Supplementary Information for

A Comprehensive Observational Based Multiphase Chemical Model Analysis of the Sulfur Dioxide Oxidations in both Summer and Winter

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Text S1. Activity coefficients of main reactants in the PKU-MARK model

The properties of electrolytes play an important role in the kinetic salt effect in the aqueous phase reaction. Atmospheric heterogeneous reactions occurring in aerosol deliquescent particles are characterized by high ionic strength ($I_s$). In these multicomponent mixture, reaction rates should be replaced by the activity coefficient, which representing the thermodynamic non-ideality caused by all-molecular interactions (Rusumdar et al., 2016; Rusumdar et al., 2020). Suitable multiphase chemistry models should apply activity coefficients instead of reaction rate constants in non-ideal solution. Heterogeneous processed in clouds and haze may be considered as occurring in dilute electrolytes and there is no need to consider the influence of ionic strength, this is not the case for high ionic strength deliquescent particles. Based on the measurement of ambient aerosol deliquescent particles (Herrmann et al., 2015), in marine areas, the ionic strength is about 6 M and in urban environments can reach about 8-18 M. Fountoukis and Nenes using the ISORROPIA–II model predicted high levels of ionic strength ranging between 13 and 43 M during the severe Beijing Haze (Fountoukis and Nenes, 2007a). In some extreme cases, the ionic strength of aerosol deliquescent particles can even reach 100 M (Cheng et al., 2016a). In two field campaign mentioned in this study, the mean value of ionic strength is 56.55 ± 39.83 M (±1σ) in winter and 24.26 ± 13.3 M (±1σ) in summer in haze periods (PM$_{2.5}$>75μg/m$^3$), and in extremely situation, 175.45 M in winter and 96.41 M in summer. In these cases, large errors can be introduced in the model calculation without considering the influence of ionic strength on aqueous phase reaction rate and heterogeneous mass transport.

Several studies are developed to evaluate the effects of ionic strength on the activity of aqueous phase ions and organic matters (Pitzer, 1991; Li et al., 1994; Polka et al., 1994; Ming and Russell, 2002; Raatikainen and Laaksonen, 2005; Clegg et al., 2008; Zuend et al., 2008; Zuend et al., 2011), and during the latest year considerable effort has been devoted to developing kinetic model frameworks for the modelling of processes in multicomponent atmospheric particles, which include both a detailed description of organic and inorganic multiphase chemistry as well as detailed thermodynamic comprehensions of its non-ideal behavior (Rusumdar et al., 2016). In this study, the activity coefficients of TMI were calculated by the Extended Debye–Hückel equation (Ross and Noone, 1991; Linder and Murray, 1982; Kontogeorgis et al., 2018). Other ions and organic oxalic acid and its complexes used the typical values predicted by AIOMFAC model by Rusumdar (Rusumdar et al., 2020). As for neutral solutes which activity coefficients are not corrected in AIOMFAC model, such as O$_3$, O$_2$ and small molecules OH and HO$_2$, logarithm of the activity coefficient of neutral solutes is a linear function of the effective ionic strength and the Sechenov coefficient (Rischbieter et al., 2000; Beltran, 2003; Clever, 1983; Ross and Noone, 1991). Unfortunately, Setchenov parameters are unknown for H$_2$O$_2$, which is an important source of aqueous OH radical and other ROS. Several studies (Ali et al., 2014; Cheng et al., 2016b; Liu et al., 2020) showed that the formation rate of S(VI) by H$_2$O$_2$ increases with aerosol condensed phase solution ionic strength and proposed different expression with the limitation of maximal ionic strength equal
to 5 M. In this case, considering the high value of ionic strength in the two field campaigns (averaged values are beyond 5 M), direct extrapolation of the observed/predicted $a-I$ relationship into such high ranges of ionic strength may not be appropriate. Thus, in this paper, the activity coefficient of $H_2O_2$ is only considered when calculating the sulfate formation rate. Corresponding typical activity coefficient values and calculation expressions are summarized in Table S2 and S3. The influence of ionic strength on gas phase molecular Henry’s law coefficients were also considered in the MARK model which are summarized in Table S3.

**Text S2. The concentration of aerosol particle transition metals in urban areas**

For the lack of Mn concentration in PM$_{2.5}$ during two field campaigns, we summarized the concentration of transition metals in urban areas, mainly in Beijing winter in Table S9. The mass concentration ratio of Fe/Mn is in the range of 8.6 to 31 in Beijing, and can up to 78 in India. In the calculation of sulfate formation, we used the mass concentration ratio of Fe/Mn as 28 which is a medium value of the ratios. The modeled ratio of soluble Fe (III) to total Fe in the whole winter field campaign was in the range of 0.02% to 27.63% with an average value of 1.63% and in the range of 0.04% to 3.29% with an average value of 0.79% in polluted and highly polluted conditions. The modeled ratio of soluble Mn (II) to total Mn in the whole winter field campaign was in the range of 0.01% to 97.21% with an average value of 21.78% and in the range of 0.01% to 80.46% with an average value of 19.83% in polluted and highly polluted conditions.

**Text S3. Four haze periods in PKU-17 observation**

Fig. S4 shows the diurnal trends of the key parameters measured in the PKU field campaign for four haze periods. All four haze periods lasted for 6 days. Due to the strict emission control policies enacted by the Chinese government, the concentration of PM$_{2.5}$ decreased compared to the same period in 2016 while still cause severe haze pollution in 2017. $H_2O_2$ exhibited a typical diurnal pattern with a maximum in the afternoon and low concentrations in the morning and night. It was worth mentioning that some studies reported high $H_2O_2$ concentrations during haze episodes, while in our study the average concentration of $H_2O_2$ was only about 0.02 ppb. Low OH radicals and $O_3$ concentrations indicated low photochemical activity. The largest PM$_{2.5}$ concentrations of period IV and II were observed exceeding 150 μg/m$^3$, which was coincident with higher concentrations of transition metal including Fe and Cu. Period IV was characterized by lower gas-phase $H_2O_2$ and higher RH as well as higher aerosol liquid water content compared to the other three periods. Due to the lack of OH radical data during Period IV, averaged OH concentrations from the other three haze periods were used in the calculation causing small biases due to the reduced gas-phase oxidant pathway during the haze period. Period II was characterized with the highest $SO_2$ concentration which was beneficial to the formation of secondary sulfate aerosol. The other two haze periods including Period I and Period III also own high levels of 24-hour averaged PM$_{2.5}$ loading exceeding 75 μg/m$^3$. However, according to the
observed $\text{SO}_4^{2-}$ concentration, high concentrations of sulfate only appeared in the fourth stage of pollution indicating the importance of RH and aerosol TMI.

Figures

Fig. S1. Ionic strength of aerosol particle solution influence on the aqTMI rate constant.

$$\log_{10}(k_{(\text{aqTMI})}/k_{(\text{aqTMI}, I_s=0)})$$

$$= (-3.02 \times \sqrt{I_s})/(1 + \sqrt{I_s})$$
Fig. S2. Distribution of ALWC and number concentration with aerosol particle bins in two campaigns.
Fig. S3. Calculated aerosol water by ISORROPIA-II model and H-TDMA method in two field campaigns during haze periods. The plots were colored with the relative humidity values. The black dashed line in the figure is the 1:1 baseline, and the red solid line is the linear fitting result assuming the intercept is zero.
Fig. S4. Time series of observed gas-phase pollutants concentrations, RH, Temperature, PM$_{2.5}$ mass loading and calculated aerosol pH and water content and sulfate formation rates in these four haze periods in PKU-17 field campaign.
Fig. S5. SOR (≡n(SO\(_2\))/n(SO\(_2\)+SO\(_4\)\(^{2-}\))) correlations with effective Fe (III) concentrations in PKU-17 winter field campaign.

