Sublimation Rates and Vapor Pressures of H_2O, CO_2, N_2O, and Xe

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The sublimation rates of H_2O, CO_2, N_2O, and Xe were measured in the temperature ranges that correspond to vapor pressures between 10^{-4} and 10^{-9} torr. The data, obtained with a quartz crystal microbalance, were compared with existing data and extrapolations. Some of the limitations of the technique are discussed.

The quartz crystal microbalance has proved to be a useful tool in conjunction with the Langmuir free evaporation technique for measuring vapor pressure (*9, 10*). Its high mass sensitivity allows the measurement of sublimation rates, n, that correspond to vapor pressures between 10^{-3} and 10^{-9} torr. Pressure measurements in this region are somewhat limited, both by the need for transpiration effect corrections and calibration problems (*1, 8*). The free evaporation technique used with a quartz crystal microbalance circumvents this problem.

In the work reported here, this technique was used to measure bulk sublimation rates for CO_2, N_2O, H_2O, and Xe. The data are compared to the extrapolation of Honig and Hook (*7*) and serve as an effective test of the accuracy of the extrapolations. For these measurements, the microbalances were used to detect a fraction of the molecules leaving a nearby surface. A more direct method is to measure the rate at which molecules leave the surface of a microbalance (*9*). The latter technique is more sensitive but is not suitable for measurements where the temperature is varied with time. In addition, accurate surface temperature measurement is more difficult.

Apparatus and Procedures

Because the apparatus used for these measurements is described in detail elsewhere (*4*), only the pertinent aspects are reviewed here for convenience.

The microbalances were mounted near a thermostated target disc in a high vacuum chamber. The chamber was suspended in a 50K pumped nitrogen bath. The target disc was manufactured out of pure copper, and its temperature was determined to within ±0.1K with Pt and Ge resistance thermometers. A molecular beam was used to deposit a thick film of the molecules to be studied on the target disc. The temperature of the disc, T, was held near the bath temperature for the deposition of the CO_2, N_2O, and Xe. For the deposition of the H_2O, T was held near 100K. A microbalance located beside the disc and in the beam was used to determine the population density, N, of the film. For the bulk sublimation measurements, N was greater than 10^{19} molecules cm^{-2}.

A microbalance located above the disc and outside of the incident beam was used to intercept a fraction F of the molecules leaving the disc. F could be calculated from the relative positions of the disc and the microbalance. The accuracy of the calculations was limited to ±20% by the probable errors in the measured positions. However, comparisons of high vapor pressures for H_2O with values obtained with conventional pressure measurement techniques showed F to be accurate to within ±3%. The latter accuracy was assumed for all sublimation rate measurements.

Previous measurements of the condensation coefficient with this apparatus have shown that, for CO_2, H_2O, N_2O, and Xe, 99.9% of the molecules that hit a 50K surface remain there (*3*) when the gas temperature is 130K for N_2O, CO_2, and Xe and 270K for H_2O.

The molecular beam used to deposit the films was equipped with a monopole mass spectrometer. The gases used were analyzed prior to deposition. The CO_2 and Xe were commercially prepared, were of high-purity grade, and showed no measurable impurities. As purchased, the N_2O was a dry, nominally 98%, pure-grade gas. Analysis showed the main impurity to be air, which was easily removed. This purification was accomplished by repeated evacuation of the bulb in which the N_2O was stored, while the N_2O was cooled to 77K. No impurity could be

