Technical Note: Adsorption and desorption equilibria from statistical thermodynamics and rates from transition-state theory

Daniel A. Knopf[1], Markus Ammann[2]

[1]School of Marine and Atmospheric Sciences, Stony Brook University, Stony Brook, New York, USA
5 [2]Laboratory of Environmental Chemistry, Paul Scherrer Institute, Villigen, Switzerland

Correspondence to: Daniel A. Knopf (daniel.knopf@stonybrook.edu) and Markus Ammann (markus.ammann@psi.ch)

Abstract.

Adsorption and desorption represent the initial processes of the interaction of gas species with the condensed phase. It has important implications for evaluating heterogeneous (gas-to-solid) and multiphase chemical kinetics involved in catalysis,
10 environmental interfaces, and, in particular, aerosol particles. When describing gas uptake, gas-to-particle partitioning, and the chemical transformation of aerosol particles parameters describing adsorption and desorption rates are crucial to assess the underlying chemical kinetics such as surface reaction and surface-to-bulk transfer. For instance, the desorption lifetime, in turn, depends on the desorption free energy which is affected by the chosen adsorbate model. To assess the impact of those conditions on desorption energy and, thus, desorption lifetime, we provide a complete classical and statistical thermodynamic
15 treatment of the adsorption and desorption process considering transition state theory for two typically applied adsorbate models, the 2D ideal gas and the 2D ideal lattice gas, the latter being equivalent to Langmuir adsorption. Both models apply to solid and liquid substrate surfaces. We derive the thermodynamic and microscopic relationships for adsorption and desorption equilibrium constants, adsorption and desorption rates, first-order adsorption and desorption rate coefficients, and the corresponding pre-exponential factors. Although, some of these derivations can be found in the literature, this study aims
20 to bring all derivations into one place to facilitate the interpretation and analysis of the variables driving adsorption and desorption for their application in multiphase chemical kinetics. This exercise allows for a microscopic interpretation of the underlying processes including the surface accommodation coefficient and highlights the importance of the choice of adsorbate model and standard states when analyzing and interpreting adsorption and desorption processes. We demonstrate how the choice of adsorbate model choice affects equilibrium surface concentrations and coverages, desorption rates, and decay of the
25 adsorbate species with time. In addition, we show how those results differ when applying a concentration- or activity-based description. Our treatment demonstrates that the pre-exponential factor can differ by orders of magnitude depending on the choice of adsorbate model with similar effects on the desorption lifetime, yielding significant uncertainties in the desorption energy derived from experimentally derived desorption rates. Furthermore, uncertainties in surface coverage and assumptions in standard surface coverage can lead to significant changes in desorption energies derived from measured desorption rates.
30 Providing a comprehensive thermodynamic and microscopic representation aims to guide theoretical and experimental

assessments of desorption energies and estimate potential uncertainties in applied desorption energies and corresponding desorption lifetimes important for improving our understanding of multiphase chemical kinetics.

Short Summary (500 character in total)

Adsorption on and desorption of gas molecules from solid or liquid surfaces or interfaces represent the initial interaction of gas-to-condensed phase processes that can define the physicochemical evolution of the condensed phase. We apply a thermodynamic and microscopic treatment of these multiphase processes to evaluate how adsorption and desorption rates and

40 surface accommodation depend on the choice adsorption model and standard states with implications for desorption energy and lifetime.

1 Introduction

Any interaction between gas-phase species and condensed matter, including liquid, semi-solid, and solid phases, commences by adsorption and desorption processes (McNaught and Wilkinson, 2014;Langmuir, 1918, 1916, 1915). Those are of

45 importance in the research areas of catalysis and, in particular, multiphase chemical kinetics or phase transfer kinetics involving environmental surfaces and interfaces (Cussler, 2009;Chorkendorff and Niemantsverdriet, 2007;Finlayson-Pitts and Pitts, 2000;Ravishankara, 1997;Solomon, 1999). Surfaces including water bodies, ice, and terrestrial and anthropogenic structures can provide interfaces at which phase transfer processes, multiphase and heterogeneous reactions can take place. In the atmospheric sciences, multiphase chemical reactions have been the foci of research since the realization that heterogeneous

50 reactions on the surface of polar stratospheric clouds lead to the activation of inert chlorine reservoir species that subsequently result in ozone depletion, manifested in the spring southern hemispheric ozone hole (Solomon, 1999;Rowland, 1991). By now it is well established that gas-particle interactions play crucial roles in particle growth by condensation, gas-particle partitioning, and the chemical evolution of particles during aerosol formation and aging (Pöschl et al., 2007;Kolb et al., 2010;Rudich et al., 2007;George and Abbatt, 2010;Pöschl and Shiraiwa, 2015;Moise et al., 2015;Ammann et al., 2013;Crowley

55 et al., 2013;Kroll et al., 2011;Donahue et al., 2011;Jimenez et al., 2009). The role of reversible adsorption and desorption has been addressed in many studies of gas uptake and multiphase chemical reactions, in particular for the decoupling of mass transport and chemical reaction (Kolb et al., 1995;Hanson and Ravishankara, 1991;Kolb et al., 2010;Ammann et al., 2013;Crowley et al., 2013;Pöschl and Shiraiwa, 2015).

In the context of atmospheric sciences, adsorption is commonly described by the surface accommodation coefficient, α_s,

60 which is the probability that a molecule undergoing a gas kinetic collision is adsorbed at the surface (see overview and definitions by (Kolb et al., 2010)). For desorption, according to the Frenkel equation, the desorption lifetime (τ_d) of a surface-

adsorbed chemical species (i.e., the adsorbate) follows an Arrhenius-type behavior (Arrhenius, 1889b;Arrhenius, 1889a;Laidler, 1949;Frenkel, 1924;Laidler et al., 1940):

$$\tau_d = \frac{1}{k_d} = \frac{1}{A} e^{\frac{E^0_{des}}{RT}} , \tag{1}$$

where E^0_{des} is the desorption energy with the energy reference of the gas molecule at rest at $T = 0\ K$ (as outlined below), k_d is a first-order desorption rate coefficient, A is a pre-exponential factor, R is the general gas constant, and T is temperature. Adsorption is treated as an activated process if an energy barrier exists. Desorption is always treated as an activated process; independent of whether an additional energy barrier exists. When describing multiphase chemical kinetics, k_d affects the overall rate of transfer of a gas molecule into the bulk by impacting the loss rate by surface reaction and the surface-to-bulk transfer and, thus, the bulk accommodation coefficient (Ammann and Pöschl, 2007;Pöschl et al., 2007;Shiraiwa and Poschl, 2021). For example, a kinetic multilayer model analysis of measured uptake coefficients for OH radicals on levoglucosan substrates yielded a tight correlation between τ_d and the chemical reaction rate coefficient at the surface, because the experimental data only allowed to constrain the product/ratio of the two (Arangio et al., 2015). A similar issue, the competition between adsorption (and uptake) and desorption, pertains to gas-particle partitioning kinetics when describing condensation of water vapor and volatile organic compounds (VOCs) and volatilization of organic reaction products (Shiraiwa et al., 2013;Shiraiwa et al., 2012;Shiraiwa and Seinfeld, 2012). Thus, accurate derivation of the chemical reaction kinetics requires accurate τ_d values. Atmospheric trace gases and water vapor can undergo reversible adsorption on aerosol, cloud, and ground surfaces over a wide range of temperatures from below 200 to above 300 K. Especially at low temperatures, large values of τ_d could counteract slow rates of chemical reaction and diffusion, enhancing the overall gas uptake which may involve reversible, reactive, and catalytic processes on the surface or in the bulk of the particles (Ammann et al., 2013;Crowley et al., 2013;Kolb et al., 2010;Pöschl et al., 2007;Rudich et al., 2007;Li et al., 2020;Li and Knopf, 2021).

Equation (1) does not explicitly show that the desorption rate depends on the choice of adsorbate model and standard states. The same applies to the surface accommodation coefficient, which is not referring to the adsorbate model. Once the pre-exponential factor A for desorption is expressed in terms of the free energy of activation (Campbell et al., 2016;Donaldson et al., 2012;Kolasinski, 2012;Campbell et al., 2013), the choice of adsorbate model and standard states has a significant impact on the values of the pre-exponential factor A and thus τ_d. Vice versa, when using experimentally observed desorption rates to derive E^0_{des}, assumptions about the adsorbate model can result, as we show in this study, in significant changes in the corresponding E^0_{des} values. It is known that the choice of standard states and adsorbate model impacts the interpretation of the equilibrium constant and the desorption process (Campbell et al., 2016;Donaldson et al., 2012;Kolasinski, 2012).

The difference in adsorbate models reflects the treatment of the potential well in which the adsorbate "sits" in (Hill, 1986;Campbell et al., 2016). The most commonly applied adsorbate model is the 2D ideal gas which lacks one translational degree of freedom compared to the 3D ideal gas (Hill, 1986). It is defined by the condition of negligible lateral potential wells; thus, it can freely move parallel across the surface. The other extreme is the 2D ideal lattice gas where the absorbate cannot overcome the potential well of the adsorption site. Thus, it exerts only vibrational movements parallel and vertical to the

95   surface. A model that can describe both extremes is, e.g., the ideal hindered translator model (Hill, 1986;Campbell et al., 2016;Sprowl et al., 2016). Which of the two models, the ideal 2D gas and the ideal lattice gas, are realized will depend on the activation barrier for adsorbate diffusion parallel to the surface. If this activation barrier is above $k_B T$ (Boltzmann constant times temperature), the ideal lattice gas model is the preferred model, whereas if it is below $k_B T$, diffusion of adsorbates parallel to the surface can commence and the adsorption is described by an ideal 2D gas (Sprowl et al., 2016). The hindered

100   translator model (Sprowl et al., 2016) is not discussed in this study. It will be shown that the choice of adsorbate model and corresponding standard states will result in different equilibrium constants, pre-exponential factors, and, thus, desorption rates, but counter-intuitively, in the same adsorption rates. Ultimately, the choice of the adsorbate model will also render E_{des}^0 and τ_d, important parameters when examining and interpreting the multiphase chemical kinetics at environmental interfaces.

      The purpose of this study is to provide a holistic description of the thermodynamic functions derived from microscopic

105   principles (i.e., corresponding partition functions) that allow for the calculation of the pre-exponential factor of the desorption rate based on transition state (TS) theory for the case of the 2D ideal gas and 2D ideal lattice gas. We will apply statistical thermodynamics to describe the microscopic, i.e., on the molecular level, processes and classical thermodynamics that define the overall energy and equilibrium conditions. The presented framework only considers physisorptive processes, within the general framework of treating adsorption in atmospheric chemistry (Kolb et al., 2010;Pöschl et al., 2007). Although, many

110   aspects of the presented derivations can be found in statistical thermodynamic textbooks (Hill, 1986;Kolasinski, 2012) and articles (Campbell et al., 2016;Donaldson et al., 2012;Savara, 2013), a complete treatment of adsorption and desorption including the TS and respective standard states is not readily available in the literature, as far as the authors are aware of. An outcome of this exercise is an improved understanding of the defining parameters that govern typically measured and reported thermodynamic parameters and their dependency on chosen standard states. For example, the presented derivations

115   demonstrate that the pre-exponential factor, commonly assumed to be around 10^{13} s^{-1} (Atkins and de Paula, 2006), can differ by orders of magnitude in response to the choice of standard state and adsorbate model (Campbell et al., 2016). This, in turn, will alter interpretation and analyses of multiphase chemical kinetics occurring at interfaces.

      The outline of this study is guided by ways of the derivation of the thermodynamic functions. TS theory assumes thermodynamic equilibrium between the adsorbed state and the TS for desorption (Kolasinski, 2012;Eyring, 1935). The

120   description of this equilibrium in terms of the basic thermodynamic functions is based on adsorption thermodynamics. Since the desorption rate and the pre-exponential factor are expressed in terms of molecular properties (i.e., the microscopic picture), the linkage between statistical thermodynamics and the thermodynamic functions have to be considered and applied. However, the foundational derivations for the thermodynamics and statistical thermodynamics of adsorption are not well established and not treated in comprehensive ways in textbooks. We therefore retrace this theory first for the case of desorption as an overall

125   process. This will then serve as the basis for applying this theory to the TS theory for desorption and adsorption and to derive the pre-exponential factor for desorption. A great part of those derivations follows the treatment by Campbell et al. (2016). Subsequently, combination of the rate expressions of desorption and adsorption establishes the links between the overall adsorption thermodynamics and the microscopic kinetic parameters including the interpretation of the surface accommodation

coefficient. In this study, the surface accommodation coefficient follows the definition by (Kolb et al., 2010) valid for physisorptive processes and consistent with the Langmuir adsorption description but not necessarily the same as the sticking coefficient used in surface sciences or catalysis, which is often inconsistently defined, and sometimes or sometimes not lumps physisorption and chemisorption. There are alternative descriptions such as the Kisliuk-type precursor mechanism that consider more complex configurations of the adsorbate (Kisliuk, 1957;Tully, 1994;Campbell et al., 2016), not discussed in this study. Lastly, we evaluate how our findings impact interpretation and analysis of measured or theoretically derived E_{des}^0 values.

Since the basis for describing desorption by TS theory requires consideration of thermodynamic equilibria, in section 2 to 5 and the Supplement, we introduce first the overall desorption thermodynamics in more detail to provide the necessary equations and terminology. Section 2 discusses the general thermodynamic functions for describing adsorption and desorption, their derivations from microscopic properties (partition functions), and definitions of the standard states. Section 3 provides the derivation of equilibrium thermodynamic functions that describe the desorption process for the two different adsorbate models. The results so far will be applied in Section 4 to derive the desorption rates and associated pre-exponential factors for the different adsorbate models in terms of thermodynamic and microscopic quantities. Section 5 presents the derivation of the adsorption rate including thermodynamic and microscopic treatment and evaluation of the surface accommodation coefficient. In Section 6, by combination of the previous results we consider the equilibrium between adsorption and desorption to derive the corresponding equilibrium constants demonstrating that the derivations are internally consistent. Section 7 provides the derivation of the kinetic parameters from equilibrium between adsorption and desorption. Section 8 discusses how the choices made for standard states and the type of adsorbate model impact surface concentration, activity, and coverage, adsorption and desorption rates, and E_{des}^0 and τ_d values and thus our interpretation of multiphase chemical kinetics. This is followed by the conclusions section.

To fundamentally follow all derivations presented in this document, an excess number of equations would need to be shown, which would have rendered this document difficult to read. In the supplement we provided all necessary definitions, equations, and derivations from first principles to follow the thoughts in the main document. The reader is encouraged to study this document side-by-side with the Supplement that contains all information leading to the results shown here. We apply the definitions of parameters and standard states given in the Supplement. The Supplement includes all necessary detailed derivations of the thermodynamic equations for 3D ideal gas, 2D ideal gas, 2D ideal lattice gas, and TS. It includes the following sections: (S1) Definition of desorption and adsorption equilibrium constants; (S2) Derivation of thermodynamic functions for desorption and adsorption; (S3) Standard molar enthalpies, entropies, and Gibbs free energies; (S4) Derivation of Equilibrium Constants; (S5) Standard molar Gibbs free energy change and equilibrium constant between the 3D ideal gas and the transition state for adsorption; (S6) Adsorption-Desorption Equilibrium.

2. Thermodynamic and Microscopic Considerations of the Adsorption/Desorption Process

In this section we define the nomenclature, signage, and units involved of partition functions, thermodynamic quantities, and standard states when describing adsorption and desorption processes.

2.1 Gibbs Free Energy, Enthalpy, and Entropy of the Adsorption and Desorption Process

The spontaneous occurrence of adsorption implies an exergonic process with the thermodynamic condition (Bolis, 2013):

$$\Delta G^0_{ads,m} = \Delta H^0_{ads,m} - T\Delta S^0_{ads,m} < 0 \tag{2}$$

$$\Delta H^0_{ads,m} = H^0_{ads,m} - H^0_{g,m} = -\Delta H^0_{des,m} \tag{3}$$

$$\Delta S^0_{ads,m} = S^0_{ads,m} - S^0_{g,m} = -\Delta S^0_{des,m} \tag{4}$$

Since adsorption of a gas on a substrate results in an increase of molecular ordering and $\Delta S^0_{ads,m} < 0$, the change in enthalpy $\Delta H^0_{ads,m}$ has to be negative. In this study, ΔG^0_m and ΔH^0_m are expressed in units J mol^{-1} and ΔS^0_m in units J mol^{-1} K^{-1}. For the remainder of the text, the subscripts denote the process direction in the order of (from left to right) process (adsorption or desorption), educt (e.g., adsorbate), and product (e.g., gas species). Subscript m denotes molar quantities.

2.2 Adsorption and Desorption Energy and Activation Barrier

We define the energy reference as the internal energy of the gas molecule at rest at $T = 0\ K$. The adsorbed or desorbing molecule is at the bottom of a potential well, at $-\epsilon^0_{des}$ with ϵ^0_{des} being a positive number in units of Joule indicating the necessary heat for the molecule to desorb as depicted in Fig. 1. Different processes can contribute to ϵ^0_{des} such as molecular rotations and vibrations or other molecular interactions. In molecular quantities and at constant volume, accounting for the number of adsorbed molecules in the system, N_{ads}, yields

$$U_{ads}(0) = -N_{ads}\epsilon^0_{des} = -\varepsilon^0_{des}, \tag{5}$$

where ε^0_{des} represents the molecular desorption energy. In molar quantities we obtain

$$E^0_{des} = N_A\epsilon^0_{des} \tag{6}$$

and, thus,

$$U_{ads,m}(0) = -E^0_{des}\ . \tag{7}$$

We treat the general case of activated adsorption/desorption here, meaning that the TS's internal energy is elevated by the barrier height above the reference level. The TS for adsorption/desorption is assumed to exist at some fixed distance from the surface but within a very thin layer of thickness d, where it experiences an increase in potential energy (relative to the gas phase at infinite separation) to a maximum value expressed by the energy barrier ϵ^0_b due to its interaction with the surface (e.g., due to Pauli repulsion) as outlined in Fig. 1. We further assume for simplicity that at this TS distance from the surface, the

potential energy does not depend on the rotational orientation of the molecule nor on the location parallel to the surface. In molecular quantities, accounting for the number of molecules in the TS in the system, N_{TS}, and at constant volume yields

190 $$U_{TS}(0) = N_{TS}\epsilon_b^0 = \varepsilon_b^0 \tag{8}$$

and in molar quantities

$$U_{TS,m}(0) = E_b^0 . \tag{9}$$

In the literature, the desorption energy often includes the energy barrier (Kolasinski, 2012), so that the activation of desorption is, expressed in our notation here, as

195 $$E_{des,act}^0 = E_{des}^0 + E_b^0 . \tag{10}$$

For the remainder of the document, we treat the desorption energy and energy barrier separately. In the absence of an energy barrier for adsorption and desorption, i.e., $E_b^0 = 0$, and all equations simplify accordingly. Note, however, and as mentioned above, in absence of a barrier, the desorption process remains an activated process with $E_{des,act}^0 = E_{des}^0$.

2.3 Relationship Between Partition Functions and Thermodynamic Quantities

200 We use statistical thermodynamics to relate the microscopic properties to the matter's bulk properties. Via the partition function Q we can express the thermodynamic functions U, S (entropy), H (enthalpy) and G (Gibbs free energy) in the following way (Atkins and de Paula, 2006)

$$U - U(0) = -\left(\frac{\partial \ln Q}{\partial \beta}\right)_V \quad \text{with} \quad \beta = \frac{1}{k_B T} \tag{11}$$

$$S = \frac{U - U(0)}{T} + k_B \ln Q \tag{12}$$

205 $$H - H(0) = -\left(\frac{\partial \ln Q}{\partial \beta}\right)_V + k_B T \mathcal{V} \left(\frac{\partial \ln Q}{\partial \mathcal{V}}\right)_T \tag{13}$$

$$G - G(0) = -kT \ln Q + k_B T \mathcal{V} \left(\frac{\partial \ln Q}{\partial \mathcal{V}}\right)_T . \tag{14}$$

T and $\mathcal{V}$ are the system's temperature and volume, respectively, and k_B is the Boltzmann constant. We first calculate the molecular quantities U, H, G, S, and then express them as molar quantities,

$U_m = U/n$, $H_m = H/n$, $G_m = G/n$, $S_m = S/n$, via $= \frac{N}{N_A}$, $R = N_A k$, and $q_m = \frac{q}{n}$, (15)

210 where q is the molecular partition function (Atkins and de Paula, 2006), N is the number of molecules in the system, n is the number of moles in the system, N_A is the Avogadro number, and R is the general gas constant.

As introduced below for the cases of 3D ideal gas, 2D ideal gas, 2D ideal lattice gas, and TS for desorption, we will apply the appropriate partition functions (see also Supplement S3). For the 3D and 2D ideal gases we will use the canonical partition function, expressed for indistinguishable and independent molecules as $Q = q^N/N!$ (Atkins and de Paula, 2006). For the 2D

215 ideal lattice gas, we will have to modify the canonical partition function to introduce adsorption sites (Hill, 1986).

2.4 Concentration, Standard States of Gas Species and Adsorbates, and Activities

The concentration of the 3D ideal gas in the gas phase is given by

$$\mathcal{N}_g = \frac{N_g}{\mathcal{V}},$$
(16)

where N_g is the number of gas molecules in the system and $\mathcal{V}$ is the volume of the system. Its standard concentration is

220
$$\left(\frac{N_g}{\mathcal{V}}\right)^0 = \frac{n_g^0 \cdot N_A}{\mathcal{V}^0} = \frac{N_A}{\mathcal{V}_m^0},$$
(17)

where n_g^0 is the standard number of moles of the gas species (typically set equal to 1), N_A is Avogadro's number, and $\mathcal{V}_m^0$ indicates the standard molar volume reflecting n_g^0. For $n_g^0 = 1$ mol, $\mathcal{V}_m^0 = 24.8$ L mol^{-1} at 298 K and 1000 hPa. We define the gas phase activity, a_g, as the concentration in the gas phase, $\mathcal{N}_g$, divided by the standard concentration, $(N_g/\mathcal{V})^0$:

$$a_g = \frac{(N_g/\mathcal{V})}{(N_g/\mathcal{V})^0} = \frac{\mathcal{N}_g}{(N_g/\mathcal{V})^0} = \frac{\mathcal{N}_g}{(N_A/\mathcal{V}_m^0)}.$$
(18)

225   The concentration for the adsorbate representing a 2D ideal gas, we define as

$$\mathcal{N}_{ads} = \frac{N_{ads}}{\mathcal{A}},$$
(19)

where N_{ads} is the number of gas molecules on the surface and $\mathcal{A}$ is the surface of the system. Its standard concentration is

$$\left(\frac{N_{ads}}{\mathcal{A}}\right)^0 = \frac{n_{ads}^0 \cdot N_A}{\mathcal{A}^0} = \frac{N_A}{\mathcal{A}_m^0},$$
(20)

where n_{ads}^0 is the standard number of moles of adsorbate and $\mathcal{A}_m^0$ indicates the corresponding standard molar surface area.

230   Several suggestions have been made for the surface concentrations (Donaldson et al., 2012;Ammann et al., 2013;Campbell et al., 2016;Kemball and Rideal, 1946;de Boer, 1968). Campbell et al. (2016) argue that when choosing $(N_{ads}/\mathcal{A})^0 = e^{1/3}(N_A/\mathcal{V}_m^0)^{2/3}$, the adsorbate considered as a 2D ideal gas has an entropy of 2/3 of that of the gas species, i.e., $S_{ads}^0 = \frac{2}{3} S_g^0$ when just considering only the translational degrees of freedom (see below). Since a 2D ideal gas is a simple and straightforward assumption especially for physisorption, this standard state has advantages. This standard surface

235   concentration corresponds to $(N_{ads}/\mathcal{A})^0 = 1.17 \times 10^{13}$ cm^{-2} at 298 K at 1000 hPa. In comparison, the IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation is using $(N_{ads}/\mathcal{A})^0 = 1.61 \times 10^{12}$ cm^{-2} (Ammann et al., 2013;Crowley et al., 2013). We define the surface activity for the 2D ideal gas, $a_{ads,2D}$, as the concentration at the surface, $\mathcal{N}_{ads}$, divided by the standard surface concentration, $(N_{ads}/\mathcal{A})^0$:

$$a_{ads,2D} = \frac{(N_{ads}/\mathcal{A})}{(N_{ads}/\mathcal{A})^0} = \frac{(\mathcal{N}_{ads})}{(N_A/\mathcal{A}_m^0)} = \frac{(\mathcal{N}_{ads})}{(N_A/\mathcal{A}_m^0)}.$$
(21)

240   The concentration for the molecule in the TS for desorption, we define as

$$\mathcal{N}_{TS} = \frac{N_{TS}}{\mathcal{A}},$$
(22)

where N_{TS} is the number of molecules in the TS and $\mathcal{A}$ is the area of the system. Its standard concentration is

$$\left(\frac{N_{TS}}{\mathcal{A}}\right)^0 = \frac{n_{TS}^0 \cdot N_A}{\mathcal{A}^0} = \frac{N_A}{\mathcal{A}_m^0},$$
(23)

where n_{TS}^0 is the standard moles of TS molecules and $\mathcal{A}_m^0$ indicates the standard molar surface area. Since the TS is assumed to exist at some fixed distance from the surface but within a very thin layer of thickness, it is treated as a 2D ideal gas, independent of the choice of model for the adsorbate. Hence, we define the surface activity for the TS, a_{TS}, as the concentration of the TS, $\mathcal{N}_{TS}$, divided by the standard concentration of the TS, $(N_{TS}/\mathcal{A})^0$:

$$a_{TS} = \frac{(N_{TS}/\mathcal{A})}{(N_{TS}/\mathcal{A})^0} = \frac{(\mathcal{N}_{TS})}{(N_A/\mathcal{A}_m^0)} = \frac{(\mathcal{N}_{TS})}{(N_A/\mathcal{A}_m^0)} . \tag{24}$$

For many applications, it has been common to normalize the surface concentration, $\mathcal{N}_{ads}$, to a maximum concentration

$$\mathcal{N}_{ads,max} = \frac{N_{ads,max}}{\mathcal{A}} . \tag{25}$$

Then, the surface concentration can also be expressed as a coverage

$$\theta = \frac{\frac{N_{ads}}{\mathcal{A}}}{\frac{N_{ads,max}}{\mathcal{A}}} = \frac{\mathcal{N}_{ads}}{\mathcal{N}_{ads,max}} \tag{26}$$

with a corresponding standard surface coverage

$$\theta^0 = \left(\frac{N_{ads}}{\mathcal{A}}\right)^0 / \frac{N_{ads,max}}{\mathcal{A}} . \tag{27}$$

Similar to the 3D ideal gas, also for the 2D ideal gas case, in principle, there is no limit to the surface concentration. To remain within physically reasonable bounds, all equations in conjunction with the 2D ideal gas model relate to conditions of surface coverages below a typical monolayer coverage of about 10^{14} cm^{-2}.

