

# Combined experiments to measure low sublimation pressures and diffusion coefficients of organometallic compounds

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Received 24 July 2006; received in revised form 27 October 2006; accepted 27 October 2006

Available online 6 December 2006

## Abstract

Vapor pressures and sublimation pressures of organometallic (metalorganic) compounds are needed in several processes like chemical vapor deposition (CVD). Thermobalances at ambient pressures are often used to study the evaporation of such compounds. At least three strategies are found in the literature to evaluate the results using different theoretical approaches. In some of the frequently used approaches the diffusion out of a crucible is neglected. We present a simple theoretical approach which describes the interrelation between the observed mass transfer rate and the physical variables of typical TGA set-ups. It turns out that the mass transfer rate at a given total pressure and temperature is mainly a function of the diffusion coefficient and the vapor pressure of the sublimating substance. The vapor pressures may be determined from an independent measurement using the Knudsen cell and combined with the TGA to obtain the diffusion coefficients. Experiments have been performed with two well studied substances naphthalene and phenanthrene to check the present strategy. Further measurements were then performed for the metal organic CVD relevant compounds: ferrocene and Tris(2,2,6,6-tetramethyl-3,5-heptanedianato)cobalt III [Co(tmhd)<sub>3</sub>].

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*Keywords:* Vapor pressure; Metalorganic compounds; Ferrocene; Cobalt salts; Diffusion coefficients; Naphthalene; Phenanthrene

## 1. Introduction

Species with low but observable vapor pressures are interesting for several applications. One of these is the chemical vapor deposition (CVD), which is of main interest for us [1]. For this process the precursor molecules (which often are metalorganic compounds) are evaporated. In such a process after the evaporation of one or more precursor molecules that include the elements which shall be present in a deposited thin film (or coating), are mixed and flown to a substrate. There the energy (thermal energy) is provided to initiate a chemical reaction so that films of metals, oxides or other compounds are formed. To engineer such a process the knowledge of the vapor or sublimation pressures is essential because they determine the maximum theoretical growth rate and the composition. Due to the low vapor pressures and consequently the requirement of a sophisticated experimental procedure, often either no information is available, or the data are contradictory. The latter may have dif-

ferent reasons: some of the used precursors are not thermally stable, so that evaporation may be accompanied by pyrolysis, also sometimes the methods might not have been appropriate. Since the thermal balances are available in many laboratories it is evident that different researchers tried to use these devices to measure the needed data. At least three approaches are found in the literature for vapor pressure data evaluation.

One approach (A) is the Knudsen effusion method [2] (thermogravimetry in vacuum). It is based on the kinetic theory of gases. As soon as the mean free path length is larger than the typical dimensions of an orifice (area:  $S$ ) which separates the sublimating substance from its surrounding, the mass loss rate from the cell ( $\Delta m/\Delta t$ ) is determined by the area of the hole (orifice) and the vapor pressure; this rate is the rate of effusion from the cell. For steady state effusion the following formula gives the mass loss rate:

$$\frac{\Delta m}{\Delta t} = \frac{p^{\text{vap}} S}{\sqrt{2\pi RT/M}} \quad (1)$$

Here  $M$  is the molecular mass and  $p^{\text{vap}}$  the vapor (or sublimation) pressure,  $T$  the temperature and  $R$  is the universal gas constant. Eq. (1) is strictly valid for an “ideal” hole, i.e., a hole in a sheet of

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infinitely small thickness. For finite sheet thicknesses (where the height of the orifice is not negligible) an additional correction factor [3] (Clausing factor),  $K$  is taken into account and the expression (1) becomes:

$$\frac{\Delta m}{\Delta t} = \frac{p^{\text{vap}} S}{\sqrt{2\pi RT/M}} \times K \quad (2)$$

The main presuppositions for the application of this formula are the low pressure regime and the evaporation of non-associated molecules. Without a recognizable reason and for the sake of easiness this method was later adopted for the thermogravimetric measurements at ambient pressures. In these experiments calibrations were necessary [4,5]. As soon as the calibration was performed with a molecule with a comparable diffusion coefficient the results are good although the applied theory is not correct. We will see why.