Table I. Vapor Pressure of H_2O vs. Temperature, T

Temp, K	Press, torr	Temp, K	Press, torr
187.02	1.48×10^{-4}	148.50	4.70×10^{-8}
186.80	1.44×10^{-4}	147.50	2.65×10^{-8}
182.64	6.91×10^{-5}	146.30	1.86×10^{-8}
176.83	2.33×10^{-5}	146.30	1.86×10^{-8}
174.57	1.49×10^{-5}	146.30	1.58×10^{-8}
169.20	5.00×10^{-6}	144.90	2.15×10^{-8}
159.78	5.78×10^{-7}	144.90	2.01×10^{-8}
159.58	7.20×10^{-7}	144.00	1.05×10^{-8}
159.50	7.04×10^{-7}	144.00	1.02×10^{-8}
159.20	4.39×10^{-7}	144.00	9.77×10^{-9}
159.20	3.95×10^{-7}	142.90	6.67×10^{-9}
159.00	3.73×10^{-7}	142.90	5.59×10^{-9}
153.50	1.16×10^{-7}	141.10	4.70×10^{-9}
153.19	1.33×10^{-7}	141.00	4.42×10^{-9}
151.10	8.64×10^{-8}	141.00	4.17×10^{-9}
151.10	8.64×10^{-8}	136.90	2.66×10^{-9}
151.00	5.75×10^{-8}	134.50	9.28×10^{-10}
151.00	5.75×10^{-8}	134.50	7.17×10^{-10}
151.00	4.99×10^{-8}	131.80	6.33×10^{-10}
149.34	3.90×10^{-8}		

Table II. Vapor Pressure of N_2O vs. Temperature, T

Temp, K	Press, torr	Temp, K	Press, torr
80.2	9.09×10^{-7}	74.7	4.75×10^{-8}
79.8	4.25×10^{-7}	74.6	4.11×10^{-8}
79.4	6.66×10^{-7}	74.5	3.27×10^{-8}
79.3	5.91×10^{-7}	74.4	3.57×10^{-8}
79.0	3.78×10^{-7}	74.3	3.57×10^{-8}
77.2	1.78×10^{-7}	74.3	3.57×10^{-8}
77.1	1.33×10^{-7}	74.3	3.13×10^{-8}
77.1	1.32×10^{-7}	74.3	3.75×10^{-8}
77.1	1.66×10^{-7}	73.9	3.16×10^{-8}
77.0	1.24×10^{-7}	73.8	2.58×10^{-8}
77.0	1.42×10^{-7}	73.4	2.31×10^{-8}
76.7	1.69×10^{-7}	73.3	1.59×10^{-8}
76.4	5.70×10^{-8}	72.4	1.06×10^{-8}
75.8	9.38×10^{-8}	71.3	7.88×10^{-9}
75.3	5.66×10^{-8}	70.3	2.61×10^{-9}
75.1	4.86×10^{-8}	69.8	2.59×10^{-9}
74.8	6.37×10^{-8}	68.6	1.29×10^{-9}
74.7	5.55×10^{-8}	68.6	1.29×10^{-9}
74.7	4.57×10^{-8}	68.1	8.55×10^{-10}

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detected after this procedure was repeated twice. The level of impurity detectability corresponded to about 0.1% O_2 in N_2O.

The H_2O proved to be more difficult to clean. After starting with doubly distilled H_2O and outgassing it for 10 min at 100°C, the H_2O still contained nominally 0.5 mol % CO_2. At least 90% of this CO_2 did not stick to the target disc when the H_2O was deposited with the disc held at 100K. The resulting H_2O film contained less than 0.05% CO_2.

Table III. Vapor Pressure of CO_2 vs. Temperature, *T*

Temp, K	Press, torr	Temp, K	Press, torr
102.50	3.16×10^{-4}	77.34	7.09×10^{-9}
100.21	1.55×10^{-4}	77.22	7.92×10^{-9}
98.22	7.92×10^{-5}	77.04	8.97×10^{-9}
96.15	3.74×10^{-5}	77.04	8.96×10^{-9}
94.19	1.84×10^{-5}	77.04	8.93×10^{-9}
91.73	7.49×10^{-6}	76.92	8.31×10^{-9}
90.00	3.23×10^{-6}	76.92	5.13×10^{-9}
89.95	3.21×10^{-6}	76.92	4.69×10^{-9}
89.42	2.87×10^{-6}	76.92	4.05×10^{-9}
88.97	1.99×10^{-6}	76.92	3.99×10^{-9}
88.73	2.02×10^{-6}	76.86	8.49×10^{-9}
88.65	1.91×10^{-6}	76.75	4.79×10^{-9}
86.91	1.02×10^{-6}	76.53	6.00×10^{-9}
86.66	7.89×10^{-7}	76.28	3.99×10^{-9}
85.03	4.13×10^{-7}	75.93	4.69×10^{-9}
85.00	4.08×10^{-7}	75.36	3.47×10^{-9}
84.60	2.76×10^{-7}	75.13	4.17×10^{-9}
84.03	2.46×10^{-7}	75.13	4.14×10^{-9}
83.96	2.27×10^{-7}	75.13	3.95×10^{-9}
82.95	1.72×10^{-7}	75.13	3.42×10^{-9}
81.37	7.61×10^{-8}	74.91	2.81×10^{-9}
81.37	7.74×10^{-8}	74.13	9.98×10^{-10}
81.10	5.22×10^{-8}	74.02	1.32×10^{-9}
80.58	4.98×10^{-8}	73.53	8.49×10^{-10}
80.00	3.58×10^{-8}	73.10	1.33×10^{-9}
79.65	3.09×10^{-8}	71.99	8.66×10^{-10}
79.36	2.71×10^{-8}	71.89	8.16×10^{-10}
79.18	2.50×10^{-8}	71.84	6.49×10^{-10}
79.05	1.93×10^{-8}	71.63	5.38×10^{-10}
78.62	1.52×10^{-8}	71.58	3.46×10^{-10}
78.00	1.34×10^{-8}	69.69	8.61×10^{-11}

