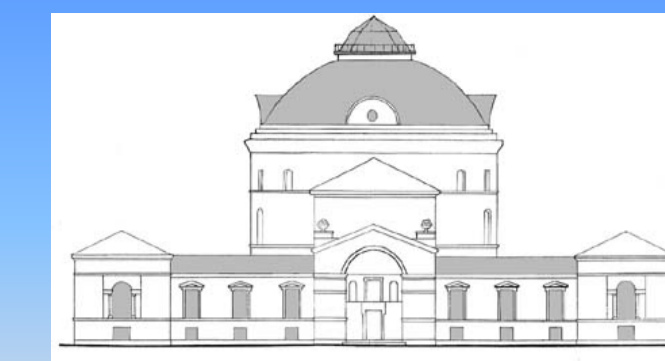# Iron catalysis of SO$_2$ oxidation in cloud droplets
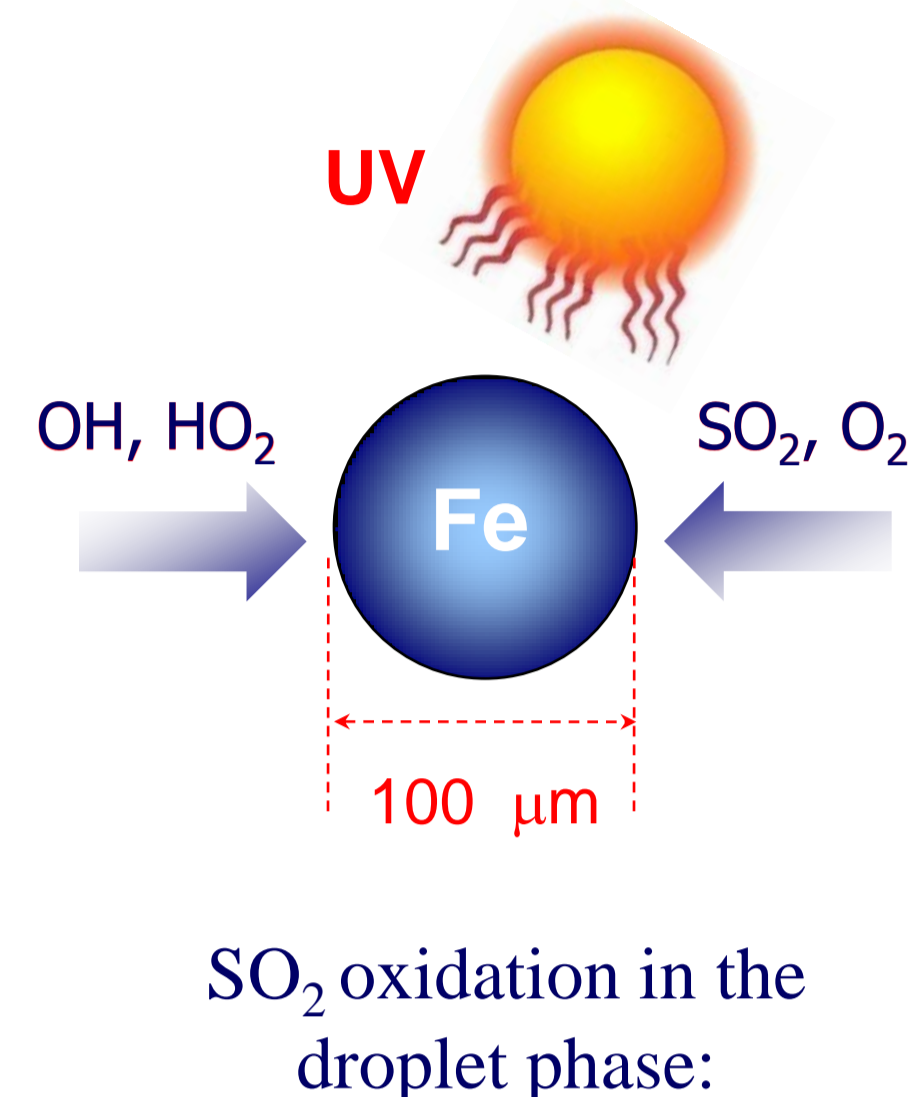
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Institute