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On Predicting Secondary Smoke Humidity Boundaries at Temperatures Below 0 °C

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ACKNOWLEDGMENTS

The vapor-liquid equilibria data and procedures discussed in this document were reviewed (but not necessarily endorsed) by Dr. David Hanson of NOAA and by Dr. Eugene Miller, consultant, both of whom have published data in this field. Dr. Miller also offered comments on certain other aspects of the secondary smoke problem discussed in the document. In addition, Dr. Maile Smith of IDA reviewed the document briefly. All comments are acknowledged and appreciated. Remaining errors and/or misinterpretations are the responsibility of the author.

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EXECUTIVE SUMMARY

The visibility or "smokiness" of a rocket's exhaust is an important consideration when selecting solid propellants for military applications. Visibility may arise either from particulates produced in the combustion process itself ("primary smoke") or from "secondary smoke" (in effect, contrails) which can form when the exhaust gases, which always include water vapor and often include hydrogen chloride (HCl) and sometimes hydrogen fluoride (HF), interact with a cold or humid atmosphere. HCl is of particular interest, since it appears in all propellants using ammonium perchlorate as an oxidizer; HF has much less effect and is much more rare. The presence of HCL vapor under most conditions depresses the amount of water vapor which air can contain at saturation, so that secondary smoke becomes more probable in humid atmospheres. The issues involved were examined in an early paper by this author (Oliver, 1969) and simple procedures were developed which permitted the prediction of temperature-relative humidity boundary curves defining regimes where secondary smoke would be expected for various propellants. The procedures have proved to be useful, and results have been widely adopted (e.g., AGARD, 1993). However (as was pointed out in the 1969 paper), a problem existed with the procedures and the results for ambient temperatures below 0 °C because the required HCl- and HF-water vapor equilibria data did not exist, which led to use of estimates based on extrapolations from existing data at higher temperatures. Experimental low-temperature HCl-water vapor-liquid data have since become available, stimulating a reexamination of this problem area, which is carried out here. This paper is limited to the HCl problem; the HF problem remains to be reworked. The paper is not intended as a general review of data or procedures used in secondary smoke methodology.

In the simple equilibrium procedures used here, prediction of secondary smoke boundaries when HCl is present in the exhaust gas involves two basic steps. First, vapor-liquid equilibrium data for the HCl-water system must be available, showing the vapor pressure of water above which condensation will occur in the presence of specified partial pressures of HCl at specified temperatures. The second step involves a heat and mass balance for the rocket exhaust as it mixes with air to see whether saturation conditions are ever exceeded. The procedures ignore all kinetic phenomena. The bulk of the work in this reexamination was devoted to the vapor-liquid equilibrium part of the problem rather than to the heat and mass balance step.

The revised equilibrium data used here for temperatures above 0 °C are based on Fritz and Fuget (1956), rather than the handbook data (based on Zeisberg, 1925) used in the 1969 work. The Fritz and Fuget data extend only from 0 to 50 °C; the data were extrapolated from 50 to 70 °C for modeling convenience and completeness, although not of importance otherwise. Data for the region below 0 °C were based on projections of the Fritz and Fuget work, coupled with phase data and recent low-temperature data. The low-temperature data were provided by Hanson (private communication, 1997; see also Hanson and Mauersberger, 1990); other published data (Miller, 1983) were also examined. Certain minor adjustments, as will be described, in the Fritz and Fuget (1956) data at 0 °C were found to be necessary to achieve internal consistency (necessary for purposes here but not necessarily useful elsewhere). Considerable uncertainty still exists in the vapor-liquid equilibria and phase equilibria of the HCl-water system.

Using the selected data, a computer vapor-pressure model of the system covering the liquid regime between +70 and –70 °C was prepared which allowed numerical evaluation at whatever resolution was desired; the trihydrate and ice regimes were handled separately. The data were converted to P/P^{o} plots showing the allowable water vapor pressure in the presence of HCl relative to that over pure ice (below 0 °C) or to that over pure water (above 0 °C) for the range of +70 to –70 °C including, where needed, estimates for the trihydrate regime. The P/P^{o} plots were then used, along with the original 1969 dilution-saturation computer program, to estimate temperature-humidity boundaries showing onset regimes for secondary smoke for several hypothetical propellants: The first propellant was a plausibly realistic one with a large amount of HCl; two were notional, carried out as an exercise which assumed use of ammonium dinitramide as a partial or total substitute for ammonium perchlorate to reduce or eliminate HCl in the exhaust. Overall changes in boundary curve estimates below 0 °C were found to be small and in the direction implied by certain open air firing results reported in AGARD (1993). Minor changes were also noted in computed results above 0 °C, due to the change in the HCl-water equilibrium source data from handbook values to those of Fritz and Fuget (1956). Propellants containing no HCl, which can form contrails at very low temperatures due to the condensation of water vapor, were, of course, unaffected by changes in HCl-water equilibrium data.

Although only a limited number of cases were examined, the general similarity of the present results to those earlier suggests that the errors introduced by using the 1969 extrapolated vapor-liquid data to temperatures below 0 °C, although conceivably significant in some cases, did not greatly affect the results. The procedures are, of course, highly simplified relative to the complex phenomena which actually are involved in the condensation process, such as supersaturation and nucleation requirements. In any event, it is believed that the revised P/P° data (Figs. II-9 and II-10 in this paper), particularly for the regime below 0 °C, are far more realistic than those presented in the 1969 work and until superseded or improved by further work should be used in future evaluations using this approach.

This work was supported by IDA under Central Research Projects (CRP) 221 and 231. The analytical work was carried out in FY 1997 and the results are so labeled. Efforts in 1998 were limited to review and some changes in presentation.

I. INTRODUCTION

Visible smoke, if present in a solid propellant exhaust, can provide a warning signal to the target under attack, leading to evasive maneuvers or other protective measures which may defeat the attack. Visible smoke can come either from combustion of metals, usually aluminum, which are added to solid propellants to increase both density and specific impulse, or by interaction of the propellant exhaust gases with an ambient atmosphere, producing, under certain conditions, a "secondary smoke," or contrail. As with aircraft, a contrail can form simply from condensation of water of combustion if the atmosphere is sufficiently cold; however, the presence of acid gases HCl or HF in the exhaust increases the probability that secondary smoke will form, because in their presence, a visible condensate may form under temperature and humidity conditions well below those in which water vapor alone would condense. This fact has of course long been recognized—early smokeless propellants were not metallized (except perhaps for small concentrations of lead or potassium salts used as combustion modifiers), nor did they use ammonium perchlorate (AP) as an oxidizer; these propellants also had very low performance.

The various issues connected with smokeless solid propellants were reviewed in a previous IDA paper (Oliver, 1969). As part of that review, the effects that HCl and HF have on allowable vapor pressures, and thus on secondary smoke formation, were predicted theoretically, accounting for effects of acid gases, using a simple equilibrium mixing model similar to that used earlier by Appleman (1953, 1957) in studies on contrail formation by aircraft. The work predicted boundary conditions showing the relative humidity at a specified ambient temperature below which secondary smoke would not be expected to form. The work also showed that typical environmental chamber tests were apt to overpredict the formation of condensate (or "fog") relative to effects in the field. Later tests showed the procedures to be reasonably satisfactory, and a new category of propellants, known as "reduced smoke" propellants, which use AP as an oxidizer in nonmetallized formulations, followed. Data showing tests of the methodology are provided in the review by Miller (1984) and in discussion in a NATO document (AGARD, 1993), wherein their adoption by NATO is indicated.

Oliver (1969) utilized available literature data on the vapor pressures of water and HCl over HCl solutions, all of which, unfortunately, were for temperatures above 0 °C, the freezing point of pure water. To explore effects below this temperature, the available thermodynamic data were simply extrapolated to lower temperatures, noting the fact, and calling for acquisition of data at lower temperatures. Some time after the publication of the IDA paper, the author learned of the work of Lewis (1968, 1969), which made it clear that the extrapolations below 0 °C were in substantial error. The propulsion community was notified, but the point was apparently not one of vital policy interest; and little interest was aroused or at least communicated to this author (it may have been addressed elsewhere). A revision by this author was published in 1979 [Oliver and Strahle (1979)], based on Lewis' work. Unfortunately, that revision was included in the appendix to a classified paper and may not have received wide distribution. (Both papers are now unclassified.) Also, some data at temperatures to –35 °C on the HCl-H_2O system were obtained and reported by Miller (1983).

The HCl-H_2O system at very low temperatures (~ 200 K) became of interest to an entirely different community in the mid-1980's, at the time when the ozone hole was becoming evident in the Antarctic stratosphere, and condensation phenomena with acid gases (nitric, sulfuric, and hydrochloric) were critical to understanding the heterogeneous reactions being considered [see, as examples, Wofsy et al. (1988); Hanson and Mauersberger (1988, 1990); Abbatt et. al. (1992); Wooldridge (1995)]. There was some disagreement on one point related to the effects of HCl vapor on water ice [this point recalled the procedures used by Lewis (1968, 1969)]. The classical presumption, and the one used by Lewis, is that the ice phase which separates out at low temperatures and at less than about 25 percent HCl (by weight) is essentially pure ice. Wofsy et al. (1988) found a distribution of HCl between liquid and solid phases, which would have affected the vapor pressure of water over the solid phase; also, Abbatt et al. (1992) reported some apparent surface effects of HCl on ice which appeared to affect HCl equilibrium vapor pressures, although no data are reported on effects on water vapor pressures. However, Hanson and Mauersberger (1990) found the vapor pressure of water over the ice phase to be essentially that of pure ice. This latter observation seems to fit other data, as shall be shown herein later, and has been used in this work.

A considerable amount of work, as detailed by Miller (1984) and in the more recent AGARD (1993) documentation, has been done on the question of secondary smoke since the IDA paper was published in 1969. There are no thermodynamic data presented in the

AGARD (1993) document other than at 0 °C. How much of the various work reported used the original erroneous extrapolations is unknown. In fact, it is not known whether use of these erroneous extrapolations makes much difference, since much of the regime of interest is at temperatures well above freezing, where previous procedures were based on reasonably good thermodynamic data, and in some low-temperature regimes, where water from combustion will form a contrail with or without HCl being present. The work reported here makes no attempt to review all prior data on secondary smoke. Instead, this paper reviews the thermodynamic data on the HCl-H_2O system at low temperatures, carries out some simple calculations using procedures as presented in the 1969 and 1979 papers, and compares the results.

Note that HCl is the only acid gas considered here. An update of the 1969 work on HF would also be of interest but remains to be carried out.

The write-up which follows is broken into procedures, results, and conclusions. Two types of procedures are described. The first, which represents the bulk of the effort carried out for this document, describes how the available thermodynamic data were reduced to a form useful in carrying out secondary smoke humidity-temperature boundary computations. The second describes how the secondary smoke calculations were carried out. Results for several cases of interest are then presented and compared.

This work was sponsored by IDA under Central Research Projects 221 and 231. Because the effort was a limited one (about 6 man-weeks were requested and allotted), many questions could not be pursued in depth.

II. PROCEDURES

A. REDUCTION OF THERMODYNAMIC DATA

The basic objective of the study of the thermodynamic data on the HCl-H_2O water system is to determine the effect that HCl vapor has on the saturation water vapor pressure relative to that over pure water, at specified temperatures and total pressures. The ratio of saturation vapor pressure (P) in the presence of HCl vapor to that over pure water (P^o) is termed the "k" factor in AGARD (1993). The reduced vapor pressure (or fugacity, assuming, as is done here, perfect gases) of water over liquid acid simply represents the reduced activity of water in the acid compared to the activity of pure water. The "k" factor (or "depression" effect, as in AGARD, 1993, or "suppression effect" as in Oliver, 1969) is a multiplier less than one and determined by examining the vapor-pressure data for both HCl and water over aqueous solutions of HCl, comparing equilibrium water vapor pressures either to those of liquid water (above 0 °C) or to pure ice (below 0 °C). A discussion of the approaches used in each of the prior reports and in this paper follows.

1. The Approach Used in Oliver (1969)

The 1969 paper used the Zeisberg (1925) data as reported in the *Chemical Engineer's Handbook*. The data are provided for water vapor over 6 to 42 percent solutions from 0 to 110 °C and (incompletely) for HCl over 2 to 46 percent solutions also from 0 to 110 °C. The depression factor P/P^o, where P is the equilibrium water vapor pressure over the acid and P^o is the equilibrium vapor pressure over pure water, was calculated over the regime of interest. The data covered only the regime above 0 °C but were needed at lower temperatures. No truly satisfactory way was found at the time to estimate vapor pressures below 0 °C, so an extrapolation procedure involving the partial molal heat content of the solvent (water) into lower temperatures was used. The complex phase behavior of the HCl-H_2O system was noted but not taken into account. The resulting plot, which should not now be used below 0 °C for anything but comparison purposes, is shown in Figure II-1. This plot, incidentally, was converted to empirical relationships suitable for computer usage by Victor [see Victor (1978)].

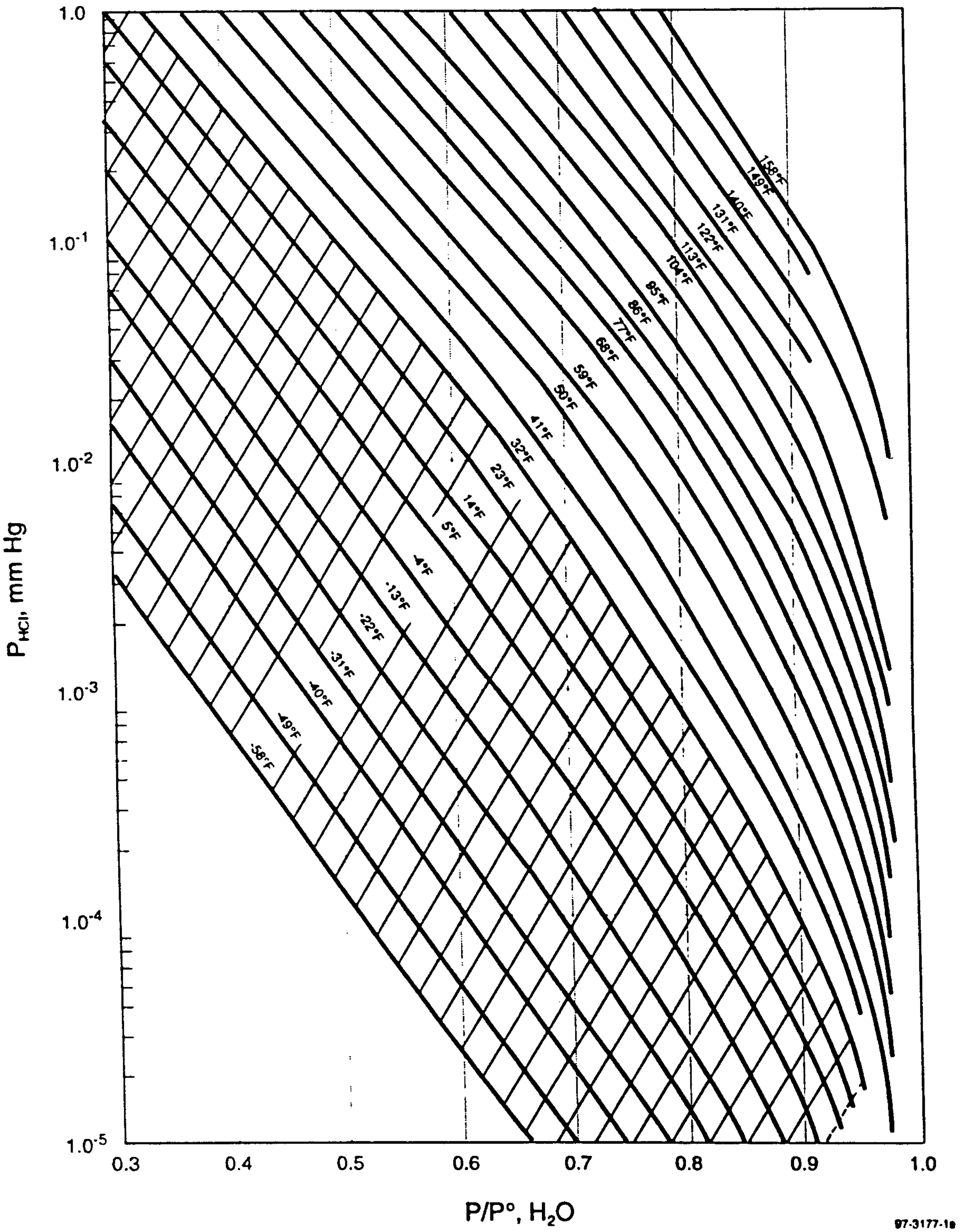

Figure II-1. HCl-H_2O Vapor Equilibria per Oliver (1969): In Error in Crosshatched Region below 32 °F

It should be noted that the P/P° term is the same as the water "activity" reported by Akerlof and Teare (1937). That work was reviewed briefly in the Oliver (1969) paper but was not used because problems were noted in the equations presented, e.g., showing activities for water above unity below about 0.25 molal. (Incidentally, it appears now that some of the objections to that work noted in Appendix A of the 1969 paper were in error due to a misreading of tabular data, where minus signs were not shown—presumably to avoid tabular clutter—but evidently expected to be understood by the reader.)

2. The Approach Used in Oliver and Strahle (1979)

As noted in the Introduction, the work of Lewis (1968, 1969) came to this author's attention after the publication of the 1969 paper. Lewis noted that a great deal could be deduced about the HCl-H_2O system at low temperatures by using the vapor pressure data (Lewis cites Schmidt, 1953, for vapor pressures), freezing point data (from Pickering, 1893; see Fig. II-2), and phase compositions, and tying all the data into a compatible whole. The critical assumption (which is often made) was that the solid phase which separates out at low temperatures in acids with concentrations less than about 25 wt. percent HCl (Region I in Fig. II-3) is, or has the water vapor pressure of, pure ice, for which the vapor pressure is known. [It would seem that this cannot be *precisely* true, since the ice phase has an HCl vapor pressure over it which is in equilibrium with HCl over the liquid phase (Region II).] At higher concentrations (over a limited range, Region III) it was also known that a trihydrate phase separates out.

Inasmuch as in the liquid region the logarithm of the HCl vapor pressure and the logarithm of the water vapor pressure are both reasonably linear in 1/T, it follows that the logarithm of the HCl pressure (for a given composition) is also (approximately) a linear function of the logarithm of the water pressure. Figure II-3 shows Lewis' plot (as redrawn somewhat imprecisely by IDA in 1979) so prepared. Note that for acid concentrations below about 25 percent HCl, the log P_{HCl} vs. log P_{H_2O} lines, the slopes of which are established at higher temperatures, can simply be extrapolated to lower temperatures until P_{H_2O} equals the known P_{H_2O} of ice, which, if everything is done correctly, occurs at the known freezing point. For concentrations above about 25 percent HCl, the water vapor and HCl vapor pressures must be extrapolated to lower temperatures, using known 1/T data, to the known freezing point at which the trihydrate comes out of solution. Isotherms in the trihydrate region are established from the Kp values ($P_{H_2O}^3 \times P_{HCl}$) at the intercept, which

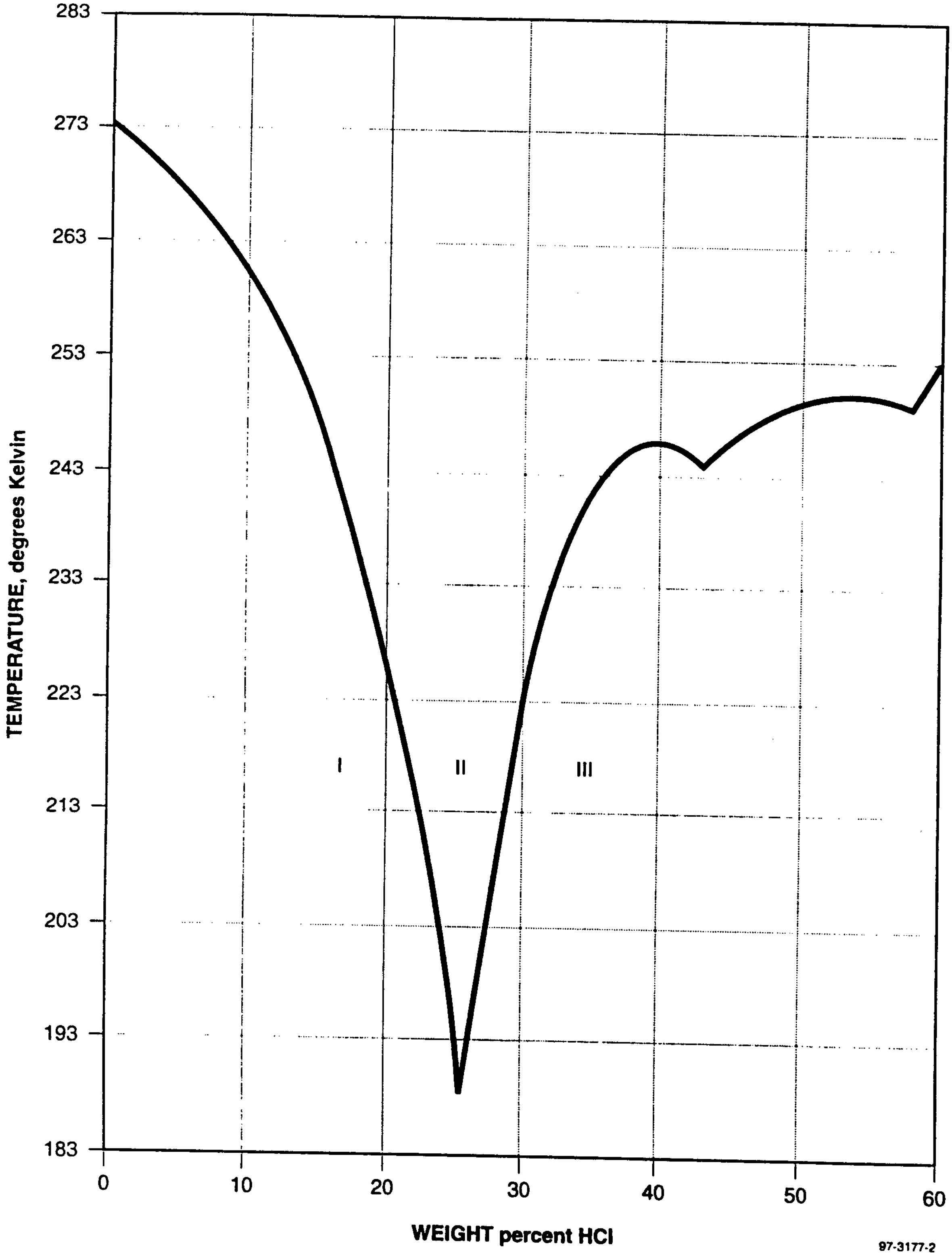

Figure II-2. HCl-H_2O Freezing Point Diagram per Lewis (1968–1969), Redrawn by IDA [in Oliver and Strahle (1979)]

