

# A Thermogravimetric Method for Determination of Vapour Pressures above $10^{-2}$ Atm. II. Vapour Pressure of Molten Sodium Chloride

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The vapour pressure of molten sodium chloride has been measured in the temperature range 1267–1438 K using the method discussed in a previous communication. Experimentally, the rate of vapour transport through a capillary opening in a cell is determined as a function of an applied inert-gas pressure at constant temperature. The vapour pressure is derived by computer fitting of the previously developed theoretical equation to the experimental data. The primary aim of the present study has been to test the validity of the method. It is found that the vapour pressure values are self-consistent and in agreement with accepted literature data even when simplified equations and porous cell materials are used. The application of the method for determination of vapour diffusivity and viscosity is also discussed.

The present work has been performed to evaluate the practical use of the method for determination of vapour pressures previously discussed by Motzfeldt, Kvande and Wahlbeck.<sup>1</sup> In this method, the sample is contained in a cell with a narrow capillary opening of length  $l$  and radius  $r$ . The cell is placed in a gas-tight thermobalance with an inert-gas pressure  $P_f$  at a furnace temperature  $T$ . The rate of mass loss  $\dot{n}$  (the mass of sample vapour which leaves the cell through the capillary per unit time)\* is measured as a function of the inert-gas pressure  $P_f$ , which is lowered stepwise during the run.

\* In the first paper<sup>1</sup> the rate of mass loss of the vapour was designated  $\dot{n}_2$  and the equilibrium vapour pressure  $P_2^*$ ; these symbols have been replaced by  $\dot{n}$  and  $P_s$ .

The theoretical treatment showed that the rate of mass loss furthermore is related to the following quantities:<sup>1</sup> The interdiffusion coefficient of the vapour and the inert gas, expressed by  $D' = DP$  ( $D'$  being independent of the total gas pressure  $P$ ), the molar heat of vaporization  $\Delta H_v$  of the sample, a heat transfer coefficient  $K$  specific to the experimental arrangement, and the viscosity  $\eta$  of the vapour. For convenience, three parameters denoted  $A$ ,  $B$  and  $C$  are defined by the following equations:

$$A = \frac{\pi r^2 D'}{RTl} \quad (1)$$

$$B = \frac{KRT^2}{\Delta H_v^2} \quad (2)$$

$$C = \frac{\pi r^4}{16RT\eta} \quad (3)$$

The rate of mass loss is also related to the ratio of the molar weights of the vapour and the inert gas, expressed by  $\gamma = (M_2/M_1)^{1/2}$  which is considered as a known constant.

The theoretical treatment gave the following relation between the rate of mass loss  $\dot{n}$ , the inert-gas pressure  $P_f$ , the equilibrium vapour pressure  $P_s$  of the sample, and the above parameters:<sup>1</sup>

$$\dot{n} = C \left[ \left( \frac{P_s \exp(-\frac{\dot{n}}{B})}{1 - \exp(-\frac{\dot{n}}{A})} \right)^2 - P_f^2 \right] - A \ln \left[ \gamma + (1 - \gamma) \exp(-\frac{\dot{n}}{A}) \right] \quad (4)$$

In some cases, including the present one with a varying monomer/dimer ratio in the vapour, the value of  $\gamma$  is not precisely known. The equation may then be used with an estimated average and constant  $\gamma$  value, since it turns out that  $\dot{n}$  is not very sensitive to the value assigned to  $\gamma$ . Still eqn. (4), with the concomitant eqns. (1), (2) and (3), looks somewhat unwieldy. The problem is simplified, however, by noting that the parameters  $A$ ,  $B$  and  $C$  may be regarded as "unknowns" together with the equilibrium vapour pressure  $P_s$ . By use of a suitable computer program to fit eqn. (4) to the experimentally obtained set of data for  $\dot{n}$  and  $P_f$ , a set of "best" values is obtained for  $A$ ,  $B$ ,  $C$  and  $P_s$ , where the value of the latter is the primary aim of the method. There is no objection in principle to this procedure. It was pointed out in the previous discussion,<sup>1</sup> however, that the computer treatment may give some trouble in practice because eqn. (4) generally may be fitted to a given set of experimental data with almost equal precision for widely different values of the two parameters  $B$  and  $C$ . For this reason, two alternative equations were also considered, each resulting from a simplifying assumption:

