Thermochimica Acta, 197 (1992) 469–478
Elsevier Science Publishers B.V., Amsterdam

TGA experimental data—analysis provided by transpiration theory

P.G. Wahlbeck

Department of Chemistry and National Institute for Aviation Research, The Wichita State University, Wichita, KS 67208 (USA)

(Received 7 July 1991)

Abstract

Thermogravimetric analysis (measurement of sample mass vs. temperature) is a frequently used laboratory technique in the analysis of materials, and commercial computer-automated equipment is available. The TGA experiment is designed in much the same way as a transpiration experiment; the transpiration experiment was theoretically analyzed using a transport mechanism coupling diffusion and viscous flow. This coupled flow analysis as applied to the TGA experiment will be discussed. The analysis allows one to calculate equilibrium vapor pressures and related thermodynamic properties. As an example, data for the vaporization of $Tl_2O_3(s)$ will be discussed.

INTRODUCTION

Previously Motzfeldt et al. [1] have theoretically analyzed the Ruff method for vapor pressure measurements using a model (the MKW model) with coupled diffusion and viscous flow as the principal means for sample transport. The coupling of diffusion and viscous flow into a transport mechanism has broad applications to several experiments.

The apparatus for the Ruff experiment is shown schematically in Fig. 1. The sample is contained in the Ruff cell, which is similar to a Knudsen cell, but the opening to the cell is a long, small diameter capillary. The cell is suspensed from a vacuum balance into a constant temperature furnace with an inert gas present at a known pressure. Inside the cell, the sample vapor and the inert gas are present. When the inert gas pressure is large compared with the equilibrium vapor pressure, the sample will diffuse from the cell. When the inert gas pressure is smaller than the equilibrium vapor pressure at high temperature, the sample will leave the cell by viscous flow; at low temperature, the limit to sample vaporization will be heat transfer to the cell as proposed by Wagner [2].

Correspondence to: P.G. Wahlbeck, Department of Chemistry and National Institute of Aviation Research, The Wichita State University, Wichita, KS 67208, USA.

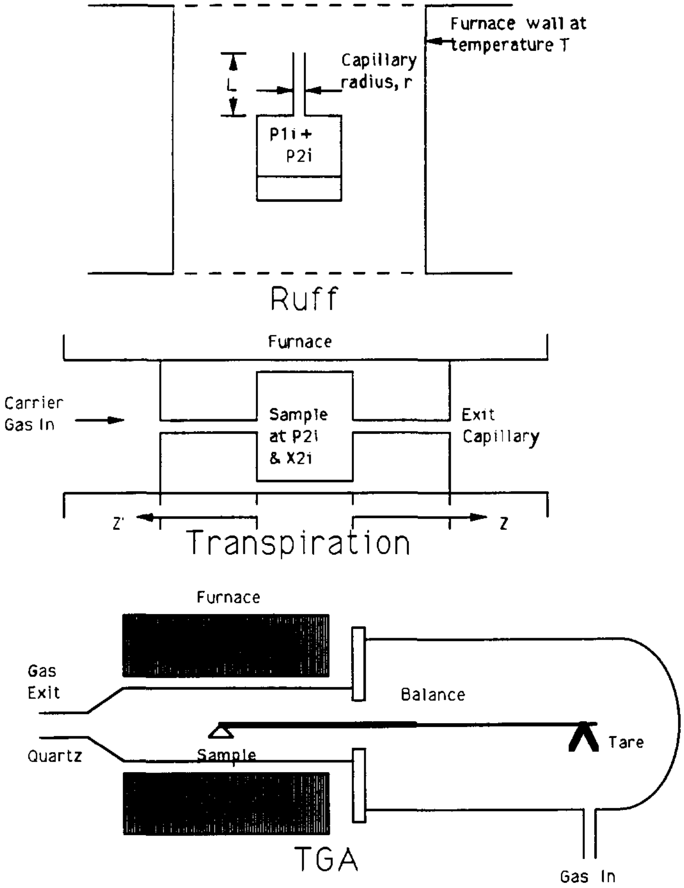

Fig. 1. Experimental apparatus designs for the Ruff–MKW experiment, the transpiration experiment, and the TGA experiment (from top to bottom). The connecting aspects of these apparatuses are discussed in the text.

