We thank the referee for carefully evaluating our manuscript. Below we provide point-by-point responses, where red-colored text indicates our response.

Referee #2:

The authors build up on (their) previous work (Knopf and Ammann, 2021), explaining desorption lifetime and desorption energy and its importance for a molecular based approach for describing trace gas uptake and surface reaction on aerosol particles. Here, they provide an overview over the different experimental and modeling approaches to determine desorption energies. In addition, they survey and compile an impressive list of desorption energies and use these data and calculations to come up with a parametrization based on compound mass, polarizability and O:C ratio.

The manuscript is well written and it will certainly serve the community by providing not only the compilation of desorption energies but also illustrating its relevance for a molecular understanding of reactive uptake.

We thank the referee for their review and this positive note.

I would like the authors to consider a few comments below for the revision of the manuscript.

(1) As a non-specialist in this particular field, after reading the introduction, I am still struggling to understand the role of the surface accommodation coefficient, αS. As the (the authors) Knopf and Amman (2021) write: “In the context of atmospheric sciences, adsorption is commonly described by the surface accommodation coefficient, which is the probability that a molecule undergoing a gas kinetic collision is adsorbed at the surface”. Hence, in the case of a “simple” physisorption, this probability need to somehow relate to the desorption lifetime as the authors explain starting in line 87: “In case of physisorption, Edes is equal to the negative value of the enthalpy of adsorption with a correction for the change in degree of freedom between gas and adsorbed phase”. I certainly will benefit from an expanded explanation on why we cannot then set the accommodation coefficient equal to one very generally, once we base the desorption process on the Frenkel equation (eq. 1). For example in equations 3, and 4 there remains this molecular interpretation of the terms Γs and Γsb with the first-order desorption rate based on the desorption energy, but there is also this unexplained (in terms of molecular properties) surface accommodation term. Furthermore, what follows for the surface accommodation coefficient when we assume reversible adsorption (line 252)?

There might be some misunderstanding in interpreting the phenomenon of adsorption and the kinetic treatment of desorption. The surface accommodation coefficient, α_s, is the key parameter to describe the adsorption process, and in terms of definition and value is independent of the formulation of the desorption process via the Frenkel equation (characteristic for activated desorption). The adsorption rate (and thus , α_s) does also not contain the binding energy of the adsorbed state that is contained in the Frenkel equation.

Γ_s and Γ_{sb} express the normalized loss rates due to surface reaction and surface to bulk transfer, driven by k_s and k_{sb} (the rate coefficients of the corresponding elementary processes), respectively. The normalization with the gas kinetic collision rate has to account for the probability for a gas molecule colliding with the surface to be accommodated at the surface. Hence α_s, is present in equations (3) and (4).

In (Knopf and Ammann, 2021) we derive the adsorption rate from transition state theory similar to that for desorption. By relating it to the Hertz-Knudsen equation, we then obtain the corresponding expressions for α_s, which is operationally defined by the ratio of the adsorption rate to the collision rate. It depends on the presence of an energy barrier (but not E_{des}^{0}, as mentioned above), the transmission coefficient (defining the probability with which an activated complex proceeds from the transition state to the adsorbed state), and the ratio of the partition functions of the transition state to those of the gas phase state (i.e., is the transition state more or less constrained than the gas phase state) (Eq. 129 in (Knopf and Ammann, 2021). Any of these parameters is typically not readily available independently in experiments, but eventually the overall α_s may be obtained from experiments (especially using molecular beam techniques). Even though α_s may often be close to 1, it may also be smaller.

In our derivations, we always assume reversible physisorption as a precursor to any further process including irreversible reactions – chemisorption would be expressed as a reaction following reversible physisorption as well.

We note that the statement (line 87) “In case of physisorption, E_{des}^{0} is equal to the negative value of the enthalpy of adsorption with a correction for the change in degree of freedom between gas and adsorbed phase” is not mentioned in connection with the adsorption rate but only with the desorption rate that contains E_{des}^{0} and this correction in the Arrhenius term.

The reviewer seems to refer to the coupling between adsorption and desorption under equilibrium conditions. Indeed, the adsorption equilibrium constant, i.e., the ratio of adsorption and desorption rates, could then, of course in principle, be related to the ratio of the accommodation coefficient and the desorption rate coefficient. This can indeed be used to obtain constraints on either of these parameters if the other two can be obtained from an experiment (Bartels-Rausch et al., 2005; Tabazadeh and Turco, 1993; Donaldson et al., 2012) and we have devoted a separate section in (Knopf and Ammann, 2021) on this topic. However, we prefer to not enter this topic as this manuscript focuses on the desorption rates. Though, we have made slight text changes throughout the manuscript to make above distinction between adsorption phenomena and desorption kinetics clearer.