1. Assume that the rate of mass loss, in the pressure range  $P_f < P_s$ , is determined by the rate of heat transfer from the furnace to the sample, with no pressure gradient in the capillary. Eqn. (4) is then reduced to

$$P_f = P_s \frac{\exp\left(-\frac{\dot{n}}{B}\right)}{1 - \exp\left(-\frac{\dot{n}}{A}\right)} \quad (5)$$

2. Assume instead that the rate of mass loss in the pressure range mentioned is determined by viscous flow through the capillary, with no temperature difference between furnace and sample. Eqn. (4) then gives

$$\dot{n} = C \left[ \left( \frac{P_s}{1 - \exp\left(-\frac{\dot{n}}{A}\right)} \right)^2 - P_f^2 \right] - A \ln \left[ \gamma + (1 - \gamma) \exp\left(-\frac{\dot{n}}{A}\right) \right] \quad (6)$$

Eqns. (5) and (6) may be fitted separately to the same set of experimental data, and the computer handling is then quite simple because each of the equations contains only one of the two parameters  $B$  and  $C$ .

In the present investigation we have compared the results for the vapour pressure derived by means of eqns. (4), (5) and (6) from the same experimental data, and we have discussed the values obtained for the parameters  $A$ ,  $B$  and  $C$  in order to test as far as possible the validity of the theoretical treatment.

The theory deals with mass transport through a capillary opening in an otherwise gas-tight cell; this is the ideal situation which cannot always be realized in high-temperature applications because of material problems. With this in mind we have included in our tests comparison between results obtained with porous and impervious cells.

## EXPERIMENTAL

*Sample.* The experiments reported here were done as a preliminary to further work on the vapour pressure of molten salt systems; hence, a molten salt was desirable as the sample substance. Sodium chloride was chosen because its vapour pressure has been accurately determined by Barton and Bloom.<sup>2,3</sup> Analytical grade reagent was recrystallized from its melt in a platinum crucible in dry nitrogen atmosphere and large, transparent crystals were picked for use.

*Cell materials.* Silica glass is a good container material for molten alkali chlorides. Fig. 1 shows the shape of the silica cells employed in the present study and in further work on chloride mixtures.<sup>4</sup> The present study was also a preliminary to investigations of molten fluorides<sup>5</sup> which should be contained in graphite cells. Two brands of graphite were used, viz., the impervious Graph-I-Tite G from Carborundum Co., U.S.A. and the high-purity, porous quality AUC from Union Carbide Co., U.S.A. The general shape of the graphite cells is shown in Fig. 2.

*Apparatus.* The experiments with silica cells were carried out in a thermobalance with the furnace

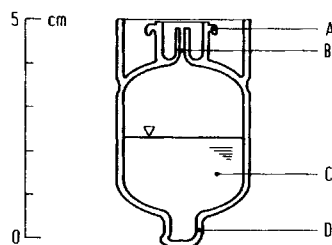


Fig. 1. Silica cell. A: Collar for protection of capillary tubing, with hooks for suspension. B: Silica capillary. C: Molten salt. D: Sealed-off tube which has been used for charging the cell with the sample.