Table IV. Vapor Pressure of Xe vs. Temperature, *T*

Temp, K	Press, torr
59.5	1.03×10^{-6}
59.3	9.19×10^{-7}
58.3	5.31×10^{-7}
57.1	2.34×10^{-7}
56.7	1.78×10^{-7}
53.9	4.73×10^{-8}
53.7	4.48×10^{-8}

Table V. Heat of Vaporization and Preexponential for Data in Tables I–IV

Material	Temp range, K	ΔH, kcal/mol	B, ln (torr)
H_2O	153–187	12.2 ± 0.1	24.0
H_2O	132–153	11.4 ± 0.3	21.7
N_2O	68.1–80.2	6.0 ± 0.1	23.6
CO_2	69.7–102.5	6.5 ± 0.1	23.8
Xe	53.7–59.5	3.4 ± 0.1	15.2

Data Treatment

If there are n molecules cm^{-2} sec^{-1} leaving a bulk surface and none is incident, the Langmuir vapor pressure, P_L, (torr) can be given by

$$P_L = (2.85 \times 10^{-23})\,(MT)^{1/2}n \qquad (1)$$

where M is the gram molecular weight of the vapor. The equilibrium vapor pressure, P_s, is related to P_L through the Langmuir sublimation coefficient, α_L, by the expression $P_L = \alpha_L P_s$. Although typically near unity, the range of possible values of α_L is 0 to 1.0 (*10*).

At equilibrium, α_L is equal to the condensation coefficient, γ. The coefficient, γ, is defined here as the ratio of the number of molecules incident on a surface that stick to the number incident. Experimentally, it has been observed that γ approaches unity as the gas temperature approaches the surface temperature (*3*). For the data that are available for those values of incident flux closest to n and for the gas temperature used for each molecular species, γ was greater than 0.9. Therefore, γ and α_L can be assumed to be near unity for the situations reported here.

Results

The data on bulk sublimation of H_2O, N_2O, CO_2, and Xe are used in Equation 2 to calculate the pressure for each temperature contained in Tables I–IV. The data on CO_2 and H_2O are from ref. *5*. Figures 1–4 show the same data along with the extrapolations of Honig and Hook (*7*), i.e., the dotted lines. The solid line represents a least-squares fit of the data to an equation of the form

$$\ln P_L = \Delta H/RT + B$$

The values obtained for the constants ΔH and B are contained in Table V.

There are two sets of constants for H_2O. One set is for the data for T above 150K, and the other is for T below 150K. This temperature is approximately the transition temperature from vitreous ice to ice *I* (*6*). From the data given here, the heat of transformation for this phase change is 740 cal mol^{-1}. This heat is nearly double the heats obtained previously for this transformation (*6*). Above 150K, the data for H_2O agree well with the extrapolation of Honig and Hook (*7*), which is based on pressure data that go down almost to 10^{-5} torr. Because the data here go above 10^{-4} torr, the data in the overlap region serve as a check on the geometrical factor introduced to relate the flux of molecules detected at the microbalance to the rate at which the molecules leave the surface.

