

# Vapor Pressure and Solid Phases of Methanol below Its Triple Point Temperature

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We present an experimental work devoted to study of the thermodynamical properties of solid methanol. We combine Fourier transform infrared spectroscopy (FTIR) and mass spectrometry (MS) to measure, for the first time, the vapor pressure of various methanol solid phases and determine their Clausius–Clapeyron equations. We perform our experiments between  $T = 130$  K and the triple point temperature  $T_t = 175.61$  K. When methanol is condensed from its vapor below  $T_t$ , we observe three different solid phases depending on temperature. A condensation at  $T = 130$  K forms a metastable phase with an enthalpy of sublimation  $\Delta H_{\text{metastable-vapor}} = 42.9 \pm 0.5 \text{ kJ}\cdot\text{mol}^{-1}$ . Upon heating, this phase transforms itself at  $T \approx 145$  K to the  $\alpha$ -phase that has an enthalpy of sublimation  $\Delta H_{\alpha\text{-vapor}} = 46.9 \pm 0.2 \text{ kJ}\cdot\text{mol}^{-1}$ . Cooling the  $\alpha$ -phase does not lead back to the metastable phase, whereas heating this  $\alpha$ -phase leads to the  $\beta$ -phase occurrence at  $T_{\alpha\text{-}\beta} = 157.36$  K. This latter one is stable until  $T_t$  and has an enthalpy of sublimation  $\Delta H_{\beta\text{-vapor}} = 44.2 \pm 0.5 \text{ kJ}\cdot\text{mol}^{-1}$ .

## 1. Introduction

Numerous studies of methanol ( $\text{CH}_3\text{OH}$ ) in the fluid state<sup>1</sup> have been carried out because of its role as a solvent, but fewer works have been devoted to studying the solid state. Solid methanol has recently become of interest in astrophysics, as it is one of the most important compounds in interstellar ices.<sup>2</sup> Laboratory studies<sup>2–4</sup> tend to replicate interstellar ice infrared spectra recorded by various satellite missions using mixtures of probable compounds<sup>5</sup> as well as different ultraviolet irradiation exposure times. However, there is still a lack of knowledge about the structural and thermodynamical properties of pure solid methanol at low temperature.

Methanol is also of interest in atmospheric chemistry, at temperatures above 180 K. This molecule belongs to the partially oxidized volatile organic compounds (POVOC's), which are involved in oxidizing chemical reactions in the gas-phase and heterogeneous reactions upon ice particles and aerosols.<sup>6</sup> Until recently, both the chemical species concentrations in the atmosphere and their evolution with time were studied through gaseous-phase models and laboratory experiments. However, discrepancies with field measurements lead to considering possible heterogeneous reactions.<sup>7</sup> Because any gaseous model cannot explain the formaldehyde excess measured in the Arctic surface air, heterogeneous chemistry upon ice particles has to be considered.<sup>8,9</sup> Furthermore, a direct correlation between concentrations of methanol and formaldehyde has been evidenced in the upper troposphere,<sup>10</sup> which supports this latter assumption.

Two stable crystalline phases of solid methanol have clearly been evidenced by Parks:<sup>11</sup> the  $\alpha$ -phase that is stable below  $T \approx 155$  K, and the  $\beta$ -phase that is stable between  $T \approx 165$  K and the triple point at  $T_t = 175.61$  K, accurately determined by Carlson and Westrum.<sup>12</sup> Dempster and Zerbi<sup>13</sup> have also shown the existence of an amorphous metastable phase below  $T = 128$  K that transforms itself to the  $\alpha$ -phase upon heating. Structures

of the crystalline methanol phases have been investigated with X-ray and neutron diffraction,<sup>14–16</sup> and both crystals have the orthorhombic symmetry with four molecules per unit cell. The  $\alpha$ -phase belongs to the  $D_4^2\text{-}P2_12_12_1$  space group, and the  $\beta$ -phase to the  $D_{2h}^{17}\text{-}Cmcn$  one. They are made of zigzag chains of hydrogen bonds, the main difference between these phases consists of a reorientation of these chains.

