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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

Technical Memorandum 33-659

Some Environmental Considerations Relating to the Interaction of the Solid Rocket Motor Exhaust With the Atmosphere: Predicted Chemical Composition of Exhaust Species and Predicted Conditions for the Formation of HCl Aerosol

Robert A. Rhein

(NASA-CR-136558) SOME ENVIRONMENTAL CONSIDERATIONS RELATING TO THE INTERACTION OF THE SOLID ROCKET MOTOR EXHAUST WITH THE ATMOSPHERE: PREDICTED CHEMICAL (Jet Propulsion Lab.) ~~24~~ 25 p HC $3.25 CSCL 21H

N74-15655

Unclas

G3/33 26761

JET PROPULSION LABORATORY
CALIFORNIA INSTITUTE OF TECHNOLOGY
PASADENA, CALIFORNIA

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Prepared Under Contract No. NAS 7-100
National Aeronautics and Space Administration

PREFACE

The work described in this report was performed by the Propulsion Division of the Jet Propulsion Laboratory.

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ABSTRACT

The exhaust products of a solid rocket motor using as propellant 14% binder, 16% aluminum, and 70% (wt) ammonium perchlorate consist of hydrogen chloride, water, alumina, and other compounds. The equilibrium and some frozen compositions of the chemical species upon interaction with the atmosphere were computed.

The conditions under which hydrogen chloride interacts with the water vapor in humid air to form an aerosol containing hydrochloric acid were computed for various weight ratios of air/exhaust products. These computations were also performed for the case of a combined SRM and hydrogen-oxygen rocket engine. Regimes of temperature and relative humidity where this aerosol is expected were identified. Within these regimes, the concentration of HCl in the aerosol and weight fraction of aerosol to gas phase were plotted.

Hydrochloric acid aerosol formation was found to be particularly likely in cool humid weather.

I. INTRODUCTION

This report discusses the interaction of the exhaust of a typical solid rocket motor (SRM) with the atmosphere. The assumed propellant is ammonium perchlorate and aluminum in a hydrocarbon binder. It deals with two aspects of the problem: composition and concentration of the chemical species and conditions for the formation of hydrochloric acid aerosol. The purpose of determining these chemical interactions relates to the effect upon the environment. In particular, the atmospheric conditions of temperature and relative humidity conducive to the formation of an HCl aerosol upon interaction with SRM exhaust and also with the combined exhaust of an SRM with the exhaust of a hydrogen-oxygen engine are presented in detail. The latter case is modeled after the proposed propulsion system of the Space Shuttle (Refs. 1 and 2).

Until recently, the primary concern over the interaction of the exhaust products with the atmosphere dealt with the problem of electromagnetic wave attenuation through the exhaust plume and its effect on ground-rocket communication (Ref. 3); other earlier studies dealt with the rocket exhaust composition, with the view of improving the specific impulse of the engine (Ref. 4). However, there has been recent concern about the toxicity of SRM exhaust gases by NASA (Refs. 1, 2, and 5), with the primary emphasis placed on the toxic aspects of HCl.

The general topic of hydrochloric acid pollution, including toxicity, HCl emission sources, etc., has been covered quite well in two reviews (Refs. 6 and 7).

II. RESULTS AND DISCUSSION

The first part of this study was concerned with the estimation of the composition and concentration of the chemical species of the exhaust gases at the nozzle exit plane and subsequently upon mixing with the atmosphere.

The solid propellant was assumed (Ref. 8) to consist of 70% (wt) ammonium perchlorate, 16% aluminum, and 14% binder (epoxy-cured PBAN, empirical formula $C_{6.497}$ $H_{9.028}$ $O_{0.628}$ $N_{0.218}$ ΔH_f-160 kcal/kg). The composition and temperature of the exhaust gases at the nozzle exit plane were calculated by a NASA-Lewis computer program (Ref. 9) modified for use in the UNIVAC-1108. The equilibrium compositions closely matched published values (Refs. 1, 2) and are presented in Figs. 1-4 (for weight ratio air/exhaust products = 0).

The equilibrium composition and concentration of the species resulting from mixing the exhaust products of the SRM were computed. Calculations were also carried out for air mixed with the combined exhaust of the SRM and liquid H_2-LOX engine, where the SRM exhaust products comprise 78.4 wt %. As for the proposed Space Shuttle (Ref. 1), the results are shown in Figs. 1-4. The equilibrium compositions were calculated with the NASA-Lewis program (Ref. 9), using as input the equilibrium composition at the SRM exhaust plane and the composition of air as in Ref. 10, p. 3076. In Figs. 1-4, the concentrations are plotted vs weight ratio air/(exhaust products) in logarithmic decrements over the range 10^{-1} to 10^5. The concentration of exhaust species in the stabilized exhaust cloud has been estimated at a weight ratio of 10^4 (Ref. 2), so the assumption is made that the actual weight ratio is in the range 10^3-10^5.

Figure 1 shows the anticipated fate of the hydrogen-oxygen species; it is seen that O_2 and H_2O are the only anticipated species for air/exhaust >10. Consequently, afterburning of H_2 is predicted. The presence of H_2 in rocket exhaust prior to mixing with air has been established experimentally (Refs. 4, 11), but H_2 was absent in the rocket plume consisting of exhaust products mixed with air (Refs. 12 and 13).

Figure 2 shows that both CO and CO_2 are present in the exhaust gas and that chemical equilibrium indicates afterburning of CO to CO_2. Published experimental results (Ref. 12) indicate a substantial, but not complete, conversion of CO to CO_2. A reaction kinetics analysis is indicated here.

Figure 3 indicates the anticipated fate of nitrogen species. Equilibrium calculations indicate that the mole fractions of all but NO_2 drop to $<10^{-10}$ for weight ratio air/exhaust >100. Nitrogen oxides were observed experimentally in SRM exhaust (Refs. 12 and 13). Plotted in Figure 3 is the hypothetical case where the NO is frozen for air/exhaust >3 after attaining an equilibrium at weight ratio air/exhaust = 3. Under these circumstances, the concentration of NO would be on the order of 1 ppm at a weight ratio air/exhaust of 10^4. Although it is beyond the scope of this paper to discuss the kinetics of the nitrogen-oxygen reaction (Ref. 14), the problem of formation, and concentration of NO_x may justify further investigation.

Figure 4 shows the anticipated fate of chlorine-HCl species under various conditions. HCl was found in SRM exhaust (Refs. 11, 12, 15 and 16), although Cl_2 was not observed. Very likely, Cl and Cl_2 are present in small concentrations and HCl reaction with O_2 from the air is frozen at weight ratio air/exhaust >10, in spite of the predicted (on an equilibrium basis) predominance of Cl_2 at air/exhaust $>10^2$. Whether or not Cl_2 is the predominant species under these conditions is an open question; on the basis of environmental input it would be very worthwhile to determine this experimentally. In this work, however, it is assumed that the HCl does not further react (frozen flow).

Although the fate of aluminum compounds was not emphasized in this study, equilibrium calculations indicated that for weight ratio air/exhaust ≥10, solid Al_2O_3 is the only aluminum species. Further discussion on the fate of aluminum species will occur later in this report.

