

# **Potential Enhancement in Atmospheric New Particle Formation by Amine-Assisted Nitric Acid Condensation at Room Temperature**

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## **Introduction**

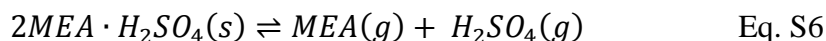
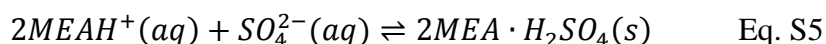
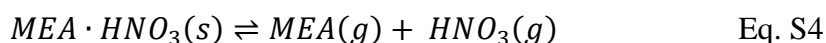
This supplement contains additional information for the theory and application of E-AIM model on reduced nitrogen compound (RNC, ammonia and amines in this study)-sulfuric acid-nitric acid chemical systems and detailed analysis of the uncertainties on simulation results. It includes the uncertainty estimates on the transitional temperature of nitric acid condensation ( $T_c$ , defined as the temperature at which the moles of total nitrate in the condensed phases equals to 5% of the initial moles of nitric acid and determined in this study) and the dependence of  $T_c$  on the amine mole fraction (mol %) and the initial relative humidity (RH) in a chemical system of RNCs, sulfuric acid and nitric acid,.

### Specific Application of Thermodynamic State Equations in a Reduced Nitrogen Compound (RNC)-Sulfuric Acid-Nitric Acid chemical system

The Extended-Aerosol Inorganics Model (E-AIM) considers the partitions of a particular chemical in four phases: gas (g), solid (s, including its salts), aqueous solution (aq) and hydrophobic organic solution (org) at any given relative humidity and temperature in a fixed total volume of 1 m<sup>3</sup> and at a fixed total pressure of 101,325 Pa. The E-AIM model (<http://www.aim.env.uea.ac.uk/aim/aim.php>) allows the users to specify the initial concentration of the chemical (as moles in 1 m<sup>3</sup>), as well as instructions regarding the properties and activity (discussed in details in following sections) of the chemical.

All possible states for water (g, aq and s) are considered by the E-AIM. However, in this study, low temperatures at which the water may start to freeze were avoided. The autoprotolysis of water and both hydrolysis equilibria of the inorganic diacid H<sub>2</sub>SO<sub>4</sub> are also considered to include H<sup>+</sup>, HSO<sub>4</sub><sup>-</sup> and OH<sup>-</sup> concentrations in the calculations. The protonation of ammonia and the formation of ammonium nitrate and sulfate solids are considered in our simulations to represent the partition of ammonia in aqueous solution and solid phases as accurately as possible. Since NH<sub>4</sub><sup>+</sup>, SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup> are the primarily inorganic ions of consideration, E-AIM Model II was used throughout our study. Thermodynamic data on ammonia and its nitrate and sulfate salts have been extensively studied and their thermodynamic properties and constants are relatively well established [Wexler and Clegg, 2002]. Therefore, default inputs (including the methods to estimate activities) in the existing E-AIM Model II on ammonia, sulfuric acid and nitric acid are used without further modification. Wang et al. [2020] identified that ammonia and nitric acid in the ammonia-sulfuric acid-nitric acid ternary system could only condense at or below 278 K, but above 263 K, suggesting that our simulation results on the ammonia-sulfuric acid-nitric acid ternary system should have an uncertainty within the range of -3.8% to +1.7%.

In this study, for example, the following series of state equations are possible for ethanolamine (MEA, with its conjugated acid labeled as MEAH<sup>+</sup>):



Each of the equation above involves an equilibrium constant  $K$  that is temperature

dependent and may have been determined experimentally or can be derived using other thermodynamic properties of MEA.

