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The Vapour Pressure of Solid and Liquid $NbCl_5$

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The vapour pressure of solid and liquid $NbCl_5$ has been measured in the temperature range 462 to 494 K by a transpiration method. From the obtained data heats and entropies of fusion, vaporization, and sublimation have been calculated.

This work comprises measurement of the vapour pressure of solid and liquid $NbCl_5$ and is part in an attempt to provide accurate data for some of the most important refractory metal chlorides. Using the same method the vapour pressure of $WOCl_4$ [1] and $TaCl_5$ [2] have earlier been investigated.

EXPERIMENTAL

The $NbCl_5$ used came from Schuchard, München, and was delivered in sealed glass ampoules. It contained > 99.9 % $NbCl_5$ and < 0.03 % $TaCl_5$, other metallic impurities where < 0.02 %. The argon used as carrier gas in the experiments was delivered by AGA, Stockholm, and had a purity better than 99.99 %. The procedure for the purification of the argon as well as the transpiration method and the apparatus and experimental technique were the same as in the work on $TaCl_5$ and has been described elsewhere.[1,2]

RESULTS AND DISCUSSION

The results from the vapour pressure determinations on solid and liquid $NbCl_5$ are given in Table 1 where values from weighing as well as from chemical analysis are given. All values are corrected for blanks, *i.e.* the amount of $NbCl_5$ vaporized during the heating up period. The data from weighings are plotted in Fig. 1 as log P *versus* $1/T$. As the results from the weighings are more accurate they have been used for the calculation of the vapour pressure equations while the values from the chemical analysis are only given as a check. The vapour pressure equations corresponding to the two lines in Fig. 1 are

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Table 1. Results from weighing and analysis.

Temperature K	$10^3/T$	From weighing						From analysis			Notes
		$NbCl_5$ mmol	Ar mmol	Mol fraction	Pressure torr	P_{NbCl_5} torr	$\log P_{NbCl_5}$	Mol fraction	P_{NbCl_5} torr	$\log P_{NbCl_5}$	
469.4	2.130	2.039	7.594	0.2117	752.0	159	2.201	0.2062	155	2.190	
469.4	2.130	1.880	6.796	0.2167	752.9	163	2.212	0.2153	162	2.210	
478.6	2.090	1.547	3.782	0.2903	760.0	221	2.344	0.2803	213	2.328	a
478.7	2.089	1.266	2.897	0.3041	760.8	231	2.364	0.2934	223	2.348	
462.7	2.161	1.625	9.076	0.1519	776.6	118	2.072	0.1545	120	2.079	
462.9	2.160	1.751	9.483	0.1559	776.1	121	2.083	0.1511	117	2.068	
477.5	2.094	2.931	7.284	0.2869	776.7	223	2.348	0.2903	225	2.352	
477.5	2.094	1.492	3.755	0.2844	776.8	221	2.344	0.2667	207	2.316	
487.2	2.052	1.221	2.612	0.3185	778.3	248	2.395	—	—	—	a
487.5	2.051	1.806	2.908	0.3831	777.6	298	2.474	—	—	—	
487.4	2.051	2.051	3.229	0.3884	761.9	296	2.471	0.3712	283	2.452	
494.1	2.024	2.065	2.216	0.4824	762.7	368	2.566	0.4682	357	2.553	
494.2	2.023	2.262	2.381	0.4872	762.7	372	2.571	0.4609	352	2.547	
483.7	2.067	1.880	3.535	0.3586	764.8	274	2.438	0.3349	256	2.408	
484.1	2.066	1.877	3.361	0.3583	766.0	274	2.438	0.3397	260	2.415	

[a] New charge.

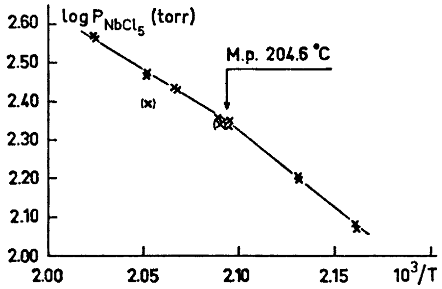

Fig. 1. Vapour pressures of $NbCl_5$ calculated from weighing results.

$$\log P_{NbCl_5(s)}(\text{torr}) = -4.033 \times 10^3/T + 10.794 \qquad (462\ K - 478\ K) \qquad (1)$$

$$\log P_{NbCl_5(l)}(\text{torr}) = -3.080 \times 10^3/T + 8.799 \qquad (478\ K - 494\ K) \qquad (2)$$

The intersection of the two lines corresponds to a melting point of 477.8 K. An extrapolation of eqn. (2) gives a boiling point of 520 K. From eqn. (1) the entropy of sublimation $\Delta S°_{subl.}$ is calculated to 36.20 cal deg.$^{-1}$ mol^{-1} and from the same equation the heat of sublimation in the temperature range investigated is obtained giving the value $\Delta H°_{subl.} = 18.45$ kcal/mol. For calculation of the $\Delta S°_{subl.(298)}$ and the $\Delta H°_{subl.(298)}$ the Δc_p value estimated by Schäfer and Kahlenberg [3] was used. According to their estimation

$$\Delta c_p = -6.4 - 0.7 \times 10^5/T^2 \text{ cal deg.}^{-1} \text{ mol}^{-1}$$

With this value $\Delta S°_{subl.(298)} = 39.4$ cal deg.$^{-1}$ mol^{-1} and $\Delta H°_{subl.(298)} = 19.64$ kcal mol^{-1} were calculated.

