Referee’s Report on
Submission to ACP by Knopf & Ammann

This is an excellent paper that is certainly important enough to be published in this journal. It provides a good review of statistical thermodynamic treatments of adsorption and desorption equilibria and transition-state theory rates, using an internally self-consistent set of equations (with probably over 100 equations here) and symbology. It emphasizes the importance of using self-consistent approximations and well-defined standard state concentrations if one wants to get accurate numbers from experiments. These issues are of very high importance in atmospheric chemistry research, so it seems a timely and worthy contribution to present to this audience.

However, I suggest several moderately important revisions:

1. The title is “Classical and statistical thermodynamic treatment of adsorption and desorption kinetics and rates”, but I think it would define the topics covered better if it were instead: “Statistical thermodynamic treatment of adsorption and desorption equilibria and transition-state theory rates”. The authors might consider a title change.

2. Although they have 22 citations to Campbell et al., 2016 in the main text, these citations of that paper are all referring to rather specific points. The fact is, most of the overall treatment here, including the symbology, is very, very similar to or identical to that by Campbell et al., 2016. I think they also should state that broad similarity somewhere very early in this paper. Even more importantly, the derivations occupy 235 Equations in the Supplementary Information (SI), and a huge fraction of these are nearly identical to the equations from Campbell et al., 2016. Yet this SI only cites that paper by Campbell et al. one time, and that citation is made when referring to a single, very specific equation (number (56)). The SI really needs to start with a statement about the very broad similarity between these derivations and their symbology and those presented by Campbell et al..
Eq. (54) in the SI (and probably others) also needs a very specific citation to Campbell et al., since it uses an equation for the configurational entropy derived in the Appendix of Campbell et al. that was a very lengthy derivation, and original.

3. The main part that is significantly different from Campbell et al. is the inclusion here of a real barrier to adsorption in treating adsorption / desorption rates. However, the premise of that addition is not written properly, and will confuse the readers. This appears at the start of Section S2.4, where it says: “The TS for desorption is assumed to exist at some fixed distance from the surface but within a very thin layer of thickness d. The molecules do not have any interactions with the surface, but it is activated to an energy level according to the barrier height above the gas phase reference.” This is physically impossible. The molecule cannot both have no interactions with the surface and at the same location be higher in potential energy than the gas

phase by the barrier height shown in Fig. 1. A better way to imagine this, that would result in the same equations as derived here, would be to say instead: "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 (at the barrier of energy E^0_b per mole) due to its interaction with the surface (e.g., due to Pauli repulsion). We further assume for simplicity that, at this TS distance from the surface, or barrier, the potential energy does not depend on the rotational orientation of the molecule nor on the location parallel to the surface (i.e., the barrier is independent of (x,y) coordinates)." This same problem occurs in the main text in several places, most importantly just after Eq. (7).

4. In my opinion, it will be very confusing to the readers to use of the symbol q to mean potential energy in Fig. 1 and all its associated text in the main paper and SI, because the symbol q is used extensively later for the molecular partition function. Please change this potential energy symbol to something else like $\in$ or V instead.

5. In several places, the paper used the words "inner energy" for what most textbooks call "internal energy". I suggest to use "internal energy" instead. I never heard of "inner energy" before.

6. Prefactors for desorption are mentioned in several places. In at least one of these places (e.g., at the very end of Section 4.1), the authors should mention that Campbell has published a paper that shows some very important experimental trends in prefactors for desorption and their statistical thermodynamic explanation (Kinetic Prefactors of Reactions on Solid Surfaces, C. T. Campbell, L. Árnadóttir and J. R. V. Sellers, *Z. Physikalische Chemie* (in special issue celebrating Eyring / Polanyi paper introducing transition states) 227, 1435–1454 (2013)).

7. The paper by Campbell et al., 2016 mentioned above has an important paragraph that starts with:

"It is clear from the derivation above that this $1/(1-\theta)$ factor in the desorption rate for an ideal 2D lattice gas applies as long as the sticking probability remains unity. The sticking probability, $P_s(\theta)$, in general varies with coverage, but is well known to remain near unity for many adsorbates up to >90% of saturation coverage because of a Kisliuk-type precursor mechanism for adsorption (whereby the transiently adsorbed precursor could easily visit 100 or even 1000 sites before it desorbs). …"

The authors need to read this paragraph carefully and recognize the importance of Kisliuk-type sticking probabilities somewhere in this paper by somehow summarizing the effects discussed here. The coverage dependence of the sticking probability has important consequences for the desorption rate equation, as pointed out initially by John Tully, I guess. Kisliuk-type sticking is more often observed than straight Langmuir type sticking.

8. On page 3 it says: "… 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). This new adsorbate model (Sprowl et al., 2016) is not discussed in this study. …" The authors should at least point out here or late in their paper that this paper by Sprowl et al. shows that, in reality, there is a pretty sharp transition between the two extreme models studied here (i.e., the ideal 2D gas and the ideal lattice gas models) when the activation barrier for adsorbate diffusion parallel to the surface goes from just below to just above kT. It is important for readers to recognize that it is this diffusion barrier (relative to kT) that determines which extreme model is most appropriate to use.