(2) At the end of section 3.2. “Gas adsorption by solid surfaces” the authors correctly discuss that most often atmospheric particles may have a condensed aqueous solution on its surface. They also state that in these cases one should consider the uptake process as proceeding on liquid substrates. However, the high vapor pressure of the relevant liquids does not allow easily to measure desorption kinetics (line 542). The authors suggest to use nevertheless the same concept although they admit (line 563) here the hydrogen bonding network is of particular importance and this may depend on the solutes being present. May be the authors could come back to this problem in their conclusion section?

Thank you for pointing this out. Indeed, this lack of knowledge of desorption energies for liquids with high vapor pressure and in the presence of solutes in the bulk and at the interface should be listed as a further research need. We now added this need in our conclusion section:

- Desorption kinetic measurements involving liquids with high vapor pressure are needed. Furthermore, the role of solutes in aqueous solutions on the hydrogen bonding network and in turn on the desorption process is not well understood. For example, adsorbates with hydrophilic functional groups exert greater E_{des}^{0}. Systematic examination of desorption kinetics as a function of varying solute concentration and gas species $O{:}C$ and dipole moment are needed to improve our understanding of adsorption and desorption processes on liquid surfaces.

(3) Same section “Gas adsorption by ice”: I recommend to cite the review by Huthwelker et al. (2006) here for those who are interested in experimental techniques and available data and a discussion with a different focus.

Thank you for pointing out this review article (Huthwelker et al., 2006). It will be included.

(4) line 793 ff: I suggest to have similar figures for the different substrates (ice, water, aqueous, solids) like Fig.8 in the SI using the parametrization of eq. 16 to show that there are no significant physical state of substrate specific differences.

We have added a new supplemental figure that similar to Fig. 8 for solid, ice, and liquid substrates individually plotted:

