# Determination of the Average Molar Mass of the Vapour Above Molten Sodium Chloride by the Transpiration Method

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The transpiration method has been used to measure the rate of mass loss of vapour from NaCl(l) at 1293 K as a function of the carrier-gas flow rate. A theoretical equation developed previously has been fitted to the experimental data by non-linear least-squares analysis using a computer. Results in the temperature range 1153 to 1382 K have been combined with total vapour-pressure values to give the average molar mass of the vapour. Literature data show that the dominating vapour species above NaCl(l) are NaCl(g) and $Na_2Cl_2$(g), and the calculated value of the average molar mass of $(81.0 \pm 4.6)$ g mol$^{-1}$ at 1273 K then is interpreted as corresponding to a dimer content of $(38 \pm 8)$ mol per cent in the vapour. For the reaction $Na_2Cl_2$(g) = 2NaCl(g) the third-law value of $\Delta H_r^\circ(298\ K) = (211.7 \pm 5.0)$ kJ mol$^{-1}$ is calculated.

In the transpiration method the mass of sample vapour transported by a known volume of carrier gas is measured at constant temperature. Kvande and Wahlbeck[1] have given a theoretical analysis of the roles of diffusion and viscous flow in transpiration experiments. The present work has been performed to evaluate the practical significance of the theoretical analysis. Furthermore, the transpiration method has been applied to determine the average molar mass of the vapour above NaCl(l) and thermodynamic data for reactions of condensed and vapour species of NaCl.

## APPLICATION OF THE THEORY

The theoretical analysis[1] showed that the flow rates $\dot{n}_1$ of carrier gas and $\dot{n}_2$ of vapour (mol per unit time) are related to the total pressure $P_f$, the

vapour pressure $P_{2i}$ and the parameter $C$ by the equation

$$\dot{n}_2 = \dot{n}_1 \frac{P_{2i}}{\left(P_f^2 + \dfrac{\dot{n}_1 + \dot{n}_2}{C}\right)^{\frac{1}{2}} - P_{2i}} \tag{1}$$

The parameter $C$ is dependent upon the experimental arrangement and the viscosity of the mixture of carrier gas and vapour,[1] but for the present purpose it may be considered as a constant at fixed temperature. In practice one measures the flow rate of vapour in mass units rather than in mol, and the simple expression

$$\dot{n}_2 = \dot{m}_2/M_2 \tag{2}$$

is introduced. Here, $\dot{m}_2$ is the measured mass of vapour carried away from the sample per unit time, and $M_2$ is the average molar mass of the vapour. In order to avoid an equation of second order with respect to $\dot{m}_2$, it is assumed that $(P_f^2 + \dot{n}_1/C) \gg \dot{n}_2/C$, that is, the term $\dot{n}_2/C$ is deleted inside the parenthesis in the denominator of eqn. (1). The largest error introduced by this assumption is 0.7 % in the present data for the molar mass, as calculated from the numerical values given later. Combination of eqns. (1) and (2) then gives

$$\dot{m}_2 = \dot{n}_1 \frac{P_{2i} M_2}{(P_f^2 + \dot{n}_1/C)^{\frac{1}{2}} - P_{2i}} \tag{3}$$

At constant temperature the vapour pressure $P_{2i}$ is fixed and is considered to be known from measurements by some other method. The average molar mass $M_2$ and the parameter $C$ are unknown

and may be determined by fitting eqn. (3) to a set of measured values for $\dot{m}_2$, $\dot{n}_1$ and $P_f$ by use of a non-linear least-squares analysis computer program.[2]

Eqn. (3) then may be used to calculate $M_2$ at any other temperature from measured values of $\dot{m}_2$, $\dot{n}_1$ and $P_f$. The vapour pressure $P_{2i}$ is considered to be known, and the value of $C$, as determined by the above procedure, may be corrected for the change in temperature $T$, since $C$ is proportional to $T^{-3/2}$.[1]

## EXPERIMENTAL

*Apparatus.* Fig. 1 shows the essential features of the transpiration apparatus. A standard Kanthal-wound furnace, as described by Motzfeldt,[3] was placed horizontally and could be moved back and forth along a tube made of Inconel 600, an alloy which consists of 76 % Ni, 15 % Cr and 9 % Fe (Henry Wiggin & Co., Ltd., Hereford, England). The tube had an outer diameter of 30 mm, an inner diameter of 24.7 mm and a length of 1.00 m.