The phase transition between 155 and 165 K is still under discussion since a recent study evidenced a metastable phase in the  $\alpha$ – $\beta$  phase transition's temperature domain.<sup>16</sup> This metastable phase may exist from 155 to 165 K upon heating and from 135 to 125 K upon cooling, but crystallization kinetic effects seem to play an important role when cooling the crystal as the  $\alpha$ -phase is mixed with the  $\beta$ -phase if the cooling rate through the transformation is too fast. However, older works of Carlson and Westrum<sup>12</sup> show a first-order phase transition at  $T_{\alpha\text{-}\beta} = 157.36$  K, and very careful attention had been paid to avoid kinetic effects. It should be mentioned that water-free methanol is very difficult to obtain and the existence of a transition at  $T = 155.7$  K corresponding to the water–methanol eutectic has been shown by Vuillard and Sanchez.<sup>17</sup> This latter transition has never been observed when very pure methanol (mol % water < 0.04) was studied.<sup>12,18,19</sup>

To date, no vapor pressure data are available in the literature and only a few studies have been undertaken either to determine the enthalpies of transition between the  $\alpha$ ,  $\beta$ , and liquid methanol phases<sup>12</sup> or to calculate the bulk cohesion energy of these solid phases.<sup>20,21</sup> We present in this paper experimental vapor pressure measurements of several methanol solid phases by combining mass spectrometry (MS) and Fourier transform infrared spectroscopy (FTIR) in the 130–175.63 K temperature range. This preliminary work is needed to undertake an experimental study of the heterogeneous oxidation reaction of methanol upon ice particles.

## 2. Experimental Setup

Experiments are performed in a stainless steel ultrahigh vacuum (UHV) chamber where a residual pressure of about  $10^{-9}$

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mbar is reached by using a turbomolecular pump (Pfeiffer Vacuum, model TPU-240). A helium closed-cycle cryocooler (APD Cryogenics, model DE-202) enables cooling of a silicon window where the methanol condenses. A laboratory-made system controls the sample holder temperature with a stability of  $\Delta T = 10^{-2}$  K between 15 and 325 K. Several class A platinum resistors ( $R = 100 \Omega$  at 273.15 K), located along the cryocooler's coldfinger, and the sample holder allow accurate temperature measurements. Pure gases are introduced in the UHV chamber through manual leak valves (Pfeiffer Vacuum, model UDV 136), and the pressure is measured either by an absolute pressure transducer (MKS Baratron, model 672B) in the  $10^{-3}$ – $10$  mbar range or a standard Bayard–Alpert type ionization gauge (Varian, model UHV-24) in the  $10^{-9}$ – $10^{-3}$  mbar range. Mass spectra in the 0–200 atomic mass unit (amu) range are recorded by a quadrupole mass spectrometer (Pfeiffer Vacuum, model Prisma QMS 200M) that enables partial or total pressure measurements in the  $2 \times 10^{-14}$ – $10^{-4}$  mbar pressure range. A FTIR spectrometer (Bruker, model Equinox 55) is used to record infrared (IR) spectra in the transmission mode. We use a spectral resolution of  $4 \text{ cm}^{-1}$  and a HgCdTe (MCT) light detector in the range  $672$ – $7500 \text{ cm}^{-1}$ . Infrared windows of the UHV chamber are made out of ZnSe.

### 3. Sample Preparation

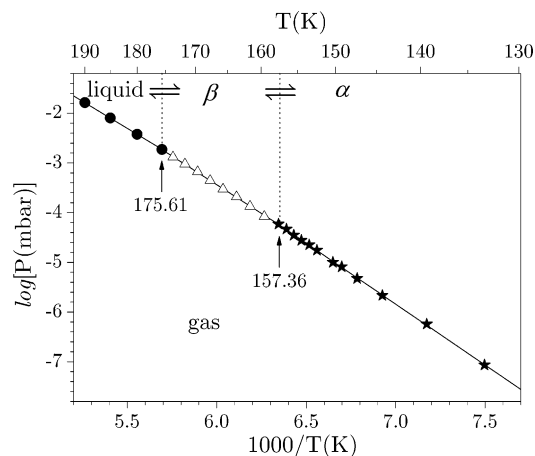
We use spectroscopy grade methanol (SDS, 99.8% purity) that contains 0.05% of water, 0.02% of ethanol, and less than 0.005% of other impurities. Liquid methanol is exposed to air for a short time when we fill the tank connected to the UHV chamber. Consequently, we apply a purification procedure consisting of a dozen freeze–pump–thaw cycles between 150 K and the ambient temperature. Note that this procedure may not lead to a complete removal of dissolved water, as methanol is more volatile than water. However, our results indicate that less than 0.04 mol % of water is present after purification (see section 5).