The second method (B) is the transpiration method [6]. The main idea is that the flowing inert gas is totally saturated by the evaporating substance. Applying Dalton's law and the known flow rate of the buffer (inert) gas one can calculate the vapor pressure of the substance of interest.

$$p^{\text{vap}} = \frac{\dot{m}RT_a}{\dot{V}M} \quad (3)$$

where  $\dot{m}$  is the mass flow rate of the transported compound,  $M$  its molar mass,  $T_a$  the temperature at which the gas flow rate is measured,  $\dot{V}$  the volumetric flow rate of the transporting gas and  $R$  is the universal gas constant. If the flow is too fast, saturation will not be achieved, if the flow is too slow back diffusion against the flow direction might be a problem. Therefore, smart flow geometries were designed and the independence of the rate of sublimation from flow rate had to be established. The geometry of typical thermo balances is not well suited for this approach, and without exact information on the used geometry and flow velocity those measurements are difficult to reproduce. In recent past the technique has been improved for the measurement of vapor pressures of high molecular weight hydrocarbons as low as  $10^{-3}$  Pa [7,8].

A third method (C) assumes that in TGA experiments where crucibles are used to contain the substance the purge rate has no effect on the vaporisation rate; at the surface of the substance a saturated mixture is assumed as one boundary condition, while the mole fraction of the evaporating substance at the top of the crucible is assumed to be zero. Thus the height of the crucible above the substance may be taken as effective boundary layer thickness [9]. Under these conditions the vapor pressure of evaporating species is related to the weight loss under isothermal conditions:

$$p^{\text{vap}} = \frac{\Delta m}{\Delta t} \frac{RTd}{SMD_{AB}} \quad (4)$$

where  $R$  is the universal gas constant,  $T$  the temperature in K,  $d$  the length of the free space above the substance in the crucible (boundary layer thickness),  $S$  the area of the substance evaporation surface,  $M$  the molar mass of the substance and  $D_{AB}$  is the diffusion coefficient of substance A in the carrier gas B. Nyman et al. [9] estimated the diffusion coefficient; however,

they did not consider the change in height (effective boundary layer thickness) during the experiment. X-ray data was used by these authors to estimate the molecular diameter which in turn is used to calculate the diffusion coefficient. The curvature of the mass versus time curves is no problem if the initial rate is evaluated, but the curvature of the slopes can be explained by a slightly more complicated theory.

In the present communication one-dimensional diffusion theory will be applied to TGA experiments to derive a simple formula for the evaluation of vapor pressure and diffusion coefficients from mass loss rates. The latter are also needed for the calculation of the Sherwood and Lewis number used to describe mass transfer processes. Naphthalene, phenanthrene, ferrocene and Tris(2,2,6,6-tetramethyl-3,5-heptanedianato)cobalt III [Co(tmhd)<sub>3</sub>] were studied. Naphthalene and phenanthrene are well known substances for which sublimation/vapor pressure and diffusion coefficient values are found in literature. Ferrocene and Co(tmhd)<sub>3</sub> are interesting and stable precursor for CVD processes [10] and were studied for this reason.

## 2. Theory

In a typical TG/DTA apparatus the sample crucible and a reference crucible are placed on a sample holder in a horizontal tube furnace in a gas stream. The sample crucible is filled to some amount with the substance to be investigated. This amount is changing with time due to evaporation. If the vapor pressure of the sample is low (below 10 mbar at a total pressure of 1000 mbar) the deviation of the mole fraction of the inert gas from unity can be neglected. The theory can also be adapted for other conditions, but this is not interesting for our purposes. According to the theory of diffusion processes the crucible may be approximated as a one-dimensional quasi-stationary system where a constant concentration of the substance is fixed at the (slowly moving) surface of the substance due to the loss of the substance from the crucible, while at the upper edge of the crucible the concentration of the substance is negligible. The mass change rate is determined by the diffusion rate out of the crucible. The derivation is adapted from the textbook by Bird et al. [11]. The starting point is the mass balance, which basically states that the molar evaporation rate of the sample is equal to the molar diffusion rate out of the pan in the gas phase:

$$S \frac{\rho_A}{M_A} \frac{dh(t)}{dt} = \frac{cD_{AB}}{H + h(t)} (x_{A,\text{surf}} - x_{A,\text{top}}) S \quad (5)$$

Here  $\rho_A$  is the apparent density of the evaporating substance A and  $M_A$  is its molecular mass.  $H$  is the initial distance between the surface of the substance and the top of the cylinder,  $S$  the surface area of the evaporating substance,  $h(t)$  the time dependent height of the sample evaporated, being zero initially and getting positive at longer times;  $c$  the molar density of the gas ( $c = p/RT$ ;  $p$  being the total pressure);  $x_{A,\text{surf}}$  the mole fraction of A at the surface and  $x_{A,\text{top}}$  is its mole fraction at the top. Since the change in height is quite slow the steady state evaporation rate at any time  $t$  has been used on the right hand side of Eq. (5).

