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Patterns, oscillations, and microtornadoes:
Extreme events in vapor-to-particle reaction zones

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Abstract

We report on a new set of topochemically organized, nanoparticulate experimental systems in which vapor diffuses and convects to form spatially defined reaction zones. In these zones, a complex sequence of catalyzed proton-transfer, nucleation, growth, aggregation, hydration, charging processes, and turbulence produce rings, tubes, spirals, pulsing crystals, oscillating fronts and patterns such as Liesegang rings. We call these beautiful 3-dimensional structures “microtornadoes,” “microstalagtites,” and “microhurricanes.” We synthesize a proposed mechanism for the chemical reactions and propose ways in which mathematical modeling of the patterns can inform studies of the nature of these extreme events.

Keywords: atmospheric aerosols; proton transfer; nucleation and growth; topochemistry; Liesegang rings

1. Introduction

A wide variety of anthropogenic and natural processes occur by vapor-to-particle transitions. The annual production of engineered nanomaterials (ENM’s) [1] such as titania (TiO$_2$, 6Mt), carbon black (C, 10Mt), silica (SiO$_2$, 1Mt) and many exotic materials for microelectronics is enormous [2]. Combustion of fuels directly produces millions of tons of nanoparticulate soot and fly ash [3] and indirectly forms atmospheric aerosols such as ammonium sulfate, nitrate, and chloride (NH$_4$)$_2$SO$_4$, NH$_4$NO$_3$, NH$_4$Cl respectively). Natural processes include cloud formation, volcanic action, sea spray, and oxidation of volatile organics from plants. Dying stars generate huge amounts of nanoparticulate dust which cycles throughout the universe [4]. Currently there is considerable concern about the effect of terrestrial nanoparticulates on health and the environment, particularly because atmospheric aerosols scatter solar radiation and can modify cloud chemistry and influence climate change [5].

Vapor-to-particle transitions generate very large numbers of very small particles because of the inherent mechanisms involved in the nucleation and growth of the condensed phase. Phase transitions proceed by two consecutive steps, namely nucleation and growth. The nucleation step is the first appearance of molecular clusters of new phase

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such as solid or liquid, and can occur in two ways, homogeneously or heterogeneously. Homogeneous nucleation occurs by random molecular fluctuations which under the system conditions produce clusters of a critical size, which then grow irreversibly. Heterogenous nucleation requires the preexistence of particles (which can be liquid, solid, or ionic) which can catalyze critical cluster formation. The formation of clusters (nuclei) of new phase requires that work be done to create surface, and consequently there is an energy barrier to nucleation. The required thermodynamic “push” to overcome the barrier is experimentally manifest as a required supercooling, superheating, or supersaturation. Post-nucleation growth may take place by simple addition of monomer to a critical cluster or by interaction of critical and postcritical clusters (aggregation, agglomeration, accumulation). The quantitative kinetic theory of nucleation was first developed for homogeneous, homomolecular nucleation of a liquid drop from vapor in one-component systems [6, 7, 8]. The rate equation has the from \( J = A \exp(-\Delta G^*/kT) \), where \( J \) is the number of critical clusters formed in unit volume and time, and \( \Delta G^* \) is the maximum Gibbs free energy barrier:

\[
\Delta G^* = \frac{16\pi\sigma^3M^2}{3(pRT\ln s)^2},
\]

where \( \sigma \) is the interfacial free energy per unit area (surface tension), \( M \) is the molar mass of the nucleated species, \( p \) is the particle density, \( T \) is the absolute temperature, \( R \) is the gas constant, and \( s \) is the supersaturation ratio. It has proven to be more difficult to develop theories of heterogeneous nucleation (even though it is far more prevalent than homogeneous nucleation) because of the problem of quantitatively characterizing the nature of the preexisting catalysts. John Aitken pioneered methods to study the effects of dust on the nucleation of water vapor [9], and his work led C.T.R. Wilson to recognize that ions (generated in the atmosphere by cosmic rays) could nucleate water vapor [10]. Wilson then applied the principle to the design of cloud chambers for use in detecting high energy particles in nuclear physics. Recently, ion-induced nucleation (ions produced artificially by synchrotron beams) of atmospheric aerosol \((\text{NH}_4)_2\text{SO}_4\) has been studied at CERN [11].

Vapor-to-particle nucleation generally produces very small particles which are arbitrarily classified into three broad size ranges, depending on the aerodynamic diameter: ultrafine (Aitkin or nucleation mode) < 0.1 \( \mu m \), fine (accumulation mode) 0.1-2.5 \( \mu m \), and coarse (giant) 2.5-10 \( \mu m \). The form of the relationship between the rate of nucleation and the supersaturation provides insight into the reasons for the very small particle sizes. The crucial experimental parameter is the supersaturation ratio, which is defined as the vapor pressure in the supersaturated vapor at temperature \( T K \) divided by the equilibrium saturated vapor pressure of the liquid at \( T K \). Clearly, high supersaturations (greater than the critical or threshold supersaturation) will generate very large numbers of new nuclei \( J \) very large). Growth rates would then be substantially reduced because the concentration of unnucleated monomers becomes small. Vapor-to-particle transitions can involve very high supersaturations because the equilibrium saturation vapor pressure of the new solid phase is usually very small. Of course, \( J \) depends on the initial vapor concentration ratios, the temperature, and the interfacial free energy per unit area. The problematical feature of the classical theory of homogeneous nucleation is the application of macroscopic particle parameters to nanoscopic entities, particularly \( \sigma \) and \( s \). Many modifications have appeared (and are still appearing!) in the literature in order to extend the theory to the formation of covalent, metallic, and ionic solids, polymers, liquid crystals, and even stardust. As mentioned earlier, heterogeneous nucleation on “foreign” catalysts is best described by dealing with the specifics of a particular catalytic interaction (often very difficult to do).

C.T.R. Wilson was also the first to experimentally produce homogeneous nucleation of water vapor in a cloud chamber. Rapid adiabatic expansion of moist air gave a cloud of droplets even when the air was dust free. In general, traditional nucleation experiments from the vapor state have involved measuring the critical supersaturation needed to produce a specific nucleation rate. More recently, it has become possible to measure actual rates of nucleation and to analyze the size, composition, and stability of critical clusters both experimentally and theoretically. A number of techniques are used, such as expansion cloud chambers, shock tubes, supersonic nozzles diffusion tubes and chambers, and turbulent mixing chambers [12]. Expansion chamber experiments produce short nucleation pulses (< 10 ms) and cannot be used with long-time-lag systems, and if high supersaturations are required the measurements become much more difficult. One of the most common methods is the thermal diffusion chamber, in which a pool of liquid at the bottom of the chamber is heated, and the vapor diffuses up and is cooled at the top of the chamber. Laser light scattering is often used to interrogate the nucleated droplets, and particle counters are used to count the number of particles. A wide variety of pure liquid substances such as alkanes, alcohols, esters, and metals have been studied...
in this way. Most binary chemical reaction systems have been studied by turbulent mixing in which two carrier gas streams containing the reacting vapors are led into a turbulent mixing chamber. Vapor-to-particle processes such as the reaction between ammonia (NH₃) and hydrogen chloride (HCl) to from the aerosol ammonium chloride (NH₄Cl) have been studied with this technique. It is important to note that it is very difficult to observe patterning and periodic behavior in these types of experimental systems. One instance, however, is a report of multiple oscillations in nucleation of methanol in a thermal diffusion chamber [13, 14].

We originally became interested in vapor-to-particle phase transitions because we wanted to introduce more dynamics of phase changes, reactions, and transport into chemistry, engineering, and mathematics courses. One of the classic lecture demonstrations, first described in 1918 [15], and still commonly used, is the counterdiffusion of NH₃(g) and HCl(g) in a long, glass tube. The specific location of the first-formed band of NH₄Cl aerosol is supposed to verify Graham’s Law of Diffusion, being inversely proportional to the square root of the ratio of molar masses of NH₃(g) and HCl(g). If the system is allowed to develop (hours to days), a series of bands are produced, which are described as Liesegang rings (see Fig. 3). The demonstration is controversial and is probably not an example of Graham’s Law (we will report in great detail elsewhere). We carried out a series of careful experiments on the NH₃(g)/HCl(g) and related systems. In the process, we discovered some new and interesting phenomena which led to a paradigm shift in our thinking about the nature of pattern formation in vapor-to-solid particle systems (both experimental and theoretical)

All the systems were allowed to evolve in order to explore possible pattern formation.

Most classical and contemporary Liesegang ring formation experiments have been carried out in condensed phase gel systems in which a more concentrated solution of a reactant is allowed to diffuse into a gel containing a less concentrated second reactant [16, 17]. Over a relatively long period of time (days to months in macroscopic containers), a series of discrete bands of precipitate form. Numerous empirical laws and many theories have been developed to describe the evolution of these pattern-forming reaction-diffusion systems. However, it is interesting to speculate about the nature of the moving reaction zone which produces these rings. A moving zone (whether diffusional or convectional or both) must slow down and/or start and stop again in order to form the first ring (band). After the first ring, there is usually a band with no observable precipitate. This change of motion of the zone constitutes a de facto temporal oscillation, and the frequency of this oscillation should correlate with the average velocity of the zone motion through the system. It is important to note that these temporal oscillations are completely different from the empirical Morse-Pierce scaling law for Liesegang ring patterns, which states that \( x_n^2 \propto t_n \), where \( x_n \) is the position of the \( n \)th band and \( t_n \) is the time of formation. Although no such oscillations have been observed in gel systems, we report in Section 4 on oscillations in the NH₃/HCl system [18].

