\ln\left(\frac{q^0_{TS,2D,m}}{N_A}\right)+E^0_b\right] - \left[-RT\ln\left(\frac{q^0_{g,m}}{N_A}\right)\right] = -RT\ln\left[\frac{q^0_{TS,2D,m}}{q^0_{g,m}}\right]+E^0_b =$$

$$-RT\ln\left[\frac{q^0_{TS,2D,m}}{q^0_{g,m}}e^{-\frac{E^0_b}{RT}}\right]. \quad (207)$$

Therefore, we can express the equilibrium constant as

$$\ln K^0_{ads,g,act} = \ln\left[\frac{q^0_{TS,2D,m}}{q^0_{g,m}}e^{-\frac{E^0_b}{RT}}\right] \quad (208)$$

and

$$K^0_{ads,g,act} = \frac{q^0_{TS,2D,m}}{q^0_{g,m}}e^{-\frac{E^0_b}{RT}}. \quad (209)$$

When setting in the expressions for the standard molar partition functions:

$$K^0_{ads,g,act} = \frac{\mathcal{A}^0_m(2\pi m k_B T/h^2)}{\mathcal{V}^0_m(2\pi m k_B T/h^2)^{3/2}}e^{-\frac{E^0_b}{RT}} = \frac{\mathcal{A}^0_m}{\mathcal{V}^0_m(2\pi m k_B T/h^2)^{1/2}}e^{-\frac{E^0_b}{RT}}. \quad (210)$$

We should obtain the same result, when assuming equilibrium and using the chemical potential of the activated state and adsorbed ideal 3D gas:

$$\mu_{act}(T) = \mu^0_{act}(T) + k_B T\ln a_{TS} = \mu_g(T) = \mu^0_g(T) + k_B T\ln\frac{p}{p^0}. \quad (211)$$

We use above derivations to write

$$-k_B T\ln\left[\left(\frac{2\pi m}{h^2\beta}\right)\frac{\mathcal{A}^0_m}{N_A}\right] + k_B T\ln a_{TS} + q^0_b = -k_B T\ln\left[\left(\frac{2\pi m}{h^2\beta}\right)^{\frac{3}{2}}\frac{kT}{p^0}\right] + k_B T\ln\frac{p}{p^0}, \quad (212)$$

Rearranging terms yields

$$k_B T\ln\left[\frac{\mathcal{N}_{TS}}{\frac{N_A}{\mathcal{A}^0_m}}\right] - k_B T\ln\frac{\mathcal{N}_g}{\frac{N_A}{\mathcal{V}^0_m}} = k_B T\ln\left[\frac{q_{TS,2D}}{\mathcal{A}}\frac{\mathcal{A}^0_m}{N_A}\right] - k_B T\ln\left[\frac{q_g}{\mathcal{V}}\frac{\mathcal{V}^0_m}{N_A}\right] - q^0_b \quad (213)$$

$$k_B T\ln\left[\frac{a_{TS}}{a_g}\right] = k_B T\ln K^0_{g,act} = k_B T\ln\left[\frac{q_{TS,2D}}{q_g}\frac{\mathcal{V}}{\mathcal{A}}\frac{\mathcal{A}^0_m}{\mathcal{V}^0_m}e^{-\frac{E^0_b}{RT}}\right]. \quad (214)$$

$$K^0_{ads,g,act} = \frac{q_{TS,2D}}{q_g}\frac{\mathcal{V}}{\mathcal{A}}\frac{\mathcal{A}^0_m}{\mathcal{V}^0_m}e^{-\frac{E^0_b}{RT}} = \frac{(2\pi m k_B T/h^2)^{2/2}}{(2\pi m k_B T/h^2)^{3/2}}\frac{\mathcal{A}^0_m}{\mathcal{V}^0_m}e^{-\frac{E^0_b}{RT}} = \frac{\mathcal{A}^0_m}{\mathcal{V}^0_m(2\pi m k_B T/h^2)^{1/2}}e^{-\frac{E^0_b}{RT}}. \quad (215)$$

This is the same result for $K^0_{ads,g,act}$ we obtained when solving for the Gibbs free energy.