Methanol vapor is introduced in the UHV chamber through a leak valve, and a thick film is condensed onto the sample holder that is maintained at a constant temperature. We then adjust the methanol vapor introduction step by step until we reach equilibrium conditions between the condensed film and its vapor phase. Infrared spectra are recorded during the whole condensation process, and we evaluate the integrated area of the first overtone of the C–O methanol stretching mode at  $\approx 2040 \text{ cm}^{-1}$  because it is well-defined and isolated (see Figure 3). This integrated area does not evolve with time when the adsorption and desorption rates are equal, and a MS measurement gives us the mass 31 ionic current ( $I_{31}$ ).

### 4. Pressure and Temperature Calibration

We measure the temperature of the methanol solid film with a pair of platinum resistance thermometers that are calibrated by using the pure liquid nitrogen boiling point ( $T = 77.35 \text{ K}$ ) as a reference. Thermometer accuracy is estimated to be  $\pm 0.01 \text{ K}$ . We also check the methanol triple point temperature<sup>1</sup> at  $T_t = 175.61 \text{ K}$  as follows: we first condense a solid methanol thick film at about 10 K below  $T_t$  and check its FTIR spectrum to make sure that only the solid  $\beta$ -phase is present. We then slowly increase the temperature until FTIR spectra indicate the coexistence of the liquid and the  $\beta$ -phases. At this stage, our temperature measurements indicate a value of  $T = 175.57 \text{ K}$ , in very good agreement with the literature.<sup>1</sup>

Before performing methanol vapor pressure measurements, we calibrate the cathode potential of the QMS by using argon



**Figure 1.** Experimental data relative to the: (●) liquid phase from ref 1, (Δ)  $\beta$ -phase, and (★)  $\alpha$ -phase. Arrows indicate the observed phase transitions and full lines correspond to the least-squares fits giving the Clausius–Clapeyron equations (see text).

gas (Linde, purity 99.999%). We adjust the cathode potential to a value of 40 eV so that we cannot observe the second ionization of argon. The emission current value is kept constant and equal to 0.6 mA. We determine the cracking pattern of methanol with these QMS parameters. During our experiments, we follow only the main mass component of methanol at 31 amu. We check numerous times both the repeatability and the linearity of  $I_{31}$  with pressure at constant temperature.

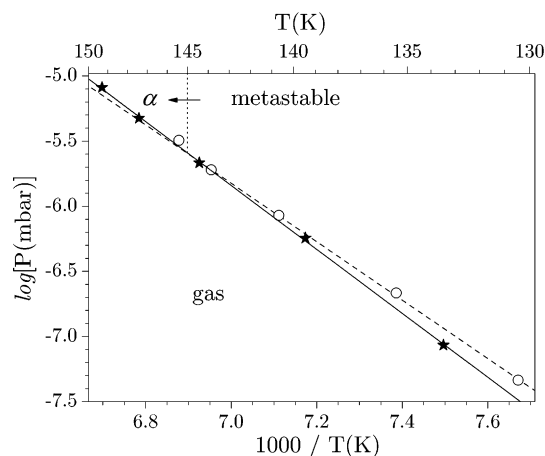
The absolute pressure determination is a challenging task, and we use the  $\text{CH}_3\text{OH}$  triple point as a reference. We condense methanol films in the  $\beta$ -phase at different temperatures below  $T_t$  and measure  $I_{31}$  at each temperature when the adsorption and desorption rates are equal (following the procedure described in the previous section). We also check that the  $I_{31}$  value remains constant for various film thicknesses to make sure that we measure the bulk vapor pressure. Because the walls of the UHV chamber are at room temperature ( $T_{\text{wall}}$ ) and the  $\text{CH}_3\text{OH}$  film at a lower temperature ( $T_{\text{sample}}$ ), and because of molecular conditions, a thermomolecular correction has to be taken into account in our pressure measurements. Thus, the relationship between the absolute pressure  $P$  and the ionic current  $I_{31}$  measured by the mass spectrometer is given by:

$$P = \left( \frac{T_{\text{sample}}}{T_{\text{wall}}} \right)^{1/2} \times S_{31} \times I_{31} \quad (1)$$