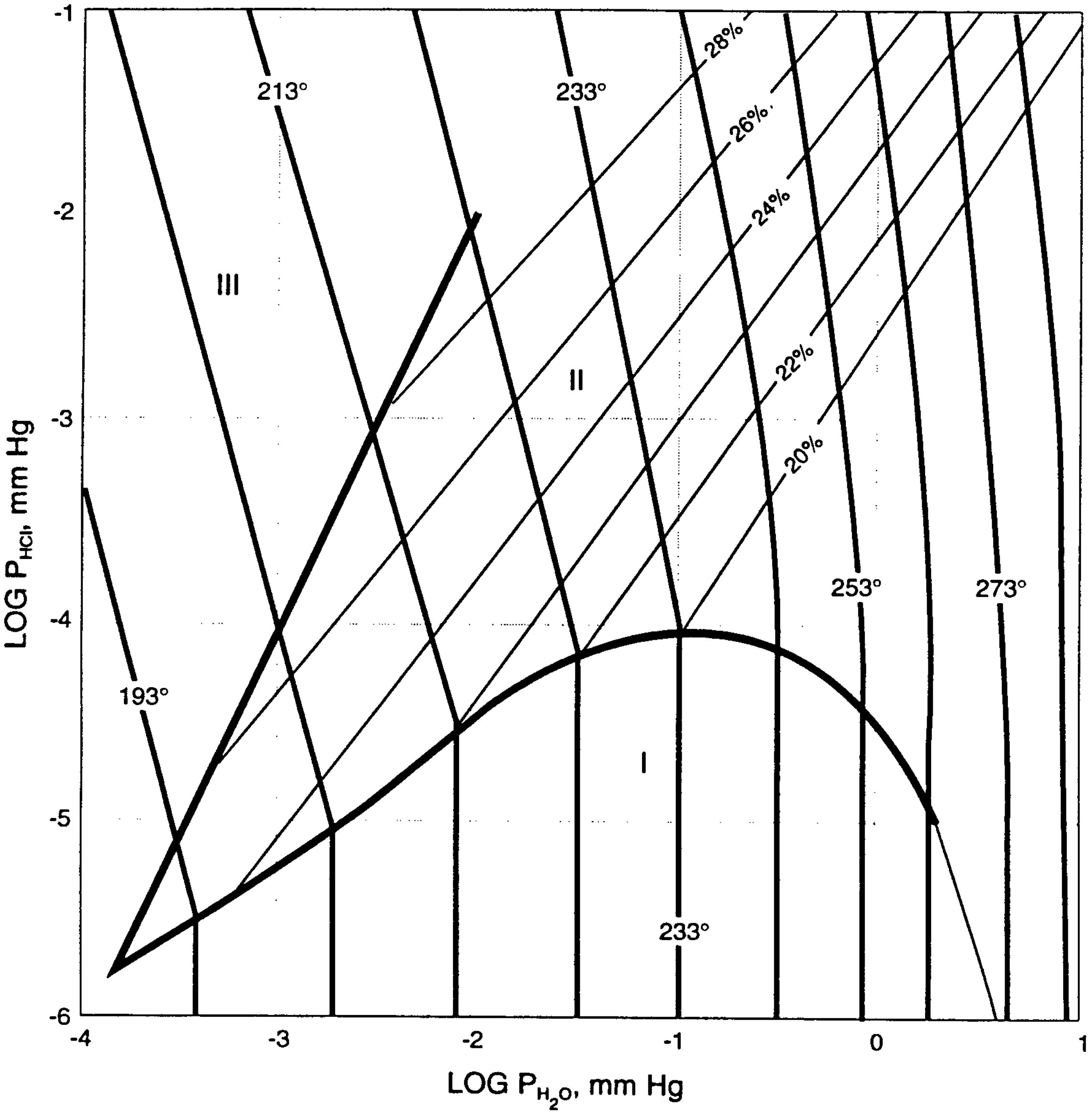

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Figure II-3. Estimated Low Temperature H_2O-HCl Vapor Equilibria per Lewis (1968–1969), Redrawn by IDA [in Oliver and Strahle (1979)] (if properly plotted) have a –3 slope on a log-log plot. Note that P/P° for water vapor (either liquid or ice) is related to the curvature of the isotherm (the negative logarithm of the water activity is the horizontal distance between the isotherm and a vertical line extended above P_{H_2O} on the abscissa) and that there is no observable depression of allowable water vapor pressure by HCl in the two-phase region where ice is one phase. It might also be noted that formation of the trihydrate solid phase would seem to be improbable kinetically in rocket gas mixing with a cold atmosphere. A trihydrate of nitric acid is believed to form in the Antarctic stratosphere (Hanson and Mauersberger, 1988), but this is presumably over periods of days to months.

The HCl-H_2O vapor system as described by Lewis (1968, 1969) was converted to a revised P/P° plot in the 1979 paper [Oliver and Strahle (1979)] and is presented as Figure II-4. The vapor pressure data used for the regime above 0 °C was again that of Zeisberg (1925). Note that this plot, while representing a substantial improvement over the 1969 plot, since it at least incorporated phase data, did not incorporate any new measurements of vapor pressures and was again based on rather lengthy log-linear extrapolations of vapor pressure data taken at higher temperatures. It was also based on the assumption that the ice phase in the low-concentration region has a water vapor pressure identical to that of pure ice.

Note that Lewis did not show a hexahydrate phase. According to recent work [Abbatt et al. (1992)] the hexahydrate is the thermodynamically stable solid phase in equilibrium with about 25 percent acid (near the ice-trihydrate eutectic), and melts at about 200 K. Further information on the hexahydrate is provided in Wooldridge et al. (1995); the region is clearly complex. Abbatt et al. (1992) note that the hexahydrate does not form unless the mixture is cooled to about 150 K and then rewarmed; Wooldridge et al. (1995) state that the hexahydrate nucleates only when cooled to below 170 K. The hexahydrate phase has thus not been considered in this work, even though all other work is based on equilibrium rather than on kinetic phenomena.

3. The Current Approach

a. General

The current approach basically follows that of Lewis (1968, 1969) but incorporates new data with the goal of tying the available data into a coherent mathematical description of vapor pressures and suppression factors for known molality systems as functions of temperature as needed for purposes here. Unfortunately, the available data are not all consistent, so this goal was not fully met. The overall goal of the thermodynamic work was to develop an improved Figure II-4, suitable for work of this type, a somewhat less demanding goal than a full rationalization of published thermodynamic data.

The linear nature of the abscissa in Figure II-4, in a data set extending over many decades, and where uncertainties may in fact be factors of 2 or more, requires internal consistency if smooth plots are to be realized. For example, a 10-percent error in P_{H_2O} converted to a P/P° value moves the plotted point in Figure II-4 by a large and obvious amount. Both extrapolated and measured values of P_{H_2O} at very low temperatures can easily be in error by more than 10 percent.

This paper primarily utilized specific molalities as used by Fritz and Fuget (1956), and did not provide routines for interpolation between molalities. Interpolation procedures to provide vapor pressures for different molalities have been proposed as far back as 1937 by Akerlof and Teare. More recently, interpolation procedures for HCl alone, up to about 9 molal, have been proposed by Stone (1985) and by Luckas and Eden (1995). Unfortunately, all have appeared to involve some difficulties so that this dimension of the modeling remains for some future effort.

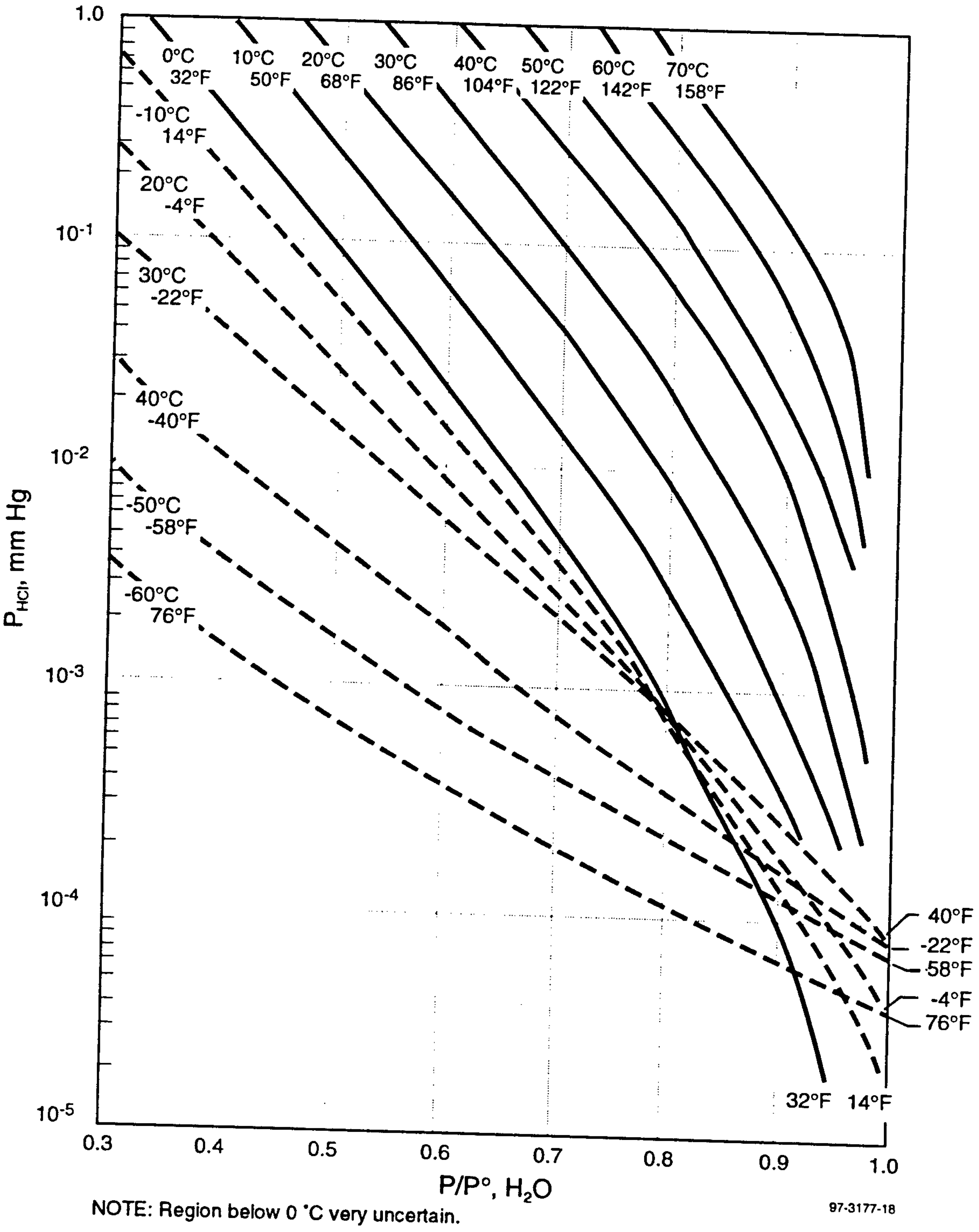
b. Data Needed

The data needed include the vapor pressures for pure ice (below 0 °C), pure water (above 0 °C), and HCl; H_2O vapor pressures in equilibrium with acids of known molality and temperature; and preferably data on the equilibrium constant for the trihydrate in equilibrium with water vapor and HCl.

Note that certain important caveats must be recognized in using equilibrium data for the type of predictions made here, since kinetics play a major role in condensation phenomena and supersaturation is required. These caveats are discussed later.

c. Data Used

Vapor Pressure Data for Water and for Ice. These data are well known. The correlation given in the Smithsonian tables (List, 1951) was used for the vapor pressure of pure liquid water above 0 °C. The same equation can be used for supercooled water, but the vapor pressures of supercooled water were not used in this work. The correlation of Jansco et al. (1970) was used for the vapor pressure of ice below 0 °C. (See, however, Section II.B.)



NOTE: Region below 0 °C very uncertain.

Figure II-4. Vapor Pressure Depression of H_2O by HCl, with Dashed Lines (below 0 °C) Based on Lewis (1968–1969), as Reported in Oliver and Strahle (1979). Updated in this work.

Freezing Point Data for Acid Solutions. The HCl-H_2O system would be expected to be well characterized in view of its long use and many published measurement efforts. Indeed, it is well characterized for most purposes. However, for work which involves integration of data from various sources and extrapolation into poorly measured areas, the data leave much to be desired. Perhaps the basic reason that this situation still pertains is that properties of interest are extremely sensitive to the acid concentration, particularly near the freezing point minimum, as are, correspondingly, the vapor pressures of HCl and of H_2O at the freezing point. The liquid is subject to supercooling. No modern studies of the freezing point were found. The International Critical Tables (ICT) give some incomplete and not always consistent data. A copy of the original work [which was cited by Wofsy et al. (1988), but which does not seem to be cited in the ICT] by Pickering (1893) reported that the first and second runs provided significantly different freezing points, presumably due to supercooling of the liquid. A preferred plot was provided by Pickering, but precise reading of the plot is difficult, particularly where the freezing point is changing rapidly with molality (in the 8–10 molal regime). The freezing point plot as used in this work is shown as Figure II-5; it is presumably based on the same data source (Pickering, 1893) used by Lewis and shown earlier as Fig. II-2, but in different concentration units. It should be recognized that Figure II-5 is simplistic in terms of equilibria phenomena, as evidenced by the complex behavior involving ice, liquid, trihydrate, and hexahydrate illustrated in Wooldridge et al. (1995) in the minimum freezing point region. The Wooldridge et al. (1995) data suggest that a minimum freezing point in the absence of hexahydrate formation occurs at about –93 °C, some 6 °C below that shown in Figure II-5, with a composition near, but not necessarily precisely at, 9 molal.

Vapor Pressure Data for Acid Solutions. The vapor pressure data are derived from Fritz and Fuget (1956) (see Table II-1). The data of Miller (1983) which extended from 0 to –35 °C were also examined and are summarized later (Fig. II-8). The principal tie to low temperatures used here [to extend the data of Fritz and Fuget (1956)] was provided by the data of Hanson and Mauersberger (1990).[1]

The vapor pressure data set (available only for temperatures above 0 °C), which seems to be preferred in the recent scientific literature, is that of Fritz and Fuget (1956). The Fritz and Fuget (1956) data set has a thermodynamic basis and shows little scatter for

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[1] Provided to the author by D. Hanson in 1997 and reproduced in Table II-2.

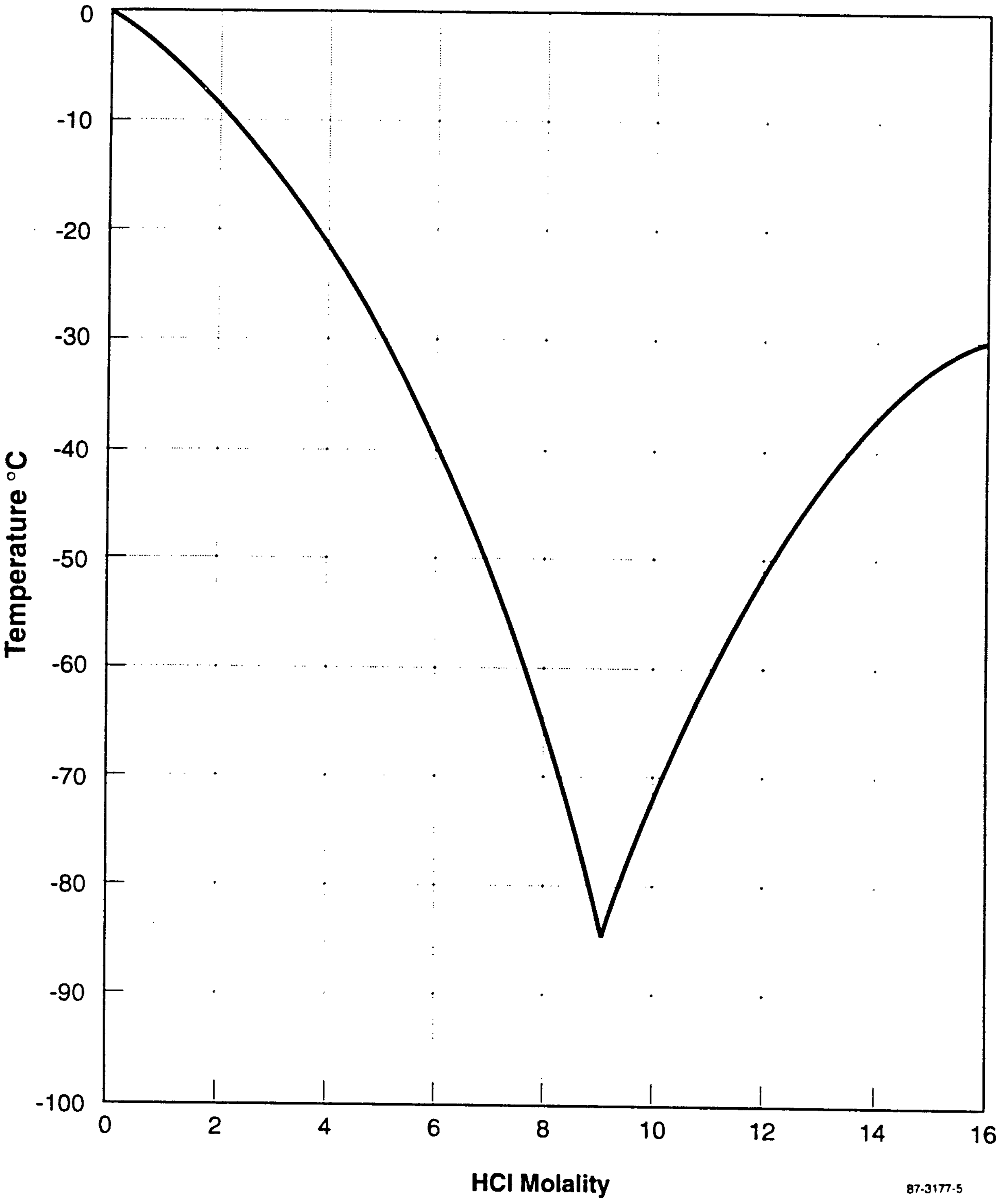

Figure II-5. Freezing Point Data for HCl-H_2O Solutions. Based on Pickering (1893).