### **Saturation vapor pressure considerations for amines**

Data on the saturation vapor pressure ( $p^0$ ) of an amine at various temperatures are needed to accurately describe its distribution between gaseous and condensed phases. However, comprehensive and high-quality experimental data on  $p^0$  of amines are not always available. Ge et al. (2011) systematically evaluated the available experimental data and several theoretical vapor pressure calculation models for amines and concluded that the method by Moller et al. (2008) provides the best estimations. Alcohol amines, such as MEA, showed the largest difference in calculated and measured vapor pressure values (up to a factor of 3.56 times). Such discrepancy was much smaller among monoamines with alkyl groups (a factor of 1.06). The default  $p^0$  values for amines in the E-AIM models were experimental data and only when these data were missing, the calculation method by Moller et al. (2008) was used, with the exception of MA, DMA, EA, DEA and AN-N (discussed in the next section). In our study, to provide the most conservative estimation of the uncertainties caused by errors in  $p^0$  of amines, the vapor pressure of each amine was increased and decreased by a factor of 3.56, representing the maximum uncertainty range by the method of Moller et al. (2008), while the rest of the conditions remained the same (initial moles of an amine, sulfuric acid and nitric acid at  $1.11151 \times 10^{-9}$ ,  $2.03777 \times 10^{-11}$  and  $8.86895 \times 10^{-8}$ , respectively, initial mole of water at 0.07848 that corresponds to 60 % RH at 263.15 K and 101,325 Pa). Figure S1(a) illustrates the results of such error analysis using PZ as an example. The corresponding  $T_c$  values are summarized in Table S1 and the relative uncertainties were generally small ( $\pm 3\%$ ).

### **Henry's Law constant considerations for monoamines**

MA, DMA, EA and DEA are monoamines with small alkyl group(s) and their measured  $p^0$  ranges (described by the Antoine equation parameters) are generally well below 298 K [Linstrom and Mallard, 2018]. Opposite to these small alkylamines, AN-N has extremely low  $p^0$  at 298 K and therefore has an Antoine equation applicable only at 415–609 K [Linstrom and Mallard, 2018]. It is therefore difficult to use  $p^0$  to study these amines, without introducing unknown levels of uncertainties by extrapolating their Antoine equations to 298 K. Alternatively, Henry's Law constant  $K_H$  for these amines can be used to describe their partition between gas and aqueous solution and has been determined on these amines previously [Sander, 2015; Linstrom and Mallard, 2018]. The values recommended by Ge et al. (2011) were considered the default input parameters in our study (corresponding results reported in Table 1).

Additional simulations were carried out using the extrapolated  $p^0$  for each of the five monoamines with initial moles of the amine, sulfuric acid and nitric acid at  $1.11151 \times 10^{-9}$ ,  $2.03777 \times 10^{-11}$  and  $8.86895 \times 10^{-8}$ , respectively, and a fixed initial mole of water at 0.07848 (corresponding to 60 % RH at 263.15 K and 101,325 Pa). The

results were plotted in Figure S1(b), except for AN-N which showed negligible difference ( $< 0.05\%$ ). While the results for the four alkylamines using the  $K_H$  and the extrapolated  $p^0$  appeared to be very different, it is important to note that in all four cases the  $T_c$  values calculated using the extrapolated  $p^0$  values are higher than those calculated using the  $K_H$  values, suggesting that the reported  $T_c$  values in our Table 1 are the lower bound estimation of the transitional temperature at which the amines can condense with nitric acid. Numerically, the choice to use  $K_H$  or extrapolated  $p^0$  for our simulations will cause a change in  $T_c$  values by 6% or less.

Due to the potentially large errors in extrapolating the  $p^0$  values, the variability in the  $T_c$  of DMA associated with its extrapolated  $p^0$  was further tested by increasing and decreasing its extrapolated  $p^0$  at 298 K by a factor of 4.8 (limited by the maximum allowed  $p^0$  value of 10 atm in E-AIM). In the case of AN-N, the extrapolated  $p^0$  value at 298 K from Antoine equation was lower by 30 times based on another vapor pressure estimation method, EPI Suite v 4.11 [US EPA, 2019]. The corresponding relative uncertainties in  $T_c$  caused by these drastic changes in extrapolated  $p^0$  values were within 2%.