There have been very few attempts to systematically investigate the spatial (topochemical arrangements) and reactant concentration ratios in vapor-to-particle systems. Studies on the kinetics of NH₄Cl aerosol formation have mainly involved experiments in which small concentrations of NH₃(g) and HCl(g) have been mixed under anhydrous or semianhydrous conditions. The objective of these studies was to measure rates of nucleation and growth and size of nuclei, not pattern formation. We report here on a new set of topochemically organized and patterned nanoparticle experimental systems performed in tubes, boxes, and petri dishes, as illustrated in Fig. 1. In these experiments, vapor diffuses, convects, and reacts in small-scale, spatially confined reaction zones. The particle characteristics, the spatial structures, and the temporal oscillations that form are determined by the modes in which the precursor gases are brought together, by the complex mechanistic sequences of the chemical reactions, and by the reactant concentration ratios. The interaction of moving, defined reaction zones, fast kinetics, exoergicity, charge redistribution, and turbulent jet streaming produce extreme conditions and exotic morphologies. Beautiful three-dimensional structures such as square, circular, and rectangular periodic bands (Fig. 1, T1-T11), tubes and tubes within tubes (Fig. 1, P17), oscillating fronts (Fig. 1, B1), and pulsing crystals form, which we call “microtornadoes,” (Fig. 1, P11) “microgeysers,” (Fig. 1, B2) and “microstalagtites” (Fig. 1, P6, P16) Tornadic structures form as vapors react in hemispherical microzones to give nanoparticulate solids or liquids which are ejected and stream downward in the form of fingered, rotating tubes. Horizontal rotating “hurricanes” can be formed by the strong coupling of large temperature gradients and the aerosol particle exhaust convected from the reaction zones. Reaction...
Fig. 1. Topochemically organized experimental systems in tubes (T), boxes (B), and petri dishes (P), including condensation on petri dish lids (PC). Red, blue, and green respectively denote acids, bases, and aerosol precipitates. T1-T11: NH₃/HCl, NH₃/HNO₃, NH₃/CH₃COOH in various diameter tubes, in various cross sections, e.g. circular, square, rectangular, of various lengths, e.g. 120, 100, 60, 30, 20, 10 cm, and in various materials, e.g. glass, quartz, polycarbonate, polystyrene. T1: > 5 cm diameter. Time sequence showing turbulent overflowing. T2: ≃ 2 cm (ID). Time sequence for NH₃/HCl system showing heterogeneous volume and wall nucleation, onset of homogeneous nucleation, convection cell generation, front motion, and Liesegang ring formation. T3: 0.5 and 1.0 cm diameter, development of reaction zone and subsequent formation of ring pattern. T4: 0.1 cm 1D capillary, formation of NH₄Cl(s) pattern. T1-T4 were carried out in a horizontal tube configuration. T5: NH₃/HCl. Aerosol fingers at reaction front. T6: NH₃/HCl. Liesegang ring formation downwards. T7: NH₃/HCl. Cell pattern instabilities. T8: NH₃/HCl. High aqueous NH₃ concentration. T9: NH₃/HCl. Low aqueous NH₃ concentration. T10: Unstable aerosol falling through rising NH₃(aq). T11: Convective cell front and subsequent pattern formation in the same system as T10 but with acid and base source reversed. All tubes in T5-T11 performed in a vertical mode. B1: Time sequence showing aerosol “tornado” diameter change and oscillating behaviour. B2: Small container (0.4 μL) of aqueous HCl generating a microgeyser convection cell and formation of solid NH₄Cl. PC1: H₂O condensation patterns around acid drops. PC2: H₂O condensation patterns around NH₃ drops. P1-P5: NH₄Cl aerosol tornadoes formed in various topochemical arrangements. P4: microtornado arising at acid source. P5: unstable vertical reaction front of NH₄Cl(aq). P6: Microstalagmite formation in the NH₃/HNO₃ system. P7: Ammonium salt formation on acid source. P8: Ammonium salt formation on NH₃ source. P9: Microtornado formation with NH₃ source at right angle. P10: unstable aerosol system formed over large planar NH₃(aq) source. P11: microhurricane pattern in NH₃/HCl/dry ice (solid CO₂) system. P12: rapid turbulent flow in NH₃/HCl/dry ice system. P13: microcyclone in NH₃/HCl system with a drop of hot H₂O. P14: microanticyclone in NH₃/HCl system with a drop of cold H₂O. P15: microtornado deflection in an external electric field. P16: microstalagmite formation in NH₃/H₂SO₄ system. P17: microtornadoic tubes within larger tubes in NH₃/HNO₃ system. P18: microdrop array of microtornadoes showing tornadoic diameter increasing with increasing distance from the NH₃ source. P20: microstalagmite formation inside microtornadoes in the NH₃/HNO₃ system.
zones can be forced to oscillate as part of a vapor-phase chaotic front or by moving into and out of a condensed phase reactant. The violent, defined motion of the "microgeysers" is generated by low-density, porous aerosols convected upwards by the heat energy released in a very fast crystal lattice formation. "Microstalagtites" result from the complex interactions between vapor base and nonvolatile acid solution drops which produce a series of unusual semifluidic hygroscopic hydrate salts which drop down in string form. We also report on many experiments designed to elucidate the nature of first and subsequent band formation in a variety of chemical vapor reactions. We have also produced the first example of the formation of a defined zone of liquid aerosol of sulfruic acid in a Petri dish (by the same mechanism which can form H$_2$SO$_4$ in the atmosphere).

This paper is organized as follows: Section 2 provides a synthesis of the NH$_3$/HCl reaction mechanism and an overview of topochemical positioning procedures we used in our experiments. Experiments in tubes are described in Sections 3 and 4, and a mathematical model for these experiments is outlined in Section 5. Section 6 describes experiments resulting in "microtornadoes" and other small-scale extreme events.

2. The reactions and topochemical positioning procedures

The vapor-to-particle reactions studied were all gas-phase proton transfer reactions from acids to bases with subsequent formation of a solid (in one case, a liquid aerosol) salt as an aerosol. Reactions between ammonia vapor (NH$_3$(g)) and vapors of hydrogen chloride (HCl(g)), nitric acid ((HNO$_3$(g)), and acetic acid (CH$_3$COOH(g)) and a solution of sulfuric acid (H$_2$SO$_4$(aq)) were carried out. Proton transfer reactions are very common and extremely important in atmospheric, biochemical, biological, and the applied sciences.

The NH$_3$(g)/HCl(g) system represents an excellent example of a proton transfer process and will now be discussed in detail. The reaction of NH$_3$ and HCl in aqueous solution rapidly produces hydrated NH$_4^+$ and Cl$^-$ ions. However, the gas-phase reaction has proven to be controversial. The literature (even back to the 1800's [19]) is replete with numerous conflicting reports about whether the proton transfer can occur in the gas phase [20]. Microwave rotational spectroscopy has clearly shown that transfer does not occur in isolated (NH$_3$)(HCL) heterodimers [21, 22, 23]. The spectra show linear, hydrogen-bonded H$_3$N\cdots HCl complexes. The fact that a white cloud of NH$_4$Cl(s) forms immediately when vapors from open bottles of aqueous NH$_3$ and HCl mix, suggests that other molecules (such as water) play a role. The mechanism may in fact be different under anhydrous or other conditions, such as the presence of excess electrons or an electric field [24, 25]. Recent theoretical work using ab initio density functional theory has shown that 2 or 3 water molecules cluster with an NH$_3$ and an HCl molecule and assist in proton transfer, thus catalyzing the formation of NH$_4^+$ and Cl$^-$ ions [26, 27, 28]. DFT calculations have also been used to analyze the properties of a variety of (NH$_4$Cl)$_n$ clusters, and it has been concluded that homogeneous nucleation of NH$_4$Cl from pure NH$_3$ and HCl gases under strictly anhydrous conditions is possible. Apparently in this case very stable ion pair clusters may be the catalysts [29, 30].

The reaction kinetics of the gas-phase process has been studied under a variety of experimental conditions, in the presence and absence of water, ions, and radicals, in different temperatures, etc. The nucleation in the presence of water vapor was first studied by Twomey [31]. Several studies under anhydrous and pseudooahydrous conditions have been reported. The most complete study was reported by Banic and Iribarne, who varied the partial pressures of NH$_3$, HCl, and H$_2$O and examined the influence of negative and positive ions and radicals, and relative humidity, on the nucleation rate of NH$_4$Cl(s). The products of the reaction were identified by means of a specially designed mass spectrometer. The main conclusions were that chloride ions could catalyze the nucleation of NH$_4$Cl(s) and that the critical cluster was likely (NH$_4$Cl)$_n$Cl$^-$, where $n = 2$ or 3, and that the critical cluster radius was 0.55 nm [32, 33, 34].

2.1. Kinetics and mechanism

The following is a suggested mechanism for the vapor-phase reaction of NH$_3$ and HCl to form aerosol NH$_4$Cl that we have synthesized from the literature. It represents the process as we envisage it under the conditions that we used in all our experiments. The overall process is

\[
\text{NH}_3(g) + \text{HCl}(g) \rightarrow \text{NH}_4\text{Cl}(s).
\]
The first step is a fast, water-catalyzed proton transfer;

\[ \text{NH}_3(g) + \text{HCl}(g) \xrightleftharpoons{\text{H}_2\text{O}} \text{NH}_4^+\text{Cl}^- \cdot \text{nH}_2\text{O}, \quad (n = 2, 3, 4). \]  

This transfer produces an ammonium ion \( \text{NH}_4^+ \) and a \( \text{Cl}^- \) ion. Several studies of the kinetics of \( \text{NH}_4\text{Cl} \) formation under anhydrous conditions have reported values for the rate constant for the forward reaction in a first step. The values have been inconsistent and are smaller than the value that we have used in our model (see later). It should be emphasized that it is highly probable that under anhydrous conditions the first step is different from that when water is present [35, 36, 37, 38]. Water molecules are still prevalent in the cluster. \( \text{Cl}^- \) ions can act as a catalyst to induce nucleation in a charge redistribution followed by stepwise addition of \( \text{HCl} \) and \( \text{NH}_3 \) monomers:

\[
\begin{align*}
\text{Cl}^- + \text{HCl} & \rightarrow \text{Cl}^- \cdot \text{HCl} \\
\text{Cl}^- \cdot \text{HCl} + \text{NH}_3 & \rightarrow \text{Cl}^- \cdot \text{NH}_4\text{Cl} \\
\text{Cl}^- \cdot \text{HCl} \cdot \text{NH}_3 & \rightarrow \text{Cl}^- \cdot (\text{NH}_4\text{Cl})_2 \\
\vdots & \vdots \\
\text{Cl}^- \cdot (\text{NH}_4\text{Cl})_n + \text{HCl} & \rightarrow \text{Cl}^- \cdot \text{HCl} \cdot (\text{NH}_4\text{Cl})_n \\
\text{Cl}^- \cdot \text{HCl} \cdot (\text{NH}_4\text{Cl})_n + \text{NH}_3 & \rightarrow \text{Cl}^- \cdot (\text{NH}_4\text{Cl})_{n+1}
\end{align*}
\]