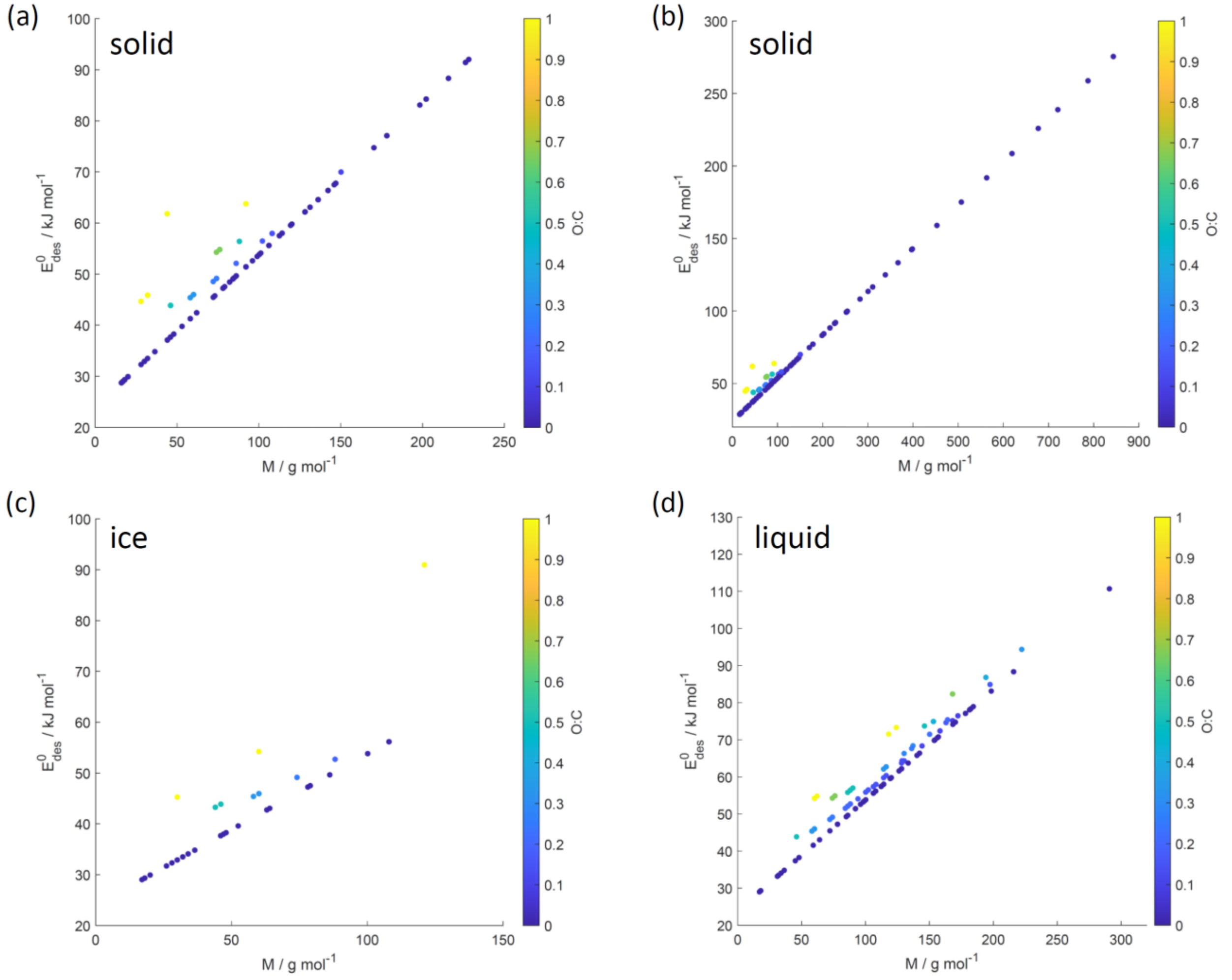

Figure S4. E^0_{des} values derived from the new parameterization (Eq. (16)) applying the training dataset of gas species with molar mass (M) and $O:C$, the latter coded as symbol color described by the color bar, similar to Fig. 8. Panels (a) and (b) show data for solid substrates where (a) is an enlarged view of (b). Panel (c) shows data for ice substrates and panel (d) represents the case of liquid substrates. Note that three gas species with $O:C$ > 1 (CO_2, formic acid, and peroxyacetyl nitrate) are included in these plots as having $O:C$ = 1 to allow for better visualization of entire data set.

We will add a reference to this figure in the main text:

"Figure S4 shows E^0_{des} values derived from the training data set separated by different substrate types corroborating the correlation displayed in Fig. 8."

(5) line 800 ff, Correlation desorption energy enthalpy of vaporization: Could it be that for the atmospherically very relevant liquid substrates, a parametrization based on this correlation including O:C (Fig. 11(c)) is as good as eq. (16) in particular for substances with O:C > 1? In this context: the statement in line 821 that Edes and ΔHsolv are better correlated than Edes and ΔHvap may be not true if using O:C for a parametrization as well.

For clarification purposes, we split our response in two parts:

i) The parameterization given by Eq. (16), i.e., E_{des}^{0} as a function of molar weight and $O{:}C$ is different from a correlation between E_{des}^{0} and the enthalpy of vaporization, ΔH_{vap} (Fig. 11c). We do not discuss $O{:}C$ values of substrates but only for gas species. We feel the reviewer meant that the correlation is better for gas species with larger $O{:}C$ ratios.

We provide a linear regression parameterization for E_{des}^{0} as a function of ΔH_{vap} and $O{:}C$. This results in:

$$E_{\mathrm{des}}^{0}\left(\Delta H_{\mathrm{vap}}, O{:}C\right) = 5.0711 + 0.8247\Delta H_{\mathrm{vap}} + 26.1822(O{:}C)$$

with an R^2 = 0.56 and RMSE = 13.0. Hence, the regression quality is similar to the parameterization given by Eq. (16).