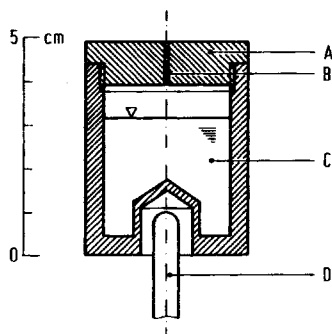


Fig. 2. General shape of graphite cells. A: Threaded lid. B: Drilled hole serving as a capillary opening. C: Molten salt. D: Thermocouple.

heated by Kanthal wire wound on an oxide tube.<sup>4,6</sup> The experiments with graphite cells were done in another thermobalance with a graphite tube heater.<sup>7,\*</sup> Both apparatuses are built on the general principle of a balance placed on a water-cooled table above the furnace. The balances are standard analytical, knife-edge type, converted to electronic recording of mass changes. Balance and furnace are jointly inside a vacuum chamber connected to an oil diffusion pump and a rotary pump. The inert-gas pressures are read on closed-end U-tube mercury manometers. Temperatures were measured by Pt/Pt 10% Rh or by Chromel/Alumel thermocouples, calibrated against the melting point of silver (1235.1 K according to IPTS-68). The temperature was kept constant within  $\pm 0.5$  K during any one run by means of electronic controllers. Special attention has to be paid to the temperature control in the use of the present method since the gas pressure inside the furnace is lowered in the course of the run, and this tends to give an increase in temperature which must be counteracted by the control equipment.

**Procedure.** The cell with contents is suspended from the balance into the furnace, and the system is closed and evacuated to about  $10^{-3}$  Pa, as read on a Penning gauge. After degassing at moderate temperature, inert gas (argon) is admitted to a pressure well above the expected vapour pressure, and the temperature is raised to the desired value. The mass of the cell with contents is recorded for some minutes at constant temperature and inert-gas pressure. The inert-gas pressure then is decreased by a short interval of pumping, the recording

\* The use of two different furnaces was owing to the different subsequent projects and was not a necessity in the present work, since either cell could be used in either furnace at the temperatures in question.

continued, and the procedure repeated. The recorder tracing at each pressure should give a straight line, and the slope of this line represents the rate of mass loss  $\dot{m}$ . When this rate has increased to a suitably high value, indicating that the inert-gas pressure is well below the vapour pressure in the cell, the run is stopped by admitting an excess pressure of inert gas, and the system is ready for another run, at another temperature if desired.

Each run yields a set of corresponding values for  $\dot{m}$  and  $P_f$ . This set is read into a computer together with a suitable program for fitting of eqn. (4) to the data, or alternatively, fitting of either eqn. (5) or (6). As regards  $\gamma$ , a constant value of 1.46 was used, derived from the data of Barton and Bloom.<sup>3</sup> The computer then gives the corresponding value of the equilibrium pressure  $P_s$ , and also of the parameters  $A$ ,  $B$  and/or  $C$  depending on the equation used. In the present work a computer program devised by Hertzberg<sup>8</sup> was used, executed on a Univac 1108 computer.

**Results.** Some typical curves for  $\dot{m}$  versus  $P_f$  are shown in Fig. 3. The figure is given merely for illustration, since graphical representation of the observed data is generally unnecessary. Numerical

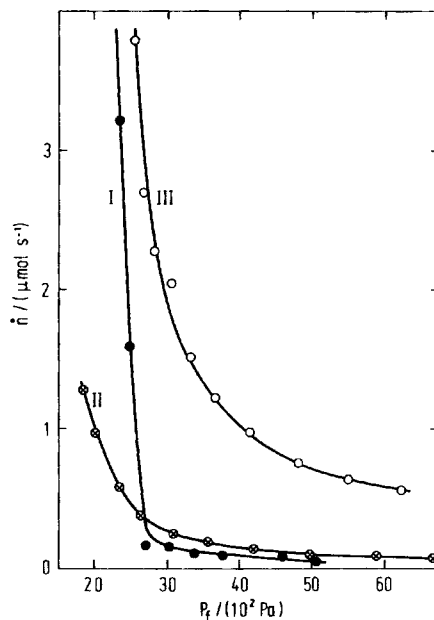


Fig. 3. Typical curves for rate of mass loss  $\dot{m}$  versus inert-gas pressure  $P_f$ . I: Silica cell,  $r=0.25$  mm,  $T=1378$  K. II: Impervious graphite cell,  $r=0.20$  mm,  $T=1380$  K. III: Porous graphite cell,  $r=0.25$  mm,  $T=1383$  K. Curves are shown as resulting from computer fitting.