6. Adsorption-Desorption Equilibrium

Considering the equilibrium, for the case that the adsorbed state is a 2D ideal gas, at low coverage, starting with the thermodynamic expressions:

$$\frac{R_{ads}}{\mathcal{A}} = \frac{R_{des}}{\mathcal{A}} \tag{216}$$

$$\kappa\left(\frac{k_B T}{h}\right) e^{-\Delta G^0_{ads,g,act,m}/RT} \frac{(N_{TS}/\mathcal{A})^0}{(N_g/\mathcal{V})^0} \mathcal{N}_g = \kappa\left(\frac{k_B T}{h}\right) \frac{(N_{TS}/\mathcal{A})^0}{(N_{ads}/\mathcal{A})^0} e^{-\Delta G^0_{des,2D,act,m}/RT} \mathcal{N}_{ads} \tag{217}$$

$$\frac{(N_{TS}/\mathcal{A})^0}{(N_g/\mathcal{V})^0} \mathcal{N}_g \frac{q^{0\prime}_{TS,m}}{q^0_{g,m}} e^{-\frac{E^0_b}{RT}} = \frac{(N_{TS}/\mathcal{A})^0}{(N_{ads}/\mathcal{A})^0} \mathcal{N}_{ads} \frac{q^{0\prime}_{TS,m}}{q^0_{ads,2D,m}} e^{-\frac{\left(E^0_{des}+E^0_b\right)}{RT}} \tag{218}$$

$$\frac{\mathcal{N}_g}{(N_g/\mathcal{V})^0} \frac{q^{0\prime}_{TS,m}}{q^0_{g,m}} = \frac{\mathcal{N}_{ads}}{(N_{ads}/\mathcal{A})^0} \frac{q^{0\prime}_{TS,m}}{q^0_{ads,2D,m}} e^{-\frac{E^0_{des}}{RT}} \tag{219}$$

$$\frac{\mathcal{N}_{ads}}{\mathcal{N}_g} \frac{(N_g/\mathcal{V})^0}{(N_{ads}/\mathcal{A})^0} = e^{\frac{E^0_{des}}{RT}} \frac{q^0_{ads,2D,m}}{q^0_{g,m}} = K^0_{ads,g,2D} = \frac{1}{K^0_{des,2D,g}} = K_{lin} \frac{(N_g/\mathcal{V})^0}{(N_{ads}/\mathcal{A})^0}\,. \tag{220}$$

For the case of the activity-based adsorption and desorption rates, starting with the thermodynamic expressions, we obtain

$$\frac{R_{ads}}{\mathcal{A}} = \frac{R_{des}}{\mathcal{A}} \tag{221}$$

$$\kappa\left(\frac{k_B T}{h}\right) e^{-\Delta G^0_{ads,g,act,m}/RT} \frac{(N_{TS}/\mathcal{A})^0}{(N_g/\mathcal{V})^0} \mathcal{N}_g = \kappa\left(\frac{k_B T}{h}\right) \frac{(N_{TS}/\mathcal{A})^0}{(N_{ads}/\mathcal{A})^0} e^{-\Delta G^0_{des,2D,act,m}/RT} \mathcal{N}_{ads} \tag{222}$$

$$\frac{(N_{TS}/\mathcal{A})^0}{(N_g/\mathcal{V})^0} \mathcal{N}_g \frac{q^{0\prime}_{TS,m}}{q^0_{g,m}} e^{-\frac{E^0_b}{RT}} = \frac{(N_{TS}/\mathcal{A})^0}{(N_{ads}/\mathcal{A})^0} \mathcal{N}_{ads} \frac{q^{0\prime}_{TS,m}}{q^0_{ads,2D,m}} e^{-\frac{\left(E^0_{des}+E^0_b\right)}{RT}} \tag{223}$$