For the 2D ideal lattice gas case, the maximum number of equivalent but distinguishable sites is $N_{ads,max} = M$, which will be important for the statistical thermodynamic derivation (Supplement S2.3). A physically reasonable choice for M is such that $\frac{M}{\mathcal{A}} = 10^{15}$ cm^{-2}. Then, the standard surface coverage is $\theta^0 = 0.0117$ at 298 K. We define the surface activity for the 2D ideal lattice gas, $a_{ads,latt}$:

$$a_{ads,latt} = \frac{(\theta/(1-\theta))}{(\theta^0/(1-\theta^0))} , \tag{28}$$

where $a_{ads,latt}$ does not depend linearly on surface coverage, θ, and standard surface coverage, θ^0. The reason for this, ultimately, lies in the canonical partition function describing equivalent but distinguishable adsorption sites (Supplement Eqs. (40 and 41)). For example, from the derivation of the chemical potential of the adsorbed 2D ideal lattice gas (Supplement Eq. (56)), it can be clearly seen that Eq. (28) provides a self-consistent definition of the activity for this adsorbate model. The difference between surface coverage and activity will be further discussed below.

3. Thermodynamic Functions of the Desorption Equilibrium

We derive the desorption equilibrium constants for the 2D ideal gas and 2D ideal lattice gas in equilibrium with the gas phase considering the corresponding standard states and partition functions. See also general definitions for equilibrium constants outlined in Supplement section S1. For both adsorbate models we also derive the change in enthalpy and entropy between the

adsorbed and the gas molecule. The derivations in this section will demonstrate the importance of standard states when calculating the equilibrium constants for the desorption processes.

3.1 Desorption equilibrium for adsorbed 2D ideal gas

275   The adsorbed 2D ideal gas is characterized by molecules moving freely parallel to the surface with a constant binding energy to the surface. In other words, the adsorbate vibrates in all directions but has only free translational motion in the horizontal plane. The thermodynamic desorption equilibrium constant is defined by the ratio of the activity in the gas phase (a_g) to that on the surface (a_{ads}),

$$K_{des,2D,g}^0 = \frac{a_g}{a_{ads,2D}} = \frac{\frac{(N_g/\mathcal{V})}{(N_g/\mathcal{V})^0}}{\frac{(N_{ads}/\mathcal{A})}{(N_{ads}/\mathcal{A})^0}} = \frac{\frac{\mathcal{N}_g}{(N_g/\mathcal{V})^0}}{\frac{(\mathcal{N}_{ads})}{(N_A/\mathcal{A}_m^0)}} = \frac{\frac{\mathcal{N}_g}{(N_A/\mathcal{V}_m^0)}}{\frac{(\mathcal{N}_{ads})}{(N_A/\mathcal{A}_m^0)}} \ . \tag{29}$$

280   As indicated by the definition of the adsorbate surface activity, $a_{ads,2D}$, used in the definition of the equilibrium constant, for the 2D ideal gas, the surface activity and thus, also the surface concentration, are linearly correlated with the gas phase activity and concentration (i.e., number density). This is often expressed with a constant (K_{lin}) directly relating gas phase number density with surface concentration (Crowley et al., 2010):

$$\mathcal{N}_{ads} = K_{lin}\mathcal{N}_g \ . \tag{30}$$

285 As mentioned above, no limitations by surface area or number of sites are convoluted in this equation. The relationship between K_{lin} and the equilibrium constant is:

$$K_{lin} = \frac{\mathcal{N}_{ads}}{\mathcal{N}_g} = \frac{(N_{ads}/\mathcal{A})^0}{K_{des,2D,g}^0 (N_g/\mathcal{V})^0} \ . \tag{31}$$

The equilibrium constant, $K_{des,2D,g}^0$, is also related to the free energy change, $\Delta G_{des,2D,g,m}^0$. Since $\Delta G_{des,2D,g,m}^0 = G_{g,m}^0 - G_{ads,2D,m}^0$, we can associate the two free energies with the two partition functions for the two states, and thus express the

290 equilibrium constant as (see Supplement Eqs. (119-123) with Supplement Eqs. (86), (89), (91), (93), (97), (98))

$$K_{des,2D,g}^0 = e^{-\Delta G_{des,2D,g,m}^0/RT} = \frac{q_{g,m}^0}{q_{ads,2D,m}^0} e^{-\frac{E_{des}^0}{RT}} \ . \tag{32}$$

The two partition functions, $q_{g,m}^0$ and $q_{ads,2D,m}^0$ are evaluated using the standard molar volume and area, respectively. Typical values for standard partition functions are given in Table S1. The desorption or activation energy at the molecule's zero-point energy reflects the energy to elevate the adsorbed molecule from the lowest vibrational state to the lowest vibrational state of

295 the activated complex, i.e., the molecular state from which the adsorbate can directly desorb into the gas phase. In other words, E_{des} corresponds to the depth of the potential well (per mole). It has a positive value as defined above (Eq. (5)). When applying the standard adsorption enthalpy and entropy in Eq. (32) (via $\Delta G_{des,2D,g,m}^0$), those have to be based on the same standard concentrations as given in Eqs. (17) and (20), to result in the same $K_{des,2D,g}^0$. Applying the expressions for the partition functions (see Supplement Eqs. (92) and (99)):

300 $\quad K_{des,2D,g}^0 = \frac{\mathcal{V}_m^0(2\pi m k_B T/h^2)^{3/2}}{\mathcal{A}_m^0(2\pi m k_B T/h^2)} e^{-\frac{E_{des}^0}{RT}} = \frac{\mathcal{V}_m^0}{\mathcal{A}_m^0}(2\pi m k_B T/h^2)^{1/2} e^{-\frac{E_{des}^0}{RT}} = \frac{(N_{ads}/\mathcal{A})^0}{(N_g/\mathcal{V})^0}(2\pi m k_B T/h^2)^{1/2} e^{-\frac{E_{des}^0}{RT}}$ (33)

and thus, it follows

$$K_{lin} = (2\pi m k_B T/h^2)^{-1/2} e^{\frac{E_{des}^0}{RT}} .$$ (34)

Hence, K_{lin} can be readily calculated if vibrations are not considered. For a molecule at 298 K with molecular weight of 60 g mol^{-1} and $E_{des}^0 = 45$ kJ mol^{-1}, K_{lin} is about 0.1 cm, a typical value also found experimentally for many species (Crowley et al., 305 2010).

The standard free energy change (and the equilibrium constant) is also related to the adsorption entropy and enthalpy via (Supplement Eqs. (119-121))

$$-RT \ln\left(K_{des,2D,g}^0\right) = \Delta G_{des,2D,g,m}^0 = \Delta H_{des,2D,g,m}^0 - T\Delta S_{des,2D,g,m}^0 = E_{des}^0 - RT \ln\left[\frac{\left(\frac{q_{g,m}^0}{N_A}\right)}{\left(\frac{q_{ads,2D,m}^0}{N_A}\right)}\right] .$$ (35)

As shown in the Supplement (Eqs. (12), (28), and (120))

310 $\quad \Delta H_{des,2D,g,m}^0 = H_{g,m} - H_{ads,2D,m} = \frac{5}{2}RT - \frac{4}{2}RT + E_{des}^0 = \frac{1}{2}RT + E_{des}^0 .$ (36)

The enthalpy difference is due to the change in translational degrees of freedom between the 3D and 2D ideal gases, and the binding energy of the 2D ideal gas on the surface.

As derived in the Supplement (Eq. (16)) from statistical thermodynamics, the entropy in the gas phase is given by the Sackur-Tetrode equation (Campbell et al., 2016;Atkins and de Paula, 2006;Hill, 1986) as

315 $\quad S_{g,m}^0 = R \ln\left(\frac{e^{5/2} q_{g,m}^0}{N_A}\right) = R \ln\left(\mathcal{V}_m^0(2\pi m k_B T/h^2)^{3/2} e^{5/2}\right) = R \ln\left(\frac{(2\pi m k_B T/h^2)^{3/2} e^{5/2}}{(N_g/\mathcal{V})^0}\right),$ (37)

while the entropy on the surface is (Supplement Eq. (33)):

$$S_{ads,2D,m}^0 = R \ln\left(\frac{e^2 q_{ads,2D,m}^0}{N_A}\right) = R \ln\left(e^2 \mathcal{A}_m^0(2\pi m k_B T/h^2)^{2/2}\right) = R \ln\left(\frac{e^2(2\pi m k_B T/h^2)^{2/2}}{(N_{ads}/\mathcal{A})^0}\right) .$$ (38)

As already mentioned above, following Campbell et al. (2016), because the standard state is chosen as $(N_{ads}/\mathcal{A})^0 = e^{1/3}(N_A/\mathcal{V}_m^0)^{2/3}$, the entropy on the surface is 2/3 of that in the gas phase (Eq. (37)), because

320 $\quad S_{ads,2D,m}^0 = R \ln\left(\frac{(2\pi m k_B T/h^2)e^2}{(N_{ads}/\mathcal{A})^0}\right) = R \ln\left(\frac{(2\pi m k_B T/h^2)e^{5/3}}{(N_A/\mathcal{V}_m^0)^{2/3}}\right) = \frac{2}{3}R \ln\left(\frac{(2\pi m k_B T/h^2)^{3/2} e^{5/2}}{(N_g/\mathcal{V})^0}\right) = \frac{2}{3}S_{g,m}^0 .$ (39)

From this follows (Supplement Eq. (121) with Supplement Eq. (89))

$\Delta S_{des,2D,g,m}^0 = S_{g,m}^0 - S_{ads,2D,m}^0 = R \ln\left(\frac{e^{5/2} q_{g,m}^0}{N_A}\right) - R \ln\left(\frac{e^2 q_{ads,2D,m}^0}{N_A}\right) = R \ln\left(\frac{e^{5/2} q_{g,m}^0 N_A}{N_A e^2 q_{ads,2D,m}^0}\right) = R \ln\left(\frac{e^{1/2} q_{g,m}^0}{q_{ads,2D,m}^0}\right) = \frac{1}{2}R +$

$R \ln\left(\frac{q_{g,m}^0}{q_{ads,2D,m}^0}\right),$ (40)

Using $\Delta H_{des,2D,g,m}^0$ (Eq. (36)) and $\Delta S_{des,2D,g,m}^0$ (Eq. (40)) together in the second part of Eq. (35) results in the last expression 325 of Eq. (35). Thus, the expressions for the thermodynamic functions are all consistent with each other.

Substituting the definition of θ (Eq. (27)) into the equation for the adsorption entropy (Eq. (39)) leads to:

$$S^0_{ads,2D,m} = R\ln\left(\frac{(2\pi mk_BT/h^2)e}{(N_{ads,max}/\mathcal{A})}\right) + R\ln(e/\theta^0) = S_{trans,2D} + S_{cov} \, . \tag{41}$$

Thus, the adsorption entropy can be considered the sum of a translational term, $S_{trans,2D}$, and a coverage-dependent term, S_{cov}. For $\theta^0 = 0.012$, $S_{cov} = 5.42R$. At room temperature, $S_{trans,2D}$ varies around $23R$.

3.2 Desorption equilibrium for adsorbed 2D ideal lattice gas

In contrast to the adsorbate being equivalent to a 2D ideal gas, where molecules freely diffuse parallel across the surface, the adsorbed molecule could also randomly populate a fixed number of adsorption sites, where the adsorbates have only vibrational degrees of freedom in three directions. This adsorption model is generally referred to as Langmuir adsorption (Langmuir, 1915, 1916, 1932). It is worthwhile noting that this concept holds for solid and liquid surfaces as long as the number of adsorption sites is given by M. In other words, it is not necessary to know how the M adsorption sites are distributed over the surface and time. The corresponding picture would be to treat the adsorbate as a 2D ideal lattice gas (Campbell et al., 2016). The activity is then given by $\frac{(\theta/(1-\theta))}{(\theta^0/(1-\theta^0))}$ (Supplement S2.3). In analogy to Eq. (29), the equilibrium constant is formulated as the ratio of activities

$$K^0_{des,latt,g} = \frac{a_g}{a_{ads,latt}} = \frac{\frac{(N_g/\mathcal{V})}{(N_g/\mathcal{V})^0}}{\frac{(\theta/(1-\theta))}{(\theta^0/(1-\theta^0))}} = \frac{\frac{\mathcal{N}_g}{(N_g/\mathcal{V})^0}}{\frac{(\theta/(1-\theta))}{(\theta^0/(1-\theta^0))}} = \frac{\frac{\mathcal{N}_g}{(N_A/\mathcal{V}^0_m)}}{\frac{(\theta/(1-\theta))}{(\theta^0/(1-\theta^0))}} \, . \tag{42}$$

In the traditional formulation of Langmuir adsorption, the coverage is related to the gas phase concentration via

$$\theta = \frac{K_{Lang}\mathcal{N}_g}{(1+K_{Lang}\mathcal{N}_g)} \, , \tag{43}$$

where K_{Lang} is the Langmuir adsorption constant. From this, we can derive

$$(\theta/(1-\theta)) = K_{Lang}\mathcal{N}_g \, . \tag{44}$$

This equation clearly demonstrates the usefulness of the definition of the adsorbate surface activity. Thus, for the relationship between the K_{Lang} and $K^0_{ads,latt}$, we obtain

$$K_{Lang} = \frac{(\theta^0/(1-\theta^0))}{K^0_{des,latt,g}(N_g/\mathcal{V})^0} \, . \tag{45}$$

This relationship demonstrates that the functional form of the dependence of the surface coverage with pressure or concentration in the gas phase is the same for both definitions of the equilibrium constants (apart from the inverse formulation of the equilibrium constant as the ratio of gas-to-surface concentrations (Eq. (42)) versus surface-to-gas concentrations). However, only $K^0_{des,latt,g}$ can be related to the free energy change directly. Also in this case, the standard free energy change, $\Delta G^0_{des,latt,g,m}$, embodied in $K^0_{des,latt,g}$, can be related to the partition functions describing the molecules in the gas phase and adsorbed phases as (see Supplement Eqs. (131, 133, 134) with Supplement Eqs. (86), (89), (91), (100), (103), 105))

$$K_{des,latt,g}^0 = \frac{\left(\frac{q_{g,m}^0}{N_A}\right)}{q_{ads,latt}\frac{(1-\theta^0)}{\theta^0}} e^{-\frac{E_{des}^0}{RT}} . \tag{46}$$

When inserting the expressions for the standard molar partition functions for the translational motions (see Supplement Eq. (92)):

$$K_{des,latt,g}^0 = \frac{\left(\frac{v_m^0(2\pi m k_B T/h^2)^{3/2}}{N_A}\right)}{q_{ads,latt}\frac{(1-\theta^0)}{\theta^0}} e^{-\frac{E_{des}^0}{RT}} = \frac{(2\pi m k_B T/h^2)^{3/2}}{(N_g/\mathcal{V})^0 q_{ads,latt}\frac{(1-\theta^0)}{\theta^0}} e^{-\frac{E_{des}^0}{RT}} . \tag{47}$$

K_{Lang} can now be expressed as

$$K_{Lang} = \frac{q_{ads,latt} e^{\frac{E_{des}^0}{RT}}}{(2\pi m k_B T/h^2)^{3/2}} . \tag{48}$$

Hence, K_{Lang} can be readily calculated. For a molecule at 273 K with molecular weight of 48 g mol⁻¹, and vibration frequency of about 10^{13} s⁻¹, and $E_{des}^0 = 70$ kJ mol⁻¹, K_{Lang} is about 10^{-13} cm³, representing a typical value (Ammann et al., 2013).

Since $K_{des,latt,g}^0$ is also related to the enthalpy and entropy of adsorption, we can write

$$-RT\ln(K_{des,latt,g}^0) = \Delta G_{des,latt,g,m}^0 = \Delta H_{des,latt,g,m}^0 - T\Delta S_{des,latt,g,m}^0 = E_{des}^0 - RT\ln\frac{\left(\frac{q_{g,m}^0}{N_A}\right)}{q_{ads,latt}\frac{(1-\theta^0)}{\theta^0}} . \tag{49}$$

In variation to the case of the 2D ideal gas, and neglecting vibrations, $U_{ads,latt,m} = -E_{des}^0$ (Supplement Eq. (45)), due to the absence of translational motion (while in the gas phase, $U_{g,m} = \frac{3}{2}RT$, or for the 2D ideal gas, $U_{ads,2D,m} = RT - E_{des}^0$). Also, as shown in the Supplement Eq. (49) (neglecting contribution of vibrations in gas and adsorbed phase), we obtain

$$H_{ads,latt,m}^0 = -E_{des}^0 - RT\frac{\ln(1-\theta^0)}{\theta^0}. \tag{50}$$

Overall, for the change in enthalpy between gas and adsorbed states (see also Supplement Eq. (133)), we obtain

$$\Delta H_{des,latt,g,m}^0 = H_{g,m}^0 - H_{ads,latt,m}^0 = \frac{5}{2}RT + E_{des}^0 + RT\frac{\ln(1-\theta^0)}{\theta^0} . \tag{51}$$

We can now obtain the relationship between the desorption energy and the adsorption enthalpy as

$$E_{des}^0 = \Delta H_{des,latt,g,m}^0(T) - \frac{5}{2}RT - RT\frac{\ln(1-\theta^0)}{\theta^0} . \tag{52}$$

Thus, in the case of the 2D ideal lattice gas, the relationship between the desorption energy and the enthalpy contains the standard surface coverage explicitly.

For the entropy of the adsorbed 2D ideal lattice gas (Supplement Eqs. (54) and (103)), we can write (Campbell et al., 2016)

$$S_{ads,latt,m}^0 = R\left(\ln q_{ads,latt} - \beta\left(\frac{\partial \ln q_{ads,latt}}{\partial \beta}\right)\right) + R\left(\ln\left(\frac{(1-\theta^0)}{\theta^0}\right) - \frac{\ln(1-\theta^0)}{\theta^0}\right) = S_{ads,latt,vib}^0 + S_{ads,latt,config}^0 . \tag{53}$$

The adsorption entropy has a contribution for the vibrations in three dimensions at the site, $S_{ads,latt,vib}$, (related to $q_{ads,latt}$, Supplement Eq. (38)) and a configurational contribution, $S_{ads,latt,config}$. Using the above standard state of $\theta^0 = 0.012$ leads to

$$S^0_{ads,latt,m} = S^0_{ads,latt,vib} + 5.42R .\tag{54}$$

Typical values for S_{vib} for 3 dimensions at room temperature, assuming a vibration frequency of 10^{14} s^{-1}, are around $4.90R$ (Campbell et al., 2016;McQuarrie, 2000;Atkins and de Paula, 2006). Note that also another choice of θ^0 has been used, i.e., $\theta^0 = 0.5$, because then, the $\theta^0/(1 - \theta^0)$ is unity. Consequently, this leads to a different numerical value for the standard adsorption entropy ($S_{ads,latt,config} = 1.39R$). The choice of the standard state adopted here and suggested by Campbell et al. (2016) has the advantage that the standard adsorbate coverage is low and the coverage dependent contributions $S_{ads,latt,config}$ for the 2D ideal lattice gas and S_{cov} for the 2D ideal gas have nearly the same value (5.417 and 5.423, respectively).

For the change in entropy upon desorption, we can derive (Supplement Eq. (135)(Campbell et al., 2016))

$$\Delta S^0_{des,latt,g,m} = S^0_{g,m} - S^0_{ads,latt,m} = R \ln\left(\frac{e^{5/2} q^0_{g,m}}{N_A}\right) - R\left(\ln q_{ads,latt} - \beta\left(\frac{\partial \ln q_{ads,latt}}{\partial \beta}\right)\right) - R\left(\ln\left(\frac{(1-\theta^0)}{\theta^0}\right) - \frac{\ln(1-\theta^0)}{\theta^0}\right).\tag{55}$$

3.3 Adsorbate model comparison of surface concentration, activity, and coverage

We can now use the results in section 3.1 and 3.2 to evaluate the equilibrium conditions between gas phase and surface concentrations and activities and respective coverages for the 2D ideal gas and 2D ideal lattice gas, presented in Figs. 2-4. The thermodynamic quantities to reproduce these figures are given in Table S1. Figure 2 illustrates the behavior of the adsorption equilibria for the 2D ideal gas and the 2D ideal lattice gas cases in terms of surface concentration versus gas phase concentration. As intuitively clear from the defining equations, for the 2D ideal gas case, the surface concentration increases linearly with gas phase concentration without a limitation, thus, increasing beyond a monolayer coverage, here assumed as 10^{19} m^{-2}. In turn, for the 2D ideal lattice gas case, the initially linear increase is followed by the well-established adsorption saturation due to the limitation by the number of available sites on the surface, known as Langmuir adsorption. Note that we purposely chose a larger desorption energy for this case, leading to the higher initial slope. Assuming the same desorption energy for both cases, the initial slopes would be the same for both adsorption models. As shown in Fig. 3, when normalizing the surface concentration to the maximum number of adsorption sites to obtain the coverage, the picture remains the same.

In contrast to Figs. 2 and 3, when considered in terms of activities, both adsorbate models exhibit a linear relationship between the surface activity and the gas phase activity as shown in Fig. 4. While trivial for the 2D ideal gas case, for the 2D ideal lattice gas case, this is related to the definition of the activity as being proportional to $\theta/(1 - \theta)$. Note that the gas phase activity range in Fig. 4 covers the same gas phase concentration range as in Figs. 2 and 3. Also note that the numerical values for the activities are completely different for the two cases. For example, for the 2D ideal gas case, at values of θ of 0.5 and 0.8, $a_{ads,2D}$ is 42.8 and 68.4, respectively, while for the 2D ideal lattice gas at the same coverages, $a_{ads,latt}$ is 85.9 and 336.8, respectively. On the one hand, the different slopes of surface activity as a function of gas phase activity are related to the normalization to the two different standard states. On the other hand, when considered as a function of θ, the relationship between the two surface activities is highly non-linear due to the diverging nature of the $\theta/(1 - \theta)$ term for high θ.

4. Derivation of the Desorption Rate and Pre-Exponential Factor A

410 Above we have outlined the determination of the equilibrium constant K^0_{des} and the importance to consider the standard concentrations. In this section we will derive the desorption rate and its pre-exponential factor A from TS theory, which starts from the free energy change between the adsorbate and the TS. This exercise will demonstrate the necessity of knowing the standard state of the entropic contribution or the standard concentrations of the TS and adsorbate for the correct derivation of A. As we will show below, the pre-exponential factor A in the desorption rate coefficient, k_{des}, includes the entropic change

415 between the adsorbed and TS of the desorbing molecule. If we like to calculate A, the standard desorption entropy has to be based on the same standard concentrations as for the definition of the activity. Again, the same activity definitions have to be applied to calculate actual desorption rates. We will see that without knowledge of the chosen standard state of the entropy or standard concentrations of TS and adsorbate species, A cannot be accurately derived. Furthermore, we examine two cases of adsorbate where we first treat the adsorbate as a 2D ideal gas and secondly as a 2D ideal lattice gas. The TS is treated as a 2D

420 ideal gas in both cases. This section follows the derivations outlined in Campbell et al. (2016). Detailed derivations are given in the Supplement.