The agreement of these data with the extrapolations of Honig and Hook for CO_2, N_2O, and Xe is not quite as good as for H_2O. However, the discrepancies are not unduly large, considering that the extrapolations are based on data for the pressure range above 10^{-3} torr. For CO_2 the earlier data by Tickner and Lossing (*11*) do not fit an extrapolation of our data to the higher pressure range. In all three cases, the data here are lower than the extrapolations. The recent data on Xe by Leming and Pollack (*8*) are also lower by approximately the same amount. On the basis of our data, the extrapolations of Honig and Hook are excellent guides for the approximate prediction of vapor pressure at lower pressures.

Two limitations associated with using the quartz crystal microbalance were encountered in this work. One was the drift in the frequency, which is associated primarily with the temperature drift of the bath. This drift provides a lower limit on the rate of change of mass that can be reliably detected. For CO_2 and N_2O this corresponds to

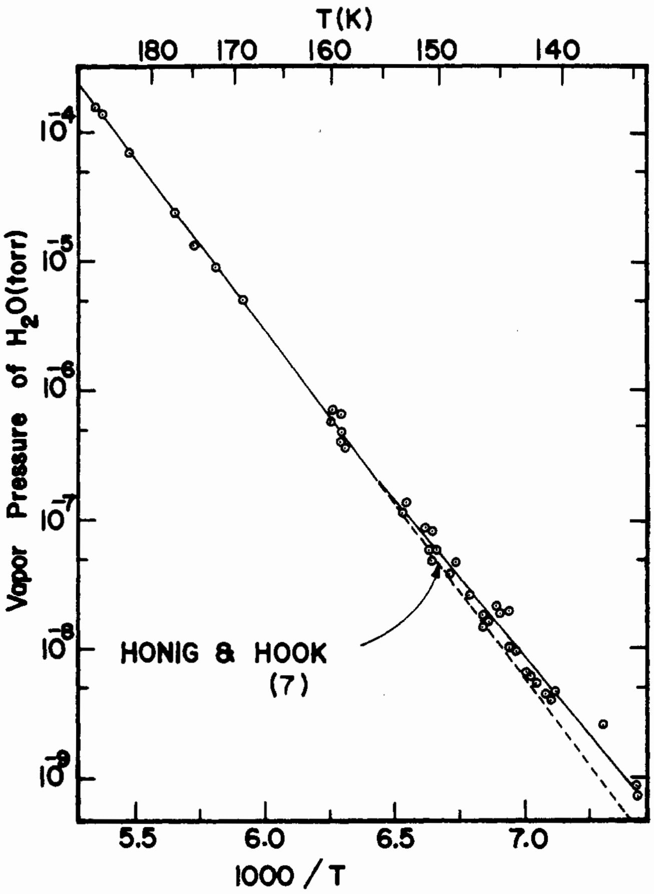

Figure 1. Vapor pressure of H_2O vs. temperature, *T*

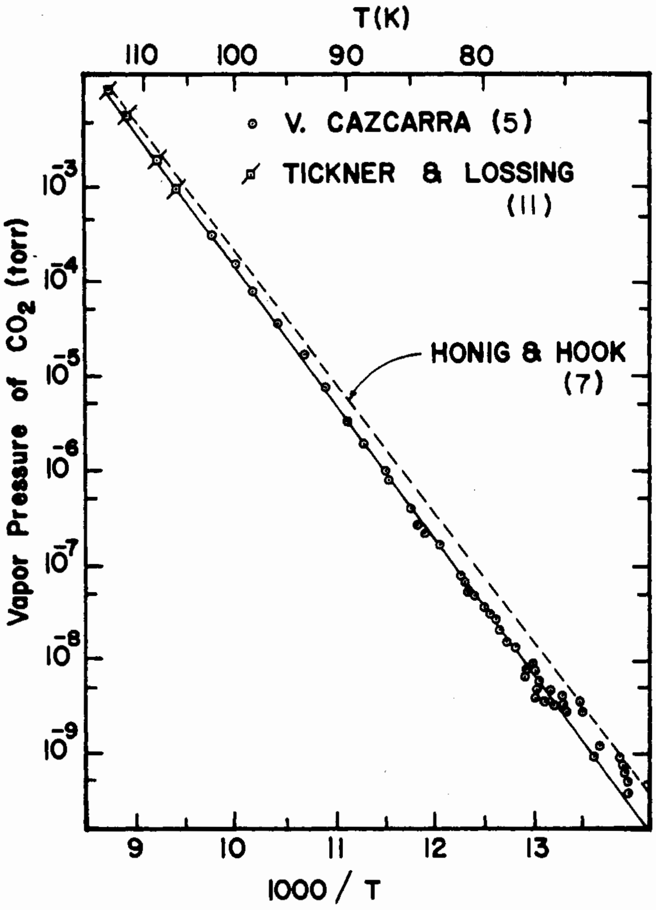

Figure 3. Vapor pressure of CO_2 vs. temperature, *T*

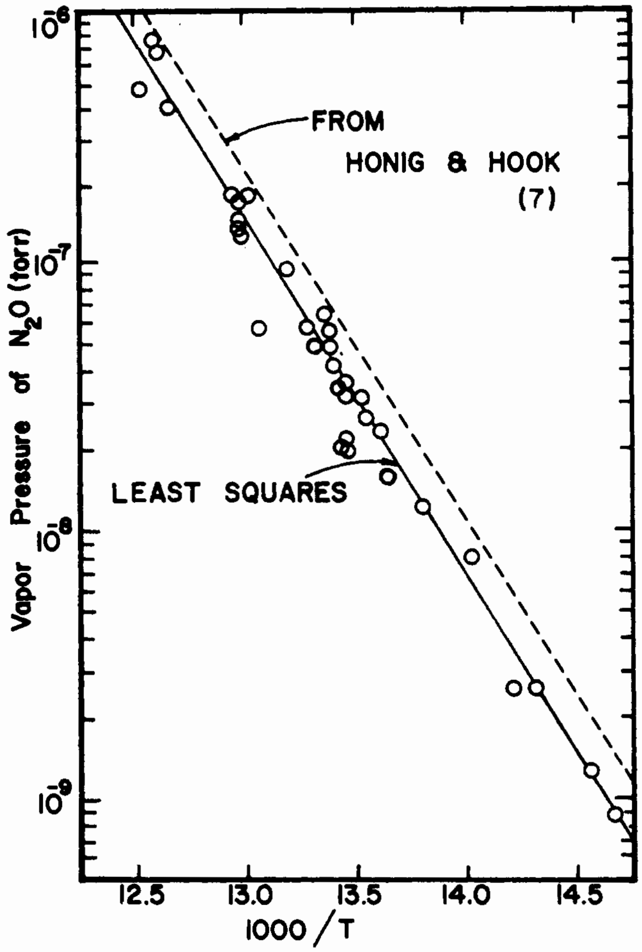

Figure 2. Vapor pressure of N_2O vs. temperature, *T*

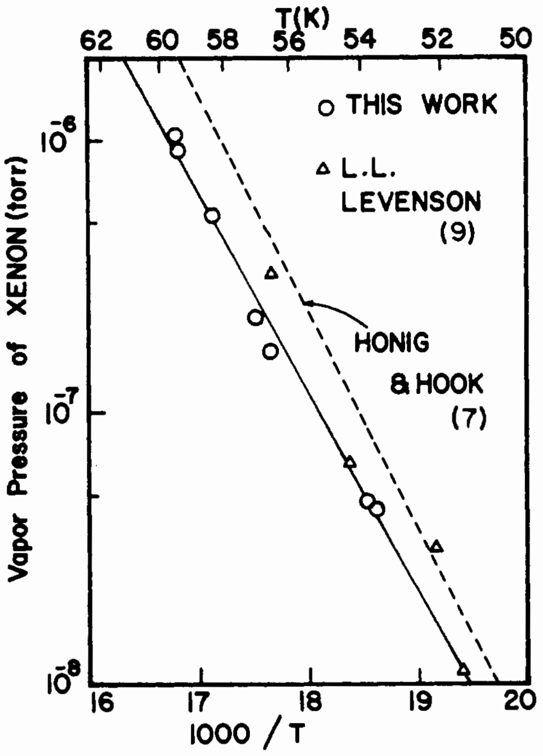

Figure 4. Vapor pressure of Xe vs. temperature, *T*

approximately 5 × 10^{-10} torr. The other limitation was that the vacuum chamber had to be at a low enough temperature so that the vapor pressure in the chamber was much less than the corresponding sublimation rates being measured. In the case of Xe, a chamber wall temperature near 50K limited the measurements to above 10^{-8} torr.