Fig. S6. SOR (≡n(SO\(_2\))/n(SO\(_2\)+SO\(_4\)\(^{2-}\))) correlations with odd oxygen ([O\(_x\)]≡[O\(_3\)]+[NO\(_2\)]) and relative humidity (RH) in WD-14 summer field campaign.
Fig. S7 The “dilution effect” of Fe mass concentration and ALWC increasing with PM mass in winter and summer.

Fig. S8. Variation of PM$_{2.5}$, ionic strength, aerosol pH, particle specific surface areas and sulphate formation rates from different pathways with aerosol liquid water content (ALWC) during summer field campaign. The total number of valid data points shown in the figure is 501. The shaded area refer to the error bar (±1 σ) of PM$_{2.5}$ mass concentration, aerosol ionic strength and pH calculated by ISORROPIA-II (Fountoukis and Nenes, 2007b). Ratio in the second panel refers to the ratio of contributions from Mn-surface and aqTMI to produce sulphate. Particle specific surface areas represent the ratio of particle surface area (μm$^2$/cm$^3$) and mass concentration (μg/m$^3$).
Tables

Table S1. Reaction rate expression and constant for SO2 oxidation by OH in the gas-phase.

| Oxidant | The reaction rate expression and constant \(^a\) | References |
|---------|-------------------------------------------------|------------|
| OH      | \( R_{SO2+OH} = k_0[SO_2(g)][OH(g)] \)         | Burkholder et al. (2020) |
|         | \( k_{0\text{low}} = 3.3 \times 10^{-31} \times (T/300\text{K})^{-4.3} \text{ cm}^6 \text{ s}^{-1} \) |            |
|         | \( k_{0\text{high}} = 1.6 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1} \) |            |
|         | \( F_c = 0.6 \) |            |

\(^a\) We report the low and the high pressure limit of \( k \) for SO\(_2\) oxidation by OH. \( F_c \) is used to calculate the dependence of \( k \) on pressure and temperature (details see the reference(Burkholder et al., 2020)).
Table S2. Aqueous-phase reaction rate expressions, rate constants (k) and influence of ionic strength (I_s) on k for sulfate production in aerosol particle condensed phase.

| Oxidants | The reaction rate expressions \((R_{\text{S(IV)+oxi})}\), constants \((k)\) and influence of \(I_s\) (in unit of M) on \(k\) | Notes | References |
|----------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------|----------------------|
| O₃       | \((k_1[\text{H}_2\text{SO}_3] + k_2[\text{HSO}_3^-] + k_3[\text{SO}_3^{2-}]) [\text{O}_3(\text{aq})]\) \n\(k_1 = 2.4 \times 10^4 \text{ M}^{-1} \text{s}^{-1}\) \n\(k_2 = 3.7 \times 10^5 \text{ e}^{-5530(1/T-1/298)} \text{ M}^{-1} \text{s}^{-1}\) \n\(k_3 = 1.5 \times 10^9 \text{ e}^{-5280(1/T-1/298)} \text{ M}^{-1} \text{s}^{-1}\) \n\(\log_{10}(\frac{k}{k_{I_s=0}}) = b_1 \left(\frac{\sqrt{I_s}}{1+\sqrt{I_s}} - 0.3I_s\right)\) \n\(b_1\) is in range of 0.7 to 1.3 \n\(\frac{k}{k_{I_s=0}} = 1 + b_2I_s\) \n\(b_2\) is in range of 1.34 to 6.13 | \(I_s, \text{max} = 0.94\) M | Maahs (1983) |
| H₂O₂     | \(k_4[\text{H}^+][\text{HSO}_3^-][\text{H}_2\text{O}_2(\text{aq})]/(1+K[\text{H}^+])\) \n\(k_4 = 7.45 \times 10^7 \text{ e}^{-4430(1/T-1/298)} \text{ M}^{-1} \text{s}^{-1}\) \n\(K = 13\) M \n\(\log_{10}(\frac{k}{k_{I_s=0}}) = 0.36I_s - \frac{1.018\sqrt{I_s}}{1+0.17\sqrt{I_s}}\) \n\(\text{ln} \left(\frac{k}{k_{I_s=0}}\right) = 30.374 - \frac{6824.2068}{215.365+I_s}\) | \(I_s, \text{max} = 5\) M | Maaß et al. (1999) |
| NO₂      | \(k_5[\text{S(IV)}][\text{NO}_2(\text{aq})]\) \n\(k_{5\text{low}} = 2 \times 10^6 \text{ M}^{-1} \text{s}^{-1}\) \n\(k_{5\text{high}} = (1.24-2.95) \times 10^7 \text{ M}^{-1} \text{s}^{-1}\) \n\(\log_{10}(\frac{k}{k_{I_s=0}}) = b_3I_s\) \n\(b_3 > 0\) | Theoretical prediction | Cheng et al. (2016b) |
| TMI+O₂   | \(k_6[\text{H}^+]^{0.74}[\text{S(IV)}][\text{Mn(II)}][\text{Fe(III)}] (\text{pH} \leq 4.2)\) \n\(k_6 = 3.72 \times 10^7 \text{ e}^{-8431.66(1/T-1/297)} \text{ M}^{-2} \text{s}^{-1}\) \n\(k_7[\text{H}^+]^{0.67}[\text{S(IV)}][\text{Mn(II)}][\text{Fe(III)}] (\text{pH} > 4.2)\) \n\(k_7 = 2.51 \times 10^{13} \text{ e}^{-8431.66(1/T-1/297)} \text{ M}^{-2} \text{s}^{-1}\) \n\(\log_{10}(\frac{k}{k_{I_s=0}}) = b_4\frac{\sqrt{I_s}}{1+\sqrt{I_s}}\) \n\(b_4\) is in range of −4 to −2 | \(I_s, \text{max} = 2\) M | Martin and Hill (1987, 1967) |
\( k_8 \times f(H^+) \times f(T) \times f(I_s) \times [\text{Mn(II)}] \times [\text{SO}_2(g)] \times A \)

\( k_8 = 11079.30 \ \mu \text{g/m}^3/\text{min} , \ A \) is the surface area concentration in nm\(^2\)/cm\(^3\), and the SO\(_2\) mixing ratio is in ppbV.