In general, the desorption rate can be expressed as

$$\frac{R_{des}}{\mathcal{A}} = -\frac{d\mathcal{N}_{ads}}{dt} = -k_{des}\mathcal{N}_{ads} \,, \tag{56}$$

where k_{des} represents the first-order rate coefficient for desorption (in units s^{-1}), describing the rate of change of surface

425 concentration. As is evident from the definitions of activity above, the surface concentration is not necessarily proportional to the surface activity. We therefore introduce a separate rate expression and corresponding desorption rate coefficient acting on surface activities, R^a_{des} and k^a_{des}, respectively, as

$$R^a_{des} = -\frac{da_{ads}}{dt} = -k^a_{des}a_{ads} \,. \tag{57}$$

4.1 Desorption of a 2D ideal gas

430 According to conventional transition state theory (CTST) (Kolasinski, 2012), E_{des} is the activation energy necessary to elevate an adsorbed species from the lowest vibrational state to the lowest vibrational state of the activated complex, i.e., the molecular state from which the adsorbate can directly desorb into the gas phase. Note that desorption is always considered an activated process, thus, also including the case of desorption of a physisorbed molecule, and irrespective of whether an energy barrier is considered or not. In CTST, rates are derived from assuming equilibrium between the adsorbed state and the TS, which is the

435 reason for discussing the overall adsorption/desorption equilibrium in detail above. The TS for desorption is assumed to exist at some fixed distance from the surface but within a very thin layer of thickness d, where it experiences an increase in potential energy to a maximum value expressed by the energy barrier ϵ^0_b due to its interaction with the surface as outlined above. In principle, the TS resembles a 2D ideal gas, but as discussed further below and in the Supplement S3.4, CTST assumes molecules in the TS exhibit translational motion along the reaction coordinate, which for the case of desorption is orthogonally

440   away from the surface. The associated equilibrium constant is related to the free energy change between the adsorbed state and the TS, each expressed with the corresponding standard molar partition function, $q_{ads,2D,m}^0$, and $q_{TS,m}^0$ (Supplement sections S1, S2, and S4, Eqs. (3), (22), (60), (117) and (152))

$$K_{des,2D,TS}^0 = \frac{\left(\frac{q_{TS,m}^0}{N_A}\right)}{\left(\frac{q_{ads,2D,m}^0}{N_A}\right)} e^{-\frac{\left(E_{des}^0 + E_b^0\right)}{RT}} = \frac{q_{TS,m}^0}{q_{ads,2D,m}^0} e^{-\frac{\left(E_{des}^0 + E_b^0\right)}{RT}} . \tag{58}$$

The equilibrium constant is also related to the ratio of activities

445     $$K_{des,2D,TS}^0 = e^{-\Delta G_{des,2D,TS,m}^0/RT} = \frac{\frac{(N_{TS}/\mathcal{A})}{(N_{TS}/\mathcal{A})^0}}{\frac{(N_{ads}/\mathcal{A})}{(N_{ads}/\mathcal{A})^0}} = \frac{\frac{\mathcal{N}_{TS}}{(N_{TS}/\mathcal{A})^0}}{\frac{\mathcal{N}_{ads}}{(N_{ads}/\mathcal{A})^0}} = \frac{a_{TS}}{a_{ads}} = \frac{q_{TS,m}^0}{q_{ads,2D,m}^0} e^{-\frac{\left(E_{des}^0 + E_b^0\right)}{RT}} . \tag{59}$$

As discussed above, the entropy values depend strongly on the configuration (i.e., degrees of freedom) of the species in the adsorbed state and the TS.

      Within this CTST approach, the desorption rate can be obtained by assuming that the TS has a finite width d across which the molecule moves with its mean thermal velocity in the direction orthogonal to the surface

450     $$\frac{R_{des,2D}}{\mathcal{A}} = \kappa \left(\frac{N_{TS}}{\mathcal{A}}\right) \frac{(k_B T/2\pi m)^{1/2}}{d} , \tag{60}$$

where κ is a transmission coefficient defining the probability with which an activated complex proceeds to desorption (Kolasinski, 2012). The partition function for the translational motion of the transition state in the direction of desorption is

$$q_{TS,des} = (2\pi m k_B T/h^2)^{1/2} d . \tag{61}$$

Solving this for d and inserting into Eq. (60) allows to express the desorption rate as a function of this partition function:

455     $$\frac{R_{des,2D}}{\mathcal{A}} = \kappa \left(\frac{k_B T}{h}\right) \left(\frac{N_{TS}}{\mathcal{A}}\right) \frac{1}{q_{TS,des}} . \tag{62}$$

The surface concentration of the TS can be derived from the equilibrium (Eq. (59))

$$\mathcal{N}_{TS} = \frac{N_{TS}}{\mathcal{A}} = \frac{q_{TS,m}^0}{q_{ads,2D,m}^0} \frac{(N_{TS}/\mathcal{A})^0}{(N_{ads}/\mathcal{A})^0} e^{-\frac{\left(E_{des}^0 + E_b^0\right)}{RT}} \mathcal{N}_{ads} . \tag{63}$$

Inserting Eq. (63) into Eq. (62) leads to

$$\frac{R_{des,2D}}{\mathcal{A}} = \kappa \left(\frac{k_B T}{h}\right) \left(\frac{1}{q_{TS,des}} \frac{q_{TS,m}^0}{q_{ads,2D,m}^0}\right) \frac{(N_{TS}/\mathcal{A})^0}{(N_{ads}/\mathcal{A})^0} e^{-\frac{\left(E_{des}^0 + E_b^0\right)}{RT}} \mathcal{N}_{ads} . \tag{64}$$

460   When considering surface activities, by dividing by the standard surface concentration we obtain

$$R_{des,2D}^a = \frac{\frac{R_{des,2D}}{\mathcal{A}}}{(N_{ads}/\mathcal{A})^0} = \kappa \left(\frac{k_B T}{h}\right) \left(\frac{1}{q_{TS,des}} \frac{q_{TS,m}^0}{q_{ads,2D,m}^0}\right) \frac{(N_{TS}/\mathcal{A})^0}{(N_{ads}/\mathcal{A})^0} e^{-\frac{\left(E_{des}^0 + E_b^0\right)}{RT}} a_{ads,2D} . \tag{65}$$

      As further discussed in Supplemental Section 3.4, the activation process can be conceptually 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. Thus, activation does not include the energy of the motion along the desorption coordinate, and as such is less than the energy associated with the TS. When defining $\Delta G_{des,2D,act,m}^0$ of desorption as $\Delta G_{des,2D,TS,m}^0$ (see Supplement Eq. (145) and (146))

minus the TS's free energy associated with the motion along the desorption coordinate, expressed by its molecular partition function, $q_{TS,des}$, we obtain

$$e^{-\Delta G^0_{des,2D,act,m}/RT} = \frac{e^{-\Delta G^0_{des,2D,TS,m}/RT}}{q_{TS,des}} = \frac{1}{q_{TS,des}} \frac{q^0_{TS,m}}{q^0_{ads,2D,m}} e^{-\frac{\left(E^0_{des}+E^0_b\right)}{RT}} . \tag{66}$$

With this definition of $\Delta G^0_{des,2D,act,m}$, we can express the desorption rate as

$$\frac{R_{des,2D}}{\mathcal{A}} = \kappa \left(\frac{k_B T}{h}\right) \left(\frac{1}{q_{TS,des}} \frac{q^0_{TS,m}}{q^0_{ads,2D,m}}\right) \frac{(N_{TS}/\mathcal{A})^0}{(N_{ads}/\mathcal{A})^0} e^{-\frac{\left(E^0_{des}+E^0_b\right)}{RT}} \mathcal{N}_{ads} = \kappa \left(\frac{k_B T}{h}\right) e^{-\Delta G^0_{des,2D,act,m}/RT} \frac{(N_{TS}/\mathcal{A})^0}{(N_{ads}/\mathcal{A})^0} \mathcal{N}_{ads} \tag{67}$$

and obtain for the activity-based desorption rate

$$R^a_{des,2D} = \kappa \left(\frac{k_B T}{h}\right) \left(\frac{1}{q_{TS,des}} \frac{q^0_{TS,m}}{q^0_{ads,2D,m}}\right) \frac{(N_{TS}/\mathcal{A})^0}{(N_{ads}/\mathcal{A})^0} e^{-\frac{\left(E^0_{des}+E^0_b\right)}{RT}} a_{ads,2D} = \kappa \left(\frac{k_B T}{h}\right) e^{-\Delta G^0_{des,2D,act,m}/RT} \frac{(N_{TS}/\mathcal{A})^0}{(N_{ads}/\mathcal{A})^0} a_{ads,2D} . \tag{68}$$

Thus, we can derive the desorption rate coefficient as

$$k_{des,2D} = k^a_{des,2D} = \kappa \left(\frac{k_B T}{h}\right) \frac{(N_{TS}/\mathcal{A})^0}{(N_{ads}/\mathcal{A})^0} e^{-\Delta G^0_{des,2D,act,m}/RT} = \kappa \left(\frac{k_B T}{h}\right) e^{-\Delta G^0_{des,2D,act,m}/RT} , \tag{69}$$

where we assume $\frac{(N_{TS}/\mathcal{A})^0}{(N_{ads}/\mathcal{A})^0} = 1$. Equation (69) is consistent with Eq. (4.4.24) in Kolasinski (2012), since the standard concentrations are the same for the TS and the adsorbed state in this case.

Following Campbell et al. (2016) defining $q^{0'}_{TS}/\mathcal{A}^0_m$ as the partition function for the TS after omitting motion in the direction of the reaction coordinate, this leaves the partition function for a 2D ideal gas (Supplement Eq. (117)):

$$\left(\frac{q^0_{TS,m}}{q_{TS,des}}\right) = q^{0'}_{TS,m} = q^0_{TS,2D,m} = \mathcal{A}^0_m (2\pi m k_B T/h^2)^{2/2} . \tag{70}$$

Using Eq. (70) in Eq. (71), we obtain

$$\frac{R_{des}}{\mathcal{A}} = \kappa \left(\frac{k_B T}{h}\right) \left(\frac{q^{0'}_{TS,m}}{q^0_{ads,2D,m}}\right) \frac{(N_{TS}/\mathcal{A})^0}{(N_{ads}/\mathcal{A})^0} e^{-\frac{\left(E^0_{des}+E^0_b\right)}{RT}} \mathcal{N}_{ads} \tag{71}$$

and

$$R^a_{des,2D} = \kappa \left(\frac{k_B T}{h}\right) \left(\frac{q^{0'}_{TS,m}}{q^0_{ads,2D,m}}\right) \frac{(N_{TS}/\mathcal{A})^0}{(N_{ads}/\mathcal{A})^0} e^{-\frac{\left(E^0_{des}+E^0_b\right)}{RT}} a_{ads,2D} . \tag{72}$$

Identifying Eq. (71) with Eq. (56) yields

$$k_{des,2D} = k^a_{des,2D} = \kappa \left(\frac{k_B T}{h}\right) \left(\frac{q^{0'}_{TS}}{q^0_{ads,2D,m}}\right) \frac{(N_{TS}/\mathcal{A})^0}{(N_{ads}/\mathcal{A})^0} e^{-\frac{\left(E^0_{des}+E^0_b\right)}{RT}} . \tag{73}$$

We can convert the standard molar partition functions back to the molecular ones. For that, we consider that $\left(\frac{N_{ads}}{\mathcal{A}}\right)^0 = \frac{n_{ads} \cdot N_A}{\mathcal{A}^0} = \frac{N_A}{\mathcal{A}^0_m}$ and analogously for the TS, then we obtain

$$\frac{1}{q_{TS,des}} \frac{q^0_{TS,m}}{q^0_{ads,2D,m}} \frac{(N_{TS}/\mathcal{A})^0}{(N_{ads}/\mathcal{A})^0} = \frac{q^{0'}_{TS,m}}{q^0_{ads,2D,m}} \frac{(N_{TS}/\mathcal{A})^0}{(N_{ads}/\mathcal{A})^0} = \frac{\frac{q'_{TS}}{\mathcal{A}}}{\frac{q_{ads,2D}}{\mathcal{A}}} = \frac{q'_{TS}}{q_{ads,2D}} . \tag{74}$$

This yields

490    $$k_{des,2D} = k^a_{des,2D} = \kappa \left(\frac{k_B T}{h}\right)\left(\frac{q'_{TS}}{q_{ads,2D}}\right) e^{-\frac{\left(E^0_{des}+E^0_b\right)}{RT}} . \tag{75}$$

Hence, we have an expression for $k_{des,2D}$ based on thermodynamic quantities (Eq. (69)) and on molecular properties (Eq. (75)). The latter is consistent with Eq. (4.4.20) given by (Kolasinski, 2012):

$$k_{des,2D} = k^a_{des,2D} = \kappa \frac{k_B T}{h} \frac{q_{\ddagger}}{q_{ads}} e^{-\frac{\left(E^0_{des}+E^0_b\right)}{RT}} , \tag{76}$$

where $q_{\ddagger}$ represents the partition function of the TS, for which, in the explanation of Kolasinski, 'the loose vibration in the

495   direction of desorption has been factored out' and can be identified with q'_{TS}. Note that factoring out a 'loose' vibration has the same effect on q_{TS} as assigning the TS a translation over the length d, as discussed above and in other text books (Hill, 1986; Pilling and Seakins, 1996). As outlined above, in the literature, the desorption energy often includes the energy barrier (Kolasinski, 2012), i.e., $E^0_{des,act} = E^0_{des}+E^0_b$.

     The above derivations include the definition of the free energy of desorption (i.e., the free energy change between the

500   adsorbed and the TS) and, thus, allow us to evaluate the pre-exponential factor A. We first formulate k_{des} using the definition of $\Delta G^0_{des,2D,act,m}$ (Eq. 66), equate it with the expression in Eq. (75) and apply the relationship $\Delta H^0_{des,2D,act,m} = E^0_b + E^0_{des}$ (Supplement Eq. (148) with Supplement Eqs. (108) and (93))

$$k_{des,2D} = k^a_{des,2D} = \kappa \left(\frac{k_B T}{h}\right)\frac{(N_{TS}/\mathcal{A})^0}{(N_{ads}/\mathcal{A})^0} e^{-\Delta G^0_{des,2D,act,m}/RT} = \kappa \left(\frac{k_B T}{h}\right)\left(\frac{q'_{TS}}{q_{ads,2D}}\right) e^{-\frac{\left(E^0_{des}+E^0_b\right)}{RT}} \equiv$$

$$\kappa \left(\frac{k_B T}{h}\right)\frac{(N_{TS}/\mathcal{A})^0}{(N_{ads}/\mathcal{A})^0} e^{\Delta S^0_{des,2D,act,m}/R} e^{-\Delta H^0_{des,2D,act,m}/RT} = \kappa \left(\frac{k_B T}{h}\right)\left(\frac{q'_{TS}}{q_{ads,2D}}\right) e^{-\frac{\left(E^0_{des}+E^0_b\right)}{RT}} \equiv$$

505    $$\kappa \left(\frac{k_B T}{h}\right)\frac{(N_{TS}/\mathcal{A})^0}{(N_{ads}/\mathcal{A})^0} e^{\Delta S^0_{des,2D,act,m}/R} e^{-\frac{\left(E^0_{des}+E^0_b\right)}{RT}} = \kappa \left(\frac{k_B T}{h}\right)\left(\frac{q'_{TS}}{q_{ads,2D}}\right) e^{-\frac{\left(E^0_{des}+E^0_b\right)}{RT}} . \tag{77}$$

With this, we can define the pre-exponential factor A as

$$A_{des,2D} = \kappa \left(\frac{k_B T}{h}\right)\left(\frac{q'_{TS}}{q_{ads,2D}}\right) = \kappa \left(\frac{k_B T}{h}\right)\frac{(N_{TS}/\mathcal{A})^0}{(N_{ads}/\mathcal{A})^0} e^{\Delta S^0_{des,2D,act,m}/R} = \kappa \left(\frac{k_B T}{h}\right)\frac{(N_{TS}/\mathcal{A})^0}{(N_{ads}/\mathcal{A})^0} e^{\frac{S^0_{act,m}-S^0_{ads,2D,m}}{R}} . \tag{78}$$

     Equation (78) demonstrates the relevance of knowing the standard state. The first expression on the right-hand side, the formulation in terms of the molecular partition functions (q'_{TS}, $q_{ads,2D}$), indicates that the value of $A_{des,2D}$ is directly linked to

510   the assumptions of the adsorbate model as a basis for the calculation of the partition functions. In contrast, when $A_{des,2D}$ is obtained from the entropy of activation ($\Delta S^0_{des,2D,act,m}$), the Arrhenius term needs to be corrected by the ratio of the standard states, $\frac{(N_{TS}/\mathcal{A})^0}{(N_{ads}/\mathcal{A})^0}$.

     Above derivations (Eq. (77)) now allow for the interpretation of $A_{des,2D}$. Let us assume $\kappa \approx 1$. Also recall that if both adsorbed and TS are 2D ideal gases and if we neglect vibrations, $\left(\frac{q'_{TS}}{q_{ads,2D}}\right) = \frac{(2\pi m k_B T/h^2)}{(2\pi m k_B T/h^2)} = 1$, which is equivalent to having

515   no significant change in entropy, i.e., $\Delta S^0_{des,2D,act,m} = 0$. This leads to the commonly applied value of $A_{des,2D} \approx \frac{k_B T}{h} \approx$ $6 \times 10^{12} \approx 10^{13}$ s^{-1} at room temperature (298 K). It is clear, that if the ratio of the partition functions deviates significantly

from one and, thus, there are significant changes in $\Delta S^0_{des,2D,act,m}$ when going from the adsorbed state to the activated state, substantial deviations from the 'benchmark' value of 10^{13} s^{-1} are expected. For example, $A_{des,2D} > 10^{13}$ s^{-1} with $\Delta S^0_{des,2D,act,m} > 0$ and $\frac{q^{0\prime}_{TS,m}}{q^0_{ads,2D,m}} > 1$, which represents the case where a greater number of accessible configurations of the TS (more degrees of freedom) are available that are more easily excited by thermal energy than the adsorbed state. In contrast, $A_{des,2D} < 10^{13}$ s^{-1}, $\Delta S^0_{des,2D,act,m} < 0$ and $\frac{q^{0\prime}_{TS,m}}{q^0_{ads,2D,m}} < 1$ indicates that the TS is constrained where, e.g., the molecule has to obtain a specific configuration in the activated complex. Campbell et al.(2013) showed that the observed variations in A for different adsorbates can be well described by a linear correlation between adsorbate entropies and gas-phase entropies provided the adsorbate's surface residence time is less than $\sim$1000 s. The underlying explanation is that the gas molecule's motions in z direction are arrested (i.e., frustrated rotational and translational modes) resulting in a steep interaction potential well in the z direction, better described by a hindered translator model.

4.2 Desorption of a 2D ideal lattice gas

For the case of the adsorbate being a 2D ideal lattice gas, but the TS a 2D ideal gas, the associated equilibrium constant is related to the free energy change between the TS and the absorbed state, each expressed with the corresponding standard molar partition function, $q^0_{TS,m}$, and $q_{ads,latt}$ (Supplement Eqs. (4), (38), and (175)):

$$K^0_{des,latt,TS} = \frac{\left(\frac{q^0_{TS,m}}{N_A}\right)}{q_{ads,latt}\frac{(1-\theta^0)}{\theta^0}} e^{-\frac{\left(E^0_{des}+E^0_b\right)}{RT}}. \tag{79}$$

The equilibrium constant is also related to the ratio of activities:

$$K^0_{des,latt,TS} = e^{-\Delta G^0_{des,latt,TS,m}/RT} = \frac{\frac{(N_{TS}/\mathcal{A})}{(N_{TS}/\mathcal{A})^0}}{\frac{(\theta/(1-\theta))}{(\theta^0/(1-\theta^0))}} = \frac{\frac{\mathcal{N}_{TS}}{(N_{TS}/\mathcal{A})^0}}{\frac{(\theta/(1-\theta))}{(\theta^0/(1-\theta^0))}} = \frac{\left(\frac{q^0_{TS,m}}{N_A}\right)}{\left(q_{ads,latt}\frac{(1-\theta^0)}{\theta^0}\right)} e^{-\frac{\left(E^0_{des}+E^0_b\right)}{RT}}. \tag{80}$$

Note that $q_{ads,latt}$ represents only vibrations and rotations. In addition, for the 2D ideal lattice gas, the surface activity is based on the coverage, and correspondingly, for the normalization to the standard state, $\theta^0/(1-\theta^0)$ is replacing $(N_{ads}/\mathcal{A})^0$. Using the same procedure as for the 2D ideal gas case, i.e., rearranging Eq. (80), leads to (Campbell et al., 2016):

$$\mathcal{N}_{TS} = \frac{N_{TS}}{\mathcal{A}} = \frac{\left(\frac{q^0_{TS,m}}{N_A}\frac{(\theta/(1-\theta))}{(\theta^0/(1-\theta^0))}\right)}{\left(q_{ads,latt}\frac{(1-\theta^0)}{\theta^0}\right)} (N_{TS}/\mathcal{A})^0 e^{-\frac{\left(E^0_{des}+E^0_b\right)}{RT}} = \frac{\left(\frac{q^0_{TS,m}}{N_A}\right)}{(q_{ads,latt})} (N_{TS}/\mathcal{A})^0 e^{-\frac{\left(E^0_{des}+E^0_b\right)}{RT}} (\theta/(1-\theta)). \tag{81}$$

Setting this into Eq. (62) yields

$$\frac{R_{des,latt}}{\mathcal{A}} = \kappa \left(\frac{k_B T}{h}\right) \frac{\left(\frac{q^0_{TS,m}}{N_A}\right)}{q_{TS,des} q_{ads,latt}} (N_{TS}/\mathcal{A})^0 e^{-\frac{\left(E^0_{des}+E^0_b\right)}{RT}} (\theta/(1-\theta)). \tag{82}$$

We note that Eq. (82) differs from Eq. (71) for the ideal 2D gas, such that $q_{ads,latt}$ has only vibrational degrees of freedom (instead of two translational motions) (Campbell et al., 2016).

