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THE ROLE OF SOOT IN TRANSPORT OF
HYDROGEN CHLORIDE FROM FIRES

J. P. Stone, et al

Naval Research Laboratory
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) As predicted by E.A. Ramskill at NRL, soot has been shown to transport HCl in fires of polyvinyl chloride and polyethylene, but less HCl is carried by the soot particles than Ramskill predicted. A nitrogen gas purge of the soot easily removes 19 milligrams of HCl per gram of soot, whereas 23 milligrams of chlorine, tightly bound, remains. The spherical, amorphous soot particles formed in the combustion vary in size from 0.03 to 0.11 microns. Simple agglomeration theory suggests that the clusters grow rapidly but remain below 2.5 microns in diameter for an hour. We estimate that, when exposed to this dense smoke (1.57		

20. Abstract (cont.)

grams/cubic meter) for 1 hour, a man would retain in his lungs 36 milligrams of easily removed HCl. Our work implies the importance of water in transport of HCl by soot. In the last section of the report, we discuss implications for future work.

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THE ROLE OF SOOT IN TRANSPORT OF HYDROGEN CHLORIDE FROM FIRES

INTRODUCTION

Toxic gases and smokes are hazardous products of fire. In confined spaces on ships these products accumulate to limit visibility and produce dangerous atmospheres, particularly if ventilation is poor. Dense smokes and deadly gases create problems not only for those who want to escape fire areas but also for firefighters who want to approach fire areas. Below decks such conditions have long harassed the Navy. Introduction of man-made polymers into construction and fitting of ships complicates these conditions further. Although the new polymeric materials are attractive and can be made "fire retardant," little is known of their burning properties, combustion and pyrolysis products, or toxic potentials. Recent naval fire experience implies that special fire hazards result from combustion of certain of these new materials.

To investigate these implications, the Navy has sponsored research typified by the following studies:

1. A survey by NRL of toxic and fire hazards on ships [1], as requested by the Chief of Naval Research following the fire on the USS *Forrestal* (CVA-59) in 1967.
2. A fire-risk criteria study of polymeric materials sponsored by NAVSEC and conducted by the Fire Research Section of the National Bureau of Standards [2]. Selected ship materials (such as deck coverings, insulations, and paints) were tested for ignition, flame spread, heat generation, and smoke generation. Establishing practical, meaningful tests and performance standards to implement discrete selection of ship materials was a goal in this study.
3. A toxicology study conducted by the Navy Toxicology Unit of the National Naval Medical Center [3,4]. Laboratory animals, including subhuman primates, were exposed to carbon monoxide and to mixtures of carbon monoxide and other likely fire gases. Information was sought on effects these added gases had on the acute toxicity of carbon monoxide to the animals. Carbon tetrachloride and benzene were additive rather than synergistic in their effects.
4. A scrutiny of naval fire problems conducted by the Advanced Technical Objectives Working Group (ATOWG) for Fire Research. Composed mostly of scientists and engineers from naval laboratories, this interdisciplinary group initiates, encourages, and supports concepts for better description, communication, and solution of naval fire problems. As its annual report for fiscal 1973 shows, the group is involved in a variety of activities [5]. For example, it has sponsored contracts for feasibility studies of design changes in ship ventilation for the purpose of controlling smoke during a fire and of

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of design changes in ship structure for the purpose of creating fire integrity zones during a fire. It has recognized how pressing the problem of obscuration of vision by "smoke" is to those who fight fires or who seek to escape fires. It has emphasized the importance of the scaling or modeling of fires, a subject basic for relating test fires to real fires, and accordingly, it sponsors such research at two universities. An important function has been communication. It acts as a direct link not only between its members but also between the fleet and the research community. In addition, it has participated in the educational process, as evidenced by (a) a presentation before the National Academy of Sciences [6]; (b) its efforts to establish fire-related short courses on both the East and West Coasts; and, (c) production of a popular, award-winning training film entitled, *Man from LOX*.

