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Tetraethoxysilane, $Si(OC_2H_5)_4$: vapour pressure measurements at temperatures from 323 to 442 K by means of a Bourdon spoon gauge

M.G.M. van der Vis*, E.H.P. Cordfunke

Netherlands Energy Research Foundation ECN, P.O. Box 1, 1755 ZG Petten, The Netherlands

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Abstract

The vapour pressure of tetraethoxysilane, $Si(OC_2H_5)_4(s,l)$, has been measured from 323 to 442 K and can be presented by the equation $\log(p/\mathrm{Pa}) = 37.5498 - 3940.10/(T/\mathrm{K}) - 8.92951 \cdot \log(T/\mathrm{K})$. The boiling point derived from this equation is 441.3 K. The enthalpy of vaporization, $\Delta_{\mathrm{vap}} H_{\mathrm{m}}^{\circ}(298.15\,\mathrm{K})$, obtained by second- and third-law evaluation is $-53.93\,\mathrm{kJ \cdot mol^{-1}}$ and $-52.33\,\mathrm{kJ \cdot mol^{-1}}$, respectively. The result has been compared with literature data and the value, $\Delta_{\mathrm{vap}} H_{\mathrm{m}}^{\circ}(298.15\,\mathrm{K}) = (52.0 \pm 2.0)\,\mathrm{kJ \cdot mol^{-1}}$, is recommended for the enthalpy of vaporization of tetraethoxysilane. Combining this value with the enthalpy of formation of liquid tetrathoxysilane results in $\Delta_{\mathrm{f}} H_{\mathrm{m}}^{\circ}(Si(OC_2H_5)_4, \mathrm{g}, 298.15\,\mathrm{K}) = -(1356.0 \pm 6.0)\,\mathrm{kJ \cdot mol^{-1}}$.

Keywords: Tetraoxysilane; Vapour pressure; Enthalpy of vaporization; Enthalpy of formation; Thermodynamics

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1. Introduction

During our investigation of the thermodynamic properties of organometallic compounds such as tetraethoxysilane (TEOS) [1–3] a vapour pressure equipment was constructed for the pressure range 500 to 10^5 Pa. Although several vapour pressure measurements of TEOS are known in the literature [4–9], it was used as a testing material for our newly built equipment. Preliminary results of the vapour pressure measurements of TEOS have already been published in a paper describing its decomposition behaviour [10].

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* Corresponding author.

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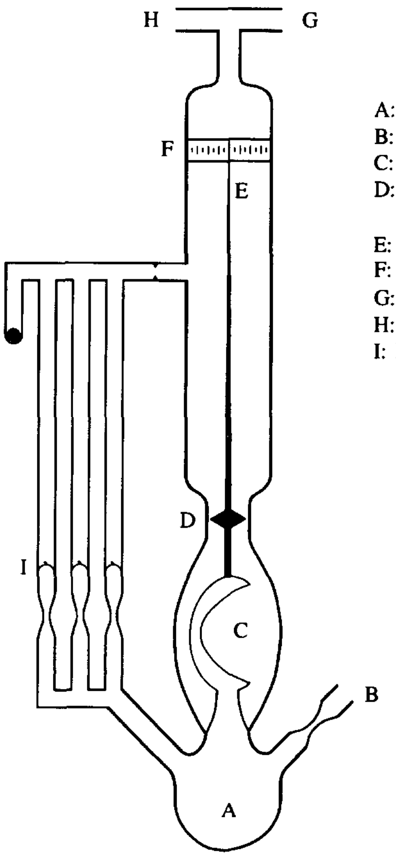
2. Experimental

Tetraethoxysilane (TEOS), purchased from Merck, was distilled twice before use. The fraction boiling at (440.0 ± 0.5) K was collected. The purity of the sample was checked with n.m.r. The ^{1}H-n.m.r. showed two peaks at $1.11 \cdot 10^{-6}$ (3 H's, triplet) and $3.75 \cdot 10^{-6}$ (2 H's, quartet). No additional lines of organic impurities were found.