Equation (82) highlights that the desorption rate is not proportional to the surface concentration but is depending non-linearly on the surface coverage θ for high θ. Figure 5 highlights this behavior. The desorption rate first changes linearly with coverage for both adsorbate models, but then strongly non-linearly for the 2D ideal lattice gas when approaching high (θ close to 1) surface coverages. This fact makes conversion of the rate expression to the surface activity challenging. The rate of change in surface activity is related to the rate of change in θ as (Supplement Eq. (2))

$$\frac{R_{des,latt}}{\mathcal{A}N_{ads,max}} = -\frac{d\theta}{dt} . \tag{83}$$

Assuming that the steady state surface concentration of the TS remains much smaller than the number of adsorbed molecules (in a time interval necessary to populate the TS), and correspondingly the desorption rate remains relatively small in comparison to the actual coverage, we can write

$$\frac{R_{des,latt}}{\mathcal{A}N_{ads,max}} = -\frac{d\theta}{dt} \approx -\frac{d(\theta/(1-\theta))}{dt} , \tag{84}$$

since

$$\lim_{\theta \to 0} \left(\frac{\theta}{1-\theta}\right) \approx \theta .$$

In other words, for small rates of change of θ, the desorption rate in terms of rate of change of activity can be assumed to depend linearly on θ. Since this concerns the rate of change of θ, Eq. (84) holds for any coverage. This allows us to express the desorption rate in terms of activity as

$$\frac{R_{des,latt}}{\mathcal{A}N_{ads,max}(\theta^0/(1-\theta^0))} \approx -\frac{d\left(\frac{(\theta/(1-\theta))}{(\theta^0/(1-\theta^0))}\right)}{dt} = -\frac{da_{ads,latt}}{dt} . \tag{85}$$

Therefore, dividing Eq. (82) by $\mathcal{N}_{ads,max}(\theta^0/(1-\theta^0))$ leads to the corresponding activity-based desorption rate expression

$$R^a_{des,latt} = \kappa \left(\frac{k_B T}{h}\right) \frac{\left(\frac{q^0_{TS,m}}{N_A}\right)}{q_{TS,des}(q_{ads,latt})} e^{-\frac{\left(E^0_{des}+E^0_b\right)}{RT}} \frac{(N_{TS}/\mathcal{A})^0}{\mathcal{N}_{ads,max}} a_{ads,latt} . \tag{86}$$

We now follow a similar derivation as for the 2D ideal gas. We define $\Delta G^0_{des,latt,act,m}$ of desorption as $\Delta G^0_{des,latt,TS,m}$ minus the TS's free energy associated with the motion along the desorption coordinate and obtain

$$e^{-\Delta G^0_{des,latt,act,m}/RT} = \frac{e^{-\Delta G^0_{des,latt,TS,m}/RT}}{q_{TS,des}} = \frac{1}{q_{TS,des}} \frac{\left(\frac{q^0_{TS,m}}{N_A}\right)}{\left(q_{ads,latt}\frac{(1-\theta^0)}{\theta^0}\right)} e^{-\frac{\left(E^0_{des}+E^0_b\right)}{RT}} . \tag{87}$$

Thus, we can express the desorption rate for an adsorbate treated as a 2D ideal lattice gas as

$$\frac{R_{des,latt}}{\mathcal{A}} = \kappa \left(\frac{k_B T}{h}\right) \frac{\left(\frac{q^0_{TS,m}}{N_A}\right)}{q_{TS,des}\left(q_{ads,latt}\frac{(1-\theta^0)}{\theta^0}\right)} e^{-\frac{\left(E^0_{des}+E^0_b\right)}{RT}} \frac{(1-\theta^0)}{\theta^0} (N_{TS}/\mathcal{A})^0 (\theta/(1-\theta)) =$$

$$\kappa \left(\frac{k_B T}{h}\right) e^{-\Delta G^0_{des,latt,act,m}/RT} \frac{(1-\theta^0)}{\theta^0} (N_{TS}/\mathcal{A})^0 (\theta/(1-\theta)) = \kappa \left(\frac{k_B T}{h}\right) e^{-\Delta G^0_{des,latt,act,m}/RT} (N_{TS}/\mathcal{A})^0 \frac{(\theta/(1-\theta))}{(\theta^0/(1-\theta^0))} . \tag{88}$$

The activity-based desorption rate expression becomes

$$R_{des,latt}^a = \kappa \left(\frac{k_B T}{h}\right) \frac{\left(\frac{q_{TS,m}^0}{N_A}\right)}{q_{TS,des}\left(q_{ads,latt}\frac{(1-\theta^0)}{\theta^0}\right)} e^{-\frac{\left(E_{des}^0 + E_b^0\right)}{RT}} \frac{(1-\theta^0)}{\theta^0} \frac{(N_{TS}/\mathcal{A})^0}{\mathcal{N}_{ads,max}} a_{ads,latt} =$$

$$\kappa \left(\frac{k_B T}{h}\right) e^{-\Delta G_{des,latt,act,m}^0/RT} \frac{(1-\theta^0)}{\theta^0} \frac{(N_{TS}/\mathcal{A})^0}{\mathcal{N}_{ads,max}} a_{ads,latt} . \tag{89}$$

570   Therefore, the desorption rate coefficient (in units s^{-1}) related to the surface activity is given by

$$k_{des,latt}^a = \kappa \left(\frac{k_B T}{h}\right) \frac{\left(\frac{q_{TS,m}^0}{N_A}\right)}{q_{TS,des}(q_{ads,latt})} \frac{(N_{TS}/\mathcal{A})^0}{\mathcal{N}_{ads,max}} e^{-\frac{\left(E_{des}^0 + E_b^0\right)}{RT}} = \kappa \left(\frac{k_B T}{h}\right) \frac{(1-\theta^0)}{\theta^0} \frac{(N_{TS}/\mathcal{A})^0}{\mathcal{N}_{ads,max}} e^{-\Delta G_{des,latt,act,m}^0/RT} . \tag{90}$$

While the activity-based desorption rate expression (Eq. (86)) clearly displays the first order decay behavior of the activity, driven by $k_{des,latt}^a$, Eqs. (82) and (88) demonstrate that when expressed in terms of molecules desorbing per unit area and time, it is not first order in the surface concentration but shows a strong dependence on the surface coverage, $(\theta/(1-\theta))$, otherwise

575   included in the activity. Therefore, for high surface coverage, an apparent $k_{des,latt}$ cannot easily be derived. For low coverage (of the adsorbate, not of the transition state), $(\theta/(1-\theta)) \approx \theta = \frac{\mathcal{N}_{ads}}{\mathcal{N}_{ads,max}}$, the rate equations (82) simplifies to

$$\frac{R_{des,latt}}{\mathcal{A}} \approx \kappa \left(\frac{k_B T}{h}\right) \frac{\left(\frac{q_{TS,m}^0}{N_A}\right)}{q_{TS,des}(q_{ads,latt})} \frac{(N_{TS}/\mathcal{A})^0}{\mathcal{N}_{ads,max}} e^{-\frac{\left(E_{des}^0 + E_b^0\right)}{RT}} \mathcal{N}_{ads} . \tag{91}$$

From this it follows, $k_{des,latt}(\theta \ll 1) = k_{des,latt}^a$. This demonstrates that the decay of surface concentration at high coverage cannot be used to derive E_{des}^0, as also pointed out by Campbell et al. (2016). In other words, the decay of the surface coverage

580   is not a first-order process at high coverages. Using Eq. (70) in Eq. (82), yields

$$\frac{R_{des,latt}}{\mathcal{A}} = \kappa \left(\frac{k_B T}{h}\right) \frac{\left(\frac{q_{TS,m}^{0'}}{N_A}\right)}{(q_{ads,latt})} (N_{TS}/\mathcal{A})^0 e^{-\frac{\left(E_{des}^0 + E_b^0\right)}{RT}} (\theta/(1-\theta)). \tag{92}$$

Note that the last equation is consistent with the desorption rate derived by Campbell et al. (2016) for the special case of $\theta^0 = 0.5$.

We can now express the desorption rate coefficient as

585    $$k_{des,latt}^a = \kappa \left(\frac{k_B T}{h}\right) \frac{\left(\frac{q_{TS,m}^{0'}}{N_A}\right)}{(q_{ads,latt})} \frac{(N_{TS}/\mathcal{A})^0}{\mathcal{N}_{ads,max}} e^{-\frac{\left(E_{des}^0 + E_b^0\right)}{RT}} = \kappa \left(\frac{k_B T}{h}\right) \frac{(q_{TS}'/\mathcal{A})}{q_{ads,latt} \mathcal{N}_{ads,max}} e^{-\frac{\left(E_{des}^0 + E_b^0\right)}{RT}} = \frac{(2\pi m k_B T/h^2)}{q_{ads,latt} \mathcal{N}_{ads,max}} e^{-\frac{\left(E_{des}^0 + E_b^0\right)}{RT}} . \tag{93}$$

For the second and third expression in Eq. (93), we have converted the standard molar partition function back to the molecular ones, using $\left(\frac{N_{TS}}{\mathcal{A}}\right)^0 = \frac{n_{TS} \cdot N_A}{\mathcal{A}^0} = \frac{N_A}{\mathcal{A}_m^0}$.

We can establish the link between the entropy and the pre-exponential factor by taking the expression for k_{des}^a and

590   inserting the definition of $\Delta G_{des,latt,act,m}^0$ accounting for the relationship between E_{des}^0 and $\Delta H_{des,latt,act,m}^0$ (Supplement Eqs. (108) and (171))

$$\Delta H^0_{des,latt,act,m} = H^0_{act,m} - H^0_{ads,latt,m} = 2RT - \frac{N_A \cdot h\nu}{e^{\beta h\nu}-1} + RT\frac{\ln(1-\theta^0)}{\theta^0} + E^0_{des} + E^0_b \ . \tag{94}$$

Neglecting vibrations, we obtain

$$\Delta H^0_{des,latt,act,m} \approx 2RT + E^0_{des} + E^0_b + RT\frac{\ln(1-\theta^0)}{\theta^0} \ . \tag{95}$$

595 Then it follows

$$k^a_{des,latt} = \kappa\left(\frac{k_BT}{h}\right)\frac{(N_{TS}/\mathcal{A})^0}{(\theta^0/(1-\theta^0))\mathcal{N}_{ads,max}}e^{-\Delta G^0_{des,latt,act,m}/RT} = \kappa\left(\frac{k_BT}{h}\right)\frac{(q'_{TS}/\mathcal{A})}{q_{ads,latt}\mathcal{N}_{ads,max}}e^{-\frac{\left(E^0_{des}+E^0_b\right)}{RT}} \equiv$$

$$\kappa\left(\frac{k_BT}{h}\right)\frac{(N_{TS}/\mathcal{A})^0}{(\theta^0/(1-\theta^0))\mathcal{N}_{ads,max}}e^{\Delta S^0_{des,latt,act,m}/R}e^{-\Delta H^0_{des,latt,act,m}/RT} = \kappa\left(\frac{k_BT}{h}\right)\frac{(q'_{TS}/\mathcal{A})}{q_{ads,latt}\mathcal{N}_{ads,max}}e^{-\frac{\left(E^0_{des}+E^0_b\right)}{RT}} \equiv$$

$$\kappa\left(\frac{k_BT}{h}\right)\frac{(N_{TS}/\mathcal{A})^0}{(\theta^0/(1-\theta^0))\mathcal{N}_{ads,max}}e^{-2}e^{\Delta S^0_{des,latt,act,m}/R}e^{-\frac{\left(E^0_{des}+E^0_b\right)}{RT}}(1-\theta^0)^{-\frac{1}{\theta^0}} = \kappa\left(\frac{k_BT}{h}\right)\frac{(q'_{TS}/\mathcal{A})}{q_{ads,latt}\mathcal{N}_{ads,max}}e^{-\frac{\left(E^0_{des}+E^0_b\right)}{RT}} \ . \tag{96}$$

With this, we can derive the pre-exponential factor as

600 $$A^a_{des,latt} = \kappa\left(\frac{k_BT}{h}\right)\frac{(q'_{TS}/\mathcal{A})}{q_{ads,latt}\mathcal{N}_{ads,max}} = \kappa\left(\frac{k_BT}{h}\right)\frac{(N_{TS}/\mathcal{A})^0(1-\theta^0)^{-\frac{1}{\theta^0}}}{(\theta^0/(1-\theta^0))\mathcal{N}_{ads,max}}e^{-2}e^{\left(\frac{\Delta S^0_{des,latt,act,m}}{R}\right)} =$$

$$\kappa\left(\frac{k_BT}{h}\right)\frac{(N_{TS}/\mathcal{A})^0}{(\theta^0/(1-\theta^0))\mathcal{N}_{ads,max}}e^{-2}e^{\left(\frac{S^0_{act,m}-S^0_{ads,latt,m}}{R}\right)} \ . \tag{97}$$

We can, thus, identify

$$\frac{(N_{TS}/\mathcal{A})^0(1-\theta^0)^{-\frac{1}{\theta^0}}}{(\theta^0/(1-\theta^0))}e^{\left(\frac{\Delta S^0_{des,latt,act,m}}{R}\right)} = e^2\frac{(q'_{TS}/\mathcal{A})}{q_{ads,latt}} \ . \tag{98}$$

Again, as for the previous case, Eqs. (96) and (97) clearly show that when using thermodynamic data to assess the TS, the 605 correct standard state needs being applied to calculate $A^a_{des,latt}$ from the entropy of activation.

4.3 Adsorbate model comparison of desorption rate and pre-exponential factor

Since, strictly speaking, the desorption rate law is representing a first-order process acting on the surface activity, it is also straightforward to understand that the desorption rate, when expressed as rate of change of activity per unit time is proportional to the surface activity, as shown in Fig. 6, independent of the adsorbate model. Thus, even when the surface coverage gets 610 high, the activity based first-order desorption rate coefficient remains constant. The consequence of this becomes then directly apparent in Fig. 7, showing the desorption rate expressed as rate of change of surface concentration per unit area and unit time, as a function of the surface coverage. For the 2D ideal gas case, the linear relationship is maintained, i.e., the surface concentration-based desorption rate coefficient is constant, and thus independent of the surface coverage. In contrast, for the 2D ideal lattice gas case, the desorption rate is rapidly increasing towards high surface coverages, clearly demonstrating the 615 non-first order behavior of desorption when expressed in terms of surface concentration. This behavior is a consequence of the high configurational entropy at high coverages and naturally results from a consistent description of the surface activity. Therefore, the dependency of the desorption rate on coverage is not due to surface sites with different desorption energies, but

a consequence of the applied lattice gas adsorption model that entails a limited number of equivalent sites. In other words, the lifetime of an individual adsorbate molecule depends on the overall surface coverage, exerting shorter adsorbate lifetimes for

620   greater surface coverages. Therefore, as also pointed out by Campbell et al. (2016), experimental desorption rate measurements need to be analyzed with care when deriving the desorption energy from measured desorption rates.

The features of the rate law for desorption acting as a first order process on the surface activity become then also manifest in the time dependent decay of the surface coverage for the two adsorbate models. As expected for the 2D ideal gas case, where surface activity and surface coverage are proportional to each other, the first order and thus single exponential decay of the

625   surface activity leads to a corresponding single exponential decay of the surface coverage, as shown in Fig. 8. In contrast, as demonstrated in Fig. 9, the single exponential decay of the surface activity of the 2D ideal lattice gas case leads to a non-exponential decay of the surface coverage. This further emphasizes the need to carefully analyze experimental data of desorption rate measurements, especially if short time scales are considered.

As discussed above, the pre-exponential factor is often assumed to be $A_{des} \approx 10^{13}$ s^{-1}. Figure 10 shows A_{des} for both

630   adsorbate models as a function of temperature. For the 2D ideal gas, A_{des} displays a weak temperature dependency and, when approaching room temperature, $A_{des,2D}$ is close to the typically applied value of 10^{13} s^{-1}. For the 2D ideal lattice gas, $A_{des,latt}^{a}$ is about 3 orders of magnitude larger and exhibits a stronger temperature dependency compared to the 2D ideal gas. The greater values for $A_{des,latt}^{a}$ can be understood in the following way. When going from a localized bound species (i.e., 2D ideal lattice gas) to a 2D ideal gas (TS), it is very likely that the ratio of partition functions is larger than one and $\Delta S_{des,latt,act,m}^{0} > 0$.

635   Hence, it can be expected that in these cases $A_{des,latt}^{a} > 10^{13}$ s^{-1}, as demonstrated in Fig. 10. Even when ignoring internal rotations, the change in translational degrees of freedom between the 2D ideal lattice gas adsorbate and the 2D ideal gas of the TS, the configurational contribution to the 2D ideal lattice gas adsorbate leads to an increase in $A_{des,latt}^{a} > 10^{15}$ s^{-1} (if κ remains 1).

5. Rate of Adsorption

640   Adsorption is treated as a physisorptive process but might exert a non-zero energy barrier E_{b}^{0} for activated adsorption. We derive the adsorption rates of gas molecules transferring into the 2D ideal and 2D ideal lattice gas absorbates. The adsorption proceeds via the TS, which is treated as a 2D ideal gas, as in the case of desorption.

When considered from the gas phase side, the equilibrium constant between the gas phase and the adsorbed state is given by the inverse ratio of activities compared to the case of desorption, as now the adsorbed state is the product:

645    $$K_{ads,g,2D}^{0} = \frac{a_{ads,2D}}{a_g} = \frac{\frac{(N_{ads}/\mathcal{A})}{(N_{ads}/\mathcal{A})^0}}{\frac{(N_g/\mathcal{V})}{(N_g/\mathcal{V})^0}} = \frac{\frac{(N_{ads})}{(N_A/\mathcal{A}_m^0)}}{\frac{(N_g/\mathcal{V})}{(N_A/\mathcal{V}_m^0)}} \equiv \frac{1}{K_{des,2D,g}^{0}} \tag{99}$$

and

$$K^0_{ads,g,latt} = \frac{a_{ads,latt}}{a_g} = \frac{\frac{(\theta/(1-\theta))}{(\theta^0/(1-\theta^0))}}{\frac{(N_g/\mathcal{V})}{(N_g/\mathcal{V})^0}} = \frac{\frac{(\theta/(1-\theta))}{(\theta^0/(1-\theta^0))}}{\frac{(N_g/\mathcal{V})}{(N_A/\mathcal{V}^0_m)}} \equiv \frac{1}{K^0_{des,latt,g}} . \tag{100}$$

The relationship to the equilibrium constant of desorption holds irrespective of whether the adsorbed state is a 2D ideal gas or 2D ideal lattice gas due to the reversible nature of the adsorption equilibrium.

650   In general, the adsorption rate can be expressed as

$$\frac{R_{ads,2D}}{\mathcal{A}} = \frac{d\mathcal{N}_{ads}}{dt} = -\frac{d\mathcal{N}_g}{dt}\frac{\mathcal{V}}{\mathcal{A}} = k_{ads}\mathcal{N}_g\frac{\mathcal{V}}{\mathcal{A}} \tag{101}$$

and

$$\frac{R_{ads,latt}}{\mathcal{A}} = \frac{d\mathcal{N}_{ads}}{dt} = \frac{d\theta}{dt}\mathcal{N}_{ads,max} = -\frac{d\mathcal{N}_g}{dt}\frac{\mathcal{V}}{\mathcal{A}} = k_{ads}\mathcal{N}_g\frac{\mathcal{V}}{\mathcal{A}} \tag{102}$$

with $\frac{d\theta}{dt} = \frac{k_{ads}}{\mathcal{N}_{ads,max}}\mathcal{N}_g\frac{\mathcal{V}}{\mathcal{A}}$, $\tag{103}$

655   where k_{ads} represents the first-order rate coefficient for adsorption (in units s^{-1}), describing the rate of change of gas phase concentration or activity. Considering the rate expression in terms of gain of adsorbed molecules per unit area and time, the rate of loss from the gas phase needs to be multiplied by $\frac{\mathcal{V}}{\mathcal{A}}$. Since adsorption proceeds via the TS that is assumed to be ~~similar to~~ a 2D ideal gas, k_{ads} is the same first-order rate coefficient for the adsorption into the 2D ideal gas and 2D ideal lattice gas adsorbate model.

660   The rate of change of surface activity for the 2D ideal gas is given by

$$R^a_{ads,2D} = \frac{R_{ads,2D}}{\mathcal{A}(N_{ads,2D}/\mathcal{A})^0} = k_{ads}\mathcal{N}_g\frac{\mathcal{V}}{\mathcal{A}(N_{ads,2D}/\mathcal{A})^0} = k_{ads}\mathcal{N}_g\frac{\mathcal{V}(N_g/\mathcal{V})^0}{\mathcal{A}(N_{ads,2D}/\mathcal{A})^0(N_g/\mathcal{V})^0} = k_{ads}\frac{\mathcal{N}_g}{(N_g/\mathcal{V})^0}\frac{\mathcal{V}(N_g/\mathcal{V})^0}{\mathcal{A}(N_{ads,2D}/\mathcal{A})^0} =$$

$$k_{ads}a_g\frac{\mathcal{V}\mathcal{A}^0_m}{\mathcal{A}\mathcal{V}^0_m} = k^a_{ads}a_g\frac{\mathcal{V}\mathcal{A}^0_m}{\mathcal{A}\mathcal{V}^0_m}, \tag{104}$$

and for the 2D ideal lattice gas by

$$R^a_{ads,latt} = \frac{da_{ads,latt}}{dt} = \frac{d}{dt}\frac{\theta}{(1-\theta)}\frac{(1-\theta^0)}{\theta^0} \approx \frac{d\theta}{dt}\frac{(1-\theta^0)}{\theta^0} = \frac{k_{ads}}{\mathcal{N}_{ads,max}}\mathcal{N}_g\frac{\mathcal{V}}{\mathcal{A}}\frac{(1-\theta^0)}{\theta^0} = \frac{k_{ads}}{\mathcal{N}_{ads,max}}\frac{\mathcal{N}_g}{(N_g/\mathcal{V})^0}\frac{\mathcal{V}(N_g/\mathcal{V})^0}{\mathcal{A}}\frac{(1-\theta^0)}{\theta^0} =$$

665   $$\frac{k_{ads}}{\mathcal{N}_{ads,max}}a_g\frac{\mathcal{V}}{\mathcal{A}}\frac{(N_g/\mathcal{V})^0(1-\theta^0)}{\theta^0} = \frac{k^a_{ads}}{\mathcal{N}_{ads,max}}a_g\frac{\mathcal{V}}{\mathcal{A}}\frac{(N_g/\mathcal{V})^0(1-\theta^0)}{\theta^0} . \tag{105}$$

We note that although k_{ads} is the same for both gas adsorbate models, $R^a_{ads,2D}$ and $R^a_{ads,latt}$ will differ, as evident from Eqs. (104) and (105), respectively and shown further below (Eqs. (126) and (127)). As outlined above and in the Supplement (S3.3), the activity of the 2D ideal lattice gas scales with $\frac{(\theta/(1-\theta))}{(\theta^0/(1-\theta^0))}$. To provide an analytical solution using our definitions, in Eq. (105), we make the assumption $\frac{d}{dt}\frac{\theta}{(1-\theta)}\frac{(1-\theta^0)}{\theta^0} \approx \frac{d\theta}{dt}\frac{(1-\theta^0)}{\theta^0}$, meaning that we consider small enough rates of change so that this

670   condition is justified. Since k^a_{ads} describes the decay of the gas phase activity, which is proportional to its concentration, we follow that $k^a_{ads} = k_{ads}$. In turn, the factor $\frac{\mathcal{V}}{\mathcal{A}}$ needs to be normalized to the corresponding ratio of standard molar volume to surface area to convert from gas phase activity change to surface activity change, in the last expression of Eq. (105).

TS theory for adsorption is encompassing the same steps as that for desorption but starting from the gas phase side. Considered from the gas phase, the equilibrium constant between the gas phase and the TS for adsorption is related to the free

675 energy change between the gas and the TS, each expressed with the corresponding standard molar partition functions, as defined by (Supplement Eqs. (193-199)

$$K^0_{ads,g,TS} = e^{-\Delta G^0_{ads,g,TS,m}/RT} = \frac{q^0_{TS,m}}{q^0_{g,m}} e^{-\frac{E^0_b}{RT}} . \tag{106}$$

Note that we treat the general case of activated adsorption here, meaning that the TS's internal energy is elevated by the barrier height above the reference level (E^0_b), leading to the corresponding Arrhenius term in Eq. (106). The equilibrium constant is

680 also related to the ratio of activities (Supplement Eq. (5)):

$$K^0_{ads,g,TS} = e^{-\Delta G^0_{ads,g,TS,m}/RT} = \frac{a_{TS}}{a_g} = \frac{\frac{(N_{TS}/\mathcal{A})}{(N_{TS}/\mathcal{A})^0}}{\frac{(N_g/\mathcal{V})}{(N_g/\mathcal{V})^0}} = \frac{\frac{(\mathcal{N}_{TS})}{(N_A/\mathcal{A}^0_m)}}{\frac{(N_g/\mathcal{V})}{(N_A/\mathcal{V}^0_m)}} . \tag{107}$$

As in the case of desorption, the adsorption rate can be obtained by assuming that the TS has the same finite width d across which the molecule moves with its mean thermal velocity in the direction orthogonal to the surface

$$\frac{R_{ads,2D}}{\mathcal{A}} = \kappa \left(\frac{N_{TS}}{\mathcal{A}}\right) \frac{(k_B T/2\pi m)^{1/2}}{d} , \tag{108}$$

685 where κ is the same transmission coefficient defining the probability with which the activated complex proceeds to adsorption as that for desorption due to microscopic reversibility (Kolasinski, 2012). The partition function for the translational motion of the TS in the direction of adsorption is

$$q_{TS,ads} = (2\pi m k_B T/h^2)^{1/2} d . \tag{109}$$

Solving this for d and inserting into Eq. (108) allows to express the adsorption rate as a function of this partition function:

690 $$\frac{R_{ads,2D}}{\mathcal{A}} = \kappa \left(\frac{k_B T}{h}\right) \left(\frac{N_{TS}}{\mathcal{A}}\right) \frac{1}{q_{TS,ads}} . \tag{110}$$

The surface concentration of the TS can be derived from the equilibrium (Eq. (107))

$$\mathcal{N}_{TS} = \frac{N_{TS}}{\mathcal{A}} = \frac{q^0_{TS,m}}{q^0_{g,m}} e^{-\frac{E^0_b}{RT}} \frac{(N_{TS}/\mathcal{A})^0}{(N_g/\mathcal{V})^0} \mathcal{N}_g . \tag{111}$$

Inserting Eq. (111) into Eq. (110) leads to

$$\frac{R_{ads,2D}}{\mathcal{A}} = \kappa \left(\frac{k_B T}{h}\right) \frac{1}{q_{TS,ads}} \frac{q^0_{TS,m}}{q^0_{g,m}} e^{-\frac{E^0_b}{RT}} \frac{(N_{TS}/\mathcal{A})^0}{(N_g/\mathcal{V})^0} \mathcal{N}_g . \tag{112}$$

695 When defining $\Delta G^0_{ads,g,act,m}$ of adsorption as $\Delta G^0_{ads,g,TS,m}$ (Supplement Eqs. (193) and (207)) minus the TS's free energy associated with the motion along the adsorption coordinate, expressed by its molecular partition function, $q_{TS,ads}$, we obtain

$$e^{-\Delta G^0_{ads,g,act,m}/RT} = \frac{e^{-\Delta G^0_{ads,g,TS,m}/RT}}{q_{TS,ads}} = \frac{1}{q_{TS,ads}} \frac{q^0_{TS,m}}{q^0_{g,m}} e^{-\frac{E^0_b}{RT}} . \tag{113}$$

With this definition of $\Delta G^0_{ads,g,act,m}$, we can express the adsorption rate as

$$\frac{R_{ads,2D}}{\mathcal{A}} = \kappa \left(\frac{k_B T}{h}\right) e^{-\Delta G^0_{ads,g,act,m}/RT} \frac{(N_{TS}/\mathcal{A})^0}{(N_g/V)^0} \mathcal{N}_g . \tag{114}$$