\( f(H^+) = -1/(1 - 8.83 \times 10^{17} \times [H^+] - 7.84 \times 10^{21} \times [H^+]) \)

\( f(T) = e^{-11576.08 \times (1/T - 1/298)} \)

\( f(I_s) = \begin{cases} 
1, & I_s < 1.52911 \times 10^{-41} \times e^{2999.19} + 13.8704 \\
10.3, & I_s \geq 1.52911 \times 10^{-41} \times e^{2999.19} + 13.8704
\end{cases} \)

Nitrate photolysis

\[ 1.64 \times EF \times [\text{NO}_3^-] \times J_{\text{HNO}_3} \times \frac{K_{\text{HONO}}}{K_{\text{HONO} + [H^+]}} \times v \times A \times 0.25 \times [\text{SO}_2] \]

\[ K_{\text{HONO}} = 10^{-3.3} \text{ M}, \ EF = 1 - 100 \]

\( a \) The aerosol pH was in the range of 4.1 to 5.2 based on the calculations of ISORRPIA II model in winter and 3.8 to 4.9 in summer, which are consistent with the observed in NCP (Liu et al., 2017; Guo et al., 2017).

\( b \) The values of \( b_1 \) and \( b_2 \) are different for different solutions (Maahs, 1983; Lagrange et al., 1994). Since these values vary largely and have a significant impact on the estimated reaction rate at high \( I_s \) in aerosol water, we used a medium value of \( b_1 = 1.0 \) and \( b_2 = 1.94 \) in according to the calculation in Cheng to show the general pattern. Due to the low concentration of O\(_3\) during haze periods, the pathway provides little contribution in the sulfate formation.

\( c \) The last expression is the fitting results from the measurement results of Liu et al. (2020) Figure S10. The typical enhancement factor of proton-catalyzed sulfate formation rate is 40 in the haze periods of the winter campaign with an averaged ionic strength as 36.3 M.

\( d \) The \( k_{\text{slow}} \) was taken from Lee and Schwartz (1983). They reported a lower-limit value of \( k_{\text{slow}} = 2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1} \) at pH of 5.8 and 6.4. The \( k_{\text{high}} \) is in the pH range of 5.3–13 as reported by Clifton et al. (1988) and it increases with increasing pH. We used the value \( k_{\text{high}} = 1.24 \times 10^7 \text{ M}^{-1} \text{ s}^{-1} \) for pH < 5.3, and \( k_{\text{high}} = (0.1239 \text{ pH} + 0.5954) \times 10^7 \text{ M}^{-1} \text{ s}^{-1} \) for pH in 5.3–7.8 in the present calculations.

\( e \) The \( b_3 \) was predicted theoretically to be positive as 0.5 (Cheng et al., 2016b), however, no specific value of \( b_3 \) was determined from laboratory work. Because of the high value of ionic strength during the PKU campaign, we proposed an expression for the activity coefficient of NO\(_2\) based on the Sechenov theory to reflect the trend of its reaction rate increasing with the concentrations and chose \( b_3 \) value as 0.01, typical value of activity enhancement of NO\(_2\) with S(IV) is 2.31 with averaged ionic strength equaling to 36.3 during the haze periods. With \( b_3 \) equaling to 0.5 proposed in Cheng et al. (2016b), however, typical value is \( 1.41 \times 10^{18} \).

Thus we didn’t consider the influence of \( I_s \) on S(IV) + NO\(_2\) in aerosol water in our calculation.

\( f \) S(IV) oxidation by O\(_2\), which is via a radical chain mechanism, can be initiated by transition metal ions (TMIs) in bulk water (\( k_6 \) and \( k_7 \)). In our calculation, the reaction rate \( k_6 \) and \( k_7 \) was used for sulfate production via S(IV) + O\(_2\). Only Fe (III) and Mn (II) are considered here, since other transition metal ions (TMIs), such as Sc (III), Ti (III), V(III), Cr (III), Co (II), Ni (II), Cu
(II) and Zn (II), showed much less catalytic activities (Huss Jr et al., 1982). In addition, it has been concluded that the decreased temperature would generally lead to a decrease in overall reaction rate. Based on the measurement results of Ibusuki and Takeuchi (1987), the correction of temperature are considered in the present study.

Impact of ionic strength on the sulfate formation rate of aqueous phase TMI-catalyzed oxidation of dissolved SO$_2$ by O$_2$ in aerosol particles was studied by Liu et al. (2020). In their results, $b_4$ is -3.02 based on the fitting modeling and in the range of -2 for Fe(III) and -4 for Mn(II) (Martin and Hill, 1987, 1967). We used $b_4$ as -3.02 in the calculations in the present study.
Table S3. Calculations of Henry’ law coefficients and influence of ionic strength.

| Gas species | Henry’s law coefficient and the influence of $I_s$ | Notes | References |
|-------------|--------------------------------------------------|-------|------------|
| SO$_2$      | $H^0_{SO_2} = 1.23 \times e^{(3145.3 \times (\frac{1}{T} - \frac{1}{298}))}$ | $I_{s, \text{max}} = 6 \text{ M}$ | Seinfeld and Pandis (2016) |
|             | $\log_{10}(\frac{H_{SO_2}}{H^0_{SO_2}}) = \left(\frac{22.3}{T} - 0.0997\right) \times I_s$ |       | Millero et al. (1989) |
| O$_3$       | $H_{O_3} = e^{(22.97 \times (2.659 \times I_s + 688 \times \frac{I_s}{T} - 12.19))}$ | $I_{s, \text{max}} = 0.6 \text{ M}$ | Kosak-Channing and Helz (1983) |
| H$_2$O$_2$  | $H^0_{H_2O_2} = 1.3 \times 10^5 \times e^{(7297.1 \times (\frac{1}{T} - \frac{1}{292}))}$ | $I_{s, \text{max}} = 5 \text{ M}$ | Seinfeld and Pandis (2016); Chung et al. (2005) |
|             | $\frac{H_{H_2O_2}}{H^0_{H_2O_2}} = 1 - 1.414 \times 10^{-3} I_s^2 + 0.121 I_s$ |       | Liu et al. (2020) |
| NO$_2$      | $H^0_{NO_2} = 1.0 \times 10^{-2} \times e^{(2516.2 \times (\frac{1}{T} - \frac{1}{298}))}$ |       | Seinfeld and Pandis (2016) |

$^a$ We didn’t consider the influence of $I_s$ on $H_{NO_2}$ in our calculation due to the lack of relevant laboratory data. $H$ is in unit of M atm$^{-1}$. 

$^b$
Table S4. Typical activity coefficient values and expressions used in the MARK model

| Species                        | Calculation expression or typical value |
|--------------------------------|-----------------------------------------|
| **Inorganic ions**             |                                         |
| H\(^{+}\)                      | 0.4                                     |
| OH\(^{-}\)                     | 0.5                                     |
| NH\(_{4}\)^{+}                 | 0.2                                     |
| Na\(^{+}\)                     | 0.3                                     |
| SO\(_{4}\)^{2-}                | 0.02                                    |
| HSO\(_{4}\)^{-}                | 1                                       |
| NO\(_{3}\)^{-}                 | 0.4                                     |
| Fe(II), Cu(I), Cu(II), Mn(II) ions and their hydroxides | \(\log_{10}(a_i) = \frac{-z_i^2 \times 0.5109 \sqrt{I_s}}{1 + 1.5 \times \sqrt{I_s}}\) |
| Fe(III) and its hydroxides     | 0.001                                   |
| **Organic matters and Fe-complex** |                                         |
| H\(_{2}\)C\(_{2}\)O\(_{4}\)    | 0.6                                     |
| HC\(_{2}\)O\(_{4}\)^{-}        | 0.05                                    |
| C\(_{2}\)O\(_{4}\)^{2-}        | 0.43                                    |
| [Fe(C\(_{2}\)O\(_{4}\))\(_{2}\)]^{+} | 0.43                                    |
| [Fe(C\(_{2}\)O\(_{4}\))]^{1+}   | 0.43                                    |
| [Fe(C\(_{2}\)O\(_{4}\))]^{3+}   | 0.001                                   |