for energy problems of chemical physics RAS. IEPCP RAS, 119334, Moscow, Leninskii avenue 38 bldg. 2,Russia   **IEPCP RAS**
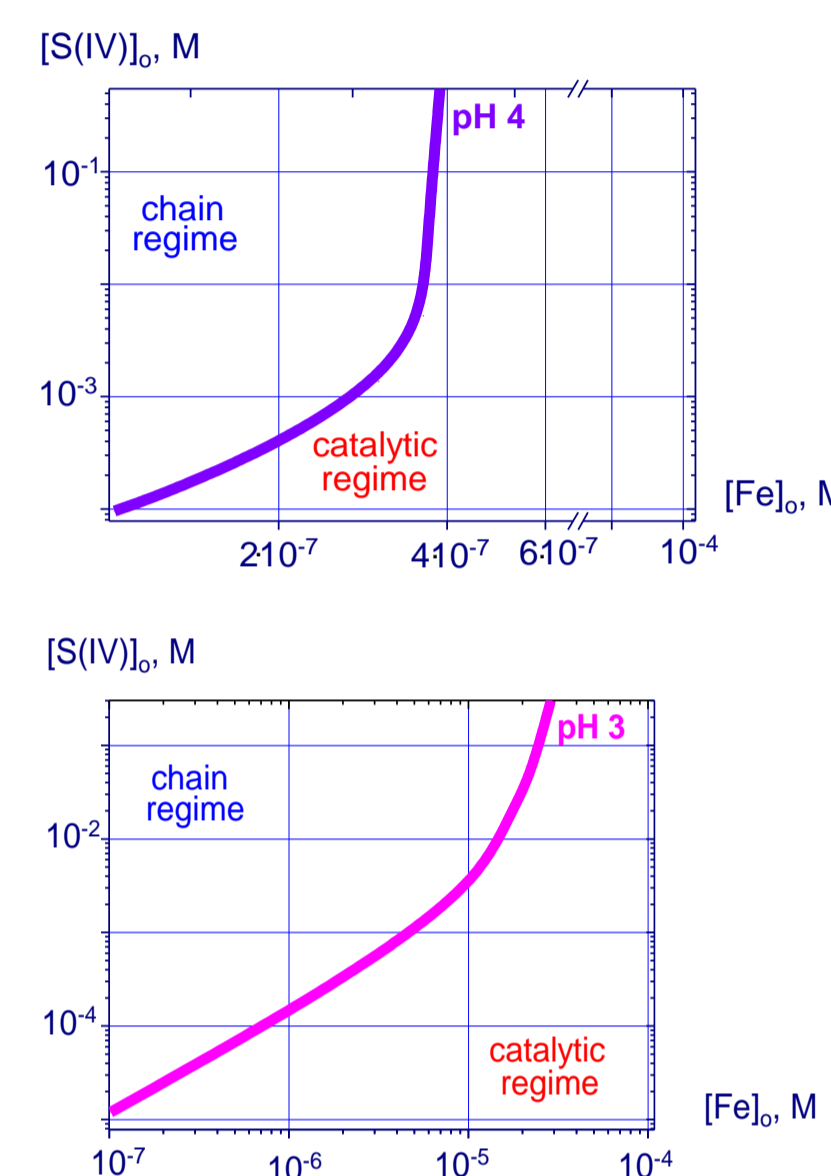
Abstract

