VAPOR PRESSURES OF ACETYLENE AT LOW TEMPERATURES

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The atmospheres of many of the outer planets and their satellites contain a large number of hydrocarbon species. In particular, acetylene (C_2H_2) has been identified at Jupiter, Saturn and its satellite Titan, Uranus and Neptune. In the lower atmospheres of these planets, where colder temperatures prevail, the condensation and/or freezing of acetylene is probable. In order to obtain accurate models of the acetylene in these atmospheres, it is necessary to have a complete understanding of its vapor pressures at low temperatures. The vapor pressures of acetylene above 90K have been measured[1,2], but these measurements were made over 30 years ago and may not be extremely accurate. For temperatures below this, no vapor pressure data exists in the literature. Therefore, to arrive at an estimate for these values, modelers are forced to extrapolate the high temperature data to temperatures more appropriate for planetary atmospheres using the Clausius-Clapeyron equation. This equation employs a linear relationship between lnp and 1/T by assuming that the enthalpy (ΔH) is not temperature dependent. This assumption may not be valid over large temperature ranges and may lead to inaccuracies in the extrapolated values. Therefore, our lab has been engaged in the determination of these vapor pressures at low temperatures for acetylene.

The vapor pressures are measured with two different techniques in order to cover a wide range of temperatures and pressures. In the first, the acetylene is placed in a sample tube which is immersed in a low temperature solvent/liquid nitrogen slush bath whose temperature is measured with a thermocouple. The vapor pressure is then measured directly with a capacitance manometer. Vapor pressures in the 10^{-3} to 10^2 Torr range are measured with this method.

For lower pressures, a second technique which we call the thin-film infrared method (TFIR) was developed.[3] It involves measuring the disappearance rate of a thin film of acetylene at a particular temperature. A thin film of the material (~1m) is deposited on a substrate (figure 1) that is cooled to 40K, where the acetylene has essentially no vapor pressure. The substrate and film are then heated to the desired temperature for a vapor pressure measurement. At low temperatures where the vapor pressure is less than 1 torr, the rate of evaporation of molecules from a surface in a vacuum is the same as the rate of evaporation of the molecules in the presence of saturated vapor. Therefore, if we have a way to measure this evaporation rate, we can determine the vapor pressure of the molecule at that temperature directly. We accomplish this by taking the spectrum of a characteristic absorption feature for the molecule (1420 cm^{-1} for acetylene) at different time intervals with a Fourier Transform Infrared Spectrophotometer (FTIR). Once the sample film reaches the desired temperature, an initial spectrum is recorded. The spectrum of the absorption feature is then monitored while part of the sample film evaporates. At a certain time, t_1, when a portion of the sample film has evaporated, another absorption spectrum is taken. At a later time, t_2, when more of the sample has evaporated, another spectrum is taken and this process is repeated until the absorption feature is too weak to use for quantitative analysis (see figure2).

The spectra are then analyzed using previously determined extinction coefficient values, to determine the disappearance rate R (where R=Δn/Δt, the number of molecules that disappear per unit time). This can be related to the vapor pressure directly using the formula

$$R = \frac{p}{(2\pi mkT)^{1/2}}$$

where p is the vapor pressure at temperature T, m is the molecular mass of the compound and k is the Boltzmann constant. This technique facilitates measurement of the lower temperatures and pressures (10^{-8} to 10^{-6} Torr). Both techniques have been calibrated using CO_2, and have shown good agreement with the existing literature data. Table I gives values for acetylene using both methods and figure 3 shows a plot of these values as well as the literature values for the higher temperature data.

