

Vapour pressures of solid and liquid NbCl₅ and TaCl₅

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The vapour pressures of solid and liquid NbCl₅ and TaCl₅ have been measured over the temperature range 425 to 525 K by a quartz Bourdon-type spiral pressure gauge. Enthalpies and entropies of sublimation, fusion, and evaporation as well as melting points and boiling points have been calculated. The present results are compared with those reported in the literature.

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A moyen d'une jauge Bourdon à spirale de quartz, on a mesuré les tensions de vapeur du pentachlorure de niobium et de tantale à l'état solide et liquide, à des températures variant entre 425 et 525 K. Les enthalpies et les entropies de sublimation, de fusion et d'évaporation ont été calculées, ainsi que les températures de fusion et d'ébullition. Les résultats obtenus sont comparés avec les données publiées dans la littérature scientifique.

Introduction

The equilibrium vapour pressures of pure solid and liquid NbCl₅ (1-6) and TaCl₅ (1-4, 7-10) have been the subject of many investigations. It is evident in Figs. 3 and 4 that the results of various investigations differ greatly. The uncertainties in values of the derived thermodynamic properties such as the enthalpies and entropies of evaporation and of sublimation are even greater since their calculation depends upon an accurate knowledge of the derivative of the logarithm of pressure with respect to the reciprocal of temperature.

In the present investigation the pressures of NbCl₅ and TaCl₅ vapours, in equilibrium with the pure compounds NbCl₅ and TaCl₅, respectively, have been measured by a direct method over a temperature range extending below and above their melting points.

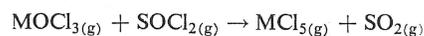
The study is part of a research program concerned with the thermodynamic and electrochemical properties of refractory-metal chlorides (11-13).

Experimental

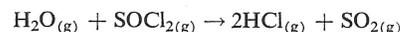
The compounds NbCl₅ and TaCl₅ were obtained commercially¹ and were certified to be of purity 99.99% and 99.9%, respectively. These were further purified by sublimation in a stream of oxygen-free and dehydrated helium gas saturated with thionyl chloride, as described

¹The salts were obtained from Research Organic/Inorganic Chemical Corporation, Belleville, New Jersey, U.S.A.

by Keneshea *et al.* (14). Any oxychloride and water impurities present should react according to



and



where M represents Nb or Ta. The purified compounds were sublimed into glass ampoules which were subsequently sealed under vacuum.

The apparatus for measuring the equilibrium vapour pressures is shown in Fig. 1. It consisted of a Bourdon-type fused quartz spiral.² This was enclosed in a quartz chamber in such a way that the salt vapour from the sample entered only the inside of the spiral while air could be admitted to the chamber surrounding the spiral to equilibrate pressures inside and outside the spiral. The gauge served only as a null point detector while the pressure was read directly on a closed-end mercury manometer. The null point of the quartz signal was determined with the aid of a telescope to the nearest 0.2 mm Hg. Mercury levels in the manometer were measured by a cathetometer.

The quartz spiral-type gauge was found to be superior to both the spoon-type Bourdon gauges (15, 16) and the molten tin isoteniscope (17, 18) used previously in this laboratory because of its ability to sustain large and sudden pressure changes without shattering. This eliminated the need for close supervision of the apparatus since it was no longer necessary to balance the pressures continuously. In addition, because of the compact size of the spiral-type gauge and because it was connected directly to the sample container, the volume of the gas phase was kept to a minimum. Furthermore, the salt sample and its vapour were contained in a closed system. This facilitated conducting experiments over extended time periods with no accompanying material losses.

Heat was supplied by a resistance furnace consisting of

²The Bourdon spiral was manufactured by Worden Quartz Products, Houston, Texas.

Sublimatic
Temperature (°C)
153.8
164.0
175.5
182.0
187.2
190.0
191.2
206.5
163.0
158.7

TO CLOSED-END
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FIG. 1. App pressure.