Diffusion is a transport mechanism in which the flow of species is dependent upon a gradient in concentration. Let the inert gas be labelled as species 1, and the sample vapor as species 2. The diffusion equations are

$$J_1 = -D_{12}(\mathrm{d}x_1/\mathrm{d}z) + cx_1v \tag{1a}$$

$$J_2 = -D_{12}(\mathrm{d}x_2/\mathrm{d}z) + cx_2v \tag{1b}$$

where J_i is the flux, D_{12} is the coefficient of interdiffusion of the two gases, x_i is the mole fraction of the species in the gaseous mixture, c is the total concentration of gas (i.e., x_ic gives the concentration of species i by Dalton's law of partial pressures), and v is the mean molar velocity in the z direction (the direction of the capillary). The velocity v is made up of two components: (1) a diffusion velocity, and (2) a viscous flow velocity caused by the pressure gradient. For the Ruff experiment, the solution to the above equations is given by Motzfeldt et al. [1].

Kvande and Wahlbeck [3] applied the same equations to the transpiration experiment. The experimental apparatus is depicted in Fig. 1 also. The sample is contained in a sample boat with entrance and exit plugs. A carrier gas flows through the apparatus, and the sample is transported from the boat area by diffusion and by bulk transport in the carrier gas. In this case, capillary flow will occur through the entrance and exit plugs. The solution of the equations applied to the transpiration experiment was given by Kvande and Wahlbeck [3]. Previous equations given by Mack and France [4] and by Merten [5] are special limiting cases of the Kvande–Wahlbeck results.

Experimental studies were performed to verify the theoretical analyses for the Ruff experiments; verifying results were given by Motzfeldt and co-workers [1,6] and by Wahlbeck et al. [7,8].

TGA EXPERIMENTAL DESIGN

The design of the TGA apparatus is shown in Fig. 1 using the design of the Du Pont apparatus. In this case the sample is contained in a sample boat which is suspended from a vacuum balance. A carrier gas is used which flows around the sample. The mass loss of the sample by vaporization is measured by the balance. Usually the temperature is ramped with $\mathrm{d}T/\mathrm{d}t$ as a constant.

In principle, the apparatus shows a remarkable likeness to the transpiration experiment. The similar parts are: (1) use of a furnace, (2) use of a carrier gas, (3) sample placement in a sample boat, (4) measurement of the temperature of the sample, and (5) measurement of the amount of sample transported. The differences are: (1) baffles in the flow of the carrier gas present in the transpiration apparatus are absent in the TGA apparatus, (2) the direct measurement of the mass of the sample by means of a balance attached to the sample in the TGA apparatus, and (3) the use of a constant temperature in the transpiration experiment and a temperature ramp in the TGA experiment.

The data are provided as mass vs. sample temperature in the TGA experiment. The software supplied with the apparatus can provide the rate of mass loss vs. sample temperature.

DEVELOPMENT OF TGA EQUATIONS

Since the transpiration and TGA experiments are related, the equations developed for the transpiration experiment can be used directly for the TGA case. Let us begin with the following equations (their equations (13) and (14)) from Kvande and Wahlbeck [3]

$$P_{2i}^2 = x_{2i}^2\left\{P_F^2 + \left[(\dot{n}_1 + \dot{n}_2)/C\right] + (A/C)\ln[1 - x_{2i}(1 - \Gamma)]\right\} \tag{2}$$

$$x_{2i} = \left[\dot{n}_2/(\dot{n}_1 + \dot{n}_2)\right]\left\{1 - \exp\left[-(\dot{n}_1 + \dot{n}_2)/A\right]\right\} \tag{3}$$

where P_{2i} is the pressure of the sample inside the furnace zone, P_F is the pressure of the carrier gas, $\dot{n}_i$ is the rate of flow of the species i

$$A = \pi r^2 D'/RTl \tag{4}$$

$$C = \pi r^4/16RTl\eta \tag{5}$$

$$\Gamma = \sqrt{M_2/M_1} \tag{6}$$

For the "capillary", r is the radius and l is the length, R is the universal gas constant, and T is the absolute temperature. The symbol D' is the product of D_{12} and pressure P, and η represents the viscosity coefficient of the gas.