Table II-1. HCl-H_2O Vapor Pressure Data [Fritz and Fuget (1956)]

(a) HCl Vapor Pressure, mm Hg

Molality	Wt. % HCl	0 °C	10 °C	20 °C	30 °C	40 °C	50 °C
.00	.0364	2.10×10^{-9}	6.37×10^{-9}	1.84×10^{-8}	5.01×10^{-8}	1.32×10^{-7}	3.35×10^{-7}
.05	.1820	4.46×10^{-8}	1.35×10^{-7}	3.88×10^{-7}	1.06×10^{-6}	2.79×10^{-6}	7.00×10^{-6}
.10	.3633	1.65×10^{-7}	1.01×10^{-6}	1.43×10^{-6}	3.88×10^{-6}	1.01×10^{-5}	2.52×10^{-5}
.20	.724	6.16×10^{-7}	1.85×10^{-6}	5.28×10^{-6}	1.43×10^{-5}	3.72×10^{-5}	9.37×10^{-5}
.50	1.790	3.87×10^{-6}	1.15×10^{-5}	3.26×10^{-5}	8.38×10^{-5}	2.20×10^{-4}	5.41×10^{-4}
1.0	3.513	1.81×10^{-5}	5.33×10^{-5}	1.49×10^{-4}	3.96×10^{-4}	1.01×10^{-3}	2.45×10^{-3}
2.0	6.796	1.20×10^{-4}	3.45×10^{-4}	9.44×10^{-4}	2.43×10^{-3}	6.05×10^{-3}	.0143
3.0	9.859	4.68×10^{-4}	1.32×10^{-3}	3.51×10^{-3}	8.88×10^{-3}	.0211	.0497
4.0	12.73	1.59×10^{-3}	4.36×10^{-3}	.0114	.0279	.0659	.149
5.0	15.42	4.89×10^{-3}	.0131	.0333	.0794	.183	.401
6.0	17.95	.0141	.0366	.0903	.210	.468	1.001
7.0	20.34	.0382	.0964	.231	.521	1.132	2.354
8.0	22.58	.0987	.242	.563	1.236	2.61	5.27
9.0	24.70	.240	.571	1.295	2.76	5.69	11.20
10.0	26.72	.0552	1.278	2.83	5.87	11.73	22.6
11.0	28.63	1.229	2.77	5.86	11.97	23.28	43.9
12.0	30.43	2.55	5.60	11.75	23.14	44.1	80.9
13.0	32.16	5.11	11.00	22.25	43.6	79.5	140
14.0	33.79	9.99	20.75	41.1	76.8	137.4	242
15.0	35.35	18.56	38.0	72.2	132.5	23.2	400
15.88	36.63	31.0	61.2	114.8	201.4	360	

(b) H_2O Vapor Pressure, mm Hg

Molality	0 °C	10 °C	20 °C	30 °C	40 °C	50 °C
0.0	4.579	9.209	17.535	31.824	55.324	92.51
0.05	4.575	9.19	17.51	31.78	55.23	92.44
0.10	4.57	9.18	17.47	31.71	55.13	92.18
0.20	4.56	9.15	17.42	31.62	54.94	91.88
0.50	4.51	9.05	17.22	31.22	54.35	90.94
1.0	4.42	8.87	16.78	30.70	53.27	89.18
2.0	4.22	8.44	16.08	29.96	50.8	87.63
3.0	3.99	7.95	15.17	27.63	48.8	80.60
4.0	3.69	7.38	14.09	25.70	45.2	75.3
5.0	3.37	6.75	12.91	23.6	41.7	69.5
6.0	3.03	6.09	11.71	21.5	38.0	63.5
7.0	2.70	5.45	10.49	19.3	34.3	57.5
8.0	2.48	4.81	9.35	17.2	30.6	51.5
9.0	2.13	4.21	8.26	15.6	27.2	45.6
10.0	1.80	3.69	7.22	13.4	24.0	40.6
11.0	1.59	3.17	6.28	11.7	21.0	35.5
12.0	1.34	2.75	5.45	10.2	18.4	31.6
13.0	1.11	2.36	4.72	8.86	16.2	27.8
14.0	0.98	2.02	4.05	7.73	14.1	24.4
15.0	0.83	1.73	3.49	6.71	12.9	21.4
15.88	0.72	1.51	3.07	6.00	11.4	

(c) Total Vapor Pressure, mm Hg

Molality	0 °C	10 °C	20 °C	30 °C	40 °C	50 °C
0.0	4.58	9.21	17.54	31.82	55.32	92.31
0.05		9.19	17.51	31.78	55.23	92.44
0.10	4.57	9.18	17.47	31.71	55.13	92.18
0.20	4.56	9.15	17.42	31.62	54.94	91.88
0.50	4.51	9.05	17.22	31.32	54.35	90.94
1.0	4.42	8.87	16.78	30.70	53.27	89.18
2.0	4.22	8.44	16.08	29.96	50.8	87.64
3.0	3.99	7.95	15.17	27.64	48.8	80.65
4.0	3.69	7.38	14.10	25.73	45.3	75.4
5.0	3.37	6.76	12.94	23.7	41.9	69.9
6.0	3.04	6.13	11.80	21.7	38.5	64.5
7.0	2.74	5.55	10.72	19.8	35.4	59.9
8.0	2.58	5.05	9.91	18.4	33.2	56.8
9.0	2.37	4.78	9.56	18.4	32.9	56.8
10.0	2.35	4.97	10.05	19.3	35.7	63.2
11.0	2.82	5.94	12.14	23.7	44.3	79.4
12.0	3.89	8.35	17.20	33.3	62.5	112.5
13.0	6.22	13.36	27.0	52.5	95.7	168
14.0	10.97	22.8	45.2	84.5	132	266
15.0	19.39	39.7	75.7	139	245	421
15.88	31.7	62.7	118	207	371	

both water vapor and for HCl when plotted on typical logarithmic pressure vs. 1/T plots. However, when fit to mathematical representations, it quickly becomes clear that in some cases the data—in particular the water vapor pressure data—involve uncertainties which are significant in terms of the modeling efforts here. Figure II-6 illustrates the point with regard to the water vapor pressure data. Figure II-6a is a "difference" plot, which shows the difference (sign reversed) between the indicated vapor pressure at 0 °C at succeeding molalities as a function of molality. Note the odd behavior above 7 molal and in particular in the 8–11 molal regime. Similarly, Figure II-6b shows the ratios of vapor pressures reported at 10 °C to those reported at 0 °C, with erratic behavior again beginning about 7 molal. In the procedures developed here, the data at 10 °C were not in fact used; however, the difference data and the ratio data both suggested that the vapor pressure at 8 molal at 0 °C is somewhat suspect.

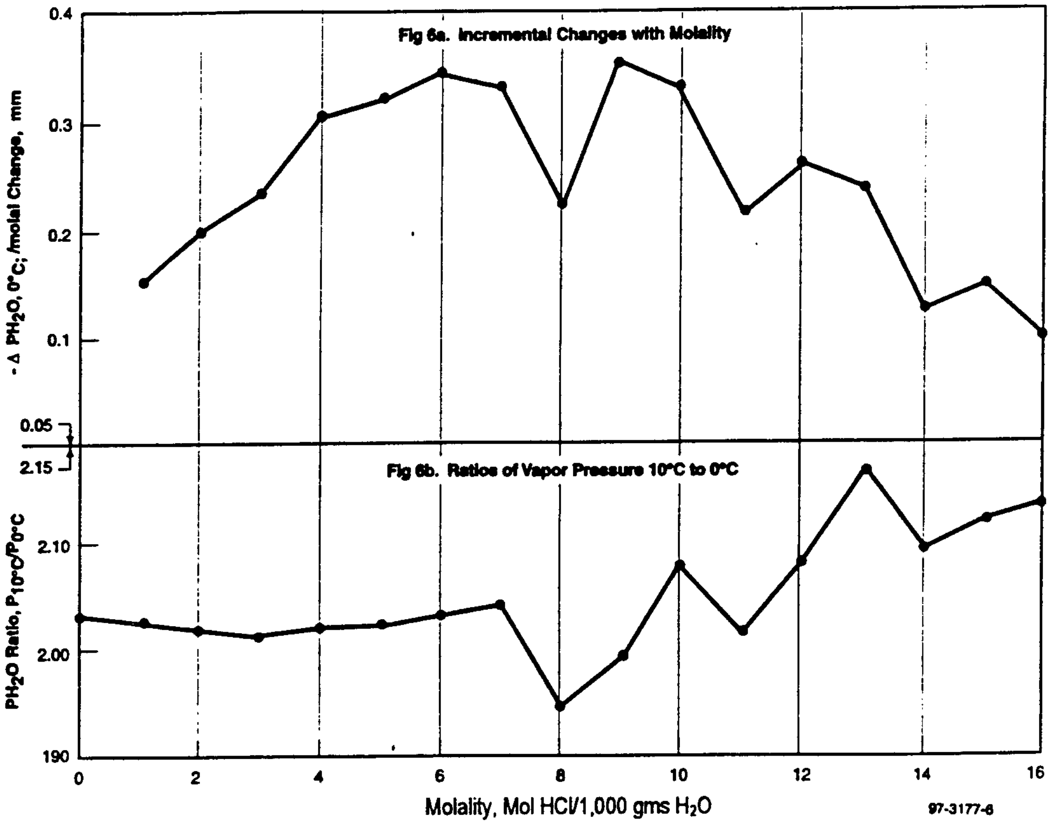

Figure II-6. H_2O Vapor Pressure Data Comparisons [Fritz and Fuget (1956)]

The HCl vapor pressures reported by Fritz and Fuget (1956) appear to behave much more reasonably than do the water vapor pressures, but this may be an artifact, in that the wide change in vapor pressures forces a logarithmic presentation, which suppresses apparent uncertainties. Also, in modeling, effects of uncertainties in P_{HCl} are less obvious, not being testable against ice vapor pressures in the one regime and entering only as the first power rather than as the cube in the trihydrate regime.

Fritz and Fuget (1956) state that their uncertainties in P_{HCl} are 1 percent at 30 °C and 2 percent at the two extreme temperatures. The stated accuracy in P_{H_2O} is estimated at 2 percent in log (P/Ps) where Ps is the saturation vapor pressure of pure water. They note that this figure means that the accuracy is within 0.1 percent at 2 molal, 1.5 percent at 9 molal, and 3.5 percent at 15 molal.

It should be noted also that the Fritz and Fuget (1956) data often differ significantly from that of Zeisberg (1925). A sample comparison carried out here used data at 0 °C for both water and HCl at different acid concentrations. It was found that the Fritz and Fuget vapor pressure for water was always higher than that from Zeisberg, from 2.4 percent higher at 6 percent HCl to 10.2 percent higher at 26 percent HCl. Use of the Fritz and Fuget data thus implies a somewhat lesser effect of HCl on allowable vapor pressures of water, an effect which will be evident later herein, but which has nothing to do with data procedural errors in the 1969 paper. Vapor pressure data for HCl at 0 °C over the same concentration range also differed, but not in a uniform manner. At low concentrations, the HCl vapor pressures reported by Zeisberg were somewhat lower than those reported by Fritz and Fuget; at high concentrations, they were higher; in the mid-concentration range, they went from being lower to being higher.

In this work, the approach was to use Fritz and Fuget data along with recent experimental data for both HCl and H_2O (independently) at each specified molality, at three temperatures, to fit a modified form of the Clausius-Clapeyron equation:

$$\ln P = A - B/T + C \ln T .$$

This form allows for differences between heat capacities of reactants and products, but it is treated here as being purely empirical. Initially, for curve-fitting purposes, to solve for A, B, and C, data were selected at 0 °C, 20 °C, and 50 °C. (In principle, of course, all the data could have been treated in some sort of least squares minimization program, but this was not done; furthermore, doing so probably would not have helped in terms of incorporating the new low-temperature data into a coherent treatment of the entire data set.) The vapor pressures were then calculated at lower temperatures.

Ice Side (Region I) Compositions. For compositions on the ice side of the minimum freezing point, the calculated (extrapolated to low temperatures) vapor pressure of water over the acid solution was compared to the vapor pressure of pure ice, it being expected that the water vapor pressure would equal that of pure ice at the known freezing point. This is a sensitive test for the extrapolation, and in some cases, the apparent freezing point derived from extrapolations of higher temperature water vapor pressure data were far from the known freezing point. The worst case encountered was at 8 molal, where the calculated freezing point using the actual Fritz and Fuget data was found to be some 25 °C high (231 K vs. about 206 K). It was soon concluded that internal consistency forced a different approach, which evolved into use of "consistency-required" vapor pressures, which for modeling purposes were found by trial and error and used at 0 °C, keeping the 50 °C and 20 °C values unaltered. For example, to fit the known freezing point at 8 molal, it was necessary to use a water vapor pressure at 0 °C of 2.39 mm instead of 2.48 mm. This 3.6-percent difference can be viewed as a measure of the fit of the ln P vs. T equation, which extends from 50 °C to about 70 °C, to the Fritz and Fuget data at 0 °C, or it can be viewed as a measure of possible experimental error in that data. If viewed as experimental error, however, the deviation is over twice that indicated by Fritz and Fuget (1.5 percent at 9 molal), and probably indicates that some of the "error" should have been ascribed to the data at 20 °C and 50 °C or to some other cause.) The consistency-required water vapor pressure at 0 °C at 13 molal also differs from the Fritz and Fuget number (1.11 mm reported vs. 1.155 mm required, a 4.05-percent difference), by an amount which is somewhat larger than their error estimate (3.5 percent at 15 molal). The differences between the consistency-required vapor pressures and the reported values were otherwise all much smaller than the discrepancies at 8 and 13 molal, and certainly unnoticeable on a typical log-log plot. These very small changes can, however, have a significant effect on, for example, the calculated Kp value at the freezing point.

Trihydrate Equilibria. On the trihydrate side, the equilibrium criterion is the thermodynamic equilibrium constant, here labeled "Kpt," which is the product of the cube of the water vapor pressure (here, in mm Hg) and the first power of the HCl vapor pressure (again, in mm Hg). The hexahydrate is again ignored, which may not be correct. A consistent data set would result in extrapolated water vapor and HCl vapor pressures at the known freezing point which would match Kpt at the freezing point. Kp, calculated at low temperatures (~ 200 K) using values for the vapor pressure of water extrapolated from higher temperature data (273 K and above), is extremely sensitive to the precise values of the vapor pressures of water as measured at the higher temperatures.

Unfortunately, Kpt, which is a function of T only, is not well known for the trihydrate. The only published value found was that given by Wooldridge et al. (1995):

$$\ln \mathrm{Kpt}' = 67.88 - 207{,}200/RT ,$$

where Kpt′ is in $(\text{atmospheres})^4$, R is 8.315 kJ/mol-K, and T is in K.

With Kpt in $(\text{mm})^4$, and substituting R, the equation becomes

$$\ln \mathrm{Kpt} = 94.413 - 24{,}919/T .$$

The equation in the form presented by Wooldridge et al. (1995) is stated to be based on Hanson and Mauersberger's (1990) measurements, but it appears to provide only an approximate match to his data. A crude expression derived by this author from the published data in the 180–200 K regime in the small log-log plot in Hanson and Mauersberger (1990) was the following:

$$\ln \mathrm{Kpt} = 91.367 - 24{,}412/T ,$$

which gives somewhat lower Kpt values at 200 K than would be indicated by the Wooldridge et al. (1995) expression (4.68×10^{-14} vs. 7.80×10^{-14}). It was noted that the data used by Wooldridge et al. (1995) for Kpt were apparently based only on very low temperature data over a limited range. An independent estimate was thus developed for use in this work using the freezing point estimates and the P_{HCl} and P_{H_2O} estimates extrapolated from Fritz and Fuget (1956), modified as necessary in certain instances,[2] and covering the range from about 240 K to 190 K. The resulting curve fit expression was

$$\ln \text{Kpt} = 96.8684 - 25{,}452.8/T, \text{ where Kpt is in } (\text{mm})^4.$$

The uncertainty in this expression has not been estimated. It should be viewed as an interim expression developed only for use in this work. Obviously, more significant figures are shown than are justified. Note that this equation yields a value of 6.30×10^{-14} mm^4 at 200 K, a value in between those noted above.

To generate a model of the system which was reasonably consistent internally, this expression was used in Region III in preparing a set of values for P_{HCl} and P_{H_2O} at 0 °C to "smooth" data at the different molalities at the freezing point data and recent experimental data. That is, the expression shown was used to generate a theoretical Kpt value at the freezing point, where the extrapolated values for P_{H_2O} and P_{HCl} should meet. The process was analogous to that used at lower concentrations, where water ice rather than trihydrate is the expected solid phase, and where "Kp" at the freezing point is simply the vapor pressure of pure ice. Here, however, the extrapolated value for P_{HCl} also entered. It was noted that only very small changes in P_{H_2O} at 0 °C could, when extrapolated to the freezing point, easily change calculated Kp for the trihydrate by a factor of 2.

Recent Experimental Data. Two primary data sets are available, that of Miller (1983) and that of Hanson and Mauersberger (1990) with details of the latter provided by Hanson in a private communication. One additional partial data set is noted from Abatt et al. (1992).

Miller (1983) carried out studies of the vapor pressures of acid solutions in the 0 to −35 °C regime. Using the Gibbs-Duhem approach, he compared his experimental results to calculated results and found substantial discrepancies—in one case, for P_{HCl}, a factor

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[2] The overall process was iterative but involved what amounted to two steps; initial adjustments were used to generate a plot from which a Kpt expression could be derived. This expression, coupled with the Fritz and Fuget (1956) data and experimental data at low temperatures, was then used for further adjustments. The final adjustments are noted below.

of 2—indicating an erroneous measurement. Again, his results are plotted and tabulated later herein, but were not used to adjust any of the modeled curves.

Table II-2 gives the original experimental results reported in graphical form in Hanson and Mauersberger (1990). A subset of the results at temperatures in the 200–220 K regime was found to be particularly useful in "anchoring" (i.e., forcing minor adjustments in) the extrapolated results of Fritz and Fuget (1956). These particular data, while unconfirmed by other investigators, appear to be quite internally consistent and reasonably free of scatter, which of course does not guarantee that the data are "correct." A problem was that none of Hanson's compositions exactly matched the molalities used by Fritz and Fuget (1956), so that a precise tie was not possible. Note that P/P° on the ice side of the freezing point minimum approaches unity as the temperature approaches the freezing point. This was the basic assumption used by Lewis (1968, 1969) and in this work. Note also that the data at 0.072 and 0.118 mole fraction showed some discrepancies or lack of reproducibility. The water vapor pressure data point at 0.118 mole fraction (7.426 molality) and 220.8 K appeared low; furthermore, the entire data set at 0.118 mole fraction did not fit well on an interpolated plot at 7.426 molal. These data were not used to make any adjustments to the Fritz and Fuget (1956) extrapolations.

A small amount of data on PHCl at the freezing points has also been reported by Abbatt et al. (1992). The data seem to be quite consistent but are two- to threefold lower than expected from other data. The issues involved were not resolved or pursued.

"Consistency-required" Adjustments. As already noted, internal consistency forced some minor adjustments which were here made in reported vapor pressures at 0 °C to bring the entire data set into a reasonably rational whole and to develop smooth and reasonable P/P° curves. These "adjusted" values are intended only for purposes of this work. The process was iterative, subjective, and clearly arbitrary but was apparently unavoidable; certainly there seemed to be no hope of finding a scientifically "best" data set from all the disparate available results. [Even so, perfect consistency was not achieved. At 9 molal, the estimated freezing point requirement was met but the trihydrate Kp value was not; the modeling may be in error or the 9 molal freezing point may not be a quadruple point. This is a complex regime, as was shown by Wooldridge et al. (1995).] The actual numbers and adjustments used are summarized in Table II-3. A check mark indicates no change was needed in the Fritz and Fuget (1956) data. The adjustments are all minor.

Table II-2. Low Temperature Vapor Pressure Data [Hanson and Mauersberger (1990)*]

HCl Mole Fraction*	Molality[1]	Estimated Fr. Pt., K[1]	T, K*	P_{HCl}, Torr*	P_{H_2O}, Torr	$(P_{H_2O}/P°_{ice})$[1]
.072	4.307	248.7	256.0	3.20 – 4(2)	1.00 + 0	0.99
.072	4.307	248.7	246.9	1.78 – 4	4.30 – 1	1.03
.118	7.426	215.0	238.4	1.30 – 4	1.49 – 1	0.86
.118	7.426	215.0	229.3	3.37 – 4	5.25 – 2	0.85
.118	7.426	215.0	220.8	6.90 – 5	1.35 – 2	0.61
.118	7.426	215.0	219.1	8.80 – 5	1.84 – 2	1.03
.128	8.148	203.7	220.0	2.87 – 4	1.53 – 2	0.77
.128	8.148	203.7	210.0	7.05 – 5	4.51 – 3	0.86
.128	8.148	203.7	205.0	3.40 – 5	2.45 – 3	0.95
.128	8.148	203.7	200.0	1.55 – 5	1.20 – 3	0.98
.132	8.441	199.2	215.0	1.79 – 4	7.39 – 3	0.71
.132	8.441	199.2	205.0	4.40 – 5	2.20 – 3	0.85
.146	9.489	195.2	220.0	1.23 – 3	1.21 – 2	0.61
.146	9.489	195.2	215.0	6.39 – 4	6.77 – 3	0.65
.146	9.489	195.2	210.0	3.15 – 4	3.57 – 3	0.68
.146	9.489	195.2	205.0	1.46 – 4	1.87 – 3	0.72
.146	9.489	195.2	200.0	7.00 – 5	9.55 – 4	0.78
.151	9.872	198.5	220.0	1.80 – 3	1.56 – 2	0.58
.151	9.872	198.5	210.0	4.60 – 4	3.30 – 3	0.63
.151	9.872	198.5	200.0	1.06 – 4	8.40 – 4	0.73

* Private communication, D. Hanson, 1997.

[1] IDA computation or estimate.

[2] Indicated by Hanson to be questionable.

d. Resulting Data

The computer-generated tabular results for all compositions used from 0.5 to 15.88 molal are provided in AppendixA. Note that the data have been extrapolated above the source upper data temperature value of 50 °C to 70 °C, as well as to the subfreezing temperatures. The extension to higher temperatures is a matter of convenience, inasmuch as prior plots of vapor pressure suppression factors extended to 70 °C. These data have not been tested against other data and should not be used where high accuracy may be needed. Data are not included for isotherms extrapolated into the solid trihydrate region, but these

Table II-3. "Consistency-Required" Vapor Pressures at 0 °C vs. Fritz and Fuget (1956) Reported Values

	P_{H_2O}, 0 °C		P_{HCl}, 0 °C	
Molality	F + F	Model*	F + F	Model*
0.5	4.51	√	3.87 – 6	√
1.0	4.42	√	1.81 – 5	√
2	4.22	√	1.20 – 4	√
3	3.99	√	4.68 – 4	√
4	3.69	√	1.59 – 3	√
5	3.39	√	4.89 – 3	√
6	3.03	3.035	.0141	√
7	2.70	√	.0382	√
8	2.48	2.39	.0987	.0994
9	2.13	2.1015	.0240	0.242
10	1.80	1.81	0.552	0.558
11	1.59	1.563	1.229	1.220
12	1.34	1.342	2.55	2.57
13	1.11	1.155	5.11	√
14	0.98	0.975	9.99	√
15	0.83	√	18.56	√
15.88	0.72	0.703	31.0	√

* A check mark indicates no change.

can be generated by hand using the Kp values at the freezing point. In Region I the vapor pressure of water is not affected by the vapor pressure of HCl, and is simply the vapor pressure of pure ice at the specified temperature.

Figure II-7 presents the HCl-H_2O system in the liquid regime principally pursued in this work, after all adjustments. The curved line at 0 °C is the Fritz and Fuget (1956) data. The isotherms at the different molalities are the modeled results, tying into Hanson and Mauersberger's (1990) data and with freezing point and Kp data as discussed earlier. The Abbatt et al. (1992) results, which are for P_{HCl} only, are plotted against the vapor pressures of pure ice at the specified temperatures. The triangular region at very low temperatures is dotted to indicate that this is a more complex region than indicated. Note also that isotherms of constant Kp could have been drawn in the trihydrate region. P_{H_2O} isotherms in the ice regime near the abscissa are simply vertical lines set by the vapor pressure of ice.