It is also important to note the complications in applying the  $K_H$  values from literatures in our thermodynamic simulations. The  $K_H$  values at 298 K for the five amines varies significantly in literatures [Sander, 2015]. In our simulations, the  $K_H$  values recommended by Linstrom and Mallard (2018) were used as default input values (corresponding results reported in Table 1). When applicable, the largest and smallest  $K_H$  values of an amine (with clearly stated method of determination) at 298 K summarized by Sander [2015] were used to estimate the possible uncertainties caused by the variability in  $K_H$  at 298 K. Figure S1(c) illustrated such uncertainty estimation on DMA as an example. The  $T_c$  values after varying the  $K_H$  values at 298 K for the four amines are included in Table S1.

Note that among available data, there are also significant uncertainties in the temperature dependence of  $K_H$  for amines. A systematic uncertainty analysis was difficult due to the lack of such literature data for most of the amines in our study, which could be a potential issue in the accurate determination of  $T_c$  values. However, for the five amines with available alternative temperature dependence coefficients of  $K_H$  [Sander, 2015], the uncertainties in  $T_c$  values caused by the alternative coefficients are within 3%.

### Activity considerations for amines

It is possible to carry out thermodynamic simulations with or without considering the activities of the chemicals in the aqueous solution, including the ammonium and aminium cations, the nitrate and sulfate anions and the dissolved amines. The scenario where activities of all chemical species are considered to be one is referred as the Raoult's law method, which is likely applicable at high relative humidity due to the much-diluted ion concentrations. However, at a higher temperature or lower relative

humidity, water condensation on the particle may be limited and the formed aqueous solution may have a very high ionic strength [Pye et al., 2020]. Therefore, it is important to evaluate the uncertainties caused by the methods used for activity estimations in our simulations.

The activities of the anions involved in our simulations were relatively well studied [Wexler and Clegg 2002]. Ge et al. (2011) showed that it is reasonable to assume the activities of the aminium cations to be the same as that of ammonium cation. As highly polar molecules, the activities of amines dissolved in an aqueous solution may be described using the UNIFAC method [Fredenslund et al., 1977].

Our  $T_c$  values reported in Table 1 were based on simulations using the UNIFAC method as default to estimate the activities of the amines. Ge et al. (2011) showed that the estimation of activities of amines using UNIFAC method will generally lead to satisfactory results yet the dataset for comparison was far from comprehensive. Therefore, additional simulations were carried out using the Raoult's law method for all the amines. One example comparing the results between Raoult's law and UNIFAC methods is shown in Figure S1(d). The relative difference in  $T_c$  using the two activity estimation methods for amines in our study was generally below 2.5%.

### **Solubility considerations for the salts of amines**

One last potential complication in our thermodynamic simulations is the possible formation of the solid aminium nitrate salts. Only a handful of the nitrates of alkylamines (such as MA, DMA, TMA), AN and MEA were studied for their solubility properties. The general trend is that the nitrate salts of alkylamines and alcohol amines are highly soluble in water, which consequentially make no impact on the thermodynamic modeling results.

In the case of AN, its nitrate salt has low solubility. Additional simulation using E-AIM while specifying the solubility of AN nitrate showed that no solid of AN nitrate may form under our simulation conditions. It is therefore reasonable to assume that the water solubility of the aminium nitrate salts had no impact on our  $T_c$  results.

### **Overall uncertainty estimations**

As discussed previously, it is assumed that the overall uncertainties of our simulation were determined by errors in  $p^0$  (or  $K_H$ ) estimations and the discrepancies in the activity estimation methods (assuming that the true value lies in the middle of the two methods), and the two sources were independent from each other. The uncertainties in the temperature dependence of  $K_H$  were not considered in our error estimations due to the large variability in the data in the literature. Instead, the values suggested by Linstrom and Mallard (2018) were used as the default values for the temperature dependence of  $K_H$ .

The overall uncertainty for the  $T_c$  value of each amine was therefore the square root of the square sum of the two independent sources (summarized in Table S1). It is worth noting that typically the uncertainty of the upper boundary for the  $T_c$  value is larger than that of the lower boundary. This is particularly pronounced in DEA and may bring its  $T_c$  value up to the 280 K range. While the uncertainty analysis presented

in Table S1 could move some of the amines from Group I to Group II, it doesn't change our conclusion that amines may contribute significantly to nitric acid condensations in the presence of high ammonia concentration, especially at higher temperature where ammonia and nitric acid are not likely to condense.