We will assume that the logarithmic term in eqn. (2) in negligible; this gives

$$P_{2i}^2 = x_{2i}^2\{P_F^2 + [(\dot{n}_1 + \dot{n}_2)/C]\} \tag{7}$$

or

$$P_{2i}^2 = [\dot{n}_2/(\dot{n}_1 + \dot{n}_2)]^2\{1 - \exp[-(\dot{n}_1 + \dot{n}_2)/A]\}^2\{P_F^2 + [(\dot{n}_1 + \dot{n}_2)/C]\} \tag{8}$$

In the usual and elementary calculations for the transpiration experiment, the vapor pressure is calculated by

$$P(\text{calc}) = [\dot{n}_2/(\dot{n}_1 + \dot{n}_2)]P_F \tag{9}$$

with the assumption that P(calc) is the equilibrium vapor pressure. Substituting eqn. (9) into eqn. (8) one obtains

$$P_{2i}^2 = P(\text{calc})^2\{1 - \exp[-(\dot{n}_1 + \dot{n}_2)/A]\}^2\{1 + [(\dot{n}_1 + \dot{n}_2)/CP_F^2]\} \tag{10}$$

This equation may be rearranged for P(calc), the usual calculated quantity

$$P(\text{calc})^2 = P_{2i}^2/\{1 - \exp[-(\dot{n}_1 + \dot{n}_2)/A]\}^2\{1 + [(\dot{n}_1 + \dot{n}_2)/CP_F^2]\} \tag{11}$$

For the usual experimental conditions, $\dot{n}_1 \gg \dot{n}_2$; i.e., the transport of the carrier gas is much larger than that of the sample. Thus, eqn. (11) becomes

$$P(\text{calc})^2 = P_{2i}^2/\{1 - \exp[-\dot{n}_1/A]\}^2\{1 + [\dot{n}_1/CP_F^2]\} \tag{12}$$

or

$$P(\text{calc}) = P_{2i}/\{1 - \exp[-\dot{n}_1/A]\}\{1 + [\dot{n}_1/CP_F^2]\}^{1/2} \tag{12a}$$

Three different cases can be considered: (1) the usual elementary calculations give $P(\text{calc}) = P_{2i}$ when it is assumed that $A = 0$ and $C = \infty$; (2) at large flow rates (large $\dot{n}_1$), the C term will be significant but the A term will not; and (3) at small flow rates, the A term will be significant but the C term will not.

TYPICAL EXPERIMENTS AND DATA

Experiment 1: temperature dependence

The typical experiment has a known sample mounted in the sample boat; the mass of the sample is measured, the carrier gas flow is initiated at a fixed flow rate, the temperature is ramped, and the mass as a function of temperature is recorded.

Consider the following model for the experiment. (1) Assume that the sample vaporizes and that the rate of vaporization corresponds to P(calc) given by eqn. (9). (2) Assume that the temperature dependence of the equilibrium pressure P_{2i} is given by the Clausius–Clapeyron equation (or the van't Hoff equation where P_{2i} is replaced by K, the equilibrium constant)

$$\ln P_{2i} = -\Delta_{\text{vap}}H^\circ/RT + \Delta_{\text{vap}}S^\circ/R \tag{13}$$

where $\Delta_{\text{vap}}H^\circ$ and $\Delta_{\text{vap}}S^\circ$ are the standard enthalpy and entropy of vaporization, respectively. No sample cooling is assumed. Substituting eqn. (13) into eqn. (12) gives

$$P(\text{calc})^2 = \exp(-2\Delta_{\text{vap}}H^\circ/RT)\exp(2\Delta_{\text{vap}}S^\circ/R)/ \\ \{1-\exp[-\dot{n}_1/A]\}^2\{1+[\dot{n}_1/CP_F^2]\} \tag{14}$$

or

$$P(\text{calc}) = \exp(-\Delta_{\text{vap}}H^\circ/RT)\exp(\Delta_{\text{vap}}S^\circ/R)/ \\ \{1-\exp[-\dot{n}_1/A]\}\{1+[\dot{n}_1/CP_F^2]\}^{1/2} \tag{14a}$$

At some temperature the sample will be exhausted, and a peak will exist at that temperature in the rate of mass loss vs. temperature.