In the gas phase $NbCl_5$ has a similar structure as $TaCl_5$, consisting of monomeric trigonal bipyramidal $NbCl_5$ according to electron defraction measurements by Skinner and Sutton.[4] This structure has also been confirmed by Gaunt and Ainscough [5] from IR and Raman spectroscopy. The Nb – Cl distance in the trigonal bipyramid has been determined to 2.28 ± 0.02 Å by Spiridonov and Romanov.[6] In the solid state, however, Zalkin and Sands [7] have shown that crystallized niobium pentachloride forms dimeric molecules Nb_2Cl_{10}. Several investigations of the vapour pressure of $NbCl_5$ have been reported in the literature.[8–15]

Schäfer and Pölert [8] obtained with a transpiration method the relation

$$\log P_{NbCl_5(s)}(\text{atm}) = -5352.57/T + 19.3779 - 3.2204 \log T - 7648.9 \times T^{-2}$$

valid between 350 – 385 K. From results of Meyer, Oosterom and van Oeveren [9] on the system $NbCl_5 - Nb_2O_5$ Schäfer and Pölert [8] derived the equation

$$\log P_{NbCl_5(s)} (\text{torr}) = -4805/T + 12.446$$

Using a boiling point method Ainscough, Holt and Trowse [10] obtained results at vapour pressures between 680 – 900 torr which they related to the boiling points with the equation

$$\log P_{NbCl_5(s)} (\text{torr}) = -2770/T + 8.201$$

't Hart and Meyer [11] studied the vapour pressure of $NbCl_5$ with a static method in the range 540 – 695 K and gave the equation

$$\log P_{NbCl_5(l)}(\text{torr}) = 313.0179 - 15664.84/T - 112.9694 \log T + 0.0460236T$$

Johnson, Silva and Cubicciotti [12] used a boiling point method in the temperature range 504 – 800 K and obtained the relation

$$\log P_{NbCl_5(l)}(\text{atm}) = 6.11621 - 5.42391 \times 10^3/T + 2.10052 \times 10^6/T^2 - 0.48558 \times 10^9/T^3$$

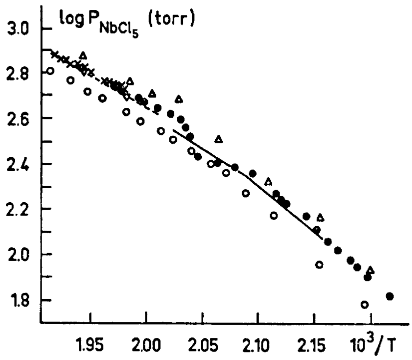

Fig. 2. Vapour pressures of $NbCl_5$ (comparison with earlier works).
△ Opichtina, Fleischer;[13]
● Tarasenkov, Komandin,[14] static method;
× Tarasenkov, Komandin,[14] boiling point method;
○ Alexander, Fairbrother;[15]
▽ Johnson, Silva, Cubicciotti;[12]
– – – Ainscough, Holt, Trowse;[10]
——— This work.

In Fig. 2 the present work – given as two lines corresponding to eqns. (1) and (2) – is compared with published results that fall within the same temperature range. In Table 2 the constants in the vapour pressure equation

$$\log P_{NbCl_5(l)}(\text{torr}) = -a \times 10^3/T + b$$

Table 2. Reported results for $NbCl_5$(l)

Temp. range K	Boiling point °C	a	b	ΔH°_{vap} kcal mol^{-1}	ΔS°_{vap} cal deg.$^{-1}$ mol^{-1}	Ref.
483 – 514	–	2.84	8.43	13.0	25.4	13
480 – 506	–	3.27	9.22	15.0	29.0	14 Static method
504 – 520	–	2.45	7.60	11.2	21.6	14 Boiling p. method
478 – 528	–	2.89	8.36	13.2	25.1	15
–	247	2.770	8.201	12.7	–	10
–	248	–	–	–	–	17
478 – 494	247	3.080	8.799	14.09	27.10	This work

and the thermodynamic quantities calculated from the constants are compared. Boiling points obtained at different investigations are also given. The values given from the work of Opichtina and Fleischer,[13] Tarasenkov and Komandin,[14] and Alexander and Fairbrother[15] have been obtained from a statistical treatment by Schäfer, Bayer and Lehman[16] and from these values Schäfer and Kahlenberg[3] have given the equation

$$\log P_{NbCl_5(l)}(\text{torr}) = -2.87 \times 10^3/T + 8.37$$

said to be valid for temperatures close to the melting point.