The observations of Fe(II) in cloud water and, in particular, its ratio to the total iron content in radiation fog and in orographic clouds were published to signify the support of potential importance of the catalytic pathway the SO$_2$ removal from the gas.

UV

OH, HO$_2$ Fe   SO$_2$, O$_2$

100 μm

SO$_2$ oxidation in the droplet phase:

Introduction

What can happen to solution of a sulfite saturated by oxygen if a small amount of Fe(III/II) is introduced? The normally slow autoxidation is specifically accelerated by these ions, see Fig (*Brandt & van Eldik*, 1995).

time, min

uncatalyzed

$\frac{[S(IV)]}{[S(IV)]} \gg 1$ catalyzed

time, min

In general, the kinetics of the reaction is characterized by bad a reproducibility. The reaction orders vary unpredictably between zero – second order both in sulfite and in iron. None of the data support the half-order dependence on iron ion concentration expected for radical-radical recombination (SO$_5^-$ + SO$_5^-$), see generalized mechanism:

Generalized mechanism

SO$_4^{2-}$ SO$_4^-$
HSO$_5^-$ M^{3+}—M^{2+} SO$_5^-$
SO$_3^-$ HSO$_5$
HSO$_3^-$
S$_2$O$_6^-$ O$_2$ SO$_5^-$
S$_2$O$_6^{2-}$

The "anomalies" receive a naturally explanation assuming a conjugation between the branching reaction, HSO$_5^-$ + Fe^{2+} and those producing HSO$_5^-$ in the chain-carriers cycle SO$_5^-$+ HSO$_3^-$ and the metal cycle SO$_5^-$ + Fe^{2+}. Being coupled these steps are able to accelerate or to slow down the production of chain-carriers at certain concentration conditions known as the chain and catalytic regimes of the reaction:

$$FeOH^{2+} + HSO_3^- \rightarrow Fe^{2+} + SO_3^- + H_2O$$
$$HSO_5^- + Fe^{2+} \rightarrow FeOH^{2+} + SO_4^-$$
$$HSO_5^- + HSO_3^- \rightarrow H_2O + SO_3^- + SO_4^-$$

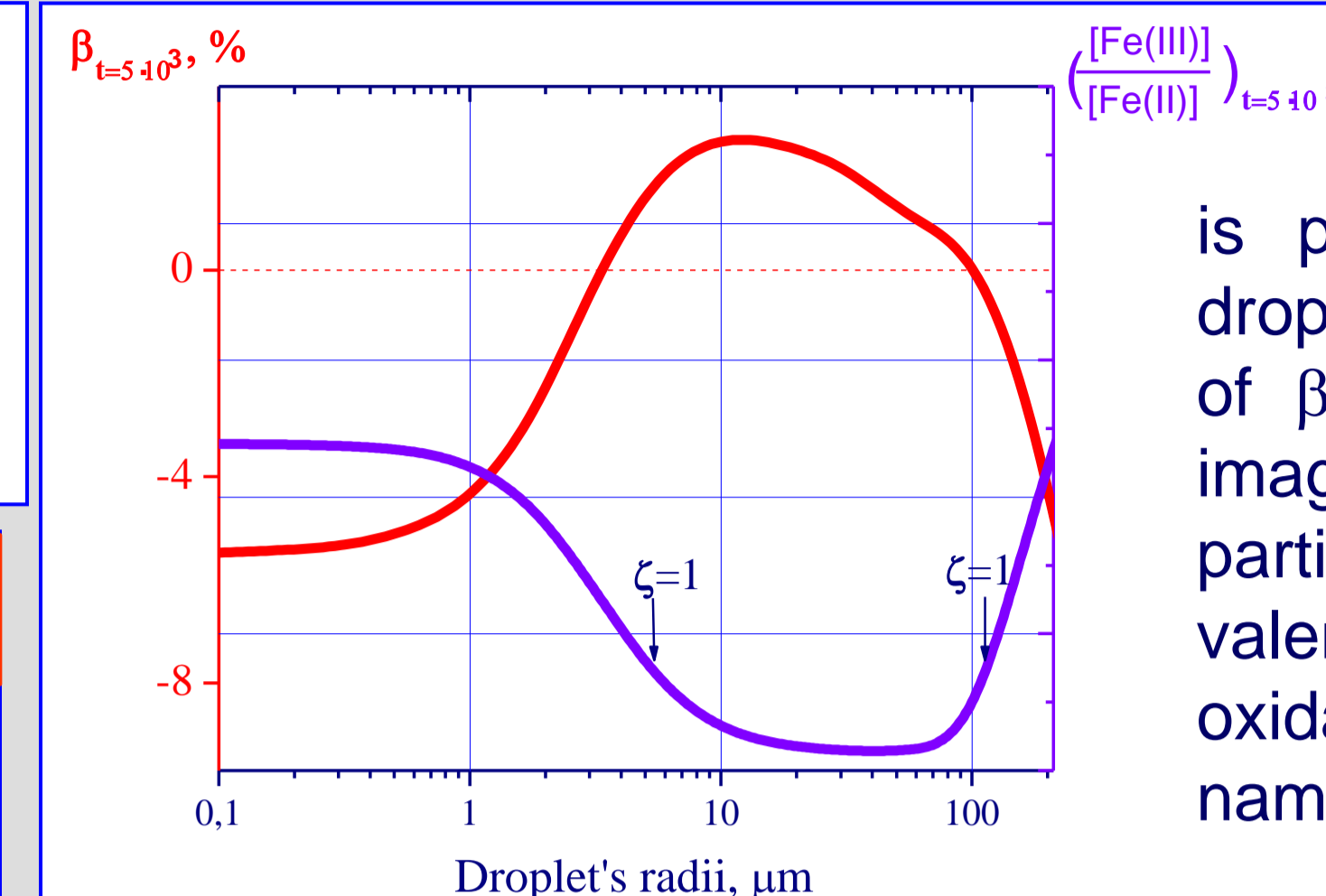**Thus two new active species are formed for the one that is consumed.**

