

VAPOUR PRESSURE MEASUREMENTS WITH A THERMOBALANCE

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Abstract

The 'Modified Entrainment Method' developed by Faktor *et al.* [1] is an attractive yet not very popular method to determine vapour pressures in the range of 0.002 to 0.1 bar at 10–1000°C. The method consists of evaporating a solid or liquid from a small bulb through a capillary into a flowing inert gas, e.g. argon. The vapour pressure of the sample is related to the rate of evaporation and some easily controlled experimental parameters. In the present paper a new convenient experimental set-up is described and its use to study the decomposition of metal complexes is illustrated.

Keywords: decomposition, metal complex, vapour pressure

Introduction

In solution, the stability of metal complexes is governed by two contributions, i) the energy of the metal–ligand bond and ii) the solvation energies of the reaction partners. In order to distinguish between the two contributions complete thermodynamic cycles have to be established i.e. the metal complex formation has to be studied in the gas phase and solvation energies have to be measured. For examples see [4–7]. A prerequisite to the study of the metal complex formation in the gas phase are the vapour pressures of the reaction partners. We found the 'modified entrainment method' particularly useful to measure vapour pressures of metal complexes and ligands and to investigate decomposition equilibria of metal complexes.

Experimental

The theory of the 'Modified Entrainment Method' has been discussed in detail by Faktor *et al.* [1]. We have modified their experimental set-up slightly by using a titanium reaction vessel (Fig. 1) resting on the platform of the thermobalance instead of a quartz vessel hanging on quartz fibres. This new arrangement has a number of advantages. The capillary is always parallel to the flow of the inert gas. The titanium cell is light, has good thermal conductivity and is easy to clean thanks to the wide opening when the capillary containing cover is screwed off the beaker. As titanium can be more easily and more precisely machined than quartz, the geometry of the reaction vessel is well defined. Capillaries of various dimensions can and have been used but Fig. 1 shows the dimensions of the most frequently used one only.

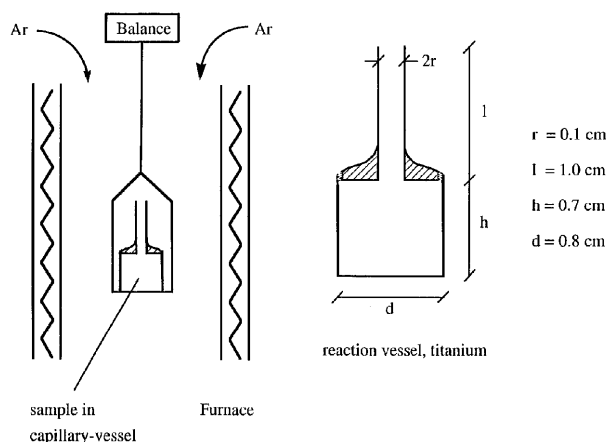


Fig. 1 Experimental set-up for 'Modified Entrainment' experiments

The thermobalance was a Mettler TA 3000. Usually it has been programmed to raise the temperature in 5 K steps with 5–10 min measuring time at each temperature. Assuming a weighing precision of ± 0.001 mg the minimum rate of mass loss is around 0.1 mg h^{-1} . The speed of the stream of argon was constant, approximately 1 m min^{-1} .

Equation (1) shows how the vapour pressure P of a sample in the capillary vessel (Fig. 1) is related to the experimental parameters and the rate of mass loss.

$$P = P_{\text{ext}}(1 - e^{-b}) \quad (1)$$

where

$$b = \frac{dW}{dt} T^{-a} \frac{RT_0^{1+a}}{Mr^2\pi D_0}$$

and dW/dt – mass loss/ g s^{-1} , T – temperature/ K , $R=83.15 \text{ bar cm}^3 \text{ K}^{-1} \text{ mol}^{-1}$, l – length of the capillary/ cm , r – radius of the capillary/ cm , P_{ext} – external pressure/ bar , D_0 – diffusion coefficient at $T_0/\text{cm}^2 \text{ s}^{-1}$, M – molar mass of evaporating substance/ g mol^{-1} , a – semiempirical factor ≈ 0.8 [1, 19, 20].