The second part of this discussion deals with the interaction of hydrogen chloride (as an exhaust product) with water vapor in the atmosphere (present as atmospheric humidity plus that emitted as a rocket exhaust product). Hydrogen chloride interacts very strongly with water to form aqueous hydrochloric acid. Although there is extensive literature regarding the interaction of water with hydrogen chloride, the gas-liquid system (water vapor/hydrogen chloride/aqueous hydrochloric acid) is well summarized by Schmidt (Ref. 17) and in Perry's Handbook, pp. 268-269 and 166-167 (Ref. 18). In this portion of this work, the objectives are to identify the regimes of air ambient temperature and relative humidity whereupon interaction with hydrogen chloride from SRM exhaust yields the aqueous hydrochloric acid phase (presumably as an aerosol) and, within the regime of aerosol formation, to show the concentration of HCl in the liquid phase and the weight fraction of liquid phase. The objectives were met through computer analysis and the results shown in Figs. 5-22.

The following is a brief discussion of the procedure used for computing these results. The published data (Refs. 17 and 18) of the vapor pressure of water and of hydrogen chloride vs temperature and hydrochloric acid concentration in the aqueous phase were entered into computer storage. Using the weight ratio air/exhaust as an independent variable, the temperature, water vapor pressure (from the rocket exhaust and from the ambient relative humidity), and partial pressure of hydrogen chloride of the air plus rocket exhaust mixture were determined; from this and the above computer-stored data, the conditions for HCl aerosol and HCl concentrations were calculated.

Figures 5-11 (each figure corresponding to a given value of weight ratio air/exhaust, ranging from 10^3, Fig. 5, to 10^5, Fig. 11) show the boundary and region of anticipated aerosol formation for an SRM under the assumption that no afterburning of H_2 and CO occurs. The independent variables are ambient air temperature and relative humidity. Figures 12-14 present this information under the assumption of afterburning of CO and H_2 (the afterburning produces higher water vapor pressure and higher cloud temperature). In these figures, the family of solid lines represents the weight percent HCl in the aerosol, or liquid phase; the dashed lines represent the weight fraction (ppm) of aerosol in the aerosol-air mixture.

Figures 15-22 deal with the combined SRM + LH_2-LOX rocket exhaust system such as that proposed for the Space Shuttle. Figures 15 and 16 show the predicted aerosol parameters (for air at an ambient temperature of 298°K) vs weight ratio air/exhaust and relative humidity; Fig. 15 assumes no afterburning; Fig. 16 assumes afterburning. Figures 17-22 present these aerosol parameters vs ambient temperature and relative humidity; each figure represents the case for fixed weight ratio air/exhaust. Figures 17-19 represent no afterburning; Figs. 20-22 represent the situation where afterburning of CO and H_2 is assumed. The data in Figs. 15-22 supersede that in a previous report (Ref. 19), wherein frozen flow was assumed from throat to nozzle of the LH_2-LOX engine.

Several observations can be inferred by inspection of Figs. 5-22. At a weight ratio air/exhaust of 10^4, there is a substantial region of ambient air temperature and relative humidity where HCl aerosol is expected. The weight percent of HCl in the aerosol depends upon temperature and relative humidity, but in any of these cases, the aerosol is that of a strong acid (e.g., 5% HCl is 1.38 N). For a given weight ratio air/exhaust, the aerosol data curves for each of the rocket exhaust alternatives (i.e., SRM with or without afterburning and SRM + LH_2-LOX rocket exhaust with or without afterburning) are fairly similar although not identical. Afterburning produces higher temperatures and water vapor pressure in the exhaust cloud; higher water vapor pressure favors liquid-phase (aerosol) formation, whereas higher temperatures favor the gas phase at the expense of the liquid phase. Apparently the two effects approximately cancel each other.

The figures indicate that aerosol formation is favored by lower ambient temperatures and higher relative humidity, as may be expected. This suggests that midday launches may be preferable to those in the morning or evening if avoidance of aerosol is desired.

Although Figs. 5-22 indicate the conditions under which aerosol is expected, based on the system liquid-gas phase equilibrium, the actual formation of aerosol depends upon droplet nucleation. It has been reported (Ref. 20) that HCl aerosol will not form (at ambient temperatures) below a relative humidity of 78%. The issue of nucleation raises an interesting conjecture, i. e., the possibility of HCl aerosol nucleation on the Al_2O_3 exhaust particles, since the SRM exhaust consists of 28% (weight) Al_2O_3 (Ref. 1). In the course of particle-size distribution studies, it was reported (Ref. 21) that the smaller particles are γ-Al_2O_3, and that γ-Al_2O_3 is soluble in aqueous hydrochloric acid. Consequently, the question is raised as to what portion of the HCl aerosol actually consists of droplets of $AlCl_3$-HCl solution; this issue is complicated by the fact that, in addition to the co-existent Al_2O_3, there are a variety of other types of nucleation sites already present in the atmosphere (Ref. 22).

III. CONCLUSIONS

Hydrogen chloride, present in the exhaust of an SRM can interact with humid air to form an aerosol of hydrochloric acid. Aerosol formation is favored by low temperature and high relative humidity, particularly as found in the morning and evening. Experimental verification of certain of these computed results is indicated; for example, determination of the HCl/Cl_2 ratio, the CO/CO_2 ratio, and the H_2 present in the exhaust/air mixture.

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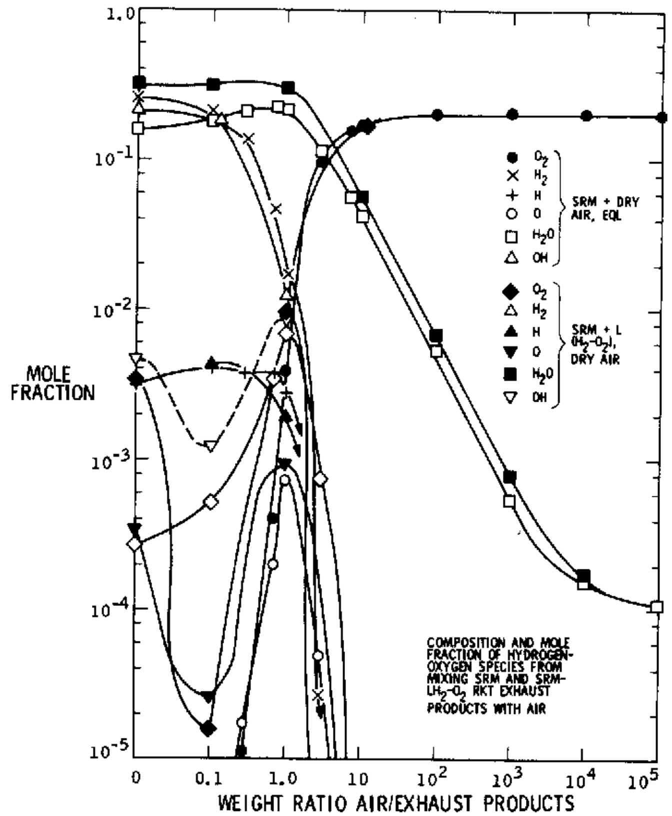

