

# Recommended vapor pressures for thiophene, sulfolane, and dimethyl sulfoxide

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## ABSTRACT

Recommended vapor pressure data for important industrial solvents, thiophene (CAS RN: 110-02-1), sulfolane (CAS RN: 126-33-0), and dimethyl sulfoxide (CAS RN: 67-68-5), were developed by the simultaneous correlation of vapor pressure and related thermal data (heat capacities of condensed phases, ideal gas heat capacities and calorimetrically determined enthalpies of vaporization). For sulfolane and dimethyl sulfoxide, new vapor pressure data were obtained using the static method in the temperature interval from 273 to 308 K. Liquid heat capacities and calorimetric enthalpies of vaporization were taken from the literature and/or determined by Calvet calorimetry. The thermodynamic properties in the ideal gaseous state were calculated using the methods of statistical thermodynamics based on experimental as well as calculated fundamental vibrational frequencies and molecular structure data. Comparisons with literature values are shown for all measured and derived properties.

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## 1. Introduction

Thiophene, sulfolane, and dimethyl sulfoxide are important industrial solvents produced on a large scale. Despite of this fact, their vapor pressures at ambient temperatures are not known with sufficient accuracy. Reliable vapor pressure data are indispensable for processes involving phase equilibria and for phase equilibrium studies on systems containing these compounds.

In this work, we first assessed all available literature vapor pressure data and examined their consistency with calorimetrically determined vaporization enthalpies and heat capacities of condensed phases and ideal gas. Literature review and consistency tests revealed that new vapor pressure data in the low pressure region for sulfolane and dimethyl sulfoxide and new liquid heat capacities for sulfolane were needed. These data were experimentally determined in this work. Also, heat capacities of ideal gas and thermodynamic properties in the ideal gaseous state for all the studied compounds were calculated using the methods of statistical thermodynamics. We employed both the experimental and calculated fundamental vibrational frequencies and compared the obtained results as part of our effort to assess the reliability of the calculations based purely on *ab initio* data. Consequently, recommended vapor pressure data for thiophene,

sulfolane, and dimethyl sulfoxide were developed by the simultaneous correlation of selected vapor pressure and related thermal data [1].

## 2. Simultaneous treatment of vapor pressures and related thermal data (SimCor method)

Vapor pressure  $p$ , enthalpy of vaporization  $\Delta_{\ell}^g H_m$  and the difference between ideal gas heat capacity and heat capacity of liquid  $\Delta_{\ell}^g C_{p,m}^0 = C_{p,m}^{g0} - C_{p,m}^{\ell}$  are linked by exact thermodynamic relationships

$$RT^2 \left( \frac{d \ln p}{dT} \right)_{sat} = \frac{\Delta_{\ell}^g H_m}{\Delta_{\ell}^g z} = \Delta H' \quad (1)$$

$$\left( \frac{d \Delta H'}{dT} \right)_{sat} = R \left\{ \frac{d[T^2(d \ln p/dT)]}{dT} \right\}_{sat} = \Delta C' \\ = \Delta_{\ell}^g C_{p,m}^0 + pVT \text{ correction} \quad (2)$$

where subscript 'sat' denotes a derivative along the saturation line,  $R$  is the molar gas constant ( $R = 8.314472 \text{ J K}^{-1} \text{ mol}^{-1}$  [2,3]),  $\Delta_{\ell}^g z$  stands for the difference between the compressibility factors of the coexisting phases.  $\Delta H'$  and  $\Delta C'$  are auxiliary quantities which can be calculated using Eqs. (1) and (2) either from the vapor pressure correlating equation (by substituting the derivative  $d \ln p/dT$  into Eqs. (1) and (2)) or from experimental values of enthalpy of vaporization  $\Delta_{\ell}^g H_m$  and  $\Delta_{\ell}^g C_{p,m}^0$  calculated from experimental data

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by combining heat capacity of ideal gas  $C_{p,m}^{g0}$  and calorimetric values of heat capacity of liquid  $C_{p,m}^l$ . The possibility to calculate  $\Delta H'$  and  $\Delta C'$  both from the experimental thermal data and vapor pressure data and from a vapor pressure correlating equation means that after selecting a suitable relationship describing  $p$  vs.  $T$  it is possible to correlate simultaneously experimental vapor pressures  $p$ , enthalpies of vaporization  $\Delta_\ell^g H_m$  and heat capacity difference  $\Delta_\ell^g C_{p,m}^0$  as a function of temperature.

The Cox equation was found to be the most adequate for describing simultaneously vapor pressure and related thermal data as a function of temperature down to the triple point [1]. The Cox equation has the form [4]

$$\ln \frac{p}{p^0} = \left(1 - \frac{T^0/K}{T/K}\right) \exp \left( \sum_{i=0}^n A_i (T/K)^i \right), \quad (3)$$

where  $p$  is the vapor pressure,  $T$  is the temperature,  $T^0$  and  $p^0$  is the temperature and pressure of an arbitrarily chosen reference point and  $A_i$  are correlation parameters.  $n=2$  is usually adequate; less or more parameters can be used when temperature range is too narrow or too wide or when temperature dependence of  $\Delta_\ell^g C_{p,m}^0$  is complex.

Equations analogous to those for the equilibrium between the liquid and vapor phases can be derived for the equilibrium between the solid and vapor phases. The SimCor method was thoroughly tested in our laboratory [1] and used to obtain recommended vapor pressure for several crystalline and liquid compounds [5–12].