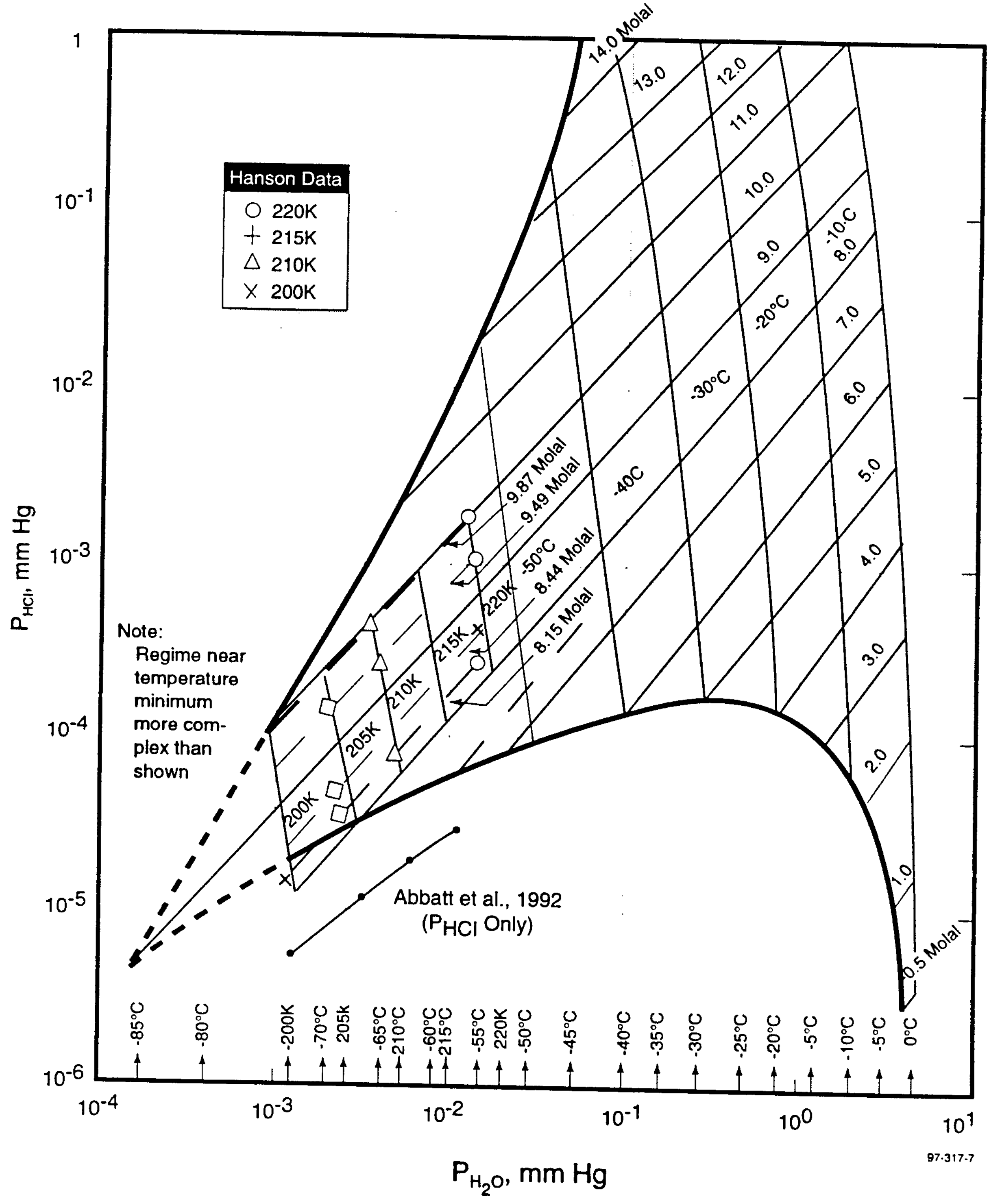


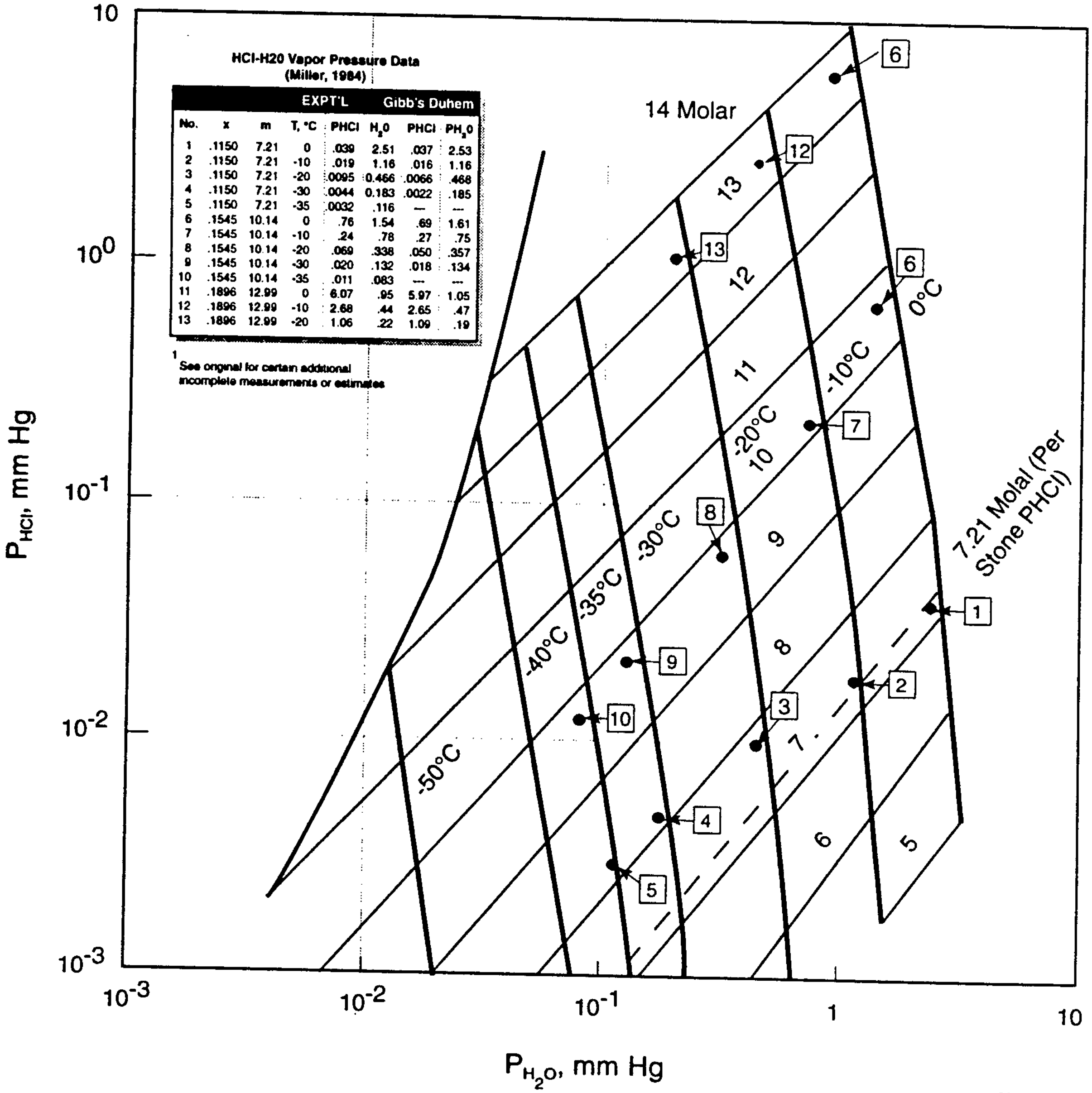
Figure II-7. HCl-H_2O Vapor Pressure Data

Figure II-8 presents a different portion of the same modeled data, showing Miller's (1983) reported data. The points are numbered and tabulated to show where the plot differs from his results. Many of the results fit reasonably well with the plot. The 0 °C results can be compared directly to Fritz and Fuget (1956) data. The three 13 molal points all lie above the extrapolated Fritz and Fuget values, suggesting that the Fritz and Fuget data, as projected, may be in error in this region; however adjustment of the Fritz and Fuget data set to accommodate these data seemed infeasible. In fact, no attempt was made here to study and weight all available data sources to provide a "best" data set, a task that appeared to be considerably beyond the scope of this effort. Certainly the Fritz and Fuget data involve uncertainties, as was noted in discussion earlier.

Figures II-9 (below 0 °C) and II-10 (above 0 °C) present the depression factor data resulting from the above work. Values extending into the trihydrate region have been calculated by hand. The curves in Figure II-9 are the primary results from this portion of the work. Detailed values at 5 °C intervals for the liquid region are given in the tabulations in Appendix A, and a computer program which could provide values at any specified temperature or at other temperature intervals is included.

B. PREDICTION OF SECONDARY SMOKE BOUNDARIES

The procedure used here is the same as that developed in Oliver (1969) which in turn was adapted from Appelman (1953, 1957). The technique is simple and simplistic, ignoring all complexities of rocketry, fluid dynamics, etc., relying instead on a combination of a heat and mass balance, in which it is assumed that the rocket propellant, with known composition and heat of formation, is burned in air at a specified pressure. Certain details change with the case being considered, but the usual procedure is as follows. The heat release per unit mass of propellant and the amount of water and acid gas formed are calculated, assuming all chlorine in the propellant goes to HCl (or fluorine to HF). The gas mixture is then assumed to be diluted with increasing amounts of ambient air. At each assumed mixture, the mixture temperature and the amount of water vapor which the mixture can hold at saturation are calculated, taking into account the "depression factor" effect of any HCl or HF present. The total water vapor, less the amount contributed by the combustion of the propellant, is the amount which can come from the ambient air. This amount of water vapor is converted to a relative humidity, which represents the highest relative humidity which can be tolerated without exceeding the saturation limit. Note that in



HCl-H20 Vapor Pressure Data (Miller, 1984)

				EXPT'L		Gibb's Duhem	
No.	x	m	T, °C	PHCl	H_2O	PHCl	PH_2O
1	.1150	7.21	0	.039	2.51	.037	2.53
2	.1150	7.21	-10	.019	1.16	.016	1.16
3	.1150	7.21	-20	.0095	0.466	.0066	.468
4	.1150	7.21	-30	.0044	0.183	.0022	.185
5	.1150	7.21	-35	.0032	.116	—	—
6	.1545	10.14	0	.76	1.54	.69	1.61
7	.1545	10.14	-10	.24	.78	.27	.75
8	.1545	10.14	-20	.069	.338	.050	.357
9	.1545	10.14	-30	.020	.132	.018	.134
10	.1545	10.14	-35	.011	.083	—	—
11	.1896	12.99	0	6.07	.95	5.97	1.05
12	.1896	12.99	-10	2.68	.44	2.65	.47
13	.1896	12.99	-20	1.06	.22	1.09	.19

[1] See original for certain additional incomplete measurements or estimates

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Figure II-8. HCl-H_2O Data from Miller (1983) Plotted on Grid as Developed in This Paper

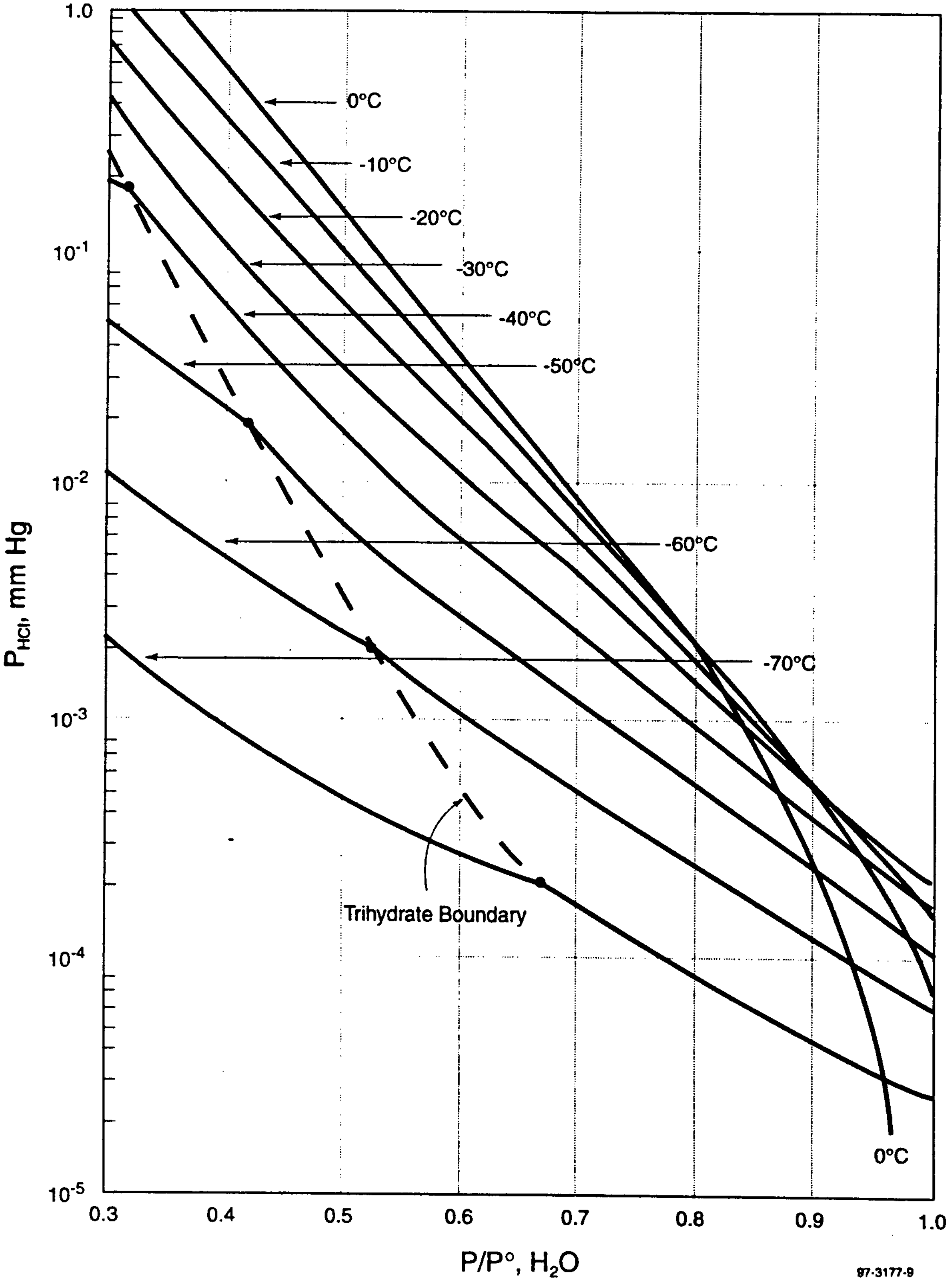

Figure II-9. HCl Depression of Water Vapor Pressure, 0 to –70 °C, Relative to Ice

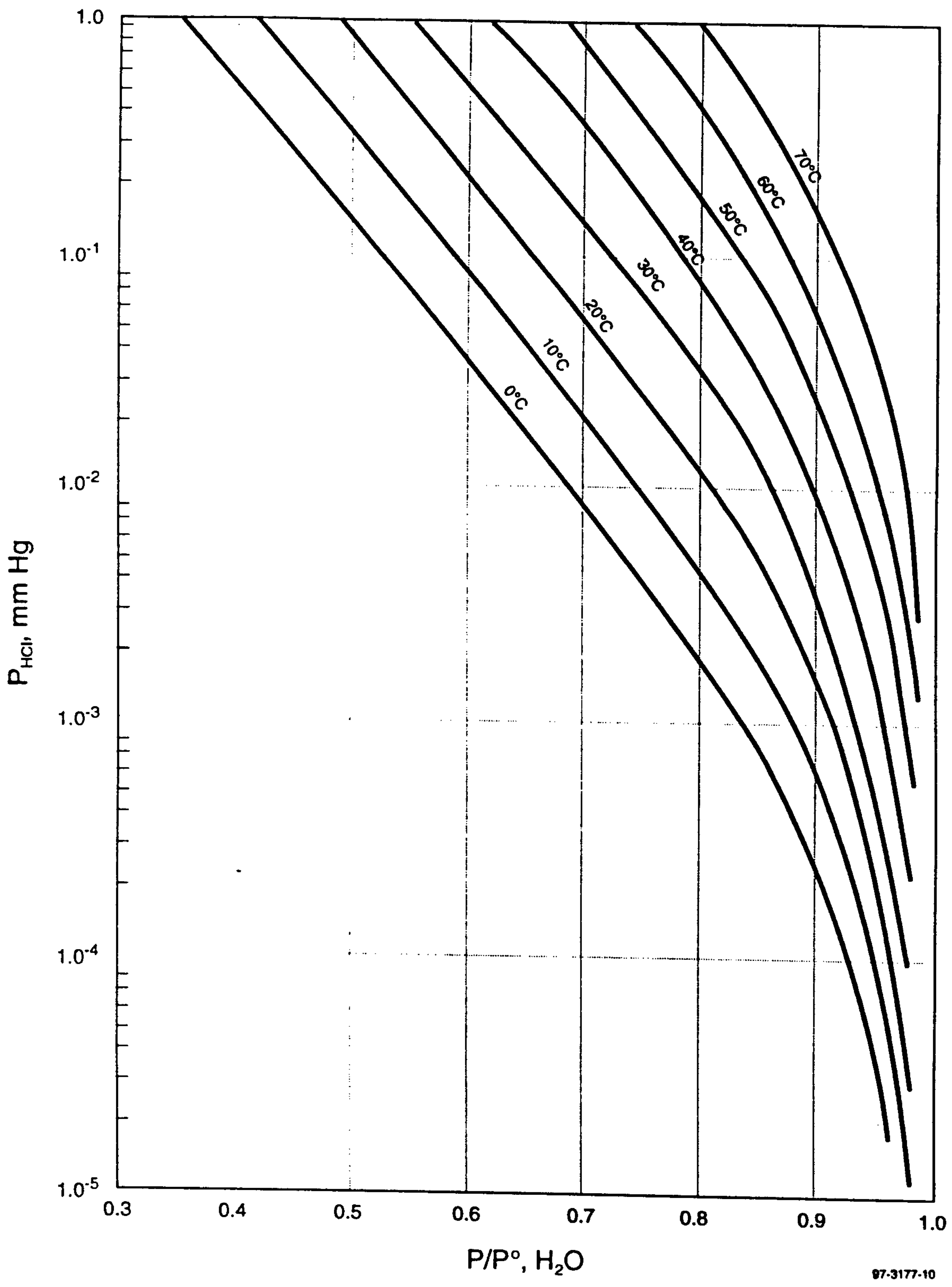

Figure II-10. HCl Depression of Water Vapor Pressure, 0 to 70 °C, Relative to Liquid Water. Data from 50 to 70 °C are based on extrapolations.

this phase of the work there is no need for extreme precision in water vapor pressure data, and the simple A – B/T representations used in Oliver (1969) continue to be used.

The calculations done here follow conceptually those done by Appleman (1953, 1957) in his pioneering work on aircraft contrail formation. Several differences do, however, exist. In the first place, Appleman allowed for supersaturation requirements by assuming that no condensed phase would form below 0 °C until the vapor pressure of water exceeded that of the supercooled liquid, which is higher than the vapor pressure of ice at the same temperature, whereas no supersaturation requirements are imposed in the rocket work done here. The second point, of course, is that aircraft exhaust should have no acid gases present (ignoring possible trace quantities of HNO_3 or sulfur-containing acids). Finally, Appleman was particularly interested in defining conditions where *visible* contrails would be expected, assuming certain ice crystal contents (0.004 and 0.01 gm/m^3) are necessary for a contrail to be visible. The work here, however, is limited to defining the thermodynamic boundary between regions where contrails (secondary smoke) would or would not be expected to form, based purely on equilibrium considerations. In principle, actual conditions needed to form a visible contrail in the rocket exhaust case should be somewhat more severe than conditions at the boundary indicated by this work. In the rocket case, an actual condensate would most likely be a concentrated liquid acid, whereas the aircraft exhaust contrail would probably be ice (assuming a supersaturated liquid would immediately freeze in the probable presence of nuclei).

The computer program developed in Oliver (1969) is included in Appendix C along with a few explanatory notes.

The base case used in this work and in the past has assumed that the rocket fuel is completely burned in air. This may or may not be the case. In Oliver (1979), effects of afterburning vs. nonafterburning were studied at various altitudes. For the cases studied, it was found that afterburning made contrail formation more rather than less probable, since the added moisture had more effect than the added heat. The same general principle should be kept in mind in considering alternative fuels, binders, or new oxidizers which may eliminate HCl as an exhaust product but produce more water.

III. SECONDARY SMOKE HUMIDITY-TEMPERATURE BOUNDARY PREDICTIONS

A. EFFECTS COMPARISONS, SEA-LEVEL CONDITIONS

A principal purpose of this work has been to develop a corrected suppression factor figure for use below 0 °C. However, it is obviously also of interest to see whether, or under what conditions, the revised charts (Figs. II-9 and II-10) would significantly alter results obtained in Oliver (1969), all of which assumed sea-level conditions. A propellant of interest for the comparison is one labeled UTX-7782. This is a simple propellant consisting of 83 percent ammonium perchlorate and 17 percent "CH_2," indicating a hydrocarbon polymeric binder. The temperature-humidity boundary value plot for this mixture, as reported in Oliver (1969), is shown in the figure.[3] (Note that Figure III-1 is not used in predictions of contrail-forming conditions for propellants containing no chlorine.) The AGARD (1993) paper includes a plot (Fig. III-2) which shows experimental firing results for what is presumed to be the same or a similar propellant, as well as for a double-based (no chlorine) formulation. Note that the test data can be argued to indicate that the original curve slopes downward somewhat too sharply, intersecting the abscissa at too high a temperature, consistent with an overestimation of the effects of HCl. The program was thus rerun, using 1969, 1979, and 1997 estimates of depression factors, yielding dilution results shown in Figure III-3 and a boundary value curve as shown in Figure III-4, along with the earlier results. Note that there is a less rapid downward slope using the new data, but the overall effect is minor.