It should be noted that, although \( \text{H}_2\text{O} \) is a required catalyst for the proton transfer, it is not clear whether the nucleated \( \text{NH}_4\text{Cl} \) clusters still retain it. The \( \text{Cl}^- \) ion produced in the proton transfer step then catalyzes the nucleation step and is therefore an autocatalyst for the overall reaction, and in fact it remains at the core of the nucleated nanoparticle. Growth of the critical cluster then proceeds, and ionically-bonded, macroscopic solid \( \text{NH}_4\text{Cl} \) particles are produced [30]. If the negative charge associated with the core \( \text{Cl}^- \) ion is not neutralized by the adsorption of an \( \text{NH}_4^+ \) ion, the resulting aerosol should be negatively charged. Another mode of charging could occur by collisional triboelectric surface charging. The extent and longevity of the charge will perhaps depend on charge leakage by adsorbed surface water [39, 40]. It is interesting to note that the deliquescence relative humidity (DRH) (at 298K) is 78% for \( \text{NH}_4\text{Cl} \), 62 % for \( \text{NH}_4\text{NO}_3 \), and 36% for \( \text{CH}_3\text{COONH}_4 \) [41]. Clearly, the aerosol surface is wetter when the DRH is smaller.

The kinetics and mechanisms of aerosol formation in other reactions reported in this paper are not as well understood as \( \text{NH}_4\text{Cl} \). However, it is known that proton transfer in the reaction of \( \text{NH}_3 \) with nitric acid (\( \text{HNO}_3 \)) [42, 43] and the reaction of \( \text{NH}_3 \) with acetic acid (\( \text{CH}_3\text{COOH} \)) are both catalyzed by water [44, 45]. The stepwise addition of ammonia and hydrogen chloride proposed in equations (3) is similar to a mechanism recently proposed for the formation of ammonium sulfate based on experiments at CERN [11]. The importance of preeucleation clusters in ion nucleation was anticipated by Castleman, et. al. in the 1970s [46].

### 2.2. Thermodynamics of ammonium chloride aerosol formation

A thermodynamic analysis of the overall reaction (1) provides some interesting insights. All of the steps in the suggested mechanism up to the cumulative ionic bonding in the crystal solid are endoergic [47]. The thermodynamic driving force for the reaction is therefore the lattice energy released in the cumulative combination

\[ \text{NH}_4^+\text{Cl}^- \rightarrow \text{NH}_4\text{Cl}(s). \]  

Note that below 458K, solid \( \text{NH}_4\text{Cl} \) has a CsCl motif. The standard enthalpy changes for reactions required to calculate the standard enthalpy change for the overall process are

\[
\begin{align*}
1. \quad & \frac{1}{2} \text{N}_2(g) + \frac{1}{2} \text{H}_2(g) \rightarrow \text{NH}_3(g), \quad \Delta H^\circ = -45.9 \text{ kJ mol}^{-1} \\
2. \quad & \frac{1}{2} \text{Cl}_2(g) + \frac{1}{2} \text{H}_2(g) \rightarrow \text{HCl}(g), \quad \Delta H^\circ = -92.3 \text{ kJ mol}^{-1} \\
3. \quad & \frac{1}{2} \text{N}_2(g) + 2 \text{H}_2(g) + \frac{1}{2} \text{Cl}_2(g) \rightarrow \text{NH}_4\text{Cl}(g), \quad \Delta H^\circ = -314.6 \text{ kJ mol}^{-1} \\
4. \quad & \text{NH}_4\text{Cl}(s) \rightarrow \text{NH}_4^+(s) + \text{Cl}^-(s), \quad \Delta H^\circ = 697 \text{ kJ mol}^{-1}
\end{align*}
\]

(For values of crystal lattice energies, see [48].) Then, for

\[
5. \quad \text{NH}_3(g) + \text{HCl}(g) \rightarrow \text{NH}_4^+(g) + \text{Cl}^-(g), \quad \Delta H^\circ = 176.4 \text{ kJ mol}^{-1},
\]

\[ \Delta H^\circ = -21 \text{ kJ mol}^{-1}. \]
and therefore, for the overall process,

\[ \text{NH}_3(g) + \text{HCl}(g) \rightarrow \text{NH}_4\text{Cl}(s), \quad \Delta H^\circ = -176.4 \text{ kJ mol}^{-1}. \quad (7) \]

The standard entropy change (\(\Delta S^\circ\)) for the overall reaction is -285.2 J mol\(^{-1}\) K\(^{-1}\), and the standard free energy change (\(\Delta G^\circ\)) is -91.4 kJ mol\(^{-1}\). The overall process is spontaneous, but catalyzed steps are required to form NH\(^+\text{4}(g)\) and Cl\(^{-}\)(g) species.

The energy landscape consists of a series of shallow potential energy wells as each cluster moves downhill to the final solid form. A similar analysis for the overall process

\[ \text{NH}_2(g) + \text{HNO}_3(g) \rightarrow \text{NH}_4\text{NO}_3(s) \quad (8) \]

gives a standard enthalpy change (\(\Delta H^\circ\)) of -185.8 kJ mol\(^{-1}\) for the formation of aerosol ammonium nitrate. Again, we emphasize that the kinetic and thermodynamic analyses presented here were carefully correlated with the experimental conditions used in our work and provide many insights into the experimental observations.

2.3. Experimental Procedure

1. Topochemical positioning. The vapor-to-particle reactions were in all cases carried out in transparent (polystyrene, glass, etc.) containers. Particle formation and reaction zones were identified and tracked by various types of light scattering (incandescent, fluorescent, LED, and blue, red, and green laser sources). Extensive imaging was accomplished by digital video with computer analysis. The reactants were topochemically positioned in such a way as to allow complete control of the reaction location anywhere in the container, and which could be followed for extended periods of time. The position of the reaction zone was controlled by both the individual reactant vapor concentrations and by the binary concentration ratios. All the vapors were produced as volatile species from the appropriate aqueous solutions of reagents. Vapor phase concentrations were carefully calculated from data presented in ICT and NIST reference tables and in research papers [49, 50, 51, 52]. Other vapor phase concentrations were calculated using appropriate diffusional models. Fig. 2 shows some of the configurations of reactant sources that we employed to qualitatively and quantitatively interrogate the spatial and temporal progress of reaction zones and their “exhaust.”

The reactions were carried out at 25°C ± 1°C in a room in which the temperature was carefully controlled. Only light sources with low wattages were employed for light scattering. Mouth masks were used when necessary to avoid heating systems by warm breathed air. It is important to note that it is often rather difficult to start gas-phase reactions in a “clean” manner. However, it became obvious that even after an initial mixing turbulence occurred, steady-state behavior of reaction zones was achieved within 2-3 seconds in closed containers.

3. Counterdiffusional Experiments

3.1. Sequence of nucleation events in counterdiffusional experiments

The counterdiffusional experiments described in this section comprise a summary of over 1500 experiments carried out mostly on the system NH\(_3\)(g) + HCl(g) → NH\(_4\)Cl(s). Aqueous solutions of varying concentrations of NH\(_3\) and HCl (quantitatively analyzed by titration) were pipetted (15mL) into fiberglass-wool plugs placed into a B24 polyethylene hollow cap machined to fit into a 120 cm-long, 2 cm-internal diameter (I.D.) pyrex glass tube. The caps were simultaneously placed onto the ends of the tube, NH\(_3\) at one end, and HCl at the other. The glass tube was held up 20 cm above the bench with two insulated clamps and was checked for horizontality. The NH\(_3\) and HCl vapors were allowed to diffuse. The tube was carefully and continuously examined by means of a He/Ne laser (632.8 nm) and solid-state laser (650 nm), which were swept continuously into the tube. The laser beams were moved so that there was no possibility of local heating. The experiments were carried out in a dark room kept at 25 ± 1°C. A mask was worn over the mouth and nose to avoid inadvertently warming the surface of the tube. The temperature of the NH\(_3\) and HCl solutions were monitored by means of a diode encased in a PTFE sheath. Each experiment at specific concentrations of NH\(_3\) and HCl was repeated a minimum of three times, often as many as five times, and the results were reproducible. The following sequence of phenomena (which has not been observed before this study) was carefully measured with respect to time of occurrence and distance along the tube.
The tube remained completely dark until suddenly a broad zone of individual crystals scattering light could be seen. The number of crystals in the zone was large at higher NH₃ and HCl concentrations and much smaller (almost countable by eye) at lower concentrations. Crystal faces could be seen in the very slowly moving crystals. Almost simultaneously, it was noticed that the walls of the tube slightly changed in appearance, indicating the start of wall nucleation. The length of the zone of crystals was about 2 cm at the highest concentrations, and became longer, to about 15 cm at the lowest concentrations. Then, a peculiar but reproducible phenomenon occurred. After a short time of about 5 seconds at highest concentrations and much longer at lowest concentrations, a completely dark zone formed and slowly enlarged in the middle of the zone of crystals. The dark zone was formed in an axial direction, and it was noted that the crystals did not appear to be moving to the walls of the tube. To calibrate the motion perception of the crystals, the tube was touched (with a finger), and about 5-10 seconds later, the crystals showed local rapid and random motion, which quickly damped. All of the evidence points to this zone as the heterogeneous nucleation of NH₄Cl crystals on dust particle surfaces and tube walls. Experiments conducted at a time when local forest fire smoke was evident in the room air gave such a large number of crystals that the experiment had to be terminated. We suggest that the dark zone in the middle of the heterogeneously nucleated crystals could be an example of thermophoresis of the NH₄Cl crystals caused by the temperature gradient produced by the onset of the second nucleation event described below [53]. It is not clear from the literature how the system’s potential energy decrease in nanoparticle formation is transduced into kinetic energy or into infrared radiation. The very fast kinetics of homogeneous nucleation produces clusters of NH₄Cl which cannot be “seen,” but it must be assumed that there is a very rapid release of energy during these processes ($\Delta H^\circ$ is -176.4 kJ mol⁻¹).