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TABLE 1. Measured vapour pressure of NbCl₅ and TaCl₅

NbCl ₅				TaCl ₅			
Sublimation		Evaporation		Sublimation		Evaporation	
Temperature (°C)	Pressure (mm Hg)	Temperature (°C)	Pressure (mm Hg)	Temperature (°C)	Pressure (mm Hg)	Temperature (°C)	Pressure (mm Hg)
153.8	17.1	230.2	485.7	169.3	52.4	236.8	807.8
164.0	30.9	230.1	483.9	185.0	106.6	229.5	672.9
175.5	57.0	240.0	623.2	215.6	425.8	229.1	665.1
182.0	77.1	241.0	638.3	208.7	316.9	226.4	621.3
187.2	99.1	213.6	310.5	201.2	228.2	229.4	672.5
190.0	111.4	235.6	561.7	193.1	161.2	226.4	626.3
191.2	116.2	251.2	813.4	183.4	106.1	224.2	592.0
206.5	247.5	213.6	307.2	219.7	492.5	231.9	723.0
163.0	26.5	209.9	276.1	183.9	111.1	227.6	644.8
158.7	22.3					234.7	777.1

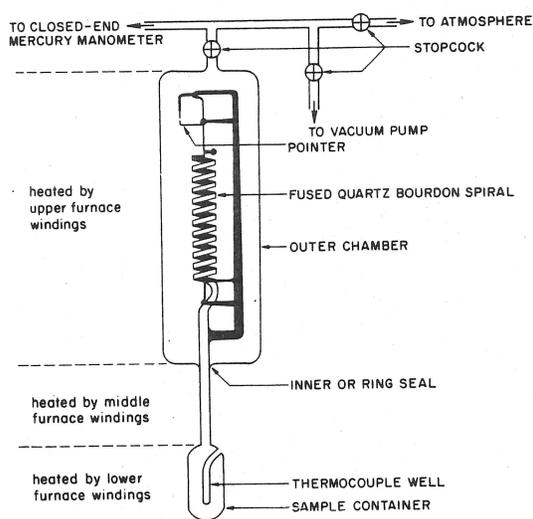


FIG. 1. Apparatus for the measurement of vapour pressure.

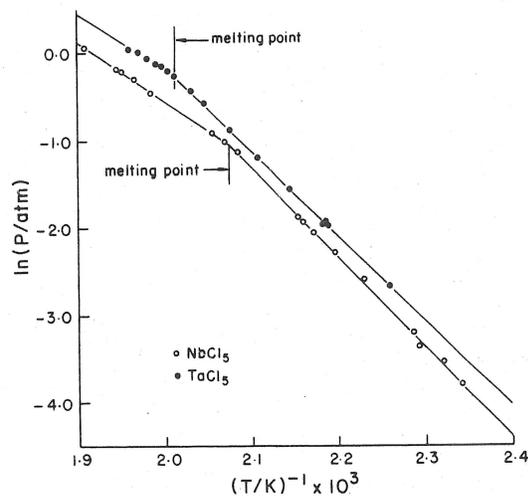
three independently controlled nichrome tape windings. The lowest winding heated the sample, while the upper two windings created a temperature profile in the spiral and the tube connecting it to the sample such that condensation of salt in these regions was prevented. The temperature variation in the zone of the furnace occupied by the sample was ± 0.25 K. Temperature was measured by means of a chromel-alumel thermocouple contained in a glass tube immersed in the salt sample. The thermocouple had been calibrated against a certified platinum-13% rhodium vs. platinum standard. Thermal emf's were measured by a volt potentiometer.

In a typical experiment the salt was distilled into the sample container. The system was then sealed under vacuum. Experiments lasted usually a period of three days. During this time the sample was subjected to repeated heating and cooling cycles over the entire temperature range of interest to demonstrate the absence

of hysteresis in the Bourdon spiral and to establish the reversibility of the measurements. In each case at the end of the experiment the pressure returned to within 2 to 3 mm Hg of zero.

Results and Discussion

The apparatus was capable of measuring the total vapour pressure in the system. Density measurements of NbCl₅ and TaCl₅ vapours from 500 K to the critical temperature by Nisel'son *et al.* (19) and by Johnson and Cubicciotti (20) have shown that in the temperature range of the present work the vapour phase may be considered a monomeric ideal gas. Accordingly, in the following thermodynamic calculations fugacity

FIG. 2. Temperature dependence of vapour pressure of NbCl₅ and TaCl₅: results of the present study.

ties have been replaced by measured vapour pressures.