700   When using the definition of the adsorption rate coefficient linking the loss rate from the gas phase with the gain of adsorbed species on the surface, i.e., $\frac{R_{ads,2D}}{\mathcal{A}} = k_{ads} \mathcal{N}_g \frac{V}{\mathcal{A}}$, the adsorption rate coefficient becomes

$$k_{ads} = \left(\frac{k_B T}{h}\right) e^{-\Delta G^0_{ads,g,act,m}/RT} \frac{(N_{TS}/\mathcal{A})^0}{(N_g/V)^0} \frac{\mathcal{A}}{V} = \kappa \left(\frac{k_B T}{h}\right) \frac{1}{q_{TS,ads}} \frac{q^0_{TS,m}}{q^0_{g,m}} e^{-\frac{E^0_b}{RT}} \frac{(N_{TS}/\mathcal{A})^0}{(N_g/V)^0} \frac{\mathcal{A}}{V} . \tag{115}$$

       Defining $q^{0'}_{TS}/\mathcal{A}^0_m$ as the partition function for the TS after omitting motion in the direction of the reaction coordinate (Campbell et al., 2016), this leaves the partition function for a 2D ideal gas (Supplement Eqs. (60) and (118)):

705
$$\left(\frac{q^0_{TS,m}}{q_{TS,ads}}\right) = q^{0'}_{TS,m} = q^0_{TS,2D,m} = \mathcal{A}^0_m (2\pi m k_B T/h^2)^{2/2} . \tag{116}$$

Using Eq. (116) in Eq. (112), we obtain

$$\frac{R_{ads,2D}}{\mathcal{A}} = \kappa \left(\frac{k_B T}{h}\right) \frac{q^{0'}_{TS,m}}{q^0_{g,m}} e^{-\frac{E^0_b}{RT}} \frac{(N_{TS}/\mathcal{A})^0}{(N_g/V)^0} \mathcal{N}_g \tag{117}$$

and identifying Eq. (117) with Eq. (104) yields

$$k_{ads} = \kappa \left(\frac{k_B T}{h}\right) \frac{q^{0'}_{TS,m}}{q^0_{g,m}} e^{-\frac{E^0_b}{RT}} \frac{(N_{TS}/\mathcal{A})^0}{(N_g/V)^0} \frac{\mathcal{A}}{V} . \tag{118}$$

710   This is the same result as in Eq. (115) when using thermodynamic quantities.

       We can convert the standard molar partition functions back to the molecular ones. For that, we consider that $\left(\frac{N_{TS}}{\mathcal{A}}\right)^0 = \frac{n_{TS} \cdot N_A}{\mathcal{A}^0} = \frac{N_A}{\mathcal{A}^0_m}$ and $\left(\frac{N_g}{V}\right)^0 = \frac{n_g \cdot N_A}{V^0} = \frac{N_A}{V^0_m}$, we obtain

$$\frac{1}{q_{TS,ads}} \frac{q^0_{TS,m}}{q^0_{g,m}} \frac{(N_{TS}/\mathcal{A})^0}{(N_g/V)^0} \frac{\mathcal{A}}{V} = \frac{q^{0'}_{TS,m}}{q^0_{g,m}} \frac{(N_{TS}/\mathcal{A})^0}{(N_g/V)^0} \frac{\mathcal{A}}{V} = \frac{\mathcal{A}^0_m (2\pi m k_B T/h^2)^{2/2}}{V^0_m (2\pi m k_B T/h^2)^{3/2}} \frac{\frac{N_A}{\mathcal{A}^0_m}}{\frac{N_A}{V^0_m}} \frac{\mathcal{A}}{V} = \frac{q'_{TS}/\mathcal{A}}{q_g/V} \frac{\mathcal{A}}{V} = \frac{1}{(2\pi m k_B T/h^2)^{1/2}} \frac{\mathcal{A}}{V} . \tag{119}$$

This yields

715
$$k_{ads} = \kappa \left(\frac{k_B T}{h}\right) \frac{1}{(2\pi m k_B T/h^2)^{1/2}} e^{-\frac{E^0_b}{RT}} \frac{\mathcal{A}}{V} . \tag{120}$$

As in the case of desorption, we can compare the thermodynamic derivation of k_{ads} (left hand side below) with the one based on the partition functions (right hand side below):

$$k_{ads} = \kappa \left(\frac{k_B T}{h}\right) e^{-\Delta G^0_{ads,g,act,m}/RT} \frac{(N_{TS}/\mathcal{A})^0}{(N_g/V)^0} \frac{\mathcal{A}}{V} = \kappa \left(\frac{k_B T}{h}\right) \left(\frac{q'_{TS}/\mathcal{A}}{q_g/V}\right) e^{-\frac{E^0_b}{RT}} \frac{\mathcal{A}}{V} \equiv$$

$$\kappa \left(\frac{k_B T}{h}\right) \frac{(N_{TS}/\mathcal{A})^0}{(N_g/V)^0} e^{\Delta S^0_{ads,g,act,m}/R} e^{-\Delta H^0_{ads,g,act,m}/RT} \frac{\mathcal{A}}{V} = \kappa \left(\frac{k_B T}{h}\right) \left(\frac{q'_{TS}/\mathcal{A}}{q_g/V}\right) e^{-\frac{E^0_b}{RT}} \frac{\mathcal{A}}{V} , \tag{121}$$

720   with $\Delta H^0_{ads,g,act,m} = -\frac{1}{2} RT + E^0_b$ (Supplement Eq. (195)), we obtain

$$\kappa \left(\frac{k_B T}{h}\right) \frac{(N_{TS}/\mathcal{A})^0}{(N_g/V)^0} e^{\Delta S^0_{ads,g,act,m}/R} e^{1/2} e^{-\frac{E^0_b}{RT}} = \kappa \left(\frac{k_B T}{h}\right) \left(\frac{q'_{TS}/\mathcal{A}}{q_g/V}\right) e^{-\frac{E^0_b}{RT}} .$$

$$\kappa \left(\frac{k_B T}{h}\right) \frac{(N_{TS}/\mathcal{A})^0}{(N_g/\mathcal{V})^0} e^{\Delta S^0_{ads,g,act,m}/R} e^{1/2} = \kappa \left(\frac{k_B T}{h}\right) \left(\frac{q'_{TS}/\mathcal{A}}{q_g/\mathcal{V}}\right). \tag{122}$$

In the case of adsorption, the Arrhenius term is only driven by the barrier height. Therefore, the pre-exponential factor for adsorption is (since $k^a_{ads} = k_{ads}$)

735    $A_{ads,2D} = A^a_{ads,2D} = \kappa \left(\frac{k_B T}{h}\right) \left(\frac{q'_{TS}/\mathcal{A}}{q_g/\mathcal{V}}\right) \frac{\mathcal{A}}{\mathcal{V}} = \kappa \left(\frac{k_B T}{h}\right) \frac{(N_{TS}/\mathcal{A})^0}{(N_g/\mathcal{V})^0} e^{1/2} e^{\Delta S^0_{ads,g,act,m}/R} \frac{\mathcal{A}}{\mathcal{V}} = \kappa \left(\frac{k_B T}{h}\right) \frac{(N_{TS}/\mathcal{A})^0}{(N_g/\mathcal{V})^0} \frac{\mathcal{A}}{\mathcal{V}} e^{1/2} e^{\left(\frac{S^0_{act,m} - S^0_{g,m}}{R}\right)}.$

$$\tag{123}$$

Thus, we can identify

$$\frac{(N_{TS}/\mathcal{A})^0}{(N_g/\mathcal{V})^0} e^{\Delta S^0_{ads,g,act,m}/R} = \left(\frac{q'_{TS}/\mathcal{A}}{q_g/\mathcal{V}}\right) e^{-1/2}. \tag{124}$$

730   This emphasizes the relationship between the entropy of activation and the ratio of the corresponding partition functions. Note that when neglecting vibrations, $\left(\frac{q'_{TS}/\mathcal{A}}{q_g/\mathcal{V}}\right) = \frac{(2\pi m k_B T/h^2)^{2/2}}{(2\pi m k_B T/h^2)^{3/2}} = \frac{1}{(2\pi m k_B T/h^2)^{1/2}}$, which allows estimating the entropy of activation for adsorption. For the examples discussed here (see Table S1), $\Delta S^0_{ads,g,act,m}$ = -53.98 J K^{-1} mol^{-1}.

Thus, essentially, the gas loses one translational degree of freedom, and the rate of adsorption (vibrations neglected) can be written as

735    $\frac{R_{ads,2D}}{\mathcal{A}} = k_{ads} \mathcal{N}_g \frac{\mathcal{V}}{\mathcal{A}} = \kappa \left(\frac{k_B T}{h}\right) \left(\frac{q'_{TS}/\mathcal{A}}{q_g/\mathcal{V}}\right) e^{-\frac{E^0_b}{RT}} \mathcal{N}_g \frac{\mathcal{A}}{\mathcal{V}} \frac{\mathcal{V}}{\mathcal{A}} = \kappa \left(\frac{k_B T}{h}\right) \frac{h}{\sqrt{2\pi m k_B T}} e^{-\frac{E^0_b}{RT}} \mathcal{N}_g = \frac{p}{\sqrt{2\pi m k_B T}} \kappa e^{-\frac{E^0_b}{RT}}. \tag{125}$

For the case considering activities, we obtain

$$R^a_{ads,2D} = k_{ads} a_g \frac{\mathcal{V}\mathcal{A}^0_m}{\mathcal{A}\mathcal{V}^0_m} = \kappa \left(\frac{k_B T}{h}\right) \left(\frac{q'_{TS}/\mathcal{A}}{q_g/\mathcal{V}}\right) e^{-\frac{E^0_b}{RT}} \frac{\mathcal{A}}{\mathcal{V}} a_g \frac{\mathcal{V}\mathcal{A}^0_m}{\mathcal{A}\mathcal{V}^0_m} = \kappa \left(\frac{k_B T}{h}\right) \frac{h}{\sqrt{2\pi m k_B T}} e^{-\frac{E^0_b}{RT}} \frac{\mathcal{N}_g}{(N_g/\mathcal{V})^0} \frac{\mathcal{A}^0_m}{\mathcal{V}^0_m} = \kappa \frac{p}{\sqrt{2\pi m k_B T}} e^{-\frac{E^0_b}{RT}} \frac{\mathcal{A}^0_m}{N_A}$$

$$\tag{126}$$

For the case of the 2D ideal lattice gas we can write, using the same definition for k_{ads}

740    $R^a_{ads,latt} = \frac{k_{ads}}{\mathcal{N}_{ads,max}} a_g \frac{\mathcal{V}}{\mathcal{A}} \frac{(N_g/\mathcal{V})^0 (1-\theta^0)}{\theta^0} = \kappa \left(\frac{k_B T}{h}\right) \left(\frac{q'_{TS}/\mathcal{A}}{q_g/\mathcal{V}}\right) e^{-\frac{E^0_b}{RT}} \frac{\mathcal{A}}{\mathcal{V}} \frac{1}{\mathcal{N}_{ads,max}} a_g \frac{\mathcal{V}}{\mathcal{A}} \frac{(N_g/\mathcal{V})^0 (1-\theta^0)}{\theta^0} =$

$\kappa \left(\frac{k_B T}{h}\right) \left(\frac{q'_{TS}/\mathcal{A}}{q_g/\mathcal{V}}\right) e^{-\frac{E^0_b}{RT}} \frac{1}{\mathcal{N}_{ads,max}} a_g \frac{(N_g/\mathcal{V})^0 (1-\theta^0)}{\theta^0} = \kappa \left(\frac{k_B T}{h}\right) \frac{h}{\sqrt{2\pi m k_B T}} e^{-\frac{E^0_b}{RT}} \frac{\mathcal{N}_g}{(N_g/\mathcal{V})^0} \frac{1}{\mathcal{N}_{ads,max}} \frac{(N_g/\mathcal{V})^0 (1-\theta^0)}{\theta^0} =$

$\kappa \frac{p}{\sqrt{2\pi m k_B T}} e^{-\frac{E^0_b}{RT}} \frac{1}{(N_g/\mathcal{V})^0} \frac{1}{\mathcal{N}_{ads,max}} \frac{(N_g/\mathcal{V})^0 (1-\theta^0)}{\theta^0} = \kappa \frac{p}{\sqrt{2\pi m k_B T}} e^{-\frac{E^0_b}{RT}} \frac{1}{\mathcal{N}_{ads,max}} \frac{(1-\theta^0)}{\theta^0}. \tag{127}$

$\frac{p}{\sqrt{2\pi m k_B T}}$ represents the Hertz-Knudsen expression of the flux of molecules impinging on surface atoms. Thus, CTST is consistent with the collision rate multiplied with κ for the case that the activated complex associated with the TS is considered

745   a 2D ideal gas, the barrier is negligible, and no internal vibrations are considered.

As discussed in the previous section, the TS for adsorption is the same as that for desorption and is considered a 2D ideal gas. This means that the adsorptive flux, i.e., the adsorption rate in terms of gain of molecules per surface area and time, is

simply proportional to the gas phase concentration, independent of the adsorption model used to describe the final state of adsorption, as shown in Fig. 11. For the same reason, also the rate of change of surface activity is linearly related to the gas phase activity, as shown in Fig. 12. However, the meaning of the rate of change of surface activity is entirely different for the two adsorbate models, as discussed for the case of desorption. While for the 2D ideal gas model, the rate of change of surface activity is linearly related to the rate of change of surface coverage, for the 2D ideal lattice gas case, the same rate of change of surface activity is governed by a strongly non-linear relationship to the rate of change of surface coverage, thus, depending on the actual coverage. This explains the visible slight deviations between $R_{ads,2D}^a$ and $R_{ads,latt}^a$ in Fig. 12 at high gas phase activity values, reflecting in fact different rates of change of surface coverages.

We can now look at the surface accommodation coefficient, α_s, which is operationally defined as the ratio between the adsorption rate and the gas-kinetic collision rate (Kolb et al., 2010;Ammann et al., 2013;Crowley et al., 2013) considering only physisorptive processes, not accounting for possibly more complex configurations involving already adsorbed molecules (Kisliuk, 1957;Tully, 1994;Campbell et al., 2016). The description of the adsorption rate follows as

$$\frac{R_{ads,2D}}{\mathcal{A}} = \kappa \frac{p}{\sqrt{2\pi m k_B T}} = \mathcal{N}_g \kappa \frac{\sqrt{k_B T}}{\sqrt{2\pi m}} = \mathcal{N}_g \kappa \frac{\sqrt{8 k_B T}}{4\sqrt{\pi m}} = \alpha_s \mathcal{N}_g \frac{\omega}{4} , \tag{128}$$

where ω represents the thermal velocity of the gas species. Keeping with this definition, but putting in the more general expression for the adsorption rate based on TS theory, the interpretation of α_s becomes different, as it is related to

$$\alpha_s = \frac{\kappa\left(\frac{k_B T}{h}\right)\frac{q_{TS}'/\mathcal{A}}{q_g/\mathcal{V}}e^{-\frac{E_b^0}{RT}}\mathcal{N}_g}{\mathcal{N}_g\frac{\omega}{4}} = \frac{\kappa\left(\frac{k_B T}{h}\right)\frac{q_{TS}'/\mathcal{A}}{q_g/\mathcal{V}}e^{-\frac{E_b^0}{RT}}}{\left(\frac{k_B T}{h}\right)(2\pi m k_B T/h^2)^{-1/2}} = \kappa \frac{q_{TS}'/\mathcal{A}}{q_g/\mathcal{V}} e^{-\frac{E_b^0}{RT}}(2\pi m k_B T/h^2)^{1/2} . \tag{129}$$

Therefore, $\alpha_s = \kappa$ (and $= 1$, if $\kappa = 1$), if $\frac{q_{TS}'/\mathcal{A}}{q_g/\mathcal{V}} = (2\pi m k_B T/h^2)^{-1/2}$ and $E_b^0 = 0$, but is different in the presence of a barrier or if other contributions are relevant in the partition functions of the activated complex associated with the TS or the gas phase species (such as internal vibrations or rotations). As mentioned above, the ratio of the partition functions is also related to the corresponding entropy of activation (i.e., non-zero if α_s deviates from κ).

Figure 13 shows how α_s depends on E_b^0 under the assumption of $\kappa = 1$ and $\frac{q_{TS}'/\mathcal{A}}{q_g/\mathcal{V}} = (2\pi m k_B T/h^2)^{-1/2}$ (see Table S1). Hence, α_s depends exponentially on the activation energy of adsorption. A transmission coefficient $\kappa < 1$ will yield lower α_s values. If the TS is more constrained than the assumed 2D ideal gas, expressed by $\Delta S_{ads,g,act,m}^0 = R \ln\left(\frac{q_{TS,2D,m}^0}{e^{1/2}q_{g,m}^0}\right)$ (Eqs. (124) and Supplement Eq. (197)), this will further lower α_s.

6. Adsorption-Desorption Equilibrium

We consider equilibrium between adsorption and desorption and demonstrate that this results in the proper equilibrium constants for gas adsorption into a 2D ideal gas and a 2D ideal lattice gas, proving that the CTST formulation of the rates leads

775 back to the equilibrium definition, from which we started off. We also show that this works both when using partition functions and thermodynamic expressions. Hence, the derivations of all thermodynamic functions are internally consistent.

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

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

$$\kappa \left(\frac{k_B T}{h}\right) \frac{q'_{TS}/\mathcal{A}}{q_g/\mathcal{V}} e^{-\frac{E_b^0}{RT}} \mathcal{N}_g = \kappa \left(\frac{k_B T}{h}\right) \left(\frac{q'_{TS}}{q_{ads,2D}}\right) e^{-\frac{\left(E_{des}^0 + E_b^0\right)}{RT}} \mathcal{N}_{ads}$$

780 $$\frac{1/\mathcal{A}}{q_g/\mathcal{V}} \mathcal{N}_g = \left(\frac{1}{q_{ads,2D}}\right) e^{-\frac{E_{des}^0}{RT}} \mathcal{N}_{ads}$$

$$\frac{\mathcal{V}}{\mathcal{A}} \mathcal{N}_g = \left(\frac{q_g}{q_{ads,2D}}\right) e^{-\frac{E_{des}^0}{RT}} \mathcal{N}_{ads}$$

$$\frac{\mathcal{N}_{ads}}{\mathcal{N}_g} = \frac{q_{ads,2D}}{q_g} \frac{\mathcal{V}}{\mathcal{A}} e^{\frac{E_{des}^0}{RT}} = (2\pi m k_B T/h^2)^{-1/2} e^{\frac{E_{des}^0}{RT}} = K_{lin} . \tag{130}$$

This is the same result as given in Eq. (31) and consistent with the relation between K_{lin} and the equilibrium constant. Performing the same derivation starting with the thermodynamic expressions is given in the Supplement (Eqs. (216-220)).

785 For the case of the activity-based adsorption and desorption rates, we obtain

$$R_{ads,2D}^a = R_{des,2D}^a$$

$$\kappa \left(\frac{k_B T}{h}\right) \left(\frac{q'_{TS}/\mathcal{A}}{q_g/\mathcal{V}}\right) e^{-\frac{E_b^0}{RT}} \frac{\mathcal{A}}{\mathcal{V}} a_g \frac{\mathcal{V} \mathcal{A}_m^0}{\mathcal{A} \mathcal{V}_m^0} = \kappa \left(\frac{k_B T}{h}\right) \frac{q'_{TS}}{q_{ads,2D}} e^{-\frac{\left(E_{des}^0 + E_b^0\right)}{RT}} a_{ads,2D}$$

$$\frac{1/\mathcal{A}}{q_g/\mathcal{V}} a_g \frac{\mathcal{A}_m^0}{\mathcal{V}_m^0} = \left(\frac{1}{q_{ads,2D}}\right) e^{-\frac{E_{des}^0}{RT}} a_{ads,2D}$$

$$\frac{\mathcal{V}}{\mathcal{A}} a_g \frac{\mathcal{A}_m^0}{\mathcal{V}_m^0} = \left(\frac{q_g}{q_{ads,2D}}\right) e^{-\frac{E_{des}^0}{RT}} a_{ads,2D}$$

790 $$\frac{a_{ads,2D}}{a_g} = \frac{q_{ads,2D}}{q_g} \frac{\mathcal{V}}{\mathcal{A}} e^{\frac{E_{des}^0}{RT}} \frac{\mathcal{A}_m^0}{\mathcal{V}_m^0} = (2\pi m k_B T/h^2)^{-1/2} e^{\frac{E_{des}^0}{RT}} \frac{\mathcal{A}_m^0}{\mathcal{V}_m^0} = K_{lin} \frac{\mathcal{A}_m^0}{\mathcal{V}_m^0} . \tag{131}$$

This is the same result as in Eqs. (130). The derivation using the thermodynamic expressions is outlined in the Supplement Eqs. (221-225).

For the case when the adsorbed state on the surface is treated as a 2D ideal lattice gas using Eqs. (92), (102), and (121):

$$\frac{R_{ads,latt}}{\mathcal{A}} = \frac{R_{des,latt}}{\mathcal{A}}$$

795 $$\kappa \left(\frac{k_B T}{h}\right) \frac{q'_{TS}/\mathcal{A}}{q_g/\mathcal{V}} e^{-\frac{E_b^0}{RT}} \mathcal{N}_g = \kappa \left(\frac{k_B T}{h}\right) \frac{\left(\frac{q_{TS,m}^{0'}}{N_A}\right)}{(q_{ads,latt})} (N_{TS}/\mathcal{A})^0 e^{-\frac{\left(E_{des}^0 + E_b^0\right)}{RT}} (\theta/(1-\theta)) ,$$

with $\left(\frac{q_{TS,m}^{0'}}{N_A}\right) (N_{TS}/\mathcal{A})^0 = \left(\frac{q_{TS,m}^{0'}}{N_A}\right) \frac{N_A}{\mathcal{A}_m^0} = \frac{q_{TS,m}^{0'}}{\mathcal{A}_m^0} = \frac{q'_{TS}}{\mathcal{A}}$, we obtain

$$\kappa \left(\frac{k_B T}{h}\right) \frac{q'_{TS}/\mathcal{A}}{q_g/\mathcal{V}} e^{-\frac{E_b^0}{RT}} \mathcal{N}_g = \kappa \left(\frac{k_B T}{h}\right) \frac{(q'_{TS}/\mathcal{A})}{q_{ads,latt}} e^{-\frac{\left(E_{des}^0 + E_b^0\right)}{RT}} (\theta/(1-\theta))$$

$$\frac{1}{q_g/\mathcal{V}}\mathcal{N}_g = \frac{1}{q_{ads,latt}}e^{-\frac{E_{des}^0}{RT}}(\theta/(1-\theta))$$

$$\frac{(\theta/(1-\theta))}{\mathcal{N}_g} = \frac{q_{ads,latt}}{q_g/\mathcal{V}}e^{\frac{E_{des}^0}{RT}} = (2\pi m k_B T/h^2)^{-3/2}e^{\frac{E_{des}^0}{RT}} = K_{Lang} \tag{132}$$

This is the expected result outlined in Eq. (44). The derivation starting with the thermodynamic expressions is given in the Supplement Eqs. (226-230).

For the case of the activity-based adsorption (Eq. (127)) and desorption rates (Eq. (86), we obtain

$$R_{ads,latt}^a = R_{des,latt}^a$$

$$\kappa\left(\frac{k_B T}{h}\right)\left(\frac{q_{TS}'/\mathcal{A}}{q_g/\mathcal{V}}\right)e^{-\frac{E_b^0}{RT}}\frac{1}{\mathcal{N}_{ads,max}}a_g\frac{(N_g/\mathcal{V})^0(1-\theta^0)}{\theta^0} = \kappa\left(\frac{k_B T}{h}\right)\frac{(q_{TS}'/\mathcal{A})}{q_{ads,latt}\mathcal{N}_{ads,max}}e^{-\frac{(E_{des}^0+E_b^0)}{RT}}a_{ads,latt}$$

$$\frac{1}{q_g/\mathcal{V}}a_g\frac{(N_g/\mathcal{V})^0(1-\theta^0)}{\theta^0} = \frac{1}{q_{ads,latt}}e^{-\frac{E_{des}^0}{RT}}a_{ads,latt}$$

$$\frac{a_{ads,latt}}{a_g} = \frac{q_{ads,latt}}{q_g/\mathcal{V}}e^{\frac{E_{des}^0}{RT}}\frac{(N_g/\mathcal{V})^0(1-\theta^0)}{\theta^0}\frac{a_{ads,latt}}{a_g}$$

$$\frac{a_{ads,latt}}{a_g} = (2\pi m k_B T/h^2)^{-3/2}e^{\frac{E_{des}^0}{RT}}\frac{(N_g/\mathcal{V})^0(1-\theta^0)}{\theta^0} = K_{Lang}\frac{(N_g/\mathcal{V})^0(1-\theta^0)}{\theta^0}$$

$$\frac{a_{ads,latt}}{a_g}\frac{\theta^0}{(N_g/\mathcal{V})^0(1-\theta^0)} = \frac{(\theta/(1-\theta))}{\mathcal{N}_g} = K_{Lang} \ . \tag{133}$$

This results in the same relationship as in Eq. (132). The derivation starting with the thermodynamic expressions is given in the Supplement Eqs. (231-235). Thus, equating the adsorption and desorption rates, both derived based on TS theory, correctly reproduces the corresponding equilibrium constant.