Vapour pressure measurements were performed using a Bourdon spoon gauge. A detailed picture of the gauge is given in Fig. 1. The pointer of the spoon was split into two parts in such a way that one of the pointers was in front of the scale and the other one was behind the scale. By aligning the two pointers parallax-free reading was ensured. A magnifying-glass (10 ×) was used for readings of the zero point of the pointer, as well as the height of the mercury column, which was used for measuring the compensating pressure. The sensitivity of the spoon was determined to be 30 Pa per scale division resulting in an accuracy of reading the zero point of about 10 Pa. Filling



A: Sample chamber
B: Filling tube
C: Spoon
D: Construction to prevent breaking of the spoon
E: Pointer
F: Scale (0.2 mm division)
G: Connection to vacuum line
H: Connection to manometer
I: Break-seal

Fig. 1. The Bourdon spoon gauge.

of the apparatus was done in an argon-filled glove box. After filling, the sample chamber was connected to the vacuum line (G) with a glass tube, and the sample was degassed by freezing several times in liquid nitrogen. Finally the sample chamber was sealed off in vacuo. After determination of the zero point of the pointer, the gauge was placed in a thermostatted bath consisting of a Dewar vessel containing silicon oil. The temperature of the vessel was controlled to within 0.05 K. Calibrated thermometers, with uncertainties ranging from 0.02 K at 323 K to 0.08 K at 450 K, were used for temperature readings. The thermometer was completely immersed in the bath. The height of the mercury column was measured with a calibrated electronic ruler, having an uncertainty of less than 0.05 mm. Errors in reading the height of the mercury column did not exceed 0.1 mm. The following procedure was used for the vapour pressure measurements: During heating or cooling of the bath the compensating pressure was adjusted in such a way that the pointer maintained about its zero position. After reaching the desired temperature the bath was stabilized for at least three hours. The compensating pressure was slowly reduced or increased at a rate of about 60 Pa per minute until the pointer had returned to its zero position. This procedure of pressure compensation was performed in triplicate at the desired temperatures. The zero point of the gauge was checked regularly, but no indication was found for any declination of the zero point.

The pressure in millimeter mercury was transformed to Pascal using the equation:

$$p(\mathrm{Pa}) = \frac{\rho_{T_{\mathrm{lab}}}}{\rho_{273.15\,\mathrm{K}}} \times 133.322 \times p(\mathrm{mmHg})$$

Mercury densities were taken from the work of Ambrose [11].

3. Results

A graphical representation of the results is given in Fig. 2. The experimental points were fitted, resulting in:

$$\log(p/\mathrm{Pa}) = 37.5498 - 3940.10(T/\mathrm{K}) - 8.92951 \cdot \log(T/\mathrm{K}).$$

From this equation the boiling point (at $p^\circ = 101325$ Pa) was calculated as 441.3 K.

For a calculation of the enthalpy of vaporization a second- and third-law evaluation of the vapour pressure measurements was performed using the thermodynamic functions of TEOS(l) [1] and TEOS(g) [2] (Table 1). The resulting second-law value, 53.95 $\mathrm{kJ \cdot mol^{-1}}$, agrees reasonably well with the third-law value, 52.33 $\mathrm{kJ \cdot mol^{-1}}$. As can be seen in Table 1 almost no temperature dependency is observed in the third-law treatment.

The second- and third-law evaluation was also performed for other vapour pressure measurements known in the literature [4–9]. The results are presented in Table 2. In general, there is good agreement with other measurements, except with those of D'yachkova et al. [7]. Since the second- and third-law enthalpies of vaporization derived from the measurements of D'yachkova et al., also show a poor agreement, their results have been disregarded here.

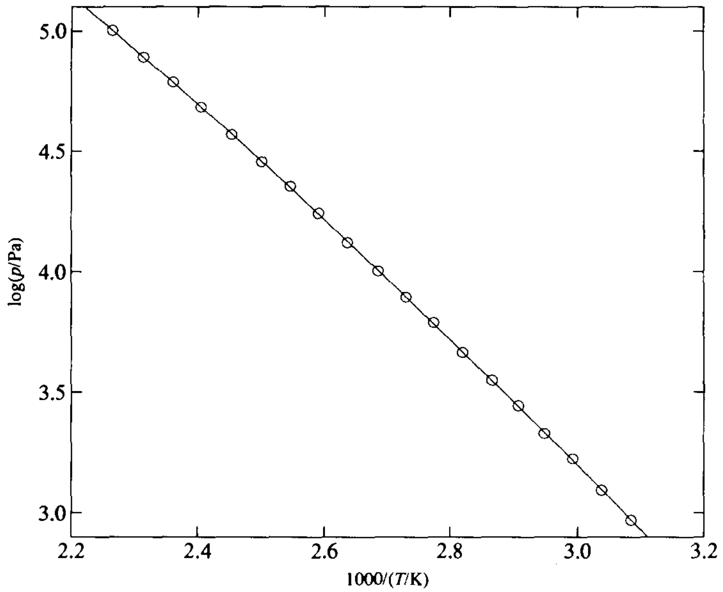


Fig. 2. Vapour pressure of tetraethoxysilane.