Perhaps most importantly is also that the radical-radical recombination SO$_5^-$ + SO$_5^-$ represents a gross but not a net loss of the chain-carriers, because nearly all of them are reformed through the branching step: HSO$_5^-$ + Fe(II) → FeOH^{2+} + H$_2$O + SO$_4^-$ and SO$_4^-$ + HSO$_3^-$ → SO$_5^-$.

Chain and catalytic regimes delimitation

[S(IV)]$_o$, M

pH 4

chain regime

catalytic regime

[Fe]$_o$, M

[S(IV)]$_o$, M

pH 3

chain regime

catalytic regime

[Fe]$_o$, M

The calculated curves depict the sulfite-iron content boundaries along which [Fe(III)]/[Fe(II)] = 1. Above the curves ferrous ions dominate and chain regime dominates. The lower pH the wider the area in which chain regime dominates, see Figs. *Yermakov & Purmal*, 2003

Atmospheric implications

The drop size effect on the rate of sulfur dioxide oxidation in tropospheric clouds is analyzed within a chemical gas-aqueous phases box model of the convective cloud; **Chem_WG** (*Yermakov & Larin*, 2003). The model includes: 34 components (54 chemical & photochemical reactions) in the gas-phase 57 components (121 chemical & photochemical reactions) in the aqueous-phase.

Conditions: daytime, [SO$_2$] = 3.5 ppbV, $L = 10^{-6}$, [Fe]$_o$ = 10^{-7} M.

[S(IV)]$_{t=0}$, cm^{-3}

[S(IV)]$_{Fe}$, cm^{-3}

$P_{H_2O_2}/RT$

10^{3}s

5·10^3 s

Droplet's radii, mm

The process has a rapid and a slow mode, see Fig. As the droplet's size grows, the difference between the rapid and slow modes becomes less. The rapid mode reflects the dynamics of hydrogen peroxide transport from the gas phase followed by the liquid-phase reaction H$_2$O$_{2(aq)}$ + HSO$_{3(aq)}^-$. At this time point, nearly all of the gases hydrogen peroxide is exhausted (initial content 1 ppb, see Fig.).