The mole fraction of the vapor at the top of the cylinder can be neglected if the buffer gas flow rate is high enough (i.e.  $x_{A,top} \approx 0$ ). The ideal gas law ( $p = cRT$ ) and Dalton's law ( $p_A = x_{A,surf}p$ ) are used to integrate between the starting time and a given time,  $t$ :

$$\int_0^h [H + h(t)] dh = \frac{p_A^{\text{vap}} D_{AB} M}{RT\rho_A} \int_0^t dt \quad (6)$$

The solution of the integration

$$h = \sqrt{\left( H^2 + \frac{2p_A^{\text{vap}} D_{AB} M}{RT\rho_A} t \right)} - H \quad (7)$$

is then used to derive an expression between the mass loss and the evaporation time, or for the product of vapor pressure and the binary diffusion coefficient:

$$\begin{aligned} p_A^{\text{vap}} D_{AB} &= \left\{ (h + H)^2 - H^2 \right\} \frac{RT\rho_A}{2Mt} \\ &= \left\{ \left( \frac{\Delta m}{S\rho_A} + H \right)^2 - H^2 \right\} \frac{RT\rho_A}{2Mt} \end{aligned} \quad (8)$$

The problem is now that the diffusion coefficient is in general unknown. However, from the kinetic theory of gases an expression can be derived for its calculation [12]:

$$D_{AB} = \frac{0.00266T^{3/2}}{pM_{AB}^{3/2}\sigma_{AB}^2\Omega_D} \quad (9)$$

Here  $p$  is the pressure in bar,  $T$  the temperature in K,  $M_{AB} = 2/(1/M_A + 1/M_B)$  where  $M_A$  and  $M_B$  are the molecular masses of substance A and the carrier gas B. The characteristic length  $\sigma_{AB}$  in Angstrom units and the diffusion collision integral  $\Omega_D$  can be calculated by selecting an intermolecular force law, e.g. Lennard-Jones.

This expression shifts the problem to two new unknowns: the collision diameter  $\sigma_{AB}$  and the collision integral  $\Omega_D$ . The latter is a function of temperature and could vary by 30–40% in the interesting temperature range, while the former can be estimated by XRD data (if available) and should be only a weak function of temperature. For organic compounds there are empirical rules for their estimation, but little is known for organometallic compounds. Both can be determined by the methods of theoretical chemistry and molecular dynamics, but for validation some experimental data are needed. If the experimental approach shall be followed further, some independent method is needed to measure either the diffusion coefficient or the vapor pressure. What is done often is to use a calibration compound, of similar size and if possible of similar intermolecular potential, with known vapor pressure. If the mass loss curve is measured with such a compound, a correlation between mass loss and vapor pressure can be established, assuming implicitly that the diffusion coefficients are the same. Since little is known about the diffusion coefficients of such compounds, the errors are difficult to estimate. Another point can easily be seen from the formula given above: the mass loss rate is a function of  $H$ , the initial distance

between the surface and the top of the cylinder and the mass loss is not a linear function of time. For short measurement times the difference to a linear curve is very small and not recognized by most workers; however, for longer measurement times the deviation from linearity is obvious, this is also observed by Nyman et al. [9] and us. Also  $H$  is in general not stated in the literature and its influence was probably neglected. So with a simple theory, several important features of an isothermal TGA evaporation experiment can be rationalized. The theory could also be easily expanded to non-isothermal conditions, but this is not of interest here.

We followed another approach and measured the vapor pressure independently with a method, which does not depend on diffusion in the continuum range. We constructed a Knudsen cell with well defined orifice and measured the vapor pressures. These experimental vapor (sublimation) pressures together with the measurements of the TG/DTA apparatus were then used to evaluate the diffusion coefficients, which are also important for the construction of mass transfer equipments. The Knudsen experiment was evaluated using Eq. (2) and a theoretical correction factor which accounts for the finite thickness of the walls of the orifice, taken from Ref. [3].

### 3. Experimental

Naphthalene (>99%), phenanthrene (purity >98%) and ferrocene (purity >99%) were purchased from Merck. For vapor pressure measurements these were purified by sublimation. Some measurements were also performed using untreated samples. The vapor pressures of purified samples did not differ from those of the untreated samples. Hence for further thermogravimetric experiments the substances were used as such.  $\text{Co}(\text{tmhd})_3$  (>99%) was purchased from ABCR GmbH & Co. and used without further purification. He (99.998%),  $\text{N}_2$  (99.98%), synthetic air (99.98) or  $\text{CO}_2$  (99.95) were used as carrier gases.