In recent years, civil fire research has gained in attention, and study of polymer combustion and combustion products is increasing. Undoubtedly, legislation has played a role in this increase. Since the Flammable Fabrics Act of 1953 and its amendment, Public Law 90-189, standards have resulted for flammability of children's sleepwear as well as for carpets [7], and standards for mattresses and blankets are expected to follow. In smoke studies, recent evidence implies that smoke and toxic gas hazards exceed the peril of uncontrolled fire [8]. And now, loss of vision in civil fires is recognized as a major cause of fire casualties. According to Hoffman [9], significant advances in kinetics relating to fire problems are emerging. The increased interest and activity is further evidenced in the sixth edition of the *Directory of Fire Research in the United States* [10], as it also is in *Fire Research Abstracts and Reviews* [11]. And finally, the report of the National Commission on Fire Prevention and Control, "America Burning," [12], clearly focuses the nation's fire problem and recommends actions for dealing with it.

Our research is directed toward understanding the nature and amounts of products from confined-space fires and the effect combustion conditions have on these products. Both gas-phase and aerosol studies of the products are used. In this report, a soot aerosol study is described. The study tests certain necessary conditions of the hypothesis by Ramskill [13]. In confined-space fires where chlorinated plastics burn or pyrolyze to give off the irritant gas, hydrogen chloride (HCl), he predicted that soot particles adsorb and carry the gas. These particles, properly sized, can escape the respiratory defenses when inhaled and be deposited in the lungs. There, the irritant is desorbed to irritate the tissue and cause pulmonary edema. Thus, Ramskill suggests a reason for the occasional delayed deaths resulting from exposure to naval fires. To test this mechanism, the partition of HCl between the vapor phase and soot particles was measured during burning of polyvinyl chloride (PVC) with polyethylene (PE). In addition, soot particles were characterized as to surface area, shape, size, crystallinity, and apparent density.

EXPERIMENTAL

Apparatus

A diagram of the apparatus is shown in Fig. 1. Air was pulled through the system by a carbon-vane pump (Bell and Gassett Hydrionics). Flow was controlled by a throttling valve (Roger Gilmont Instruments, Inc.). Air entered the reaction tube via ports A and B. The reaction tube, 25.5 in. in length and 1-5/8 in. in inner diameter, was fabricated

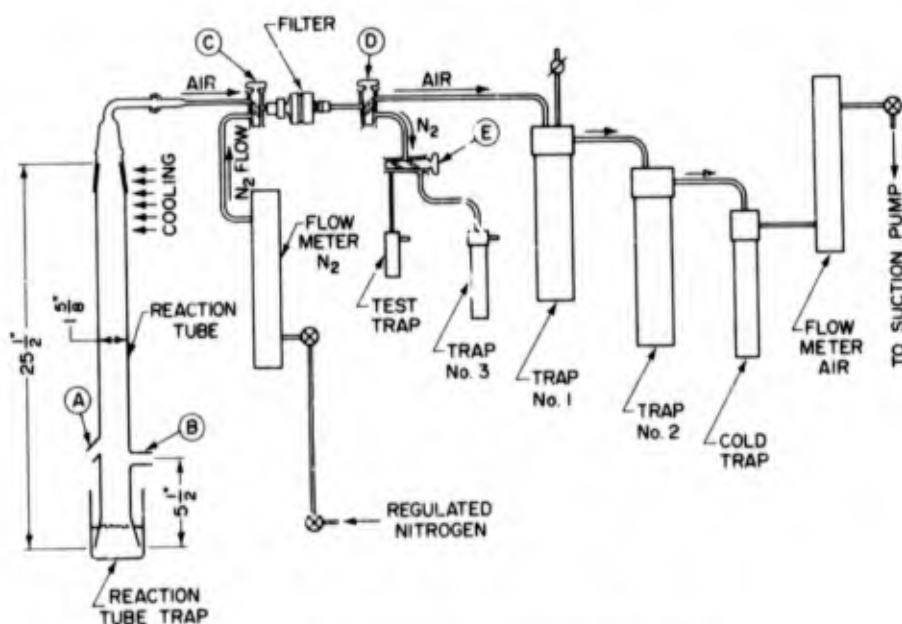


Fig. 1—Flow diagram of experimental apparatus

from borosilicate glass. Glass fiber filters (2-in. Gelman Type A) with a $0.3\text{-}\mu\text{m}$ particle retentivity of $99.8 \pm 0.3\%$ [14] were held by Millipore "Swinnex-47" type filter holders. These polypropylene holders were fitted into the flow system with tetrafluoroethylene and polyethylene adaptors. Traps No. 1 and 2 were 2-l filter flasks containing 750 ml of a 0.027N sodium hydroxide solution. In the purge circuit, dry nitrogen was passed through the glass fiber filters to either trap 3 or the test trap. Trap 3 contained 10 ml of 0.3N sodium hydroxide solution. The influent nitrogen stream was dispersed into fine bubbles at the bottom of the liquid by a drawn capillary tube. The test trap was of similar construction with 0.6 ml of 0.5N sodium hydroxide solution in a 1-ml graduate.