Table S1. Uncertainty estimations of the  $T_c$  values for the reduced- nitrogen compounds (RNCs) in this study.

RNC	$T_c^a$	Upper limit of $T_c$ due to $p^0$ (298 K) <sup>b</sup>	Lower limit of $T_c$ due to $p^0$ (298 K) <sup>b</sup>	Difference in $T_c$ due to activity <sup>c</sup>	Overall uncertainty in $T_c$ , upper limit <sup>d</sup>	Overall uncertainty in $T_c$ , lower limit <sup>d</sup>
NH <sub>3</sub>	273.4	-	-	-	+ 1.7% <sup>**</sup>	- 3.8% <sup>**</sup>
MA	274.1	288.4 <sup>*</sup>	274.1 <sup>*</sup>	-2.5% <sup>†</sup>	+ 5.4%	- 1.3%
DMA	270.6	287.3 <sup>*</sup>	270.6 <sup>*</sup>	-2.2% <sup>†</sup>	+ 6.3%	- 1.1%
TMA	274.8	279.6	270.6	-2.4%	+ 2.1%	- 2.0%
EA	272.7	288.0 <sup>*</sup>	272.0 <sup>*</sup>	-0.2% <sup>†</sup>	+ 5.6%	- 0.3%
DEA	263.9	287.4 <sup>*</sup>	257.9 <sup>*</sup>	3.5% <sup>†</sup>	+ 9.1%	- 2.9%
TEA	273.8	278.4	269.7	6.7%	+ 3.8%	- 3.7%
AN	256.6	256.6	256.6	2.2%	+ 1.1%	- 1.1%
AN-M	256.6	256.6	256.6	3.6%	+ 1.7%	- 1.7%
AN-N	256.6	256.5 <sup>*</sup>	256.7 <sup>*</sup>	< 0.05% <sup>‡</sup>	<+0.05% <sup>#</sup>	<- 0.05% <sup>#</sup>
MEA	304.5	309.6	299.9	-0.9%	+ 1.7%	- 1.6%
IBA	307.0	314.0	300.0	-1.1%	+ 2.3%	- 2.3%
PZ	302.4	308.8	296.5	-2.5%	+ 2.5%	- 2.3%
AN-O	289.0	293.0	284.7	1.7%	+ 1.6%	- 1.7%
DAE	323.5	328.5	318.6	-0.2%	+ 1.5%	- 1.5%
DGA	323.7	330.6	317.3	0.1%	+ 2.1%	- 2.0%
DIPA	313.5	319.5	307.5	1.9%	+ 2.1%	- 2.1%

<sup>a</sup> The transitional temperature (in K) of nitric acid condensation assisted with the amine by using default E-AIM input parameters.

<sup>b</sup> The limits of the  $T_c$  (in K) resulting from the uncertainties in vapor pressure  $p^0$  at 298 K of the amine (unless noted otherwise). The upper and lower limits of  $T_c$  were obtained by decreasing and increasing  $p^0$  at 298 K of the amine by a factor of 3.56, respectively.

<sup>c</sup> The relative difference in  $T_c$  between the UNIFAC and the Raoult's law methods to determine activities of the amine in an aqueous solution.

<sup>d</sup> It is assumed that the uncertainty in  $T_c$  was caused mainly by the uncertainties of the  $p^0$  (or  $K_H$  when applicable) and activity estimations.

<sup>†</sup> This uncertainty was within  $\pm 0.05\%$  when the Henry's law constant  $K_H$  of the amine was used. It was then conservatively estimated by using the extrapolated vapor pressure at 298 K based on the Antoine Equation of the amine [Linstrom and Mallard, 2018]. The enthalpy change at 298 K was extrapolated based on compiled data by Linstrom and Mallard (2018). The heat capacity was assumed to be the same as that of TMA,  $-90 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ .

<sup>‡</sup> Both enthalpy change values of 70.0 kJ/mol and 77.9 kJ/mol [Linstrom and Mallard, 2018] produced similar results ( $<0.05\%$  difference).