The pressure measurements are displayed in Table 1. Pressures were measured in mm Hg, and corrections were made for scale expansion, mercury expansion, and gravity (21, 22) to give the corresponding mercury column height under standard conditions, *i.e.* at 273.15 K and an acceleration of free fall of 9.80665 m/s². These corrected values appear in the table. Temperatures reported are based on the IPTS-68 (23). In Fig. 2 these data are plotted.

Since the heat capacities of NbCl₅ are known (14) it was possible to calculate the complete temperature dependence of its vapour pressure by applying the Σ function method (24). Enthalpy contents of solid and liquid NbCl₅ were measured by drop calorimetry by Keneshea *et al.* (14) and the molar heat capacities of solid and liquid NbCl₅ are given as 35.35 cal/K and 57.26 - 22.06 × 10⁻⁶ T² cal/K, respectively.³

Werder, Frey, and Guenthard (26) measured the vibrational spectra of solid NbCl₅ and calculated the molar heat capacity of the gas from theory based on the harmonic-oscillator rigid-rotator approximation. These results have been fitted herein to the equation

$$[1] \quad C_{P,\text{gas}} = 31.73 - 2.678 \times 10^5 T^{-2} \text{ cal/K mol}$$

which is valid in the temperature range 300 to 600 K.

Linear regression of Σ vs. 1/T yields the following equations for NbCl₅:

$$[2] \quad \Delta H_{\text{sublimation}} = 21651 - 3.62T + 2.678 \times 10^5 T^{-1} \pm 450 \text{ cal/mol}$$

$$[3] \quad \ln(P_{(s)}/\text{atm}) = 33.116 - 10896T^{-1} - 1.8217 \ln T - 6.738 \times 10^4 T^{-2} \pm 0.029$$

$$[4] \quad \Delta H_{\text{evaporation}} = 24530 - 25.53T + 2.678 \times 10^5 T^{-1} + 7.340 \times 10^{-6} T^3 \pm 100 \text{ cal/mol}$$

$$[5] \quad \ln(P_{(l)}/\text{atm}) = 103.801 - 12344T^{-1} - 12.8474 \ln T - 6.738 \times 10^4 T^{-2} \\ + 1.8468 \times 10^{-6} T^2 \pm 0.004$$

Figure 3 shows a comparison of various vapour pressure studies of NbCl₅. It may be seen that the results of this investigation are within the range of reported values and agree well with the work performed on this system since 1970 by Johnson *et al.* (5) and Staffansson and Enghag (6).

In the case of TaCl₅, heat capacity data could not be found in the literature. However, Schaefer and Kahlenberg (27) have estimated the following values based on the properties of ZrCl₄ and HfCl₄

$$C_{P,\text{solid}} = 38 - 3 \times 10^5 T^{-2} \text{ cal/K mol}$$

and

$$C_{P,\text{gas}} = 31.6 - 3.7 \times 10^5 T^{-2} \text{ cal/K mol}$$

The Σ function analysis of the sublimation vapour pressures yields the following approximate equations for TaCl₅

$$[6] \quad \Delta H_{\text{sublimation}} = 22100 - 6.4T + 7 \times 10^4 T^{-1} \pm 450 \text{ cal/mol}$$

$$[7] \quad \ln(P_{(s)}/\text{atm}) = 42.180 - 11123T^{-1} - 3.2207 \ln T - 1.761 \times 10^4 T^{-2} \pm 0.024$$

In the absence of any estimate of the heat capacity of molten TaCl₅ least-squares analysis of the evaporation vapour pressures gives the following equations

$$[8] \quad \Delta H_{\text{evaporation}} = 12810 \pm 400 \text{ cal/mol}$$

$$[9] \quad \ln(P_{(l)}/\text{atm}) = 12.710 - 6.4478 \times 10^3 T^{-1} \pm 0.005$$

³The molar heat capacity of NbCl₅ was misprinted in eq. 7 of ref. 14 as 57.36 - 22.02 × 10⁻⁶ T² cal/K along with the statement that its value is 56.8 cal/K at the melting point. The correct value is 57.26 - 22.02 × 10⁻⁶ T² with a value of 52.2 at the melting point quoted in the paper. Both errors also appear in the GMELIN handbook (25). These corrections have been confirmed in a private communication by D. Cubicciotti, Stanford Research Institute, Menlo Park, California.