Procedure

Torches of PVC interleaved with PE were prepared by rolling into cylinders, 3-in. by 5-in. sheets of commercial film, 4 mil and 1.5 mil in thicknesses, respectively. The finished cylinders were about 1/4 in. in diameter and 3 in. in length and weighed slightly less than 1.5 g each. In each experiment a torch was burned in the reaction tube at atmospheric pressure in an air stream. In preparation for a burn, weights of the torch, the torch holder, the glass fiber filter, and the assembled filter including adaptors, were determined with a semimicrobalance.

With the apparatus assembled, nitrogen flow was directed through the filter and trap 3 and adjusted to 12 ml/min. The on-off valve was then closed, stopcocks C and D repositioned, and the air flow adjusted to 12.7 l/min. A torch mounted on a torch holder was positioned through port A into the reaction tube at an angle of about 45° to vertical. It was ignited by a natural gas flame extended through port B.

During a burn, the torch was rotated so as to maintain a flame height of 2 in. or less and to avoid excessive dripping. A fairly steady, yellow, sooty flame was maintained as the torch burned. About 8 min were required to complete a burn. A flame temperature of about 1100°C was measured with an optical pyrometer. As soot collected on the filter, the flow resistance of the system increased slightly. Reaction tube walls remained cool except for a 4-in. section just above the flame position. Condensate collected on the upper tube wall was concentrated below the top of the tube, upon which a jet of cool air was directed. About 1.1 g of water was produced from the combustion, and about 0.9 g entered with the room air (relative humidity of 40% at 23°C).

On burnout of the torch, the air flow was stopped within 1 s. The filter system was isolated during the 4 s required to adjust to the desired nitrogen flow conditions. The reaction tube trap, which served to close the lower end of the tube and to collect any crippings or falling char, was quickly replaced and the reaction tube, including the tubing to the filter, was thoroughly washed with a dilute sodium hydroxide solution. All condensate and soot were removed. The soot was filtered and the wash solution quantitatively collected in a 1-ℓ volumetric flask. Likewise, solutions from traps 1 and 2 were each quantitatively transferred to 1-ℓ flasks.

The purge nitrogen from the soot filter bed was diverted at the end of 1 hr to the test trap for 5 min and then back to trap 3. Chloride analyses were made on 10-μℓ aliquots of the 0.6-ml test-trap solution. This procedure was repeated at desired intervals to determine the completeness of chloride removal. Except for the small amounts collected in the test trap, chloride purged from the filtered soot bed was accumulated in trap 3. Upon completion of a purge, the filter assembly was removed from the system and the weight of soot was obtained. Soot from the filter was then analyzed for tightly bound chloride.

Chloride Analysis

Three analytical methods for chloride analysis were used in this study. The coulometric method by Coulson and Cavanagh [15,16] was particularly suitable for analyzing chlorides trapped from the effluent nitrogen stream. The method features rapid determinations with good accuracy and low detection limits. The Dohrmann Titration Cell T-300-S and Microcoulometer C-200-B were used in conjunction with an electronic integrator (Hewlett Packard). Aliquots were taken from the traps with calibrated syringes for injection into the titration cell.

A standard test method, ASTM D 1303-55 (1961), was used to determine the chloride content of the PVC film. This method, which makes use of the Parr peroxide bomb [17], was also applied in analyzing the soot for tightly bound chloride.

The Volhard method [18] was used to determine chloride content of solutions in traps 1 and 2.

RESULTS

Typical weights of combustible material and soot collected are listed in Table 1. Ten to twelve percent of the combustible material was recovered as soot. About 80%

Table 1
Soot Produced from Burning Polyvinyl
Chloride with Polyethylene

Burn No.	Torch Material			Soot			
	Polyethylene (mg)	PVC (mg)	Total (mg)	Reactor Tube (mg)	Filter (mg)	Total (mg)	Soot Yield (%)
11	301	1186	1487	37.8	134.4	172.2	12
12	297	1153	1450	24.9	122.6	147.5	10
13	305	1166	1471	29.7	122.9	152.6	10

of the soot was collected in the filter with the remainder found on the walls of the reaction tube. The PVC film was found to contain $36.4 \pm 0.2\%$ by weight of chloride. No chloride was detected in the PE.