7. Derivation of Kinetic Parameters from the Equilibrium Constants

In previous studies (Bartels-Rausch et al., 2005;Tabazadeh and Turco, 1993) equilibrium thermodynamic data or equilibrium coverage data have been used to constrain kinetic parameters of either adsorption or desorption. If $K_{ads,g,latt}^0$ or $K_{ads,g,2D}^0$ are known as a function of temperature from measurements or extracted from fundamental thermodynamic data, the Arrhenius plot of its temperature dependence delivers $\Delta H_{ads,g,2D}^0$ or $\Delta H_{des,2D,g}^0$ as a slope and $\Delta S_{ads,g,2D}^0$ or $\Delta S_{des,2D,d}^0$ as an offset.

For the case of an adsorbed 2D ideal gas, we can derive the pre-exponential factor from equilibrium, $R_{ads,2D}^a = R_{des,2D}^a$, starting off with the molecular descriptions of respective rates (Eq. (131). In addition, we make use of α_s and its relationship to microscopic properties (Eq. (129)) and the definition of $A_{des,2D}$ obtained from the derivation of the desorption rate (Eq. (78)). By applying the thermodynamic equilibrium constant, we can then relate the microscopic picture to thermodynamic functions, obtaining $A_{des,2D}$ under equilibrium conditions (the full derivation is given in Supplement Eq. (236)):

$$\kappa\left(\frac{k_B T}{h}\right)\left(\frac{q_{TS}'/\mathcal{A}}{q_g/\mathcal{V}}\right)e^{-\frac{E_b^0}{RT}}\frac{\mathcal{A}}{\mathcal{V}}a_g\frac{\mathcal{V}\mathcal{A}_m^0}{\mathcal{A}\mathcal{V}_m^0} = \kappa\left(\frac{k_B T}{h}\right)\frac{q_{TS}'}{q_{ads,2D}}e^{-\frac{(E_{des}^0+E_b^0)}{RT}}a_{ads,2D}$$

$$\left(\frac{k_B T}{h}\right)\alpha_s a_g \frac{\mathcal{A}_m^0}{\mathcal{V}_m^0}(2\pi m k_B T/h^2)^{-1/2} = A_{des,2D} e^{-\frac{\left(E_{des}^0 + E_b^0\right)}{RT}} a_{ads,2D}$$

$$A_{des,2D} = \left(\frac{k_B T}{h}\right)\alpha_s \frac{\mathcal{A}_m^0}{\mathcal{V}_m^0}(2\pi m k_B T/h^2)^{-1/2} e^{-1/2} e^{\frac{E_b^0}{RT}} e^{\Delta S_{des,2D,g,m}^0/R} \ . \tag{134}$$

825   If the energy barrier E_b^0 is negligible, this simplifies to

$$A_{des,2D} = \alpha_s e^{\Delta S_{des,2D,g,m}^0/R} e^{-1/2}\left(\frac{\mathcal{A}_m^0}{\mathcal{V}_m^0}\right)\left(\frac{k_B T}{h}\right)(2\pi m k_B T/h^2)^{-1/2} \ . \tag{135}$$

$A_{des,2D}$ derived from equilibrium is the same result as for $A_{des,2D}$ derived from desorption using TS theory (Eq. (78)). Thus, the pre-exponential factor of desorption can be calculated from the desorption entropy ($\Delta S_{des,2D,g,m}^0$) and from the known value of α_s but only if the standard state, which has been used to obtain the entropy, is known.

830   For the case of an adsorbed 2D ideal lattice gas, we can derive the pre-exponential factor from equilibrium, $R_{ads,latt}^a = R_{des,latt}^a$ (Eq. (133), in a similar ways as for the 2D ideal gas discussed above, using $A_{des,latt}$ from the derivation of the desorption rate (Eq. (97)) and α_s (Eq. (129)) as (the full derivation is given in Supplement Eq. (244))

$$\kappa\left(\frac{k_B T}{h}\right)\left(\frac{q_{TS}'/\mathcal{A}}{q_g/\mathcal{V}}\right)e^{-\frac{E_b^0}{RT}}\frac{1}{\mathcal{N}_{ads,max}}a_g\frac{(N_g/\mathcal{V})^0(1-\theta^0)}{\theta^0} = \kappa\left(\frac{k_B T}{h}\right)\frac{(q_{TS}'/\mathcal{A})}{q_{ads,latt}\mathcal{N}_{ads,max}}e^{-\frac{\left(E_{des}^0+E_b^0\right)}{RT}}a_{ads,latt}$$

$$\kappa\left(\frac{k_B T}{h}\right)\left(\frac{q_{TS}'/\mathcal{A}}{q_g/\mathcal{V}}\right)e^{-\frac{E_b^0}{RT}}\frac{1}{\mathcal{N}_{ads,max}}a_g\frac{(N_g/\mathcal{V})^0(1-\theta^0)}{\theta^0} = A_{des,latt}^a e^{-\frac{\left(E_{des}^0+E_b^0\right)}{RT}}a_{ads,latt}$$

835   $$A_{des,latt}^a = \alpha_s\left(\frac{k_B T}{h}\right)(2\pi m k_B T/h^2)^{-1/2}\frac{1}{\mathcal{N}_{ads,max}}\frac{(N_g/\mathcal{V})^0(1-\theta^0)}{\theta^0}e^{-\frac{5}{2}}(1-\theta^0)^{-\frac{1}{\theta^0}}e^{\frac{E_b^0}{RT}}e^{\frac{\Delta S_{des,latt,g,m}^0}{R}} \ . \tag{136}$$

If the energy barrier E_b^0 is negligible, this simplifies to

$$A_{des,latt}^a = \alpha_s e^{\Delta S_{des,latt,g,m}^0/R} e^{-5/2}\frac{(1-\theta^0)}{\theta^0}\left(\frac{1}{\mathcal{N}_{ads,max}}\right)\left(\frac{N_A}{\mathcal{V}_m^0}\right)(1-\theta^0)^{-1/\theta^0}\left(\frac{k_B T}{h}\right)(2\pi m k_B T/h^2)^{-1/2}. \tag{137}$$

$A_{des,latt}^a$ derived from equilibrium is the same result as for $A_{des,latt}^a$ derived from desorption using TS theory (Eq. (97)).

As can be seen, the activity-based $A_{des,latt}^a$ does not depend on the surface coverage. However, the standard surface
840   coverage θ^0, for which $\Delta S_{des,latt,g,m}^0$ has been derived, must be known (similar to the case described in Eq. 97). Hence, the pre-exponential factor $A_{des,latt}$ has a strong non-linear dependence on the standard surface coverage. When the underlying standard surface coverages are not known, additional uncertainties are introduced. When deriving the desorption rate (Eq. 82), the dependence on surface coverage is accounted for.

8. Implications for the Assessment of Desorption Energy and Rate and Pre-exponential Factor

845   The thermodynamic derivations above indicate that the underlying adsorption model, i.e., 2D ideal gas or 2D ideal lattice gas, will have a significant impact on desorption rates and the pre-exponential factor and, thus, on the evaluation of E_{des}^0 and τ_d. This is particularly important for the case of the 2D ideal lattice gas model for which the desorption rate varies non-linearly

with surface coverage, i.e., proportional to $(\theta/(1-\theta))$ (Eq. 82) since the surface activity is defined by $\frac{(\theta/(1-\theta))}{(\theta^0/(1-\theta^0))}$ (Eq. 42). This implies that for same E_{des}^0, $\frac{R_{des}}{\mathcal{A}}$ can vary significantly depending on adsorbate coverage. Vice versa, if the coverage is not well-known, derivation of E_{des}^0 from measured $\frac{R_{des}}{\mathcal{A}}$ is associated with large uncertainties.

Figure 5 displays the variation of $\frac{R_{des}}{\mathcal{A}}$ for different θ, covering a pristine surface to a fully occupied surface. As discussion of Fig. 7 alluded to (above), Fig. 5 demonstrates that the assumption of the underlying substrate model significantly impacts $\frac{R_{des}}{\mathcal{A}}$. The differences in $\frac{R_{des}}{\mathcal{A}}$ when applying a 2D ideal gas or a 2D ideal lattice gas are about 3 to 6 orders of magnitude over a typical θ range. Furthermore, variation of $\frac{R_{des}}{\mathcal{A}}$ for the 2D ideal lattice gas is greater with θ due to its non-linear dependence on θ. The observed non-linearity of $\frac{R_{des}}{\mathcal{A}}$ of the 2D ideal lattice gas, being proportional to $(\theta/(1-\theta))$, is a direct result of the non-linear increase of the configurational entropy (e.g., Eqs. (53) and (98)). Figure 5 implies that the different sensitivities of the two adsorbate models on surface coverages can result in large differences in experimentally derived desorption rates besides uncertainties in the pre-exponential factor and E_{des}^0.

As outlined above, Fig. 10 highlights how the underlying adsorbate model impacts the pre-exponential factor. If the actual adsorbate system more closely behaves as a 2D ideal lattice gas but is analyzed assuming a 2D ideal gas, significant uncertainties in A_{des} can arise which, in turn, increase the uncertainty in the derivation of E_{des}^0 and estimation of the desorption lifetime.

Figure 14 presents estimates of τ_d for given E_{des}^0 as a function of temperature when applying a 2D ideal gas and 2D ideal lattice gas adsorbate model. For both adsorbate models, the temperature sensitivity of τ_d increases with increasing E_{des}^0. For given τ_d the difference in E_{des}^0, when applying the different adsorbate models can range from 10 to 15 kJ mol^{-1}, where larger differences occur at higher temperatures. Hence, when deriving E_{des}^0 from τ_d values, in absence of knowledge of the underlying adsorbate model, E_{des}^0 is likely uncertain by 10 to 15 kJ mol^{-1}. Vice versa, the corresponding uncertainty in τ_d is up to about 3 orders of magnitude. As outlined in the introduction, for experimental studies where τ_d is coupled to the surface reaction rate, the first-order surface reaction rate could also be uncertain by up to 3 orders of magnitude.

Figure 15 displays E_{des}^0 values derived from a variation of desorption rates applying a 2D ideal gas or 2D ideal lattice gas adsorbate model as a function of surface coverage θ. For example, for $\frac{R_{des}}{\mathcal{A}} = 1$ m^{-2} s^{-1}, reflected by the uppermost red and blue curves, it is evident that the chosen adsorbate model results in significantly different E_{des}^0 values differing by at least 20 kJ mol^{-1}. These results further support the importance of accurate knowledge of θ. The E_{des}^0 values can vary by tens of kJ mol^{-1}, if θ is incorrectly determined or assumed. For example, if the substrate surface is assumed to be pristine but in fact $\theta = 0.2$, E_{des}^0 can be overestimated by $10 - 20$ kJ mol^{-1}.

Figures 5, 10, 14, and 15 highlight the potential uncertainties that arise by choice of the absorbate models for derivation of E_{des}^0. In addition to those uncertainties, standard states applied in adsorption and desorption studies are often not known or well documented. This can lead to additional uncertainties as also outlined above. A_{des} values shown in Fig. 10 will be the

same for different choices of standard states as long as they have been consistently applied to the entropic contributions
$\Delta S^0_{des,2D,act,m}$, $\Delta S^0_{des,2D,g,m}$, $\Delta S^0_{des,latt,act,m}$, and $\Delta S^0_{des,latt,g,m}$ (Supplement Eqs. (150), (121), (173), and (134), respectively) and within the equations for A_{des} (Eqs. (87), (134), (97), (136)). The standard molar volume, $\mathcal{V}^0_m = 24.8$ L mol^{-1} at 298 K and 1000 hPa, is the typically applied parameter but one has to make sure to adjust this value to observational conditions, i.e., temperature and pressure, for both the entropic contribution and the derivation of the partition functions. The latter depends linearly on the molar volume (Supplement Eqs. (7) and (92)). The actual surface coverage and applied standard surface coverages are often less clear and furthermore, different standard states may have been chosen for the entropic contributions and experimental conditions. To further complicate matters, standard surface coverages can be defined applying $\theta^0 = 0.012$ or 0.5, which both have their advantages as outlined above. If the standard surface coverage for the entropic contribution is based on $\theta^0 = 0.012$ but the remainder of thermodynamic functions on $\theta^0 = 0.5$, A_{des} will be erroneous and thus E^0_{des} and τ_d.

9. Conclusions

Reversible adsorption is a key process for any gas-condensed phase interaction, and particularly important when environmental interfaces are involved including aerosol particles. This study provides a comprehensive treatment of the classic and statistical thermodynamics of the adsorption and desorption processes considering transition state theory for two typically applied adsorbate models, the 2D ideal gas and the 2D ideal lattice gas which apply to solid or liquid substrate surfaces. We established thermodynamic and microscopic relationships for adsorption and desorption equilibrium constants, adsorption and desorption rates, first-order adsorption and desorption rate coefficients, and corresponding pre-exponential factors. These derivations allow the interpretation of thermodynamic functions such as equilibrium constants in terms of their molecular properties, as well as the calculation of explicit numeric expressions for the latter. This exercise demonstrates the importance of applied assumptions of adsorbate model and standard states when analyzing and interpreting adsorption and desorption processes, the latter being often ill-defined in experimental studies (Donaldson et al., 2012). The derivations allow for a microscopic interpretation of the surface accommodation coefficient including the entropic contribution. Our treatment demonstrates that the pre-exponential factor, when deriving the desorption lifetime from the desorption energy, can differ by orders of magnitude depending on the choice of adsorbate model. Clearly, such a difference yields similar effects on the desorption lifetime, and when used to estimate desorption energies (e.g., from interfacial residence times estimated from molecular dynamics simulations or from measured desorption rates) significant uncertainties in the desorption energy are incurred. Furthermore, uncertainties in surface coverage and assumptions in standard surface coverage can lead to significant changes in desorption rates and thus in evaluated desorption energies for the rather common case of a 2D ideal lattice gas. The objective of providing this comprehensive thermodynamic and microscopic treatment of the adsorption and desorption processes is to guide the theoretical and experimental assessments of adsorption and desorption rates, desorption energies and choice of standard states with implications for the corresponding desorption lifetimes. This in turn will improve, specifically, the analyses and

910 interpretation of surface layer reaction rates and surface-to-bulk transport, and thus, bulk mass accommodation. More generally, this provides a better basis for the prediction of gas-particle partitioning, multiphase chemical reactions, and the chemical evolution of atmospheric aerosol.

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Data availability. All data needed to draw the conclusions in the present study are shown in the paper and/or the Supplement.

Supplement. The supplement related to this article is available online at:

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References

Ammann, M., and Pöschl, U.: Kinetic model framework for aerosol and cloud surface chemistry and gas-particle interactions - Part 2: Exemplary practical applications and numerical simulations, Atmos. Chem. Phys., 7, 6025-6045, 2007.

Ammann, M., Cox, R. A., Crowley, J. N., Jenkin, M. E., Mellouki, A., Rossi, M. J., Troe, J., and Wallington, T. J.: Evaluated kinetic and photochemical data for atmospheric chemistry: Volume VI - heterogeneous reactions with liquid substrates, Atmos. Chem. Phys., 13, 8045-8228, 10.5194/acp-13-8045-2013, 2013.

Arangio, A. M., Slade, J. H., Berkemeier, T., Pöschl, U., Knopf, D. A., and Shiraiwa, M.: Multiphase Chemical Kinetics of OH Radical Uptake by Molecular Organic Markers of Biomass Burning Aerosols: Humidity and Temperature Dependence, Surface Reaction, and Bulk Diffusion, J. Phys. Chem. A, 119, 4533-4544, 10.1021/jp510489z, 2015.

Arrhenius, S. A.: Über die Dissociationswärme und den Einfluß der Temperatur auf den Dissociationsgrad der Elektrolyte, Z. Phys. Chem., 4, 96-116, 1889a.

Arrhenius, S. A.: Über die Reaktionsgeschwindigkeit bei der Inversion von Rohrzucker durch Säuren, Z. Phys. Chem., 4, 226-248, 1889b.

Atkins, P., and de Paula, J.: Physical Chemistry, 8th ed., W. H. Freeman and Company, New York, 1040 pp., 2006.

Bartels-Rausch, T., Huthwelker, T., Gaggeler, H. W., and Ammann, M.: Atmospheric pressure coated-wall flow-tube study of acetone adsorption on ice, J. Phys. Chem. A, 109, 4531-4539, 10.1021/jp0451871, 2005.

Bolis, V.: Fundamentals in Adsorption at the Solid-Gas Interface. Concepts and Thermodynamics, in: Calorimetry and Thermal Methods in Catalysis, edited by: Auroux, A., 154, Springer-Verlag Berlin Heidelberg, Berlin, 3-50, 2013.

Campbell, C. T., Arnadottir, L., and Sellers, J. R. V.: Kinetic Prefactors of Reactions on Solid Surfaces, Z. Phys. Chemie-Int. J. Res. Phys. Chem. Chem. Phys., 227, 1435-1454, 10.1524/zpch.2013.0395, 2013.

Campbell, C. T., Sprowl, L. H., and Arnadottir, L.: Equilibrium Constants and Rate Constants for Adsorbates: Two-Dimensional (2D) Ideal Gas, 2D Ideal Lattice Gas, and Ideal Hindered Translator Models, J. Phys. Chem. C, 120, 10283-10297, 10.1021/acs.jpcc.6b00975, 2016.

Chorkendorff, I., and Niemantsverdriet, J. W.: Concepts of Modern Catalysis and Kinetics, 2nd ed., Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 477 pp., 2007.

Crowley, J. N., Ammann, M., Cox, R. A., Hynes, R. G., Jenkin, M. E., Mellouki, A., Rossi, M. J., Troe, J., and Wallington, T. J.: Evaluated kinetic and photochemical data for atmospheric chemistry: Volume V - heterogeneous reactions on solid substrates, Atmos. Chem. Phys., 10, 9059-9223, 10.5194/acp-10-9059-2010, 2010.

Crowley, J. N., Ammann, M., Cox, R. A., Hynes, R. G., Jenkin, M. E., Mellouki, A., Rossi, M. J., Troc, J., and Wallington, T. J.: Evaluated kinetic and photochemical data for atmospheric chemistry: Volume V - heterogeneous reactions on solid substrates (vol 10, pg 9059, 2010), Atmos. Chem. Phys., 13, 7359-7359, 10.5194/acp-13-7359-2013, 2013.

Cussler, E. L.: Diffusion - Mass Transfer in Fluid Systems, 2009.

de Boer, J. H.: The Dynamical Character of Adsorption, Clarendon Press, Oxford, 1968.

Donahue, N. M., Epstein, S. A., Pandis, S. N., and Robinson, A. L.: A two-dimensional volatility basis set: 1. organic-aerosol mixing thermodynamics, Atmos. Chem. Phys., 11, 3303-3318, 10.5194/acp-11-3303-2011, 2011.

Donaldson, D. J., Ammann, M., Bartels-Rausch, T., and Pöschl, U.: Standard States and Thermochemical Kinetics in Heterogeneous Atmospheric Chemistry, J. Phys. Chem. A, 116, 6312-6316, 10.1021/jp212015g, 2012.

Eyring, H.: The activated complex in chemical reactions, J. Chem. Phys., 3, 107-115, 10.1063/1.1749604, 1935.

Finlayson-Pitts, B. J., and Pitts, J. N.: Chemistry of the Upper and Lower Atmosphere: Theory, Experiments and Applications, Academic Press, San Diego, Calif. ; London, xxii, 969 pp., 2000.

Frenkel, J.: Theory of the adsorption and related occurrences, Z. Phys., 26, 117-138, 10.1007/bf01327320, 1924.

George, I. J., and Abbatt, J. P. D.: Heterogeneous oxidation of atmospheric aerosol particles by gas-phase radicals, Nat. Chem., 2, 713-722, 10.1038/Nchem.806, 2010.

Hanson, D. R., and Ravishankara, A. R.: The Loss of CF_2O On Ice, Nat, and Sulfuric-Acid-Solutions, Geophys. Res. Lett., 18, 1699-1701, 1991.

Hill, T. L.: An Introduction to Statistical Thermodynamics, Dover Publications, Inc., New York, 501 pp., 1986.

Jimenez, J. L., Canagaratna, M. R., Donahue, N. M., Prevot, A. S. H., Zhang, Q., Kroll, J. H., DeCarlo, P. F., Allan, J. D., Coe, H., Ng, N. L., Aiken, A. C., Docherty, K. S., Ulbrich, I. M., Grieshop, A. P., Robinson, A. L., Duplissy, J., Smith, J. D., Wilson, K. R., Lanz, V. A., Hueglin, C., Sun, Y. L., Tian, J., Laaksonen, A., Raatikainen, T., Rautiainen, J., Vaattovaara, P.,

Ehn, M., Kulmala, M., Tomlinson, J. M., Collins, D. R., Cubison, M. J., Dunlea, E. J., Huffman, J. A., Onasch, T. B.,
990   Alfarra, M. R., Williams, P. I., Bower, K., Kondo, Y., Schneider, J., Drewnick, F., Borrmann, S., Weimer, S., Demerjian, K.,
Salcedo, D., Cottrell, L., Griffin, R., Takami, A., Miyoshi, T., Hatakeyama, S., Shimono, A., Sun, J. Y., Zhang, Y. M.,
Dzepina, K., Kimmel, J. R., Sueper, D., Jayne, J. T., Herndon, S. C., Trimborn, A. M., Williams, L. R., Wood, E. C.,
Middlebrook, A. M., Kolb, C. E., Baltensperger, U., and Worsnop, D. R.: Evolution of Organic Aerosols in the Atmosphere,
Science, 326, 1525-1529, 10.1126/science.1180353, 2009.

995   Kemball, C., and Rideal, E. K.: The adsorption of vapours on mercury .1. Non-polar substances, Proceedings of the Royal
Society of London Series a-Mathematical and Physical Sciences, 187, 53-73, 10.1098/rspa.1946.0065, 1946.

Kisliuk, P.: The sticking probabilities of gases chemisorbed on the surfaces of solids, J. Phys. Chem. Solids, 3, 95-101,
10.1016/0022-3697(57)90054-9, 1957.

Kolasinski, K. W.: Surface Science: Foundations of Catalysis and Nanoscience, 3rd ed., John Wiley & Sons, Ltd., West
1000   Sussex, United Kingdom, 556 pp., 2012.

Kolb, C. E., Worsnop, D. R., Zahniser, M. S., Davidovits, P., Keyser, L. F., Leu, M.-T., Molina, M. J., Hanson, D. R.,
Ravishankara, A. R., Williams, L. R., and Tolbert, M. A.: Laboratory Studies of Atmospheric Heterogeneous Chemistry, in:
Progress and Problems in Atmospheric Chemistry, edited by: Barker, J. R., World Scientific, Singapore, 771-875, 1995.

Kolb, C. E., Cox, R. A., Abbatt, J. P. D., Ammann, M., Davis, E. J., Donaldson, D. J., Garrett, B. C., George, C., Griffiths, P.
1005   T., Hanson, D. R., Kulmala, M., McFiggans, G., Pöschl, U., Riipinen, I., Rossi, M. J., Rudich, Y., Wagner, P. E., Winkler, P.
M., Worsnop, D. R., and O' Dowd, C. D.: An overview of current issues in the uptake of atmospheric trace gases by aerosols
and clouds, Atmos. Chem. Phys., 10, 10561-10605, 2010.

Kroll, J. H., Donahue, N. M., Jimenez, J. L., Kessler, S. H., Canagaratna, M. R., Wilson, K. R., Altieri, K. E., Mazzoleni, L.
R., Wozniak, A. S., Bluhm, H., Mysak, E. R., Smith, J. D., Kolb, C. E., and Worsnop, D. R.: Carbon oxidation state as a
1010   metric for describing the chemistry of atmospheric organic aerosol, Nat Chem, 3, 133-139,
http://www.nature.com/nchem/journal/v3/n2/abs/nchem.948.html#supplementary-information, 2011.

Laidler, K. J., Glasstone, S., and Eyring, H.: Application of the Theory of Absolute Reaction Rates to Heterogeneous
Processes II. Chemical Reactions on Surfaces, J. Chem. Phys., 8, 667-676, 10.1063/1.1750737, 1940.

Laidler, K. J.: The mechanisms of some elementary surface reactions, J. Phys. Colloid Chem., 53, 712-732,
1015   10.1021/j150470a010, 1949.

Langmuir, I.: A theory of adsorption, Phys. Rev., 6, 79-80, 1915.

Langmuir, I.: The evaporation, condensation and reflection of molecules and the mechanism of adsorption, Phys. Rev., 8,
149-176, 10.1103/PhysRev.8.149, 1916.

Langmuir, I.: The adsorption of gases on plane surfaces of glass, mica and platinum, J. Am. Chem. Soc., 40, 1361-1403,
1020   10.1021/ja02242a004, 1918.