\(^{a}\) Non-ideality is treated with the approach by Zuend et al. (2008); Zuend et al. (2011) applied in the AIOMFAC model (Aerosol Inorganic–Organic Mixtures Functional groups Activity Coefficients, http://www.aiomfac.caltech.edu/index.html, last access: 18 July 2020).
Table S5. Kinetic data for the simulation of reactions in the aerosol particle condensed phase.

| Number | Reaction                                                                 | $k_{298}$ (M$^{\text{a+1}}$ s$^{-1}$) | $Ea/R$ (K) |
|--------|--------------------------------------------------------------------------|----------------------------------------|------------|
|        | **Iron reactions**                                                       |                                        |            |
| A1     | $\text{Fe}^{2+} + \text{H}_2\text{O}_2(a) \rightarrow \text{Fe}^{3+} + \text{OH}_{(a)} + \text{OH}^{-}$ | 70                                     | 5050       |
| A2     | $\text{Fe}^{2+} + \text{O}_3(a) \rightarrow \text{FeO}^{2+} + \text{O}_2(a)$     | $8.2 \times 10^5$                     | 4690       |
| A3     | $\text{FeO}^{2+} + \text{H}_2\text{O}_2(a) \rightarrow \text{Fe}^{3+} + \text{HO}_2(a) + \text{OH}^{-}$ | $9.5 \times 10^3$                    | 2766       |
| A4     | $\text{FeO}^{2+} + \text{HO}_2(a) \rightarrow \text{Fe}^{3+} + \text{O}_2(a) + \text{OH}^{-}$ | $2 \times 10^6$                      | 0          |
| A5     | $\text{FeO}^{2+} + \text{OH}_{(a)} + \text{H}^+ \rightarrow \text{Fe}^{3+} + \text{H}_2\text{O}_2(a)$ | $1 \times 10^7$                      | 0          |
| A6     | $\text{FeO}^{2+} + \text{H}_2\text{O}_{(a)} \rightarrow \text{Fe}^{3+} + \text{OH}_{(a)} + \text{OH}^{-}$ | $2.3 \times 10^{-2}$                 | 4100       |
| A7     | $\text{FeO}^{2+} + \text{Fe}^{2+} + \text{H}_2\text{O}_{(a)} \rightarrow 2 \text{Fe}^{3+} + 2 \text{OH}^+$ | $7.2 \times 10^4$                    | 842        |
| A8     | $\text{FeO}^{2+} + \text{Fe}^{2+} + \text{H}_2\text{O}_{(a)} \rightarrow \text{Fe(OH)}_2\text{Fe}^{4+}$ | $1.8 \times 10^4$                    | 5052       |
| A9     | $\text{Fe(OH)}_2\text{Fe}^{4+} + 2 \text{H}^+ \rightarrow 2 \text{Fe}^{3+} + 2 \text{H}_2\text{O}_{(a)}$ | 2                                      | 5653       |
| A10    | $\text{Fe(OH)}_2\text{Fe}^{4+} \rightarrow 2 \text{Fe}^{3+} + 2 \text{OH}^{-}$                      | 0.49                                  | 8780       |
| A11    | $\text{FeO}^{2+} + \text{HNO}_2(a) \rightarrow \text{Fe}^{3+} + \text{NO}_2(a) + \text{OH}^{-}$ | $1.1 \times 10^4$                    | 4150       |
| A12    | $\text{FeO}^{2+} + \text{H}^+ + \text{NO}_2 \rightarrow \text{Fe}^{3+} + \text{NO}_2(a) + \text{OH}^{-}$ | $2.5 \times 10^5$                    | 0          |
| A13    | $\text{FeO}^{2+} + \text{HSO}_3 \rightarrow \text{Fe}^{3+} + \text{OH}^{-} + \text{SO}_3$ | $1 \times 10^5$                      | 0          |
| A14    | $\text{Fe}^{2+} + \text{OH}_{(a)} \rightarrow \text{Fe(OH)}^{2+}$                             | $4.3 \times 10^8$                    | 1100       |
| A15    | $\text{Fe(OH)}_2^{2+} + \text{HO}_2(a) \rightarrow \text{Fe}^{2+} + \text{O}_2(a) + \text{H}_2\text{O}_{(a)}$ | $1.3 \times 10^5$                    | 0          |
| A16    | $\text{Fe(OH)}_2^{2+} + \text{O}_2 \rightarrow \text{Fe}^{2+} + \text{O}_2(a) + \text{OH}^{-}$ | $1.5 \times 10^8$                    | 0          |
| A17    | $\text{Fe}^{3+} + \text{O}_2^{-} \rightarrow \text{Fe}^{2+} + \text{O}_2(a)$                     | $1.5 \times 10^8$                    | 0          |
| A18    | $\text{Fe}^{2+} + 2 \text{H}^+ + \text{O}_2 \rightarrow \text{Fe}^{3+} + \text{H}_2\text{O}_2(a)$ | $1 \times 10^7$                      | 0          |