Chloride Material Balance

The chloride from the combustible material was found (a) as a volatile chloride compound in the gas phase, (b) as a volatile chloride compound easily desorbed from the soot, and (c) as a tightly bound chloride on the soot, as shown in Table 2. The chloride in the gas phase and that easily desorbed from the soot is presumed to be HCl based on PVC decomposition studies by other workers [19-22]. The bulk of the HCl was carried as a vapor and was collected in caustic trap 1. Little or no chloride was found in trap 2. A significant amount of HCl was found in the wash solution of the reaction tube, probably held in the condensate. Only small amounts of chloride were found adsorbed, loosely or tightly, on the soot—less than 2% of the total. Over 95% of the chloride in the combustion products was recovered. No appreciable chloride was detected in the drippings or char or the caustic solution in the reaction tube trap. The small amount of soot collected on the walls of the reaction tube was not analyzed for tightly bound chloride, and the amounts shown in Table 2 were calculated on the basis of the filtered soot analysis.

The data in Table 2 also show that an average of 18 mg of loosely bound chloride was purged from a gram of soot and that 27 mg per gram of tightly bound chloride was found.

Results of repetitive test trap analyses of the effluent nitrogen made at hourly intervals during one run are presented in Fig. 2. Most of the loosely bound chloride was removed in 4 hr and all was removed in 22 hr.

Soot Properties

The soot was characterized by means of surface area measurements, electron micrographs, and x-ray diffraction. A summary of the findings is presented in Table 3. The

Table 2
Chloride Material Balance

Experiment No.	Chloride Determination *										Percent Chloride Recovered
	Starting Material (mg)	Combustion Products						Total Recovered (mg)			
		Reaction Tube		Bound on Filtered Soot		Caustic Traps					
		Wash (mg)	Soot† (mg)	Loosely‡ (mg)	Tightly§ (mg)	No. 1 (mg)	No. 2 (mg)				
11	431.5	70.2	1.7	2.7	2.5	330	None	407.1	94.3		
12	419.5	73.0	1.1	1.7	3.2	323	3.5	405.5	96.7		
13	424.3	98.6	1.4	2.6	3.2	299	None	404.8	95.4		

* Char and drippings yielded insignificant amounts of chloride.

† Calculated on basis of filtered soot.

‡ By nitrogen purge and coulometric method.

§ By Parr bomb combustion and Volhard method.

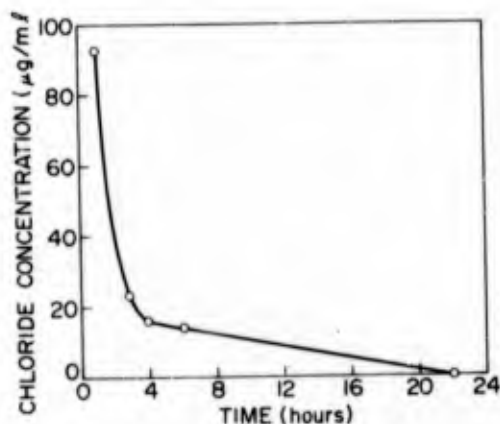


Fig. 2—Description of hydrogen chloride

soot was comprised of agglomerates of particles which are roughly spherical and range from 0.03 to 0.11 microns in diameter. A typical electron micrograph is shown in Fig. 3. The B.E.T. surface area [23], as determined by nitrogen gas adsorption, was 32 square meters per gram. The dispersion of particles in the electron micrographs was not satisfactory for a particle size distribution analysis. Thus, a surface area based on the mean particle diameter is not available. An x-ray diffraction pattern of the soot particles exhibited no crystallinity and the soot was judged to be amorphous. Using the thickness, diameter, and weight of the soot filter cakes, an apparent density of $1.83 \pm 0.07 \text{ g/cm}^3$ was obtained. The properties of the soot formed compare closely with those of certain carbon blacks, especially the high modulus and semi-reinforcing furnace blacks [24], as seen in Table 3.