Langmuir, I.: Vapor pressures, evaporation, condensation and adsorption, J. Am. Chem. Soc., 54, 2798-2832,
10.1021/ja01346a022, 1932.

Li, J., and Knopf, D. A.: Representation of Multiphase OH Oxidation of Amorphous Organic Aerosol for Tropospheric
Conditions, Environ. Sci. Technol., 10.1021/acs.est.0c07668, 2021.

1025   Li, J. N., Forrester, S. M., and Knopf, D. A.: Heterogeneous oxidation of amorphous organic aerosol surrogates by O_3, NO_3,
and OH at typical tropospheric temperatures, Atmos. Chem. Phys., 20, 6055-6080, 10.5194/acp-20-6055-2020, 2020.

McNaught, A. D., and Wilkinson, A.: IUPAC. Compendium of Chemical Terminology, 2nd ed. (the "Gold Book"). 2nd ed.,
Blackwell Scientific Publications, Oxford, 2014.

McQuarrie, D. A.: Statistical mechanics, University Science Books, Sausalito, CA, 631 pp., 2000.

1030   Moise, T., Flores, J. M., and Rudich, Y.: Optical properties of secondary organic aerosols and their changes by chemical
processes, Chem. Rev., 115, 4400-4439, 10.1021/cr5005259, 2015.

Pilling, M. J., and Seakins, P. W.: Reaction Kinetics, 2nd ed., Oxford Science Publications, Oxford University Press, USA,
New York, 320 pp., 1996.

Pöschl, U., Rudich, Y., and Ammann, M.: Kinetic model framework for aerosol and cloud surface chemistry and gas-particle
1035   interactions - Part 1: General equations, parameters, and terminology, Atmos. Chem. Phys., 7, 5989-6023, 2007.

Pöschl, U., and Shiraiwa, M.: Multiphase Chemistry at the Atmosphere-Biosphere Interface Influencing Climate and Public
Health in the Anthropocene, Chem. Rev., 115, 4440-4475, 10.1021/cr500487s, 2015.

Ravishankara, A. R.: Heterogeneous and multiphase chemistry in the troposphere, Science, 276, 1058-1065, 1997.

Rowland, F. S.: Stratospheric ozone depletion, Annu. Rev. Phys. Chem., 42, 731-768, 10.1146/annurev.physchem.42.1.731, 1991.

Rudich, Y., Donahue, N. M., and Mentel, T. F.: Aging of organic aerosol: Bridging the gap between laboratory and field studies, Annu. Rev. Phys. Chem., 58, 321-352, 10.1146/annurev.physchem.58.032806.104432, 2007.

Savara, A.: Standard States for Adsorption on Solid Surfaces: 2D Gases, Surface Liquids, and Langmuir Adsorbates, J. Phys. Chem. C, 117, 15710-15715, 10.1021/jp404398z, 2013.

Shiraiwa, M., Pfrang, C., Koop, T., and Pöschl, U.: Kinetic multi-layer model of gas-particle interactions in aerosols and clouds (KM-GAP): linking condensation, evaporation and chemical reactions of organics, oxidants and water, Atmos. Chem. Phys., 12, 2777-2794, 2012.

Shiraiwa, M., and Seinfeld, J. H.: Equilibration timescale of atmospheric secondary organic aerosol partitioning, Geophys. Res. Lett., 39, L24801, 10.1029/2012gl054008, 2012.

Shiraiwa, M., Zuend, A., Bertram, A. K., and Seinfeld, J. H.: Gas-particle partitioning of atmospheric aerosols: interplay of physical state, non-ideal mixing and morphology, Phys. Chem. Chem. Phys., 15, 11441-11453, 10.1039/c3cp51595h, 2013.

Shiraiwa, M., and Poschl, U.: Mass accommodation and gas-particle partitioning in secondary organic aerosols: dependence on diffusivity, volatility, particle-phase reactions, and penetration depth, Atmos. Chem. Phys., 21, 1565-1580, 10.5194/acp-21-1565-2021, 2021.

Silbaugh, T. L., Karp, E. M., and Campbell, C. T.: Surface kinetics and energetics from single crystal adsorption calorimetry lineshape analysis: Methyl from methyl iodide on Pt(111), J. Catal., 308, 114-121, 10.1016/j.jcat.2013.05.030, 2013.

Solomon, S.: Stratospheric ozone depletion: A review of concepts and history, Rev. Geophys., 37, 275-316, 1999.

Sprowl, L. H., Campbell, C. T., and Arnadottir, L.: Hindered Translator and Hindered Rotor Models for Adsorbates: Partition Functions and Entropies, J. Phys. Chem. C, 120, 9719-9731, 10.1021/acs.jpcc.5b11616, 2016.

Tabazadeh, A., and Turco, R. P.: A Model for Heterogeneous Chemical Processes on the Surfaces of Ice and Nitric-Acid Trihydrate Particles, J. Geophys. Res., 98, 12727-12740, 1993.

Tully, J. C.: The dynamics of adsorption and desorption, Surf. Sci., 299, 667-677, 10.1016/0039-6028(94)90688-2, 1994.

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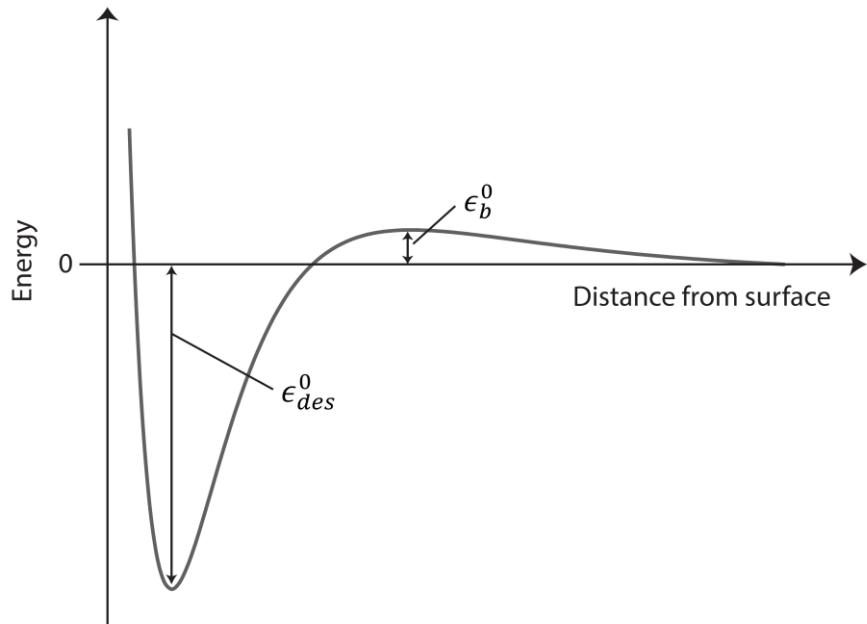
Figure 1. Potential energy curve for adsorption and desorption processes expressed by the heat of desorption, ϵ_{des}^0. For activated adsorption and desorption processes an additional energy barrier, expressed by ϵ_b^0, must be overcome.
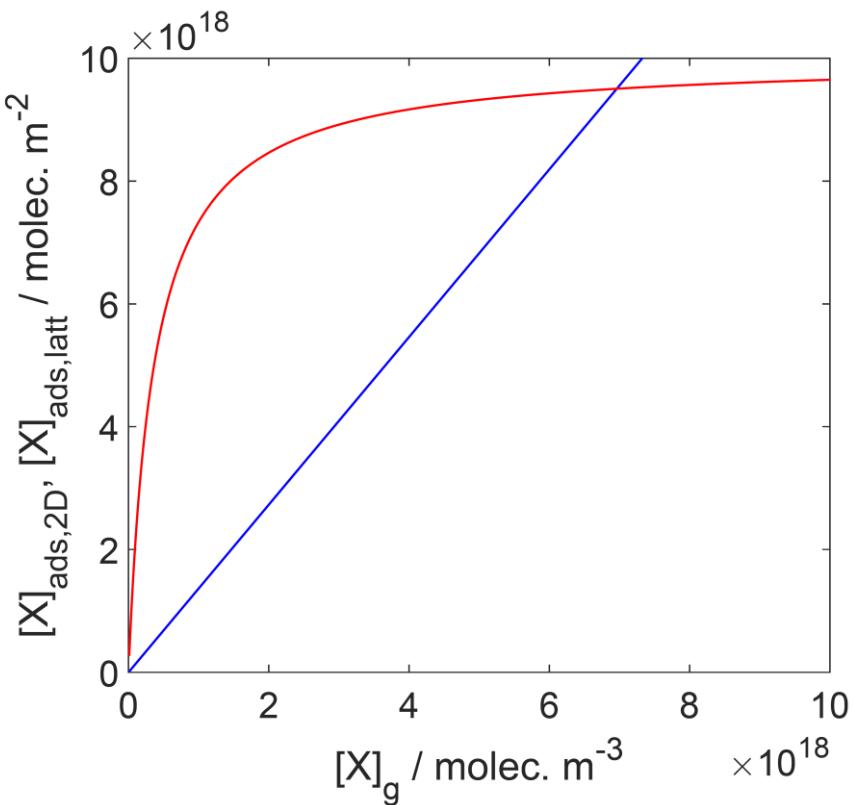
Figure 2. Equilibrium adsorbate surface concentration as a function of gas phase concentration for the case of a 2D ideal gas (blue line) and 2D ideal lattice gas (red line). Applied E_{des}^0 are 63 kJ mol^{-1} and 88 kJ mol^{-1}, respectively. We assume a desorption process without additional barrier, $E_b^0 = 0$. Thermodynamic quantities for calculation are given in Table S1.

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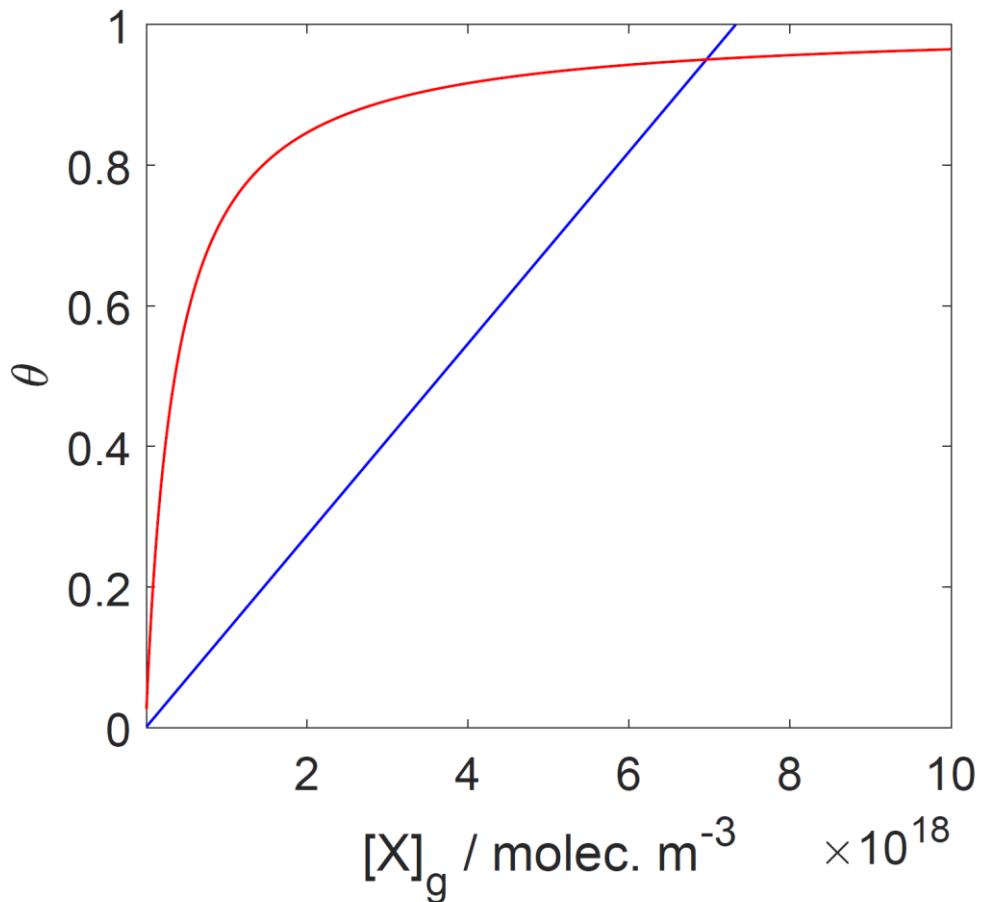
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Figure 3. Equilibrium surface coverage as a function of gas phase concentration for the case of a 2D ideal gas (blue line) and 2D ideal lattice gas (red line). The data are the same as used for derivation of Fig. 2, but surface coverages are derived by normalization with maximum number of adsorption sites. Thermodynamic quantities and standard states necessary for calculation are given in Table S1.

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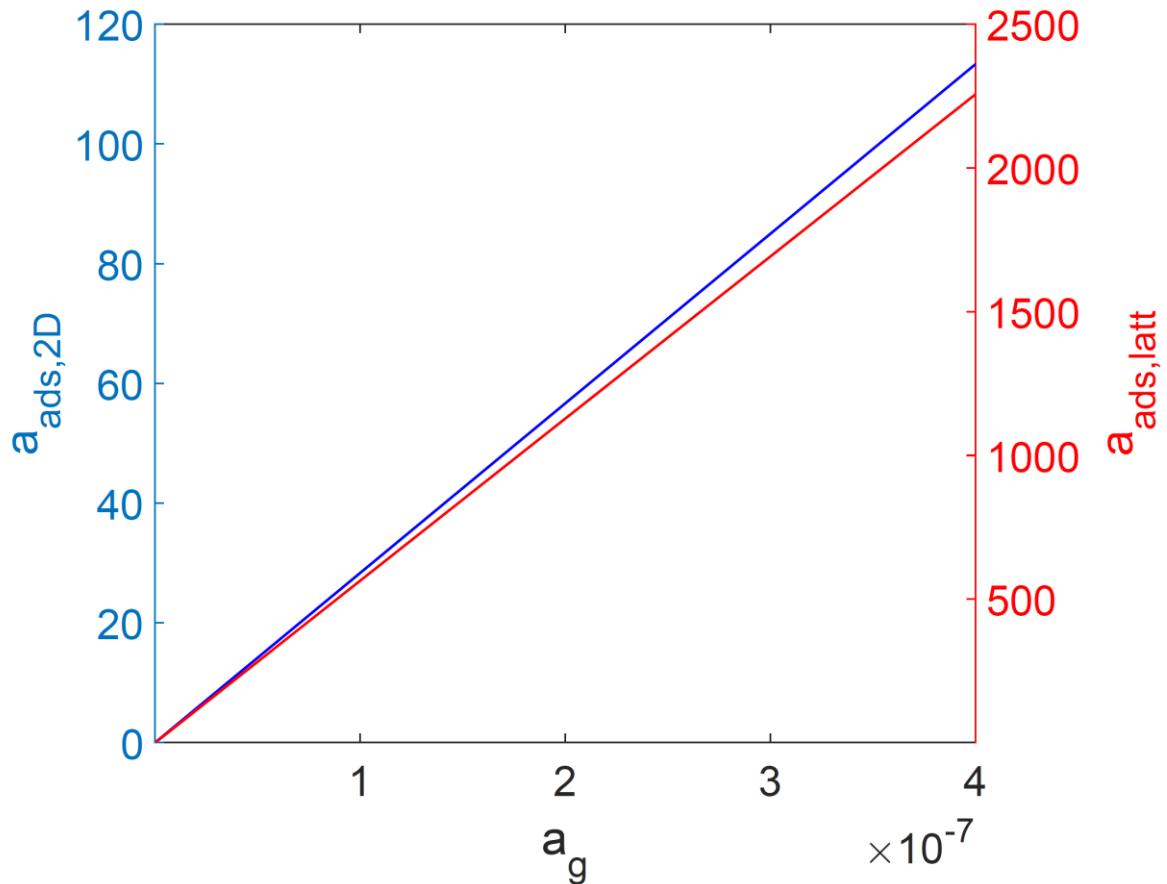
Figure 4. Equilibrium surface activity as a function of gas phase activity for the case of a 2D ideal gas (blue line) and 2D ideal lattice gas (red line). The data are the same as used for derivation of Fig. 2. Thermodynamic quantities and standard states necessary for calculation are given in Table S1.

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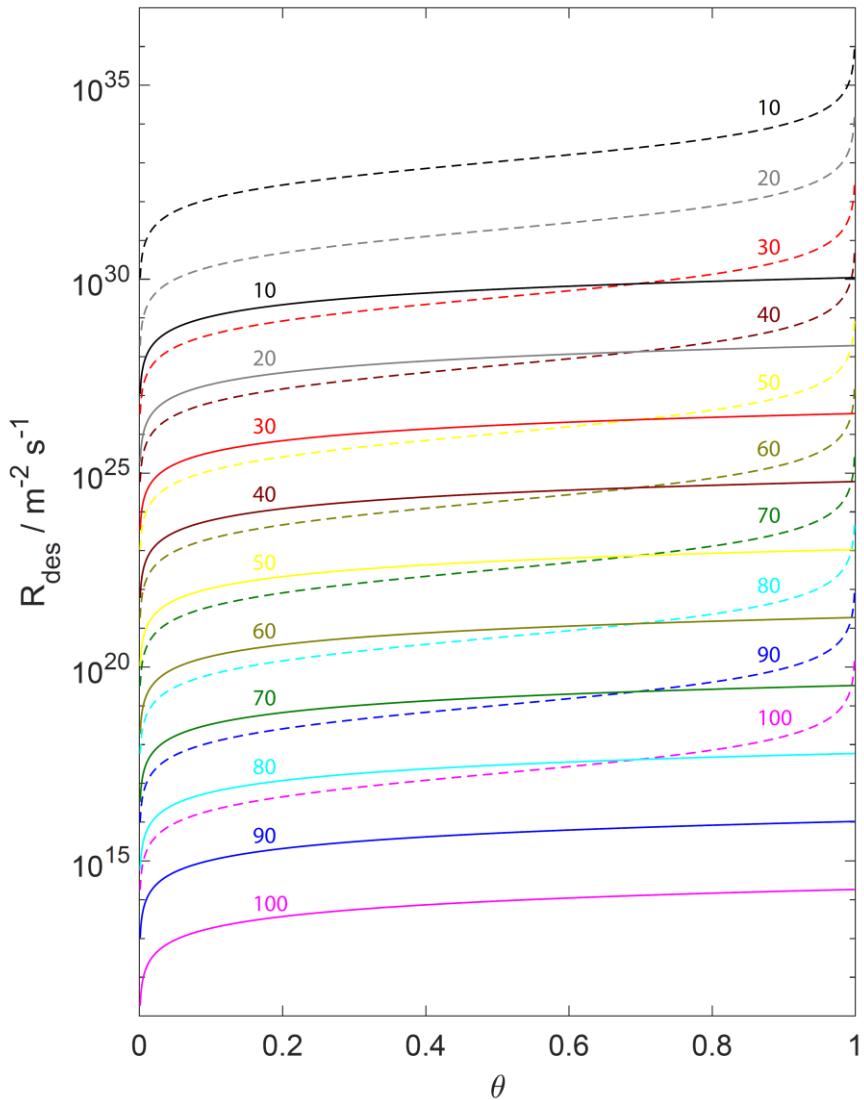
Figure 5. The change in the desorption rate for the assumption of a 2D ideal gas (solid lines) and 2D ideal lattice gas (dashed lines) are plotted as a function of adsorbate fractional surface coverage θ and variation of E_{des}^{0} from 100 (bottom) to 10 kJ mol^{-1} (top) indicated by colored numbers. We assume a desorption process without additional barrier, $E_{b}^{0} = 0$. Thermodynamic quantities and standard states necessary for calculation are given in Table S1.

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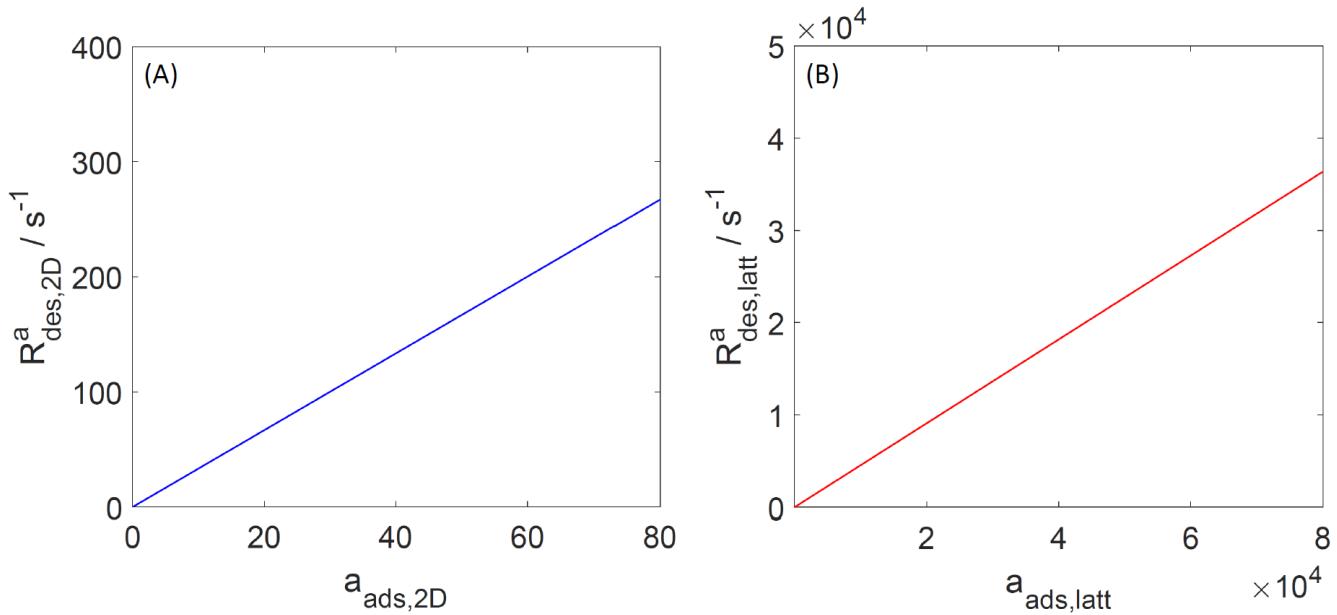
1145 **Figure 6. The activity-based desorption rate for the case of a 2D ideal gas (blue line, A) and 2D ideal lattice gas (red line, B). Applied E_{des}^0 are 70 kJ mol^{-1} and 92 kJ mol^{-1}, respectively. We assume a desorption process without additional barrier, $E_b^0 = 0$. Thermodynamic quantities and standard states necessary for calculation are given in Table S1.**

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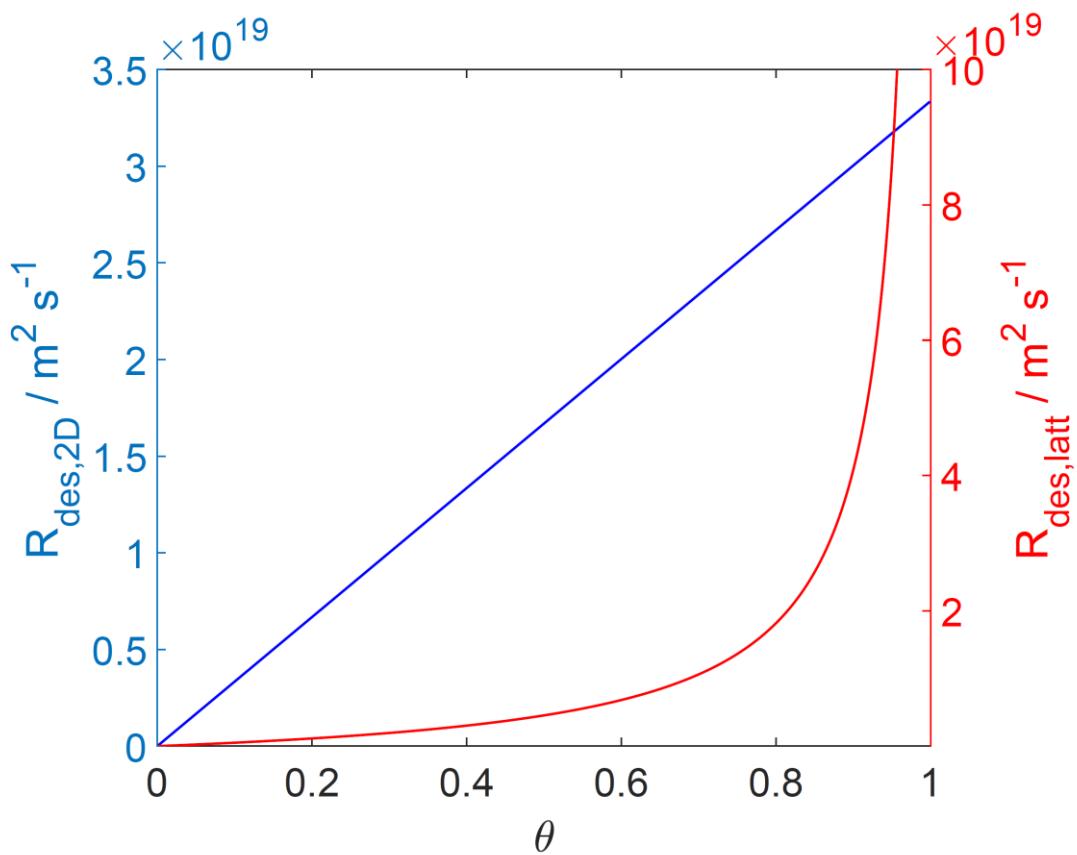
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Figure 7. The desorption rate for the case of a 2D ideal gas (blue line) and 2D ideal lattice gas (red line). Applied E_{des}^0 are 63 kJ mol^{-1} and 88 kJ mol^{-1}, respectively. We assume a desorption process without additional barrier, $E_b^0 = 0$. Thermodynamic quantities and standard states necessary for calculation are given in Table S1.