The effect of iron becomes pronounced in the slow mode. As a measure of the effect, the quotient $\beta_{t=5·10^3} = ([S(IV)]_{Fe} - [S(IV)])/[S(IV)]_{Fe}$

$\beta_{t=5·10^3}$, %

$\left(\frac{[Fe(III)]}{[Fe(II)]}\right)_{t=5·10^3}$
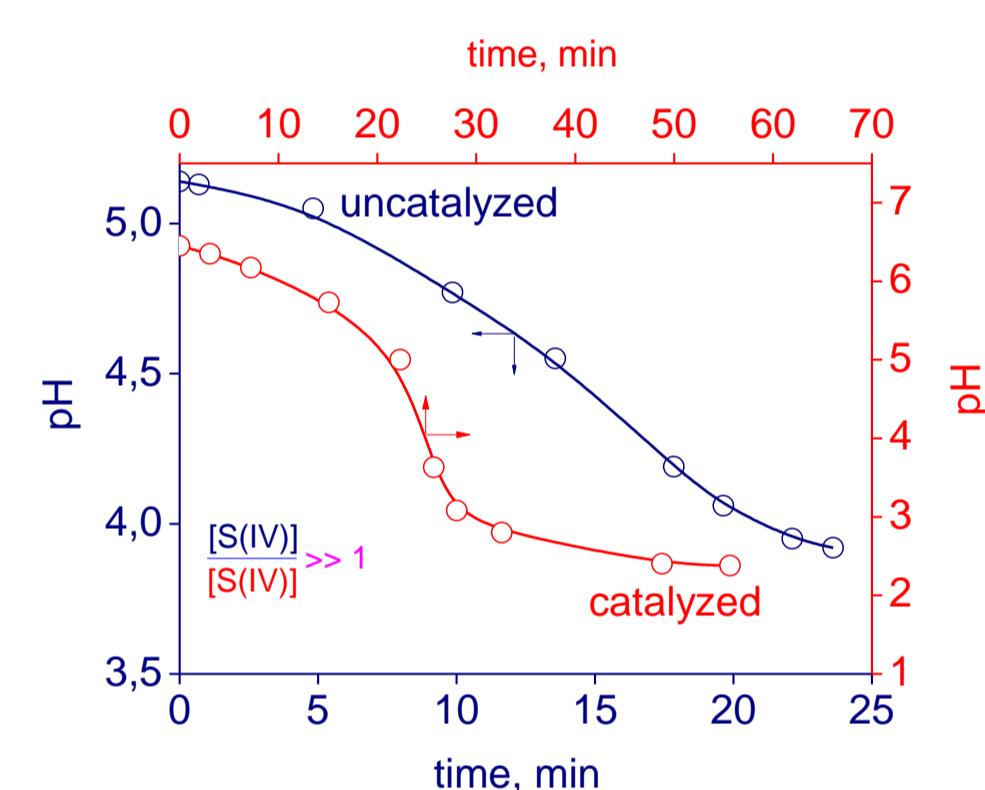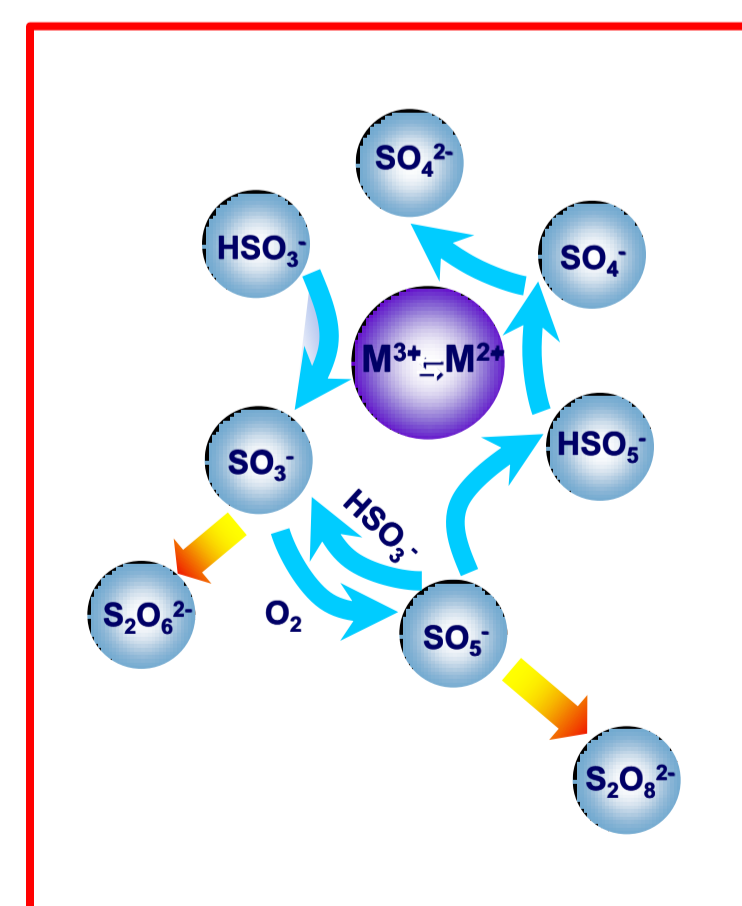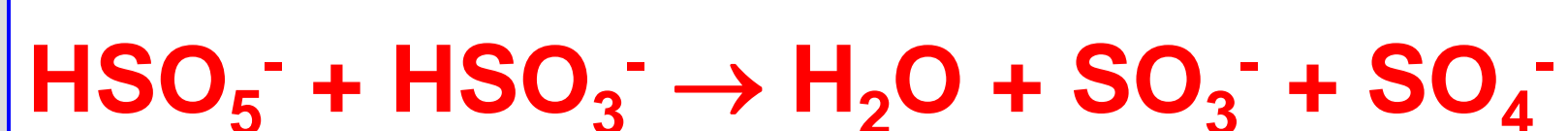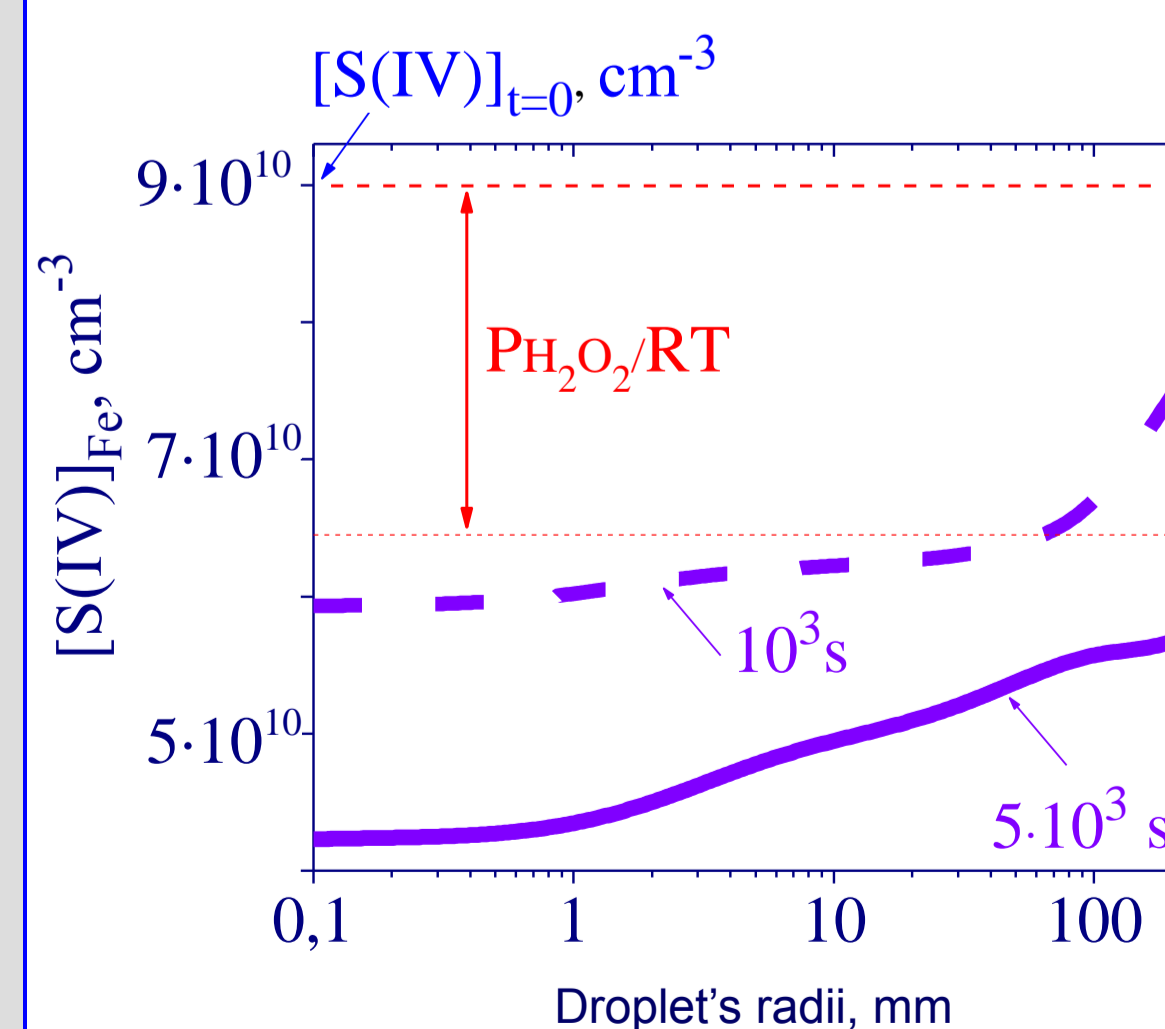
ζ=1   ζ=1

