Asian Journal of Chemistry Vol. 18, No. 1 (2006), 351–355

Measurement of Vapour Pressure and Heats of Sublimation of *o*-Nitro Benzyl Chloride by Knudsen Effusion Method

SAYED MOHAMMAD ALI HOSSEINI*, H. NAGHIBI, M. H. PEIKAR and E. JAMALIZADEH

Department of Chemistry, Shahid Bahonar University of Kerman, Kerman 76175, Iran
Fax: (98)(341)3222033; Tel.: (98)(341)3222033; E-mail: s.m.a.hosseini@mail.uk.ac.ir

An experimental method based on Knudsen effusion apparatus has been designed to measure very low vapour pressure of benzoic acid and *o*-nitro benzyl chloride at different temperatures and by means of the well known Clausius-Clapyron relationship and from slope of the logarithm of the vapour pressure against reciprocal of absolute temperature. Heats of sublimation are calculated for benzoic acid $\Delta H_{sub} = 91.74 \pm 3.45$ kJ mol^{-1} and for *o*-nitro benzyl chloride $\Delta H_{sub} = 96.20 \pm 3.45$ kJ mol^{-1}. The precision measurements of vapour pressure and heats of sublimation have been tested using benzoic acid; the results are in good agreement with literature values.

Key Words: Vapor pressure, Heats of sublimation, Knudsen effusion method, Benzoic acid, *o*-Nitro benzyl chloride.

INTRODUCTION

Vapour pressures of liquids and solids are the keys for thermodynamic parameters. Not only for determining their enthalpy of vaporization and sublimation but also it is important in several studies such as Henry's constant for solubility of solids in water, extension of models for behaviour of chemical substances in their environments[1] and some technological applications and assessment of thermodynamic values[2]. Sublimation enthalpies are also important macroscopic measures of the magnitude of intermolecular interactions in the solid state[3, 4].

Langmuir free evaporation and Knudsen effusion techniques are extensively used and are direct methods for measurement of vapour pressure[5, 6]; both are based on kinetic observation[7–9]. In using them, the weight loss during a free evaporation is measured[6, 9, 10]. Knudsen effusion cell technique is the most common method for determining vapour pressures and heats of sublimation. Kinetically also, it is important for the measurement of low vapour pressure for appointing thermodynamic properties when the equilibrium between the vapour and solid phase has been established. This technique essentially measures the rate of mass effusion from an orifice and translates this rate into the internal pressure of a cell[9]. By this method, the reliable values of vapour pressure of low volatile

solids can be measured; in addition this is highly sensitive at low pressure and can work at very high temperatures.

In the present work, a Knudsen effusion apparatus is designed to measure very low vapour pressure of benzoic acid and *o*-nitro benzyl chloride at different temperatures, and then heats of sublimation are calculated for them.

EXPERIMENTAL

In the present work, a Knudsen effusion method is used to measure vapour pressure of benzoic acid and ortho-nitro benzyl chloride at several temperatures. Benzoic acid used was obtained from Moline (U.S.A) and *o*-nitro benzyl chloride from Merck with purities more than 98%. Benzoic acid and o-nitro benzyl chloride were purified by repeated sublimation under reduced pressure, after weighing and these were kept in vacuum desiccators for experimental use.

A mass-loss Knudsen effusion apparatus is designed to measure the vapour pressure which is containing a vacuum system, Knudsen cell and thermostatic bath[5-10]. In this technique, the pumping system consists of a rotary pump Ed-30 model which can maintain 10^{-1} Pa vacuum and one oil diffusion pump No. OD 15 model that is backed by the rotary pump which can maintain a vacuum better than 10^{-4} Pa. The rotary pump is used for pre-evacuating the system before connecting to the main vacuum pump (diffusion pump). One Pirani gauge, A6 STM model with two sensor Pirani gauge heads, PR-3 model, is used during the experimental run to measure the vacuum maintained in the rotary pump and one Pening gauge, STP4M-1 model with one Pening gauge head sensor, PNG-2 model, are connected to the diffusion pump to measure the vacuum maintained in it. The cylindrical cells are constructed of aluminum with an internal diameter of 2 cm and depth 2.3 cm, a brass lid with a hole of 1 cm diameter which can be screwed to the top, using a fine thread (10 threads per cm). It was experimentally verified that escape of vapour between the cell and the lid is negligible compared with that through the effusion orifice. Effusion orifice area was built 1.0201×10^{-2} cm^2 at the centre of a thin brass foil (thickness 5.0×10^{-2} cm) which is soldered on the hole of the brass lid. The effusion cell fits tightly in the aluminum block, which sits in a glass tube (cell-holder) connected to the cold finger and consequently to the vacuum system. The inside diameter of the cell-holder is 4.5 cm and the aluminum block is fitted in such a way that the thermal resistance is minimized. The thermostatic bath is raised by means of a car jack until the bath liquid is higher than the top of the cell. The bath temperature is controlled electronically and maintained within ±0.005°C. After allowing the sample temperature to reach equilibrium, the cold finger is filled with liquid nitrogen after reaching a system vacuum of about 10^{-3} Pa. The main vacuum maintained by the diffusion pump is connected and time is recorded. After a suitable time (2–8 h, depending on the volatility of the substance) the pumps are disconnected and when the pressure returns to atmospheric, the cell is removed to a desecrator. After cooling to room temperature the cell is weighed to a constant weight (±0.01 mg) and the weight loss (Δm) calculated. Bath temperature T (K) is recorded throughout the experiment[10].