Special care was taken to reduce the effect of diffusion in these measurements. The following equipment was found to work satisfactorily. A long tube was made, consisting of an end-to-end connection of a stainless-steel tube and three tubes made of gas-tight graphite (Graph−I−Tite G, Carborundum Co., USA), as shown in Fig. 1. The whole assembly could then be slid back and forth inside the Inconel tube. A part of the first graphite tube was fitted tightly inside the steel tube and formed a permanent construction. The two other graphite tubes were threaded, and by careful machining of the tubes and the threads, they could be screwed on to each other to make gas-tight connections. With this construction two narrow capillary openings were formed (radius 0.5 mm,

length 10 mm). In the space between the capillaries the sample was placed, contained in a boat made of graphite (Graph−I−Tite G, inner dimensions: length 73 mm, width 10 mm, height 9 mm).

The carrier gas was passed through the steel tube and the three graphite tubes. Thus, the gas was forced through the two capillaries, into and out of the region where the boat was placed. The speed of the carrier gas, which was expected to increase significantly when passing through the narrow entrance capillary, was reduced by a graphite shield positioned between the entrance capillary and the boat. A water-cooled coldfinger made of copper, with a protective graphite cylinder on the outside, was used to condense the vapour.

The temperature was measured by a Pt/Pt + 10 mass % Rh thermocouple, calibrated against the melting point of silver (1235.1 K, according to IPTS − 68). The thermovoltage was indicated by a digital voltmeter. The temperature variation over the length of the boat was less than ± 1.0 K. During the measurements the temperature was kept constant within ± 0.5 K by use of a Eurotherm PID-controller, Model 070, connected to a Pt/Pt + 10 mass % Rh thermocouple placed close to the windings in the middle of the furnace.

The carrier gas was argon (99.997 volume %, Norsk Hydro). The flow rate was adjusted by a pressure reduction valve and kept constant as indicated by a rotameter. The carrier gas passed through absorption towers filled with Dehydrite and Ascarite to remove traces of $H_2O$ and $CO_2$. The volume of the carrier gas was measured by a gas-flow meter (Elster 00, Mainz). Calibration was performed by slowly adding water to a large burette and passing the replaced air through the gas-flow meter at a rate corresponding to that of argon during the measurements. The reproducibility in the measured gas volume was of the order of 0.1 %.

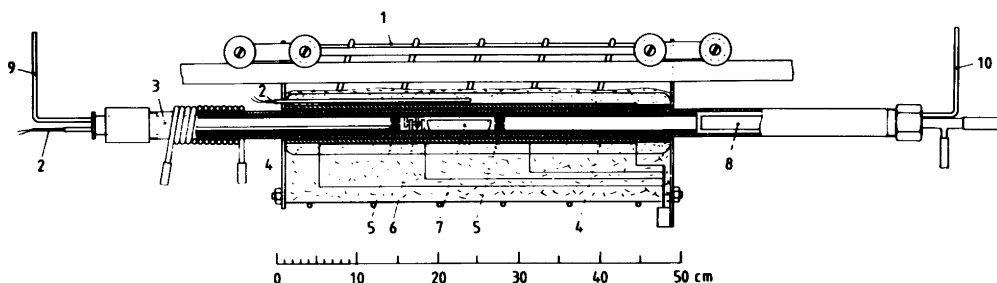Analytical grade sodium chloride was recrystallized from its melt in a platinum crucible in dry



*Fig. 1.* Essential features of the apparatus used in the transpiration experiments. 1, Furnace. 2, Thermocouple. 3, Inconel tube. 4, Graphite tube. 5, Capillary opening. 6, Graphite shield. 7, Graphite boat. 8, Coldfinger. 9, Gas entrance. 10, Gas exit.

nitrogen atmosphere, and large, transparent crystals were selected for use.