results are presented in Table 1. The observed values of  $A$ ,  $B$  and  $C$  have been converted from mass to molar units by dividing by  $85 \text{ g mol}^{-1}$ , which is the average molar weight of the vapour over molten sodium chloride in the actual temperature range, reported by Barton and Bloom.<sup>3</sup> The values for the vapour pressures are also shown in Fig. 4. Pressures in Table 1 and in Fig. 4 are given in pascal (remember that  $10^2 \text{ Pa} = 1 \text{ mbar} = 0.750 \text{ Torr}$ ).

## DISCUSSION

*Validity of equations.* It is seen from Table 1 that the values derived for the parameter  $A$  (related to

diffusivity, *cf.* eqn. (1)) are roughly the same for any one run regardless of whether eqn. (4), (5) or (6) is used. This is consistent with the fact that all three equations are essentially equivalent in the region of diffusive transport, *i.e.*, for  $P_t > P_s$ .

It is furthermore seen that the value of  $B$  derived from eqns. (4) and (5) for the same run are widely discrepant, this is particularly striking for Series I with silica cells where the ratio of the values amounts to a factor of  $10^5$ . One may estimate that a reasonable value of  $B$  for the cells in question should be about  $700 \mu\text{mol s}^{-1}$  (*cf.* below). None of the  $B$  values obtained from the experimental data are anywhere near this value; this is taken to indicate that these values lack physical significance.

Table 1. Results from vapour pressure measurements for NaCl(l).

Capillary radius and length:

Cell No.	1	2	3	4	5
$r/\text{mm}$	0.25	0.20	0.25	0.25	0.25
$l/\text{mm}$	10.0	10.0	5.6	8.6	5.6