Two other minor points should be noted. First, on comparing Figure III-3(a) to Fig. III-1, it is seen that the −22 °F plots look somewhat different. This difference was traced to an apparent plotting error in Figure III-1, which gave too much curvature to the

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[3] The abscissa "no-fog relative humidity" in Figure III-1 is the somewhat unfortunate label used in the 1969 paper to show the boundary between secondary smoke and no secondary smoke humidities, or "fog" in an environmental chamber.

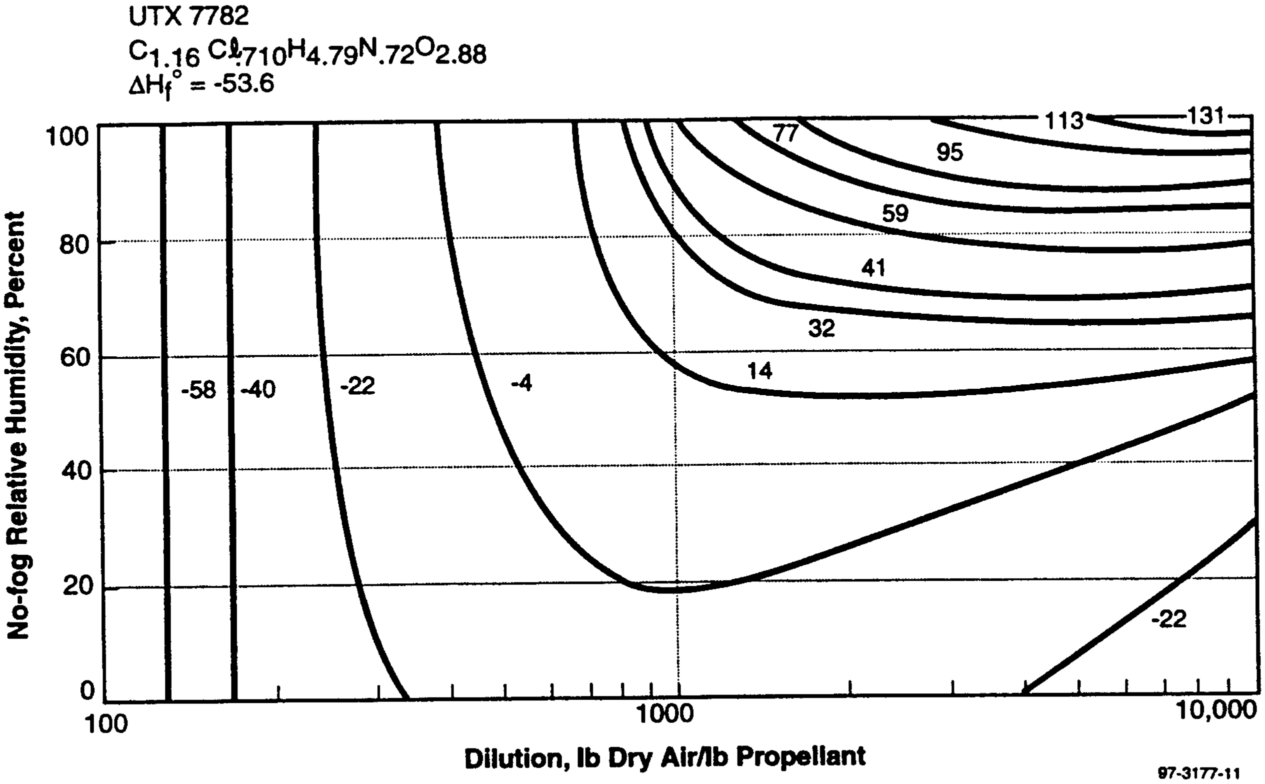


Figure III-1. Dilution Results for an 83AP/17CH$_2$ Propellant, as Reported in Oliver (1969). Temperature in °F.

lower portion of the left-hand –22 °F curve; fortunately, this error had no effect on the boundary value plot. It can also be noted that a difference is evident at 32 °F and above on Figure III-4, which evidently results from use of Fritz and Fuget (1956) data rather than the older data used in the 1969 work. Neither change would seem of much significance for most purposes.

The small apparent effect of the change in the P/P° plots (Figs. II-9 and II-10 vs. Fig. II-1) is encouraging in that it implies that previous evaluations based on Fig. II-1 are probably not in serious error. The HCl content of this mixture is high, however, and the HCl partial pressures in the diluted mixture are in the range of roughly 10^{-3} to 10^{-1} mm, a region where the extrapolated P/P° values developed in 1969 are not drastically altered. To explore the issue further, a pair of hypothetical propellants were compared. The first contained only a small amount of ammonium perchlorate (5 percent), with the rest of the oxidizer (78 percent) assumed to be ammonium dinitramide, an oxidizer containing no chlorine; the second contained no ammonium perchlorate at all, the AP having been replaced with ADN. A hydrocarbon binder was used for the second two runs; its composition differed in a minor way from that apparently used in the

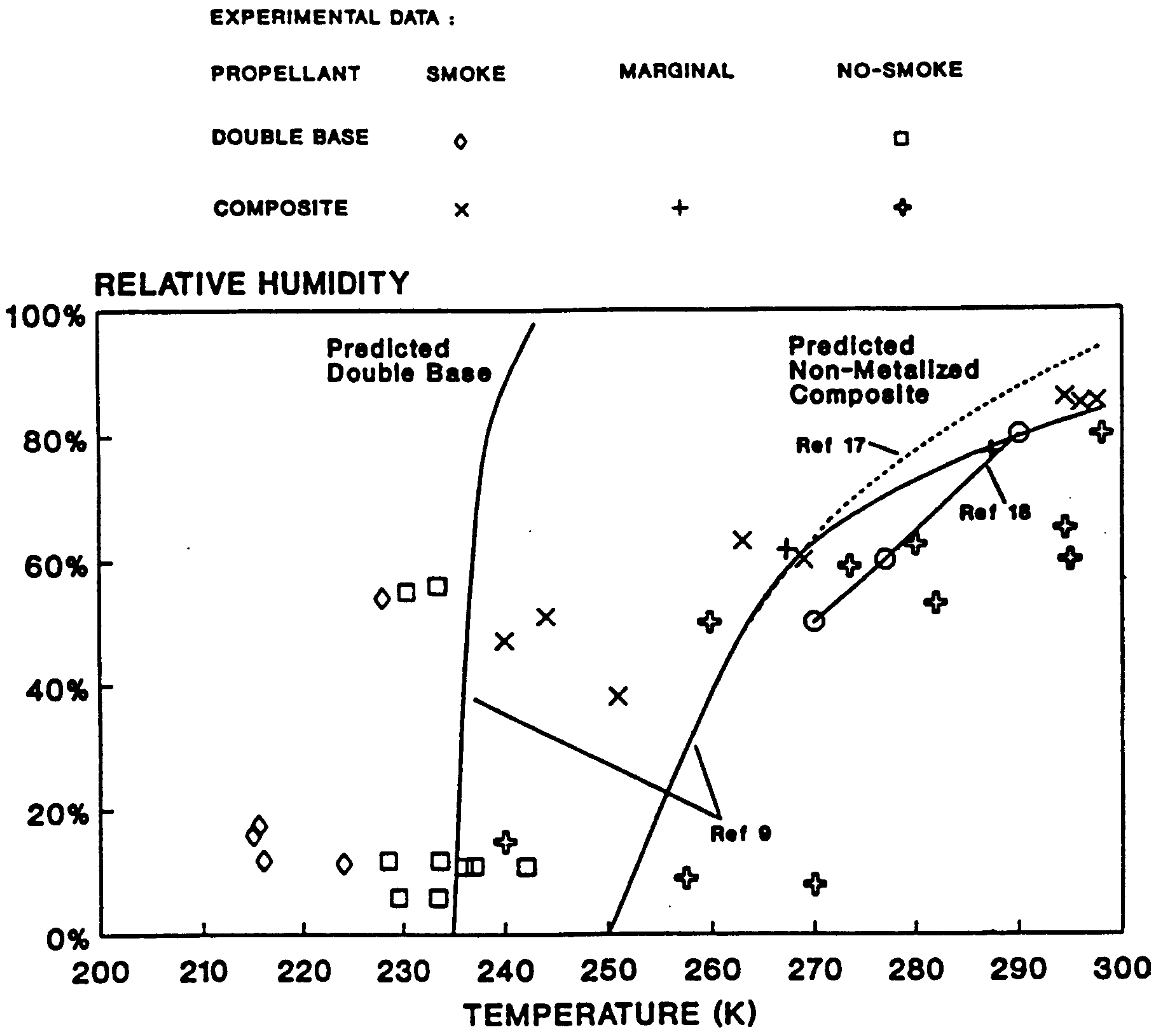


Figure III-2. Predicted and Measured "Smoke/No Smoke Boundaries" [AGARD (1993)]. AGARD (1993) references are as follows: Ref. 9 is "Oliver, Graphical Data" (unpublished); Ref. 17 is "Victor, A. Rocket Exhaust Smoke Signature" (unpublished); Ref. 18 is "Adjari, E., Secondary Smoke Occurrence Comparison Between Predictions and Experiments in a Climatic Chamber, 1988" (unpublished).

earlier UTX-7782 composition. The point of the exercise was to compare allowable relative humidity effects for large (Fig. III-4), small, and no HCl propellants. Heat release and water liberated also changed with composition, which confounds the results somewhat, but such changes cannot be avoided.

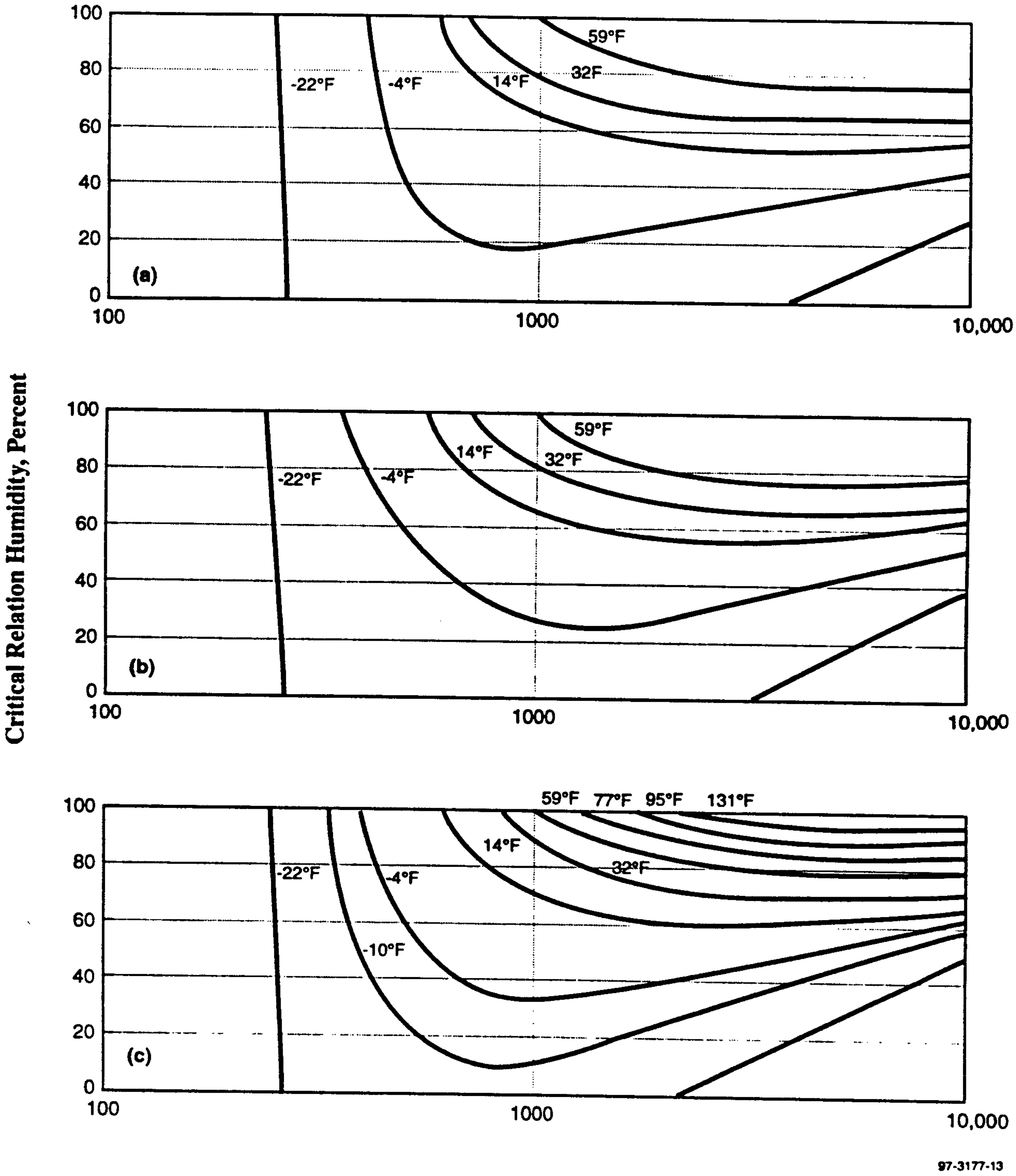


Figure III-3. Dilution Results for an 83AP/17CH$_2$ Propellant, Using (a) 1969, (b) 1979, and (c) 1997 Procedures. Temperatures in °F.

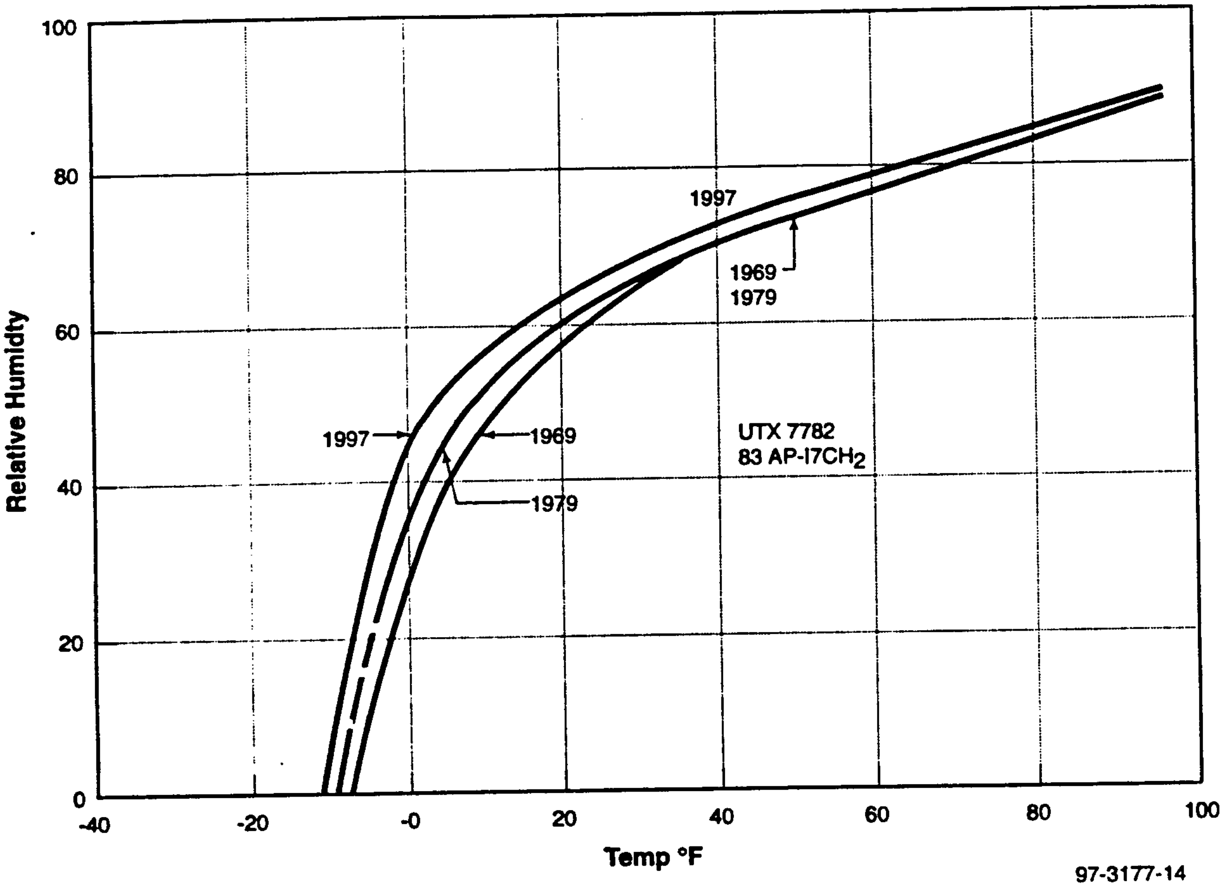
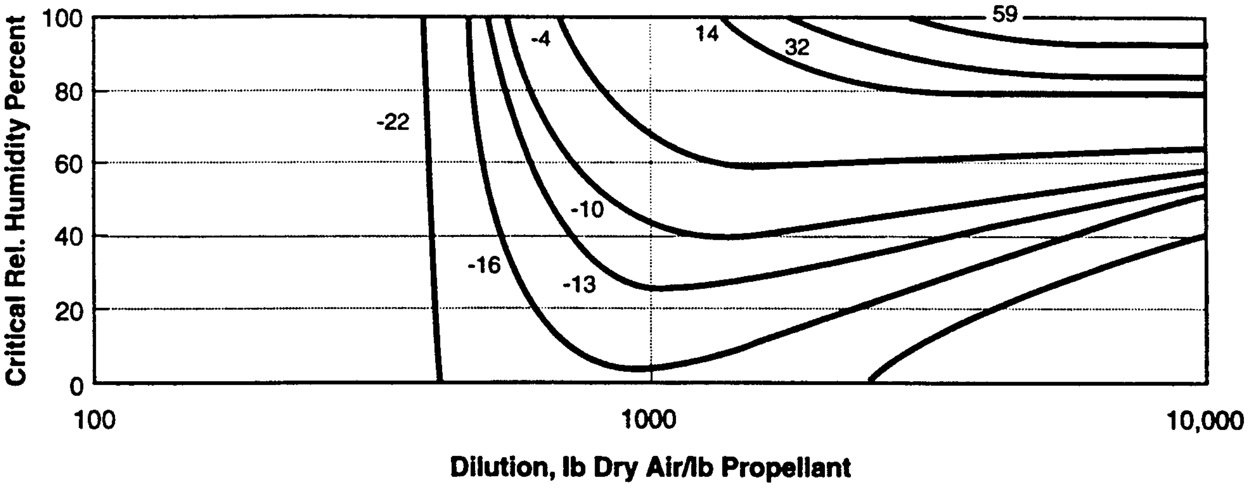
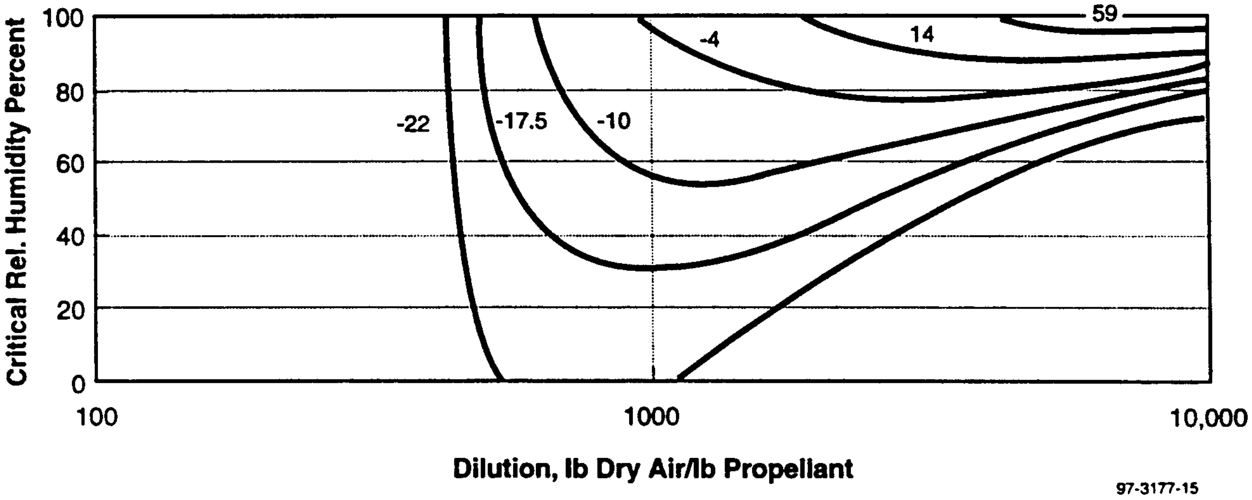


Figure III-4. Relative Humidity-Temperature Boundary Curves for an $83AP/17CH_2$ Propellant Based on 1969, 1979, and 1997 P/P° Equilibria Estimates

The results of these runs using the old (Fig. II-1) and new (Figs. II-9 and II-10) P/P° plots are shown in Figures III-5, III-6, and III-7. Figure III-7 includes the results for 1969 and 1997 P/P° estimates for the UTX-7782 83-percent AP propellant, as well as results for the hypothetical low (5-percent AP) and 0-percent AP propellants. The results are as might be expected. The presence of even small quantities of chlorine significantly increases the temperature-humidity regime in which secondary smoke would be expected, but climatic probabilities may be such that either is acceptable. The 1997 estimates also show that more severe, and presumably more unusual, conditions are needed to form secondary smoke than did the 1969 predictions.



(a) 1969 Procedures



(b) 1997 Procedures

Figure III-5. Comparative Dilution Results. 1969 and 1997 Procedures. HP-1 Low Chlorine Propellant. Temperatures in °F.