All the experimental parameters and measured quantities contributing to the vapour pressure according to Eq. (1) are known or easily determined except D_0 and a . From the kinetic theory of gases it follows that for $T=\text{const}$. $D_0=f(1/(\sqrt{M}\sigma^2))$ where M is the molar mass and σ is the diameter of the diffusing molecule. Neglecting, in a first approximation, variations of σ the $D_0=f(1/\sqrt{M})$ plot of the values listed in [2] can be approximated by a straight line (Fig. 2) which allows a reasonable estimate of D_0 for substances where the diffusion coefficient in argon is not known. The change of the diffusion coefficient if nitrogen would be used instead of argon as an inert gas is within the precision of the estimate. The semiempirical factor a accounts for the

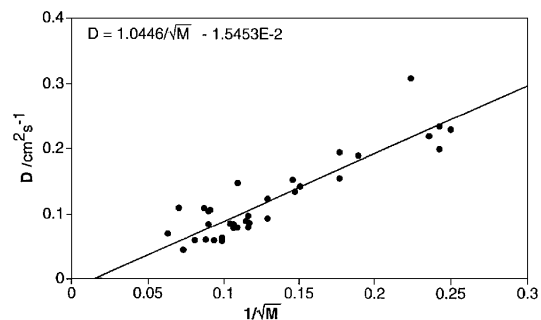


Fig. 2 Estimate of unknown diffusion coefficients [1, 2, 19, 20]

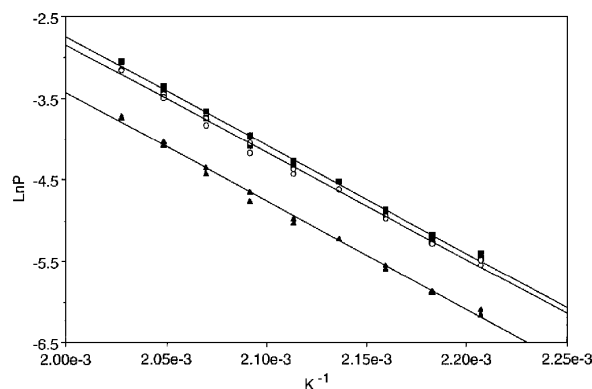


Fig. 3 The influence of D and a in Eq. (1) on the calculated vapour pressure of bis(2,2,6,6-tetramethylheptan-3,5-dionato)nickel(II)

	$D=[\text{cm}^2\text{s}^{-1}]$;	$\Delta H=[\text{kJmol}^{-1}]$;	$\Delta S=[\text{JK}^{-1}\text{mol}^{-1}]$
■	$D_0=0.035, a=0.8,$	$\Delta H_{\text{subl}}=110.7$	$\Delta S_{\text{subl}}=198.6$
▲	$D_0=0.053, a=0.8,$	$\Delta H_{\text{subl}}=110.0$	$\Delta S_{\text{subl}}=196.0$
○	$D_0=0.035, a=1.0,$	$\Delta H_{\text{subl}}=110.0$	$\Delta S_{\text{subl}}=196.4$
	Spectrophotometry	$\Delta H_{\text{subl}}=113$	$\Delta S_{\text{subl}}=198$

temperature dependence of the diffusion coefficient. It has been found to have the value 0.8 for most gases [1, 19, 20]. It turns out that the uncertainty of D and a influence very little the values of the enthalpy of evaporation [1]. This is illustrated in Fig. 3.

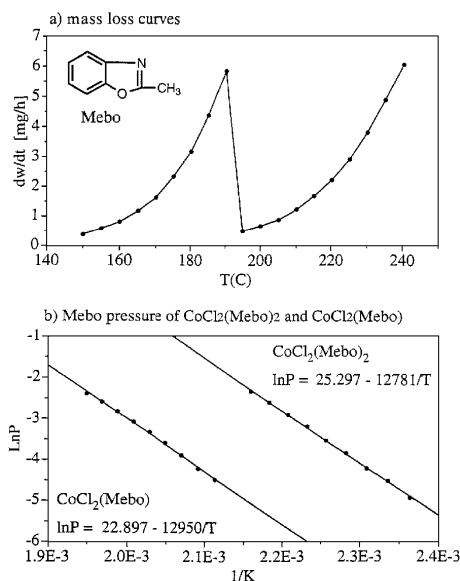
There, doubling of the diffusion coefficient or the unlikely high value of $a=1$ change the enthalpy of evaporation by less than 1%. The influence of D and a on the entropy of evaporation is somewhat larger but still small. It might be added that entropy determinations from van't Hoff plots are, in general, not very precise anyhow. Figure 3 also indicates the typical scatter of the data obtained by this method of vapour pressure determination.

In Table 1 vapour pressures of various classes of substances are presented to show the versatility of the method.