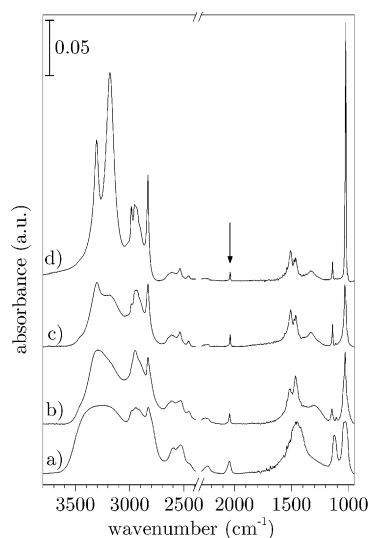
with  $P$  in mbar,  $T_{\text{wall}} = 295 \text{ K}$ ,  $T_{\text{sample}}$  in K,  $I_{31}$  in A, and where  $S_{31}$  is the methanol sensitivity factor in  $\text{mbar} \cdot \text{A}^{-1}$ .<sup>22</sup> Because the  $\text{CH}_3\text{OH}$  absolute pressure is known at  $T_t$ , a fit of our experimental data leads to a value of  $S_{31} = 1588 \pm 1 \text{ mbar} \cdot \text{A}^{-1}$  with our QMS parameters.

### 5. Results

Figures 1 and 2 represent vapor pressure measurements versus inverse temperature. When methanol films are condensed at  $T = 130 \text{ K}$  and heated, we observe a solid phase that is stable until  $T \approx 145 \text{ K}$ , where it transforms itself to the known  $\alpha$ -phase (Figure 2). A further heating leads to the occurrence of the  $\beta$ -phase at  $T \approx 158 \text{ K}$ , this latter being stable until  $T_t$ , in agreement with the literature.<sup>1</sup> We have to point out that the solid phase observed between  $T = 130 \text{ K}$  and  $T \approx 145 \text{ K}$  is metastable, as we cannot observe it again by lowering the temperature from the  $\alpha$ -phase (Figure 1). Infrared spectra of



**Figure 2.** Experimental data relative to the: (★)  $\alpha$ -phase and (○) metastable phase. The full and dashed lines correspond respectively to the  $\alpha$  and metastable Clausius–Clapeyron lines (see text for equations). The arrow indicates the observed phase transition at  $T \approx 145$  K.



**Figure 3.** Infrared spectra of the (a) liquid phase at  $T = 176$  K, (b)  $\beta$ -phase at  $T = 169$  K, (c)  $\alpha$ -phase at  $T = 139$  K, and (d) metastable phase at  $T = 140$  K. The arrow indicates the first overtone of the C–O stretching mode. The 2290–2390  $\text{cm}^{-1}$  range where  $\text{CO}_2$  vapor bands appear has been removed from spectra.

this metastable phase are similar to those of the  $\alpha$ -phase (Figure 3). A detailed analysis of each solid-phase vibrational spectra will be presented in a forthcoming paper. We have to mention that even if we cannot rule out kinetic effects, we tried to take them into account during our experiments by waiting up to 2 h for some measurements. We also do not observe the water–methanol eutectic at  $T = 155.7$  K<sup>17</sup> because we do not observe the liquid water bending mode that should occur at  $\approx 1645$   $\text{cm}^{-1}$  in the infrared spectra when  $T \geq 155.7$  K. It indicates that our methanol is very pure (mol % water < 0.04) according to previous works.<sup>12,18,19</sup>

Least-squares fits are performed on the data presented in Figures 1 and 2 to yield the Clausius–Clapeyron equation of each solid phase:

$$\log P = -\frac{A}{T} + B \quad (2)$$

with  $P$  in mbar and  $T$  in K. The Clausius–Clapeyron equation of the  $\beta$ -phase, thermodynamically stable in the 157.36–175.61

K temperature range, is:

$$\log P = -\frac{2308}{T} + 10.41 \quad (3)$$

with statistical errors of  $\sigma_A = 26$  and  $\sigma_B = 0.16$ . The enthalpy of sublimation of the  $\beta$ -phase is then determined to be  $\Delta H_{\beta\text{-vapor}} = 44.2 \pm 0.5$   $\text{kJ}\cdot\text{mol}^{-1}$ . We determine the Clausius–Clapeyron equation of the liquid phase between  $T_l = 175.61$  K and  $T = 210$  K from the literature:<sup>1</sup>