| A19    | $\text{Fe}^{2+} + \text{HO}_2(a) + \text{H}^+ \rightarrow \text{Fe}^{3+} + \text{H}_2\text{O}_2(a)$ | $1.2 \times 10^6$                    | 5050       |
| A20    | $\text{Fe(OH)}_2^{2+} + \text{O}_2 \rightarrow \text{Fe}^{2+} + \text{O}_2(a) + 2 \text{OH}^{-}$ | $1.5 \times 10^8$                    | 0          |
| A21    | $\text{Fe(OH)}_2^{2+} + \text{HSO}_3 \rightarrow \text{Fe}^{2+} + \text{SO}_3 + \text{H}_2\text{O}_{(a)}$ | 30                                    | 0          |
| A22    | $\text{Fe}^{2+} + \text{SO}_3 + \text{H}_2\text{O}_{(a)} \rightarrow \text{Fe(OH)}_2^{2+} + \text{HSO}_5$ | $2.65 \times 10^7$                  | 5809       |
| A23    | $\text{Fe}^{2+} + \text{HSO}_5 \rightarrow \text{Fe(OH)}_2^{2+} + \text{SO}_4^2$               | $3 \times 10^4$                      | 0          |
| A24    | $\text{Fe}^{2+} + \text{SO}_4 \rightarrow \text{Fe}^{3+} + \text{SO}_4^2$                   | $4.6 \times 10^9$                    | -2165      |
| A25    | $\text{Fe}^{2+} + \text{S}_2\text{O}_8^{2-} \rightarrow \text{Fe}^{3+} + \text{SO}_4 + \text{SO}_4^2$ | 17                                    | 0          |
|        | **Copper reactions**                                                     |                                        |            |
| A26    | $\text{Cu}^+ + 2 \text{H}^+ + \text{O}_2 \rightarrow \text{Cu}^{2+} + \text{H}_2\text{O}_2(a)$  | $8 \times 10^9$                      | 0          |
| Reaction | Equation | Kinetic Parameter | Catalyst | Product |
|----------|----------|-------------------|----------|---------|
| A27 | Cu⁺ + HO₂\(_{(a)}\) + H⁺ → Cu²⁺ + H₂O₂\(_{(a)}\) | 2.2×10⁹ | 0 | |
| A28 | Cu⁺ + OH\(_{(a)}\) → Cu²⁺ + OH⁻ | 3×10⁹ | 0 | |
| A29 | Cu²⁺ + HO₂\(_{(a)}\) → Cu⁺ + H⁺ + O₂\(_{(a)}\) | 1×10⁸ | 0 | |
| A30 | Cu²⁺ + O₂ → Cu⁺ + O₂\(_{(a)}\) | 1×10⁹ | 0 | |
| A31 | Cu⁺ + O₂\(_{(a)}\) → Cu²⁺ + O₂ | 4.6×10⁵ | 0 | |
| A32 | Cu⁺ + H⁺ + O₃\(_{(a)}\) → Cu²⁺ + O₂\(_{(a)}\) + OH\(_{(a)}\) | 3×10⁷ | 0 | |
| A33 | Cu⁺ + H₂O₂\(_{(a)}\) → Cu²⁺ + OH\(_{(a)}\) + OH⁻ | 7×10⁴ | 0 | |
| A34 | Cu⁺ + SO₄²⁻ → Cu²⁺ + SO₄²⁻ | 3×10⁸ | 0 | |
| **Mn reactions** | | | | |
| A35 | Mn⁴⁺ + H₂O₂\(_{(a)}\) → Mn²⁺ + O₂\(_{(a)}\) + 2H⁺ | 7.3×10⁴ | 0 | |
| A36 | Mn³⁺ + H₂O₂\(_{(a)}\) → Mn²⁺ + HO₂\(_{(a)}\) + H⁺ | 7.3×10⁴ | 0 | |
| A37 | MnOH²⁻ + H₂O₂\(_{(a)}\) → MnO²⁻ + H⁺ | 2.8×10³ | 0 | |
| A38 | MnO²⁻ + HO₂\(_{(a)}\) + H⁺ → H₂O₂\(_{(a)}\) + Mn²⁺ + O₂\(_{(a)}\) | 1×10⁷ | 0 | |
| A39 | Mn²⁺ + OH\(_{(a)}\) → Mn³⁺ + OH⁻ | 3.4×10⁷ | 0 | |
| A40 | 2 MnO₂⁺ + 2H⁺ → 2Mn²⁺ + H₂O₂\(_{(a)}\) | 6×10⁶ | 0 | |
| A41 | MnO²⁻ + 2H⁺ + Mn²⁺ → 2Mn³⁺ | 1×10⁵ | 0 | |
| A42 | Mn²⁺ + O₃\(_{(a)}\) + H⁺ → Mn³⁺ + O₂\(_{(a)}\) + OH\(_{(a)}\) | 1.65×10⁵ | 0 | |
| A43 | Mn²⁺ + NO₃\(_{(a)}\) → Mn³⁺ + NO₃⁻ | 1.5×10⁶ | 0 | |
| A44 | Mn²⁺ + HSO₅⁻ → Mn³⁺ + SO₄²⁻ + OH⁻ | 3×10⁴ | 0 | |
| A45 | Mn²⁺ + SO₅⁻ → Mn³⁺ + HSO₅⁻ + OH⁻ | 1×10¹⁰ | 0 | |
| A46 | Mn²⁺ + SO₄²⁻ → Mn³⁺ + SO₄²⁻ | 1.4×10⁷ | 4089 | |
| A47 | MnHSO₅⁺ + Mn³⁺ → H⁺ + 2Mn²⁺ + SO₄²⁻ | 1.3×10⁶ | 0 | |
| **Cu-Fe-Mn redox reactions** | | | | |
| A48 | Cu⁺ + Fe³⁺ → Cu²⁺ + Fe²⁺ | 1.3×10⁷ | 0 | |
| A49 | Cu⁺ + FeOH²⁻ → Cu²⁺ + Fe²⁺ + OH⁻ | 1.3×10⁷ | 0 | |
| A50 | Cu⁺ + Fe(OH)₂ → Cu²⁺ + Fe²⁺ + 2 OH⁻ | 1.3×10⁷ | 0 | |
| A51 | Mn³⁺ + Fe²⁺ → Mn²⁺ + Fe³⁺ | 1.6×10⁴ | 0 | |
| A52 | Mn²⁺ + FeO²⁻ + 2H⁺ → Mn³⁺ + Fe³⁺ | 1×10⁴ | 2562 | |
| **Hydroxide redox reactions** | | | | |
| A53 | O₂ + O₃\(_{(a)}\) → O₂\(_{(a)}\) + O³⁻ | 1.5×10⁹ | 2200 | |
| A54 | 2 HO$_2$(a) → H$_2$O$_2$(a) + O$_2$(a) | 8.3×10$^7$ | 2700 |
| A55 | HO$_2$(a) + O$_2$ + H$_2$O(a) → H$_2$O$_2$(a) + O$_2$(a) + OH$^-$ | 9.7×10$^7$ | 1060 |
| A56 | HO$_2$(a) + OH$_2$(a) → O$_2$(a) + H$_2$O(a) | 1×10$^{10}$ | 0 |
| A57 | O$_2$ + OH$_2$(a) → O$_2$(a) + OH$^-$ | 1.1×10$^{10}$ | 2120 |
| A58 | H$_2$O$_2$(a) + OH$_2$(a) → HO$_2$(a) + H$_2$O$_2$(a) | 3×10$^7$ | 1680 |