Table 1
Experimental points and a third-law evaluation of the vapour pressure of $Si(OC_2H_5)_4$

T/K	p/Pa	$\Delta_{vap}H^\circ_m$(298.15 K)/kJ·mol^{-1}
323.94	928	52.57
328.87	1232	52.55
333.94	1668	52.48
338.94	2127	52.53
343.71	2770	52.46
348.62	3532	52.44
354.45	4626	52.45
360.25	6159	52.37
366.17	7866	52.39
372.16	10100	52.37
379.13	13308	52.36
385.78	17561	52.27
392.63	22718	52.22
399.72	28761	52.24
407.62	37291	52.22
415.62	48525	52.15
424.42	61642	52.21
431.86	78466	52.07
441.43	101632	52.03
		mean: 52.33 ± 0.06

Table 2
Comparison of statistical and second-law entropies for $Si(OC_2H_5)_4(g)$ and comparison of the enthalpies of vaporization by second- and third-law evaluation of vapour pressure measurements

Reference	Method[a]	T_{mean}/K[b]	$S^\circ(T)/J \cdot K^{-1} \cdot mol^{-1}$		$\Delta_{vap}H^\circ_m(298.15\,K)/kJ \cdot mol^{-1}$	
			Exp.	Calc.	2nd law	3rd law
4[c]	S	386.6	733.0	734.8	51.52	52.14
5	S	304.2	662.2	656.7	54.17	51.83
6	S	360.0	711.6	711.8	52.13	51.73
7	M	308.5	622.2	666.1	34.84	48.36
8	E	366.1	719.1	717.1	53.17	52.21
9	E	420.3	761.1	763.5	50.66	51.68
This study	M	373.7	727.6	723.6	53.93	52.33
					selected value: 52.0 ± 2.0	

[a] E = ebulliometry; M = membrane null manometer; S = static.
[b] $T_{mean} = 2/(1/T_{min} + 1/T_{max})$.
[c] Points below 340 K have been rejected because of large scatter.

Ogier [12], and Voronkov et al. [13] determined the enthalpy of vaporization by calorimetry resulting in $\Delta_{vap}H^\circ_m(298.15\,K) = 40.5\ kJ \cdot mol^{-1}$, and $\Delta_{vap}H^\circ_m(298.15\,K) = (48.5 \pm 0.5)\ kJ \cdot mol^{-1}$, respectively. From the vapour pressure and calorimetric measurements we select the value: $\Delta_{vap}H^\circ_m(298.15\,K) = (52.0 \pm 2.0)\ kJ \cdot mol^{-1}$ for the enthalpy of vaporization of TEOS. Combining the selected value for the enthalpy of vaporization with the standard molar enthalpy of formation of liquid TEOS [3, 10], $-(1408.0 \pm 5.0)\ kJ \cdot mol^{-1}$, gives for the enthalpy of formation of gaseous TEOS:

$$\Delta_f H^\circ_m(Si(OC_2H_5)_4, g, 298.15\,K) = -(1356.0 \pm 6.0)\,kJ \cdot mol^{-1}.$$

4. Discussion

As described in our previous paper [2], the thermodynamic functions of gaseous TEOS have been calculated from molecular parameters, using the vapour pressure data for internal consistency. Especially the low lying torsional frequencies have a large influence on the thermodynamic properties. For example: by reducing the two lowest torsional frequencies with 1 cm^{-1} results in an increase of $S^\circ_m(298.15\,K)$ of 3.9 $J \cdot K^{-1} \cdot mol^{-1}$, which in turn results in an increase of the third-law enthalpy of vaporization of 1.5 $kJ \cdot mol^{-1}$.

Although such a treatment brings our second- and third-law values in better agreement, we have to bear in mind that the use of torsional frequencies is one of the possible approximations for the calculation of the thermodynamic properties of gaseous molecules possessing internal rotation. Another approximation is the use of parameters (potential barrier, reduced moment of inertia, symmetry) describing the 'restricted' internal rotation of the methyl, ethyl, and ethoxy groups, using the method described by Pitzer and Gwinn [14]. Problems arising with this approach are: 1) the potential barrier of the ethyl group cannot be described by a simple cosine, which makes it impossible to use the tables of Pitzer and Gwinn [14], and 2) the moment of inertia of the ethoxy group cannot be given by a constant, since it depends strongly on the rotation of the ethyl group.

Calculations, with the methyl torsional frequency replaced with the parameters describing the internal rotation, have shown that mainly the heat capacity is affected by this approach, $C^{\circ}_{p,m}(298.15\,K)$ increases with $6\ J\cdot K^{-1}\cdot mol^{-1}$, resulting in a lowering of the second-law enthalpy of vaporization of about $0.5\ kJ\cdot mol^{-1}$.

From these calculations it can be concluded that the uncertainty in the enthalpy of vaporization amounts $2\ kJ\cdot mol^{-1}$ due to the uncertainty in the thermodynamic functions of the gas phase.

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