FIG.

Figure various in results of recent work. Table 2 melting point, enthalpies at melting point, Table 3 calorimetric thermodynamic data of the pres

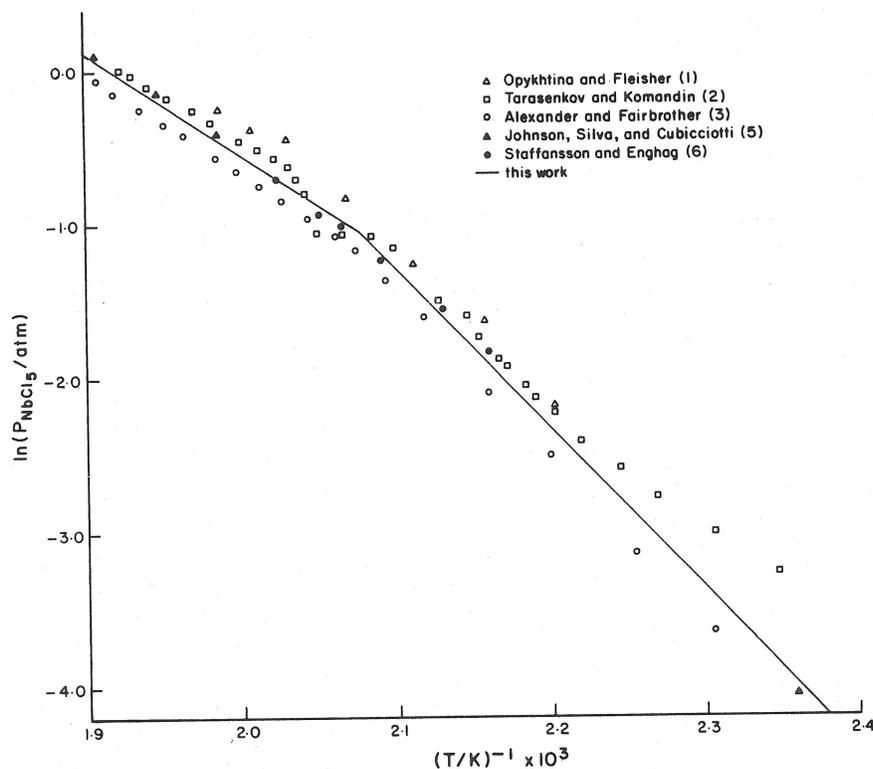


FIG. 3. Temperature dependence of vapour pressure of NbCl_5 : comparison with other investigations.

Figure 4 compares the pressure results of various investigations of the TaCl_5 system. The results of this study agree very well with the recent work by Saeki *et al.* (8).

Table 2 displays calculated values of the boiling point, melting point, and the various enthalpies and entropies of transition of NbCl_5 . Table 3 compares various determinations of the thermodynamic properties of NbCl_5 . The results of the present study lie within the range of values

reported in the literature for any given property. Noteworthy in Table 3 are the values for the molar enthalpy and entropy of sublimation at 298.15 K which compare well with values reported by Schaefer and Poelert (4) who measured vapour pressures of NbCl_5 from 350 to 384 K.

Table 4 shows calculated values of thermodynamic properties of TaCl_5 . The melting point is determined in this work to be 496.9 K, which is about 2 K higher than that quoted elsewhere.

TABLE 2. Thermodynamic properties of NbCl_5 *

Temperature	Phase transition	ΔH_T (kcal/mol)	ΔS_T (cal/K mol)
Boiling point: 521.4 K	Liquid-gas	12.77 ± 0.10	24.5 ± 0.1
Mean temperature: 502.3 K	Liquid-gas	13.17 ± 0.10	25.3 ± 0.1
Melting point: 481.5 K	Liquid-gas	13.61 ± 0.10	26.2 ± 0.1
Melting point: 481.5 K	Solid-liquid	6.85 ± 0.55	14.3 ± 1.2
Melting point: 481.5 K	Solid-gas	20.46 ± 0.45	40.5 ± 1.1
Mean temperature: 449.8 K	Solid-gas	20.62 ± 0.45	40.8 ± 1.1
Standard temperature: 298.15 K	Solid-gas	21.47 ± 0.45	43.1 ± 1.1

* All entries in Table 2 were calculated with the use of only [2] through [5]. The mean temperature is defined as the reciprocal of the mean value of T^{-1} for the reported data points.