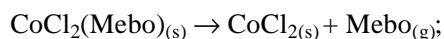
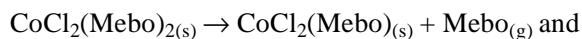
Table 1 Enthalpies and entropies of evaporation determined by modified entrainment

Substance	$T_{\text{range}}/^{\circ}\text{C}$	$\Delta H_{\text{evap}}/\text{kJ mol}^{-1}$		$\Delta S_{\text{evap}}/\text{J mol}^{-1} \text{K}^{-1}$		Ref.
		measured	Ref.	measured	Ref.	
Toluene _(l)	20–55	35.5	35.7	91.2	93.5	[8]
Nitrobenzene _(l)	70–120	51.1	51.6	111.8	107.7	[9]
Bipyridyl _(l)	105–150	61.6	63.9	122		[10]
<i>o</i> -Phenanthroline ^(l)	250–300	81.8	82.6	122.5		[11]
CHCl _{3(l)}	25–55	32.1	31.4	94.2	93.6	[12]
<i>o</i> -Phen·CHCl _{3(s)} ^A	70–100	51.2		121.5		[17]
Anthracene _(s)	150–215	94.5	97.8	175.2	182	[13]
HgCl _{2(s)}	135–200	81.7	80.0	157.2	140.1	[9]
Ni(tmhd) _{2(s)}	180–220	111		199		Fig. 3
Co(tmhd) _{2(l)}	170–225	73		128		[6]
Co(tmhd) ₂ ·bpy _(s)	185–245	129		127		[6]

A: equilibrium CHCl₃ pressure
Standard state: 1 bar

**Fig. 4** Thermal decomposition of $[\text{CoCl}_2(2\text{-methylbenzoxazol})_2]_{2(s)}$

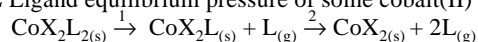
As an example, the results of a study of the equilibrium vapour pressures in the course of the stepwise decomposition of a metal complex are presented in Fig. 4. The mass loss curves of Fig. 4a represent the two decomposition steps



(Mebo=2-methylbenzoxazol, Fig. 4).

This decomposition is one of the many examples where previously the equilibrium pressure of the ligand had been taken falsely for the vapour pressure of the complex [3]. Additional results of studies dealing with the thermal decomposition of $[\text{CoX}_2\text{L}_{1,2}]_{(s)}$ complexes are presented in Table 2.

Table 2 Ligand equilibrium pressure of some cobalt(II) complexes



Reaction	X	L	$\Delta H/\text{kJ mol}^{-1}$		$\Delta S/\text{J mol}^{-1} \text{K}^{-1}$		Ref.
			measured	ref.	measured	ref.	
1	Cl	pyridine	62	64.4–74.0	124	126	[14]
2	Cl	pyridine	126	101.8	218	163	[14]
1+2	Cl	pyridine	188	119.7–189.5	342	290	[14]
1	Cl	4-picoline	88		174		[15]
2 ^A	Cl	4-picoline	139		232		[15]
1	Cl	2-methylbenzoxazol	106		210		Fig. 4
2	Cl	2-methylbenzoxazol	108		190		Fig. 4
1+2 ^B	Cl	aniline	170		327		[17]
1	Br	benzothiazole	110		199		[17, 3]
2	Br	benzothiazole	124		210		[17, 3]
1	Br	pyridine	89		157		[5]
2	Br	pyridine	119		212		[5]
1+2	Br	pyridine	208	114–193	368		[18]
1	Br	pyrazin	105				[17]
2	Br	pyrazin	130				[17]

A: $\text{CoCl}_2(4\text{-picoline})_{0.66}$ is formed as an intermediate [16]

B: reaction 1 and 2 are barely separated

Standard state: 1 bar

The vapour pressure of $\text{L}_{(g)}$ in equilibrium with $[\text{CoX}_2\text{L}_{1,2}]_{(s)}$ depends on the stability of the complex, the volatility of L and the lattice energy of $[\text{CoX}_2\text{L}_{1,2}]_{(s)}$ but more data are needed to make trends apparent.

Conclusions

With the 'Modified Entrainment' vapour pressures are measured by continuously monitoring the rate of mass loss of a sample evaporating through a capillary into a

stream of inert gas. The described experimental set-up is shown to be convenient for quite different classes of substances. An interesting application is the study of decomposition equilibria of metal complexes containing a volatile ligand.

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