Thermochimica Acta, 9 (1974) 7–13

# GAS EVOLUTION DETECTION TECHNIQUES

## I. PRESSURE–TEMPERATURE

W. W. WENDLANDT
*Department of Chemistry, University of Houston, Houston, Texas 77004 (U.S.A.)*
(Received 7 November 1973)

## ABSTRACT

A simple pressure–temperature apparatus is described which can be used for thermal analysis investigations. The apparatus contains a recording mercury manometer, the output of which is directly proportional to the pressure change of the system. Use of the system is illustrated by the *P–T* curves of $KHCO_3$, cobalt(III) ammine complexes, $CaC_2O_4 \cdot H_2O$, and magnesium, nickel and cobalt(II) carbonates.

## INTRODUCTION

The gaseous products evolved by a chemical reaction of the type: $\text{solid}_1 \rightarrow \text{solid}_2 + \text{gas}$ can be detected by numerous experimental techniques. In general, these techniques can be divided into two main types: (a) variable pressure; and (b) constant pressure. The first type, which is widely used in the investigation of solid-state heterogeneous kinetics by the isothermal method, usually consists of the measurement of the system pressure as a function of time. In the second type, the pressure is maintained constant and the evolved gases are detected by a thermal conductivity detector or other instrumental technique (mass spectrometry, infrared cell, gas chromatography, etc.). Since the concentration of the evolved gases is determined as a function of temperature, this mode is commonly used in thermal analysis investigations.

No attempt will be made here to review the vast literature of previous investigations using the variable pressure mode of detection. Illustrative studies in which the change in pressure is plotted as a function of system temperature include those by Charles et al.[1,2], Wiedemann[3,4], Wendlandt and Chou[5,6], Vaughan[7], and Findeis et al.[8]. Recording the change in pressure of the system simultaneously with thermogravimetry led Bancroft and Gesser[9] to call the technique *thermobarogravimetric analysis*. Maycock and Pai Verneker[10] made extensive use of this technique to study the dissociation of explosive materials.

The purpose of this investigation is to describe a simple variable pressure system, equipped with a recording manometer, and to determine the effect of the system parameters on the resulting pressure versus temperature data for various compounds. Use of the apparatus is illustrated by the determination of the *P–T* curves for several chemical systems.

## EXPERIMENTAL

### *Chemicals*

All of the compounds used were of C.P. quality.

### *Apparatus*

The pressure change of an enclosed system can be detected by many different types of detectors. These include manual and recording liquid manometers[11–15], various mechanical and electronic pressure transducers[9,12,13,16], and adsorption–TG methods[17]. The system used here contains a recording mercury manometer, the design of which was first suggested by Svec and Gibbs[15]. It is a simple and low-maintenance technique suitable for pressure measurements from about 1 to 760 torr, a convenient pressure range for this type of investigation.

The apparatus is illustrated schematically in Fig. 1. The sample, contained in a nickel foil boat, is placed in a Vycor tube, 15 mm in diameter by 230 mm in length.

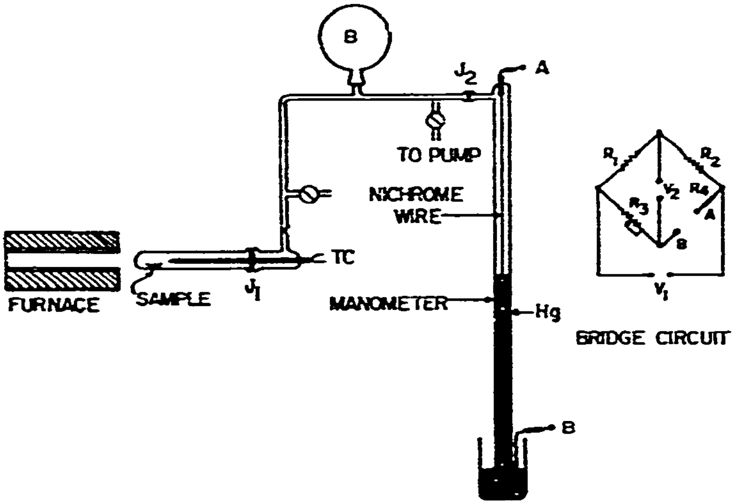

Fig. 1. Apparatus employed for variable pressure studies. $R_1$ and $R_2 = 1200\ \Omega$; $R_3 = 50\ \Omega$, 10 turn; $R_4 = 10\ \Omega$; $V_1 = 1$–$4$ V; $V_2$ is bridge output voltage. Volume of B, 50 to 500 ml.