RESULTS AND DISCUSSION

The vapour pressure is calculated by[5-13]:

$$p_m = \frac{\Delta m\sqrt{2\pi RT/M}}{Awt} \quad (1)$$

where p_m is pressure near the orifice, Δm is the weight loss of vapour which escapes through the orifice surface area A in time t, W is the Clausing probability factor for the orifice (varying from zero to one[11]), R is the universal gas constant, T is temperature and M is molecular weight of the sample. Value of W according to the orifice area is given as 0.9712. If the size of particles in the sample is very small and vacuum is very low, p_m will be equal to the equivalent vapour pressure, p.[13, 14]

According to the Clausius-Clapeyron equation, if the heat of sublimation of a substance is assumed independent of temperature over the range used, the plot of the logarithm of vapour pressure *vs.* reciprocal absolute temperature would yield a straight line.

$$\ln p = -\Delta H_{sub}/RT + c \quad (2)$$

where ΔH_{sub} is the molar heat of sublimation and c is the logarithm of the theoretical pressure at infinite temperature.

The reliability of the present implementation of the standard isothermal Knudsen effusion technique was tested using benzoic acid. Generally the result is in very good agreement with literature values of heat of sublimation of benzoic acid ($\Delta H_{sub} = 92.3 \pm 0.4$ kJ mol^{-1}); then vapour pressure, temperature dependence of vapour pressure and heat of sublimation of *o*-nitro benzyl chloride were measured.

The values of vapour pressure of benzoic acid and *o*-nitro benzyl chloride at different temperatures are listed in Tables 1 and 2.

TABLE-1
EXPERIMENTAL RESULTS FOR KNUDSEN VAPOUR PRESSURE OF BENZOIC ACID

T (K)	t (s)	Δm (mg)	P (Pa)
313.25	28800	41.4	0.526
316.68	26280	54.9	0.769
316.70	25200	53.9	0.787
320.97	18000	59.7	1.229
320.97	21000	57.3	1.272
324.14	12600	58.6	1.732
324.15	14460	66.2	1.705

TABLE-2
EXPERIMENTAL RESULTS FOR KNUDSEN VAPOR PRESSURE OF *o*-NITRO BENZYL CHLORIDE

T (K)	t (s)	Δm (mg)	P (Pa)
308.28	25200	22.1	0.269
308.29	25200	22.3	0.271
310.66	25200	29.0	0.354
310.66	25200	29.2	0.356
313.05	25200	40.0	0.490
313.06	12000	19.0	0.489
315.64	21600	45.0	0.646
315.68	25200	54.0	0.664
318.21	20400	56.4	0.860
318.22	25200	56.5	0.862

All the data are well approximated by the Clasius-Clapeyron equation, with a constant enthalpy of sublimation which is calculated from plotting the logarithm of the vapour pressure against reciprocal absolute temperature, Figs. 1 and 2. Temperature dependence of vapour pressure in the temperature range of 313–325 K for benzoic acid and 308–319 K for *o*-nitro benzyl chloride are found to be $\ln p = 11034 \times 1/T + 34591$ and $\ln p = 11571 \times 1/T + 36224$, respectively. Consequently, the calculated values of heats of sublimation for benzoic acid and *o*-nitro benzyl chloride are $\Delta H_{sub} = 91.74 \pm 3.45$ kJ mol^{-1} and $\Delta H_{sub} = 96.20 \pm 3.45$ kJ mol^{-1}, respectively, while these values are not in references.