Fig. 1. Predicted hydrogen-oxygen chemical species resulting from the mixing of air with SRM exhaust and of air with the combined SRM exhaust and LH_2-LO_2 liquid rocket exhaust, where SRM exhaust products/total exhaust products = 0.784

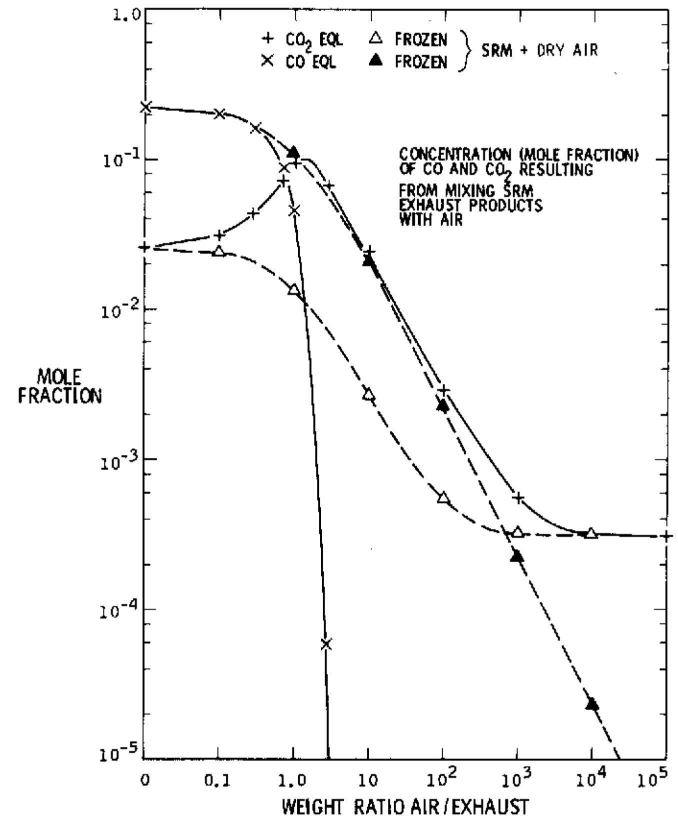

Fig. 2. Predicted CO and CO_2 concentration resulting from the mixing of SRM exhaust products with dry air

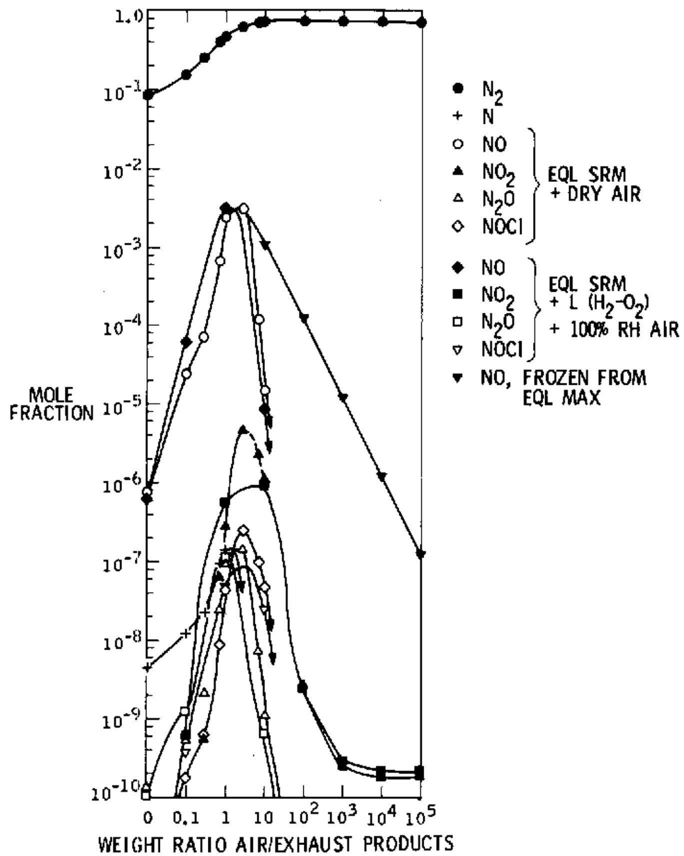

Fig. 3. Composition and mole fraction of nitrogen-oxygen species from mixing SRM exhaust products with air

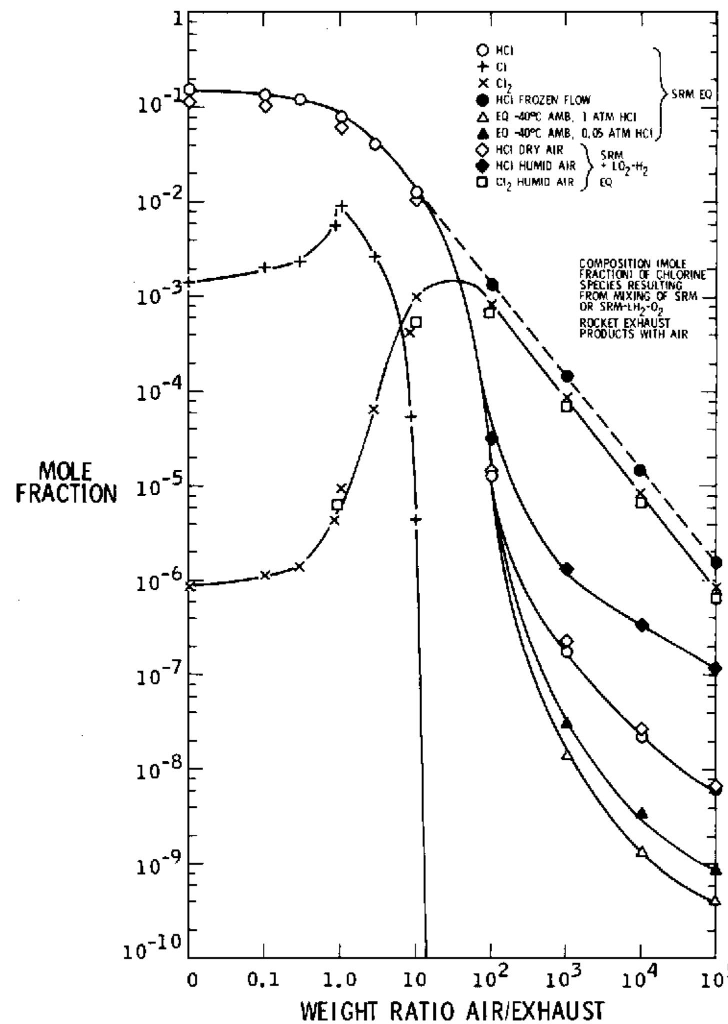

Fig. 4. Predicted chlorine species resulting from mixing SRM or SRM-LH_2-O_2 rocket exhaust products with air