**Organic reactions**

| A59 | H$_2$C$_2$O$_4$ + OH$_2$(a) → H$_2$O$_2$(a) + C$_2$O$_4$ + H$^+$ | 1.9×10$^8$ | 2800 |
| A60 | C$_2$O$_4^2-$ + OH$_2$(a) → OH$^-$ + C$_2$O$_4^-$ | 1.6×10$^8$ | 4300 |
| A61 | C$_2$O$_4$ + O$_2$(a) → 2 CO$_2$(a) + O$_2$ | 2×10$^9$ | 2800 |
| A62 | HC$_2$O$_4$ + SO$_5$ → C$_2$O$_4$ + HSO$_5^-$ | 5×10$^3$ | 0 |
| A63 | HC$_2$O$_4$ + SO$_4$ → C$_2$O$_4$ + H$^+$ + SO$_4^{2-}$ | 3.35×10$^5$ | 0 |
| A64 | HC$_2$O$_4$ + NO$_3$(a) → C$_2$O$_4$ + H$^+$ + NO$_3^-$ | 6.8×10$^7$ | 0 |
| A65 | C$_2$O$_4^2-$ + H$^+$ + SO$_5$ → C$_2$O$_4$ + HSO$_5^-$ | 1×10$^4$ | 0 |
| A66 | C$_2$O$_4^2-$ + SO$_4$ → C$_2$O$_4$ + SO$_4^{2-}$ | 1.05×10$^6$ | 0 |
| A67 | C$_2$O$_4^-$ + NO$_3$(a) → C$_2$O$_4$ + NO$_3^-$ | 2.2×10$^8$ | 0 |
| A68 | HCOOH+OH (+ O$_2$) → Products | 3.2×10$^9$ | 0 |