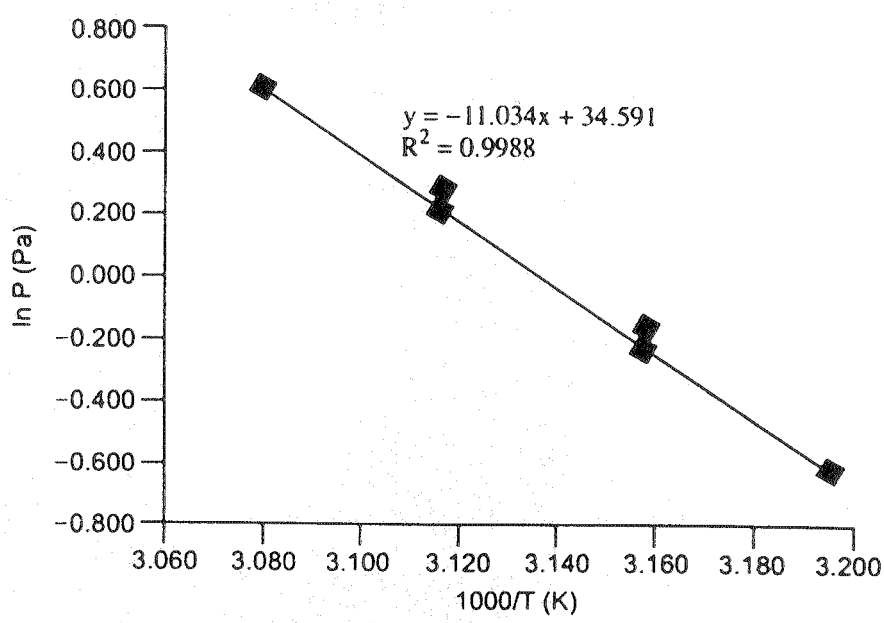

Fig. 1. Correlation between ln P and 1000/T for benzoic acid

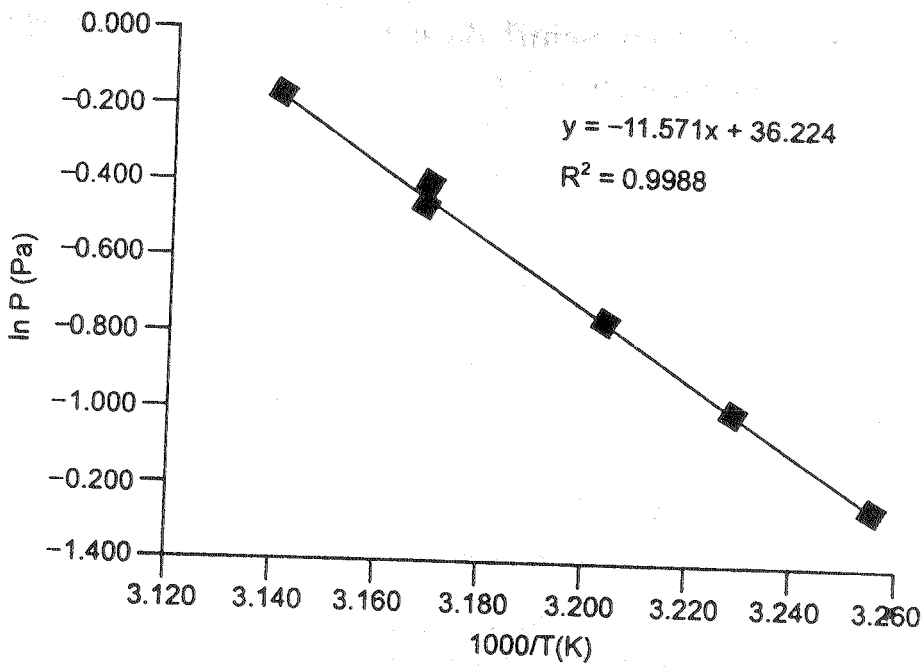

Fig. 2. Correlation between ln P and 1000/T for ortho-nitro benzyl chloride.

REFERENCES

1. M.S. Monte and D.M. Hillesheim, *J. Chem. Eng. Data*, **4**, 1088 (2000).
2. L. Malaspina, R. Gilgli and G. Bardi, *J. Chem. Thermodyn.*, **3**, 827 (1971).
3. A. Gavezzotti, *J. Am. Chem. Soc.*, **111**, 1835 (1989).
4. ———, *J. Phys. Chem.*, **95**, 8948 (1991).
5. I. Langmuir, *Phys. Rev.*, **2**, 329 (1913).
6. M. Knudsen, *Ann. Physik.*, **29**, 179 (1909).
7. R. Speiser and H.L. Johnson, *Trans. Am. Soc. Metals*, **42**, 283 (1950).
8. A.N. Nesmeyanov, Vapour Pressure of the Chemical Elements, Elsevier, Amsterdam (1990).
9. E.H. Kennard, Kinetic Theory of Gases, McGraw-Hill Book Co., New York (1938).
10. M. Ribero da Silva and M. Monte, *J. Thermochim. Acta*, **171**, 169 (1990).
11. P. Clausing, *Ann. Physik.*, **12**, 961 (1932).
12. S. Dushman, Scientific Foundatation of Vacuum Techniques, John Wiley & Sons, Inc., New York (1962).
13. K. Motzfeldt, *J. Phys. Chem.*, **59**, 139 (1955).
14. C.L. Whiman, *J. Phys. Chem.*, **20**, 161 (1952).

(*Received*: 21 February 2005; *Accepted*: 26 September 2005) AJC-4408