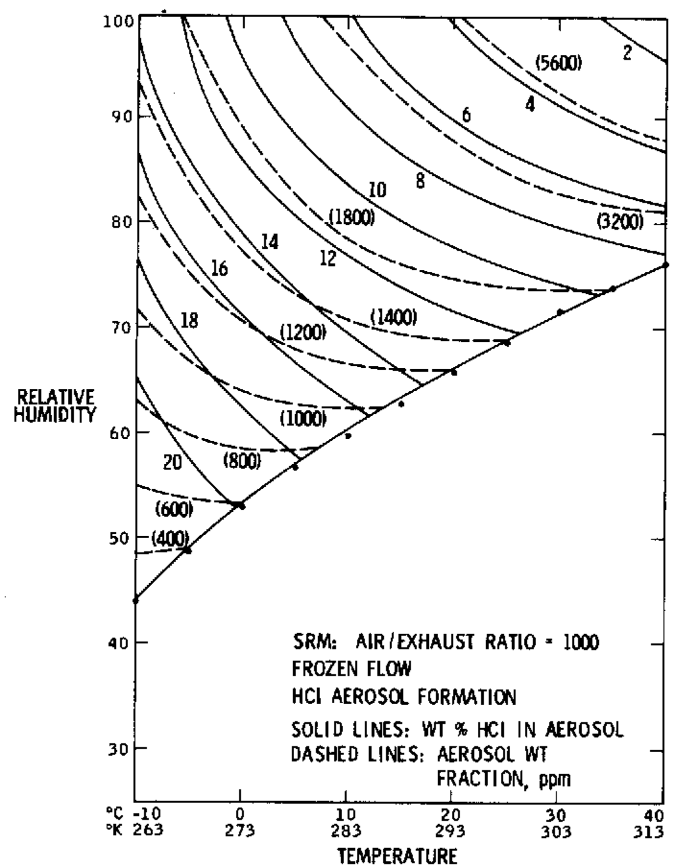

Fig. 5. Formation and properties of HCl aerosol resulting from the mixing of (1000 parts) air with SRM exhaust vs ambient air temperature and relative humidity

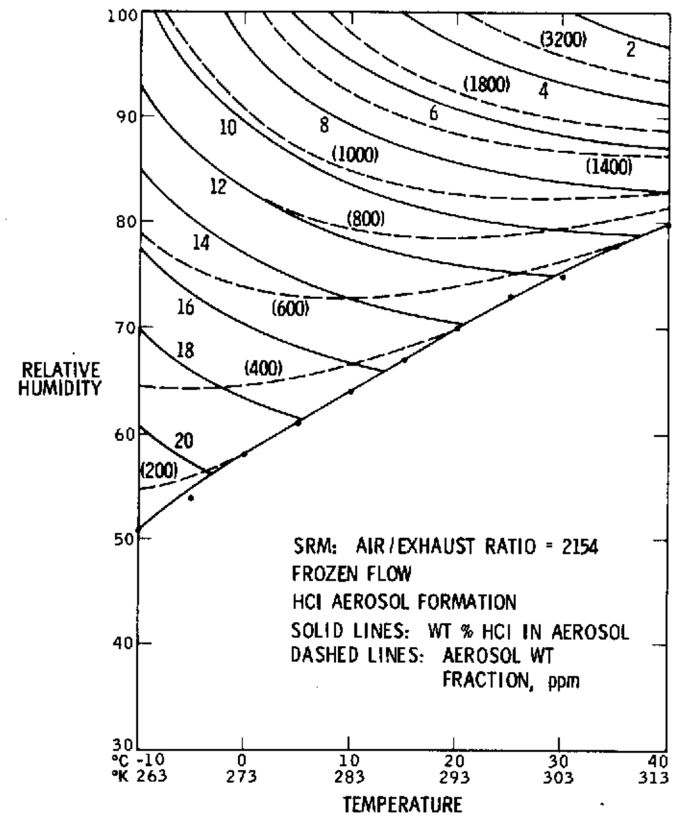

Fig. 6. Formation and properties of HCl aerosol resulting from the mixing of (2154 parts) air with SRM exhaust vs ambient air temperature and relative humidity

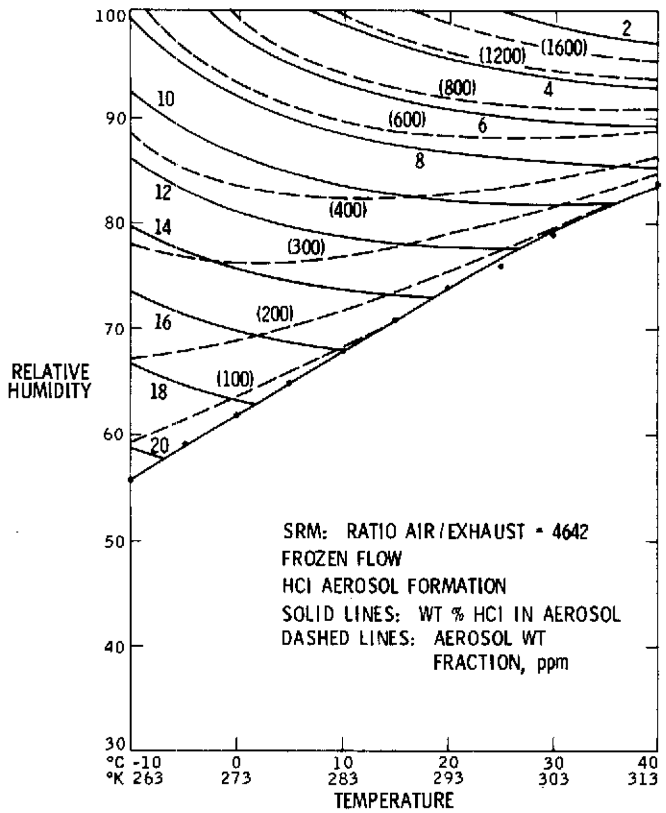

Fig. 7. Formation and properties of HCl aerosol resulting from the mixing of (4642 parts) air with SRM exhaust vs ambient air temperature and relative humidity

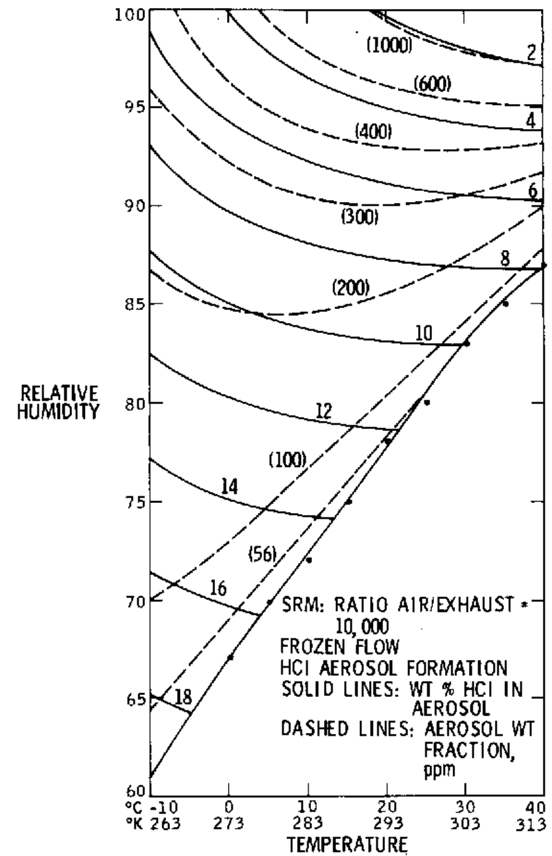

Fig. 8. Formation and properties of HCl aerosol resulting from the mixing of (10^4 parts) air with SRM exhaust vs ambient air temperature and relative humidity

