

Response to reviewer #2

This technical note derives the desorption rates for adsorbed species using thermodynamics and statistical mechanics. The authors do these derivations with two models of the sorbed species: a 2D ideal gas and a 2D ideal lattice gas. The authors demonstrate that these models will retrieve very different values of e.g. desorption energy and timescale. This work is valuable and relevant to the study of atmospheric chemistry.

We thank the referee for the careful evaluation of our manuscript and for this positive evaluation.

The authors aim to save space and increase the readability of the manuscript by moving many of the equations to the Supplement. This was a good decision, however the reader who is reliant on the additional information found in the supplement is also the reader who needs to be guided most closely through those equations. The manuscript would benefit from additional text informing readers when equations and assumptions detailed in the Supplement have been brought into the main text. This added text should specify the range of equation numbers over which a derivation has been conducted, and not simply list the equation number of the final result.

We are aware that following the equations is challenging. As the referee requested, for crucial derivations in the main text we will provide more information on which supplemental equations are needed to derive the shown results.

This concerns references to the Supplement on lines:

Line 269: (see Supplement Eqs. (119-123) with Supplement Eqs. (86), (89), (91), (93), (97), (98))

Line 285: We change “Supplement Eq. (119ff.)” to “Supplement Eqs. (119-121)”.

Line 299: (Supplement Eq. (121) with Supplement Eq. (89))

Line 330: (see Supplement Eqs. (131, 133, 134) with Supplement Eqs. (86), (89), (91), (100), (103), 105))

Line 478: (Supplement Eq. (148) with Supplement Eqs. (108) and (93))

Line 563: (Supplement Eqs. (108) and (171))

Line 647: (Supplement Eqs. (193-199))

Line 754: ... given in the Supplement (Eqs. (216-220)).

Line 761: ...is outlined in the Supplement Eqs. (221-225).

Line 770: ... given in the Supplement Eqs. (226-230).

Line 780: ... is given in the Supplement Eqs. (231-235).

237: It seems like the atmospheric chemists most likely to rely on this work are those conducting lab experiments of adsorption and desorption, where coverages may not be small. The authors should provide a quantitative estimate of the level of coverage where they believe the 2D ideal gas is no longer an appropriate model to use.

Thank you for this comment. The text may have left the reader in confusion. In short, the level of coverage will not define the application of either model. Referee #1 requested to add a description under which conditions the 2D ideal gas model and the 2D ideal lattice gas model manifest. This information will be added on line 91:

“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 kBT (Boltzmann constant times temperature), the ideal lattice gas model is the preferred model, whereas if it is below kBT , diffusion of adsorbates parallel to the surface can commence and the adsorption is described by an ideal 2D gas (Sprowl et al., 2016).”

The interaction between the adsorbate and the adsorbent is different for the different models. Surface coverage will not define which model to use. We wanted to point out the fact that mathematically the 2D ideal gas has no limit on surface coverage since no maximum site number is implemented. Though, coverages above 10^{14} cm^{-2} are likely not physically reasonable since those would go beyond a monolayer. As mentioned on line 235, this approach is conceptually similar to the 3D ideal gas that, by definition, does not have a limit of the applied gas species concentration (or pressure) below which the assumption of ideality is correct.

We will change the sentence on line 235:

“To remain within physically reasonable bounds, all equations in conjunction with the 2D ideal gas model relate to conditions of small surface coverages only.”

To

“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} .”

285: *“Supplement Eq. (119ff.)” is likely a broken equation number link?*

We wanted to point the reader to the derivations of the free energy, enthalpy, and entropy used in Eq. 35. We change

“Supplement Eq. (119ff.)” to “Supplement Eqs. (119-121)”.

765 & 792 & 808: *Can these derivations be moved to the SI?*

Regarding derivations following line 779:

We would prefer to leave those derivations in this section to keep consistency in section 6. Its structure is calculating the equilibrium first for 2D ideal gas based on concentrations followed by activities. Then (line 764), this derivation is repeated for the 2D ideal lattice gas. First on the basis of concentrations and then on the basis of activities. Leaving out the derivations on line 765 would interrupt the line of thought for the entire section.

However, we will shorten the derivations on lines 792 and 808 by not showing all necessary intermediate steps. The full derivations have been moved to the supplement section 6 after the last derivation Eq. (235).

Fig 2: extend axes to zero

Figure 2 will be corrected as suggested.

Fig 5. I recommend labelling each line with its E_{0des} value

Figure 5 will be corrected as suggested.

Fig. 15. I recommend reducing the number of lines plotted and labelling each line with its desorption rate

Figure 15 will be corrected as suggested.