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Thermodynamic Equilibrium Constant of Ethyl Alcohol-Acetaldehyde-Hydrogen System

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Thermodynamic equilibrium constants of the ethyl alcohol-acetaldehyde-hydrogen system were determined experimentally at temperatures from 456 to 540K. Equilibrium was established utilizing a commercially available cupric oxide-chromia catalyst. The equilibrium constants obtained in the present investigation were compared with those of published literature and with estimates obtained from thermochemical data. The values of ΔH_T° and ΔS_T° were estimated for the above temperature range: $\Delta H_T^\circ = 17.09 \pm 0.71$ kcal mol^{-1} and $\Delta S_T^\circ = 28.02 \pm 1.01$ cal mol^{-1} K^{-1}.

Accurate values of thermodynamic equilibrium constants are vitally needed for rate modeling near chemical equilibrium as well as for the determination of equilibrium concentrations. The equilibrium constants of the ethyl alcohol-acetaldehyde-hydrogen system have been experimentally determined by a few investigators (*5, 9, 11*). But some discrepancy exists among the constants so far reported.

In this investigation an attempt was made to obtain accurate values of thermodynamic equilibrium constants for the ethyl alcohol-acetaldehyde-hydrogen system at temperatures between 456 and 540K. The constants so obtained were compared to the literature values and those estimated from existing thermochemical data (*10*). Thermodynamic equilibrium was established utilizing a commercially available copper-chromia catalyst. The dehydrogenation reaction of ethyl alcohol and the hydrogenation reaction of acetaldehyde on the catalyst were quite fast at these temperatures so that thermodynamic equilibrium was attained rather easily.

Materials

Pure ethyl alcohol was supplied by U.S. Industrial Chemicals Co., New York, N.Y. Kodak CP grade acetaldehyde was used, with a minimum purity of 99%. Electrolytic hydrogen gas was purchased from Carbide Reduction Inc., Linden, N.J. This cylinder gas contained approximately 0.5 vol % oxygen. Hydrogen was purified before being transferred to a reactor. Hydrogen passed through a Matheson deoxo gas purifier, which catalytically converted oxygen contaminated to water.

A commercial cupric oxide-chromia catalyst, Harshaw Cu-1407 T-⅛, was used as supplied by the Harshaw Chemical Co., Cleveland, Ohio. It consisted of 37 wt % of CuO, 52 wt % of Cr_2O_3, and 11 wt % of binder. Typical physical properties are:

Size, ⅛ in. diam, ⅛ in. long (extruded)
Pellet density, 1.65 g cm^{-3}
Surface area, 17.9 m^2 g^{-1}

This catalyst was crushed and screened to −8 + 14 mesh.

Apparatus

A schematic flow diagram of the experimental equipment is shown in Figure 1. The reactor body consisted of a 1-in. i.d. Pyrex tube of 3-ft length, which provided for a catalyst chamber 1 in. in diameter by 1 in. long. Three thermocouples inserted into a ¼-in. thermocouple well measured, respectively, the top, middle, and bottom sections of the catalyst bed of the reactor. An electrically heated aluminum-bronze block served as a heat sink which provided an adequate temperature control to the catalyst bed. During a run the overall temperature gradient in the catalyst bed never exceeded 2°C.

The feed to the reactor contained ethyl alcohol, acetaldehyde, and hydrogen. A mixture of ethyl alcohol and acetaldehyde was transferred to the reactor with a mini pump. The flow rate of the mixture was measured from the volume change in the liquid reservoir. The hydrogen flow rate was controlled with a precision needle valve and was metered with a rotameter.

Analysis

Analysis of 20-ml gas samples collected at 120°C and 1 atm was performed by a gas-liquid chromatograph by

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