Suddenly, a small patch of light (in the laser beam) appeared in the middle of the dark zone. Individual crystals could not be seen at the beginning. The patch grew, quickly at high concentrations and much more slowly at lower concentrations, and very small crystals could be seen. Quickly an extreme convection event formed. Crystals zoomed downwards on either side of a narrow (1-2mm) dark zone and began to form two beautiful convection cells. At the same time, a transverse observation showed that the reaction zone was moving in a slow, clockwise circular motion.
with a dark zone at the center. These dark zones may be another example of thermophoresis. It should be emphasized that none of the phenomena described could be seen in ordinary room light or in LED or fluorescent light. Eventually, the reaction zone and the associated convection zones could be seen in room light as a collection of white particles moving in a coherent pattern in an axial direction down the tube. The direction and extent of the motion along the tube depended on the ratio of the initial concentrations of NH₃ and HCl. Movement in both directions was observed, and at one ratio of initial concentrations the reaction zone did not move from its initial place of inception. In this event, all the above phenomena appeared on top of each other, and the tube walls were covered with solid NH₄Cl so that viewing was obscured. We suggest that this second nucleation event is homogeneous nucleation of NH₄Cl which occurs in a region of the tube which has been cleared of heterogeneous nucleation catalysts by the prior heterogeneous nucleation event. It must be assumed that both the first and second nucleation events occurred in the presence of water vapor which was codiffusing from the aqueous solutions at both ends of the tube (see the water-catalyzed proton transfer step in the mechanism). The phenomenon of homogeneous nucleation occurring in a region cleared of heterogeneous nucleation catalysts is reminiscent of the drop technique developed by Bernard Vonnegut many years ago [54].

One remarkable aspect of the movement of the structurally very complex zone of particles down the tube was that the central reaction zone (with its associated dark space) remained coherent for days. Eventually a detritus of solid NH₄Cl was deposited mostly on the bottom third of the tube. Some of this deposit was chemically analyzed and found to be pure NH₄Cl. A microscopic examination revealed a mass of aggregated tiny crystals 0.1 μm in diameter. Wall nucleation was detected by simply blowing down the tube at the end of the experiment. Water vapor from breath condensed onto the wall-nucleated NH₄Cl and made it visually obvious.

Quantitative measurement of the time and position of the first (heterogeneous) and second (homogeneous) nucleation events were recorded. Data (at 25°C) for the initial vapor concentrations of NH₃ and HCl over the initial aqueous solutions were calculated as described earlier. The concentrations of the aqueous NH₃ and HCl solutions were analytically checked both before and after each experiment. The initial water vapor concentrations over both the aqueous reagent solutions were also calculated. This was in order to be able to assess the water vapor concentrations in the tube at the position of the first and second nucleation events. Some experiments were videotaped, although it proved to be difficult to image the heterogeneously nucleated crystals as well as the first patch of light from the homogeneous nucleation event because of the extremely low amount of scattered light. Red (632nm and 650nm), green (546nm) and blue (436nm) lasers were all tried, and red light proved to be optimal. The scattered light from the NH₄Cl crystals had a definite angular dependence, being maximally scattered at about 120° [55].

Many other experiments were carried out in which the 120 cm long, 2 cm diameter circular tube was held vertically, and the NH₃ and HCl solutions were variously placed at the top and bottom. With HCl at the bottom (HCl vapor is denser than air) and NH₃ at the top (NH₃ vapor is less dense than air), the results were similar to the horizontal-tube experiments except that the solid NH₄Cl appeared to fall through the reaction zone and cause turbulence. The diameter of the tube was varied from 5 cm down to 0.2 cm. At 5 cm, the system quickly (20 seconds) produced an aerosol over a large volume of the tube as the two vapors flowed over each other and caused a huge convective flow. At tube diameters of 0.6 cm or less, it proved impossible to see all the initial phenomena (first and second nucleation). However, after an initial parabolic shape formed, the reaction zone became a beautiful thin (≈ 1 mm) transverse reaction zone. It seemed that only wall nucleation was occurring in tubes of less than 0.3 cm diameter. Vertical experiments carried out in rectangular tubes of thin cross section (i.e. 100 cm × 15 cm × 0.1 cm) produced some exotic fingering and cell-like patterns at the reaction zone. These experiments will be reported on elsewhere. Numerous experiments were carried out with shorter tubes of circular, square, and rectangular cross section, the smallest being 10 cm × 0.2 cm and 10 cm × 0.1 cm × 0.1 cm. Counterdiffusional experiments in these small tubes were simultaneously carried out in bundles of up to 50 tubes in order to check the reproducibility of the phenomena; see Fig. 3 (a,b). A series of similar counterdiffusional experiments (in 120 cm-long, 2 cm I.D. tubes) have also been carried out on NH₃/NH₄O₃, NH₃/CH₃COOH, NH₃/HI, and NH₃/HBr. Similar phenomena are seen, except that Liesegang rings are not observed in the NH₃/CH₃COOH system.

### 3.2. Liesegang ring patterns in counterdiffusional experiments

Classical Liesegang ring systems are generally not designed as counterdiffusional (see above), and the dynamics of ring formation have seldom been observed experimentally. It is not clear whether these are nucleation events,
heterogeneous or homogeneous, which are distinct from aggregation and other growth events. Post-nucleation processes have also been suggested as being solely responsible for ring formation. We suggest that the counterdiffusional vapor-to-particle systems described in the last section represent an opportunity to analyse the dynamical details of pattern formation. Many of the long-tube (120 cm-long, 2 cm-diameter) experiments were left to proceed for long periods of time after the formation of the first and second nucleation events. In the NH$_3$/HCl system, reproducible patterns of varying degree of complexity are formed, depending on the initial NH$_3$ and HCl concentrations. Here is a brief description of one of the 310 patterned systems we carried out: The experimental procedure described in the last section was followed. In this instance, the reagent solutions were concentrated NH$_3$ (14.6 M) and concentrated HCl (11.81 M). The first and second nucleation events were as described previously. Homogeneous nucleation, seen in NH$_3$ vapor was diffused into a 20 cm-long, 0.6 cm I.D. pyrex tube which already contained an HCl vapor of known concentration. This topochemical configuration of reactants is analogous to typical Liesegang ring experiments, except that the medium was air and not gel. A diagram of the apparatus is shown in Fig. 4.

4. Diffusion of NH$_3$ vapor into a constant concentration of HCl (equilibrated, saturated-vapor experiments)

In order to simplify the NH$_3$/HCl vapor-to-particle dynamical system, we designed a series of experiments in which NH$_3$ vapor was diffused into a 20 cm-long, 0.6 cm I.D. pyrex tube which already contained an HCl vapor of known concentration. This topochemical configuration of reactants is analogous to typical Liesegang ring experiments, except that the medium was air and not gel. A diagram of the apparatus is shown in Fig. 4.

About 200 experiments were completed using various NH$_3$ and HCl concentrations, and in some of these we noticed some very interesting oscillations of the reaction zone. One experiment with 3.00 M NH$_3$ and 11.00 M HCl at 25°C will be described in detail. (Throughout this paper, M means moles·dm$^{-3}$.) The reaction was initialized by withdrawing a teflon spacer to allow NH$_3$ vapor to enter the tube. A thin disk-like zone was formed and moved down the tube. No convection cells were formed, unlike the situation in tubes of larger diameter. The disk zone maintained its coherence, and slowed down as it moved further from the NH$_3$ source. The disk was followed using a sophisticated video system. Astoundingly, it was observed that the disk zone appeared to be oscillating as it moved. The oscillations started at about 3 minutes after initialization, and at 6.7 cm from the NH$_3$ source. As the zone slowed, the frequency of the oscillations decreased, and the amplitude increased. Eventually, the morphology of
the oscillations became irregular and irreproducible, leading to a chaotic interpretation of events. In addition, these spatial oscillations correlate with fluctuations in the scattered white light intensity at the reaction zone front. All of the phenomena were shown to be experimentally reproducible over six separate experiments. A complete analysis with data will be presented elsewhere.