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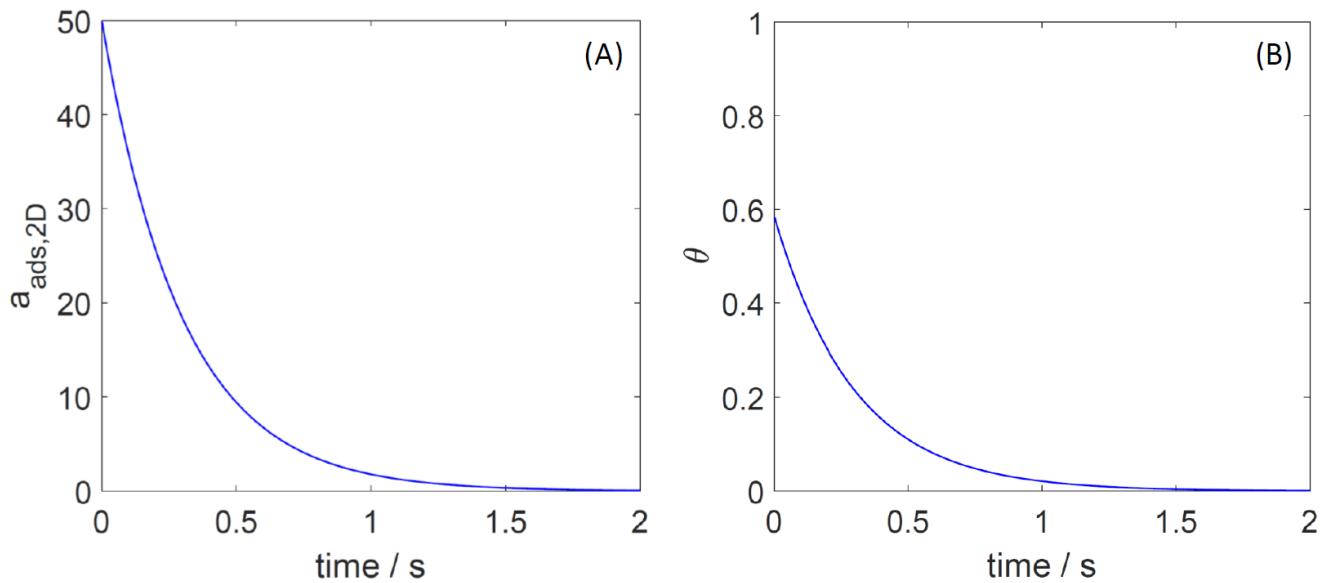
Figure 8. The decay of surface activity (A) and surface coverage (B) of the 2D ideal gas adsorbate as a function of time due to desorption. The applied E^0_{des} is 70 kJ mol^{-1} and the initial surface activity is 50. We assume a desorption process without additional barrier, $E^0_b = 0$. Thermodynamic quantities and standard states necessary for calculation are given in Table S1.

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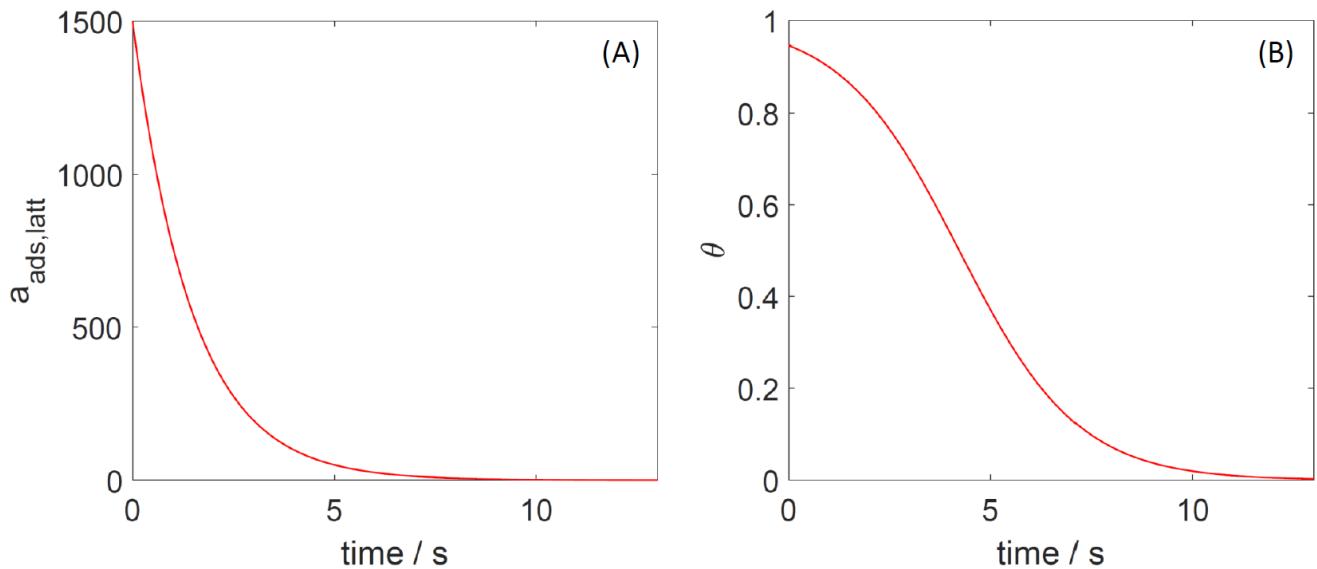
Figure 9. The decay of surface activity (A) and surface coverage (B) of the 2D ideal lattice gas adsorbate as a function of time due to

1195 **desorption. The applied E_{des}^{0} is 91 kJ mol^{-1} and the initial surface activity is 1500. We assume a desorption process without additional barrier, $E_{b}^{0} = 0$. Thermodynamic quantities and standard states necessary for calculation are given in Table S1.**

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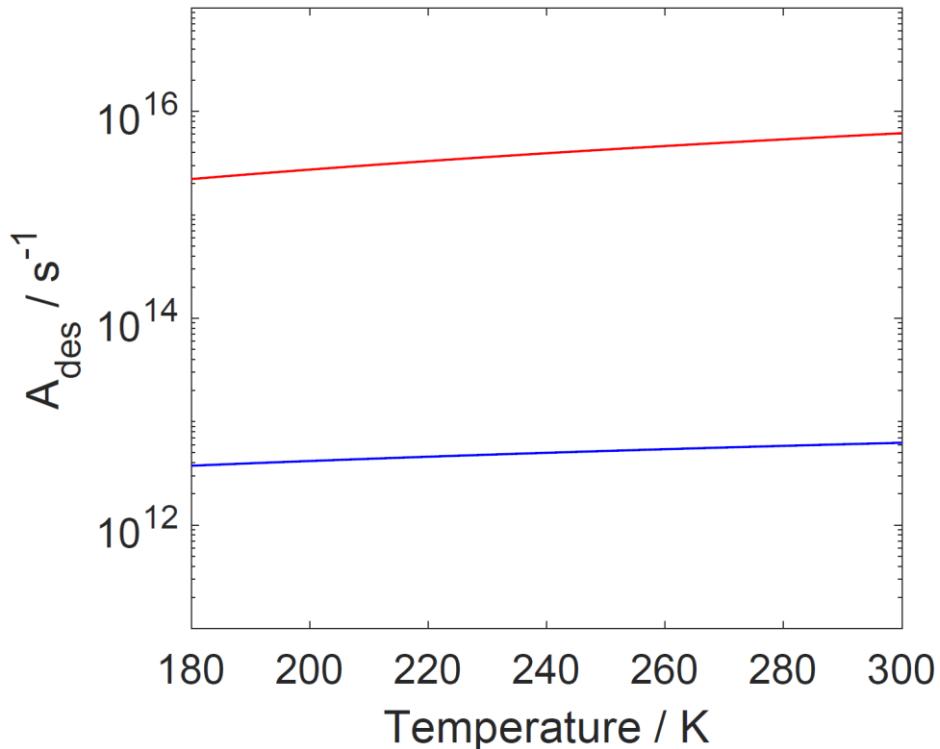
Figure 10. The pre-exponential factor A_{des} as a function of temperature is plotted for the case of a 2D ideal gas (blue) and a 2D ideal lattice gas (red). Thermodynamic quantities and standard states necessary for calculation are given in Table S1.

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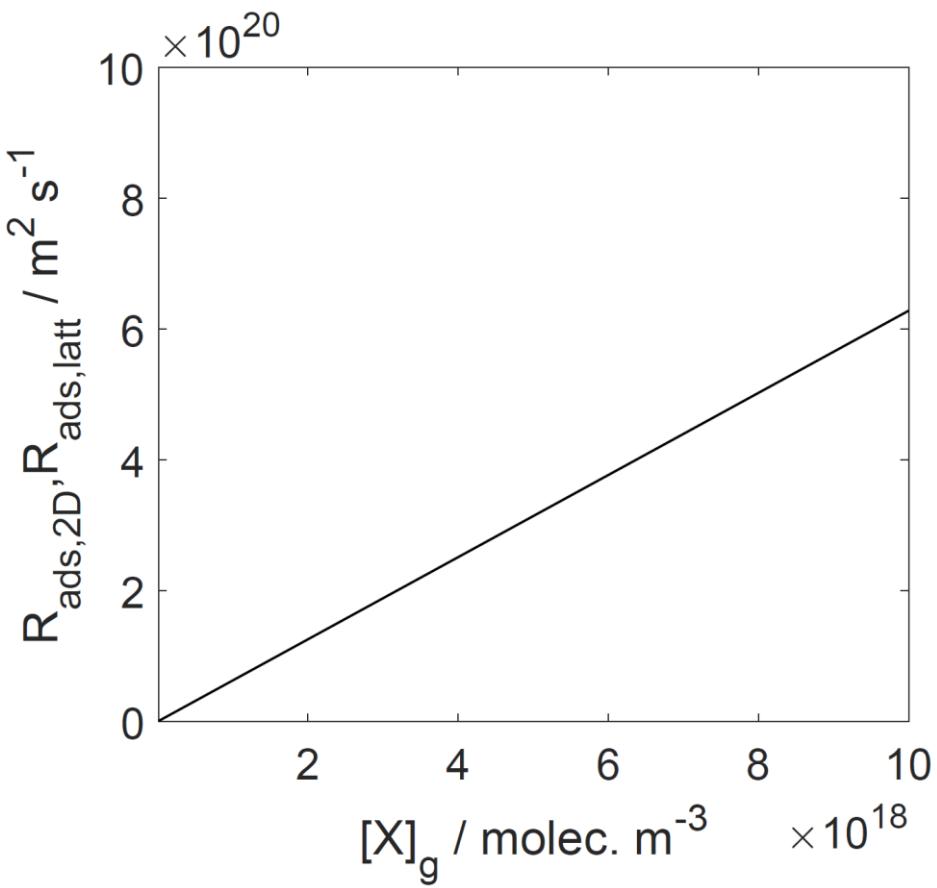
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Figure 11. The adsorption rate for the case of a 2D ideal gas and 2D ideal lattice gas is depicted. We assume a non-activated adsorption process, $E_b^0 = 0$. Thermodynamic quantities and standard states necessary for calculation are given in Table S1.

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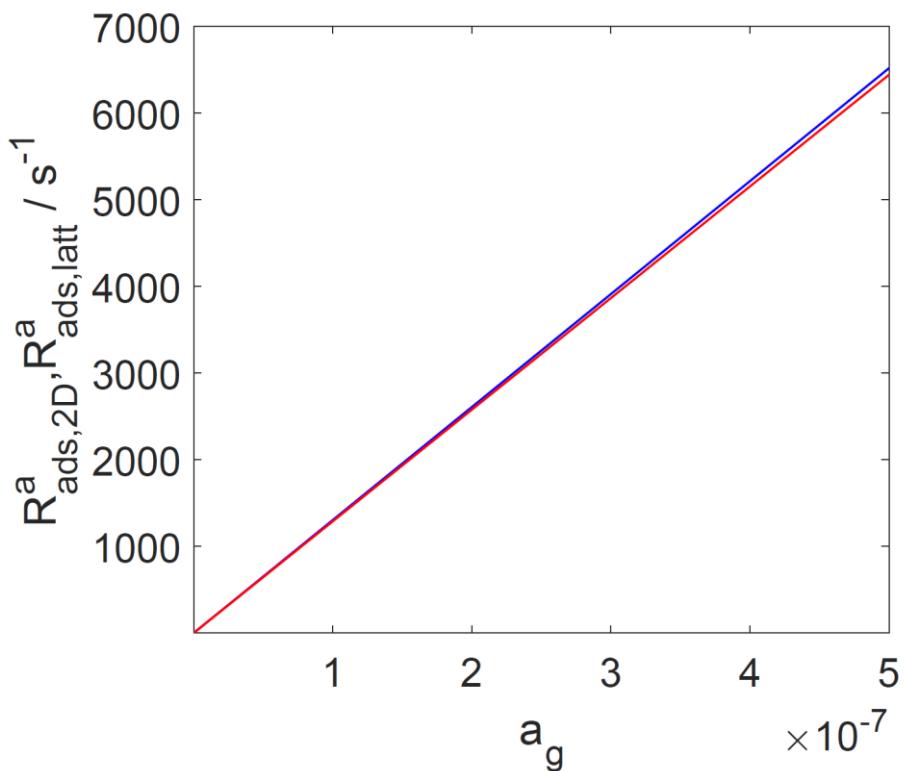


Figure 12. The activity-based adsorption rates for the case of a 2D ideal gas (blue line) and 2D ideal lattice gas (red line) are depicted. We assume a non-activated adsorption process, $E_b^0 = 0$. Thermodynamic quantities and standard states necessary for calculation are given in Table S1.

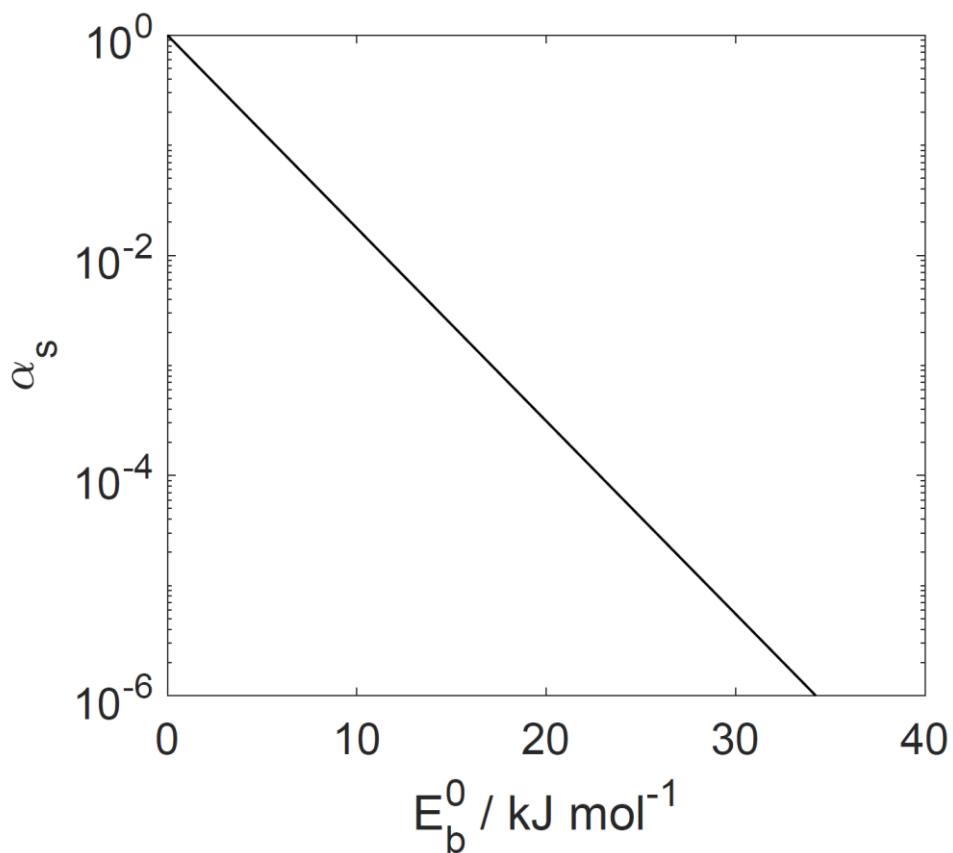



Figure 13. The dependency of the mass accommodation coefficient, α_s, on the adsorption activation energy, E_b^0. Thermodynamic quantities and standard states necessary for calculation are given in Table S1.

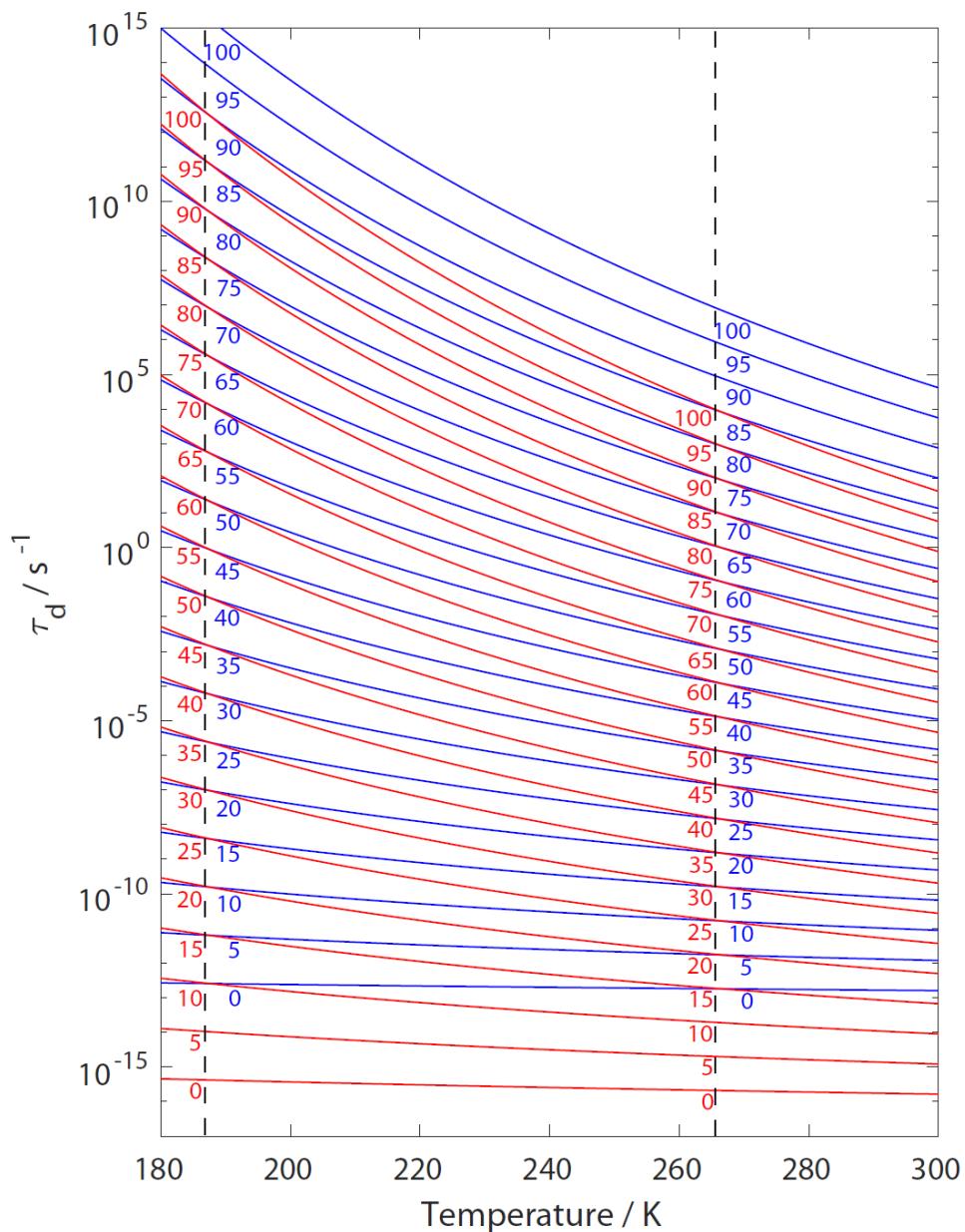
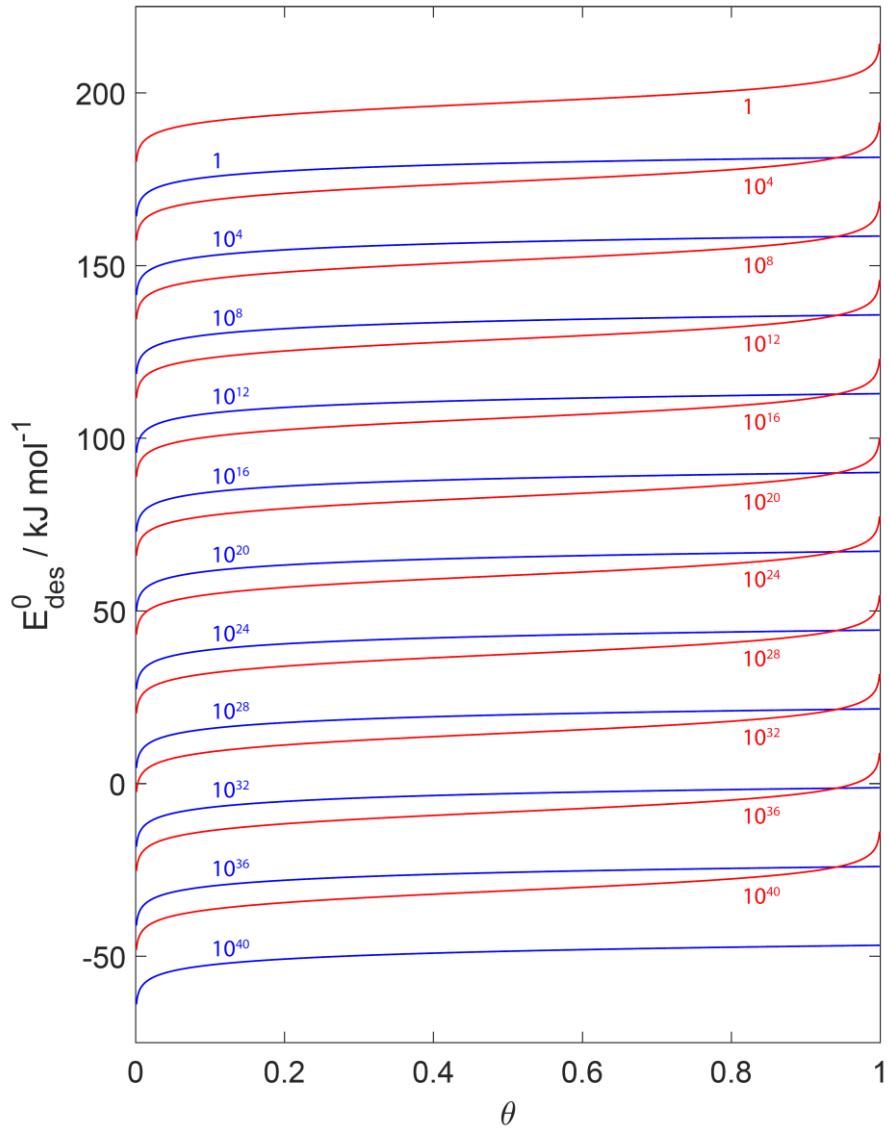



Figure 14. Estimates of τ_d as a function of temperature applying results from Fig. 3 Blue and red lines represent the 2D ideal gas and 2D ideal lattice gas model, respectively. E_{des}^0 varies from 0 to 100 kJ mol^{-1} in 5 kJ mol^{-1} steps from bottom to top and is indicated by numbers on lines. We assume a desorption process without additional barrier, $E_b^0 = 0$. Thermodynamic quantities and standard states necessary for calculation are given in Table S1.

1280 **Figure 15. Estimates of E_{des}^0 as a function of coverage for desorption rates from 1 m^{-2} s^{-1} to 10^{40} m^{-2} s^{-1} (from top to bottom and indicated by colored numbers) for T = 298 K. Blue and red lines indicate desorption model based on a 2D ideal gas and 2D ideal lattice gas, respectively. We assume a desorption process without additional barrier, $E_b^0 = 0$. Thermodynamic quantities and standard states necessary for calculation are given in Table S1.**