*Procedure.* The boat with a fresh sample was placed in the graphite tube between the two capillaries. The steel-graphite-tube assembly was positioned such that the boat came as close as possible to the entrance end of the Inconel tube, while the furnace was located at the opposite end of the Inconel tube. Carrier gas was then passed through the tube to remove all air. After 10−15 min the gas flow was stopped, and the steel-graphite-tube assembly and the furnace were pushed towards each other into their correct positions. When the sample reached the selected temperature, the experiment was started by passing carrier gas over the sample at constant flow rate. This temperature, being somewhat lower than the desired temperature, was found from accurately determined temperature-time curves.

During the measurements the temperature was read every 5 min. After exactly 1 h the gas flow was stopped. The steel-graphite-tube assembly was pulled quickly towards the entrance end of the Inconel tube, while the furnace was pushed towards the opposite end. Cooling of the sample was pursued by use of a fan. After less than 1 min the temperature had decreased to about 1000 K, and the rate of mass loss from the sample then was reduced to about 0.1 %. When the temperature of the boat had reached 298 K, it was removed and weighed, and the amount of vapour transport was determined from the mass loss of the sample during the measurement.

The total gas volume, as read on the gas-flow meter, was reduced to STP conditions (273 K and 760 Torr*) by use of the values for the room temperature and the barometric pressure. These values were read half an hour after the commencement of the experiment. The room temperature was set equal to the temperature of the oil in the gas-flow meter.

## RESULTS AND DISCUSSION

Measurements of the mass of vapour carried away from NaCl(l) were performed for different carrier-gas flow rates at 1293 K. The results are presented graphically in Fig. 2. The solid line resulted from a non-linear least-squares analysis computer fitting of a three-parameter equation developed in our previous paper.

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\* The SI pressure concept of Pascal (Pa) is not considered appropriate, while the unit Torr is more readily understandable and is preferred here; 1 Torr = 133.3 Pa.
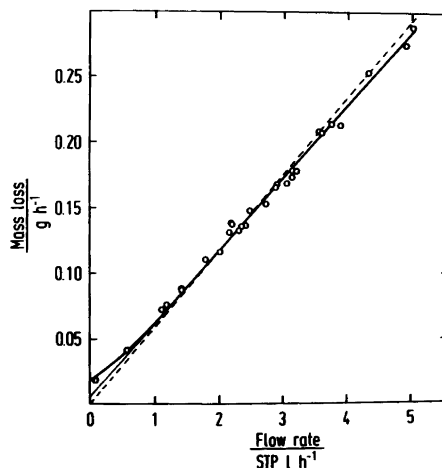
*Fig. 2.* Rate of mass loss *versus* carrier-gas flow rate for the vapour above NaCl(l) at 1293 K. Circles and heavy solid line: Data treated by the present theory. Thin solid line: Extrapolation of the data, giving a non-zero intercept. Dashed line: Data treated by Merten's theory,[4] extrapolation of the data gives a zero intercept.

At low flow rates gaseous diffusion may cause a significant contribution to the vapour transport. This is indicated by the two lower points in Fig. 2. For flow rates above 1 l h$^{-1}$, however, the contribution from diffusion may be neglected. In this region eqn. (3) was fitted to the data by non-linear least-squares analysis, and results closely identical to those obtained with the three-parameter equation were calculated. Thus, for practical purposes eqn. (3) is adequate outside the diffusion region.

One other observation was made during the transpiration measurements. If the flow rate of carrier gas was very large, the gas became unsaturated, and the measured amount of vapour transported was too small. This is a trivial effect which has been avoided in the present work by suitable design of the apparatus and by avoiding extention of the measurements to very large flow rates.

