Thermochimica Acta, 9 (1974) 399–407

EVOLVED GAS DETECTION APPARATUS FOR QUANTITATIVE VACUUM THERMAL ANALYSIS OF ALKALINE-EARTH CARBONATES

A. BOUWKNEGT, J. DE KOK AND J. A. W. DE KOCK
Philips' Gloeilampenfabrieken, Light Division, Eindhoven (The Netherlands)
(Received 21 February 1974)

ABSTRACT

An analysis is given of the requirements to be fulfilled in order to make quantitative measurements of dissociation phenomena with an evolved gas detection (EGD) apparatus, operating at pressures below 1 Torr*. This is done with the aim of measuring the dissociation temperature, the rate of decomposition, and the gas pressure above a dissociating sample of alkaline-earth carbonates. The considerations can also be applied to other thermal analysis techniques operating at these low gas pressures.

A reliable pressure determination can only be made if the gas pressure in the system is below the Knudsen limit, which is of the order of 10^{-3} Torr for usual vacuum systems. From this condition there follows an upper limit for the product of the weight of the material to be dissociated, and the rate of heating, a typical value being 10^{-3} g K sec^{-1} for $BaCO_3$. It is shown that the necessary calibration of the vacuum gauge and the determination of the pump resistance of an EGD apparatus can be made with the apparatus itself. Finally the quantitative nature of the analysis technique is illustrated with an EGD curve of a mixture of alkaline-earth carbonates.

1. INTRODUCTION

The decomposition of alkaline-earth carbonates at pressures below 1 Torr is an important step in the processing of electron-emissive coatings, as used in both electron tubes and low-pressure gas-discharge lamps. Despite the technical importance of this decomposition process, reliable data are scarce, especially at pressures below 1 Torr under non-equilibrium conditions. A critical review of data of the dissociation-rates and -temperatures of metal carbonates has been given by Stern and Weise[1]. These authors emphasize the general importance of low-pressure experiments in the study of the kinetics of dissociation reactions. Webb and Krüger[2] give differential thermal analysis (DTA) data on the decomposition of a large number of carbonate minerals at atmospheric pressure. Recently, Judd and Pope[3–8] published data con-

---

*1 Torr = 1 mm Hg.

cerning the decomposition, at pressures of the order of 10^{-1} Torr, of both the carbonates of Ca, Sr and Ba as such, and coprecipitated mixed crystals of these compounds.

A look at the results of different measurements of decomposition temperatures at lower pressures reveals a large scatter, in certain cases differences as high as about 200 K are found. It is known that differences in the chemical history of the species, in grain size distribution, or in the rate of temperature change, etc., can cause such differences in observed dissociation temperatures. However, closer inspection of the experimental circumstances in which the results were obtained shows that, in most cases reported, the description of the experimental vacuum equipment is inadequate. Since dissociation temperatures may depend strongly on pressure, it is possible that at least part of the discrepancies between various results must be attributed to less accurate measurements of the pressure just above the sample.

It is the purpose of this paper to discuss the limits set by the vacuum system used to a reliable measurement of a heterogeneous dissociation at lower pressures. The aim is to measure the dissociation temperature, the rate of decomposition and the pressure above the sample during the dissociation process.

2. THE VACUUM SYSTEM

A schematic drawing of the vacuum system is given in Fig. 1. In general outline it consists of a tube, with circular cross-section of diameter d and length L, which is connected to a vacuum pump. The carbonate sample is placed at $x = 0$, the end of the tube, which end can be heated over a length l_f by an electric oven, the rest is at room temperature. The pressure at $x = l_m$ (see Fig. 1) is indicated by gauge M and this pressure must be related to the pressure just above the carbonate sample S.

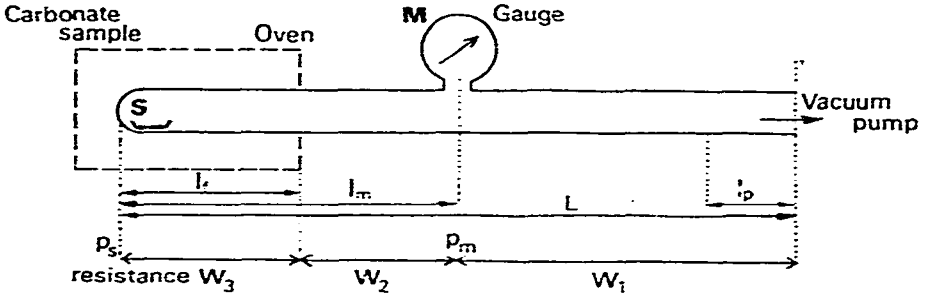

Fig. 1. Schematic drawing of vacuum system with notation of resistances and pressures.