In these experiments in the 20 cm-long 0.6 cm i.d. tubes, no ring patterns were visually observed to be deposited on walls as a result of these oscillations. Calculations show that the high zone velocity, the relatively small number of moles of NH₄Cl solid produced, and the shortness of the tube were all factors that led to extremely small variations in deposit. These latter observations led us to a realization that Liesegang ring patterns are only visually observed (in any system) when the container walls intercept the reaction product formed in a moving zone. Experiments carried out in a 120 cm-long, 0.6 cm i.d. tube with 3.00 M NH₃ and 11.00 M HCl for several hours produce Liesegang rings. Interestingly, a perusal of the hundreds of photographic images of both gel and vapor Liesegang ring systems [56] reveal an enormous variation in the precipitate morphology and a surprising lack of uniformity in where the precipitated material is deposited–at the wall, or across the gel, or both. We have been able to find only one reference in which a careful analysis of a gel Liesegang ring system was carried out before ring formation occurred. Higuchi and Matuura [57] state that “It is obvious from these results that the distribution of concentrations of metal ions of inner electrolyte, i.e. Mg²⁺ and Mn²⁺ becomes periodic if the outer electrolyte diffuses into the gel, until at last the periodic precipitation takes place.” A graph of metal ion concentrations versus distance from origin showed clearly significant spatial oscillations at and in between precipitation bands. Clearly any theory of Liesegang ring formation must be able to predict the oscillatory characteristics displayed in the vapor-to-particle NH₄Cl systems.
5. The reaction zone in a mathematical model

The vast literature on mathematical models for precipitation (Liesegang ring) patterns (for example [58, 59, 60, 61, 62, 63, 64]) has been motivated primarily by patterns forming in gel systems. We take a look in this section on how these models apply to gas-to-vapor systems and how they may be modified based on our synthesized mechanism for reactions such as those in the NH3/HCl system. For reactants A (e.g. HCl) and B (e.g. NH3) and product C (e.g. NH4Cl(g) monomer gas) that may precipitate to form precipitate D (e.g. NH4Cl(s)), models that assume that patterning is the result of prenucleation events (in contrast post-nucleation events such as Ostwald ripening) have the form [58, 59]

$$\frac{\partial a}{\partial t} = D_a \frac{\partial^2 a}{\partial x^2} - kab,$$

$$\frac{\partial b}{\partial t} = D_b \frac{\partial^2 b}{\partial x^2} - kab,$$

$$\frac{\partial c}{\partial t} = D_c \frac{\partial^2 c}{\partial x^2} + kab - f_1(c,d),$$

$$\frac{\partial d}{\partial t} = +f_1(c,d),$$

where \(a(x,t), b(x,t), c(x,t),\) and \(d(x,t)\) are respectively the concentrations of species \(A, B, C\) and \(D\) as functions of position \(x\) (for example, distance along a tube) and time \(t\). Keller and Rubinow [64] propose a model of the form (9), with

$$f_1(c,d) = \begin{cases} 
0, & \text{for } c < c_s(d), \\
-c - c_s, & \text{for } c \geq c_s(d), 
\end{cases} \quad \text{where } c_s(d) = \begin{cases} 
c_1 > 0, & \text{for } d > 0, \\
 c_{ss} > c_s, & \text{for } d = 0.
\end{cases}$$

For the NH3/HCl system, \(c_{ss}\) in (10) would be the threshold value of monomer NH4Cl(g), required before homogeneous nucleation to solid NH4Cl(s) in the absence of any heterogeneous nucleation catalysts (including NH4Cl(s)), and \(c_s\) would be the heterogeneous nucleation threshold for nucleation by NH4Cl(s). Smooth kinetic functions \(f_1(c,d)\) may approximate results given by (10) and be more stable [58, 59]. For example, Scheel, et al. [58, 59] study patterns produced by smooth kinetic functions which approximate (10).

A more general model that incorporates stepwise addition of NH3 and HCl to NH4Cl clusters would allow for reactants \(a\) and \(b\) to react directly with precipitate \(d\):

$$\frac{\partial a}{\partial t} = D_a \frac{\partial^2 a}{\partial x^2} - kab - f_2(a,b,c,d),$$

$$\frac{\partial b}{\partial t} = D_b \frac{\partial^2 b}{\partial x^2} - kab - f_2(a,b,c,d),$$

$$\frac{\partial c}{\partial t} = D_c \frac{\partial^2 c}{\partial x^2} + kab - f_1(c,d) - f_2(a,b,c,d),$$

$$\frac{\partial d}{\partial t} = +f_1(c,d) + f_2(a,b,c,d),$$

where \(f_2(a,b,c,d) = 0\) for \(c < c_s\). The effect of a function \(f_2(a,b,c,d)\) and the potential for such a modified model to yield Liesegang ring patterns that do not obey the classical Morse-Pierce scaling laws as discussed in the Introduction,
but rather Liesegang rings consistent with our experimental data for the NH₃/HCl data, is a subject of current studies. Here, we focus on estimating the kinetic rate constant \( k \) for NH₃/HCl system. This constant has implications for the nature of the reaction zone and the formation of extreme events through large heat production in a small reaction zone if \( k \) and the flux of reactants into the reaction zone are large. Measuring kinetic rate constants for gas-to-particle reactions is experimentally difficult. Rate constants for the formation of NH₄Cl under anhydrous conditions have been reported [36, 65, 66] and disputed. However, these studies assumed a simple mechanistic first step which is probably relatively slow and unrelatable to the mechanism in hydrous conditions. This is in stark contrast to the mechanism that we have synthesized in Section 2 which is catalyzed by water and is the relevant mechanism for our experiments (and atmospheric conditions). No direct experimental determination of the kinetic rate constant \( k \) for the NH₃/HCl system under hydrous conditions is available. Data from the counterdiffusional tube experiment, together with our model, however, can shed some light on this value.

The counterdiffusional experiment in a tube of length \( L \) may be modeled by the system (9) or (11) with the boundary conditions

\[
\begin{align*}
    a(0,t) &= a_0, \quad \frac{\partial a}{\partial x}(L,t) = 0, \\
    \frac{\partial b}{\partial x}(0,t) &= 0, \quad b(L,t) = b_0, \\
    \frac{\partial c}{\partial x}(0,t) &= 0, \quad \frac{\partial c}{\partial x}(L,t) = 0, \\
    \frac{\partial d}{\partial x}(0,t) &= 0, \quad \frac{\partial d}{\partial x}(L,t) = 0,
\end{align*}
\]

and initial conditions

\[
a(x,0) = 0, \quad b(x,0) = 0, \quad c(x,0) = 0, \quad d(x,0) = 0.
\]

Values of the diffusion coefficients for HCl, \( D_a = 0.16 \text{cm}^2/\text{s} \) [67], and NH₃, \( D_b = 0.22 \text{cm}^2/\text{s} \) [68] at 25°C have been experimentally determined: given these values for \( D_a \) and \( D_b \), a reasonable value for the diffusion coefficient of \( \text{NH}_4\text{Cl}_{(g)} \) monomer gas is \( D_c = 0.1 \text{cm}^2/\text{s} \). For large values of \( a_0 \) and \( b_0 \), we may assume that the first, heterogeneous nucleation of the precipitate \( \text{NH}_4\text{Cl}_{(s)} \) does not convert a significant amount of \( \text{NH}_4\text{Cl}_{(g)} \) into precipitate. In this case, the system up to the time of the second, homogeneous nucleation is governed by equations (9) with \( f_1(c,d) = 0 \), so that the only experimentally unknown parameter in the model up to the time of first homogeneous nucleation is the kinetic rate \( k \). We can compare the results of counterdiffusional experiments with the model by noting that the spatial concentration profile of monomer gas \( c(x,t_n) \) at the time \( t_n \) of first homogeneous nucleation should have a maximum value of \( c_{ss} \), located at the position \( x_n \) of first homogeneous nucleation: \( c(x_n,t_n) = c_{ss} \).

In experiments with parameters \( L = 120, a_0 = 164 \text{ mm Hg} \) (the vapor pressure of 11.81 M HCl), and \( b_0 = 103 \text{ mm Hg} \) (the vapor pressure of 5.763 M NH₃), the first homogeneous nucleation occurred at an average (over two trials) position \( x_n = 0.4643 \text{ L} \) from the HCl side of the tube, at an average time of \( t_n = 665 \text{ seconds} \) from the start of the experiment. Values of \( c_{ss} \) and \( x_n \), determined in this manner by the model (9,12,13) with known parameter values corresponding to this experiment and varying values of kinetic rate constant \( k \) are given in Table 1. The model-determined value of \( x_n \) increases up to \( x_n = 0.466 \text{ L} \) as \( k \) increases, with the experimentally determined value being attained at approximately \( k = 10^2 \text{l/(mm Hg \cdot sec)} \). The model-determined value for \( c_{ss} \) at larger values of \( k \) is consistent with experimental data on the homogeneous nucleation threshold for the NH₃/HCl system determined using a cloud chamber method, which indicates that \( c_{ss} \) is of the order of \( 10^{-2} \text{ mm Hg} \) [31]. These data and comparisons with the model therefore suggest that the kinetic rate constant \( k \) for the formation of \( \text{NH}_4\text{Cl} \) for the reaction mechanism we propose in Section 2 is of the order of \( 10^2 \text{l/(mm Hg \cdot sec)} \). Note that such a large value of \( k \) relative to the diffusion constants is also consistent with the very narrow width of the reaction zone observed in counterdiffusional and saturated-vapor tube experiments; for the saturated-vapor tube experiments described in Section 4, this zone (pictured in Fig. 4 (b)) has a width of approximately 0.2 mm. This conclusion can be tested by comparing model and experiment under varying boundary conditions \( a_0,b_0 \) as well as comparing front direction and speeds in the counterdiffusional and saturated-vapor experiments with the model. We will report in detail on such studies (which yield results consistent with what we report here) elsewhere.

The rate at which \( \text{NH}_4\text{Cl}_{(s)} \) is produced in a reaction zone, and therefore the amount of heat generated (see the discussion of the thermodynamics of \( \text{NH}_4\text{Cl}_{(s)} \) formation in Section 2.2), is also a function of the flux of reactants into that reaction zone. The counterdiffusional and saturated-vapor tube experiments complement each other in this regard,
Table 1. Theoretical values of $x_n/L$ and $c_{ss}$ determined by model (9,12,13) for varying values of kinetic rate constant $k$.

<table>
<thead>
<tr>
<th>$k$ (1/(mm Hg · sec))</th>
<th>$x_n/L$ ($L = 120$ cm)</th>
<th>$c_{ss}$ (mm Hg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^{-2}$</td>
<td>0.418</td>
<td>6.84·$10^{-6}$</td>
</tr>
<tr>
<td>$10^{-1}$</td>
<td>0.420</td>
<td>6.77·$10^{-5}$</td>
</tr>
<tr>
<td>$10^0$</td>
<td>0.434</td>
<td>6.21·$10^{-4}$</td>
</tr>
<tr>
<td>$10^1$</td>
<td>0.457</td>
<td>4.24·$10^{-3}$</td>
</tr>
<tr>
<td>$10^2$</td>
<td>0.464</td>
<td>1.25·$10^{-2}$</td>
</tr>
<tr>
<td>$10^3$</td>
<td>0.466</td>
<td>1.92·$10^{-2}$</td>
</tr>
<tr>
<td>$10^4$</td>
<td>0.466</td>
<td>2.28·$10^{-2}$</td>
</tr>
</tbody>
</table>

As the flux into the reaction zone increases over time up to a maximum value for the counterdiffusional experiments but decreases for the saturated-vapor experiments, which are governed by (9,12) together with the initial conditions

$$a(x,0) = a_0, \quad b(x,0) = 0, \quad c(x,0) = 0, \quad d(x,0) = 0.$$  \hspace{1cm} (14)

Concentration profiles $a(x,t)/a_0$ and $b(x,t)/a_0$ at a sequence of times are shown for the model of counterdiffusional experiments in Fig. 5 (a) and for the saturated-vapor experiments in Fig. 5 (b).