TABLE 3. Comparative values of the thermodynamic properties of NbCl₅
(a) Sublimation

ΔH_T^\ddagger (kcal/mol)	ΔS_T^\ddagger (cal/K mol)	ΔH_{298} (kcal/mol)	ΔS_{298} (cal/K mol)	Reference
20.0 ± 0.8*	39.8 ± 1.8*	20.9†	42.4†	1
18.3 ± 0.5*	36.1 ± 1.0*	19.4†	39.1†	2
20.0 ± 0.5*	38.9 ± 1.1*	21.0†	41.7†	3
—	—	22.8	46.2	4
18.5	—	19.6	39.4	6
22.00 ± 0.23	43.8†	23.1†	46.8†	28
20.62 ± 0.45	40.7 ± 1.1	21.47 ± 0.45	43.1 ± 1.1	This work

* Analysis of data performed by Schaefer *et al.* (33).

† Analysis of data performed by Schaefer and Poelert (4).

‡ T is the mean temperature of the measured vapour pressures.

(b) Evaporation

ΔH_T^\ddagger (kcal/mol)	ΔS_T^\ddagger (cal/K mol)	Reference
13.0 ± 1.3*	25.4 ± 2.7*	1
11.2 ± 0.2*	21.6 ± 0.5*	2 (Boiling points)
15.0 ± 1.7*	29.0 ± 3.5*	2 (Static method)
13.2 ± 0.05*	25.1 ± 0.1*	3
12.77 ± 0.42†	24.6 ± 0.8†	5
14.09	27.10	6
12.6 ± 0.1	24.3 ± 0.3	28
13.69 ± 0.18	—	34
13.17 ± 0.10	25.3 ± 0.1	This work

* Analysis performed by Schaefer *et al.* (33).

† These values were calculated herein using only the 3 points of ref. 5 which lie in the temperature range of the present study.

‡ T is the mean temperature of the measured vapour pressures.

(c) Fusion

ΔH_T^* (kcal/mol)	Experimental method	Reference
9.95	Visual synthetic method – phase diagram	35
8.30 ± 0.4	Phase equilibria	34
8.15	Visual synthetic method – phase diagram	36
8.09 ± 0.23	Drop calorimetry	14
6.85 ± 0.55	Vapour pressures	This work

* T is the melting point determined in the respective investigation.

TABLE 4. Thermodynamic properties of TaCl₅*

Temperature	Phase transition	ΔH_T (kcal/mol)	ΔS_T (cal/K mol)
Boiling point: 507.3 K	Liquid–gas	—	—
Mean temperature: 502.7 K	Liquid–gas	12.81 ± 0.40	25.3 ± 0.8
Melting point: 496.9 K	Solid–liquid	6.25 ± 0.85	12.5 ± 1.7
Melting point: 496.9 K	Solid–gas	19.06 ± 0.41	37.8 ± 0.9
Mean temperature: 468.2 K	Solid–gas	19.26 ± 0.41	38.2 ± 0.9
Standard temperature: 298.15 K	Solid–gas	20.43 ± 0.41	41.3 ± 0.9