In order to calculate the pressure above the sample the relation between pressure gradient and gas flow in the tube must be known. This relation is known in two distinct pressure regions characterized by the relation between the characteristic dimension of the system—in this case d—and the mean free path λ of the gas molecules. For $d/\lambda < 1$, that is at low pressures, the tube resistance is determined by the collisions of the gas molecules with the walls of the system. This gas flow is known as molecular flow or Knudsen flow. For $d/\lambda > 100$ the viscous properties of the gas determine the tube resistance. In both regions the resistance can reasonably be calculated, the intermediate region is, however, more difficult to handle. Accordingly, in order to relate the pressure measured by the gauge to that above the sample, it is reasonable to restrict our attention to a vacuum system for which the relation $d/\lambda < 1$ is valid everywhere in the system. As λ is proportional to $1/p$, where p is the gas pressure, the Knudsen limit $d/\lambda = 1$ can be expressed as $d \cdot p_{\mathrm{Kn}} = C_1$, C_1 being a constant depending on the gas species and the temperature. For CO_2 this relation is, for room temperature, expressed in the usual vacuum units[9]:

$$p_{\mathrm{Kn}} \cdot d = 3.3 \times 10^{-3}\ (\mathrm{Torr\ cm}) \tag{1}$$

It follows that p should not exceed 10^{-3} Torr much in a vacuum system of reasonable dimensions.

If there are no temperature gradients in the system, it is usual in vacuum calculations to define a quantity of gas q by the relation $q = pV$, p being the pressure and V the volume of the gas[9,10]. By analogy with an electric circuit the gas flow through a cross-section of the tube is given by the time derivative $\mathrm{d}q/\mathrm{d}t$. If the pressure drop over a tube of radius r and length l is ΔP, then the resistance R of that tube is defined by $R \cdot \mathrm{d}q/\mathrm{d}t = \Delta P$. This resistance is computed from

$$\frac{1}{R} = \frac{2}{3}\pi \frac{r^3}{l} v_a, \qquad v_a = \left(\frac{8kT}{\pi m}\right)^{1/2} \tag{2}$$

In this relation v_a is the average velocity of a gas molecule, m its mass, and kT is defined as usual. If M is the molecular weight of the gas, one obtains by inserting known constants in relation (2):

$$\frac{1}{R} = 3.048 \times 10^4 \frac{r^3}{l}\left(\frac{T}{M}\right)^{1/2} (\mathrm{cm}^3\ \mathrm{sec}^{-1}) \tag{3}$$

In eqn (3) all length values are given in cm. It is seen that in the case of molecular flow the resistance does not depend on pressure.

If temperature gradients exist in the vacuum system the matter is more complicated. Firstly it is more convenient to consider the particle current. The number of molecules n in a quantity of gas is given by

$$n = C_2 \frac{pV}{T} \tag{4}$$

The numerical value of C_2 is 7.244×10^{15} if p is expressed in dyne/cm^2 (μ bars) and V in cm^3. The relation between pressure drop ΔP and particle current $\mathrm{d}n/\mathrm{d}t$ is now, analogous to the foregoing:

$$W \cdot \mathrm{d}n/\mathrm{d}t = \Delta P, \quad \text{with} \quad W = R \cdot T/C_2 \tag{5}$$

Here R is computed from eqn (2) or (3) again.

Secondly, the pressure of a Knudsen gas in a vessel depends on the local temperature of the wall. If two vessels with temperatures T_1 and T_2, connected with each other by a small aperture in a common wall, contain a Knudsen gas, then the relation between the pressures p_1 and p_2 is in case of equilibrium:

$$p_1/p_2 = (T_1/T_2)^{1/2} \tag{6}$$

This can easily be shown by equating the number of particles flowing through the aperture in both directions. In a tube as considered in Fig. 1, the pressure changes gradually of course, over a distance of the order of the mean free path of the molecules in the tube. Taking this relation between pressure and wall temperature into account, the pressures p_s and p_m (see Fig. 1) are in a good approximation:

$$p_s = ((W_1 + W_2)(T_f/T_m)^{1/2} + W_3)\,\mathrm{d}n/\mathrm{d}t; \quad p_m = W_1\,\mathrm{d}n/\mathrm{d}t \tag{7}$$

T_f and T_m are the temperatures of oven and gauge, respectively. Elimination of $\mathrm{d}n/\mathrm{d}t$ gives the relation between p_s and p_m

$$\frac{p_s}{p_m} = \frac{(W_1 + W_2)(T_f/T_m)^{1/2} + W_3}{W_1} \tag{8}$$

The quantity W_3 is proportional to $(T_f)^{\frac{1}{2}}$. The quantity W_1 includes the flow resistance of the vacuum pump. This can be considered as a constant[10] if the pressure in the system exceeds the background pressure of the pump by a factor 10 at least. As a consequence in that case

$$p_s/p_m = C_3(T_f)^{1/2} \tag{9}$$

C_3 being a constant which depends only on the dimensions of the system and the gas in it.

In the case of time-dependent phenomena the characteristic time τ of pressure decay is of importance. For normal systems this time is given in order of magnitude by

$$\tau \simeq \tfrac{1}{2} R_s V_s \tag{10}$$

where R_s is the total resistance of the system and V_s its volume. If τ is smaller than the time in which significant changes in temperature or pressure take place, time-lag effects in the system can be ignored. In that case the vacuum system is the analogy of an electric circuit with only resistors and no capacitors.

