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Vapor Pressure of Solid Chloromethane

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The vapor pressure of solid chloromethane has been determined between 130 and 172 K. The molar enthalpy of condensation at 0 K, calculated by using the pressure values that we have determined and previously published heat capacity measurements, is estimated to be $\Delta_g^{cr}H(0) = -(31.94 \pm 0.016)$ kJ·mol^{-1}.

Introduction

In the measurement of adsorption isotherms involving chloromethane (CH_3Cl), it was necessary to know the vapor pressure of the bulk adsorbate in the range 130−182 K. Earlier measurements (Messerly and Aston, 1940; Ganeff and Jungers, 1948) had only been made on the liquid, above the melting point (175.44 K). No data were available at lower temperatures.

The results of our vapor pressure measurements between 130 and 172 K are presented and discussed in this paper.

Experimental Details

CH_3Cl of 99.9% volume purity was supplied by L'Air Liquide. Before each set of measurements, it was purified by pumping on the condensed phase at 193 K (dry ice temperature). An indication for the purity of the gas is given by the verticality of the first step of a CH_3Cl adsorption isotherm on graphite at 129 K shown in Figure 1. This step is representative of a well-defined adsorbed phase. It would be no more vertical if the adsorbate contained any impurity.

The experimental device was the same as used in our adsorption studies and previously described by Thomy and Duval (1966). For the vapor pressure determinations, the gas was condensed in the adsorption cell contained in a cryostat previously described by Bah (1994). The temperature of the cell was maintained constant and uniform within ±0.05 K. Its value was measured by means of a calibrated platinum resistance.

The lower pressures (<35 Pa) were measured by a home-made McLeod gauge (quadratic reading, (281.6 ± 0.05) cm^3 volume, calibrated capillary of 1 mm diameter), and the higher values with a Barocel manometer from Datametric with a sensor having a range of 0−1.33 kPa. The accuracy of the McLeod gauge readings depends on the height of the mercury column; it has been estimated to be about ±10% at 0.5 Pa and increases with increasing pressure; it is better than 1% for values higher than 10 Pa. The Barocel accuracy is ±0.15% of the reading. Thermal transpiration was taken into account by means of the semiempirical equation of Takaishi and Sensui (1963). For temperatures higher than 153 K, where the pressure is >50 Pa, this correction is less than 1% of the pressure value.

Results and Discussion

Our results can be represented by the equation

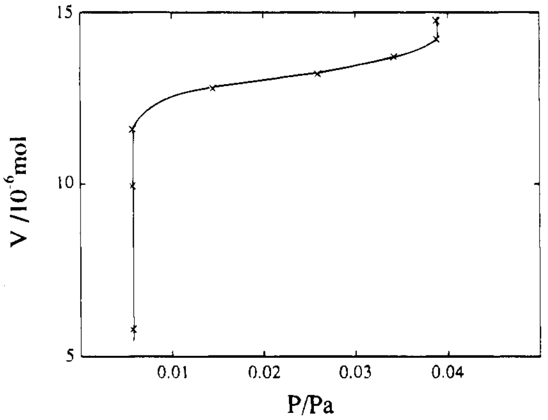

Figure 1. Adsorption isotherm of CH_3Cl on graphite at 130 K. P = equilibrium pressure. V = adsorbed volume.

$$\log(P/Pa) = -\frac{1763}{(T/K)} + 14 - 0.0052(T/K) \qquad (1)$$

the standard deviations of the constants being, respectively, 18, 0.25, and 0.0008.

A more precise thermodynamic analysis of our results can be made from the equation previously used by Grutter and Shorrock (1964) and by Tessier *et al.* (1982):

$$\Delta_g^{cr}H(0) - T\Delta_g^{cr}S(0) = A°(g,T) + RT + BP + T\int_0^T \frac{C_p}{T}\,dT - \int_0^T C_p\,dT + RT\ln P \qquad (2)$$

where $\Delta_g^{cr}H(0)$ and $\Delta_g^{c}S(0)$ are, respectively, the molar enthalpy and the molar entropy of condensation from the gas to the solid at 0 K, T is the temperature, $A°(g,T)$ is the molar Helmholtz free energy of the gas, considered as perfect, B is the second virial coefficient, and P is the sublimation pressure.

$A°(g,T)$ is related to the partition function Q by the equation

$$A°(g,T) = -RT\ln(Q) \qquad (3)$$

where R is the ideal gas constant.

When the expression of the partition function is expanded according to usual statistical thermodynamics, eq 2 becomes

$$\Delta_g^{cr}H(0) - T\Delta_g^{cr}S(0) = RT\ln\left(\frac{P}{kT}\right) + BP + T\int_0^T \frac{C_p}{T}\,dT - \int_0^T C_p\,dT - RT\ln\left(\frac{q_{rot}q_{vib}}{\Lambda^3}\right) \qquad (4)$$

where $\Lambda^{-3} = (2\pi mkT/h^2)^{3/2}$.

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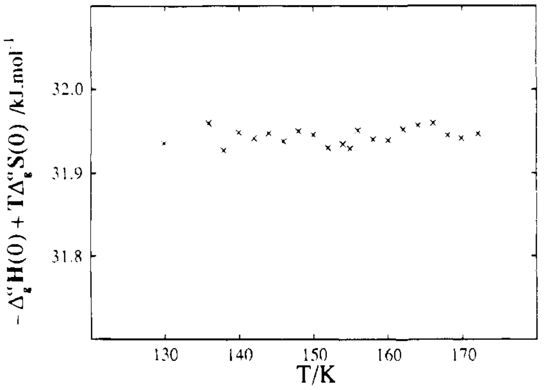

Figure 2. Dependence of $\Delta_g^{cr}H(0) - T\Delta_g^{cr}S(0)$ on temperature for $130 \le T \le 172$ K. $\Delta_g^{cr}H(0)$ and $\Delta_g^{cr}S(0)$ are, respectively, the molar enthalpy and entropy of condensation from the gas to the solid at 0 K.