<sup>\*</sup> The limits of the  $T_c$  (in K) resulting from the uncertainties in the Henry's law constant  $K_H$  at 298 K. The upper and lower limits of  $T_c$  were obtained by choosing the maximum and minimum  $K_H$  values at 298 K from available literature values with stated method of determination in Sander (2015). The temperature dependence of the Henry's law constants was based on the values recommended by Linstrom and Mallard (2018).

<sup>\*\*</sup> The relative uncertainties were estimated by comparing with the experimental observations (263 – 278 K) by Wang et al. (2020).

<sup>#</sup> The relative uncertainties were less than 0.05%.



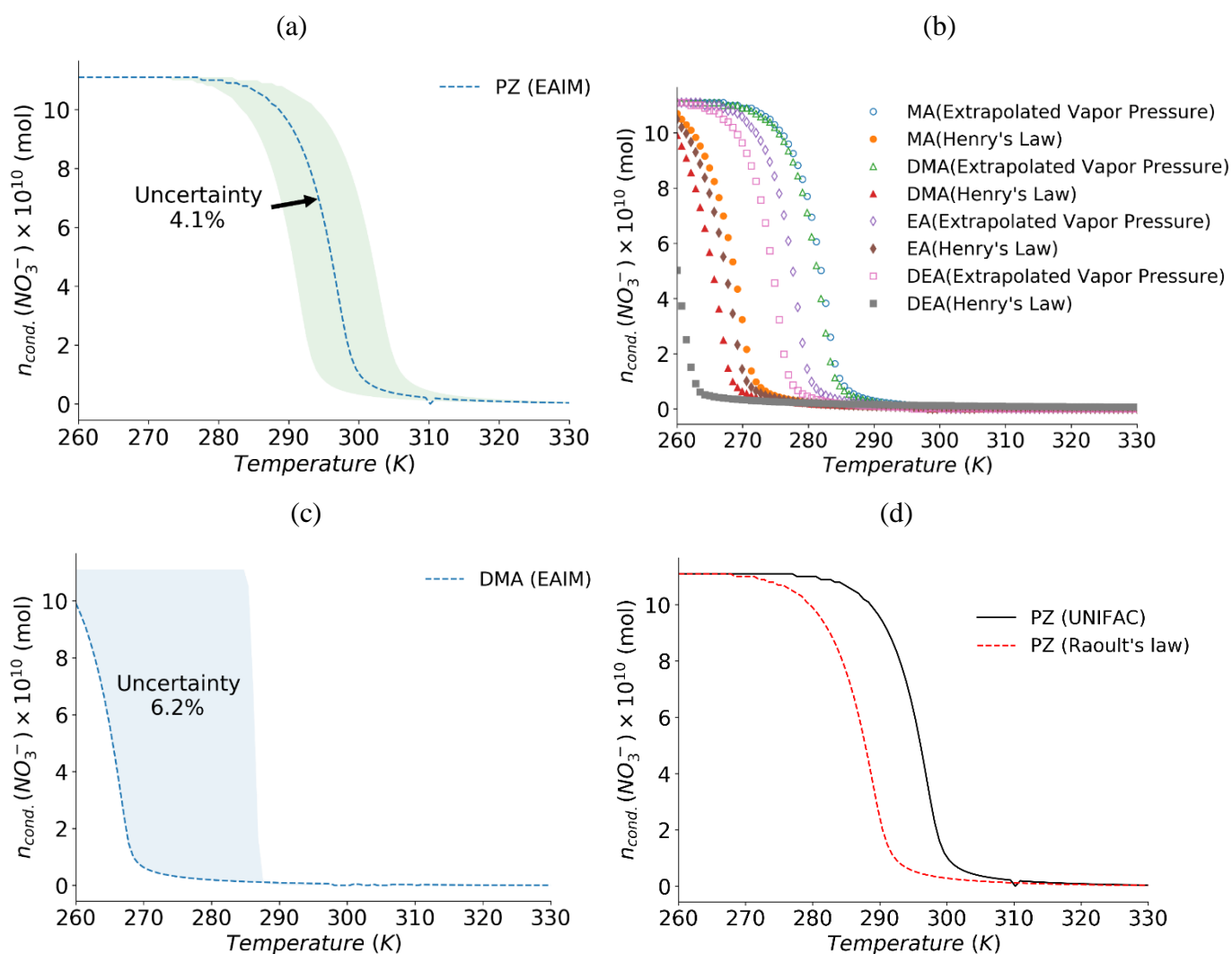


Figure S1. (a) The uncertainties in  $T_c$  of PZ (gray area) resulting from the uncertainties in its saturation vapor pressure  $p^0$ . The dash line represents the results using  $p^0$  values recommended by Ge et al. (2011). The lower and upper boundaries of the gray area were derived by increasing and decreasing the vapor pressure by a factor of 3.56, respectively. (b) The differences in  $T_c$  for MA, DMA, EA and DEA when using Henry's law constant  $K_H$  (hallow markers) and the extrapolated vapor pressure  $p^0$  at 298 K (solid markers). The extrapolated vapor pressures were based on their Antoine Equations at low temperatures [Linstrom and Mallard, 2018]. (c) The uncertainties in  $T_c$  of DMA (gray area) resulting from the uncertainties in its Henry's law constant  $K_H$  at 298 K. The dash line represents the results using the  $K_H$  at 298 K value recommended by Linstrom and Mallard (2018). The lower and upper boundaries of the gray area were derived by using the minimum and maximum  $K_H$  at 298 K values (with clearly stated methods of determination) in Sander (2015), respectively. (d) The comparison in  $T_c$  values of PZ using different activity estimation methods. The black solid line was calculated with the UNIFAC method and the red dash line was based on Raoult's law.