$T/\text{K}$	Cell No.	$A/\mu\text{mol s}^{-1}$			$B/\mu\text{mol s}^{-1}$		$C/\mu\text{mol s}^{-1}\text{Pa}^{-2}$		$P_s/10^2 \text{ Pa}^a$		
		eqn. (4)	eqn. (5)	eqn. (6)	eqn. (4)	eqn. (5)	eqn. (4)	eqn. (6)	eqn. (4)	eqn. (5)	eqn. (6)
<b>I. Silica cells</b>											
1285	1	0.020	0.042	0.023	$3.83 \times 10^5$	2.1	$7.5 \times 10^{-7}$	$7.6 \times 10^{-7}$	8.9(1)	7.6(14)	8.9(1)
1300	1	0.027	0.041	0.027	$0.45 \times 10^5$	2.0	$7.3 \times 10^{-7}$	$7.2 \times 10^{-7}$	10.7(1)	11.4(19)	10.7(1)
1314	1	0.032	0.045	0.032	$4.45 \times 10^5$	3.8	$7.3 \times 10^{-7}$	$7.3 \times 10^{-7}$	12.6(1)	13.7(7)	12.6(1)
1317	1	0.032	0.036	0.032	$3.55 \times 10^5$	5.1	$7.4 \times 10^{-7}$	$7.4 \times 10^{-7}$	12.5(1)	12.9(1)	12.5(1)
1326	1	0.032	0.033	0.033	$0.20 \times 10^5$	5.3	$6.4 \times 10^{-7}$	$6.4 \times 10^{-7}$	15.2(6)	15.3(11)	15.2(5)
1338	1	0.025	0.026	0.025	$6.93 \times 10^5$	4.7	$5.6 \times 10^{-7}$	$5.6 \times 10^{-7}$	15.8(2)	16.0(8)	15.8(2)
1340	1	0.039	0.041	0.038	$1.65 \times 10^5$	5.9	$5.9 \times 10^{-7}$	$5.9 \times 10^{-7}$	17.7(2)	17.9(14)	17.7(2)
1361	1	0.028	0.022	0.028	$2.88 \times 10^5$	8.7	$5.6 \times 10^{-7}$	$5.6 \times 10^{-7}$	20.8(1)	21.5(2)	20.8(1)
1378	1	0.071	0.071	0.071	$0.31 \times 10^5$	15.7	$5.4 \times 10^{-7}$	$5.4 \times 10^{-7}$	26.9(2)	26.9(10)	26.9(2)
<b>II. Impervious graphite cells</b>											
1285	2	0.042	0.057	0.041	8.5	0.3	$2.3 \times 10^{-7}$	$2.1 \times 10^{-7}$	7.7(2)	8.1(3)	7.7(2)
1301	2	0.047	0.053	0.046	7.3	0.3	$1.9 \times 10^{-7}$	$1.6 \times 10^{-7}$	10.2(5)	11.3(10)	10.1(4)
1316	2	0.051	0.054	0.057	5.6	0.5	$2.1 \times 10^{-7}$	$1.7 \times 10^{-7}$	11.8(2)	12.4(7)	11.6(3)
1335	2	0.056	0.069	0.054	8.7	0.8	$1.6 \times 10^{-7}$	$1.3 \times 10^{-7}$	15.7(2)	16.1(5)	15.7(2)
1380	2	0.148	0.147	0.148	8.3	3.3	$2.4 \times 10^{-7}$	$1.1 \times 10^{-7}$	26.3(5)	27.2(5)	26.8(8)
<b>III. Porous graphite cells</b>											
1289	3	0.64	0.83	0.64	220	6	$2.8 \times 10^{-6}$	$2.6 \times 10^{-6}$	8.1(3)	8.0(13)	8.1(2)
1318	4	0.56	0.50	0.67	11	4	$1.3 \times 10^{-5}$	$7.4 \times 10^{-6}$	11.8(5)	11.9(11)	11.8(3)
1353	5	0.87	1.02	0.90	63	33	$3.6 \times 10^{-6}$	$1.9 \times 10^{-6}$	18.5(9)	17.2(14)	18.2(3)
1383	5	0.86	0.96	0.84	68	41	$2.2 \times 10^{-6}$	$9.3 \times 10^{-7}$	28.0(3)	27.2(11)	27.9(4)
1421	5	1.08	0.86	1.07	220	63	$2.7 \times 10^{-6}$	$1.2 \times 10^{-6}$	39.4(5)	41.6(17)	39.4(5)

<sup>a</sup> The number in parentheses indicates the standard deviation of the last digit(s).

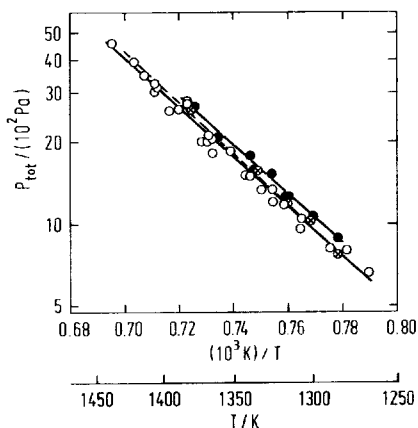


Fig. 4. Total vapour pressure over molten sodium chloride. Filled circles: Silica cells. Crossed circles: Impervious graphite cells. Open circles: Porous graphite cells. Upper solid line: Least-squares fit to results from silica cells. Lower solid line: Least-squares fit to all results from graphite cells. Dashed line: Barton and Bloom.<sup>2</sup>

The values obtained for  $C$  from eqns. (4) and (6) are in very good agreement, again with Series I as the best example where the agreement is almost perfect. This indicates that eqn. (6) is a valid approximation to the complete eqn. (4) for the present experiments while eqn. (5) is not. In other words, the rate of transport under the conditions of the present experiments is governed by viscous flow through the capillary, and not by heat transfer to the cell, in the pressure region  $P_f < P_s$ . This is in agreement with expectation; from the previous theoretical discussion it was concluded that heat transfer should be of importance in determining the rate of mass transport only at considerably lower temperatures.<sup>1</sup>