$$\frac{\mathcal{N}_g}{(N_g/\mathcal{V})^0} \frac{q^{0\prime}_{TS,m}}{q^0_{g,m}} = \frac{\mathcal{N}_{ads}}{(N_{ads}/\mathcal{A})^0} \frac{q^{0\prime}_{TS,m}}{q^0_{ads,2D,m}} e^{-\frac{E^0_{des}}{RT}} \tag{224}$$

$$\frac{\mathcal{N}_{ads}}{\mathcal{N}_g} \frac{(N_g/\mathcal{V})^0}{(N_{ads}/\mathcal{A})^0} = e^{\frac{E^0_{des}}{RT}} \frac{q^0_{ads,2D,m}}{q^0_{g,m}} = K^0_{ads,g,2D} = \frac{1}{K^0_{des,2D,g}} = K_{lin} \frac{(N_g/\mathcal{V})^0}{(N_{ads}/\mathcal{A})^0}\,. \tag{225}$$

This is again consistent with our findings above.

In case the adsorbed state on the surface is treated as a 2D ideal lattice gas, using the thermodynamic expressions as a starting point:

$$\frac{R_{ads,2D}}{\mathcal{A}} = \frac{R_{des,latt}}{\mathcal{A}} \tag{226}$$

$$\kappa\left(\frac{k_B T}{h}\right) e^{-\Delta G^0_{ads,g,act,m}/RT} \frac{(N_{TS}/\mathcal{A})^0}{(N_g/\mathcal{V})^0} \mathcal{N}_g = \kappa\left(\frac{k_B T}{h}\right) \frac{(N_{TS}/\mathcal{A})^0}{(\theta^0/(1-\theta^0))} e^{-\Delta G^0_{des,latt,act,m}/RT} (\theta/(1-\theta)) \tag{227}$$

$$\frac{(N_{TS}/\mathcal{A})^0}{(N_g/\mathcal{V})^0} \mathcal{N}_g \frac{q^{0\prime}_{TS,m}}{q^0_{g,m}} e^{-\frac{E^0_b}{RT}} = \frac{(N_{TS}/\mathcal{A})^0}{(\theta^0/(1-\theta^0))} (\theta/(1-\theta)) \frac{\left(\frac{q^{0\prime}_{TS,m}}{N_A}\right)}{\left(q_{ads,latt} \frac{(1-\theta^0)}{\theta^0}\right)} e^{-\frac{\left(E^0_{des}+E^0_b\right)}{RT}} \tag{228}$$

$$\frac{\mathcal{N}_g}{\left(N_g/\mathcal{V}\right)^0}\frac{1}{q^0_{g,m}} = \frac{(\theta/(1-\theta))}{(\theta^0/(1-\theta^0))}\frac{\frac{1}{N_A}}{q_{ads,latt}\frac{(1-\theta^0)}{\theta^0}}e^{-\frac{E^0_{des}}{RT}} \tag{229}$$

$$\frac{(\theta/(1-\theta))}{\mathcal{N}_g}\frac{\left(N_g/\mathcal{V}\right)^0}{(\theta^0/(1-\theta^0))} = e^{\frac{E^0_{des}}{RT}}\frac{q_{ads,latt}\frac{(1-\theta^0)}{\theta^0}}{\left(\frac{q^0_{g,m}}{N_A}\right)} = K^0_{ads,g,latt} = \frac{1}{K^0_{des,latt,g}} = K_{Lang}\frac{\left(N_g/\mathcal{V}\right)^0}{(\theta^0/(1-\theta^0))}. \tag{230}$$