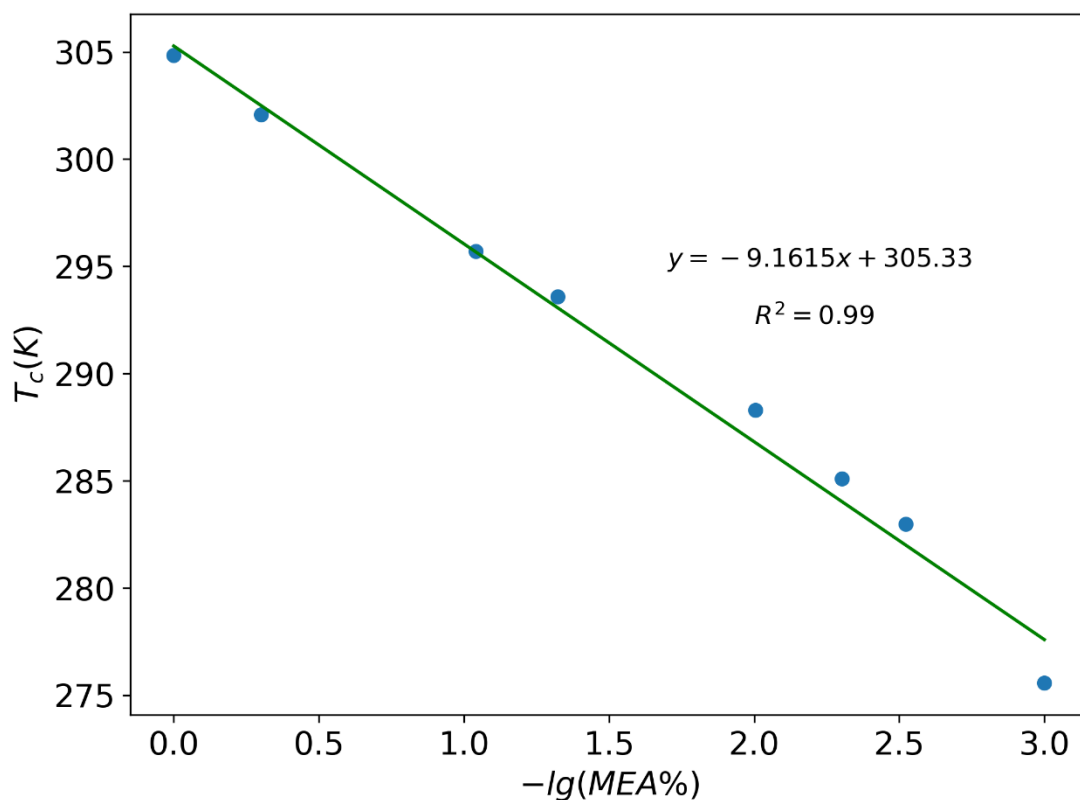


Figure S2. Linear relationships between the transitional temperature of nitric acid condensation ( $T_c$ , defined as the temperature at which the moles of total nitrate in the condensed phases equals to 5% of the initial moles of nitric acid and determined in this study.) and logarithm of MEA mole fraction (mol %) in total moles of RNCs (ammonia and MEA) in the system at 298K. All simulations have the same total moles of RNCs as  $8.86895 \times 10^{-8}$  and the same initial moles of  $HNO_3$  and  $H_2SO_4$  as  $1.11151 \times 10^{-9}$  and  $2.03777 \times 10^{-11}$ , respectively. The system has a fixed initial moles of water vapor as 0.07848 (equivalent to 60% RH at 263.15 K and 101,325 Pa in  $1 \text{ m}^3$ ).