It is noted from Table 1 that the values for the vapour pressures obtained with eqn. (4) and with eqn. (6) are in almost perfect agreement through all the series. It is also seen, however, that the values obtained by eqn. (5) are in good agreement with the rest, in spite of the fact that this is not the appropriate equation for the present case. This shows, on one hand, that agreement of vapour pressures is an insensitive test for the validity of the equations and, on the other, that fairly good results may be obtained even with the wrong choice of equation. For best results, however, either the full equation (4), or the simplified equation

appropriate to the experimental conditions, should be used.

*Influence of cell material.* The values of  $A$  within any one series in Table 1 show some scatter, which is ascribed to the fact that these values derive from measurements of low rates of mass loss where the experimental relative accuracy is lower. Considering averages, however, it is seen that the  $A$  values increase by a factor of two when going from silica cells to impervious graphite. The probable explanation is that a cell with a screwed-on lid will provide some leakage, even with careful machining of the lid. Going further to cells of porous graphite, it is seen that the  $A$  values increase by another factor of ten, which is ascribed to gaseous diffusion through the pores. The  $C$  values likewise are considerably larger for porous graphite, which would seem to indicate that some of the pores or leaks are of sufficient dimensions to permit gas flow in addition to diffusion. A further discussion of these parameter values follows below.

In spite of large variations in the values of the parameters  $A$ , ( $B$ ) and  $C$  from one series to another, it is seen from Table 1 that the values obtained for the vapour pressures are in quite good agreement throughout. This is more clearly borne out by Fig. 4, where it is seen that the results obtained with porous graphite cells show somewhat more scatter than those from the other two series, but otherwise all results are in good agreement. This leads to the conclusion that one may indeed obtain reliable measurements of vapour pressures with the present method, even in cases where no impervious cell material is available.

A total of 27 runs were made with the porous graphite cells; numerical data are given only for a few representative examples in Table 1, while all of the vapour pressure results are included in Fig. 4.

*Vapour pressures, monomer-dimer equilibrium, and vaporization thermodynamics.* The straight line representing the results from silica cells in Fig. 4 may be expressed by the equation\*

$$\log_{10}(P_s/\text{atm}) = -8961/T + 5.163 \quad (1285 - 1378 \text{ K}) \quad (7)$$

with a standard deviation in  $P_s$  of  $\pm 3.9\%$ . The

\* In eqns. (7) to (11) pressures are expressed in atm. which means that they are expressed relative to the chosen standard pressure of  $1.013 \times 10^5$  Pa. Thus, pressure values in atm are really dimensionless numbers, and not in conflict with the SI system.

straight line representing the results from both types of graphite cells may be expressed by

$$\log_{10}(P_s/\text{atm}) = -9080/T + 5.206 \quad (1267 - 1438 \text{ K}) \quad (8)$$

with a standard deviation in  $P_s$  of  $\pm 6.4\%$ . The data of Barton and Bloom,<sup>2</sup> represented by the dashed line in Fig. 4, fall in-between the two sets of present results, showing general agreement.

The measured values represent the total pressure of the vapour, which contains both monomeric and dimeric species, while higher polymers may be neglected. Thus we have

$$P_s = P_{\text{NaCl}} + P_{\text{Na}_2\text{Cl}_2} \quad (9)$$

From data given in the JANAF Tables,<sup>9</sup> the equilibrium constant for the dimer-monomer equilibrium in the temperature range 1100–1600 K is

$$\log_{10} K = \log_{10}(P_{\text{NaCl}}^2/P_{\text{Na}_2\text{Cl}_2}) = -10242/T + 6.442 \quad (10)$$