From Fig. 2 it can be seen that the present work shows a good agreement with the result from Ainscough, Holt and Trowse,[10] Tarasenkov and Komandin,[14] and Johnson *et al.*[12] for liquid $NbCl_5$.

The heat of vaporization, 14.09 kcal/mol, derived from the present work is in fair agreement with the value 13.8 kcal/mol which can be evaluated from the curve of $\Delta H°_{vap}$ *versus* temperature, given by Johnson, Silva and Cubicciotti,[12] and which they have derived with the aid of the Clapeyron equation from vapour pressures combined with the vapour and liquid densities. For solid $NbCl_5$ the corresponding constants in the vapour pressure equation

Table 3. Reported results for $NbCl_5$(s).

Mean temp. K	$10^3/T$	a	b	Ref.
434.4	2.30	4.38	11.57	13
462.7	2.16	4.01	10.77	14
449.0	2.23	4.36	11.38	15
457.4	2.19	4.805	12.446	9
469.9	2.13	4.033	10.794	This work

are given in Table 3. The a- and b-values from earlier results are taken from the article by Schäfer and Pölert.[8] As can be seen from this table the best agreement with the present work is obtained in the work by Tarasenkov and Komandin.[14] Over a large temperature range there is, however, likely to be a significant deviation from linearity in the log P *versus* $1/T$ relation. This was also found in the investigation of the vapour pressure of $WOCl_4$ [1], and has been discussed in connection with the work on $TaCl_5$.[2] It is therefore not surprising that at lower temperatures, not covered by the present work, Schäfer and Pölert from their own investigations in the range 350 to 384 K give an a-value of 4.875 at a $10^3/T$-mean value of 2.693 which indicates that the curvature of the log P *versus* $1/T$ curve is even greater for $NbCl_5$ than for $TaCl_5$.

To study the influence of temperature on the slope the log P results from different investigations near the melting point were plotted *versus* $1/T$ and compared to the results of Schäfer and Pölert at low temperatures. The slopes from these curves were evaluated graphically and are given in Table 4 together with the corresponding heats of sublimation.

Table 4. Slopes from published results and corresponding heats of sublimation.

Temp. range $10^3/T$	a graphically evaluated	$\Delta H°_{subl.}$ kcal mol^{-1}	Ref.
2.6 – 2.85	4.85	22.2	8
2.1 – 2.2	4.5	20.6	15
2.1 – 2.2	4.2	19.2	13
2.1 – 2.25	4.05	18.5	14
2.1 – 2.2	4.05	18.5	This work

If we assume that the low temperature values of Schäfer and Pölert are correct it is now possible to obtain an equation that takes into account the difference in slope of the log P curve at high and low temperature. With an a-value of 4.85 and 4.10 at $10^3/T = 2.7$ and 2.1, respectively, the following relations is obtained valid from 350 K to the melting point.

$$\log P_{NbCl_5(s)}(\text{torr}) = -7500/T - 16.45 \log T + 1.32 \times 10^3 T + 61.496 \quad (3)$$

This equation shows a good agreement with the present work as well as with the low temperature work of Schäfer and Pölert. The $\Delta H°_{subl.(298)} = 19.6$ kcal mol^{-1} and $\Delta S°_{subl.(298)} = 39.4$ cal K^{-1} mol^{-1} calculated from this work are smaller than the corresponding values from the work of Schäfer and Pölert which are 22.8 and 46.2, respectively. The reason for this descrepancy is probably the uncertainty in the Δc_p-value used for the integration. As the experimental values in this work are obtained at temperatures higher than those of Schäfer and Pölert the influence of the error in the Δc_p is also much greater why it is plausible to assume that the latter values are closer to the true values. The melting point 204.6°C obtained in the present work is in fair agreement with the results from previous investigations as can be seen in Table 5. The heat of fusion has been determined calorimetrically by Keneshea *et al.*[19] to 8.09 kcal/mol, cryoscopicly by Nisel'son and Perekhrest[21] to 9.95 kcal/mol, and from the difference in $\Delta H°_{subl.}$ and $\Delta H°_{vap.}$ by Alexander and Fairbrother[15] to 7.7 kcal/mol and by Meyer *et al.*[9] to 8.3 kcal/mol. The value in this work 4.36 kcal/mol shows a pronounced lower value than those mentioned. One should, however, not attach to much importance to this value as a calculation of the heat of fusion as a difference between $\Delta H°_{subl.}$ and $\Delta H°_{vap.}$ is not a very accurate method. The low heat of fusion obtained in this work corresponds to an entropy of fusion of 9.1 cal $deg.^{-1}$ mol^{-1} or about 1.8 cal K^{-1} g $atom^{-1}$ which is low even for a molecular substance.

Table 5. Melting point for $NbCl_5$.

°C (Ref.): 204.7 (18); 204.4 (17); 206.8 (9); 205.7 (19); 205.3 (20); 204.6 (this work).

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