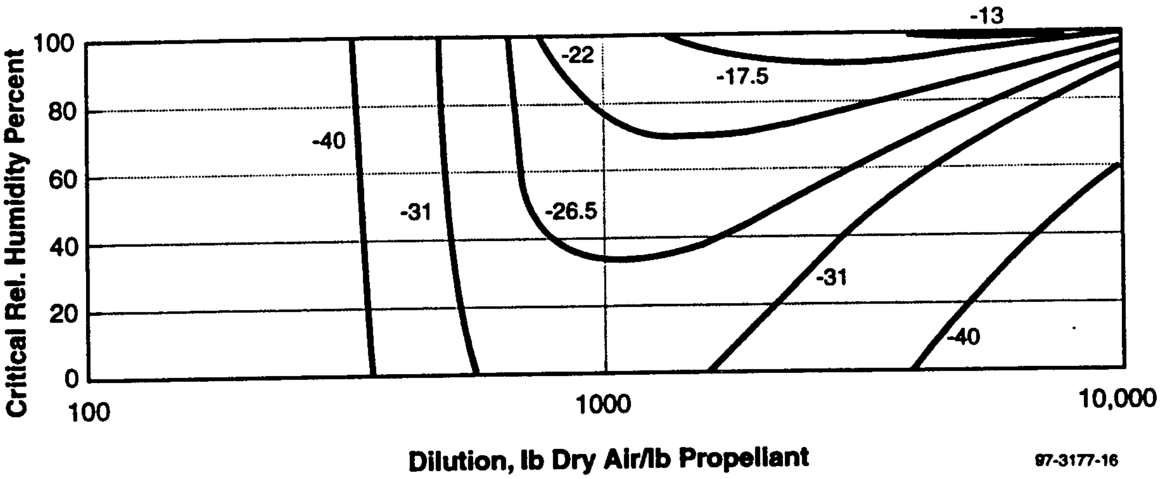


Figure III-6. Propellant HP-2 (No Chlorine). Temperatures in °F.

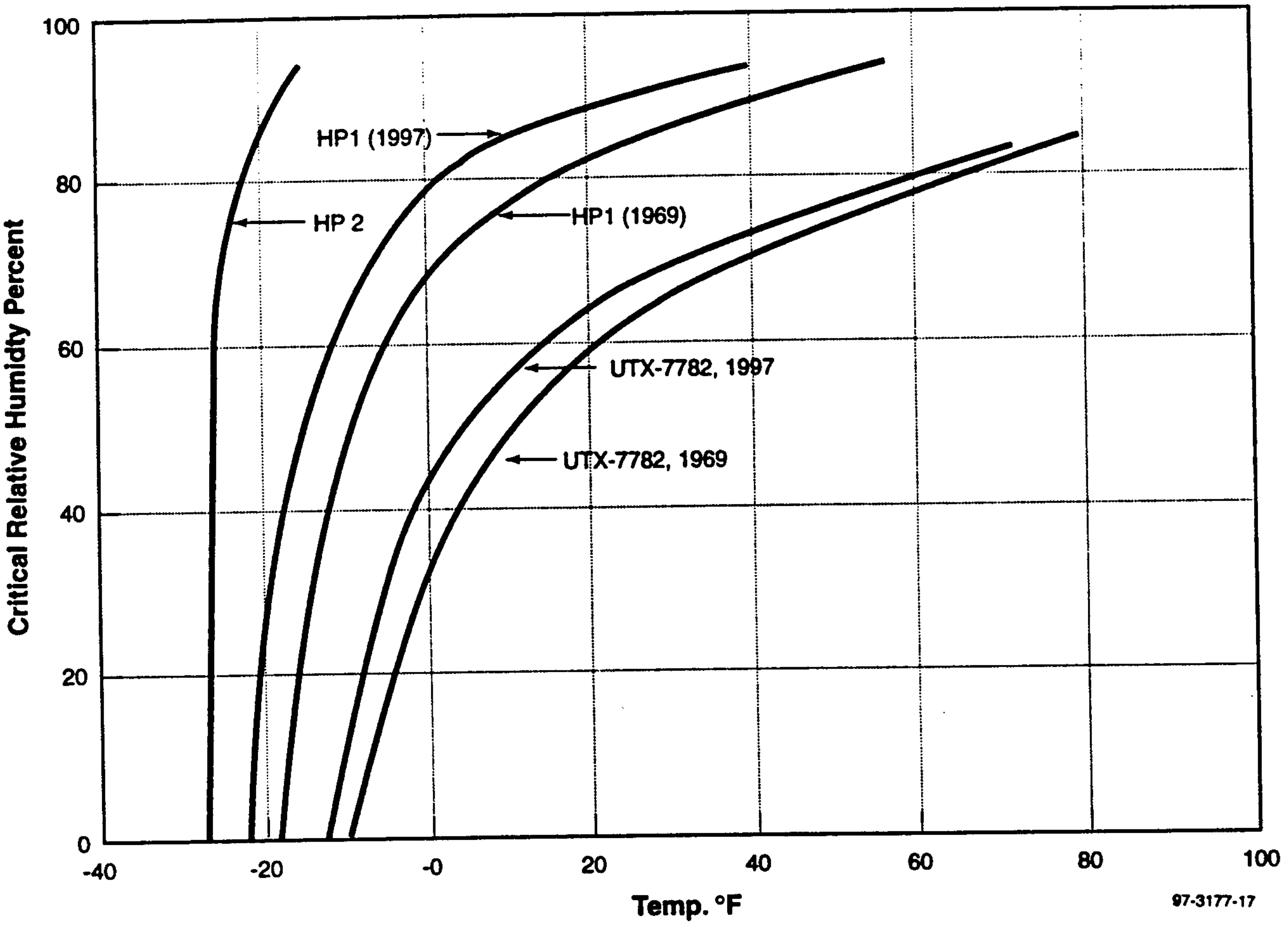


Figure III-7. Critical Boundary Line Curves for a High-Chlorine Propellant (83% AP, 17% CH_2, UTX-7782), a Hypothetical Low-Chlorine Propellant (5% AP, 78 % ADN; HP-1), and a No-Chlorine Propellant (83% ADN; HP-2). Changes above 32 °F (0 °C) are due to changes in data source.

As a matter of interest, although such conditions were not encountered in the work just described, the current model, like the 1979 work, has within it HCl partial pressure-temperature regimes where HCl has no depression effect. However, above 0 °C, the presence of HCl vapor always has a depressing effect on the amount of water vapor that can be present in the ambient air.

B. EFFECTS OF ALTITUDE AND AFTERBURNING

The foregoing results are all for sea level (1 atm.) total pressure, and all assume complete afterburning. At higher altitudes and lower air pressures, the "holding capacity" per unit mass of air at any given temperature is increased since water (or ice) vapor pressure is determined by temperature and not by the atmospheric pressure. Curves showing the effect of pressure and presented in AGARD (1993) indicate that the temperature-humidity boundary above which secondary smoke would be expected is moved upward and to the left with increasing altitude in a plot such as Figure III-2 or III-4. However, it is generally true that temperature also changes, decreasing with altitude (in the troposphere), and this effect is usually more powerful in terms of secondary smoke formation than is the pressure change. (In the stratosphere, where temperatures stay the same or increase with altitude and relative humidities are usually very low, the pressure effect is important, and aircraft contrails become less probable than they are near the tropopause.) A second effect is that complete afterburning may not occur or actually may be suppressed through additives, and this effect also affects the probability of secondary smoke formation.

Effects of altitude and afterburning based on P/P° derived from the Lewis representation of the HCl-H_2O system were also studied in the 1979 work. These effects differ to a minor degree from Figures II-9 and II-10. Temperature-humidity mean data over Berlin from sea level to 16-km altitude were used as an example. In January 1976, for example, the data showed that temperature dropped with altitude from a degree or so below 0 °C at the surface to –40 °C at about 7 km to about –55 °C at 10 km and above, with relative humidities variable but dropping from about 80 percent at the surface, to 50 percent at 6 km, to 30 percent at 10 km, and to about 22 percent at 14 km. It was found that the 87-percent AP propellant contrail formation was marginal at the surface but expected above about 6 km. Nonchlorine-containing propellants were not predicted to yield secondary smoke below about 9 km. At about 10 km, contrails were predicted both for a low-performance, nonchlorine-containing propellant (N-5), whether or not it afterburned, and for an HMX-double-base propellant (assuming afterburning, apparently). Above about 14 km, contrails were not expected with the N-5 or the HMX-DB propellant; the 87 percent AP propellant was not tested. It was also noted that in the cases studied, afterburning, which increases the amount of H_2O present in the plume, increased the probability of secondary smoke formation, the extra water having more effect than the extra heat release. This afterburning effect was, however, of much less importance than the temperature effect. High-performance propellants will probably afterburn in any case, except at very high altitudes, much above those discussed here.

IV. CONCLUSIONS

Revised charts have been prepared showing the reduction in saturation vapor pressure for water vapor in the presence of HCl vapor relative to liquid water (for mixtures above 0 °C) or relative to pure ice (for mixtures below 0 °C). These charts are recommended over earlier charts, primarily those originally prepared in Oliver (1969) but also those in Oliver and Strahle (1979), which was not widely distributed. The changes for mixtures above 0 °C are small and due entirely to selection of a different data set [Fritz and Fuget (1956) rather than handbook values, which are based on Zeisberg (1925)] showing water and HCl partial pressures above acid mixtures at various temperatures. The changes for mixtures below 0 °C are major, reflecting an approach originally described by Lewis (1968, 1969) and used in Oliver and Strahle (1979) but incorporating rather limited modern data as well. The modern data used are primarily in very low temperature regimes of interest in terms of stratospheric effects; there is some but not much data in regions of interest at ground level; the gap was filled here tying extrapolations of high-temperature (0 to 50 °C) data to the low-temperature data. A necessary assumption, supported by at least some recent data, was that the vapor pressure of ice that separates from low acid concentration two-phase mixtures (those below about 9 molal) at low temperatures has the same vapor pressure as pure ice. Above 9 molal, the solid phase was assumed to be the trihydrate in all cases, ignoring the hexahydrate, which has been argued in the literature to *not* form, even though called for thermodynamically, unless the mixture is cooled well below any temperatures of interest here. This paper, which is otherwise intended to represent equilibrium thermodynamics, thus does not adequately model the narrow region at the minimum freezing point; fortunately, this region is not applicable to this work. Also, discrepancies exist among recently published low-temperature (~190–220 K) vapor pressure data from various laboratories, so that uncertainties still exist. With these caveats, it is believed that Figure II-9, in particular, and Figure II-10 represent a substantial improvement over the 1969 work.

Several dilution runs (humidity-temperature boundary value determinations) were made to determine the effect of the changes P/P° called for in Figure II-9 relative to those in the 1969 work (Fig. II-1) or the 1979 work (Fig. II-4). As in most such work, complete afterburning and sea-level pressures were assumed in these calculations. Results showed that the overall effect on the predicted boundary values, at specified temperatures, of relative humidity below which secondary smoke (contrails) will not form is fairly small, although its operational significance, in terms of climatic humidity-temperature data, has not been evaluated. The basic effect of the revisions is to show that secondary smoke formation with HCl-containing propellants at temperatures below the freezing point of water was somewhat overpredicted in the prior work. The effect is greater at low concentrations of HCl in the exhaust. A few sample calculations were made using hypothetical propellants with varying levels of HCl in the exhaust to illustrate the point.

Some discussion of the effects of altitude and of afterburning or nonafterburning is included. It is noted that afterburning increases the probability of secondary smoke formation, but its significance is less important than the temperature profile with altitude. A sample profile based on midwinter midlatitude (mean data over Berlin for January 1976) was considered in Lewis (1968, 1969). It showed that in this instance, where temperatures above about 10 km dropped to about –55 °C, contrail (secondary smoke) formation could be expected whether or not the propellant contained chlorine; however, above about 14 km, the decreasing pressure and relative humidity suggested no contrail formation, at least with non-chlorine-containing propellants. Further study of this issue has not been attempted.

It is acknowledged that the procedures described are simplistic, ignoring the fluid dynamics of a vehicle in flight, kinetics of condensation and required supersaturation ratios, and other phenomena that enter into whether secondary smoke will actually form under flight conditions. Nevertheless, the procedures appear to have been remarkably useful in predicting the boundaries sought and in terms of propellant selection.

It is recommended that Figures II-9 and II-10 should replace the 1969 plot (Fig. II-1 in this document) in theoretical studies of secondary smoke formation, at least until superseded or replaced by further work. Uncertainties in the data are still recognized to have significant effects, which might be reduced if all the available data could be subjected to detailed scrutiny and evaluation. This appears however to be a difficult task.

Note that the 1969 P/P° plot for HF involved the same sort of erroneous extrapolation below 0 °C that the HCl plot did, and remains to be reexamined.