SAMPLE CHAMBER

To Vacuum
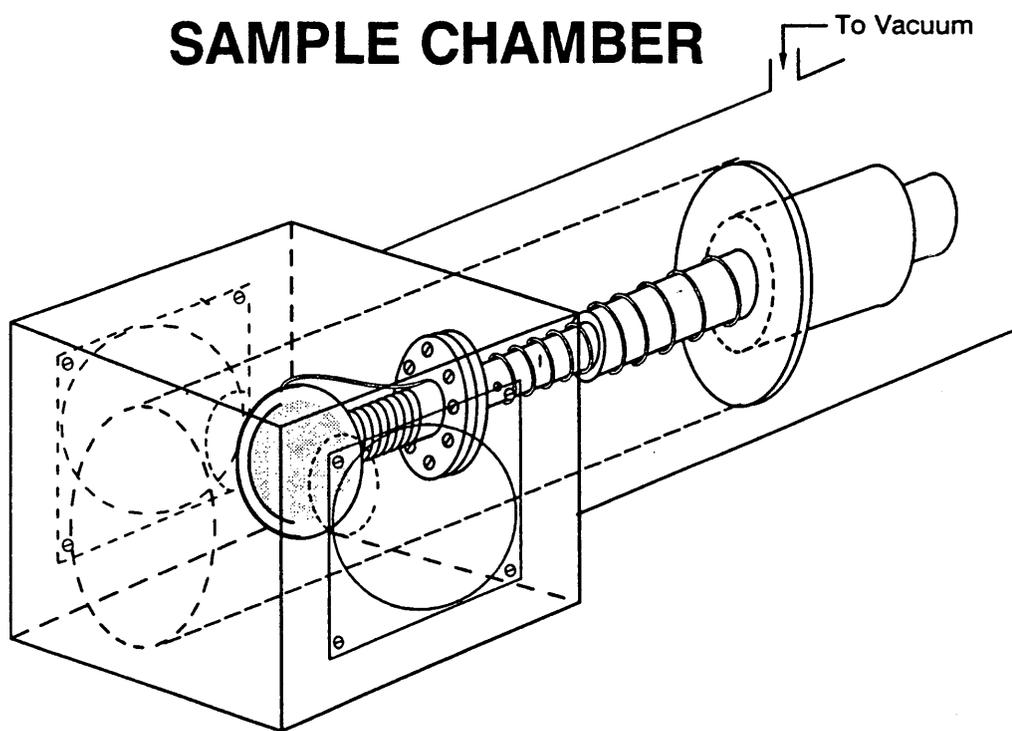
J107.009

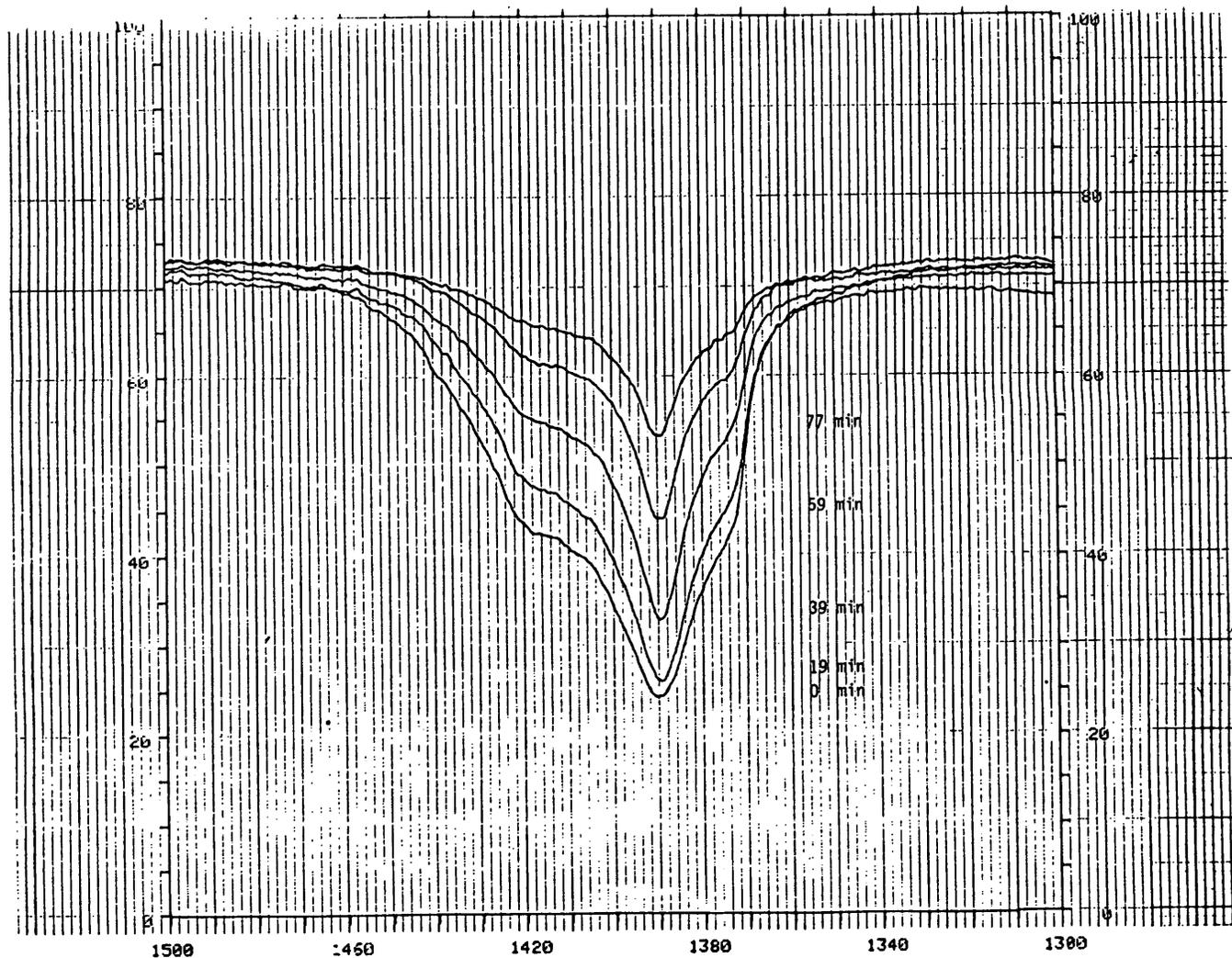Figure 1. Sample chamber for TFIR vapor pressure experiments.

Figure 2. Transmission spectra, at different times of acetylene at 80K.

Table I - Acetylene Vapor Pressures

Capacitance Manometer			TFIR	
T(K)	P(Torr)		T(K)	P(Torr)
118	5.07×10^{-3}		80.0	1.68×10^{-7}
143	8.12		81.0	3.41×10^{-7}
145	7.69		86.0	1.13×10^{-6}
148	7.82		86.2	1.29×10^{-6}
155	30.3		88.0	1.74×10^{-6}
158	42.8		90.0	5.24×10^{-6}
159	38.0		91.0	4.24×10^{-6}
160	48.5			
171	137			
176	217			
178	361			
180	367			
188	637			

As shown in figure 3, at the lowest recorded temperature, our data differs from the extrapolated value by almost 2 orders of magnitude. This produces a significant difference in the haze production models of Romani[4], for acetylene in the atmospheres of Saturn, Uranus and Neptune. Our laboratory is continuing to make vapor pressure measurements for other molecules such as diacetylene (C_4H_2), hydrogen cyanide (HCN), cyanoacetylene (HC_3N) and dicyanoacetylene (C_4N_2), that are of importance to planetary atmospheres.

References

1. W. T. Ziegler, NBS Tech. Note, **4**, (1959).

2. P. S. Bourbo, J. Phys., **8(6)**, 286 (1943).

3. R. K. Khanna, J. E. Allen, Jr., C. M. Masterson and G. Zhao, J. Phys. Chem., In Press (1989).

4. P. N. Romani, Private Communication, (1989).

Acetylene Vapor Pressure Data

□ Literature*
■ Literature+
○ Capacitance Manometer
● TFIR

*Ziegler,W.T., NBS Tech. Note,4,(1959)
+Bourbo,P.S., J. Phys.,8(6),(1943)

1/T (x1000)

Lnp (p in Torr)

10

0

-10

-20

4   6   8   10   12   14

Figure 3. Plot of the literature, capacitance manometer and TFIR vapor pressure data for acetylene.