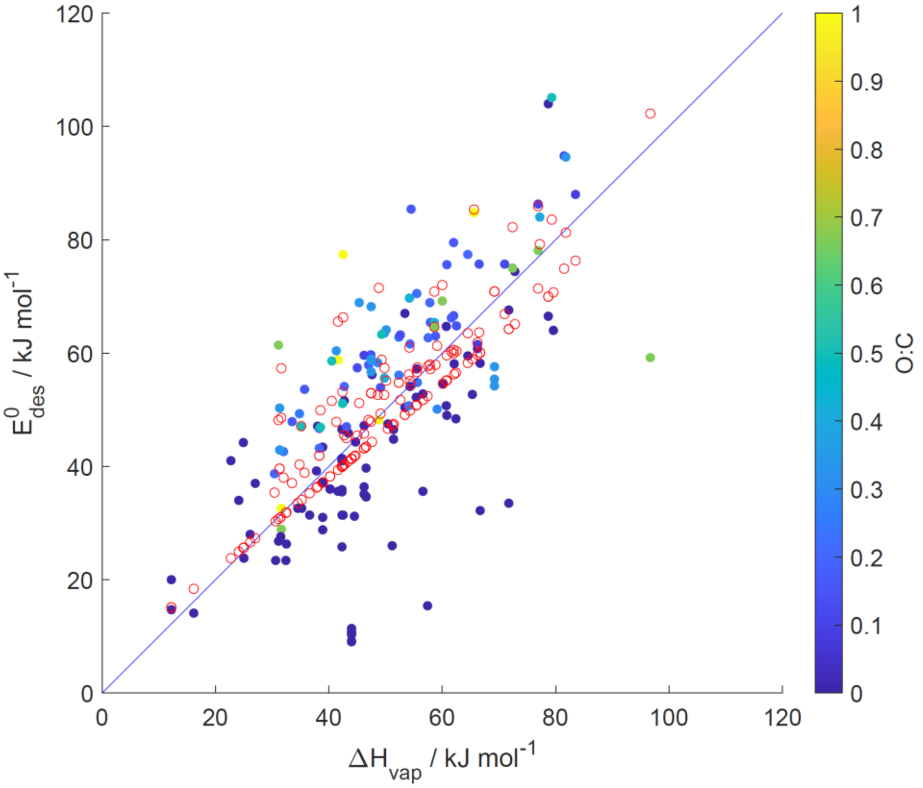

Figure S7. Same as Fig. 11c. Red open circles depict the linear regression model applying the training data set: $E_{\mathrm{des}}^{0}\left(\Delta H_{\mathrm{vap}}, O{:}C\right) = 5.0711 + 0.8247\Delta H_{\mathrm{vap}} + 26.1822(O{:}C)$ with an R^2 = 0.56 and RMSE = 13.0.

We will call out this figure:

“Figure S7 provides a linear regression model for the case of liquid substrates.”

ii) The statement on line 896 is indeed confusing, if one only looks at the liquid case. Originally this was meant to compare the E^0_{des} correlation with ΔH_{solv} to all cases of E^0_{des} correlation with ΔH_{vap}. This is misleading. We provide a linear regression parameterization for E^0_{des} a function of ΔH_{solv} and O:C. This results in

$$E^0_{\mathrm{des}}(\Delta H_{\mathrm{solv}}, O{:}C) = 16.5830 + 0.6923\Delta H_{\mathrm{solv}} + 9.6772(O{:}C)$$

with an $R^2 = 0.39$ and RMSE = 14.3. The lower R^2 value indicates that the linear regression using ΔH_{solv} results in a slightly less representative parameterization model compared to the case of using ΔH_{vap}.