The sample tube is connected to a simple vacuum system by means of an O-ring joint ($J_1$). A recording mercury manometer is connected to the system at the O-ring joint, $J_2$. The manometer consists of a glass tube, 10 mm in diameter by 1000 mm in length, which contains a length of 30 gauge Nichrome wire (total resistance of 22.9 Ω) as the variable resistance element. This resistance element is connected into the Wheatstone bridge at contact points A and B. As the mercury column decreases or increases in length, the resistance of the wire changes accordingly, and causes an unbalance voltage in the bridge. This unbalance voltage is recorded as a function of temperature on an X–Y recorder (Hewlett-Packard Model 135). A Chromel–Alumel thermocouple, contained in a two-holed ceramic insulator tube, is used to detect the sample chamber temperature. The thermojunction was enclosed by a nickel foil sheath.

The furnace consisted of a Nichrome wire wound tube, 12.3 mm in diameter by 200 mm in length, suitably insulated with asbestos cloth. A motor-driven variable voltage type programmer was used to control the furnace temperature heating-rate.

The range of pressure change in the system could be adjusted by a change in one or more of the following parameters: (a) sample size; (b) system volume via bulb B; (c) bridge voltage, $V_1$; or (d) recorder sensitivity.

### *Procedure*

The procedure for a run consisted of the following: from 20–300 mg of the weighed sample was transfered into the sample chamber and the system evacuated using a mechanical vacuum pump. The furnace was placed into position and the bridge output voltage balanced by means of $R_3$. After 5–10 min of pumping, the system was closed off and the $P$–$T$ curve recorded by activating the furnace programmer. Heating-rates employed usually ranged from 5 to 20°C/min, with a maximum furnace temperature of about 1000°C. Initial starting pressures ranged from $<1$ torr to about 500 torr; however, the former was most frequently used. Pressure changes of from 2 to 100 torr/in. could be recorded although the most convenient range was 4 torr/in.

The derivative of the $P$–$T$ curve could be recorded by passing the bridge output voltage into a Harrop computer and then into the Y-axis of another X–Y recorder. Both recorders plotted the same temperature signal from the furnace thermocouple.

## RESULTS AND DISCUSSION

### *Effect of sample and system parameters*

The effect of sample size on the $P$–$T$ curves of $KHCO_3$ is illustrated in Fig. 2. Using the thermal dissociation of $KHCO_3$ as the reference compound, the pressure increase in the system is due to the reaction:

$$2KHCO_3(s) \rightarrow K_2CO_3(s) + H_2O(g) + CO_2(g)$$

The larger the sample, the greater the pressure change observed in the system. There were slight changes in $T_i$ (initial temperature) and $T_f$ (final temperature) values and also the reaction interval ($T_f$–$T_i$). Values for $T_i$ (145°C) did not change appreciable with sample size but $T_f$ values did increase slightly: 200°C (73 mg), 205°C (111 mg) and 210°C (149 mg). The initial pressure, $P_i$, was $<1$ torr in all cases, at a heating-rate of 10°C/min.

The effects of furnace heating-rate and initial system pressure on the $P$–$T$ curves of $KHCO_3$ are shown in Fig. 3. As illustrated in (A), the changes in furnace

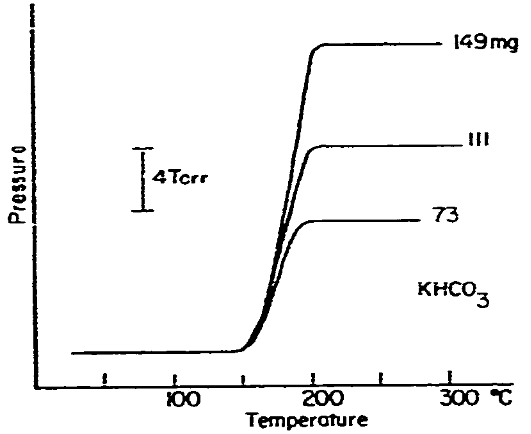

Fig. 2. Effect of sample size on *P–T* curves of $KHCO_3$. Heating-rate of 10 °C/min.

