Review, Opinion paper by Abbatt and Ravishankara , ’Opinion: Atmospheric Multiphase Chemistry: Past, Present, and Future’

General

This is an ‘Opinion’ contribution to ACPD/ ACP and, as such, hard to review. More than in a regular paper, an ‘Opinion’ piece must be intended to be subjective and focus according to what the authors rate important. However, a review could assist a bit to at least a bit widen the scope and make the contribution a bit more equilibrated between different work directions which might have contributed to the topic of the contribution. There is considerable confusion with the use of ‘multiphase’. It would be great to clarify that.

All in all I would like to suggest to clear the scope and meaning of ‘multiphase’ and, possibly address some of the details below.

Details

Title / Intro: I was a quite surprised when reading the contribution, whether its topic really “Atmospheric multiphase chemistry’ or wouldn’t ‘Atmospheric multiphase and heterogeneous chemistry’ possibly be a better fit ? The authors explain they naming in the introduction and it seems to me that their new suggestion is retiring the term “heterogeneous chemistry”. I feel it woul be too much do do this. The authors now change from the nomenclature of Ravishankara, A.R.. (1997). Heterogeneous and Multiphase Chemistry in the Troposphere. Science. 276. 1058-1065. 10.1126/science.276.5315.1058 and update in such a way that ‘multiphase chemistry’ should now include all processes from 2D- interfacial interactions to classical volume reactions. This is understandable as reacto-diffusive lengths can continuously change and there are not only the water droplet and the solid/air interface as extreme cases. However, I would like to suggest the authors offer more explanations for this use of nomenclature which is different from the common use of ‘multiphase’ not only in the’ late 20th century’ but also today.

Line 45ff: Do these reviews only cover what was called ‘heterogeneous chemistry’ or do they also cover ‘multiphase multiphase’ ? I feel some reviews should be amended here.

Line 48ff: I do not feel the discussion of the ‘three-legged stool’ really fits here and would suggest to skip this section. Interplay of lab and field measurements with modeling is a topic different from multiphase chemistry. I would also skip the corresponding remark in the abstract, line 16/17. The topic has been well addressed 10 aears ago in the cited Abbatt et al. (2014).

Line 64ff: Now the term ‘multiphase chemistry’ is being discussed. I feel the text explains what it can be but there is no sharp and applicable definition. What about these cases:

(a) A reaction of two molecules at a surface A(surf) + B(surf) → Products
(b) A reaction ‘at the end of the 20th century’ clearly addressed as a heterogeneous reaction A(surf) + B(g) → Products

I am wondering if the authors would like to see that the terms ‘heterogeneous reaction’ or ‘heterogeneous process’ are to be retired ?

Also, if the new meaning of ‘multiphase’ is now mainly, and ‘in the language of the late 20th century’, ‘heterogeneous’ – what should those groups do which say they study multiphase chemistry ? Change their laboratories ? This is kind of funny.

In summary, under the present title nobody would expect what is treated in the opinion piece. If ‘multiphase’ is really intended to be treated, add bulk processes. If only heterogeneous processes are to be treated, make it clear from the start. While it is true that the reacti-diffusive length coveres a wide range of distances, it appears useful to discuss its limiting cases, maybe you want to address them as Multiphase process limiting case I = interfacial process and Multiphase process limiting case II = bulk process.

Line 97: ‘Thus,…’ – No, that is too much said and an incorrect way of using the term ‘catalysing’. Catalysing would mean action through the involvement of a catalyst, cf. https://goldbook.iupac.org/terms/view/C00876. Maybe just exchange ‘catalysing’ by ‘… can lead to increased reaction rates through concentration enhancements’.

Line 114: Is there examples of a solvent shell in the gas phase ? If no, skip ‘(generally)’

Lines 107 -114: There is more distinguishing features. The lower effective quantum yields for photolysis processes in solution against the gas phase quantum yields. There is species which do not exist in the gas phase and can get involved in chemical reactions, think of metal ions. On aspect full ymissing in recent work: The role and impact of acidity, Pye et al. (2020), Tilgner et al.(2021).

Line 146: Maybe not only ‘cloud water’ chemistry but ‘aqueous cloud and aerosol chemistry’. I am missing nitrate photolysis for renoxification, role of TMI, and these early studies could be put in perspective with the more recent ones, some of them with severe problems regarding plausible quantum yields.

Line 159 & 160: I don’t think this is really true. Both aspects are still treated a lot.

Line 167 : A few examples for particle chemistry would fit well here.

Line 176 ff: Here would be a good place to add work on bulk-phase organic accretion reactions

Line 193: Put earlier and more recent nitrate photolysis work in perspective, see above.

Line 248/249: I would suggest to add Sasho Gligorovski’s work here.

Line 338: Here, it could be mentioned that photosensitizer chemistry has in fact been suggested for surface waters early, Canonica, S.; Hoigné, J. (1995)

Line 343/344: There heve been studies where it is shown that the observed effects have to do with extraordinary strong UV radiation and might become negligible under natural UV irridiation. Cf. Fankhauser et al., *ACS Earth and Space Chemistry* 2019, 1485-1491

Line 354: What about development in laboratory techniques ?

Line 373/374: Modern multiphase chemistry modelling can predict the composition of that filter sample by travelling box approaches. What about that ? This part with observational capabilities could be improved considering multiphase modelling.

Line 383 In this part, there are many specific examples but the modelling part is of a quite limited scope. It would be good to strengthen and also link to the preceeding observational capabilities section. Maybe these examples can be kept and discussed but where is a a section dealing with mechanism development, mechanism reduction, automated mechanism generation ? Assess the state of models. How to improve ? Do we have enough computer capacity - Moore's law still holds. And, then, for what ?

Maybe a few more thoughts: There is again and again re-investigation of certain issues which are well implemented into leading models and everybody could look up what certain processes could do – look at S(VI) production in China – how many claims to explain did we see in the last decade ? I 'd say, 100. Fm NO2 to TMI, the uncatalyzed S(IV) oxidation, photosensitization, nitrate photolysis with artificial enhancement - you can find everything. But: problem solved ? No, they are all not doing the job.

But there is exciting new fields (besides those you mention) : Continental halogen multiphase chemistry. Release of hydrated formaldehyde into the gas phase fm aqueous systems. Hydroperoxide and peroxyl radical chemistry. Role of TMI. Coupling of cloud process to aerosol composition (cf. sulfate as a role model !) Accretion product formation in gas and particle phase. Is there interesting NOx(aq) chemistry ? Condensed phase photochemistry.

There is stuff where we must get better: DMS oxidation, aromatics oxidation, multiphase mechanism kernels beyond C4. Having an up-to-date versatile gas-phase backbone mechanism to which everything couples. Have multiphase chemistry mechanisms with interfacial and bulk parts coupled correctly.