Droplet's radii, μm

is plotted as a function of droplet size, see Fig. The plot of β is similar to the mirror image of the curve showing a partitioning of iron between its valence state during sulfite oxidation in the atmosphere, namely ζ = [Fe(III)]/[Fe(II)],

For smallest of the droplets $\beta_{t=5·10^3} \approx$ - 6%, see Fig. This is does not imply that the catalytic activity of metal ions is low indeed. In the droplets the HO$_2$ radicals coming from the gas are scavenged by the ferric ions. As a sequence the recombination HO$_{2(aq)}$ + O$_{2(aq)}^-$ → H$_2$O$_{2(aq)}$ is suppressed in turn slow down the reaction H$_2$O$_{2(aq)}$ + HSO$_{3(aq)}^-$ which plays key role in the absence of metal ions.

Next the catalytic effect depends on the droplet's size. The catalytic oxidation of SO$_2$ is faster ($\beta_{t=5·10^3} < 0$) than the non catalytic pathway (if no iron) only in the droplets in which the dominant iron form is Fe(III) i.e. for small and large droplets, see violet curve in Fig. In the former, for instance, the iron ions accelerate the liquid-phase sulfite oxidation due the following steps: HSO$_5^-$ + Fe^{2+} → SO$_4^-$) and then SO$_{4(aq)}^-$ + HSO$_{3(aq)}^-$. This reactions provide SO$_2$ removal with a rate exceeding those that provide HO$_2$ radicals uptake from the gas. The calculated net effect of the catalyst is thus a sum of the cited "negative" and the "positive" impacts of the iron.

Conclusions

A fairly coherent picture emerges when existing data on the kinetics of iron-catalyzed sulfite oxidation are compared with those predicted on the basis of a concept about a conjugation between the branching reaction, HSO$_5^-$ + Fe^{2+} and those producing HSO$_5^-$ in the chain-carriers and the metal cycle. Size effect of iron ions activity as a catalyst in cloud droplets is revealed. The smallest the droplets the higher catalyst activity. The driving force of the catalysis is a conjugation between branching reaction and fast reduction of ferric ions by incoming HO$_2$/O$_2^-$ radicals.

Literature

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