Finally, we return to the observation of oscillations in the saturated-vapor experiments. Are such oscillations consistent with the pre-nucleation mechanism proposed by model (9) or model (11)? Simulations of equations (9) with

$$f_1(c,d) = k_2 \left( -\beta \left( \frac{d}{\delta} - \alpha \right) e^{-\frac{d}{\delta}} + \delta d - \gamma + c \right)$$  \hspace{1cm} (15)

do yield oscillations in the position of the reaction zone (as determined by the position where the maximum amount of precipitate is formed) as well as the amount of precipitate being formed. Fig. 6 shows these oscillations in the amount of precipitate being formed in one such simulation with $k_1 = 10^2$, $k_2 = 10^4$, $\alpha = 1$, $\beta = 0.0009$, $\delta = 0.01$, and $\gamma = 0.005$. A period-doubling transition occurs at approximately $t = 0.5$ in the simulation, and integration past time $t = 1$ yields chaotic behaviour. We will report in detail on comparisons of model to data for these oscillations elsewhere. Note that we have neglected, in the basic model presented here, convection resulting from heat generated by the reaction. This is more relevant for tubes of larger diameters.


6.1. Microtornadoes

We discovered a simple, elegant method of generating vapor-to-particle reaction fronts in any position in a container. Small volumes (1 μL - 30 μL) of aqueous reagent solutions (e.g. NH$_3$, HCl, HNO$_3$, CH$_3$COOH, and H$_2$SO$_4$)
of known concentrations were delivered, via calibrated microburets, to a polystyrene or glass surface of a container. The container size was varied from very small (< 1.0 cm³) to fairly large (∼ 250 cm³). Container shape was of cylindrical, square, or rectangular cross sections. Most of the experiments were carried out by dropping drops onto a clean, hydrophobic surface such as a new polystyrene Petri dish. A typical experiment involves placing a 30 μL drop of 6.0 M NH₃ on the bottom of a 10 cm-diameter × 1 cm-tall standard polystyrene Petri dish. A 30 μL drop of 6.0 M HCl is placed on the bottom of the dish. Almost immediately, a thin aerosol forms throughout the dish (and can be seen in a red laser beam) and then a reaction zone forms at a small distance (< 0.1 cm) from the hemispherical drop of HCl. The reaction zone, which appears to self-adjust in position, produces aerosol NH₄Cl(s). The aerosol is subject to gravitational, thermal, and charging forces, and appears to slide down the zone in a turbulent stream. As it falls, it forms a “tube” of aerosol which falls to the bottom of the dish, leaving a single ring of deposit at the surface. If the dish lid is removed for a short period of time, there is immediate turbulence produced. However, when the lid is replaced, the steady-state tornadic structure returns in less than 2-3 seconds. Different phenomena can be produced simply by varying the topochemical relationship and concentrations of the drops of reagent solutions. Fig. 7 shows some examples.

![Fig. 7. Topochemical relationships between drops of NH₃ (blue) and HCl (red) whose vapors react to produce NH₄Cl(s) (green).](image)

Topochemical arrays of reagent drops can be constructed in which the individual binary systems act semiindependently (Fig. 8). Observation at point A shows that the aerosol zone consists of four finger-like aerosol zones rotating around (and off) the HCl drops in a clockwise direction. If the concentrations of reagents are made much smaller (e.g. 0.5 M HCl (on top) and 3.0 M NH₃ (on the bottom of the dish)), the tornado cannot be seen by normal room light, but
can easily be seen in a red laser beam. The tornado direction can be reversed (i.e. with NH$_3$ at the top, and HCl at the bottom) by simply increasing the HCl and lowering the NH$_3$ concentrations. The structural characteristics and morphology of the tornado can vary tremendously, depending on how fast the NH$_4$Cl aerosol is generated at the reaction front. It seems as if all of the possible fluid dynamics structures, such as von Kármán streets and vortices, can form. Of particular interest are the oscillatory effects which can be produced by increasing the HCl and NH$_3$ concentrations. With 10.0 M HCl and 6.0 M NH$_3$, the reaction zone is a long way from the HCl drop (on top), and a diffuse, fingered zone forms. If the reaction is allowed to go for a long time (> 5 minutes), the zone begins to approach the HCl drop, forming Liesegang rings of white NH$_4$Cl on the underside of the lid. This is clearly an example of a vapor-phase titration in which the NH$_3$ vapor is in excess and is depleting the HCl vapor concentration, allowing the zone to move towards the HCl. We observe zone oscillations which occur with the zone outside the HCl drop as a series of smoke shapes (see Fig. 9) in the exhaust (which is not a tornado at this point).
Fig. 10. A time sequence of a “microtornado” experiment. The images show an HCl drop at the bottom of the lid of a polystyrene box. A drop of NH₃ (not shown) is on the floor of the box. The reaction to produce NH₄Cl is occuring just off of the HCl drop. Oscillations in the reaction yield pulses of NH₄Cl(s) aerosol precipitate (one such pulse is shown in the first five panels) and a series of Liesegang rings surrounding the HCl drop (last panel).

a complex dendritic structure at the top of the spike; see Fig. 6.1.

Fig. 11. A time sequence of the formation of a spike of NH₄NO₃ in the reaction of HNO₃ vapor from a source consisting of a drop of 10.0 M NH₄OH at the top of a polystyrene box (shown in the images) and NH₃ vapor from a source consisting of a drop of 9.0 M NH₃ at the bottom of the box (not shown).

The combination of NH₃ vapor with acetic acid (CH₃COOH, a weak organic acid) produced a tornado with a very different appearance. The ammonium acetate, CH₃COONH₄ formed in the reaction zone has a deliquescent relative humidity of about 40% DRH, and apparently there is enough water vapor to adsorb to the aerosol surface and dissolve the salt, forming aqueous solution droplets with a density much larger than the NH₄Cl aerosols. The formation of aerosol sulfuric acid is another interesting system which also produces dense liquid droplets which collectively look like a “shower” of liquid particles rather than the tornado shapes shown earlier. We were able to achieve a liquid sulfuric acid (H₂SO₄) aerosol by generating sulphur dioxide (SO₂) and diffusing the vapor to a reaction zone with vapor of hydrogen peroxide from a 10% V/V drop of aqueous hydrogen peroxide. The SO₂ was generated in the container by adding a drop of 1.0 M H₂SO₄ to one drop of 0.50 M Na₂SO₃.

Fig. 12. A topochemical drop arrangement giving rise to liquid aerosol formation via reactions (16). Drops of H₂O₂ (red) and Na₂SO₃ (blue) are vapor sources, leading to the formation of SO₂(g) (grey), H₂O₂(g) (green) and liquid H₂SO₄(l) (purple).

The reactions are

\[
\begin{align*}
\text{Na}_2\text{SO}_3 + \text{H}_2\text{SO}_4 & \longrightarrow \text{SO}_2(g) + \text{Na}_2\text{SO}_4 + \text{H}_2\text{O} \\
\text{SO}_2(g) + \text{H}_2\text{O}_2(g) & \longrightarrow \text{SO}_3(g) + \text{H}_2\text{O}(g) \\
\text{SO}_3(g) + \text{H}_2\text{O}(g) & \longrightarrow \text{H}_2\text{SO}_4(l) \quad \text{(liquid aerosol)}
\end{align*}
\]

(16)
The tiny droplets of liquid aerosol H$_2$SO$_4$ can be seen easily in a red laser beam.

A superposition of a temperature gradient on a tornadic structure can produce some very exotic patterns. Microscale cyclone and anticyclone convection cells be be set up, and easily observed with a red laser beam, by simply placing a drop of ice-cold water or a drop of hot water (≈ 70°C) into a dish in which a tornado is present. We are currently developing this as part of a small-scale sustainable science course on atmospheric chemistry, physics, fluid dynamics, and climate change. A very large temperature gradient can be obtained by placing a small piece (≈ 0.5 cm) of dry ice (solid CO$_2$) into a Petri dish containing a tornado. In certain positions of the dry ice in relation to the drops of NH$_3$ and HCl, the tornado becomes a horizontally swirling “microhurricane”. One unique phenomenon occurs upon placement of the dry ice and reagents as shown in Fig. 13 (a). Bent tornadoes were formed at all three HCl drops, but an amazing pattern of a set of 15 rings appears in the larger-diameter tube of the tornado formed under drop 3 of HCl. It is tempting to speculate that this is the first example of vapor-phase Liesegang rings! Fig. 13 (b) shows an example of vapor-phase Liesegang rings in the exhaust of a microtornado experiment.

![Fig. 13. (a) The experimental setup for bent tornadoes: Red, respectively blue dots represent drops of 6 M HCl, respectively 6 M NH$_3$, and the rectangular shape represents a block of dry ice. (b) A schematic diagram of vapor-phase Liesegang rings.](image)

We have recently carried out many experiments in which we cut out various small shapes of Whatman 3M filter paper (such as circles, squares, and stars). The experiments on “microtornadoes” were repeated with one of the reagents dropped onto the paper which were glued to the bottom of the dish lid. Very interestingly shaped “microtornadoes” with different cross sections were produced.