* All entries in Table 4 were calculated with the use of only [6] through [9]. The mean temperature is defined as the reciprocal of the mean value of T^{-1} for the reported data points.F
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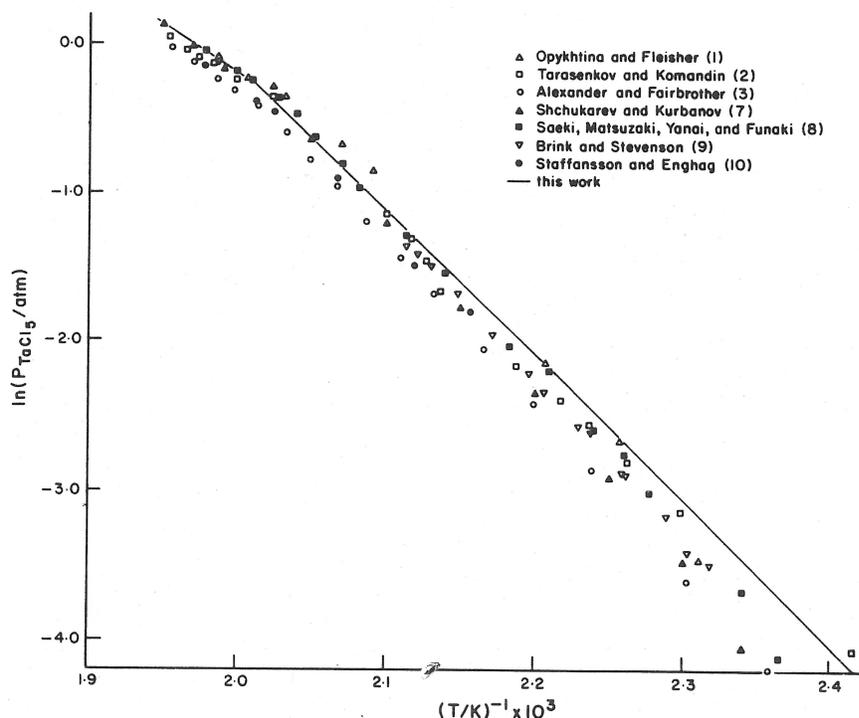


FIG. 4. Temperature dependence of vapour pressure of TaCl_5 ; comparison with other investigations. Data of Saeki *et al.* were estimated herein from Figs. 7 and 8 of ref. 8. Data of Shchukarev and Kurbanov were calculated herein at selected temperatures using equations for the least-squares lines quoted on p. 146 of ref. 7.

The melting point is reported to lie in the range of 488 K (28) to 495 K (29). The boiling point of 507.3 K falls within the reported range of 506 K (28) to 515 K (30, 31). Table 5 compares various determinations of the thermodynamic properties of TaCl_5 . The enthalpy and entropy of sublimation are lower by approximately 10% than those

previously reported. The enthalpy and entropy of evaporation agree well with other studies. The enthalpy of fusion with a value of 6.25 ± 0.85 kcal/mol lies well below the value of 8.6 kcal/mol determined calorimetrically by Dobrotin *et al.* (32). No error limits were quoted in their work.

TABLE 5. Comparative values of the thermodynamic properties of TaCl_5
(a) Sublimation

$\Delta H_{T\dagger}$ (kcal/mol)	$\Delta S_{T\dagger}$ (cal/K mol)	ΔH_{298} (kcal/mol)	ΔS_{298} (cal/K mol)	Reference
22.4*	45.2*	23.4†	47.9†	1
20.4*	40.5*	21.5†	43.6†	2
22.4*	44.3*	23.5†	47.3†	3
—	—	22.8	46.4	4
22.7 \pm 1	45.2 \pm 1	23.8	48.3	7
21.63	43.19	—	—	8
21.1 \pm 0.2	41.9	22.1	44.8	9
20.10	39.80	21.3	42.98	10
19.26 \pm 0.41	38.2 \pm 0.9	20.43 \pm 0.41	41.3 \pm 0.9	This work

* Analysis of data obtained by Schaefer *et al.* (33).

† Analysis of data obtained by Schaefer and Poelert (4).

‡ T is the mean temperature of the measured vapour pressures.

(b) Evaporation

ΔH_T^\dagger (kcal/mol)	ΔS_T^\dagger (cal/K mol)	Reference
11.7 \pm 2.3*	23.0 \pm 4.7*	1
11.7 \pm 0.7*	23.0 \pm 1.4*	2
13.64 \pm 0.26*	26.6 \pm 0.5*	3
14.9 \pm 1.0	29.3 \pm 1.0	7
13.71	27.04	8
14.03	27.51	10
13.1 \pm 0.4	25.9 \pm 1.3	28
12.81 \pm 0.4	25.3 \pm 0.8	This work

*These values were calculated herein by numerical analysis of the experimental data.

$\dagger T$ is the mean temperature of the measured vapour pressures.

(c) Fusion

ΔH_T^* (kcal/mol)	Experimental method	Reference
9.15	Visual synthetic method - phase diagram	35
8.6	Calorimetry	32
8.4	Visual synthetic method - phase diagram	36
6.25 \pm 0.85	Vapour pressures	This work

$\dagger T$ is the melting point determined in the respective investigations.

Acknowledgement

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