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APPENDIX A

TABULAR RESULTS
P/P° H_2O vs. P_{HCl}

```
HCl SUPPRESSION              05-18-1997
tfreeze =       271.66
Molality =      .5           Tmin =          265
PHCL1           PHCL2        PHCL3
 .00000387       .0000326     .000541
PH2O1           PH2O2        PH2O3
 4.51            17.22        90.94
AHCL =         -72.05493695455071
BHCL =          4665.905974745776
CHCL =          13.66722233736323
AH2O =          50.48258007870145
BH2O =          6613.401266728715
CH2O =         -4.414493074621383
TEMP,K          PHCL,mm      PH2O,mm          K
 343.16          2.851551E-03 229.9448         .9829972
 338.16          1.908314E-03 184.5053         .9827249
 333.16          1.265615E-03 146.9259         .9824519
 328.16          8.315168E-04 116.0745         .9821948
 323.16          5.410002E-04 90.94            .9819607
 318.16          3.484175E-04 70.6278          .9817624
 313.16          2.220187E-04 54.35128         .9816151
 308.16          1.399162E-04 41.42426         .9815298
 303.16          8.71596E-05  31.25343         .9815289
 298.16          5.364321E-05 23.32947         .9816184
 293.16          3.260001E-05 17.22            .9818229
 288.16          1.955115E-05 12.5608          .9821577
 283.16          1.15639E-05  9.048469         .9826434
 278.16          6.740964E-06 6.432848         .9833047
 273.16          3.870006E-06 4.51             .9836466
 268.16          2.186458E-06 3.115613         1.033459
 271.66          3.266395E-06 4.042735         .9982802
```

```
HCl SUPPRESSION             05-18-1997
tfreeze =      269.76
Molality =     1            Tmin =        260
PHCL1          PHCL2        PHCL3
 .0000181       .000149      .00245
PH2O1          PH2O2        PH2O3
 4.42           16.78        89.18
AHCL =         -87.79651216804773
BHCL =          3852.262437790924
CHCL =          16.21721383877054
AH2O =          38.84361054380771
BH2O =          6099.40976060589
CH2O =         -2.678831299178661
TEMP,K         PHCL,mm      PH2O,mm       K
 343.16         1.299639E-02  228.1089      .9751486
 338.16         8.676848E-03  182.424       .9716392
 333.16         5.743805E-03  144.8271      .9684178
 328.16         3.768624E-03  114.1033      .9655152
 323.16         2.450001E-03  89.17999      .9629563
 318.16         1.577555E-03  69.1178       .9607726
 313.16         1.005691E-03  53.09893      .9589969
 308.16         6.344937E-04  40.41704      .9576641
 303.16         3.959773E-04  30.46654      .9568164
 298.16         2.443426E-04  22.73227      .9564904
 293.16         .000149       16.77999      .9567351
 288.16         8.974371E-05  12.24675      .9576014
 283.16         5.335866E-05  8.832084      .9591445
 278.16         3.129857E-05  6.289739      .9614295
 273.16         .0000181      4.42          .9640172
 268.16         1.031264E-05  3.062675     1.0159
 263.16         5.784601E-06  2.090803     1.071854
 269.76         1.236725E-05  3.449606      .9988704
```

```
HCl SUPPRESSION             05-18-1997
tfreeze =      264.86
Molality =     2            Tmin =         255
PHCL1          PHCL2        PHCL3
 .00012         .000944      .0143
PH2O1          PH2O2        PH2O3
 4.22           16.08        85.1
AHCL =         -65.83916031219277
BHCL =          4553.053937984328
CHCL =          13.09776730192305
AH2O =          46.40050011298222
BH2O =          6435.576047782947
CH2O =         -3.814744298557124
TEMP,K         PHCL,mm      PH2O,mm        K
 343.16         7.137236E-02 216.0284       .9235058
 338.16         4.839945E-02 173.1413       .9221969
 333.16         3.253501E-02 137.7329       .9209808
 328.16         2.167215E-02 108.71         .9198778
 323.16         .0143        85.09996       .9189006
 318.16         9.34283E-03  66.04565       .9180682
 313.16         6.041505E-03 50.79584       .9174018
 308.16         3.864944E-03 38.69745       .9169192
 303.16         2.444891E-03 29.18754       .9166486
 298.16         1.528561E-03 21.78438       .9166064
 293.16         9.440001E-04 16.08          .9168241
 288.16         5.755479E-04 11.73169       .9173274
 283.16         3.462152E-04 8.454568       .9181471
 278.16         2.053435E-04 6.014253       .9193196
 273.16         .00012       4.22           .9203966
 268.16         6.904386E-05 2.918361       .9680305
 263.16         3.908076E-05 1.987431       1.01886
 258.16         2.174278E-05 1.3316         1.073124
 264.86         4.751312E-05 2.26879        1.001211
```

```
HCl SUPPRESSION                 05-18-1997
tfreeze =       259.66
Molality =      3               Tmin =          255
PHCL1           PHCL2           PHCL3
 .000468         .00351          .0497
PH2O1           PH2O2           PH2O3
 3.99            15.17           80.6
AHCL =          -59.25797506299091
BHCL =           4613.958616054726
CHCL =           12.20700186878658
AH2O =           40.60139714115951
BH2O =           6183.604169952826
CH2O =          -2.955461493918731
TEMP,K          PHCL,mm         PH2O,mm         K
 343.16          .2377336        205.8686        .8800731
 338.16          .1629068        164.7091        .8772848
 333.16          .1106722        130.8134        .8747124
 328.16          7.451259E-02    103.0968        .8723806
 323.16          .0497           80.6            .8703104
 318.16          3.282803E-02    62.48165        .8685268
 313.16          2.146406E-02    48.00833        .8670577
 308.16          1.388564E-02    36.54553        .8659304
 303.16          8.883719E-03    27.54873        .865181
 298.16          5.618088E-03    20.554          .8648367
 293.16          3.510001E-03    15.17           .8649391
 288.16          2.16524E-03     11.06923        .8655278
 283.16          1.318018E-03    7.980344        .8666474
 278.16          7.911687E-04    5.680811        .8683508
 273.16          .000468         3.99            .8702328
 268.16          2.726034E-04    2.762963        .9164843
 263.16          1.562341E-04    1.884767        .9662289
 258.16          8.802429E-05    1.265419        1.019789
 259.66          1.04751E-04     1.428534        1.003299
```

```
HCl SUPPRESSION                  05-18-1997
tfreeze =       252.16
Molality =      4                Tmin =          245
PHCL1           PHCL2            PHCL3
 .00159          .0114            .149
PH2O1           PH2O2            PH2O3
 3.69            14.09            75.3
AHCL =          -39.2154112689426
BHCL =           5262.965626111394
CHCL =           9.275905215921579
AH2O =           40.27193449388823
BH2O =           6187.474783597071
CH2O =          -2.908141550119591
TEMP,K          PHCL,mm          PH2O,mm          K
 343.16          .6719141         193.0133         .8251178
 338.16          .467414          154.291          .8217954
 333.16          .3222951         122.4319         .8186675
 328.16          .2201933         96.40511         .8157571
 323.16          .149             75.30001         .8130818
 318.16          9.981986E-02     58.31903         .8106643
 313.16          .0661764         44.76768         .8085298
 308.16          4.339518E-02     34.04587         .8067021
 303.16          2.813256E-02     25.63926         .8052132
 298.16          1.802108E-02     19.11021         .8040871
 293.16          .0114            14.09            .8033614
 288.16          7.11737E-03      10.27045         .8030699
 283.16          4.382729E-03     7.396586         .8032526
 278.16          2.659978E-03     5.259532         .8039554
 273.16          .00159           3.69             .8048017
 268.16          9.353177E-04     2.552314         .8466115
 263.16          5.409934E-04     1.739045         .8915244
 258.16          3.073927E-04     1.166191         .9398218
 253.16          1.714126E-04     .7689343         .9917964
 248.16          9.370698E-05     .4979868         1.047788
 252.16          1.52157E-04      .7059823         1.002664
```

```
HCl SUPPRESSION                05-18-1997
tfreeze =        244.16
Molality =       5             Tmin =         240
PHCL1            PHCL2         PHCL3
 .00489           .0333         .401
PH2O1            PH2O2         PH2O3
 3.37             12.91         69.5
AHCL =           -24.75778068834102
BHCL =            5656.513424886586
CHCL =            7.155882347956943
AH2O =            37.52548529530955
BH2O =            6085.401645710706
CH2O =           -2.50136136213829
TEMP,K           PHCL,mm        PH2O,mm        K
 343.16           1.709261       179.2216       .7661591
 338.16           1.205996       143.0412       .7618756
 333.16           .8433881       113.3315       .7578159
 328.16           .5843651       89.10701       .7540023
 323.16           .401           69.49997       .7504535
 318.16           .2724082       53.75277       .7471909
 313.16           .1831106       41.20799       .7442397
 308.16           .1217348       31.29931       .7416235
 303.16           8.000128E-02   23.54281       .7393734
 298.16           5.194289E-02   17.52801       .737514
 293.16           3.329999E-02   12.91          .736082
 288.16           2.106598E-02   9.401335       .7351116
 283.16           1.314163E-02   6.764808       .734643
 278.16           8.078596E-03   4.8066         .7347217
 273.16           4.889999E-03   3.37           .7350087
 268.16           2.912145E-03   2.3297         .7727695
 263.16           1.704767E-03   1.586692       .8134202
 258.16           9.800546E-04   1.063714       .8572369
 253.16           5.527516E-04   .701263        .9045116
 248.16           3.055084E-04   .4541648       .9555848
 243.16           1.652774E-04   .2886272      1.010827
 244.16           1.872165E-04   .316515        .9994292
```

```
HCl SUPPRESSION             05-18-1997
NOTE.  PH2O 0 DEG. ADJUSTED TO 3.035 FROM 3.03 MM
tfreeze =      233.16
Molality =     6            Tmin =         225
PHCL1         PHCL2         PHCL3
 .0141         .0903         1.001
PH2O1         PH2O2         PH2O3
 3.035         11.71         63.5
AHCL =        -20.41478879408127
BHCL =         5588.782221743577
CHCL =         6.526305296193995
AH2O =         39.03768393263125
BH2O =         6178.377040461699
CH2O =        -2.728904524341204
TEMP,K        PHCL,mm       PH2O,mm      K
 343.16        4.058583      164.2585      .7021931
 338.16        2.898627      131.0114      .6978018
 333.16        2.052354      103.7238      .693572
 328.16        1.440088      81.48686      .6895224
 323.16        1.001         63.5          .6856665
 318.16        .6889755      49.0645       .6820216
 313.16        .4693581      37.57396      .6786071
 308.16        .3163227      28.50615      .6754409
 303.16        .2107947      21.41498      .6725478
 298.16        .1388235      15.92215      .6699456
 293.16        9.030001E-02  11.71         .6676623
 288.16        5.797892E-02  8.513934      .6657238
 283.16        3.672197E-02  6.115776      .6641595
 278.16        .0229272      4.33742       .6630042
 273.16        .0141         3.035         .661944
 268.16        8.534582E-03  2.093622      .6944615
 263.16        5.08001E-03   1.422623      .72931
 258.16        2.970706E-03  .9513628      .7666938
 253.16        1.705052E-03  .6255263      .8068241
 248.16        9.594581E-04  .4039576      .8499464
 243.16        5.287114E-04  .2559323      .8963238
 238.16        2.849504E-04  .1588839      .9462411
 233.16        1.499967E-04  9.652082E-02  1.000018
 228.16        7.700369E-05  5.729522E-02  1.058001
 233.16        1.499967E-04  9.652082E-02  1.000018
```

```
HCl SUPPRESSION                05-18-1997
tfreeze =       221.66
Molality =      7              Tmin =          210
PHCL1           PHCL2          PHCL3
 .0382           .231           2.354
PH2O1           PH2O2          PH2O3
 2.7             10.49          57.5
AHCL =          -10.58240233186722
BHCL =           5770.994242556418
CHCL =           5.070228624853127
AH2O =           37.35335484179038
BH2O =           6135.103456110062
CH2O =          -2.477757169137707
TEMP,K          PHCL,mm        PH2O,mm        K
 343.16          9.037442       149.8242       .6404876
 338.16          6.542375       119.2813       .635324
 333.16          4.695729       94.2652        .6303247
 328.16          3.340284       73.9214        .6255053
 323.16          2.354          57.5           .620879
 318.16          1.642814       44.34806       .6164606
 313.16          1.134839       33.90077       .6122673
 308.16          .7756007       25.67318       .6083147
 303.16          .5241757       19.25219       .6046243
 298.16          .3501219       14.28861       .6012122
 293.16          .231           10.49          .5981022
 288.16          .1504489       7.613509       .5953175
 283.16          9.666395E-02   5.459446       .5928836
 278.16          6.122548E-02   3.865256       .5908308
 273.16          .0382          2.7            .5888794
 268.16          2.345887E-02   1.859393       .616767
 263.16          1.416721E-02   1.261367       .6466419
 258.16          8.405936E-03   .8421483       .678679
 253.16          4.895281E-03   .5528314       .7130598
 248.16          2.795004E-03   .3564535       .7499955
 243.16          1.56275E-03    .2254911       .7897127
 238.16          8.545673E-04   .1397785       .8324583
 233.16          4.564053E-04   8.479292E-02   .8785092
 228.16          2.37712E-04    5.026422E-02   .9281681
 223.16          1.20542E-04    2.907054E-02   .9817644
 218.16          5.94071E-05    1.637548E-02   1.039664
 213.16          2.83992E-05    8.967314E-03   1.102265
 221.66          9.77881E-05    2.454222E-02   .9986656
```

```
HCl SUPPRESSION                05-18-1997
NOTE:  P H2O 0 DEG. REVISED FROM 2.48 MM TO 2.39 MM. PHCL 0 DEG. REVISED FROM 0.
0987 TO 0.0994 MM
tfreeze =        206
Molality =       8             Tmin =         200
PHCL1            PHCL2          PHCL3
 .0994            .563           5.27
PH2O1            PH2O2          PH2O3
 2.39             9.35           51.5
AHCL =           -8.926720281107024
BHCL =            5579.532172350705
CHCL =            4.820626796206784
AH2O =            40.65842546944569
BH2O =            6304.362468090116
CH2O =           -2.978179107742114
TEMP,K           PHCL,mm        PH2O,mm        K
 343.16           19.25502       134.2542       .5739271
 338.16           14.10612       106.8909       .5693296
 333.16           10.24897       84.46853       .5648171
 328.16           7.382486       66.22752       .5604015
 323.16           5.27           51.5           .5560917
 318.16           3.726717       39.70344       .551898
 313.16           2.60953        30.33309       .5478329
 308.16           1.808502       22.95493       .543907
 303.16           1.239885       17.19878       .540136
 298.16           .8404772       12.75133       .536529
 293.16           .563           9.349999       .5331035
 288.16           .3724532       6.776553       .529874
 283.16           .2431868       4.851459       .5268575
 278.16           .1566092       3.428527       .5240737
 273.16           9.940002E-02   2.39           .5212673
 268.16           6.213104E-02   1.642111       .544694
 263.16           3.821357E-02   1.111105       .5696097
 258.16           2.310567E-02   .7397097       .5961247
 253.16           1.372117E-02   .4840521       .6243461
 248.16           7.994223E-03   .3110192       .6543995
 243.16           4.564358E-03   .1959957       .6864141
 238.16           2.550749E-03   .1209836       .7205238
 233.16           1.393348E-03   .073053        .756876
 228.16           7.428911E-04   4.308634E-02   .7956228
 223.16           3.859934E-04   2.478168E-02   .836922
 218.16           1.951084E-04   1.387545E-02   .8809398
 213.16           9.576301E-05   7.548328E-03   .9278426
 208.16           4.55459E-05    3.981303E-03   .9778129
 203.16           2.09437E-05    2.031228E-03   1.031012
 206              3.270033E-05   2.989513E-03   1.000388
```

```
HCl SUPPRESSION                05-18-1997
NOTE:  P H2O 0 DEG. REVISED FROM 2.48 MM TO 2.39 MM. PHCL 0 DEG. REVISED FROM 0.
0987 TO 0.0994 MM
tfreeze =      206
Molality =     8               Tmin =        200
PHCL1          PHCL2           PHCL3
 .0994          .563            5.27
PH2O1          PH2O2           PH2O3
 2.39           9.35            51.5
AHCL =         -8.926720281107024
BHCL =          5579.532172350705
CHCL =          4.820626796206784
AH2O =          40.65842546944569
BH2O =          6304.362468090116
CH2O =         -2.978179107742114
TEMP,K         PHCL,mm         PH2O,mm        K
 220            2.516267E-04    1.723252E-02   .8644129
 215            1.248757E-04    9.476767E-03   .9102372
 210            6.009935E-05    5.056952E-03   .9590581
 205            2.798881E-05    2.612522E-03   1.011048
 200            1.258292E-05    1.30347E-03    1.06638
 206            3.270033E-05    2.989513E-03   1.000388
```

```
HCl SUPPRESSION                  05-18-1997
NOTE. PH2O ADJUSTED FROM 2.13 TO 2.1015 MM. PHCL ADJUSTED FROM 0.240 TO 0.242 MM
tfreeze =          187.16
Molality =          9                Tmin =          180
PHCL1              PHCL2             PHCL3
 .242               1.295             11.2
PH2O1              PH2O2             PH2O3
 2.1015             8.26              45.6
AHCL =             -2.860120457951562
BHCL =              5607.940567682049
CHCL =              3.916390908657999
AH2O =              43.71012060902718
BH2O =              6455.608842613315
CH2O =             -3.446382132992563
TEMP,K             PHCL,mm           PH2O,mm           K
 343.16             38.95786          118.7741          .5077507
 338.16             28.88624          94.59948          .5038622
 333.16             21.24544          74.77504          .4999995
 328.16             15.49396          58.63692          .4961717
 323.16             11.2              45.59999          .492384
 318.16             8.021532          35.15296          .4886441
 313.16             5.689769          26.85191          .4849609
 308.16             3.995144          20.31439          .4813407
 303.16             2.775612          15.21375          .4777953
 298.16             1.907004          11.27307          .4743295
 293.16             1.295             8.26              .4709556
 288.16             .8686772          5.981189          .4676827
 283.16             .575234           4.277451          .4645216
 278.16             .3757811          3.019069          .4614853
 273.16             .242              2.1015            .4583444
 268.16             .1535147          1.441474          .4781418
 263.16             9.584644E-02      .9734918          .4990622
 258.16             .058844           .6467031          .5211717
 253.16             3.549046E-02      .4221699          .5445285
 248.16             2.100624E-02      .2705272          .5692024
 243.16             1.218772E-02      .1699677          .5952592
 238.16             6.923163E-03      .1045682          .6227613
 233.16             3.845191E-03      6.290876E-02      .6517751
 228.16             2.085147E-03      3.695277E-02      .6823616
 223.16             1.102253E-03      2.115892E-02      .7145748
 218.16             5.670341E-04      1.178885E-02      .7484631
 213.16             2.833411E-04      6.378624E-03      .7840623
 208.16             1.372437E-04      3.344461E-03      .8214039
 203.16             6.429626E-05      1.695264E-03      .8604834
 198.16             2.906141E-05      8.285676E-04      .9012864
 193.16             1.263878E-05      3.893546E-04      .9437648
 188.16             5.272843E-06      1.753482E-04      .9878238
 183.16             2.103248E-06      7.54149E-05       1.033331
 187.16             4.403747E-06      1.486843E-04      .9968169
KP =                1.447498E-17 PSAT =               1.491591E-04
KPt =               1.017628E-17 Ratio =              .7030258
```

```
HCl SUPPRESSION              05-18-1997
NOTE. PH2O ADJUSTED FROM 2.13 TO 2.1015 MM. PHCL ADJUSTED FROM 0.240 TO 0.242 MM
tfreeze =      187.16
Molality =     9             Tmin =       180
PHCL1          PHCL2         PHCL3
 .242           1.295         11.2
PH2O1          PH2O2         PH2O3
 2.1015         8.26          45.6
AHCL =         -2.860120457951562
BHCL =          5607.940567682049
CHCL =          3.916390908657999
AH2O =          43.71012060902718
BH2O =          6455.608842613315
CH2O =         -3.446382132992563
TEMP,K         PHCL,mm       PH2O,mm      K
 220            7.265487E-04  1.466843E-02  .7357936
 215            3.670372E-04  8.024651E-03  .7707624
 210            1.798771E-04  4.257603E-03  .8074604
 205            8.533378E-05  2.185785E-03  .8459001
 200            3.909402E-05  1.083077E-03  .8860737
 195            1.725063E-05  5.165505E-04  .9279418
 190            7.310494E-06  2.363924E-04  .9714334
 185            2.965819E-06  1.034519E-04 1.016426
 180            1.147761E-06  4.313026E-05 1.062751
 187.16         4.403747E-06  1.486843E-04  .9968169
KP =            1.447498E-17 PSAT =        1.491591E-04
KPt =           1.017628E-17 Ratio =        .7030258
```

```
HCl SUPPRESSION                    05-18-1997
NOTE. PH2O 0 DEG. REVISED TO 1.81 MM FROM 1.80 MM.  PHCL 0 DEG. C. REVISED TO 0.
558 MM FROM 0.552 MM
tfreeze =       202.16
Molality =      10              Tmin =          195
PHCL1           PHCL2           PHCL3
 .558            2.83            22.6
PH2O1           PH2O2           PH2O3
 1.81            7.22            40.6
AHCL =          7.110764910509862
BHCL =          5815.503368105899
CHCL =          2.423428239086507
AH2O =          44.01298467997708
BH2O =          6524.730546593024
CH2O =         -3.481879773185592
TEMP,K          PHCL,mm         PH2O,mm         K
 343.16          74.61189        106.8492        .4567725
 338.16          56.04494        84.89283        .452162
 333.16          41.76082        66.93238        .4475579
 328.16          30.85658        52.34931        .4429674
 323.16          22.6            40.6            .4383946
 318.16          16.40116        31.21072        .4338449
 313.16          11.78849        23.7714         .4293249
 308.16          8.388056        17.92983        .4248395
 303.16          5.905679        13.3861         .420397
 298.16          4.112058        9.886804        .4160004
 293.16          2.83            7.22            .4116586
 288.16          1.92395         5.209945        .4073774
 283.16          1.291235        3.712453        .4031641
 278.16          .8549182        2.610466        .3990275
 273.16          .558            1.81            .3947672
 268.16          .3587515        1.236493        .410149
 263.16          .2270055        .8315349        .4262877
 258.16          .1412428        .5499706        .4432159
 253.16          8.632966E-02    .3573772        .4609566
 248.16          5.177934E-02    .2279128        .4795397
 243.16          .030441         .1424789        .4989882
 238.16          1.751981E-02    8.719916E-02    .5193192
 233.16          9.857872E-03    5.217326E-02    .5405485
 228.16          5.414837E-03    3.047169E-02    .5626836
 223.16          2.898979E-03    .0173435        .5857211
 218.16          1.510106E-03    9.602426E-03    .6096493
 213.16          7.639205E-04    5.161384E-03    .6344389
 208.16          3.745101E-04    .0026875        .6600535
 203.16          1.775265E-04    1.352339E-03    .6864211
 198.16          8.116261E-05    6.558916E-04    .7134556
 202.16          1.522564E-04    1.173688E-03    .6917775
KP =            2.46169E-13     PSAT =          1.696626E-03
KPt =           2.454135E-13    Ratio =         .9969309
```

```
HCl SUPPRESSION              05-18-1997
NOTE. PH2O 0 DEG. REVISED TO 1.81 MM FROM 1.80 MM.  PHCL 0 DEG. C. REVISED TO 0.
558 MM FROM 0.552 MM
tfreeze =       202.16
Molality =      10             Tmin =          195
PHCL1           PHCL2          PHCL3
 .558            2.83           22.6
PH2O1           PH2O2          PH2O3
 1.81            7.22           40.6
AHCL =           7.110764910509862
BHCL =           5815.503368105899
CHCL =           2.423428239086507
AH2O =           44.01298467997708
BH2O =           6524.730546593024
CH2O =          -3.481879773185592
TEMP,K          PHCL,mm        PH2O,mm        K
 220             1.926075E-03  1.197608E-02  .6007406
 215             9.851346E-04  6.509356E-03  .6252194
 210             4.886923E-04  3.430169E-03  .6505363
 205             2.34604E-04   1.748408E-03  .6766351
 200             1.087282E-04  8.598331E-04  .7034364
 195             4.85172E-05   4.068267E-04  .7308318
 202.16          1.522564E-04  1.173688E-03  .6917775
KP =             2.46169E-13   PSAT =         1.696626E-03
KPt =            2.454135E-13  Ratio =        .9969309
```

```
HCl SUPPRESSION                  05-18-1997
NOTE. PH2O 0 DEG. SET TO 1.155 MM FROM 1.11 MM.  PHCL 0 DEG. SET TO  1.220 MM FR
OM 1.229 MM.
tfreeze =       213.16
Molality =      11           Tmin =        205
PHCL1           PHCL2        PHCL3
 1.22           5.86          43.9
PH2O1           PH2O2        PH2O3
 1.563          6.28          35.5
AHCL =          2.827457547266068
BHCL =          5416.069916026082
CHCL =          3.065718525296731
AH2O =          47.2998764653914
BH2O =          6695.359897181041
CH2O =          -3.982580839297184
TEMP,K          PHCL,mm      PH2O,mm       K
 343.16         140.1614      93.49327      .3996769
 338.16         106.1054      74.28118      .3956415
 333.16         79.71015      58.5591       .3915681
 328.16         59.40292      45.78977      .3874622
 323.16         43.89999      35.5          .3833253
 318.16         32.16007      27.27679      .3791613
 313.16         23.34467      20.76203      .3749741
 308.16         16.78375      15.64774      .3707664
 303.16         11.9459       11.67134      .3665442
 298.16         8.41327       8.610726      .3623077
 293.16         5.86          6.28          .3580631
 288.16         4.034352      4.524915      .3538133
 283.16         2.743675      3.218871      .3495621
 278.16         1.842021      2.259074      .3453148
 273.16         1.22          1.563         .3408957
 268.16         .7965394      1.0652        .3533304
 263.16         .5122603      .714434       .3662558
 258.16         .3242178      .4711279      .3796773
 253.16         .2017653      .3051473      .3935889
 248.16         .1233345      .1939062      .4079881
 243.16         7.397468E-02  .1207422      .4228623
 238.16         4.348462E-02  .0735768      .4381905
 233.16         2.502019E-02  4.381452E-02  .4539466
 228.16         1.407183E-02  2.545749E-02  .4700925
 223.16         7.724388E-03  1.440778E-02  .4865766
 218.16         4.131628E-03  .0079279      .5033352
 213.16         2.149546E-03  4.232702E-03  .520285
 208.16         1.085647E-03  2.187818E-03  .537331
 213.16         2.149546E-03  4.232702E-03  .520285
KP =            1.630045E-10 PSAT =         8.135353E-03
KPt =           1.627809E-10 Ratio =        .9986278
```

```
HCl SUPPRESSION                 05-18-1997
NOTE. PH2O 0 DEG. C. SET TO 1.342 MM FROM 1.34 MM.  PHCL 0 DEG. C     SET TO 2.57
 MM FROM 2.55 MM.
tfreeze =          223.16
Molality =         12                Tmin =          215
PHCL1              PHCL2             PHCL3
 2.57               11.75             80.9
PH2O1              PH2O2             PH2O3
 1.342              5.45              31.6
AHCL =             21.36273242788057
BHCL =             6006.62962341908
CHCL =             .279960086835329
AH2O =             37.27756732725052
BH2O =             6311.316675750543
CH2O =            -2.47387337653297
TEMP,K             PHCL,mm           PH2O,mm          K
 343.16             243.0627          85.01674         .3634404
 338.16             186.8676          67.16951         .3577629
 333.16             142.544           52.66595         .3521623
 328.16             107.8472          40.96599         .3466444
 323.16             80.89999          31.6             .3412135
 318.16             60.14414          24.16273         .3358742
 313.16             44.29526          18.30685         .3306321
 308.16             32.30295          13.73699         .3254919
 303.16             23.31506          10.20395         .3204601
 298.16             16.64621          7.499237         .3155403
 293.16             11.75             5.45             .3107395
 288.16             8.19495           3.914239         .3060632
 283.16             5.643722          2.776464         .3015178
 278.16             3.835308          1.943719         .2971107
 273.16             2.57              1.342            .2926948
 268.16             1.696773          .9130718         .3028691
 263.16             1.102823          .6116758         .3135766
 258.16             .7049926          .4030917         .3248476
 253.16             .4428269          .2610478         .3367079
 248.16             .2730196          .165961          .3491899
 243.16             .1650312          .1034563         .3623237
 238.16             9.768119E-02      .0631576         .3761384
 233.16             5.653825E-02      3.770667E-02     .3906654
 228.16             3.195383E-02      2.198306E-02     .4059344
 223.16             .0176059          1.249481E-02     .4219722
 218.16             9.440397E-03      6.911509E-03     .4388054
 223.16             .0176059          1.249481E-02     .4219722
KP =               3.43437E-08       PSAT =           .0296105
KPt =              3.430816E-08      Ratio =          .9989652
```

```
HCl SUPPRESSION                   05-18-1997
NOTE. PH2O 0 DEG. SET TO 1.155 MM FROM 1.11 MM
tfreeze =          230.76
Molality =         13             Tmin =            225
PHCL1             PHCL2           PHCL3
 5.11              22.25           140
PH2O1             PH2O2           PH2O3
 1.155             4.72            27.8
AHCL =             45.23297942690686
BHCL =             6828.61675384879
CHCL =            -3.316041513125719
AH2O =             30.64135657473313
BH2O =             6056.32602131823
CH2O =            -1.484103557837408
TEMP,K            PHCL,mm         PH2O,mm          K
 343.16            393.0971        75.80573         .324064
 338.16            307.5077        59.68051         .3178744
 333.16            238.6114        46.63391         .3118277
 328.16            183.5867        36.15428         .3059289
 323.16            140             27.79999         .3001814
 318.16            105.7705        21.1927          .2945893
 313.16            79.13194        16.01041         .2891571
 308.16            58.59711        11.98118         .2838888
 303.16            42.92521        8.877113         .27879
 298.16            31.08967        6.508749         .2738642
 293.16            22.25           4.72             .2691175
 288.16            15.72445        3.383394         .2645553
 283.16            10.96618        2.395848         .2601838
 278.16            7.54139         1.674838         .2560104
 273.16            5.11            1.155            .2519095
 268.16            3.408748        .7851498         .2604369
 263.16            2.236544        .5256841         .2694928
 258.16            1.441922        .3463472         .2791178
 253.16            .9124806        .2243331         .2893521
 248.16            .566142         .1426981         .3002437
 243.16            .3439581        8.904219E-02     .3118427
 238.16            .2043507        5.443709E-02     .3242029
 233.16            .1185496        3.256405E-02     .3373845
 228.16            6.704761E-02    1.903261E-02     .351452
 230.76            9.047221E-02    .0252396         .3440223
KP =               1.454663E-06 PSAT =             7.336616E-02
KPt =              1.468193E-06 Ratio =            1.009301
```

```
HCl SUPPRESSION                  05-18-1997
NOTE. PH2O 0 DEG. SET TO 0.975 MM FROM 0.98 MM
tfreeze =       236.06
Molality =      14               Tmin =          230
PHCL1           PHCL2            PHCL3
 9.99            41.1             242
PH2O1           PH2O2            PH2O3
 .975            4.05             24.4
AHCL =           40.36982502234029
BHCL =           6401.334699315797
CHCL =          -2.608504975814467
AH2O =           29.06728536199365
BH2O =           6051.709414261564
CH2O =          -1.236734901015479
TEMP,K          PHCL,mm          PH2O,mm          K
 343.16          656.4058         67.47404         .2884466
 338.16          517.6232         52.9391          .2819678
 333.16          405.0491         41.22252         .2756433
 328.16          314.4108         31.84635         .2694762
 323.16          242              24.4             .2634686
 318.16          184.6226         18.53334         .2576229
 313.16          139.5458         13.94983         .2519418
 308.16          104.4504         10.40018         .2464277
 303.16          77.38403         7.676491         .2410839
 298.16          56.71653         5.606771         .2359123
 293.16          41.1             4.05             .2309165
 288.16          29.42961         2.891587         .2260997
 283.16          20.80928         2.03932          .2214656
 278.16          14.51973         1.419751         .2170186
 273.16          9.989998         .975             .2126509
 268.16          6.772195         .6599749         .218916
 263.16          4.519354         .4399667         .2255497
 258.16          2.96622          .288598          .2325783
 253.16          1.912812         .1860918         .2400273
 248.16          1.210635         .1178334         .2479273
 243.16          .7511295         7.318563E-02     .25631
 238.16          .456271          4.453134E-02     .2652087
 233.16          .2709792         2.651005E-02     .2746611
 236.06          .3676309         3.591288E-02     .2691091
KP =            1.702796E-05 PSAT =               .133451
KPt =           1.746985E-05 Ratio =              1.025951
```

```
HCl SUPPRESSION                 05-18-1997
tfreeze =       240.26
Molality =      15              Tmin =          235
PHCL1           PHCL2           PHCL3
 18.56          72.2             400
PH2O1           PH2O2           PH2O3
 .83            3.49             21.4
AHCL =          31.61312362792597
BHCL =          5812.923012595505
CHCL =         -1.321168082279718
AH2O =          27.25393476406388
BH2O =          6022.589642540221
CH2O =         -.9612055466267225
TEMP,K          PHCL,mm         PH2O,mm         K
 343.16          1054.149        59.85018        .2558551
 338.16          836.6591        46.82674        .2494118
 333.16          659.2576        36.36058        .2431329
 328.16          515.558         28.01075        .2370203
 323.16          400             21.4            .231075
 318.16          307.7788        16.2079         .2252981
 313.16          234.7681        12.16413        .2196912
 308.16          177.4492        9.042374        .2142551
 303.16          132.8453        6.654629        .2089918
 298.16          98.45609        4.846           .2039019
 293.16          72.2            3.49            .1989873
 288.16          52.35849        2.484258        .1942497
 283.16          37.52604        1.746732        .1896911
 278.16          26.56416        1.212339        .1853142
 273.16          18.56           .83             .1810259
 268.16          12.78959        .5600845        .185782
 263.16          8.685344        .3722116        .1908149
 258.16          5.807594        .2433877        .1961438
 253.16          3.820156        .1564443        .2017869
 248.16          2.469491        9.874626E-02    .2077669
 243.16          1.567126        6.113503E-02    .2141065
 238.16          .9751232        3.707967E-02    .2208299
 240.26          1.19309         4.586312E-02    .2179579
 KP =            1.150969E-04 PSAT =             .210422
 KPt =           1.150474E-04 Ratio =            .9995694
```

```
HCl SUPPRESSION                    05-18-1997
NOTE. PH2O 0 DEG. SET TO 0.703 MM FROM 0.72 MM
tfreeze =       243.66
Molality =      15.88          Tmin =          230
PHCL1           PHCL2          PHCL3
 31              114.8          360
PH2O1           PH2O2          PH2O3
 .703            3.07           11.4
AHCL =           21.20218409131297
BHCL =           5181.484525960859
CHCL =           .213987551053147
AH2O =          -18.59413753871204
BH2O =           4205.727723611891
CH2O =           5.99607267368617
TEMP,K          PHCL,mm        PH2O,mm          K
 343.16          1559.561       63.83054         .2728709
 338.16          1243.595       48.76486         .2597347
 333.16          984.9749       37.00451         .2474387
 328.16          774.652        27.88325         .2359414
 323.16          604.7593       20.85661         .2252076
 318.16          468.4907       15.48154         .2152013
 313.16          359.9999       11.4             .2058905
 308.16          274.2934       8.324496         .1972453
 303.16          207.1371       6.02562          .1892375
 298.16          154.9658       4.321755         .1818436
 293.16          114.8          3.07             .1750404
 288.16          84.16928       2.158904         .1688096
 283.16          61.04267       1.502196         .1631352
 278.16          43.76506       1.033676         .1580044
 273.16          30.99999       .703             .1533267
 268.16          21.67916       .4722506         .1566472
 263.16          14.95734       .3131459         .1605348
 258.16          10.17318       .2048168         .1650598
 253.16          6.815256       .1320382         .1703072
 248.16          4.492976       8.382738E-02     .1763769
 243.16          2.911944       5.236438E-02     .18339
 238.16          1.853375       .0321537         .1914931
 233.16          1.157098       1.938714E-02     .2008633
 243.66          3.043435       5.492854E-02     .1826421
KP =             5.043804E-04 PSAT =             .3007442
KPt =            5.045148E-04 Ratio =            1.000266
```