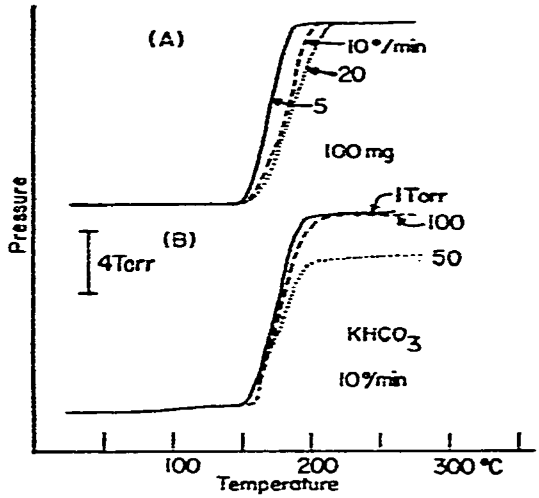

Fig. 3. Effects of furnace heating-rate and intial system pressure on *P–T* curves of $KHCO_3$.

heating-rate cause a change in the $T_f$ values and also the reaction interval. There was no apparent change in $T_i$ (145 °C); values for $T_f$ increased with an increase in heating-rate according to: 5 °C/min (190 °C); 10 °C/min (210 °C) and 20 °C/min (220 °C).

There was a slight change in the $T_i$ and $T_f$ values with initial system pressures in the range from 1 to 100 torr. Changes in $T_f$ ranged from 205 °C (<1 torr) to 220 °C (100 torr). The different total pressure changes observed were due to the slightly different sample masses employed.

*Application to coordination compounds*

Wendlandt and Chou[5,6] have previously reported the use of the *P–T* technique to detect the gaseous reaction products formed during the dissociation of $[Cr(NH_3)_6]X_3$ and $[Cr(NH_3)_5X]X_2$ complexes. The $P$–$T$ curves of $[Co(NH_3)_6]X_3$ ($X = Cl, Br$) and $[Co(NH_3)_5Cl]Cl_2$ are illustrated in Fig. 4. It has been previously

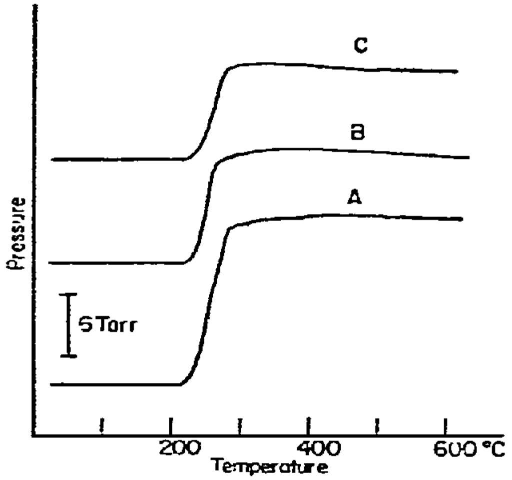

Fig. 4. $P$–$T$ curves of cobalt(III) ammine complexes. (A) $[Co(NH_3)_6]Cl$; (B) $[Co(NH_3)_6]Br_3$; and (C) $[Co(NH_3)_5Cl]Cl_2$. Heating-rate of 10 °C/min.

established[18] that the $[Co(NH_3)_6]X_3$ complexes dissociate thermally according to the reaction:

$$6[Co(NH_3)_6]X_3(s) \rightarrow 6CoX_2(s) + 6NH_4X(g) + N_2(g) + 28NH_3(g)$$

This stoichiometry has been confirmed by chemical analysis[19] and more recently by the TG–EGA–MS technique[20]. All three of the complexes undergo the oxidation–reduction reaction beginning at a $T_i$ of about 215 °C. After a very rapid change in pressure due to nitrogen and ammonia evolution, which terminates at a $T_f$ of 270–290 °C, there is a region of gradual pressure increase up to about 400 °C. No decrease in pressure was observed in the system as was found with the chromium(III) ammine complexes[5,6] at higher temperatures.

### *Miscellaneous applications*

The $P$–$T$ and derivative $P$–$T$ curves for the thermal dissociation of $CaC_2O_4 \cdot H_2O$ are shown in Fig. 5. As expected, a three-step increase in pressure is observed, due to the formation of $CaC_2O_4$, $CaCO_3$, and CaO, respectively.

The $P$–$T$ curves of magnesium, nickel and cobalt carbonates are illustrated in Fig. 6. All three of the carbonates indicated the formation of intermediate compounds, the composition of which was not determined. The first stage of dissociation is due to the evolution of water and this is followed by the carbon dioxide release. The metal oxides were obtained at temperatures above 300–400 °C.