Consider data at constant flow rate of carrier gas $\dot{n}_1$ for rate of mass loss vs. temperature prior to the temperature of the peak. The values of P(calc) may be calculated by eqn. (9) from the rate of mass loss, $\mathrm{d}G/\mathrm{d}t$. The fitting of such data to eqn. (14a) can generate values of $\Delta_{\text{vap}}H^\circ$ and a quantity which is a constant including $\Delta_{\text{vap}}S^\circ$ for the substance, $\dot{n}_1$, A, C and P_F. See Fig. 2 for a plot of $\ln(\mathrm{d}G/\mathrm{d}t)$ vs. $1/T$ as an example; the data were obtained with Tl_2O_3(s) as sample with O_2 as a carrier gas. The vaporization reaction was

$$Tl_2O_3(s) \rightarrow Tl_2O(g) + O_2(g) \tag{15}$$

The slope of the data in Fig. 2 gives the $\Delta_{\text{vap}}H^\circ$ at 973 K, the mid temperature of the data. These data are reported in Exhibit 1.

From the initial mass of the sample, and by summing the calculated amount of vaporization of the sample as the temperature increases, the

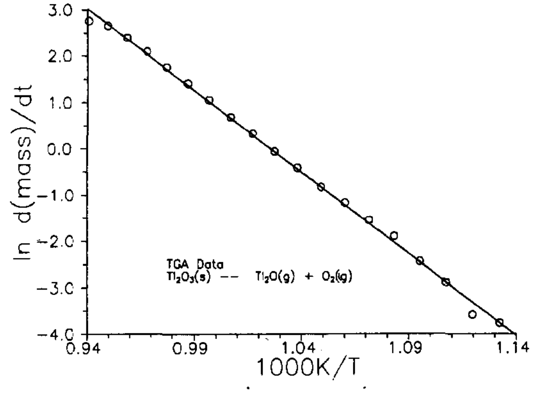

Fig. 2. Logarithm of (dG/dt) (arbitrary units) vs. reciprocal temperature for TGA data for the vaporization of $Tl_2O_3(s)$. The line is a least-squares fitted line to the data with parameters reported in Exhibit 1. The quantity dG/dt is proportional to $P[Tl_2O(g)]$, which is equal to $P[O_2(g)]$.

Exhibit 1

Estimation of typical data for the TGA experiment

$r = 3 \times 10^{-3}$ m $\quad l = 3 \times 10^{-2}$ m $\quad T = 1000$ K
$D' = DP = 30$ N s^{-1} [1]
$\eta = 1.1 \times 10^{-4}$ N s m^{-2} [1]

For $Tl_2O_3(s) = Tl_2O(g) + O_2(g)$
$\Delta_{vap}H° = 297.37 \pm 3.29$ kJ mol^{-1} of gas
$\Delta_{vap}S° = 203.24 \pm 3.41$ J deg^{-1} mol^{-1} of gas [9]

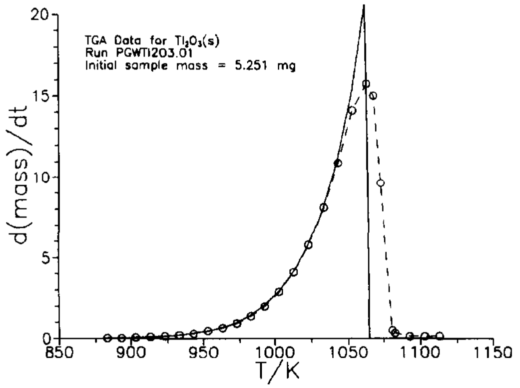

Fig. 3. TGA data for rate of mass loss vs. temperature for $Tl_2O_3(s)$. The temperature dependence of the vapor pressure determines the curve up to the peak temperature. The peak results from the sample being totally exhausted. The solid line is a calculated curve (see text).

peak position in the TGA experiment may be computed; i.e. the temperature at which the sample is exhausted. Figure 3 shows an experimental TGA data set with a calculated plot using the total mass and the data parameters obtained from Exhibit 1. The value of $\Delta_{\mathrm{vap}}H^\circ$ was taken from the data given in Fig. 2, and the value of $\Delta_{\mathrm{vap}}S^\circ$ was supplied by Wahlbeck et al. [9]. If vapor pressure data from Cubicciotti and Keneshea [10] were to be used, the value of $\Delta_{\mathrm{vap}}S^\circ$ would be different. In the experimental data, the peak is less sharp than in the calculated curve; this may be caused by sample cooling during rapid vaporization of the sample at or near the peak temperature.

Experiment 2: carrier gas flow rate dependence

The experiment cited above gives $\Delta_{\mathrm{vap}}H^\circ$, and an additional experiment is needed to obtain $\Delta_{\mathrm{vap}}S^\circ$. In order to use eqn. (12) to determine the equilibrium vapor pressure, P_{2i}, it is necessary to do experiments at different flow rates. The data for P(calc) at a fixed temperature will be fitted to eqn. (12).