$$\log P = -\frac{2174}{T} + 9.65 \quad (4)$$

with statistical errors of  $\sigma_A = 3$  and  $\sigma_B = 0.02$ . It corresponds to an enthalpy of vaporization  $\Delta H_{\text{liquid-vapor}} = 41.62 \pm 0.06$   $\text{kJ}\cdot\text{mol}^{-1}$ . By taking into account this latter value, the variation of enthalpy between the  $\beta$  and the liquid phases is then  $\Delta H_{\beta\text{-liquid}} = 2.58 \pm 0.56$   $\text{kJ}\cdot\text{mol}^{-1}$ , in quite good agreement with the value of  $\Delta H_{\beta\text{-liquid}} = 3.215 \pm 0.004$   $\text{kJ}\cdot\text{mol}^{-1}$  given by Carlson and Westrum.<sup>12</sup> In the 145–157.36 K temperature range, the  $\alpha$ -phase is stable and its Clausius–Clapeyron equation is:

$$\log P = -\frac{2453}{T} + 11.33 \quad (5)$$

with statistical errors of  $\sigma_A = 11$  and  $\sigma_B = 0.07$ . The corresponding enthalpy of sublimation is  $\Delta H_{\alpha\text{-vapor}} = 46.9 \pm 0.2$   $\text{kJ}\cdot\text{mol}^{-1}$ , and the variation of enthalpy between the  $\alpha$ - and the  $\beta$ -phases is then  $\Delta H_{\alpha\text{-}\beta} = 2.7 \pm 0.7$   $\text{kJ}\cdot\text{mol}^{-1}$ . This value is larger than the value of  $\Delta H_{\alpha\text{-}\beta} = 0.636 \pm 0.002$   $\text{kJ}\cdot\text{mol}^{-1}$  given by Carlson and Westrum<sup>12</sup> and less accurate because of the indirect measurement method that we use compared to the direct adiabatic calorimetry measurements of these authors. Concerning the metastable phase evidenced during our experiments, we did not fully investigate its existence domain, and we give hereafter a Clausius–Clapeyron equation that is only valid between  $T = 130$  K and  $T \approx 145$  K:

$$\log P = -\frac{2242}{T} + 9.87 \quad (6)$$

with statistical errors of  $\sigma_A = 29$  and  $\sigma_B = 0.21$ . The enthalpy of sublimation of this metastable phase is  $\Delta H_{\text{metastable-vapor}} = 42.9 \pm 0.5$   $\text{kJ}\cdot\text{mol}^{-1}$ , which is less than  $\Delta H_{\alpha\text{-vapor}}$ . The variation of enthalpy between the metastable and the  $\alpha$ -phase is then  $\Delta H_{\text{metastable-}\alpha} = -4.0 \pm 0.7$   $\text{kJ}\cdot\text{mol}^{-1}$ . Its negative value confirms the metastable behavior of this low-temperature phase. Note that, among the previous works, an amorphous phase has been evidenced when methanol vapor was condensed at temperatures below  $T = 128$  K,<sup>13</sup> whereas all other studies conducted by freezing liquid methanol never did observe any amorphous or metastable solid phase. Even if we cannot rule out kinetic effects during the growth and crystallization of the methanol film, our observations agree with the experimental work of Dempster and Zerbi.<sup>13</sup> A determination of the metastable  $\alpha$ -phase transition's temperature from the Clausius–Clapeyron equations leads to a value of  $T = 145 \pm 55$  K, where the statistical error is huge because of the close values of the slopes of the Clausius–Clapeyron lines. As already mentioned, a more detailed analysis of the phase transitions, the thermodynamics, and the infrared spectra behavior of each solid phase will be presented in a forthcoming paper.

## 6. Conclusion

The combination of MS and FTIR has been used to investigate thermodynamical properties of solid bulk methanol

below its triple point temperature. Vapor pressures of three different solid phases have been measured for the first time, and the enthalpy of sublimation of each phase was determined. This work is in agreement with the literature regarding the existence of both the crystalline  $\alpha$  and  $\beta$  solid phases, the temperature of the  $\alpha$ - $\beta$  phase transition, and the variation of enthalpy between these phases. We have also evidenced a metastable solid phase that exists between  $T = 130$  K and  $T \approx 145$  K when methanol is condensed at 130 K from its vapor. We have shown that combining FTIR and MS is a way of getting thermodynamical data with a fairly good accuracy if we compare them with adiabatic calorimetry measurements. These experimental techniques also represent an interesting alternative when direct calorimetric measurements are not possible, as they can be used at any temperature and in a wide pressure range.

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