The Knudsen cell was home built from stainless steel (internal diameter: 12 mm, height: 28 mm). The lid had a central hole (9 mm diameter). This was covered with a thin aluminium foil. A small circular effusion orifice was drilled in the foil. The thickness of the aluminium foil was 80  $\mu\text{m}$ . The lid together with the foil was well tightened with screws, so that the system was vacuum tight. The diameter of the orifice was measured with a microscope to be 0.765 mm. From the ratio of orifice diameter to the foil thickness, the correction factor for the correlation between mass loss rate and vapor pressure can be derived [3] to be 0.9058. The Knudsen cell is situated in a stainless steel vessel [vacuum chamber] with good thermal contact around the cell, which in turn is in a thermostated fluid. The temperature of the thermostated fluid was measured with a mercury thermometer. It was ensured that the thermal equilibrium between the sample and the thermal reservoir was attained. A silicone thermal paste was used as thermal conducting material. The Knudsen cell is evacuated with the help of a vacuum system consisting of a turbo molecular pump (Pfeifer TMH 071P), a pre-vacuum pump (diaphragm backing pump, Pfeifer MVP 055-3) and a pressure gauge (Pfeifer TPG 261). The experimental setup is shown in Fig. 1. The pressure in the system was always below

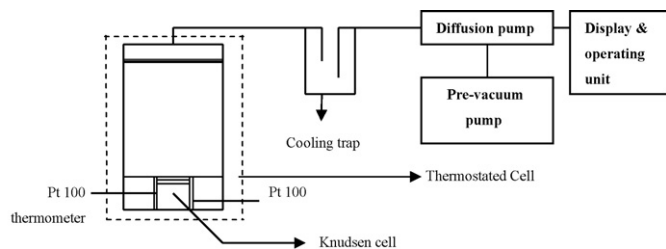


Fig. 1. Schematic representation of the measuring system (Knudsen cell).

$10^{-7}$  Pa during each experimental run. A well defined amount of the substance (depending upon the temperature of the measurement and the substance) was weighed (accuracy: 0.03 mg) into the cell. The cell was then tightened and put into the vacuum chamber. The whole assembly was thermostated in the thermal bath whose temperature was maintained constant to better than  $\pm 0.1$  K. Enough time (at least 30 min) was allowed for the attainment of a constant temperature which was recorded with the help of a calibrated Pt-100 thermometer. After evacuating the vacuum chamber the time was measured between the time when the vacuum reached the pressure of around  $10^{-3}$  Pa and the time when the high vacuum pump was turned off and the pressure was above  $10^{-3}$  Pa. Typical times were 1–3 h (in this time the weight losses were between 20 and 50 mg depending on the hole size, the temperature and the substance). The cell was then brought to room temperature in a desiccator and weighed again. The uncertainties in the evaporation time and in the mass loss are estimated to be 0.5 min and 0.05 mg, respectively. In the evaluation of the data, no additional calibration was performed. The maximum overall uncertainty in vapor pressure measurements was estimated to be  $\pm 0.1$  to  $\pm 0.5$  Pa in the pressure range 10–50 Pa and  $\pm 0.02$  to  $\pm 0.1$  Pa in the pressure range 0.4–10 Pa. This overall uncertainty was calculated assuming that the uncertainties in evaporation time, mass loss and the correction factor are independent and random.

A commercial TGA/DTA (Bähr STA 503) was used to perform the thermogravimetric experiments. The atmosphere was well defined: either He or N<sub>2</sub> or CO<sub>2</sub> or synthetic air. The flow rate of 100 cm<sup>3</sup>/min (for nitrogen) was controlled by a calibrated mass flow controller. This flow rate was found to be sufficient to ensure that the concentration of substance at the top of the crucible remains nearly zero throughout the measurement as proved experimentally: a change in flow rate did not change the mass loss rate measurably. The pressure was throughout atmospheric. Open alumina crucibles were used in all experiments; the inner diameter being 5.35 mm, the inner height is 7.2 mm. The samples were filled inside the crucible, so that the initial height of the sample inside the crucible was between 3.0 and 5.0 mm. From the initial height, which was measured in the beginning of each experiment with an estimated accuracy of  $\pm 0.2$  mm, the volume of the sample was calculated. Using the initial mass the apparent density of the sample was derived. The temperature was typically reached within 30 min, and then the temperature was held constant, in some experiments until all the sample was evaporated, in other experiments the temperature was changed after 2 h to the next temperature, so that several temperatures

could be investigated within one run. The temperature sensor was calibrated by measuring the melting points of reference substances (4-nitrotoluene, naphthalene, indium and potassium perchlorate) which cover the whole temperature range for the measurements. The uncertainty in mass loss rate was estimated to be  $\pm 1$  and  $\pm 10\%$  for the apparent density and for the diffusion coefficient  $\pm 0.005$  to  $\pm 0.015$  cm<sup>2</sup> s<sup>-1</sup> depending on the system and arising mainly from the uncertainties in the initial distance between the sample surface and the top of the crucible. This overall uncertainty in diffusion coefficient was calculated considering the uncertainties in vapor pressure, initial height of the sample and the mass loss rate given above to be independent and random.