DISCUSSION

If the chloride in these experiments is considered as hydrogen chloride [19-22], that which was easily removed from the soot amounted to 19 mg/g of soot. If a molecular

Table 3
Soot Properties

Property	Method	Soot	Sterling F Carbon Black*
Surface area	B.E.T. (N ₂ adsorption)	32 m ² /g	20 m ² /g
Particle shape	Electronmicrograph	Spherical	Spherical
Particle diameter Range	Electronmicrograph	300 to 1100 Å	800 Å (av)
Crystallinity	X-ray diffraction	Amorphous	Amorphous

*From Ref. 24.

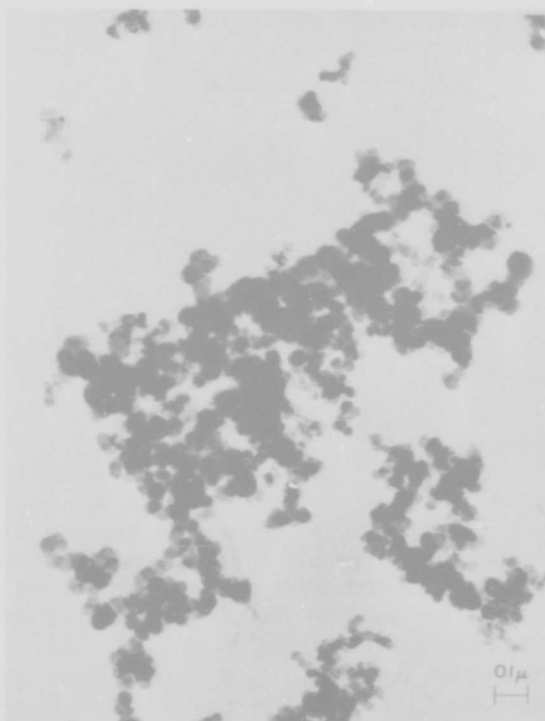


Fig. 3—Typical electronmicrograph of filter soot

area of 15 sq Å is used for one HCl molecule, we calculated, according to Emmett and Brunauer [25], that a coverage of the soot by the HCl would be about 1.5 monolayers, if evenly adsorbed. If a steady rate of burning and an average burn time of 8 min. are assumed, the soot particles were exposed to an average HCl concentration of 2700 ppm in these experiments.

The relative pressure, which is the ratio of the partial pressure to the vapor pressure, for dry HCl at the temperature of the filter bed is very low ($\sim 10^{-4}$). Physical adsorption of a gas onto a solid at such a relative pressure would be expected to be much less than 1.5 monolayers according to the B.E.T. theory [26]. A relative pressure of the order of 0.1 is usually expected for a monolayer coverage. The significant HCl adsorption observed on the soot in these experiments is most readily explained by mixed adsorption of water vapor and HCl. The fact that these two compounds form an azeotropic mixture supports this thesis.

The tightly bound chloride found in the soot may be chemically bound. The 2.7% chloride represents one atom per hundred atoms of carbon. Vinyl chloride, the monomer of PVC, has been reported from combustion of PVC [27,28], and its incorporation into the soot structure is reasonable.

Possible inhalation hazards of such soot as produced in these experiments are strongly related to sizes of the soot particles and particle agglomerates. It has been shown that the amounts and locations of particle deposition in the respiratory system

depend strongly on particle size [29,30]. It has also been shown [31] that particles sized in the range as those produced in these experiments (0.03 to 0.11 μm) coagulate rapidly to form larger particle clusters.

The time history of average cluster diameters of this soot may be estimated by coagulation theory [32] provided (a) the coagulation constant given for carbon [33] is assumed for the soot, and (b) the initial particle concentration of the soot is determined from its mass concentration as calculated from the average weight of soot produced (157 mg) and the average volume of air that was used (102 ℓ) in these experiments. Initial particle concentrations, then, become 5.9×10^{10} and 1.2×10^9 particles/cc for 0.03 and 0.11 μm diameters, respectively. The integrated form of the Smoluchowski [32] coagulation equation is

$$\frac{1}{N} - \frac{1}{N_0} = kt$$

where

N_0 is the initial particle concentration, particles/cc
 N is the particle concentration, particles/cc, at time t , min
 k is the coagulation constant, 14.1×10^{-8} cc/min for carbon.