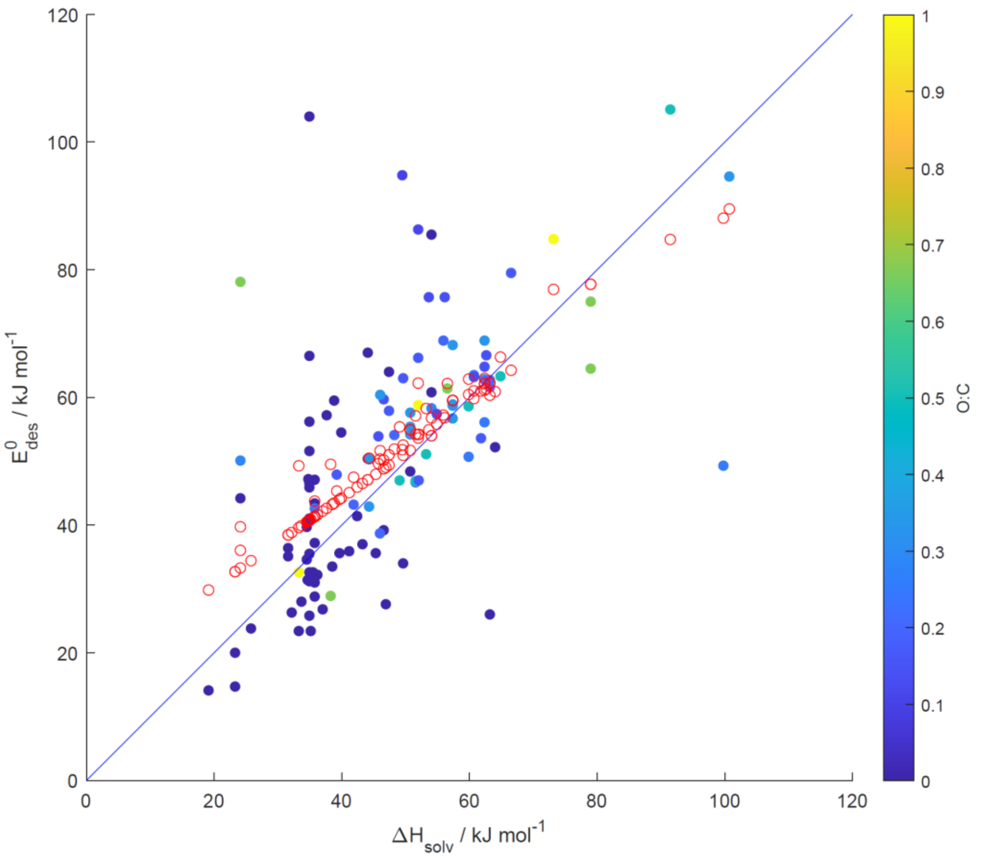

Figure S8. Same as Fig. 12. Red open circles depict the linear regression model applying the training data set: $E^0_{\mathrm{des}}(\Delta H_{\mathrm{solv}}, O{:}C) = 16.5830 + 0.6923\Delta H_{\mathrm{solv}} + 9.6772(O{:}C)$ with an $R^2 = 0.39$ and RMSE = 14.3.

We change the statement to:

"Thus, E^0_{des} and ΔH_{solv} values are much closer correlated than E^0_{des} and ΔH_{vap} (Fig. 11)."

To

“In the case of liquid substrates, the correlation between E_{des}^{0} and ΔH_{solv} is comparable to that observed between E_{des}^{0} and ΔH_{vap} (Fig. 11c). Figure S8 provides a linear regression model for the data shown in Fig. 12.”

(6) line 968 ff: “glass transition”: I do not feel that the correlation between glass transition temperature and Edes goes much beyond that both correlate with molecular mass. I think this section deviates very much from the more solid molecular picture of the other sections and should be omitted.

Referee #1 voiced a similar criticism. However, as in response to Referee #1, we feel that our empirical observation of the positive correlation between E_{des}^{0} and T_g is worthwhile reporting. We also would like to clarify that in our discussion we do not imply a causal relationship between E_{des}^{0} and T_g but wanted to point out this observational evidence.

There is a reasonable physical argument on the positive correlation between E_{des}^{0} and T_g. Based on Eq. (16), E_{des} should positively depend on molar mass and $O:C$ ratio. Shiraiwa *et al.* (2017) has shown that T_g can also be parameterized as a function of molar mass and $O:C$ ratio. As both E_{des}^{0} and T_g depend linearly on the same two molecular properties, it is sensible to expect a positive correlation between E_{des}^{0} and T_g. As shown in Fig. 15, we observe the expected trend that higher molar mass leads to higher E_{des}^{0} and T_g, while T_g is modulated stronger by the $O:C$ ratio compared to E_{des}^{0}. While this analysis serves as empirical and observational evidence, the theoretical and physical basis is yet to be established. Hence we feel that the observed correlation is still meaningful for advancing our understanding of interfacial processes.

For these reasons, we would like to keep this discussion in the manuscript. However, to give it less emphasis, we move this section to the Appendix.

We have moved the section “Glass transition” to Appendix A1 (line 1178). In addition, we have made the following changes:

In the “Summary and Conclusions” section we refer to the new Appendix section:

“Furthermore, in the Appendix A1 we outline the correlation of glass transition points with E_{des}^{0} which adds another layer of complexity when modeling multiphase chemical reactions (through the potential of viscous phase states).”

References:

Huthwelker, T, Ammann, M. and Peter, T.: The Uptake of Acidic Gases on Ice, Chem. Rev., 106, 1375-1444, 2006

Knopf, D. and Ammann, M.: Technical note: Adsorption and desorption equilibria from statistical thermodynamics and rates from transition state theory, Atmos. Chem. Phys., 21, 15725–15753, 2021

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Shiraiwa, M., Li, Y., Tsimpidi, A. P., Karydis, V. A., Berkemeier, T., Pandis, S. N., Lelieveld, J., Koop, T., and Pöschl, U.: Global distribution of particle phase state in atmospheric secondary organic aerosols, Nat. Commun., 8, 15002, 10.1038/ncomms15002, 2017.

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.