### 3. Experimental

#### 3.1. Materials

Sulfolane was obtained from Novasol Belgium. The mass fraction purity (determined by gas chromatography (GC)) and mass fraction of water (determined by Coulometric titration, UOP 481) were  $w=0.9985$  and  $w(\text{H}_2\text{O})=3 \times 10^{-4}$ , respectively, as stated in the certificates of analysis provided by the supplier. The sample was stored over 4 Å molecular sieves for approximately 2 weeks. The mass fraction of water determined prior to taking vapor pressure and heat capacity measurements was  $w(\text{H}_2\text{O})=6.5 \times 10^{-5}$  (determined by Coulometric titration with Metrohm 831). Dimethyl sulfoxide was purchased from Aldrich. The mole fraction purity (determined by GC) and mass fraction of water (determined by Coulometric titration) were  $x=0.9999$  and  $w(\text{H}_2\text{O})=2.7 \times 10^{-5}$ , respectively, as stated in the certificates of analysis provided by the supplier. Considering the assessed purities, the compounds were studied without further purification.

#### 3.2. Vapor pressure measurements

Prior to vapor pressure measurements, the samples were thoroughly degassed using an apparatus shown in Fig. 1. The samples were directly pumped with a turbomolecular vacuum pump for 2 weeks at approximately 298 K. The sample loss was prevented by cooling the upper part of the measuring cell with Peltier thermoelectric modules.

Vapor pressure measurements were performed using the static method with an apparatus internally denoted as STAT6, which was previously described in detail [13]. Therefore, only a short description is presented here. The apparatus is constructed of stainless steel internally electrochemically polished tubing with ConFlat DN 16 CF and VCR connections and all-metal, pneumatically operated, angle valves VAT series 57 (VAT Vacuumvalves AG, Switzerland) for UHV. The pressure is measured simultaneously by two capacitance diaphragm absolute gauges MKS Baratron 690A01TRA and MKS

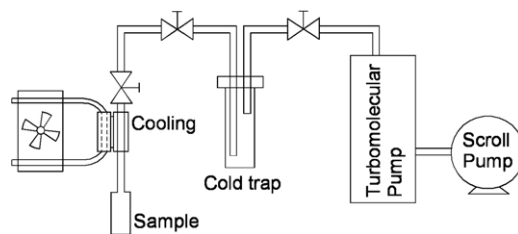


Fig. 1. An apparatus for sample degassing.

Baratron 690A11TRA (MKS Instruments Inc., USA). Their measuring upper limits are 133 and 1333 Pa, respectively. The temperature of the pressure sensors is kept at  $T=318$  K by an internal temperature controller which constrains the upper temperature limit of vapor pressure measurements to about 310 K. Calibrations of the pressure gauges at 318 K performed by the manufacturer at 11 equally spaced pressures from 0 to 130 Pa and from 0 to 1300 Pa, respectively, with a maximum relative deviation of 0.03%, are traceable to the National Institute of Standards and Technology (NIST). Additional calibrations focusing on the beginning of a pressure span ( $p < 10$  Pa) were performed by the Czech Metrology Institute. The resulting relative uncertainty of the pressure reading is less than 0.05% which is in accordance with the uncertainty stated by the manufacturer. The sample temperature is measured by a platinum resistance thermometer Burns Engineering 12001-A-12-6-2-A in a four-wire connection calibrated by the manufacturer at the ice point and/or by comparison to standard platinum resistance thermometer (SPRT). This SPRT was calibrated to the ITS-90, and its calibration was traceable to NIST. The uncertainty of the measurement of sample temperature is 0.02 K, which is insignificant in the pressure range investigated in this work. All temperatures reported here are based on the international temperature scale ITS-90. The performance of the STAT6 apparatus was checked by the measurement with naphthalene, which is recommended for calibrating vapor pressure apparatuses [11]. The agreement with the recommended data [11] was within the uncertainty of vapor pressure measurement with the STAT6 apparatus, which is adequately described by the expression  $\sigma(p/\text{Pa})=0.005(p/\text{Pa})+0.05$ .

#### 3.3. Heat capacity measurements

The  $\mu$ DSC IIIa calorimeter (Setaram, France) was used for the heat capacity determination of sulfolane in the temperature range from 304 to 355 K. The measurements were carried out in the incremental temperature scanning mode (step method) [14] with a number of 5 K steps and a heating rate of 0.5 K  $\text{min}^{-1}$  followed by isothermal delays of 3600 s. The mass of the sample was approximately 1 g. The relative uncertainty of heat capacity measurements performed using the step method is estimated to be less than 1%. A detailed description of the calorimeter and calibration can be found in a recent paper by Straka et al. [15].

Three successive runs were performed in order to obtain heat capacity of sulfolane. The measuring cell was empty in the first run and filled with the reference material and the measured sample in the second and third runs, respectively. Synthetic sapphire, NIST SRM 720, was used as the reference material. The reference cell was empty during all runs. Heat capacity was calculated from the equation

$$c_{\text{sat},s} = \frac{m_{\text{sapp}} c_{p,\text{sapp}} (A_s - A_E)}{m_s (A_{\text{sapp}} - A_E)} \quad (4)$$

where  $c_{\text{sat},s}$  is the saturation specific heat capacity of the measured sample;  $c_{p,\text{sapp}}$  is the specific heat capacity of the reference substance (synthetic sapphire);  $m_s$  is the mass of the sample;  $m_{\text{sapp}}$  is

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