The rotation contribution to the partition function, q_{rot}, was calculated by using the moments of inertia given by Messerly and Aston (1940): $I_x = I_y = 61.3 \times 10^{-47}$ kg·m^2· the CH_3Cl molecule being a symmetrical rotator, and $I_z = 5.46 \times 10^{-47}$ kg·m^2.

The CH_3Cl molecule exhibits six frequencies: $\nu_1 = 732.1$ cm^{-1}, $\nu_2 = 1015$ cm^{-1}, $\nu_3 = 1354.9$ cm^{-1}, $\nu_4 = 1454.6$ cm^{-1}, $\nu_5 = 2966.0$ cm^{-1}, and $\nu_6 = 3041.8$ cm^{-1}. ν_4, ν_5, and ν_6 are degenerate (Herzberg, 1945). However, only ν_1 brings a significant contribution to the vibration contribution to the partition function, q_{vib}.

No experimental values of the second virial coefficient were available in the investigated temperature range. This coefficient was then estimated by means of the Guggenheim semiempirical formula (Guggenheim, 1966):

$$\frac{B}{V_c} = 0.44 + 1.4\left(1 - \exp\left(0.75\frac{T_c}{T}\right)\right) \qquad (5)$$

where V_c and T_c are, respectively, the critical volume and the critical temperature. The imprecision of this equation does not significantly affect the value of $\Delta_g^{cr}H(0) - T\Delta_g^{cr}S^*(0))$, insofar as the contribution of BP to this quantity is about 0.02%.

Heat capacity measurements have been performed by Messerly and Aston (1940), and by Eucken and Hauck (1948). Their results are consistent, although slightly different. The integrals of eq 4 have been estimated graphically for each experimental temperature by using the values of Messerly and Aston which cover a larger temperature range and seem more reliable.

The dependence on temperature of $\Delta_g^{cr}H(0) - T\Delta_g^{cr}S(0)$ values that we have calculated is presented on Figure 2. For the whole set of results, $\Delta_g^{cr}H(0) - T\Delta_g^{cr}S(0)$ remains constant, which shows that the zero temperature entropy is 0. The average value of $\Delta_g^{cr}H(0)$ at 0 K is estimated to be (-31.94 ± 0.016) kJ·mol^{-1}. The experimental pressures and $\Delta_g^{cr}H(0)$ values calculated for each temperature are reported in Table 1, as well as the pressure values calculated by using eq 4 with $\Delta_g^{cr}H(0) = -31.944$ kJ·mol^{-1}. Experimental and calculated values are in good agreement. This calculation, performed at lower temperatures, makes it possible to calculate accurate sublimation pressures in a temperature range for which accurate measurements are difficult, owing to the very low values of these pressures.

In conclusion, the dependence of $\Delta_g^{cr}H(0)$ on temperature was calculated by using the heat capacity values of Messerly and Aston (1940) and our vapor pressure results. The entropy $\Delta_g^{cr}S(0)$ at 0 K deduced from these calculations is 0, in agreement with the third law of thermodynamics. The enthalpy $\Delta_g^{cr}H(0)$ at 0 K is estimated to be (-31.94 ± 0.016) kJ·mol^{-1}. The constancy of the value of $\Delta_g^{cr}H(0)$ shows the self-consistency of the pressure data. By using this $\Delta_g^{cr}H(0)$ determination, the sublimation pressures of CH_3Cl can be calculated for temperatures lower than those of the investigated range, where their very low values make difficult or even impossible any accurate measurements.

Table 1. Values of the Enthalpy at 0 K, $\Delta_g^{cr}H(0)$, Calculated from Each Temperature[a]

T/K	P_{exptl}/ Pa	$\Delta_g^{cr}H(0)$/ (kJ·mol^{-1})	P_{calcd}/ Pa	$100(P_{calcd} - P_{exptl})/P_{exptl}$
129.87	0.51	−31.936	0.50	−0.9
135.88	1.84	−31.959	1.87	−1.2
137.89	2.86	−31.927	2.82	−1.5
139.93	4.22	−31.948	4.23	0.3
141.97	6.28	−31.941	6.26	−0.3
143.96	9.06	−31.947	9.08	0.2
145.94	13.07	−31.938	13.00	−0.5
147.96	18.49	−31.950	18.56	0.4
149.93	25.99	−31.946	26.00	0.006
151.94	36.76	−31.930	36.34	−1.1
153.97	50.86	−31.935	50.46	−0.8
154.94	59.56	−31.929	58.84	−1.2
156.00	69.10	−31.951	69.44	0.5
158.01	94.73	−31.940	94.40	−0.3
160.02	127.7	−31.939	127.1	−0.4
162.08	170.6	−31.952	171.6	0.6
164.09	225.08	−31.957	227.8	0.9
166.11	297.3	−31.959	300.5	1.0
168.03	388.4	−31.945	388.4	0.0
169.86	493.0	−31.942	491.9	−0.3
172.13	657.3	−31.947	658.3	0.1

[a] P_{exptl} is the measured value of the vapor pressure, and P_{calcd} is calculated from eq 4 with $\Delta_g^{cr}H(0) = -31.944$ kJ·mol^{-1}.

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