### 6.2. Microstalagtites

“Microstalagtites” and other interesting morphologies are produced when NH$_3$ is diffused into drops of aqueous sulfuric acid solution. All attempts to produce “microtornadoes” with NH$_3$ and H$_2$SO$_4$ failed, presumably because of the extraordinarily low vapor pressure of aqueous solutions of H$_2$SO$_4$ (at 25°C, ≈ 10$^{-5}$ mmHg). A fascinating sequence of events, however, occurs in the array system shown in Fig. 14. 30 μL drops of 10M, 5M, 2M, 1M and 0.5M H$_2$SO$_4$ were placed 1 cm apart on the bottom of the Petri dish lid. 4 × 3 drops of 8 M NH$_3$ were placed on the bottom of the dish. The lid was inverted very carefully (so that the drops did not slide) and placed on the bottom. Nothing visually happened until 30 seconds, when a MELC showed significant heating in the H$_2$SO$_4$ drops. A halo then formed around the 1M H$_2$SO$_4$ drop, and then around the 2M H$_2$SO$_4$ drop. These haloes grew and ran around the areas of the 5M and 10M H$_2$SO$_4$ drops. However, very quickly the areas around the 5 and 10 M drops grew to be clear and completely transparent. The 10M H$_2$SO$_4$ drop began a pulsing motion and occasionally the drop shrank and expanded as the hemispherical surface layer seethed. One or two small crystals appeared and moved around. After about 5 minutes, the 10M drop looked like a wet semisolid and then went into the following strange sequence of events: The semisolid drop began to elongate and suddenly dropped as if on a rubber band while remaining attached to the solid above. The end bulged and flattened, and the whole structure oscillated up and down and stopped just before it hit the drops of NH$_3$ on the bottom of the dish. Slowly, the string column thinned and twisted helically and then lost its definition and eventually became a crystalized solid at the top. These events are illustrated in Fig. 14. The sequence from panels 1 to 4 took about an hour, and from 5 to 9 took about 20 seconds. The experiment is
reproducible! This complex sequence clearly involves the formation of a large amount of heat energy from the heat of neutralization of the $\text{H}_2\text{SO}_4$ by $\text{NH}_3$, and there are probably a large number of hydrate and ammoniate salts such as letovicite ($\text{NH}_4\text{H}_2\text{SO}_4$) being produced. The molar volume and viscosity of these various species must be changing dramatically as the reaction proceeds through to ammonium sulfate (panel 10), ($\text{NH}_3$)$_2\text{SO}_4$.

6.3. Experiments with synthetic 2-dimensional clouds

2-dimensional clouds of condensed water are easily made by placing the lid of a polystyrene Petri dish over a styrofoam coffee cup about 3/4 full of $\approx 70^\circ\text{C}$ warm water. A cloud of condensed water drops $< 1\mu\text{m}$ in diameter is formed on the bottom of the Petri dish lid. If the lid (with cloud) is placed on a bottom with 2 or 3 crops of water in it, then the cloud will stay for > 20 minutes. If the cloud is exposed to air, evaporation occurs in about 10 seconds. Very interesting patterns form and disappear if drops of different acids, such as 6M HCl, 4M HNO$_3$, or 2M H$_2$SO$_4$ are placed on the bottom of a Petri dish lid. The lid is then inverted and placed onto the coffee containing warm water. The pattern around each drop is completely different. That is, rings of different size droplets (with different spectral colors of blue, red, brown, and yellow) form around the 6M HCl. A clear, transparent area forms around the 2M H$_2$SO$_4$. We are currently continuing these experiments and trying to rationalize the pattern formation. We believe that we are forming a series of evolving vapor-to-liquid Liesegang ring systems which are really occurring in microdiffusion chambers.

6.4. “Antigravity” vapor-to-particle systems: “Microgeysers”

A topochemical arrangement in which $\text{NH}_3$ and acid solution drops were both placed, at varying distances apart, at the bottom of a container produced an interesting set of morphologies. If a drop of $\text{NH}_3$ solution (14.8M) and a drop of HCl solution (11.8M) are placed about 1 cm apart, an instantaneous cloud of $\text{NH}_4\text{Cl}$ aerosol is produced throughout the dish. Then, a rising tornado over the HCl drop, which quickly collapses as a sheath of solid $\text{NH}_4\text{Cl}$ is formed at and around the base of the drop of HCl. An experiment in which we placed these concentration $\text{NH}_3$ and HCl solutions into single wells (0.4 cm$^3$ well from a 1 × 12 microwell strip) about 3 cm apart and placed the strip into a 10 × 5 × 5 cm rectangular polystyrene container produced a spectacular (not as micro!) “microgeyser” shooting upwards for 7 cm from the mouth of the well containing concentrated HCl. Solid $\text{NH}_4\text{Cl}$ built up at the HCl wall and slowly closed the opening at the mouth of the well as the microgeyser began to narrow until a thin (about 1 mm-wide) vertical stream of about 5 cm high was left. As the gap closed, interesting solid shapes formed at the mouth of the HCl well. The lid was removed from the 10 × 5 × 5 cm container, and the open side was fitted with a polyethylene curtain side (in the vertical direction) in order to allow for observation of the microgeyser system with and infrared camera (FLIR i7). As the solutions were dropped into the wells and placed into the box, it was immediately noticed that each of the solutions had cooled about 2 – 3$^\circ\text{C}$ (evaporative cooling), and it became clear from the infrared radiation emanating from the microgeyser that the aerosol was emitting heat energy. The process was, in fact, an extreme, defined rising convection cell driven by the heat energy generated in the overall reaction $\text{NH}_3(g) + \text{HCl}(g) \rightarrow \text{NH}_4\text{Cl}(s)$ ($\Delta H^\circ = -176.4 \text{kJ mol}^{-1}$). A similar experiment carried out with concentrated $\text{NH}_3$ and HNO$_3$ solutions did not produce a geyser! The $\Delta H^\circ$ for $\text{NH}_3(g) + \text{HNO}_3(g) \rightarrow \text{NH}_4\text{NO}_3(s)$ is -185.8 kJ mol$^{-1}$, so the lack of a thermally driven convection cell must be due to the small vapor pressure of concentrated HNO$_3$ at 25$^\circ\text{C}$ (about 6 mm Hg).
7. Conclusions and discussion

7.1. Organizing principles

In this study, we have begun to unravel some of the complex factors that interact temporally and spatially to generate a great variety of structures and patterns in vapor-to-particle systems. Two aspects have proven to be powerful organizing principles in exploring and explaining the evolution of patterns: first, the remarkably simple experimental design which allowed for topochemical positioning of vapor sources and confined reaction zones; and secondly, the unique characteristics of the aerosol-forming process and product in the NH$_3$/HCl/NH$_4$Cl system. Surprisingly, there has been little rational exploration of the role of container size, shape, and material properties in Liesegang ring systems. The very name implies a particular mode of arrangement of reacting species and a specific container shape. The traditional tubular gel systems actually produce disks, whereas the original experiments (by Liesegang) produced rings and spirals [56]. Most of the studies of Liesegang ring formation in the NH$_3$/HCl system reported in the literature have been carried out in circular cross-section tubes in a horizontal position. In the tubular counterdiffusional experiments we report here, we discovered that the observational clarity and the fortuitous fluid dynamics in long, 2cm-diameter pyrex glass tubes allowed for a detailed analysis of the evolution of pattern formation. The NH$_3$/HCl system developed a sequence of heterogeneous volume and wall nucleation followed by a thermophoretic separation and a “burst” of homogeneous nucleation. The reaction zone enlarged, and local heat energy release drove two jets of streaming aerosol particles separated by a narrow, transverse, dark thermophoretic zone. Two convectional cells set up, one upstream, and one downstream. The reaction zone and cells began to move, depositing a smooth continuous precipitate more prevalent on the lower part of the tube. After a short time (≃15-30 minutes, depending on the reactant concentrations), discrete bands of deposited NH$_4$Cl formed. These bands (rings) were relatively uniform around the tube wall and were tilted at an angle (away from the ammonia source) which depended on the concentration of ammonia (maximum approximately 10°). The band pattern appeared to form as the moving zone slowed and/or stopped and then resumed. Remarkably, this behavior of the reaction zone was coherent for a long time (hours to days) even though it was embedded in two large, moving convection cells.

Experiments in 20 cm-long, 0.6 cm-diameter pyrex tubes in which NH$_3$ is diffused into a constant HCl concentration allowed us to construct a vapor-to-particle system analogous to the traditional Liesegang ring systems. This experimental container and topochemical positioning produced a reproducible, thin, white disk moving along the tube. In the first 15 seconds after the initial entrance of NH$_3$ vapor, a white zone with a parabolic flow profile formed. The profile quickly became vertical, and as the zone (about 0.5 cm) moved down the tube, the zone width decreased rapidly to the consistent 0.02 cm disk that made oscillations visible and enabled quantitative analysis. We interpret this sequence as follows: The parabolic profile is expected when the initial flux of NH$_3$ is so large that the rate of wall nucleation can only deplete the NH$_3$ at the wall surface. Adsorbed HCl on the glass wall acts as a reactant sink. The rate of wall nucleation is so much slower than the diffusional movement of NH$_3$ during the interval that a visible parabolic profile develops. As the flux of NH$_3$ decreases rapidly, the zone speed decreases, which allows wall nucleation to catch up. As the zone slows, nucleation and/or growth deplete “NH$_4$Cl monomers” in the wide zone, and it narrows. The zone still moves towards the HCl, so it appears as if the trailing edge of the zone catches up with
the leading edge. As the flux of \( \text{NH}_3 \) decreases, homogeneous nucleation becomes the dominant process as it marks the leading edge of the 0.02 cm zone. As the flux decreases still further, spatial oscillations occur as homogeneous nucleation supercedes the location of the visible zone to create a new zone.