## 4. Results and discussion

### 4.1. Vapor pressures from the Knudsen cell

The sublimation pressure, vapor pressure and the diffusion coefficients of phenanthrene are known over a range of temperatures and so this compound was investigated first. The measured vapor pressure results are shown in Fig. 2 as a function of  $1/T$ . Some well known literature values are also shown as lines. The agreement with the data from literature [13] is excellent. The enthalpy of sublimation derived from these vapor pressure values (from the slopes of the  $\ln(p)$  versus  $1/T$  plots) is  $87970 \pm 2000$  which is in good agreement with the values reported in literature [13] and reproduced in Table 1 for a ready reference. This shows the reliability of the method.

The vapor pressure as a function of temperature was fitted to an Antoine expression, with pressures in kPa and temperatures in K:

$$\log(p/\text{kPa}) = A_i - \frac{B_i}{(T/\text{K} + C_i)} \quad (10)$$

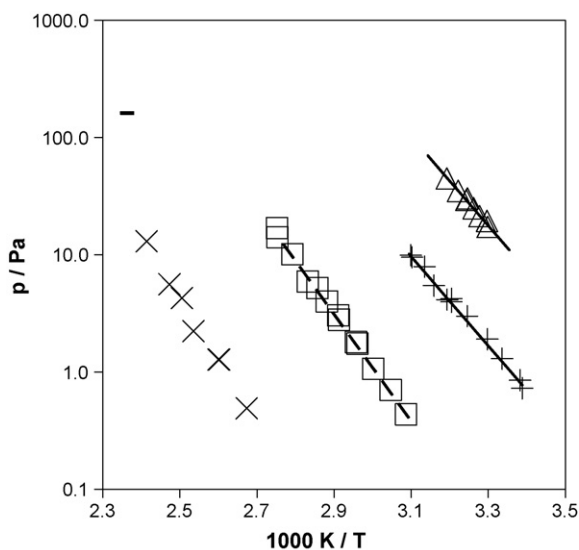


Fig. 2. Vapor pressure of phenanthrene (□), naphthalene (Δ), ferrocene (+), and Co(tmhd)<sub>3</sub> (×) as a function of inverse temperature (---) and (—) literature values.

Table 1  
The constants for Eq. (10)

Substance	$A_i$	$B_i$	$C_i$	$\Delta_{\text{sub}}H_m$ (exp.) (temperature, J mol <sup>-1</sup> )	$\Delta_{\text{sub}}H_m$ (lit.) (temperature, J mol <sup>-1</sup> )
Phenanthrene	10.83	4591.0	0.0	87970 ± 1000 (323–363 K)	90500 ± 2000 [14] (315–335 K), 87240 ± 2200 [14] (350 K)
Naphthalene	8.61	2619.8	-50.1	71780 ± 1000 (303–313 K)	73000 ± 500 [14] (220–353 K)
Ferrocene	9.78	3800.0	0.0	72700 ± 1000 (295–325 K)	72070 ± 720 [14] (278–309 K); 72370 ± 1080 [14] (293–309 K)
Co(tmhd) <sub>3</sub>	11.19	5423.6	0.0	103790 ± 1000 (374–414 K)	132000 [17] (433–463 K)

The Antoine equation constants are given in Table 1.

The sublimation pressures for naphthalene, ferrocene and Co(tmhd)<sub>3</sub> were also measured at different temperatures and fitted to obtain Antoine equation constants which are listed in Table 1. The derived enthalpy of sublimation is also shown in Table 1 together with the temperature range. The values for the sublimation pressures at various temperatures and the enthalpy of sublimation for naphthalene and ferrocene compare well with the values found in literature [14–16]. For Co(tmhd)<sub>3</sub> the available values [17] for vapor pressure 1.211 Torr (=161 Pa) at 150 °C and enthalpy of sublimation (132 kJ mol<sup>-1</sup> for temperature range 160–190 °C) are higher than our extrapolated values (24 Pa at 150 °C and 103.8 kJ mol<sup>-1</sup>, respectively).