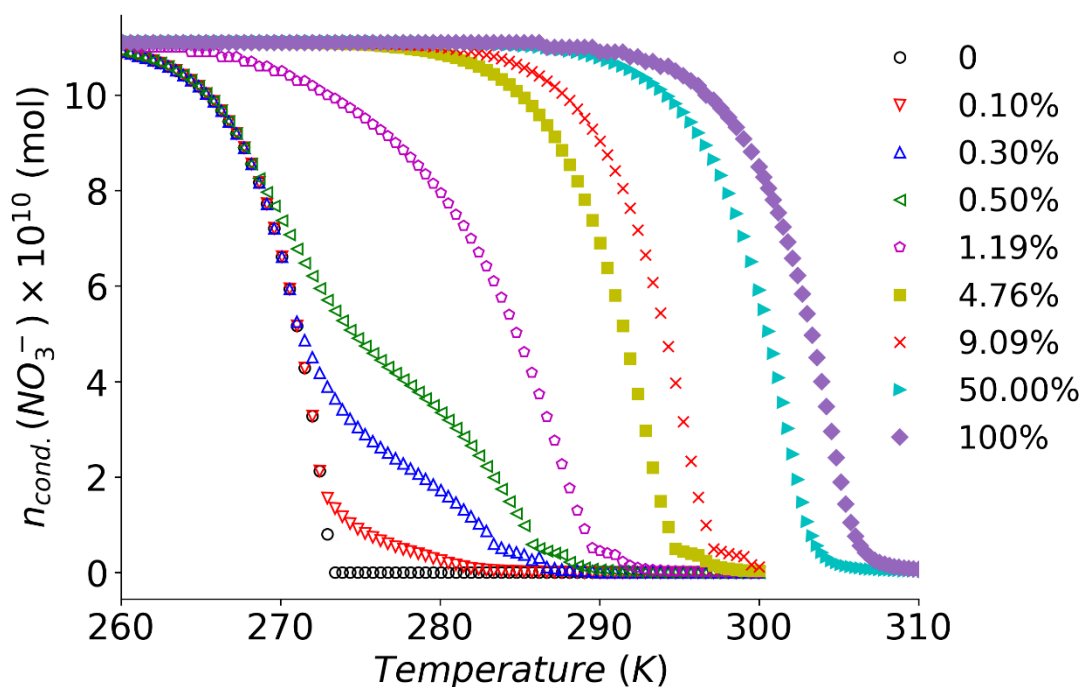


Figure S3. The moles of condensed nitric acid against temperature with different proportion of MEA at varying initial total water in a chemical system of ammonia, MEA, sulfuric acid and nitric acid. All curves have the same total moles of RNCs as  $8.86895 \times 10^{-8}$  and the same initial moles of  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$  as  $1.11151 \times 10^{-9}$  and  $2.03777 \times 10^{-11}$ , respectively. The percentage refers to the mol % of MEA in moles of all RNCs (ammonia and MEA) in the system. For each temperature point, the initial RH of the system was fixed at 60%. When the system temperature increases, the actual total water in the system will increase.

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