Typical and estimated data for the above parameters are given in Exhibit 1.

From eqn. (9), P(calc) will be a function of the carrier gas flow rate, $\dot{n}_1$. For the parameters given in Exhibit 1, the predicted data are given in Fig. 4. The usual elementary value of P(calc) from eqn. (9) is indicated as a constant at unity independent of $\dot{n}_1$. Also indicated on Fig. 4 are the calculated curves with C given by eqn. (5) and data from Exhibit 1 for the cases of $A = 0$ and A given by eqn. (4) and data from Exhibit 1. The intercept of the plot at unity gives the value of P_{2i}. As the flow rate increases to large values, P(calc) decreases from the value of P_{2i} leading to

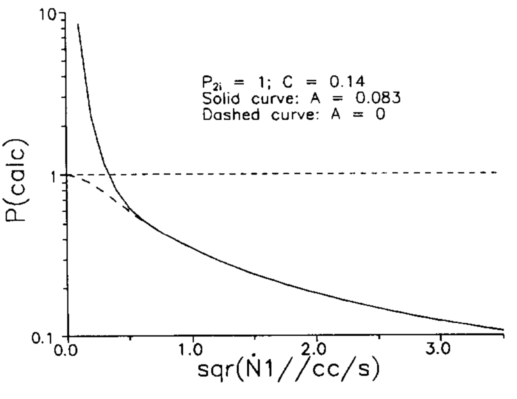

Fig. 4. Calculated curves for P(calc) vs. square root of the flow rate for the carrier gas. Parameters used in the plots are indicated on the figure. The fine broken line is a result of the usual elementary calculation giving P_{2i} independent of $\dot{n}_1$.

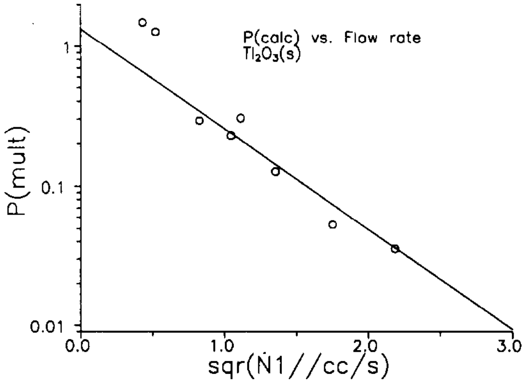

Fig. 5. Experimental data for P(mult) vs. square root of the flow rate for the carrier gas; P(mult) = P(calc)/P(ref). The data are for the vaporization of Tl_2O_3(s). The straight line is a least-squares fitted line to data excluding the two lowest rates. The intercept of the line at zero flow rate corresponds to P_{2i}/P(ref).

the typical condition of desaturation of the carrier gas. At very small flow rates, P(calc) can be larger than P_{2i}, caused by diffusion of the sample from the apparatus.

Figure 5 gives an illustration of the principles discussed above and shown in Fig. 4. The case is again the vaporization of Tl_2O_3(s) performed in the TGA apparatus. In this case, reference vapor pressure data are calculated from the enthalpy and entropy data of Exhibit 1. The ordinate of Fig. 5 is given as

$$P(\text{mult}) = P(\text{calc})/P(\text{ref}) \tag{16}$$

where P(ref) is the reference vapor pressure data. Note that the data shown in Fig. 5 are following the predicted shape given by Fig. 4. The data were analyzed in a simple way by fitting a straight line through the points with a flow rate greater than 0.676 $cm^3\ s^{-1}$ to give an intercept value of

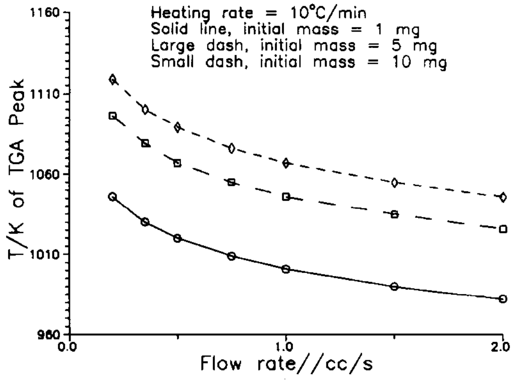

Fig. 6. Predicted peak temperatures in the TGA experiment as a function of initial sample mass with a heating rate of 10°C min^{-1} plotted against carrier gas flow rate.