#### 4.2. Diffusion coefficients from thermogravimetric measurements

The thermogravimetric experiments with the four substances were performed at four temperatures between 307 and 367 K keeping the sample at each temperature for 2 h before going to the next temperature, using different carrier gases: helium, nitrogen (synthetic air) and carbon dioxide. This was done to test the effect of diffusion, because the binary diffusion coefficient should strongly depend on the molecular weight of the carrier gas (see Eq. (9)). The mass loss rates were found to be different in all the three cases as expected from the theory given above. The mass loss rate in helium atmosphere was greater than that in nitrogen atmosphere which again was greater than in carbon dioxide atmosphere. Fig. 3 shows typical mass loss curves for naphthalene at four temperatures (307, 327, 347 and 367 K) with different carrier gases as an example. Four different slopes (depending upon the temperature) can be observed in each curve. The same behaviour was observed with all other substances studied here. Such differences could not be explained using the approaches (A) and (B), both should give mass loss rates which are independent of the molecular weight of the buffer gases. A typical isothermal experiment is shown in Fig. 4 where the slight curvature is easily noticed. It may be emphasized here that the slope of this curve is -0.098 mg/min in the first 20 min (dashed curve) and -0.067 mg/min in the last 20 min.

The binary diffusion coefficients of the substances in carrier gases were calculated from the experimental mass loss ( $\Delta m$ ) as a function of time  $t$ , the initial distance between the surface of the investigated substance and the top of the crucible  $H$  observed in thermogravimetric experiments and the sublimation pressures using Eq. (8). Fig. 5 shows the diffusion coefficients of naphthalene in air (or nitrogen: no difference could be observed between the two values). No error bars are included in the figures, because

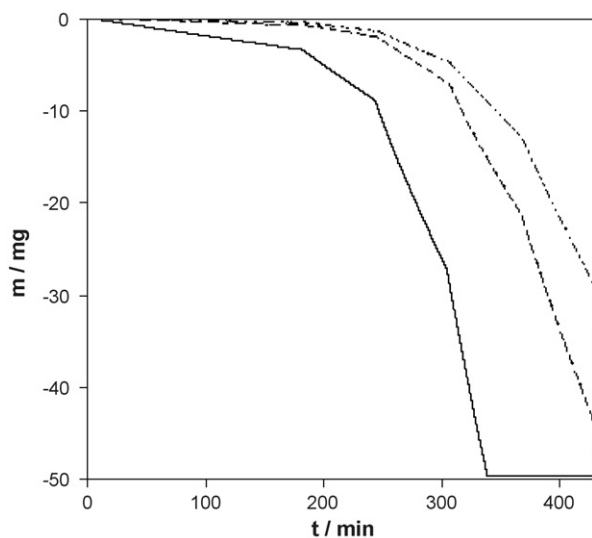


Fig. 3. The mass loss for naphthalene (50.6 mg) at 307, 327, 347 and 367 K under different carrier gas atmospheres, (—) helium, (---) nitrogen, and (···) carbon dioxide.

the symbol size selected are large enough to include the errors. The mean values for at least three runs are given in Table 2. Two different values for  $D_{12}$  for naphthalene-air system are found in the literature [18–21], which are also shown on the plot. Our mean value  $0.085 \text{ cm}^2 \text{ s}^{-1}$  at 307 K is higher than the value of Chen et al.,  $0.072$  [18] but agrees quite well with  $0.086 \text{ cm}^2 \text{ s}^{-1}$

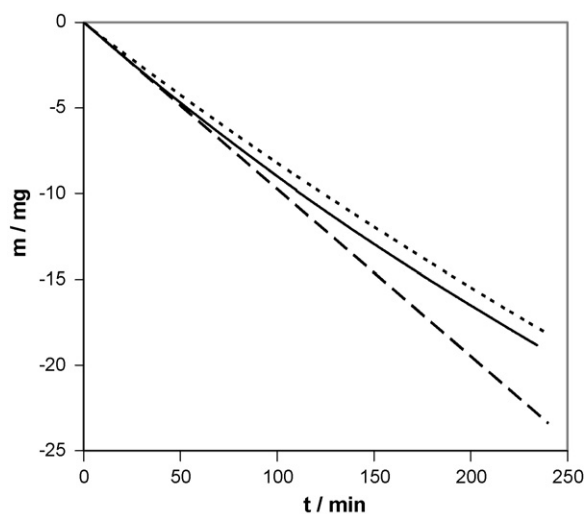


Fig. 4. The mass loss for naphthalene (50 mg) at 343.6 K as a function of time under nitrogen atmosphere, (---) initial slope, (—) experimental, and (···) theoretical.