APPENDIX B

P/P° VAPOR PRESSURE PROGRAM
(9 MOLAL EXAMPLE)

APPENDIX B
P/P° VAPOR PRESSURE PROGRAM
(9 MOLAL EXAMPLE)

The program is written to run in GWBASIC.

The program requires modification for each case run. Comments and printout instructions are entered as desired.

Each run is for a specific molality (line 9) of HCl in water.

The program requires vapor pressures at three temperatures (lines 250, 260, 270) for water (lines 200, 210, 220) and HCl (lines 130, 140, 150). Fritz and Fuget data, sometimes modified, have been used in this work. The program prints out the constants of the data fit equation for vapor pressure (A, B, C for both water and HCl vapor). (See text.)

The temperature at which solid is expected to be formed is entered at line 85. The selected printout minimum temperature is entered at line 80.

The initial temperature of interest is entered at line 670. The temperature resolution desired (e.g., each 5 degrees) is entered at line 760. The program stops at the minimum temperature set in line 85.

The program prints out the vapor pressures for water and for HCl at each temperature. The program also prints out "K," the ratio of the vapor pressure of water to the vapor pressure of ice. By the assumptions in the program, K should be unity at the freezing point on the ice side of the composition mixture. On the trihydrate side, the program calculates KP (the product of the cube of the water vapor pressure and the first power of the HCl vapor pressure) and compares it to the theoretical value (KPt) at the specified freezing point, which is a sensitive test of the data.

The ratio of these two values (KPt/KP) is printed out, and should equal unity if the freezing point and all other data are correct. After the adjustments described in the text the agreement is good except at a molality of 9, which is known to represent a complex region involving not only the trihydrate but the hexahydrate and ice.

```
10 REM This program calculates vapor depression factors for water vapor in the
presence of HCl vapor.  It uses the Fritz and Fuget data.
20 REM  This program was updated from a prior program on 12 March 1997.
30 REM This program also calculates the vapor pressures of ice according to Jans
co et al, 1970, and of water according to the Smithsonian tables.  Prepared Marc
h 7, 1997.
40 REM Fritz and Fuget data for both water and HCL at 0, 20 and 50 C are used to
 find A, B and C needed for ln P = A - B/T + C ln T.
45 REM  The program first calculates HCl vapor pressures and then water vapor pr
essures.  The water vapor pressures are compared to the vapor pressure of pure w
ater above 273.16 and to pure ice at temperatures below 273.16.
47 REM  THE PROGRAM WAS REVISED MARCH 18, 1997!
48 REM The program was also revised March 25, 1997.
50 PRINT "HCl SUPPRESSION",DATE$
60 LPRINT "HCl SUPPRESSION",DATE$
65 PRINT "NOTE. PH20 ADJUSTED FROM 2.13 TO 2.1015 MM.  PHCL ADJUSTED FROM 0.240
TO 0.242 MM"
66 LPRINT "NOTE. PH2O ADJUSTED FROM 2.13 TO 2.1015 MM. PHCL ADJUSTED FROM 0.240
TO 0.242 MM"
70 M = 9
80 TMIN#= 180#
85 TFRZ# = 187.16#
86 LPRINT "tfreeze =",TFRZ#
90 PRINT "Molality =",M, "Tmin =",TMIN#
100 LPRINT "Molality = ",M,"Tmin =",TMIN#
110 PRINT "PHCL1","PHCL2","PHCL3"
120 LPRINT "PHCL1","PHCL2","PHCL3"
130 PHCL1#= .242#
140 PHCL2# = 1.295#
150 PHCL3# = 11.2#
160 PRINT PHCL1#,PHCL2#,PHCL3#
170 LPRINT PHCL1#,PHCL2#,PHCL3#
180 PRINT "PH2O1","PH2O2","PH2O3"
190 LPRINT "PH2O1","PH2O2","PH2O3"
200 PH2O1# = 2.1015#
210 PH2O2# = 8.26#
220 PH2O3# = 45.6#
230 PRINT PH2O1#,PH2O2#,PH2O3#
240 LPRINT PH2O1#,PH2O2#,PH2O3#
250 T1# = 273.16#
260 T2# = 293.16#
270 T3# = 323.16#
280 REM This section calculates the three constants needed for HCL vapor pressur
e calculations.
290 YHCL1# = LOG(PHCL1#)
300 YHCL2# = LOG(PHCL2#)
310 YHCL3# = LOG(PHCL3#)
320 F1# = (1/T1# - 1/T2#)
330 F2# = (1/T2# - 1/T3#)
340 G1# =  LOG(T1#) - LOG(T2#)
350 G2# = LOG(T2#) - LOG(T3#)
360 CHCL# = (F2#*(YHCL1#-YHCL2#) - F1#*(YHCL2# - YHCL3#))/(F2#*G1# - F1#*G2#)
370 BHCL# = (CHCL#*G1# - (YHCL1#-YHCL2#))/F1#
380 AHCL# = YHCL1# + BHCL#/T1# - CHCL#*LOG(T1#)
390 PRINT "AHCL= ",AHCL#
400 LPRINT "AHCL =",AHCL#
410 PRINT "BHCL= ", BHCL#
420 LPRINT "BHCL = ",BHCL#
430 PRINT "CHCL= ", CHCL#
```

```
440 LPRINT "CHCL = ",CHCL#
540 REM This section calculates the three constants needed for H2O vapor pressur
e calculations.
550 YH2O1# = LOG(PH2O1#)
560 YH2O2# = LOG(PH2O2#)
570 YH2O3# = LOG(PH2O3#)
580 CH2O# = (F2#*(YH2O1#-YH2O2#) - F1#*(YH2O2# - YH2O3#))/(F2#*G1# - F1#*G2#)
590 BH2O# = (CH2O#*G1# - (YH2O1#-YH2O2#))/F1#
600 AH2O# = YH2O1# + BH2O#/T1# - CH2O#*LOG(T1#)
610 PRINT "Ah2o =",AH2O#
620 LPRINT "AH2O =",AH2O#
630 PRINT "BH2O = ", BH2O#
640 LPRINT "BH2O =",BH2O#
650 PRINT "CH2O = ", CH2O#
660 LPRINT "CH2O = ",CH2O#
670 T# = 343.16#
680 PRINT "TEMP,K","PHCL,mm","PH2O,mm","K"
690 LPRINT "TEMP,K","PHCL,mm","PH2O,mm","K"
695 PHCL# = EXP(AHCL# - BHCL#/T# +CHCL#*LOG(T#))
700 PH2O# = EXP(AH2O# - BH2O#/T# +CH2O#*LOG(T#))
710 IF T# >= 273.16 THEN 790 ELSE 870
720 'PRINT "t =",T#, "ph2o =", CSNG(PH2O#),"psat=",CSNG(PSAT#),"k =", CSNG(PH2O#
/PSAT#)
730 'lPRINT "t =",T#, "ph2o =", CSNG(PH2O#), "psat =",CSNG(PSAT#),"k =",CSNG(PH2
O#/PSAT#)
740 LPRINT T#,CSNG(PHCL#),CSNG(PH2O#),CSNG(PH2O#/PSAT#)
750 PRINT T#,CSNG(PHCL#),CSNG(PH2O#),CSNG(PH2O#/PSAT#)
755 IF T# = TFRZ# THEN 1000
760 T# = T# -5#
770 IF T# <TMIN# THEN 920
780 GOTO 695
790 TS# = 373.16#
800 LIQ# = -7.90298*(TS#/T# - 1#) + 5.02808*(LOG(TS#/T#))/(LOG(10#))
810 U1# = 10#^(11.344*(1-T#/TS#)) -1#
820 U2# = 10#^(-3.19149#*(TS#/T# -1)) -1#
830 LIQ# = LIQ# -.00000013816#*U1# + .0081328#*U2# + LOG(1013.246#)/LOG(10#)
840 PLIQ# = (10#^(LIQ#))
850 PSAT# = PLIQ#*(760#/1013.246#)
860 GOTO 720
870 Z# = -2481.604/T# + 3.5721988#*LOG(T#)/(LOG(10!))-.003097203#*T#
880 Z# = Z# - .00000017649#*(T#)^2 + 1.901973#
890 PICE# = EXP((LOG(10#)*Z#))
900 PSAT# = PICE#
910 GOTO 720
920  T# = TFRZ#
930 GOTO 695
1000 IF M > 8 THEN 1010 ELSE 1050
1010 LPRINT "KP = ",CSNG(PHCL#*PH2O#^3),"PSAT =",CSNG(PSAT#)
1011 KP# = PHCL#*PH2O#^3
1012 KPT#=EXP(96.8684#-25452.8#/T#)
1013 LPRINT "KPt =",CSNG(KPT#),"Ratio =", CSNG(KPT#/KP#)
1014 PRINT "KP = ",CSNG(PHCL#*PH2O#^3),"PSAT =",CSNG(PSAT#)
1015 PRINT "KPt =",CSNG(KPT#),"Ratio =", CSNG(KPT#/KP#)
1050 END
```

APPENDIX C

DILUTION EFFECTS PROGRAM

APPENDIX C
DILUTION EFFECTS PROGRAM

This program was originally written in 1969. It is written in GWBASIC. It is reused here with only one trivial connection in line 220, in which the term (P1–P2*R1/100) was substituted for (P1–P2) in the denominator. This change made no evident difference in any calculation. The program is easily modified for specific cases.

The program is self explanatory for the most part, requiring propellant composition inputs in terms of each element per 100 grams of propellant mix (see line 30), the heat of formation (in cal/100 grams), and the heat loss (usually 0) in cal/100 grams. The heat loss term allows isothermal calculations to be made by setting Q2 equal to Q1. P1 is the ambient pressure, in mm Hg.

The inputs at line 140 need some explanation. T1 is the ambient temperature in degrees F. R1 is the ambient relative humidity. (This term makes a difference only at extremely warm and moist conditions. An arbitrary value can usually be selected.) Z1 is the problem selection variable. Z1 is set to 0, 1, or 2. Z1 is normally set to 0 or 1, depending on whether a new set of temperature (Z1 = 0) or a new propellant composition (Z1 = 1) is desired when dilution calculations are completed. Z1 is set to 2 for cases where there is no acid gas present, and simple saturation effects for water are considered.

A1 is the initial dilution selected.

D1 is the limiting difference between the mixture temperature and the original ambient temperature beyond which calculations are discontinued.

I1 is the dilution factor used in exploring for regimes where condensation would be expected (Line 540). I2 is the factor used when acid gases are not present. In most case I2 is ignored, I1 being input in line 410.

Y1 is the factor (read from Figs. II-9 or II-10, for HCl effects) by which the saturation vapor pressure is multiplied to determine the saturation vapor pressure in the mix.

The program calculates the term NFRH, which indicates the relative humidity in the ambient air above which a condensate would be expected. (NFRH was termed the "no fog relative humidity" in Oliver, 1969, the concept, if memory serves, building on "fog" in the test environmental chambers in use at that time.)

```
5 PRINT DATE$,TIME$
6 LPRINT DATE$,TIME$
10 REM This is a rewrite of a program written in 1969.  It is used to find the t
emperature-humidity boundaries for contrails from rocket exhausts.
20 REM This was rewritten March 27, 1997 and April 1, 1997 by R. C. Oliver
30 PRINT "Input Al,C,Cl,F,H,N,O,PB,Q1,Q2,P1"
40 INPUT X1,X2,X3,X4,X5,X6,X7,X8,Q1,Q2,P1
45 LPRINT X1,X2,X3,X4,X5,X6,X7,X8,Q1,Q2,P1
50 M1 = 26.97*X1 +12.01*X2 + 35.457*X3 + 19!*X4 + 1.008*X5 + 14.008*X6 + 16!*X7
+ 207.21*X8 -100!
60 IF ABS(M1)>1! THEN 30
70 S1 = 1.5*X1 + 2*X2 - .5*X3 - .5*X4 +.5*X5 - X7 +X8
80 A2 = S1*14.5/21
90 PRINT "stoich. air ratio =",A2
95 LPRINT "stoich. air ratio =",A2
100 S3 = X1*(-200.2) + X2*(-94.05) + X3*(-22.06) + X4*(-64.8) + (X5-X3-X4)*(-28.
9) + X8*(-51) -Q1 -Q2
120 PRINT "HT. RELEASE = ",S3
125 LPRINT "ht. release =",S3
130 PRINT "DILUTION","T,DEG.F","PH2O","PHCL","PHF"
135 LPRINT "dilution","T,DEG.F","PH20","HCL","PHF"
140 PRINT "INPUT R1,T1,Z1,A1,D1,I2"
150 INPUT R1,T1,Z1,A1,D1,I2
155 LPRINT P1,R1,T1,Z1,A1,D1,I2
160 T2 = (T1 + 459.69)/1.8
170 IF T2 > 273.16 THEN 200
180 IF T2 < 273.16 THEN 210
200 P2 = EXP(20.9484- 5306.7/T2)
205 GOTO 220
210 P2 = EXP(24.047 - 6153/T2)
220 H1 = P2*(R1/100)/(P1-P2)
230 N1 = X5/2 + 100*A1*H1/29 - X3/2 -X4/2
240 S2 = X2 + X3 + X4 + + N1 + X6/2 + 79*A1/29 + 21*(A1-A2)/29
250 P3 = (X5 - X4 - X3)*P1/(2*S2)
260 P4 = X3*P1/S2
270 P5 = X4*P1/S2
280 S5 = X1*17.43/2 + X2*8.47+X3*6.96+X4*6.96 + N1*8.020001
290 S6 = S5 + (X6/2 + A1*79/29)*6.96+(A1-A2)*21*7.02/29 + X8*11.2
300 T3 = -1000*S3/S6 + T2
310 IF T3>273.16 THEN 350
320 IF T3 < 273.16 THEN 360
350 P6 = EXP(20.9484 - 5306.7/T3)
355 GOTO 370
360 P6 = EXP(24.047 - 6153/T3)
370 T4 = 1.8*T3 - 459.69
380 IF Z1 = 2 THEN 400
390 PRINT A1,T4,P3,P4,P5
395 LPRINT A1,T4,P3,P4,P5
400 IF (P4+P5)=0 THEN 500
410 INPUT Y1,I1
415 LPRINT "Y1 =",Y1, "I1 = ",I1
420 Y2 = S2/(A1*100*(1+H1)/29)
430 P7 = (Y1*P6 -P3)*Y2
440 R2 = 100*P7/P2
450 PRINT "NFRH = ",R2
455 LPRINT "NFRH =",R2
460 GOTO 530
500 R3 = (100/P2)*(P6-P3)*S2/(A1*100*(1+H1)/29)
510 PRINT "NFRH =",R3
515 LPRINT "NFRH =",R3
520 I1 = I2
530 IF (T3-T2) <D1 THEN 560
540 A1 = I1*A1
550 GOTO 230
560 IF Z1 = 0 THEN 700
570 IF Z1 = 1 THEN 710
700 GOTO 140
710 GOTO 30
900 END
```

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On Predicting Secondary Smoke Humidity Boundaries at Temperatures Below 0 °C

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13. ABSTRACT *(Maximum 180 words)*

This work reexamines work originally done in 1969 which estimated the humidity-temperature boundary conditions under which solid rocket exhaust gases containing hydrogen chloride (HCl) or hydrogen fluoride (HF) would be expected to interact with ambient moist air to form a "secondary smoke" or contrail. The original work has seen wide acceptance. However, the original work relied on extrapolations of water-HCl and water-HF vapor-pressure data taken at higher temperatures to regions below 0 °C, which under some conditions were in substantial error. Low-temperature vapor-pressure data for the HCl-water system have since become available, permitting improved treatment of this regime, which is the major point of this work; the HF work remains to be updated. In reworking the HCl problem, a decision was also made to use an alternative (later) set of literature data (Fritz and Fuget, 1956) at temperatures above 0 °C, rather than the handbook data used in the 1969 paper. The various data sources involve significant disagreements, affecting results. Some minor adjustments to the Fritz and Fuget data were necessary to achieve internal consistency for modeling purposes; these adjustments appeared to be reasonable but cannot be justified in any scientific sense. The revised data are used here to recompute boundary conditions for a number of cases of interest. Results show minor changes, which might be significant in some applications. The revised charts included here, until superseded or replaced by further work, are recommended for use in further work of this nature.

14. SUBJECT TERMS
Secondary smoke; solid propellants; smokeless propellant; hydrogen chloride-water solution-vapor equilibria

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