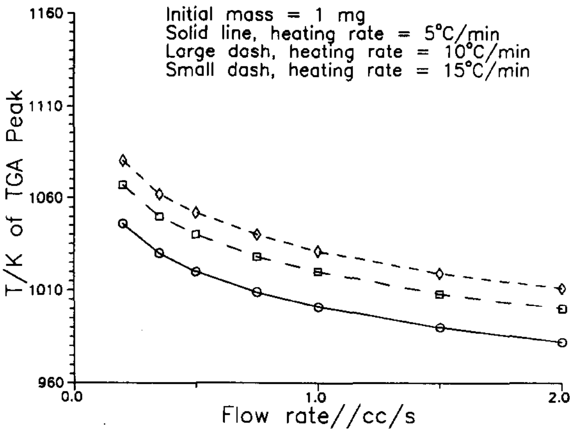

Fig. 7. Predicted peak temperatures in the TGA experiment as a function of heating rate with an initial sample mass of 1 mg plotted against carrier gasflow rate.

P(mult) at zero flow rate which corresponds to P_{2i}/P(ref). In the case of Tl_2O_3(s), the value of P_{2i}/P(ref) was given as 1.44 ± 1.38; this indicates that the intercept is close to unity within the uncertainty. Similar calculations can be performed using the data of Cubicciotti and Keneshea [10] as reference data.

CONCLUSIONS

The following conclusions were reached based on the study reported in this paper.

(1) TGA experimental data can be analyzed with the transpiration theory.

(2) The TGA peak position is dependent upon the amount of sample, the carrier gas pressure (P_F), the carrier gas flow rate, the vapor pressure (T dependent) of the sample, and dT/dt.

(3) The data for rate of mass loss vs. T yields $\Delta_{vap}H°$.

(4) Data for P(calc) vs. flow rate yields $\Delta_{vap}S°$ information.

In view of point (2), peak positions in TGA experiments are meaningful and useful only if the variables of the experiment are specified; i.e. the vapor pressure dependence on temperature, the mass of the sample, the carrier gas, the carrier gas pressure and flow rate, and the temperature ramp rate.

Figures 6 and 7 show predicted changes in the peak temperature of the TGA data depending on the independent variables of carrier gas flow rate, mass of sample, and heating rate.

ACKNOWLEDGMENTS

This paper was originally presented at a symposium honoring Professor Ketil Motzfeldt upon his retirement at Norges tekniske høgskole in Trondheim, Norway. The author thanks Professors Motzfeldt and Kvande for the many years of collaboration which led to the present research. This collaboration was aided in 1974–75 by a NATO Research Grant, Grant 836, and in 1978 by the Senior Scientist program of the Royal Norwegian Council for Scientific and Industrial Research (NTNF).

The author also thanks Wichita State University for its continued support and Los Alamos National Laboratory for its hospitality and support during a sabbatical leave during 1991.

REFERENCES

1 K. Motzfeldt, H. Kvande and P.G. Wahlbeck, Acta Chem. Scand., Ser. A, A31 (1977) 444.
2 C. Wagner, Z. Phys. Chem., 192 (1943) 85.
3 H. Kvande and P.G. Wahlbeck, Acta Chem. Scand., Ser. A, A30 (1976) 297.
4 E. Mack, Jr. and W.G. France, Laboratory Manual of Elementary Physical Chemistry, Van Nostrand, New York, 2nd edn., 1934, p. 44.
5 U. Merten, J. Phys. Chem., 63 (1959) 443.
6 H. Kvande, H. Linga, K. Motzfeldt and P.G. Wahlbeck, Acta Chem. Scand., Ser. A, A33 (1979) 281.
7 P.G. Wahlbeck, D.L. Myers, T.L. Hendrixson, F.D. Pierson and S.A. Pyles, J. Chem. Phys., 81 (1984) 915.
8 P.G. Wahlbeck, D.L. Myers, and V.V. Troung, J. Chem. Phys., 83 (1985) 2447.
9 P.G. Wahlbeck, R.R. Richards and D.L. Myers, J. Chem. Phys., 95 (1991).
10 D. Cubicciotti and F.J. Keneshea, J. Phys. Chem., 71 (1967) 808.