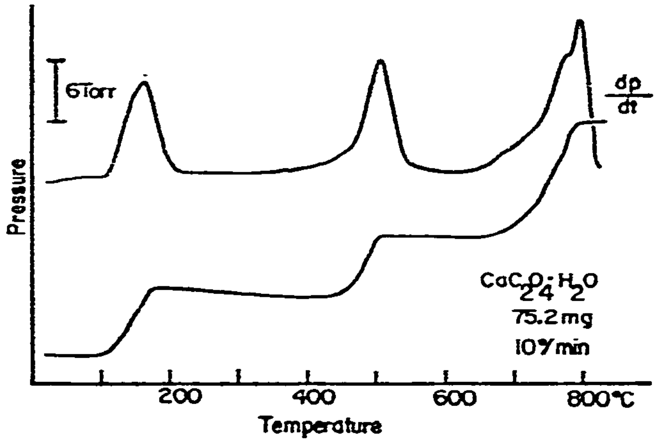

Fig. 5. *P–T* and derivative *P–T* curves of $CaC_2O_4 \cdot H_2O$. Heating-rate of 10°C/min and sample size of 75.2 mg.

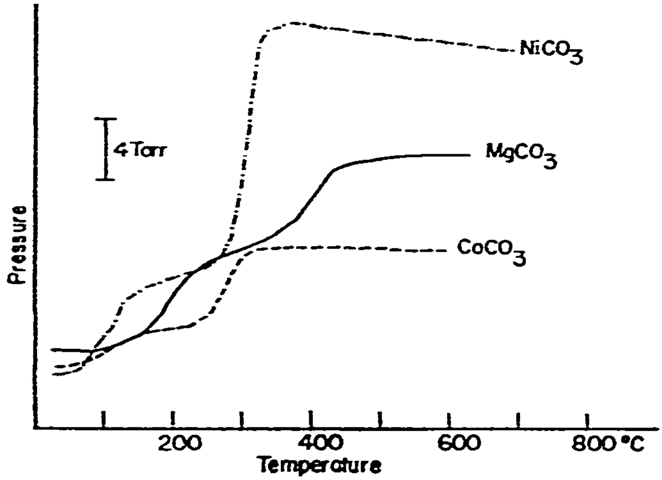

Fig. 6. *P–T* curves of magnesium, nickel and cobalt(II) carbonates. Heating-rate of 10°C/min.

## ACKNOWLEDGMENT

The financial support of this work by the Robert A. Welch Foundation of Houston, Texas, is gratefully acknowledged.

## REFERENCES

1 R. G. Charles, *Anal. Chim. Acta*, 31 (1964) 405.
2 R. G. Charles, A. Perotto and M. A. Dolan, *J. Inorg. Nucl. Chem.*, 25 (1963) 45.
3 H. G. Wiedemann in R. F. Schwenker and P. D. Garn (Eds.), *Thermal Analysis*, Academic Press, New York, Vol. 1, 1969, p. 229.
4 R. Giovanoli and H. G. Wiedemann, *Helv. Chim. Acta*, 51 (1968) 1134.
5 W. W. Wendlandt and C. Y. Chou, *J. Inorg. Nucl. Chem.*, 26 (1964) 943.

6 W. W. Wendlandt and C. Y. Chou, *Tex. J. Sci.*, 16 (1964) 62.
7 H. P. Vaughan, *Amer. Lab.*, *Jan.* (1970) 10.
8 A. F. Findeis, K. D. W. Rosinski, P. P. Petro and R. B. W. Earp, *Thermochim. Acta*, 1 (1970) 383.
9 G. M. Bancroft and H. D. Gesser, *J. Inorg. Nucl. Chem.*, 27 (1965) 1537.
10 J. N. Maycock and V. R. Pai Verneker, *Thermochim. Acta*, 1 (1970) 191.
11 T. B. Joyner, *J. Phys. Chem.*, 71 (1967) 3431.
12 T. B. Joyner, *J. Phys. Chem.*, 72 (1968) 703.
13 N. Tanaka and K. Sato, *Bull. Chem. Soc. Japan*, 43 (1970) 789.
14 F. Solymosi and T. Bansagi, *Acta Chim. Acad. Sci. Hung.*, 74 (1972) 9.
15 H. J. Svec and D. S. Gibbs, *Rev. Sci. Instrum.*, 24 (1953) 202.
16 H. G. Wiedemann, *Thermochim. Acta*, 3 (1972) 355.
17 S. Kleinberg and F. P. Stein, *Ind. Eng. Chem. Fundam.*, 11 (1972) 134.
18 W. W. Wendlandt and J. P. Smith, *The Thermal Properties of Transition Metal Ammine Complexes*, Elsevier, Amsterdam, 1967, Ch. 3.
19 W. W. Wendlandt, *J. Inorg. Nucl. Chem.*, 25 (1963) 545.
20 L. W. Collins, W. W. Wendlandt and E. K. Gibson, *Thermochim. Acta*, 8 (1974) 315.