The various microstructures that we report are topochemically shaped by the diffusion-reaction-convection interactions which are arranged in small-scale zones close to one of the reactant sources. The resulting aerosol field is then organized by gravitational, convectional, or charging forces. Accessing instability regions is accomplished by varying the initial boundary concentrations and concentration ratios and/or by allowing a temporarily continuous gas-phase “titration” of one of the reactions to occur. This “titration” process has demonstrated that it is possible to sweep through all of the evolutionary stages of pattern formation in one simple experiment. With hemispherical cap drops of \( \text{NH}_3 \) and HCl (on top) solutions in a 3 \( \times \) 5 \( \times \) 5 cm polystyrene box, the following sequence is observed: First, at the top (with a drop of HCl on the underside) is placed on the box, a turbulent container-wide “smoke” of NH\(_4\)Cl aerosol forms by heterogeneous nucleation. Then, as the \( \text{NH}_3 \) flux drives upwards, a hemispherical reaction zone of homogeneous nucleation moves towards the roof. As it does so, the edges of the zone are intercepted by the roof plane, and a set of Liesegang rings form as the zone moves in on the HCl drop. As the zone approaches the HCl, a tubular “microtornado” forms, which slowly diminishes in diameter as the zone becomes steady state. An oscillatory mode, producing “pulses” of aerosol is established. The number and frequency of pulses is determined by the initial \( \text{NH}_3 \) and HCl concentrations. The \( \text{NH}_3 \) flux pushes the reaction zone across the vapor-liquid interface and into the condensed phase. The “microtornado” ceases. Finally, as the reaction in the HCl drop produces a sufficient temperature rise (from the heat of reaction) to increase the vapor pressure of the HCl, the zone is forced out of the drop, and a new “microtornado” ensues.

Another interesting topochemical mode is that the binary reactants may be arranged in arrays in which multipositional and multifractional parameters can be explored and real solutions to extremely complex diffusional and convectional problems can be found. We have also discovered that all of these pattern-forming systems can be scaled in size, and we have designed and built a new compound microscope setup to explore vapor-to-particle systems confined in very small dimensions. The effect of externally imposed vibrations on pattern-forming processes will also be examined. We have been able to carry out hundreds of individual simultaneous Liesegang ring experiments by bundling capillary (0.1 cm) tubes and allowing \( \text{NH}_3 \) and HCl to counterdiffuse. Recent literature reports on confinement of nucleation and growth processes have shown interesting results in theoretical, chemical, physical, industrial, and biological systems [56, 70, 71, 72, 73].

One interesting aspect of our studies are the dramatic differences observed in the morphological structures produced when the system products from chemical reactions and mass and energy transfer interact or are intercepted by various boundaries, such as container walls. Phenomenologically, the clearest example of this behavior is the influence of the size and shape of containers on the counterdiffusional \( \text{NH}_3 / \text{HCl} / \text{NH}_4\text{Cl} \) system. The formation of aerosol \( \text{NH}_4\text{Cl} \) by a vapor-to-particle transition involves a significant rapid energy release in a small-scale gas phase environment. Any oscillatory reaction kinetics will necessarily lead to significant periodic variations in both mass of the solid product phase and in the subsequent mass and energy transfer processes. These simultaneous energy transfers can generate large temperature gradients and radiation fluxes which are juxtaposed with the formation of particles with high Schmidt numbers. Complex, extreme mass transfer events ensue. The particle motion is visualized by the ideal self-sensor \( \text{NH}_4\text{Cl} \) aerosol and includes strong jet streaming, complex convection cell formation, fingering, von Kármán streets, thermophoresis and IR photophoresis. The coupled mass and energy output in the “exhaust” reaches spatial regions which are almost at equilibrium and eventually encounters late thermal mass walls of containers. The movement of reaction zones superimposed on the particular depositional characteristics of particulate \( \text{NH}_4\text{Cl} \) on walls ultimately generate the amazing variety of structures we report.

### 7.2. Characteristics of the typical vapor-to-particle aerosol systems

I. M. Kennedy, et. al., in four insightful papers [74, 75, 76, 77] have used an isothermal stagnation flow reaction chamber, an axi-symmetric co-flow jet system, and a wind-tunnel flow apparatus to examine the effect of flow and turbulence on particle formation in the \( \text{NH}_3 / \text{HCl} / \text{NH}_4\text{Cl} \) reaction. Numerical simulations of the nucleation kinetics of \( \text{NH}_4\text{Cl} \) showed that aerosol formation responded sensitively to the Damköhler number. Another important conclusion was that the \( \text{NH}_3 / \text{HCl} / \text{NH}_4\text{Cl} \) system is an excellent choice when studying models of chemically reacting turbulent...
flows for several reasons: 1. The aerosol particle diameter remains effectively constant at different strain rates, and light scattering gives good information about the number concentration of product. 2. The reaction is relatively slow and is therefore useful to study the interaction of turbulence and chemical reaction in non-premixing flow. 3. The small size of the particles indicates that the particles faithfully follow the convective motion of turbulent flow. 4. The particles do not spread out via diffusion due to their large Schmidt number. We have been able to take advantage of all of these system characteristics in designing and analyzing pattern-forming processes. Note that Falkovich, et. al. have shown that the structure of turbulent fields plays an important role in accelerating the formation of large rain-inducing droplets initiated by homogeneous nucleation [78].

All of the NH₃ and HCl (and other acid) sources in our experiments were aqueous solutions. The presence of and concentration of water vapor is regarded as being critical to the rate of proton transfer from HCl to NH₃ in the first elementary step of the reaction mechanism. In fact, this catalytic effect is central to our use of rate constants which considerably exceed those reported in the literature for the reaction carried out in anhydrous and pseudoanhydrous conditions. However, the fate of the clustered water remains unclear. The water molecules that assist in the gas-phase proton transfer are likely to hydrate the ions (NH₄⁺ and Cl⁻) formed in the transfer and would accompany the clusters through the ion-induced nucleation steps. One of the most important, and problematical, parameters in the classical theory of nucleation is the interface free energy per unit surface area (surface tension). Clearly, the nature of clusters through the ion-induced nucleation steps. One of the most important, and problematical, parameters in the classical theory of nucleation is the interface free energy per unit surface area (surface tension). Clearly, the nature of the interfaceal region (between the old and new phases) is highly modified by the presence of water molecules. All of the theoretical calculations show considerable stability for these entities—in fact, the water may be regarded as a “solvent” for the ions. It is interesting to note in this context that the deliquescence relative humidity (DRH) for macroscopic NH₄Cl is 78%, and at relative humidities below this, the surface should not be hygroscopic. However, DRH is an equilibrium parameter, and nucleating clusters are certainly not at equilibrium. Our studies on NH₄/HNO₃ and NH₄/CH₃COH vapor-to-particle transitions show some important differences, in spite of the fact that these proton transfer processes are also catalyzed by water molecules. The DRH values for NH₄NO₃ and CH₃COONH₄ are 62% and 36% respectively. The nucleation of ammonium acetate aerosols clearly shows that very hygroscopic (indeed, wet) crystals are formed, and in counterdiffusional experiments, this system does not form Liesegang rings. Our experimental observation (by laser-light scattering) of both heterogeneously and late-stage homogeneously nucleated NH₄Cl clearly showed distinct crystalline faces which might indicate no absorbed water. Perhaps the temperature rise which is associated with the overall reaction NH₃(g) + HCl(g) → NH₄Cl(s) drives the water into the surrounding gas phase.

In a density and electron microscopy study of submicron NH₄Cl particles formed in a turbulent mixing reactor, Peters et. al. [79, 80] observed that the particles had only about one tenth of the density (0.146 g/cm³) of macroscopic crystals (1.53 g/cm³). Micrographs of particles formed at 10% relative humidity showed remarkable porosity, whereas particles produced under anhydrous conditions were far less porous. It is tempting to suggest that water molecules in clusters stay at the surface of NH₄Cl and “cement” the nanoparticles together, forming a highly porous mass. Other factors, such as temperature variation of adhesion (NH₄Cl sublimes!) and/or electrostatic charging could also play a role.

Another factor which certainly plays a role in the nucleation process (and in postnucleation) is the enthalpy change for the spontaneous overall reaction 7. Nucleation is a very nonlinear process with respect to the difference in chemical potential between old (vapor) and new (solid) phases, and heat exchange and mass transfer are intimately coupled. Theories of nonisothermal nucleation have shown that these rates are 20% of the isothermal rates [81]. A recent mesoscopic nonequilibrium thermodynamic approach emphasizing measurable heat effects has shown only small differences [82]. In most of our experiments, the heat energy released produced thermophoretic effects and extreme jet turbulent behaviour which led to interesting modes of kinetic energy dissipation. It seems that the thermal characterististics of nanoparticles and aerosols are very unusual.

Finally, we note that all of the aerosol systems that we examined produced charged particles. Many of the containers we used were made of polystyrene, and even though this material is almost in the center of the triboelectric series, these containers are insulating; they are, in fact, inside-out Faraday cages. The microstructures were extremely susceptible to external static fields. We intend to build an apparatus to study the mechanism and scale of charging.

The experimental systems reported in this paper probe complex proton- and electron-transfer, nucleation, growth, aggregation, and charging processes in chemical reactions producing atmospheric aerosols and small-scale extreme events. The approach of using simple experimental apparatus follows in the tradition of Raphael Eduard Liesegang.
My father’s life-long dislike of machinery struck home; I did not want any apparatus. A couple of glass plates, some test tubes, and a few dishes were all I needed. I am glad that I never had to teach; it allowed me to remain a student all my life.

In the course of demonstrating many of the microstructures described in this paper we found that almost everyone from elementary school students to research faculty were enchanted with the dynamics of these systems. We are incorporating these processes into a new learning system called Small-Scale Sustainable Science (S4) in which we fuse together theory and practice, mathematics and science. We have designed modular learning units on atmospheric science, atmospheric air pollution chemistry, cloud physics and chemistry, weather science, climate change, heat transfer, and fluid dynamics, etc. which are suitable at all levels. S4 is a low cost, high-tech, way to get students totally engaged in doing science and mathematics. Students who have the opportunity to explore extreme events using the simple experiments reported in this paper also follow a rich tradition: aerosol ammonium chloride was useful to Michael Faraday [83] and John Tyndall [84], and was one of Isaac Newton’s favorite chemicals [85].

Fig. 16. The alchemical symbol for ammonium chloride, NH₄Cl.

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