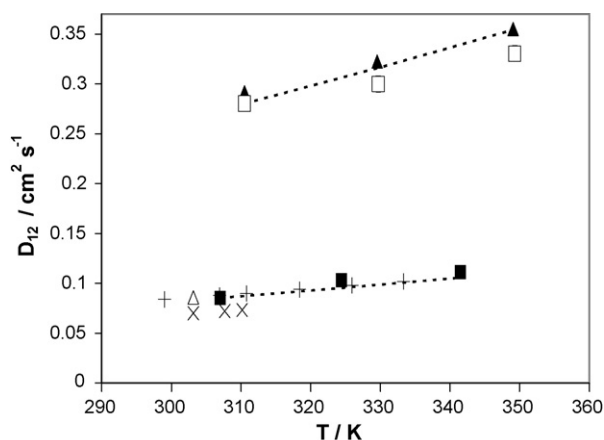


Fig. 5. Diffusion coefficient of naphthalene at various temperatures: (■) mean value (nitrogen or air), (□) mean value (helium), (▲) theory (helium), (×) Ref. [18], (Δ) Ref. [19], (+) Ref. [20], and (---) temperature dependence  $\sim T^2$ .

at 303.15 K measured by Caldwell [19] and 0.088 measured by Delgado et al. [20] at 307 K. A value of  $0.0834 \text{ cm}^2 \text{ s}^{-1}$  at 298.15 K for the diffusion coefficient of naphthalene–air system is quoted in a recent publication [21]. The variation of diffusion coefficient with the square of absolute temperature is shown as dotted line. This dependence can be obtained from the kinetic theory of gases if both the  $T^{1.5}$  dependence of hard sphere diffusion and the temperature dependence of the collision integral are taken into account [12,22]. The diffusion coefficients of naphthalene in helium are also shown in Fig. 5. No experimental values are available for  $D_{12}$  of the naphthalene–helium system and so the results are compared with theoretical values calculated with Eq. (9) using the characteristic parameters evaluated from the critical data from literature [12] and following the method of Neufeld et al. [23] quoted in [9] (see p. 11.6). As expected

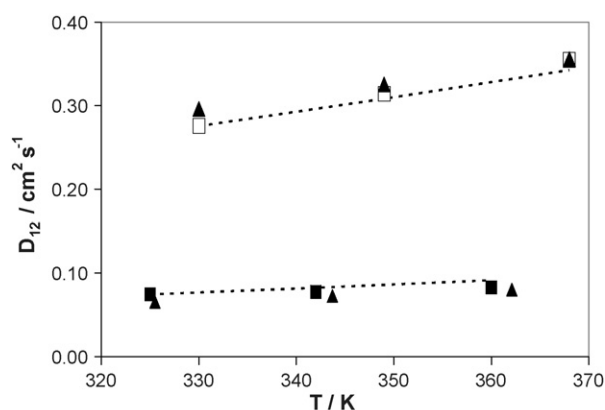


Fig. 6. Diffusion coefficient of phenanthrene at various temperatures: (■) mean value (nitrogen), (□) mean value (helium), (▲) theory, and (---) temperature dependence  $\sim T^2$ .

the  $D_{12}$  values for naphthalene in helium are higher than in air.

The  $D_{12}$  for phenanthrene–nitrogen and phenanthrene–helium systems are shown in Fig. 6 together with the values calculated from theory. The variation of diffusion coefficient with the square of absolute temperature is shown as dotted line. The values for  $D_{12}$  (in air) quoted in literature are 0.0597 and 0.0731 at 298.15 K [21]. Figs. 7 and 8 show the results for the diffusion coefficient of ferrocene and  $\text{Co}(\text{tmhd})_3$  in nitrogen and helium, respectively.

Measurements were also performed in  $\text{CO}_2$  atmosphere. The  $D_{12}$  values were  $0.05 \text{ cm}^2 \text{ s}^{-1}$  for naphthalene at 307.05 K,  $0.050 \text{ cm}^2 \text{ s}^{-1}$  for phenanthrene at 343.15 K and  $0.034 \text{ cm}^2 \text{ s}^{-1}$  for  $\text{Co}(\text{tmhd})_3$  at 415.15 K and followed the quadratic temperature dependence. These values were lower than the corresponding values in air as expected from the theory.