For the case of the activity-based adsorption and desorption rates, starting with the thermodynamic relationships, we obtain:

$$R^a_{ads,2D} = R^a_{des,latt} \tag{231}$$

$$\kappa\left(\frac{k_BT}{h}\right)e^{-\Delta G^0_{ads,g,act,m}/RT}\frac{(N_{TS}/\mathcal{A})^0}{\left(N_g/\mathcal{V}\right)^0}a_g\frac{\mathcal{A}^0_m}{\mathcal{V}^0_m} = \kappa\left(\frac{k_BT}{h}\right)e^{-\Delta G^0_{des,latt,act,m}/RT}\frac{(1-\theta^0)}{\theta^0}\frac{(N_{TS}/\mathcal{A})^0}{\mathcal{N}_{ads,max}}a_{ads,latt} \tag{232}$$

$$\frac{(N_{TS}/\mathcal{A})^0}{\left(N_g/\mathcal{V}\right)^0}\frac{\mathcal{A}^0_m}{\mathcal{V}^0_m}\frac{q^{0\prime}_{TS,m}}{q^0_{g,m}}e^{-\frac{E^0_b}{RT}}a_g = \frac{(1-\theta^0)}{\theta^0}\frac{(N_{TS}/\mathcal{A})^0}{\mathcal{N}_{ads,max}}\frac{\left(\frac{q^{0\prime}_{TS,m}}{N_A}\right)}{\left(q_{ads,latt}\frac{(1-\theta^0)}{\theta^0}\right)}e^{-\frac{\left(E^0_{des}+E^0_b\right)}{RT}}a_{ads,latt} \tag{233}$$

$$\frac{a_g}{\left(N_g/\mathcal{V}\right)^0}\frac{\mathcal{A}^0_m}{\mathcal{V}^0_m}\frac{1}{q^0_{g,m}} = \frac{\frac{1}{N_A}}{q_{ads,latt}}e^{-\frac{E^0_{des}}{RT}}\frac{a_{ads,latt}}{\mathcal{N}_{ads,max}} \tag{234}$$

$$\frac{a_{ads,latt}}{a_g} = \frac{\mathcal{N}_{ads,max}}{\left(N_g/\mathcal{V}\right)^0}\frac{\mathcal{A}^0_m}{\mathcal{V}^0_m}\frac{q_{ads,latt}}{\left(\frac{q^0_{g,m}}{N_A}\right)}e^{\frac{E^0_{des}}{RT}} = \mathcal{N}_{ads,max}(2\pi mk_BT/h^2)^{-3/2}e^{\frac{E^0_{des}}{RT}}\frac{\mathcal{A}^0_m}{\mathcal{V}^0_m} = \mathcal{N}_{ads,max}K_{Lang}\frac{\mathcal{A}^0_m}{\mathcal{V}^0_m}. \tag{235}$$

This is again consistent with our findings above.

Table S1. Physical Parameters and Standard States Applied in Calculations for Figures 2 to 15.

T / K	M / g mol^{-1}	m / kg	R / J K^{-1} mol^{-1}	k_B / J K^{-1}	h / J s	N_A / molec. mol^{-1}
298	100	1.6605×10^{-25}	8.3145	1.38065×10^{-23}	6.62607×10^{-34}	6.02214×10^{23}

$\mathcal{V}_m^0$ / m^3 mol^{-1}	$\left(\frac{N_g}{\mathcal{V}}\right)^0$ / m^{-3}	$\mathcal{A}_m^0$ / m^2 mol^{-1}	$\left(\frac{N_{ads}}{\mathcal{A}}\right)^0$ / m^{-2}	$\mathcal{N}_{ads,max}$ / m^{-2}	θ^0
0.0248	2.4283×10^{25}	5.1471×10^{6}	1.17×10^{17}	1×10^{19}	0.0117

d / m	κ	$q_{g,m}^0$	$q_{ads,2D,m}^0$	$q_{ads,latt}$	$q_{TS,m}^0$	$q_{TS,des}$	$q_{TS,2D,m}^0 = q_{TS,m}^{0\prime}$
1×10^{-10}	1	2.3976×10^{31}	5.0325×10^{28}	1	4.9761×10^{29}	9.8880	5.0325×10^{28}

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