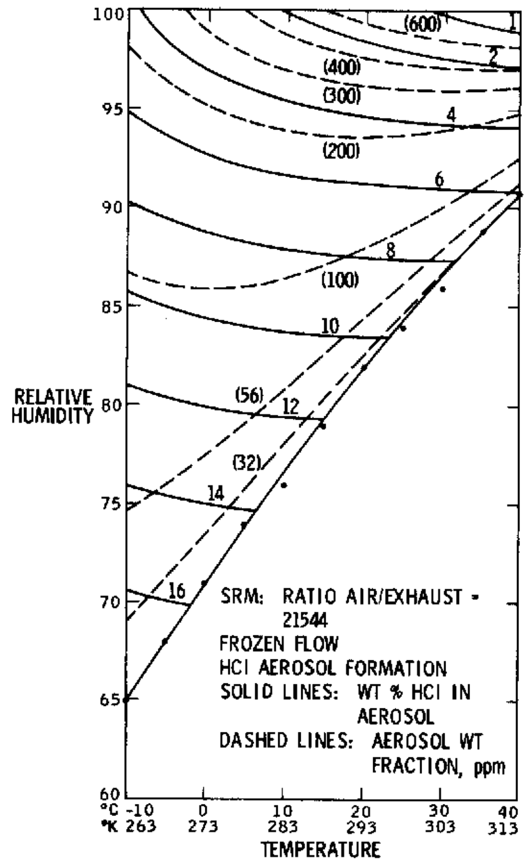

Fig. 9. Formation and properties of HCl aerosol resulting from the mixing of (21544 parts) air with SRM exhaust products vs ambient air temperature and relative humidity

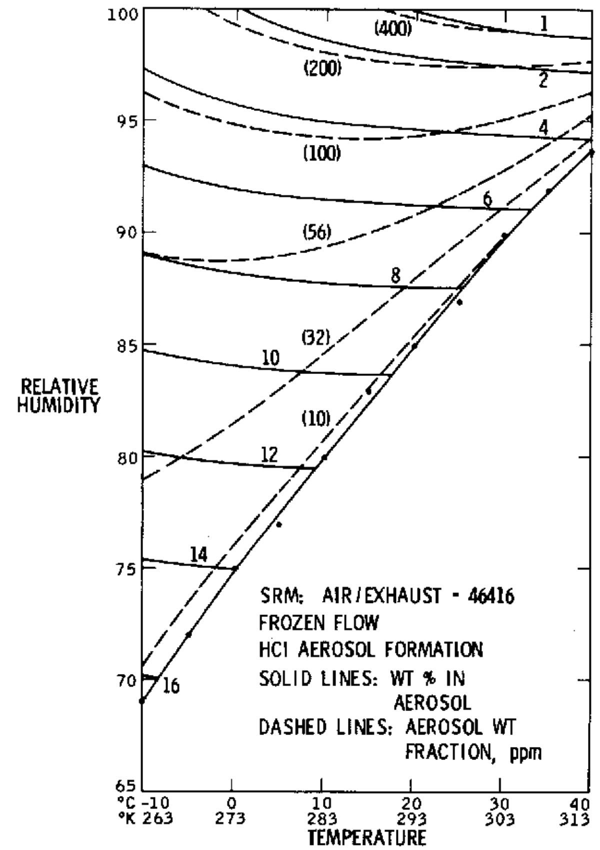

Fig. 10. Formation and properties of HCl aerosol resulting from the mixing of (46416 parts) air with SRM exhaust products vs ambient air temperature and relative humidity

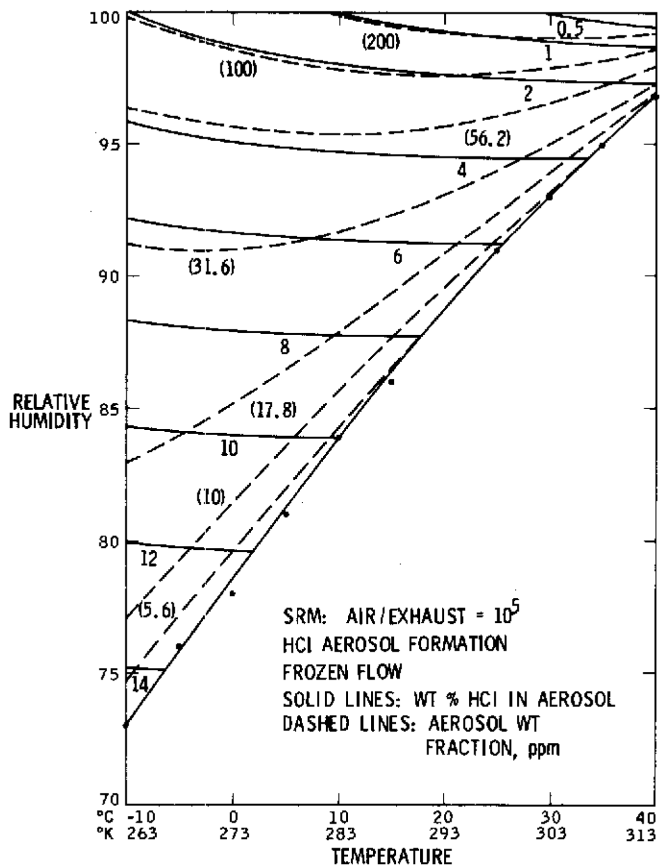

Fig. 11. Formation and properties of HCl aerosol resulting from the mixing of (10^5 parts) air with SRM exhaust products vs ambient air temperature and relative humidity

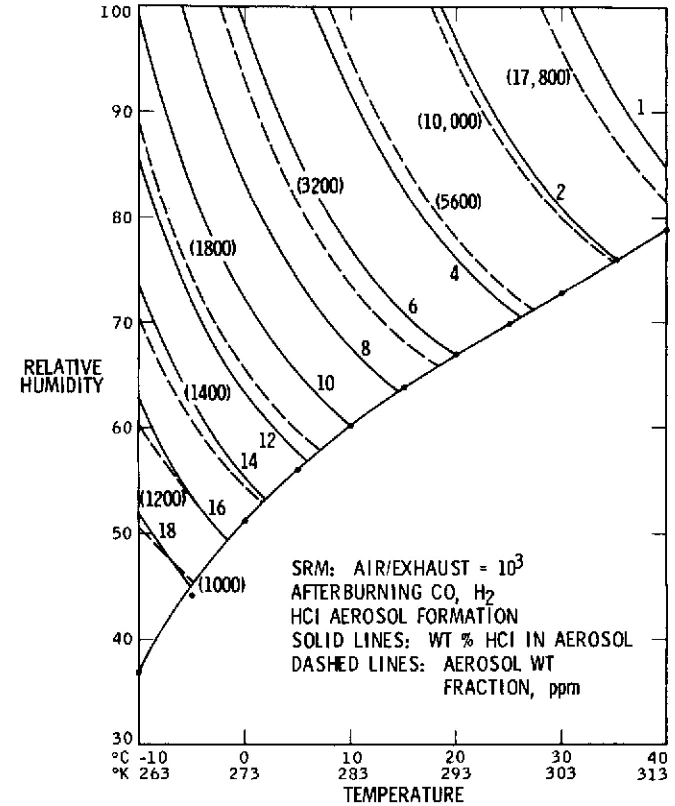

Fig. 12. Formation and properties of HCl aerosol resulting from the mixing of (10^3 parts) air with SRM exhaust, assuming afterburning of CO and H_2 vs ambient air temperature and relative humidity