**Fe-oxalate complex reactions**

| A69 | Fe$^{2+}$ + C$_2$O$_4^{2-}$ → FeC$_2$O$_4$(a) | 1×10$^6$ | 0 |
| A70 | FeC$_2$O$_4$(a) → Fe$^{2+}$ + C$_2$O$_4^{2-}$ | 1×10$^3$ | 0 |
| A71 | FeC$_2$O$_4^{+}$ + O$_2$ → FeC$_2$O$_4$(a) + O$_2$(a) | 1×10$^6$ | 0 |
| A72 | FeC$_2$O$_4^{+}$ + HO$_2$(a) → FeC$_2$O$_4$(a) + O$_2$(a) + H$^+$ | 1.2×10$^5$ | 0 |

**Sulfur and Nitrate compound reactions**

| A73 | HSO$_3^-$ + OH$_2$(a) → SO$_3^-$ + H$_2$O$(a)$ | 2.7×10$^9$ | 0 |
| A74 | OH$_2$(a) + SO$_3^2-$ → OH$^-$ + SO$_3$ | 4.6×10$^9$ | 0 |
| A75 | H$_2$O$(a)$ + N$_2$O$_5$(a) → 2 H$^+$ + 2 NO$_3^-$ | 5×10$^9$ | 0 |
| A76 | N$_2$O$_5$(a) → NO$_2^-$ + NO$_3^-$ | 1×10$^9$ | 0 |
| A77 | H$_2$O$(a)$ + NO$_2^+$ → 2 H$^+$ + NO$_3^-$ | 8.9×10$^7$ | 0 |
| A78 | Fe$^{2+}$ + NO$_3$(a) → Fe$^{3+}$ + NO$_3^-$ | 8×10$^6$ | 0 |
| A79 | H$_2$O$_2$(a) + NO$_3$(a) → HO$_2$(a) + H$^+$ + NO$_3^-$ | 4.9×10$^6$ | 2000 |
| A80 | HO$_2$(a) + NO$_3$(a) → H$^+$ + NO$_3^-$ + O$_2$(a) | 3×10$^9$ | 0 |
| Reaction | Equation | Rate Constant | Efficiency |
|----------|----------|---------------|------------|
| A81 | $\text{NO}_3(a) + \text{O}_2 \rightarrow \text{NO}_3 + \text{O}_2(a)$ | $3 \times 10^9$ | 0 |
| A82 | $\text{HSO}_3 + \text{NO}_3(a) \rightarrow \text{H}^+ + \text{NO}_3 + \text{SO}_3$ | $1.3 \times 10^9$ | 2000 |
| A83 | $\text{NO}_3(a) + \text{SO}_3^2- \rightarrow \text{NO}_3 + \text{SO}_3^-$ | $3 \times 10^8$ | 0 |
| A84 | $\text{HSO}_4 + \text{NO}_3(a) \rightarrow \text{H}^+ + \text{NO}_3 + \text{SO}_4$ | $2.6 \times 10^5$ | 0 |
| A85 | $\text{NO}_3(a) + \text{SO}_4^2- \rightarrow \text{NO}_3 + \text{SO}_4^-$ | $1 \times 10^5$ | 0 |
| A86 | $\text{NO}_2(a) + \text{OH}(a) \rightarrow \text{HOONO}(a)$ | $1.2 \times 10^{10}$ | 0 |
| A87 | $\text{NO}_2(a) + \text{O}_2 \rightarrow \text{NO}_2 + \text{O}_2(a)$ | $1 \times 10^8$ | 0 |
| A88 | $2 \text{NO}_2(a) + \text{H}_2\text{O}(a) \rightarrow \text{HNO}_2(a) + \text{H}^+ + \text{NO}_3$ | $8.4 \times 10^7$ | -2900 |
| A89 | $\text{NO}_2 + \text{OH}(a) \rightarrow \text{NO}_2(a) + \text{OH}^-$ | $9.1 \times 10^9$ | 0 |
| A90 | $\text{NO}_2 + \text{SO}_4 \rightarrow \text{NO}_2(a) + \text{SO}_4^2-$ | $7.2 \times 10^8$ | 0 |
| A91 | $\text{NO}_2 + \text{NO}_3(a) \rightarrow \text{NO}_2(a) + \text{NO}_3$ | $1.4 \times 10^9$ | 0 |
| A92 | $\text{NO}_2 + \text{O}_3(a) \rightarrow \text{NO}_3 + \text{O}_2(a)$ | $5 \times 10^5$ | 6900 |
| A93 | $\text{HNO}_2(a) + \text{OH}(a) \rightarrow \text{NO}_2(a) + \text{H}_2\text{O}(a)$ | $1.1 \times 10^{10}$ | 0 |
| A94 | $\text{HNO}_4(a) + \text{HSO}_3 \rightarrow \text{HSO}_4 + \text{H}^+ + \text{NO}_3$ | $3.3 \times 10^5$ | 0 |
| A95 | $\text{H}_2\text{O}(a) + \text{SO}_3(a) \rightarrow 2 \text{H}^+ + \text{SO}_4^2-$ | $1 \times 10^{10}$ | 0 |
| A96 | $\text{O}_3(a) + \text{SO}_5^2- \rightarrow \text{O}_2(a) + \text{SO}_4^2-$ | $1.5 \times 10^9$ | 5280 |
| A97 | $2 \text{SO}_5^2- \rightarrow \text{O}_2(a) + \text{S}_2\text{O}_8^2-$ | $4.8 \times 10^7$ | 2600 |
| A98 | $2 \text{SO}_5^- \rightarrow \text{O}_2(a) + 2 \text{SO}_4$ | $2.2 \times 10^8$ | 2600 |
| A99 | $\text{H}^+ + \text{O}_2 + \text{SO}_5^- \rightarrow \text{HSO}_5 + \text{O}_2(a)$ | $2.34 \times 10^8$ | 0 |
| A100 | $\text{O}_2(a) + \text{SO}_3(a) \rightarrow \text{SO}_5^-$ | $2.5 \times 10^9$ | 0 |
| A101 | $\text{HSO}_3 + \text{SO}_5 \rightarrow \text{HNO}_2 + \text{SO}_3$ | $8.6 \times 10^3$ | 0 |
| A102 | $\text{HSO}_4 + \text{SO}_2 \rightarrow \text{H}^+ + \text{SO}_4 + \text{SO}_2^2-$ | $3.6 \times 10^2$ | 0 |
| A103 | $\text{H}^+ + \text{SO}_3^2+ + \text{SO}_4 \rightarrow \text{HSO}_5 + \text{SO}_3$ | $2.1 \times 10^5$ | 0 |
| A104 | $\text{SO}_3^2+ + \text{SO}_5 \rightarrow \text{HSO}_5 + \text{SO}_4^2+$ | $5.5 \times 10^5$ | 0 |
| A105 | $\text{HSO}_4 + \text{OH}(a) \rightarrow \text{SO}_4 + \text{H}_2\text{O}(a)$ | $3.5 \times 10^5$ | 0 |
| A106 | $2 \text{SO}_4 \rightarrow \text{S}_2\text{O}_8^2-$ | $6.1 \times 10^8$ | 840 |
| A107 | $\text{HSO}_3 + \text{SO}_4 \rightarrow \text{H}^+ + \text{SO}_3 + \text{SO}_4^2-$ | $5.8 \times 10^8$ | 0 |
| A108 | $\text{SO}_5^2+ + \text{SO}_4 \rightarrow \text{SO}_3 + \text{SO}_4^2-$ | $3.4 \times 10^8$ | 1200 |
| A109 | $\text{H}_2\text{O}_2(a) + \text{SO}_4 \rightarrow \text{HO}_2(a) + \text{H}^+ + \text{SO}_4^2-$ | $1.7 \times 10^7$ | 0 |
| A110 | $\text{HO}_2(a) + \text{SO}_4 \rightarrow \text{H}^+ + \text{O}_2(a) + \text{SO}_4^2-$ | $3.5 \times 10^9$ | 0 |
| Reaction | Equation | Rate Constant | pH |
|----------|----------|---------------|----|---|
| A111 | O₂ + SO₄ → O₂(a) + SO₄²⁻ | 3.5×10⁹ | 0 | 0 |
| A112 | NO₃ + SO₄ → NO₃(a) + SO₄²⁻ | 5×10⁴ | 0 | 0 |
| A113 | OH⁻ + SO₄ → OH(a) + SO₄²⁻ | 1.4×10⁷ | 0 | 0 |
| A114 | H₂O(a) + SO₄ → H⁺ + OH(a) + SO₄²⁻ | 11 | 1100 | |
| A115 | HSO₅ + HSO₅ + H⁺ → 3 H⁺ + 2 SO₄²⁻ | 7.14×10⁶ | 0 | 0 |
| A116 | SO₅²⁻ + HSO₅ + H⁺ → 2 H⁺ + 2 SO₄²⁻ | 7.14×10⁶ | 0 | 0 |
| A117 | HSO₅ + OH(a) → SO₅ + H₂O(a) | 1.7×10⁷ | 0 | 0 |
| A118 | OH(a) + SO₄ → HSO₅ | 1×10¹⁰ | 0 | 0 |
| A119 | H₂O₂(a) + HSO₃ + H⁺ → 2 H⁺ + SO₄²⁻ + H₂O(a) | 7.2×10⁷ | 4000 | |
| A120 | O₃(a) + SO₂(a) + H₂O(a) → HSO₄ + H⁺ + O₂(a) | 2.4×10⁴ | 0 | 0 |
| A121 | HSO₅ + O₃(a) → SO₄²⁻ + H⁺ + O₂(a) | 3.7×10⁵ | 5530 | |
| A122 | NO₃(a) + OH⁻ → NO₃ + OH(a) | 9.4×10⁷ | 2700 | |
| Number | Reaction | $J_0$ (s$^{-1}$) |
|--------|----------|-----------------|
| J1     | $H_2O_2(a) + h\nu \rightarrow 2 OH(a)$ | $6.98\times10^{-6}$ |
| J2     | $Fe^{3+} + H_2O(a) + h\nu \rightarrow Fe^{2+} + OH(a) + H^+$ | $9.3\times10^{-6}$ |
| J3     | $Fe(OH)^{2+} + h\nu \rightarrow Fe^{2+} + OH(a)$ | $4.39\times10^{-3}$ |
| J4     | $Fe(OH)^{2+} + h\nu \rightarrow Fe^{2+} + OH(a) + OH^-$ | $5.63\times10^{-3}$ |
| J5     | $NO_2 + h\nu \rightarrow NO(a) + OH(a)$ | $2.51\times10^{-5}$ |
| J6     | $NO_3 + h\nu \rightarrow NO_2(a) + OH(a)$ | $4.15\times10^{-7}$ |
| J7     | $Fe[(C_2O_4)_2]^+ + h\nu \rightarrow C_2O_4^{2-} + C_2O_4^- + Fe^{2+}$ | $2.30\times10^{-2}$ |
| J8     | $Fe[(C_2O_4)_3]^{3+} + h\nu \rightarrow 2 C_2O_4^{2-} + C_2O_4^- + Fe^{2+}$ | $5.76\times10^{-2}$ |
| J9     | $FeC_2O_4^{+} + h\nu \rightarrow Fe^{2+} + C_2O_4$ | $7.20\times10^{-4}$ |
| J10    | $NO_3(a) + h\nu \rightarrow NO_2(a) + O_2(a)$ | $2.32\times10^{-2}$ |
| J11    | $NO_3(a) + h\nu \rightarrow NO_2(a) + O_3^p(a)$ | $2.01\times10^{-1}$ |