The combination of eqns. (7), (9) and (10) is solved numerically, and the results for the pressure of monomer may be expressed by the equation

$$\log_{10}(P_{\text{NaCl}}/\text{atm}) = -9229/T + 5.232 \quad (\text{silica cell}) \quad (11a)$$

and the combination of eqns. (8), (9) and (10) yields

$$\log_{10}(P_{\text{NaCl}}/\text{atm}) = -9308/T + 5.255 \quad (\text{graphite cells}) \quad (11b)$$

Comparison with monomer pressures calculated from JANAF data<sup>9</sup> for the temperature range 1200–1500 K shows that the values represented by eqn. (11a) deviate about 10%, while the values from eqn. (11b) agree with the JANAF data within 0.5%.

The data for the monomer pressure yield directly the second-law value for the enthalpy of vaporization of monomeric NaCl from the melt, and the third-law value is obtained by combination with free-energy functions from the JANAF Tables. The results are given in Table 2. It is seen that the second- and third-law enthalpies are in excellent agreement and also in agreement with the accepted JANAF value. The second-law value of Barton and Bloom, on the other hand, appears to be about 8 kJ too high, as is also revealed by the somewhat steeper slope in Fig. 4.

*The parameter A and diffusivity.* From the kinetic theory of gases,  $D'$  is expected to vary with  $T^{3/2}$ , and it is seen from eqn. (1) that  $A$  should then vary with  $T^{1/2}$ . This slight temperature variation, however, is masked by the spread in the values in Table 1. Limiting the discussion to the results with silica cells, it is seen that  $A$  may be considered approximately constant (excepting the discordant value at 1378 K). By use of eqn. (1), the  $A$  values from silica cells then give  $D' = 17 \pm 3 \text{ N s}^{-1}$ .

No previous experimental data are available for the diffusivity of sodium chloride vapour in argon. One may obtain a check on the value, *e.g.*, by calculating the mutual effective collision diameter  $d$  by means of the expression for  $D'$  from the hard-sphere model of the kinetic theory of gases:<sup>10</sup>

Table 2. Vaporization thermodynamics for NaCl (g).

Authors	Temperature range (K)	Heat of vaporization, $\Delta H_{v,1353}^\circ/\text{kJ mol}^{-1 a}$		Heat of sublimation, $\Delta H_{298}^\circ/\text{kJ mol}^{-1 a}$	
		Apparent value from total pressures	Value from partial pressure of monomer	Second-law value	Third-law value
Barton and Bloom <sup>2</sup>	1340–1540	180.3(17)		237.1	228.8
JANAF <sup>9</sup>			177.4		229.7
This work, silica cells	1285–1378	171.5(71)	176.6(54)	228.9(54)	228.9(3)
This work, graphite cells	1267–1438	173.6(38)	178.2(29)	230.5(29)	229.8(6)

<sup>a</sup> The uncertainties are standard deviations.

$$D' = \frac{3}{8} \frac{(kT)^{3/2}}{(2\pi m^*)^{1/2}} \times \frac{1}{d^2} \quad (12)$$

In this expression,  $k$  is the Boltzmann constant, and  $m^* = m_1 m_2 / (m_1 + m_2)$  where  $m_1$  and  $m_2$  are the molecular masses of the inert gas and the vapour. In the present case the application of eqn. (12) meets with problems since the vapour is a mixture of two species. According to eqns. (10) plus (11) it contains about 75 mol% monomer and 25 mol% dimer at 1330 K, the average temperature of the experiments in Series I. For the purpose of an approximate calculation, however, we may assume that the vapour contains monomer only. From eqn. (12) this gives the mutual collision diameter  $d = 340 \pm 60$  pm.