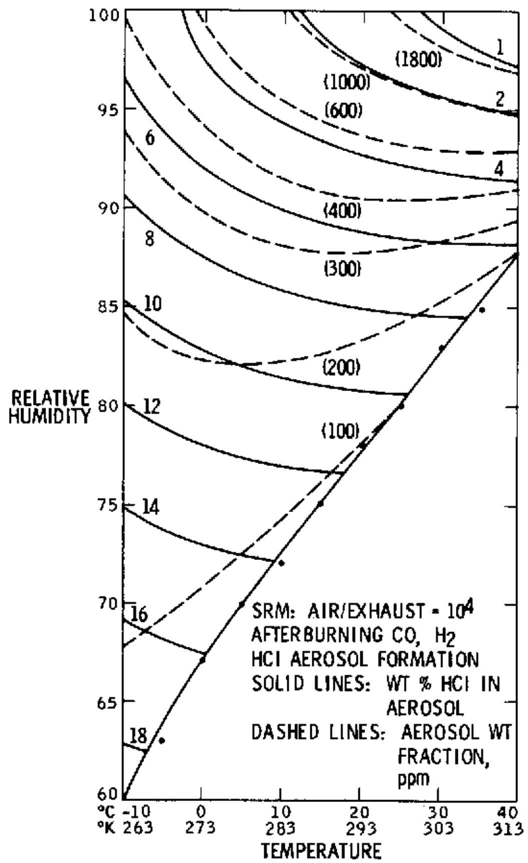

Fig. 13. Formation and properties of HCl aerosol resulting from the mixing of (10^4 parts) air with SRM exhaust, assuming afterburning of CO and H_2 vs ambient air temperature and relative humidity

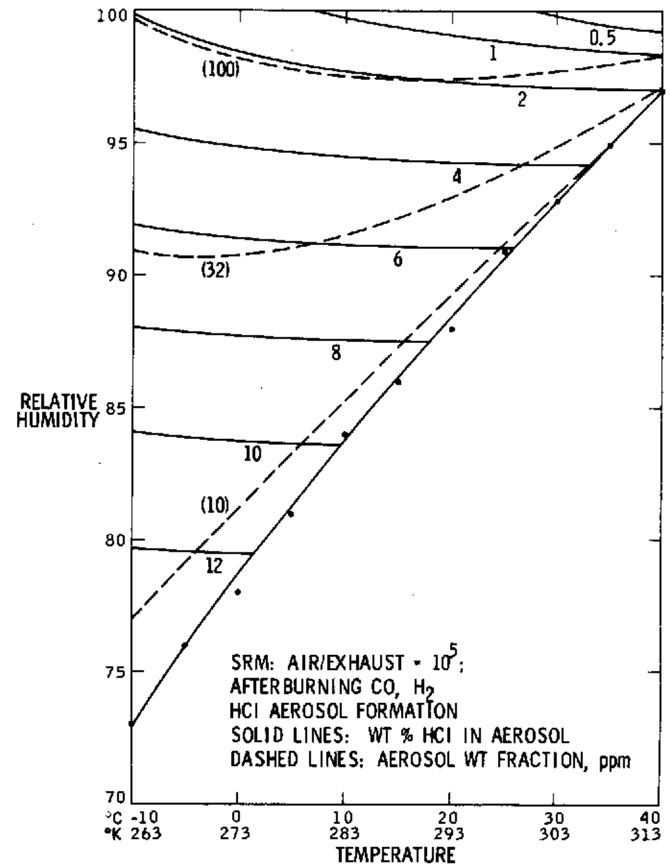

Fig. 14. Formation and properties of HCl aerosol resulting from the mixing of (10^5 parts) air with SRM exhaust, assuming afterburning of CO and H_2 vs ambient air temperature and relative humidity

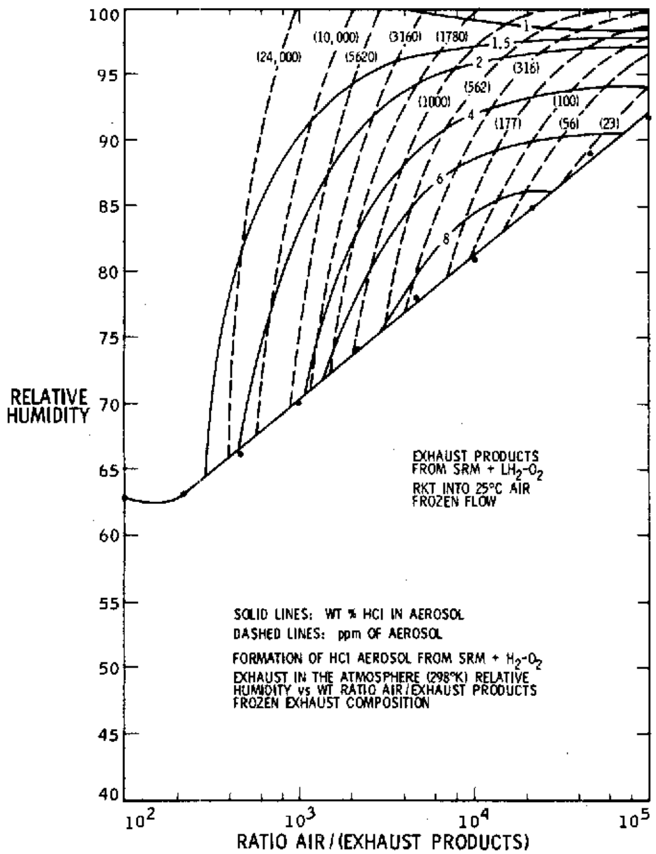

Fig. 15. Formation and properties of HCl aerosol resulting from the mixing of the combined exhaust products of an SRM and LH_2-LO_2 rocket with the atmosphere at 25°C vs relative humidity and wt ratio air/total exhaust products