*Comparison with Merten's theory.* Merten[4] presented a theoretical approach to the transpiration experiment. He made the assumption of a uniform pressure throughout the apparatus, while allowance for a pressure gradient has been made in our theory.[1] Fig. 2 shows that at flow rates below 3 l h$^{-1}$, the difference between the two theories is lost in the limited precision of the measurements,

while at larger flow rates the present theoretical model fits the experimental data more closely than Merten's model. Furthermore, a line through the apparently linear range has a non-zero intercept. This is contrasted with an actual zero intercept in Merten's theory.

Merten's equation

$$m_2 = \dot{n}_1 \frac{P_{2i}M_2}{P_f} \tag{4}$$

may be derived from eqn. (3) by assuming that $C = \infty$ and that $\dot{n}_1 \gg \dot{m}_2/M_2$. By comparison of eqns. (3) and (4) one finds that the term $(P_f^2 + \dot{n}_1/C)^{\frac{1}{2}} - P_{2i}$ may be either larger or smaller than $P_f$. Typical values from the present measurements are $P_f = 745$ Torr (average value), $\dot{n}_1 = 0.1$ mol $h^{-1}$ and $C = 1 \times 10^{-6}$ mol $h^{-1}$ Torr$^{-2}$. While these data showed little variation from one measurement to another, $\dot{m}_2$ varied from 18 to 365 mg $h^{-1}$. Merten's equation then will give a too small value for $M_2$ when $P_{2i}$ is below about 60 Torr and a too large value at higher vapour pressures. Quantitatively, the value of $M_2$ predicted by Merten's equation will be 7 or 8 % low when $P_{2i}$ is 10 Torr or smaller, while it will be about 5 % high when $P_{2i}$ is 100 Torr. The latter percentage increases rapidly with increasing vapour pressure.

The present measurements gave $M_2 = (87.2 \pm 2.3)$ g mol$^{-1}$, while Merten's equation would give $M_2 = 83.8$ g mol$^{-1}$ at 1293 K, when the vapour pressure $P_{2i}$ is 11.6 Torr.[5] The difference of 3.9 % is smaller than the expected value of 6.6 %, but agrees qualitatively with the above considerations. Good quantitative agreement has been found in recent measurements with molten cryolite.[6]

*Molar masses at other temperatures.* Additional measurements were made at fourteen other temperatures in the range 1153 to 1382 K. All measurements were made in duplicate. The results were combined with our previous values for the total vapour pressure over NaCl(l), as measured by a thermogravimetric method.[5] Average molar masses calculated from eqn. (3) are shown in Fig. 3.

The molar masses show good agreement with those of Barton and Bloom[7] and Topor.[8] Values calculated from data given in the JANAF Thermochemical Tables[9] show a nearly linear relationship between molar mass and temperature, when the temperature range is not too large. The average molar mass of the vapour above NaCl(l) from the
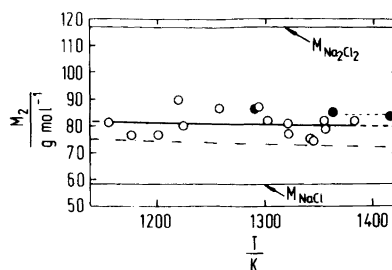


Fig. 3. Average molar mass of the vapour above NaCl(l). Filled circles: Barton and Bloom.[7] Dotted line: Topor.[8] Dashed-dotted line: JANAF Thermochemical Tables.[9] Open circles and solid line: This work.

present data then may be expressed as a function of the absolute temperature $T$ by the equation

$$M_2/(\text{g mol}^{-1}) = [91.75 - 0.008475(T/K)] \pm 4.6 \tag{5}$$

The error limit is the standard deviation determined by the least-squares analysis. From eqn. (5) the average molar mass is $(81.0 \pm 4.6)$ g mol$^{-1}$ at 1273 K. The species present in the vapour were NaCl(g) and its dimer Na$_2$Cl$_2$(g), while the mol fraction of higher polymeric species is of the order of $10^{-3}$ or less.[10] Thus, the average molar mass given above is interpreted as corresponding to a dimer content of $(38 \pm 8)$ mol per cent Na$_2$Cl$_2$(g) at 1273 K. The negative sign of the coefficient multiplied by $T$ in eqn. (5) indicates that the content of dimer in the vapour decreased slightly with increasing temperature.