The interatomic distance in the gaseous NaCl molecule is 236 pm.<sup>9</sup> Combined with the ionic radii, this gives a mean cross-sectional diameter of about 400 pm. Solid argon has an FCC structure with lattice constant 530 pm,<sup>11</sup> this gives the atomic diameter 375 pm, so that one would expect a mutual collision diameter of about 390 pm. Taking into account the presence of dimer, the value of  $d$  would slightly decrease as calculated from eqn. (12), while it would increase as expected from molecular dimensions. Nevertheless, the agreement is satisfactory in view of the assumptions made, which means that the value obtained for  $D'$  appears reasonable.

It may be added that one would not expect to obtain very accurate values for  $D'$  from experiments performed primarily to determine vapour pressures because the relative accuracy may then be rather poor in the diffusion range ( $P_f > P_s$ ). Measurements of diffusivity preferably should be done in separate experiments, with the capillary radius increased to give good accuracy in this range.

*The parameter B and heat transfer.* Assuming as a first approximation that heat transfer takes place by radiation only, it was shown in the first paper<sup>1</sup> that we have  $K \cong 2\sigma T^3 s$ , where  $\sigma$  is the Stefan-Boltzmann radiation constant, and  $s$  is the surface area of the cell. With a surface area of about 50 cm<sup>2</sup> for the cell shown in Fig. 1, and a temperature of 1330 K, this gives from eqn. (2):  $B = 700 \mu\text{mol s}^{-1}$ . It is seen from Table I that the application of eqn. (5) gives much lower  $B$  values throughout, showing that something else is rate-determining. The very high values obtained in Series I by application of eqn. (4), on the other hand, just indicate that the heat transfer is ample. When  $B$  goes towards infinity in eqn. (4), eqn. (6) is obtained.

*The parameter C and viscosity.* The viscosity of a gas is expected to increase with  $T^{1/2}$ ; from eqn. (3) it is seen that  $C$  should then be inversely proportional to  $T^{3/2}$ . The values of  $C$  from Series I in Table I show a temperature variation in the right direction. At an average temperature of 1330 K these values give the vapour viscosity  $\eta = (1.1 \pm 0.1) \times 10^{-5} \text{ N s m}^{-2}$ . From the measurements with impervious graphite cells the value  $\eta = (1.4 \pm 0.2) \times 10^{-5} \text{ N s m}^{-2}$  is obtained, thus these values are in agreement within their standard deviations.

No experimental value for the viscosity of sodium chloride vapour has been found in the literature. An indirect check may again be obtained by reference to the kinetic theory of gases:<sup>10</sup>

$$\eta = \frac{5}{16} \left( \frac{mkT}{\pi} \right)^{1/2} \times \frac{1}{d^2} \quad (13)$$

As in the previous case of diffusivities, one has the problem of the monomer – dimer mixture. Assuming the molecular mass of the monomer only, the viscosity from measurements with silica cells gives the collision diameter  $d = 800 \pm 100$  pm. This is about twice the value obtained from the diffusivity, while the value estimated from ionic dimensions, with the dimer content taken into consideration, lies in between the two calculated values. Strict agreement is not to be expected, however, since the hard-sphere model represents only a rough approximation to the real system consisting of non-spherical monomer and dimer molecules. We believe the present viscosity data to be rather reliable. A possible source of error is the radius of the capillary; e.g., an error of 5% in the value assigned to this radius gives an error of 22% in the calculated viscosity. The difference between viscosity values from silica and impervious graphite cells may have been caused by such inaccuracy since precision machining and measurement on graphite is difficult.

## CONCLUSIONS

The present experimental method has given reliable values for the vapour pressure of molten sodium chloride and it appears to be of general utility. The vapour pressure data appear consistent even when simplified theoretical equations and porous cell materials are used. The experimental evidence shows that viscous flow is rate-determining for the mass transport of vapour through the

capillary opening in the cell under the present high-temperature conditions. Capillary diameters in the range 0.3 to 0.6 mm have been found to give suitable rates of mass loss. Values obtained for the interdiffusion coefficient of argon and sodium chloride vapour, and for the viscosity of sodium chloride vapour, appear of reasonable magnitude and further corroborate the soundness of the theoretical basis for the method.

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