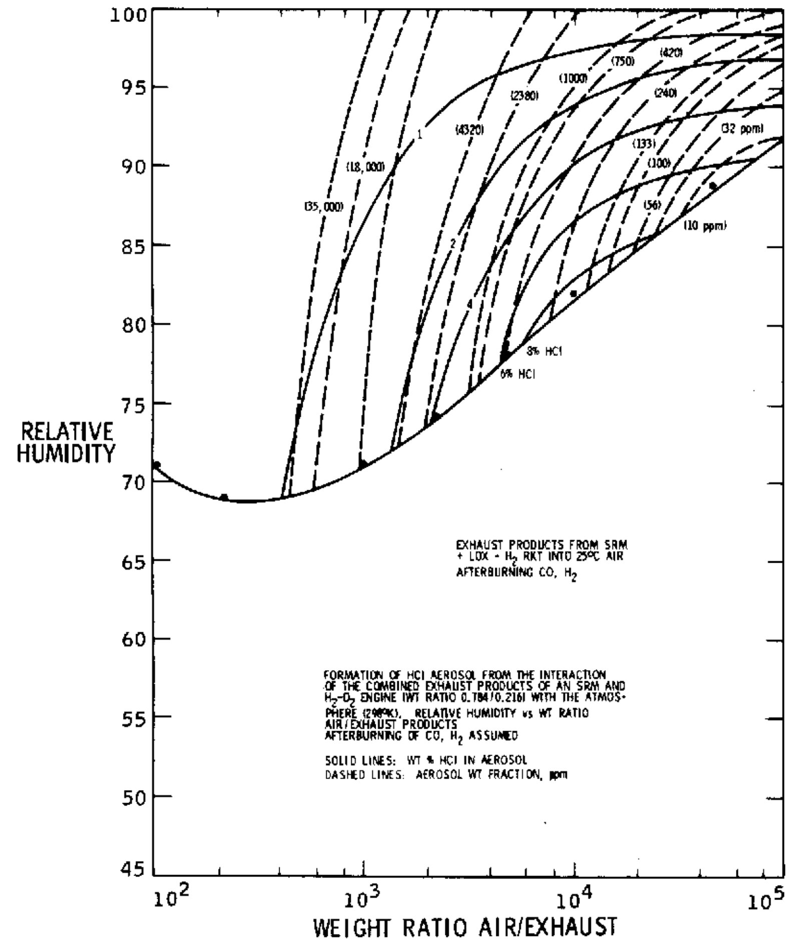

Fig. 16. Formation and properties of HCl aerosol resulting from the mixing of the combined exhaust products of an SRM and an LH_2-LO_2 rocket with the atmosphere at 25°C vs relative humidity and wt ratio air/total exhaust products

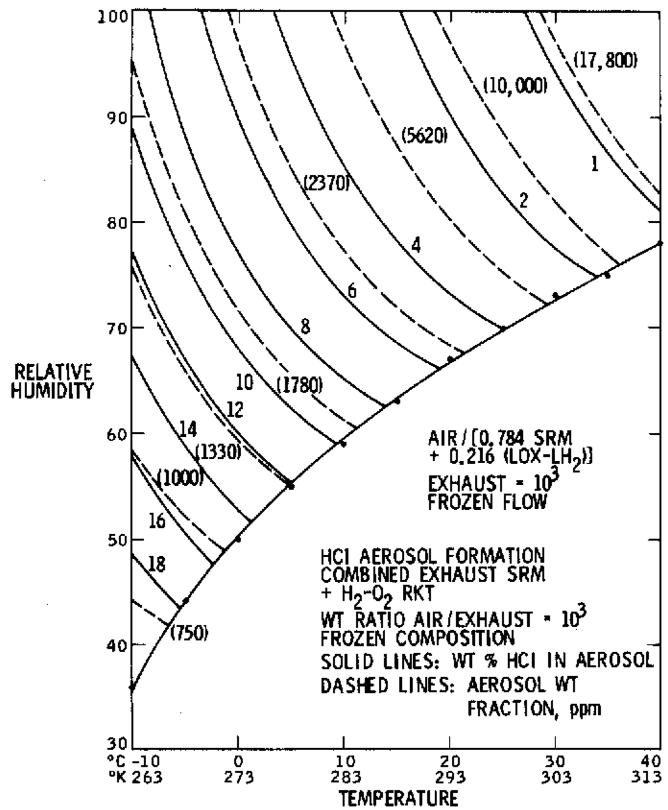

Fig. 17. Formation and properties of HCl aerosol resulting from the mixing of (10^3 parts) air with the combined exhaust of an SRM and an LH_2-LO_2 rocket vs ambient air temperature and relative humidity

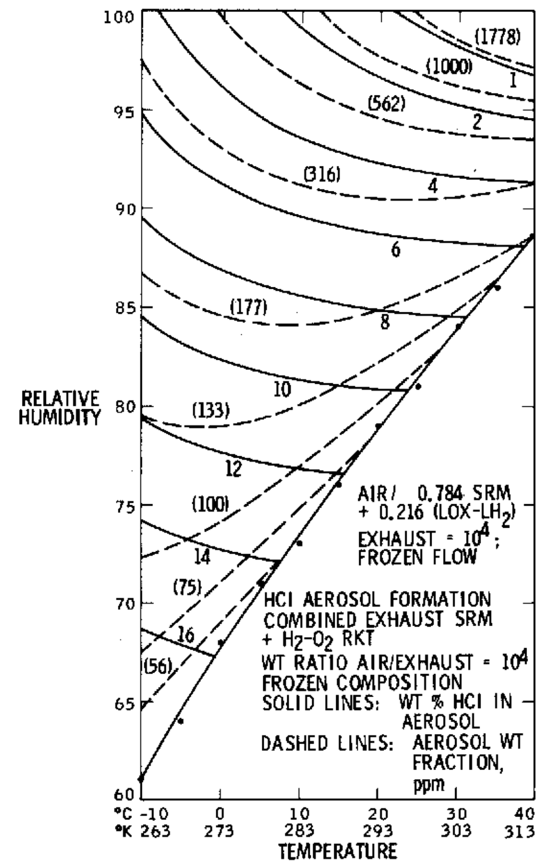

Fig. 18. Formation and properties of HCl aerosol resulting from the mixing of (10^4 parts) air with the combined exhaust of an SRM and an LH_2-LO_2 rocket vs ambient air temperature and relative humidity