*Estimated as in the gas phase*
Table S7. Aqueous equilibrium reactions

| Number | Reaction | $K_{298}$ (M) | $k_{298}$ (M$^{-n}$ s$^{-1}$) | $E_a/R$ (K) | $k_{298}$ (M$^{-n}$ s$^{-1}$) | $E_a/R$ (K) |
|--------|----------|---------------|-------------------------------|-------------|-------------------------------|-------------|
|        |          | forward       | backward                      |             | forward                      | backward    |
| E1     | H$_2$O$_{(a)}$ ↔ H$^+$+OH$^-$ | 1.8×10$^{-16}$ | 2.34×10$^{-5}$ | 6800 | 1.3×10$^{11}$ | 0 |
| E2     | NH$_3(a) + H_2O(a)$ ↔ NH$_4^+$+OH$^-$ | 1.17×10$^{-5}$ | 6.02×10$^{5}$ | 560 | 3.4×10$^{10}$ | 0 |
| E3     | HO$_2(a) ↔ H^++O_2$ | 1.6×10$^{-5}$ | 8.0×10$^{5}$ | 0 | 5×10$^{10}$ | 0 |
| E4     | HNO$_3(a) ↔ H^++NO_3^-$ | 22 | 1.1×10$^{12}$ | -1800 | 5×10$^{10}$ | 0 |
| E5     | HNO$_2(a) ↔ H^++NO_2$ | 5.30×10$^{-4}$ | 2.65×10$^{7}$ | 1760 | 5×10$^{10}$ | 0 |
| E6     | HNO$_4(a) ↔ H^++O_2N_2O_2^-$ | 1×10$^{-5}$ | 5×10$^{5}$ | 5×10$^{10}$ | 5×10$^{10}$ | 0 |
| E7     | HO$_2(a) + NO_2(a) ↔ HNO_3(a)$ | 2.17×10$^{9}$ | 1×10$^{7}$ | 4.6×10$^{-3}$ | 2×10$^{5}$ | 0 |
| E8     | HO$_2(a) + SO_2(a) ↔ HSO$_3^{-} + H^+$ | 3.14×10$^{-4}$ | 6.27×10$^{4}$ | -1940 | 2.0×10$^{8}$ | 0 |
| E9     | HSO$_3^{-} ↔ H^++SO_3^{2-}$ | 6.22×10$^{-8}$ | 3110 | -1960 | 5×10$^{10}$ | 0 |
| E10    | H$_2$SO$_4(a) ↔ HSO$_4^+ + H^+$ | 1×10$^{3}$ | 5×10$^{13}$ | 5×10$^{10}$ | 5×10$^{10}$ | 0 |
| E11    | HSO$_4^- ↔ H^++SO_4^{2-}$ | 1.02×10$^{-2}$ | 1.02×10$^{-9}$ | -2700 | 1×10$^{11}$ | 0 |
| E12    | Fe$^{3+}$ + H$_2$O$_{(a)}$ ↔ Fe(OH)$_{2}^{2+} + H^+$ | 1.09×10$^{-4}$ | 4.7×10$^{4}$ | 4.3×10$^{8}$ | 4×10$^{5}$ | 0 |
| E13    | Fe(OH)$_{2}^{2+} + H_2O_{(a)} ↔ Fe(OH)$_2^{+} + H^+$ | 1.38×10$^{-7}$ | 1.1×10$^{3}$ | 8×10$^{9}$ | 5×10$^{10}$ | 0 |
| E14    | Fe$^{3+}$ + SO$_4^{2-} ↔ Fe(SO_4)_2^{+}$ | 1.78×10$^{-2}$ | 3.2×10$^{3}$ | 1.8×10$^{5}$ | 5×10$^{10}$ | 0 |
| E15    | Cu$^{2+} + OH_{(a)} ↔ Cu(OH)_2^{+}$ | 1.17×10$^{-4}$ | 3.5×10$^{8}$ | 3×10$^{4}$ | 5×10$^{10}$ | 0 |
| E16    | HO$_3(a) ↔ H^++O_3^-$ | 5×10$^{-9}$ | 330 | 5.2×10$^{10}$ | 5×10$^{10}$ | 0 |
| E17    | HOONO$_{(a)} ↔ H^++OONO^-_1$ | 1×10$^{-6}$ | 5×10$^{4}$ | 5×10$^{10}$ | 5×10$^{10}$ | 0 |
| E18    | Fe(C$_2$O$_4$)$_2^{+} ↔ C_2$O$_4^{2-} + Fe^{3+}$ | 4.0×10$^{-10}$ | 3×10$^{-3}$ | 7.5×10$^{6}$ | 5×10$^{10}$ | 0 |
| E19    | Fe(C$_2$O$_4$)$_2^{+} ↔ C_2$O$_4^{2-} + Fe(C_2O_4)_2^{+}$ | 1.59×10$^{-7}$ | 3×10$^{-3}$ | 1.89×10$^{4}$ | 5×10$^{10}$ | 0 |
| E20    | Fe(C$_2$O$_4$)$_3^{3-} ↔ C_2$O$_4^{2-} + Fe(C_2O_4)_2^{+}$ | 2.65×10$^{-5}$ | 3×10$^{-3}$ | 114 | 5×10$^{10}$ | 0 |
| Number | Reaction                  | $k_{298}$ (M$^{-a+1}$ s$^{-1}$) forward | $k_{298}$ (M$^{-a+1}$ s$^{-1}$) backward |
|--------|---------------------------|------------------------------------------|------------------------------------------|
| T1     | CO$_2$(g) ↔ CO$_2$(a)     | $k_{mt\text{CO}_2}\times\text{ALWC}$                         | $k_{mt\text{CO}_2}(H\text{CO}_2RT)$       |
| T2     | NH$_3$(g) ↔ NH$_3$(a)     | $k_{mt\text{NH}_3}\times\text{ALWC}$                         | $k_{mt\text{NH}_3}(H\text{NH}_3RT)$       |
| T3     | O$_3$(g) ↔ O$_3$(a)       | $k_{mt\text{O}_3}\times\text{ALWC}$                         | $k_{mt\text{O}_3}(H\text{O}_3\text{RT})$  |
| T4     | HO$_2$(g) ↔ HO$_2$(a)     | $k_{mt\text{HO}_2}\times\text{ALWC}$                         | $k_{mt\text{HO}_2}(H\text{HO}_2\text{RT})$|
| T5     | OH$_1$(g) ↔ OH$_1$(a)     | $k_{mt\text{OH}}\times\text{ALWC}$                          | $k_{mt\text{OH}}(H\text{OH}\text{RT})$    |
| T6     | H$_2$O$_2$(g) ↔ H$_2$O$_2$(a) | $k_{mt\text{H}_2\text{O}_2}\times\text{ALWC}$                     | $k_{mt\text{H}_2\text{O}_2}(H\text{H}_2\text{O}_2\text{RT})$ |
| T7     | NO$_3$(g) ↔ NO$_3$(a)     | $k_{mt\text{NO}_3}\times\text{ALWC}$                         | $k_{mt\text{NO}_3}(H\text{NO}_3\text{RT})$ |
| T8     | N$_2$O$_5$(g) ↔ N$_2$O$_5$(a) | $k_{mt\text{N}_2\text{O}_5}\times\text{ALWC}$                   | $k_{mt\text{N}_2\text{O}_5}(H\text{N}_2\text{O}_5\text{RT})$ |
| T9     | NO$_2$(g) ↔ NO$_2$(a)     | $k_{mt\text{NO}_2}\times\text{ALWC}$                         | $k_{mt\text{NO}_2}(H\text{NO}_2\text{RT})$ |
| T10    | SO$_2$(g) ↔ SO$_2$(a)     | $k_{mt\text{SO}_2}\times\text{ALWC}$                         | $k_{mt\text{SO}_2}(H\text{SO}_2\text{RT})$ |

$*k_{mt}$ is related to the particle diameters and the aerosol liquid water in different diameter bins. For this reason, the mass transfer rates are corrected by the particle 11 bins diameters in the two field campaigns. The rate $k_{mt}$ equals to $\sum_{i=1}^{11} k_{mt,i} \times L_i$.
| Sampling site                | Period     | Method | Fe  | Mn  | Cu  | References         |
|-----------------------------|------------|--------|-----|-----|-----|--------------------|
| China, Beijing, Urban       | 2018.8-2019.8 | XRF    | 596 | 27.9| 7.37| Zhao et al. (2021) |
| China, Beijing, Urban       | 2015.9-2016.1 | XRF    | 686 | 60.2| 25.1| Zhang et al. (2019) |
| China, Beijing, Urban       | 2016.6-2017.5 | ED-XRF | 738 | 37  | 32  | Cui et al. (2019)  |
| China, Beijing, Urban       | 2014.1-10          | ICP-AES | 1650 | 55  | 108 | Gao et al. (2018)  |
| China, Beijing, Urban       | 2016.1-2017.5      | XRF    | 629 | 32  | 24  | Cui et al. (2020)  |
| China, Beijing, Urban       | 2016.1           | ICP-AES | 2823 | 92.3| 48  | Duan et al. (2012) |
| China, Zhengzhou, Urban     | 2017.10-2018.7    | XRF    | 1361| 157 | 29.2| He et al. (2019)   |
| China, Nanjing, Urban       | 2016.12-2017.12   | XRF    | 577 | 48.9| 27.2| Yu et al. (2019)   |
| China, Shanghai, Urban      | 2016.3-2017.2     | ED-XRF | 410 | 32  | 12  | Chang et al. (2017) |
| Canada, Hamilton, Urban     | 2014.1-2017.6     | XRF    | 49.6| 0.83| 2.76| Sofowote et al. (2019) |
| India, New Delhi, Urban     | 2013.1-2016.12    | WD-XRF | 780 | 10  | 100 | Jain et al. (2020) |
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