Table 2

Binary diffusion coefficients  $D_{12}$  for various systems at 1 bar

Naphthalene–air (or nitrogen)						
Temperature (K)	307.0	324.4	341.5			
$D_{12}$ ( $\text{cm}^2 \text{ s}^{-1}$ )	0.085	0.103	0.111			
Naphthalene–helium						
Temperature (K)	310.5	329.7	349.3			
$D_{12}$ ( $\text{cm}^2 \text{ s}^{-1}$ )	0.280	0.300	0.331			
Phenanthrene–nitrogen						
Temperature (K)	325.0	342.0	360.0			
$D_{12}$ ( $\text{cm}^2 \text{ s}^{-1}$ )	0.075	0.078	0.083			
Phenanthrene–helium						
Temperature (K)	330.0	349.0	368.0			
$D_{12}$ ( $\text{cm}^2 \text{ s}^{-1}$ )	0.276	0.314	0.355			
Ferrocene–nitrogen						
Temperature (K)	308.2	325.0	341.0	359.0	376.0	392.9
$D_{12}$ ( $\text{cm}^2 \text{ s}^{-1}$ )	0.079	0.088	0.097	0.106	0.119	0.128
Ferrocene–helium						
Temperature (K)	329.5	348.8	368.0	387.5		
$D_{12}$ ( $\text{cm}^2 \text{ s}^{-1}$ )	0.254	0.283	0.315	0.359		
$\text{Co}(\text{tmhd})_3$ –nitrogen						
Temperature (K)	376.3	395.0	413.0	432.0	450.0	
$D_{12}$ ( $\text{cm}^2 \text{ s}^{-1}$ )	0.057	0.065	0.068	0.080	0.087	
$\text{Co}(\text{tmhd})_3$ –helium						
Temperature (K)	388.6	408.0	415.7	427.7	447.0	466.5
$D_{12}$ ( $\text{cm}^2 \text{ s}^{-1}$ )	0.145	0.147	0.152	0.161	0.179	0.184

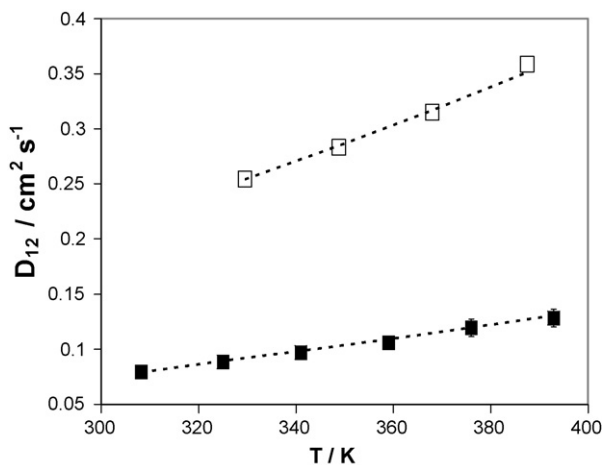


Fig. 7. Diffusion coefficient of ferrocene at various temperatures: (■) mean value (nitrogen), (□) mean value (helium), and (---) temperature dependence  $\sim T^2$ .

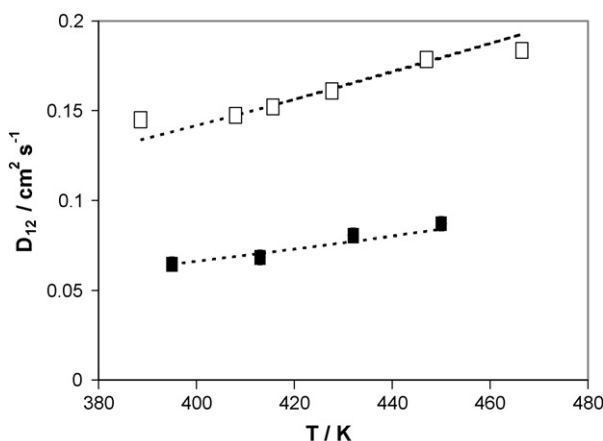


Fig. 8. Diffusion coefficient of  $\text{Co}(\text{tmhd})_3$  at various temperatures: (■) mean value (nitrogen), (□) mean value (helium), and (---) temperature dependence  $\sim T^2$ .

## 5. Conclusions

The present work offers a method for the evaluation of diffusion coefficients of less volatile substances in gas mixtures. Easily performed experimental thermogravimetric measurements for organometallic compounds may be combined with accurate vapor pressure data to determine their diffusion coefficients in various gases with reasonable accuracy. It has been shown that the mass loss rate in TG measurements depends on the product vapor pressure and diffusion coefficient and hence if vapor pressures are to be drawn from thermogravimetric measurements the effect of diffusion must be taken into account.

Alternatively, if the diffusion coefficients of reasonable accuracy are available from theoretical methods (cf. Eq. (9)) or from molecular dynamics simulations [24], these may be combined with the experimental thermogravimetric data to derive the vapor pressures.

## Acknowledgement

The authors thank A. Görnt and M. Richter for technical assistance. We are grateful to the Deutsche Forschungsgemeinschaft (Schwerpunktprogramm SPP 1119) for financial support.

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