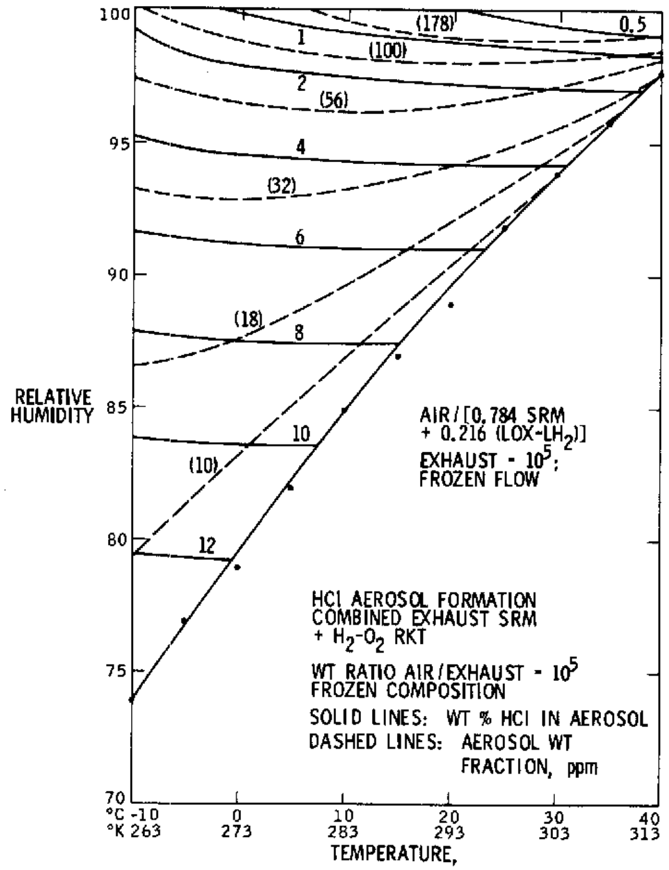

Fig. 19. Formation and properties of HCl aerosol resulting from the mixing of (10^5 parts) air with the combined exhaust of an SRM and an LH_2-LO_2 rocket vs ambient air temperature and relative humidity

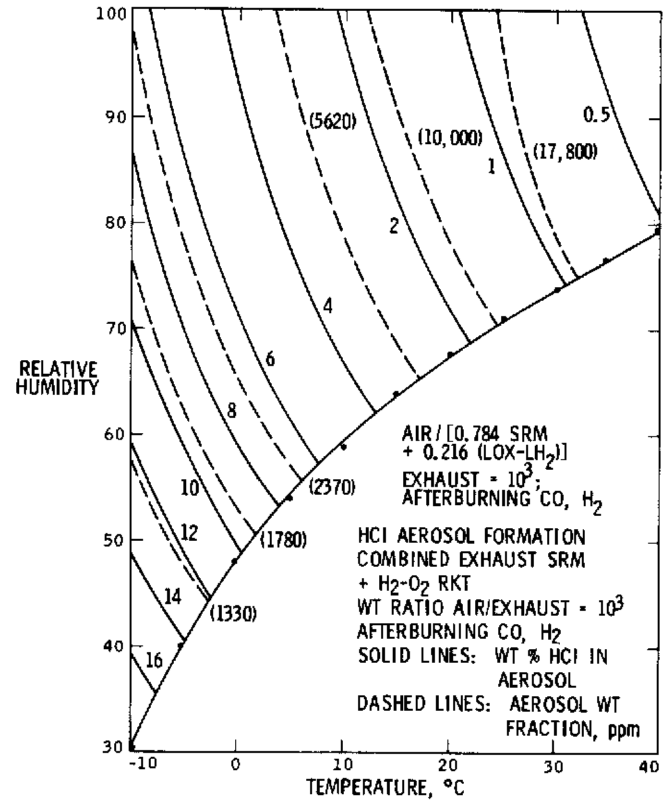

Fig. 20. Formation and properties of HCl aerosol resulting from the mixing of (10^3 parts) air with the combined exhaust of an SRM and an LH_2-LO_2 rocket (afterburning of CO, H_2 assumed) vs ambient air temperature and relative humidity

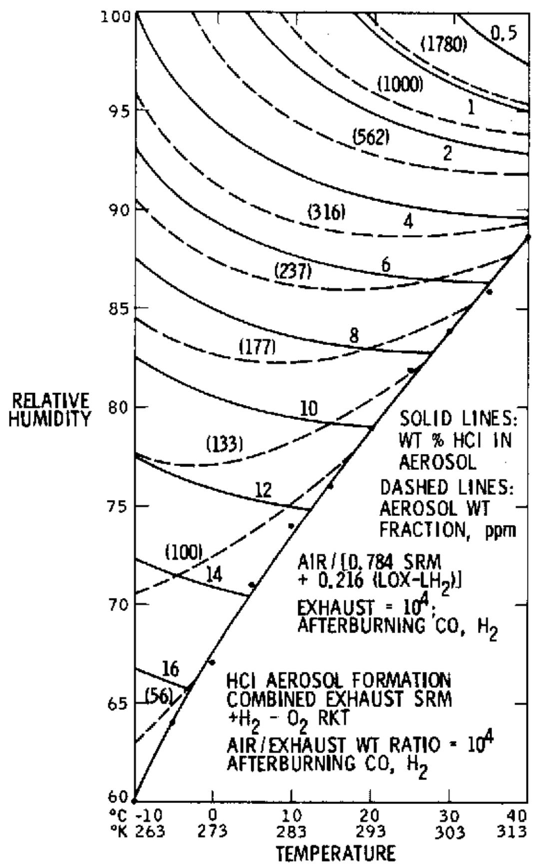

Fig. 21. Formation and properties of HCl aerosol resulting from the mixing of (10^4 parts) air with the combined exhaust of an SRM and an LH_2-LO_2 rocket (afterburning CO, H_2 assumed) vs ambient air temperature and relative humidity

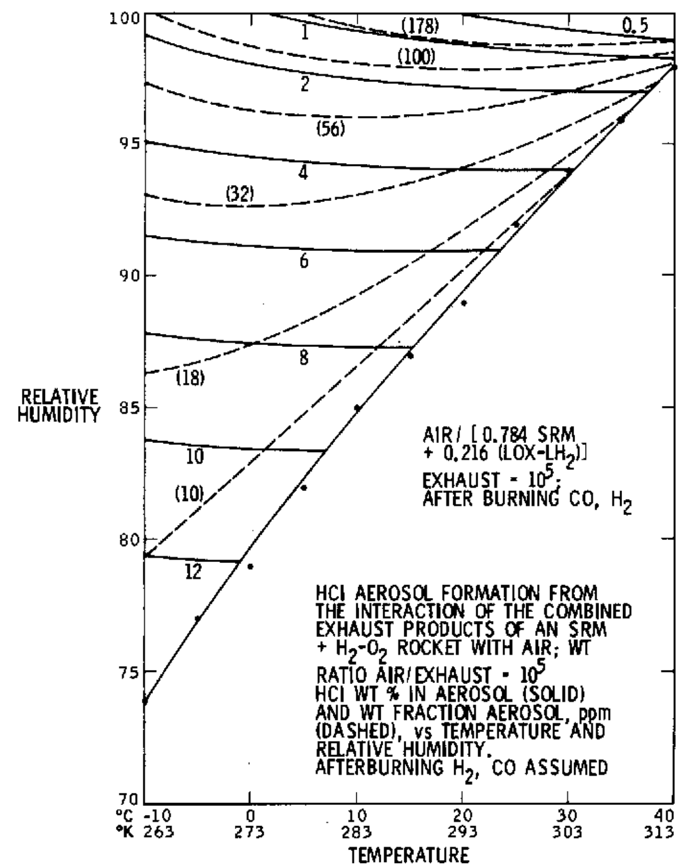

Fig. 22. Formation and properties of HCl aerosol resulting from the mixing of (10^5 parts) air with the combined exhaust of an SRM and an LH_2-LO_2 rocket (afterburning CO, H_2 assumed) vs ambient air temperature and relative humidity