Accordingly, by this simplest form of coagulation theory, regardless of which initial particle diameter is assumed (0.03 or 0.11 μm), cluster diameters calculated for various lapsed times are given in Table 4.

Upon inhalation, soot aerosols produced in these experiments would undoubtedly enter the lower lungs and to an extent be retained there. The charts of Davies [29,34], with the findings of Landahl [35] and of Altshuler et al [36], indicate particle clusters with sizes ranging from 0.1 to 2.5 μm in diameter would be retained in the alveolar sacs to an extent of from 20 to 40% of those inhaled. This range of particle diameters corresponds to soot aged from sec to 1 hr, according to the calculated values given in Table 4.

Table 4
 Cluster Diameters for Soot Agglomerates
 as Calculated for Various Times

Lapsed Time (min)	Cluster Diameter (μm)
0.17 (10 s)	0.3
1	0.6
10	1.3
30	1.9
60	2.4
180	8.8

Transport of loosely bound HCl by soot particles into the lungs can then be estimated from the preceding arguments if a rate of inhalation and a time of exposure are assumed. For the purpose of discussion, let us consider the two extreme conditions: (a) A dense HCl-laden smoke equivalent to the soot aerosol as produced in these experiments, 1.57 g of soot per m^3 of air, but with no HCl in the gas phase, and (b) a gas phase HCl concentration of $150 \text{ mg}/\text{m}^3$, with no soot aerosol present.

For condition (a), if an extreme breathing rate of 50 ℓ/min and an exposure of 1 hr is assumed (reasonable values for a man fighting a complex fire), a maximum of 1.9 g of soot bearing 36 mg of loosely bound HCl would be retained in the lower lungs.

Condition (b) was chosen so as to correspond to maximum tolerable conditions for exposure to HCl in the gas phase, according to Sax [37]. These conditions are represented by an HCl concentration of $150 \text{ mg}/\text{m}^3$, a normal breathing rate of 18 ℓ/min , and an exposure time of 1 hr. According to Henderson and Hagger [38], it is estimated that two-thirds of the HCl inhaled is retained in the body. On this basis, an HCl dosage of 108 mg would be indicated.

From the viewpoint of simple mass exposure, it would be concluded that condition (b), gas phase exposure, is three times as severe an exposure as condition (a), aerosol exposure. If the breathing rate of condition (a) were adjusted to that of (b), 18 ℓ/min , then the factor of severity would increase from 3 to 9 times, as just stated.

The effect of HCl in the gas phase is known to be largely limited to irritation affecting the upper respiratory tract [39], whereas, loosely bound HCl condensed on soot aerosol would gain access to the lower lungs, an area more vulnerable to attack by the acid. The question as to the quantitative significance of the HCl carried on the soot is a toxicological one.

The findings of this study demonstrate that soot can transport adsorbed HCl during combustion of PVC.

IMPLICATIONS FOR FUTURE WORK

The importance of water implied by our burning experiments as described above prompted studies on HCl adsorption onto soot in controlled humidity environments. However, gross wall condensation (and perhaps gas-phase nucleation) occurs in the experimental apparatus at relative humidities of 30 to 35% for the lowest HCl concentrations attainable in our flow system. With a liquid phase in the system, control of gas-phase concentration is lost. Thus to eliminate the liquid phase and regain control, either the HCl concentration must be reduced or the system temperature increased. The best approach to this experimental difficulty is to refine flow control of the HCl.

Ramskill predicted [13], as he did with soot aerosol, that water aerosol combines with HCl. Thus, properly sized liquid droplets, as with solid particles, could elude the upper respiratory defenses to penetrate into the lungs. Study of this prediction requires separation of HCl in the gas phase from that adsorbed in the water aerosol. A wetted-wall type of apparatus shows promise in this separation and is being used in a study of certain conditions necessary to test this prediction.

Since relative humidity in the respiratory tract (including the mouth) is almost 100%, conditions that promote nucleation in moist air are pertinent. If conditions of pressure, temperature, and concentration are favorable and rates of nucleation processes fast enough, then a hazardous aerosol could form within the respiratory tract. Vapor-liquid equilibrium and kinetic data for the HCl-water system in the dilute region are needed to examine this mechanism.

Following completion of the HCl-water aerosol work, plans are to study the oxides of nitrogen. Our present laboratory systems should be satisfactory for these studies.

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