*Thermodynamic data.* Table 1 shows enthalpy data for reactions involving NaCl(g). The enthalpy of vaporization of NaCl(g) from molten sodium chloride reported by Barton and Bloom,[11] $\Delta H_v^\circ$ (1353 K) = $(180.3 \pm 1.7)$ kJ mol$^{-1}$ is larger by 6.7 kJ mol$^{-1}$ compared to the present data. This is reflected by their large second-law value for the enthalpy of sublimation at 298 K for the reaction

$$\text{NaCl(s)} = \text{NaCl(g)} \tag{6}$$

For this reaction the third-law data of Kvande et al.[5] were calculated from measured vapour pressures in combination with JANAF[9] data for the vapour composition. The present data employed these vapour pressure values combined with average molar masses given by eqn. (5) and necessary free-energy functions from the JANAF Tables. For

| Researchers | Temp. range (K) | NaCl(l)=NaCl(g) $\Delta H_v^\circ$(1353 K)/kJ mol⁻¹ | | NaCl(s)=NaCl(g) $\Delta H_s^\circ$(298 K)/kJ mol⁻¹ | | 2NaCl(s)=Na₂Cl₂(g) $\Delta H_s^\circ$(298 K)/kJ mol⁻¹ | Na₂Cl₂(g)=2NaCl(g) $\Delta H_r^\circ$(298 K)/kJ mol⁻¹ |
|---|---|---|---|---|---|---|---|
| | | From total pressures | From monomer pressures | Second law | Third law | Third law | Third law |
| Barton and Bloom[7,11] | 1340–1540 | 180.3±1.7 | | 237.11 | 228.78 | 240.2 | 217.6 |
| Datz et al.[10] | 1277–1406 | | | | | | 226.4 |
| JANAF Tables[9] | | | 177.4 | | 229.7 | 256.1 | 203.3 |
| Topor[8] | 1323–1442 | 184.5±2.1 | | | | | |
| Kvande et al.[5] | 1285–1378[a] | 171.5±7.1 | 176.6±5.4 | 228.9±5.4 | 228.86±0.33 | | |
| Kvande et al.[5] | 1267–1438[b] | 173.6±3.8 | 178.2±2.9 | 230.5±2.9 | 229.79±0.59 | | |
| This work | 1267–1438 | 173.6±3.8 | 177.0±6.7 | 229.3±6.7 | 231.8 ±1.3 | 251.9±2.1 | 211.7±5.0 |

Table 1. Vaporization thermodynamics of NaCl. The uncertainties are standard deviations.

[a] With silica cells. [b] With graphite cells.

reaction (6) the third-law value of $\Delta H_s^\circ$(298 K)= (231.8±1.3) kJ mol⁻¹ is about 2 kJ mol⁻¹ larger than the other third-law values given in Table 1.

For the sublimation of the dimer

$$2NaCl(s) = Na_2Cl_2(g) \tag{7}$$

data are scarce in the literature. The present third-law value for this reaction is 4.2 kJ mol⁻¹ smaller than the JANAF value, while it is significantly larger than the value of Barton and Bloom.[7,11] The standard enthalpy of formation of $Na_2Cl_2$(g) at 298 K of (−570.3±2.1) kJ mol⁻¹ from this work is in agreement with the JANAF value of (−566.1±8) kJ mol⁻¹.

For the dimer-monomer reaction

$$Na_2Cl_2(g) = 2NaCl(g) \tag{8}$$

the value of $\Delta H_r^\circ$ (298 K)=203.3 kJ mol⁻¹ has been used in the calculations in the JANAF Tables. As seen from the last column in Table 1, the values of Barton and Bloom[7,11] and Datz et al.[10] as well as the present value are significantly larger than the JANAF value. The latter value rests heavily on mass-spectrometric data. There are difficulties with interpretation of fragmentation with this technique, and reconsideration of the data should be made.

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