3. CALCULATION OF MAXIMUM SAMPLE MASS LOADING

The requirement that the pressure limit for molecular flow should be exceeded nowhere in the vacuum system, interrelates the rate of heating of the sample to be dissociated with its mass, while this relationship depends on the dimensions of the system. To get an impression of this interrelationship a few calculations have been made for a rough model of the dissociation of a sample of $BaCO_3$. The kinetics of the dissociation reaction have been ignored in this model, and the CO_2 pressure above the carbonate sample was assumed to be equal to the equilibrium pressure. The latter can be found in the literature[11], and is: $p = A \exp(-B/T)$, with $A = 4.05 \times 10^{10}$ Torr and $B = 30 \times 10^3$ K. It was further assumed that the temperature of the part of the tube inserted in the oven was equal to the sample temperature, whereas the other part was at room temperature. The rate of heating was supposed to be constant during an experiment. The dimensions of the tube were chosen as: $L = 70$ cm, $l_f = 20$ cm, $l_m = 35$ cm, whereas the diameter was a variable parameter in the calculation.

The pressure rises exponentially with time on the above assumptions. The temperature T_{Kn} at which the CO_2 pressure at $x = 0$ surpassed the Knudsen limit p_{Kn}, as given by eqn (1), was calculated, together with the amount of carbonate dissociated up to that moment. This value has been taken as the maximum permissible load of the vacuum system, for which quantitative pressure measurements could be made. Results of the calculations are given in the following table. The value $1/R$ given is that of the vacuum system as a whole at room temperature.

TABLE 1

MAXIMUM $BaCO_3$ LOAD, AS A FUNCTION OF TUBE DIAMETER AND RATE OF HEATING

Diam.	*1/R tube*	p_{Kn}	T_{Kn}	*Maximum carbonate load (mg)*		
(mm)	*(dm³/sec)*	*(mTorr)*	*(K)*	*dT/dt (K min⁻¹)*		
				6	*12*	*30*
30	3.83	1.10	972	7.6	3.80	1.52
25	2.22	1.32	977	5.2	2.60	1.04
20	1.14	1.65	984	3.36	1.68	0.67
16	0.58	2.06	991	2.16	1.08	0.43
12	0.245	2.75	1001	1.25	0.63	0.25
10	0.142	3.30	1007	0.88	0.44	0.18

The time constant of the system described above is of the order of 0.1 sec, consequently time-lag effects can be ignored.

Inspection of the table shows that in this specific case the maximum permissible material load of the vacuum system is rather small, if reliable measurements of low non-equilibrium dissociation pressures are to be obtained. The values in actual experiments will, of course differ to some degree from this very simplified model situation, in which no reaction kinetics were considered. This is especially the case for materials with other activation energies than that assumed in the example given above. Nevertheless, the values in the table can serve as a guide to the set-up of other experiments.

In general a number of relations can be given for experimental conditions whose decay time τ is small, rate of heating dT/dt is constant and reaction kinetics cause no serious complications:

(a) The amount of material M_c, dissociated until the Knudsen limit p_{Kn} is reached, is inversely proportional to the rate of heating dT/dt, or $M_c \cdot dT/dt = C$. The value of the constant C depends on the dimensions of the system.

(b) The value M_c is inversely proportional to the length of the system, assuming that all lengths—L, l_f etc.—of the system are changed proportionally.

(c) The amount of material dissociated until a certain pressure is reached is proportional to the third power of the diameter of the tube.

(d) The influence of the volume of the pressure gauge can be neglected if it is of the same order of magnitude as the system itself.

A condition for a good calculation of the pressure just above the sample with eqn (8) is that the pump resistance is known, and the gauge calibrated. Fortunately this can be done with the EGD equipment itself.

4. CALIBRATION OF PRESSURE GAUGE AND DETERMINATION OF PUMP RESISTANCE

If the pressure in the system is about an order of magnitude above the background pressure, the pump resistance is approximately constant[10] and can be approximated by a resistance of a piece of pipe of length l_p (see Fig. 1). Assuming that this resistance, together with that of the tubes connecting the pump with the gauge is W_1, and that the pressure meter is calibrated, the application of the vacuum analogy of Ohm's law gives:

$$W_1 \, dn/dt = p_M \tag{11}$$

If a known amount of material, for example $BaCO_3$, is decomposed at S between time t_1 and t_2, the pressure can be measured as a function of time. As W_1 does not depend on time, integration of eqn (11) gives

$$W_1 = \frac{1}{n}\int_{t_1}^{t_2} p_M \, dt \tag{12}$$

in which n is the number of gas molecules evolved during the decomposition. The right-hand side of eqn (12) is thus determined if the calibration of the pressure meter is known.

If there is doubt about the calibration of the gauge M, a check can be made by inserting a known resistance, for example a certain length of tube with appropriate diameter, between gauge and pump, and repeating the experiment. In this case the pressure meter should be approximately linear in the pressure range considered. This requirement is in general fulfilled by ionization and Penning gauges[9].

5. EXAMPLE OF MEASUREMENT

In order to obtain an impression of the applicability of the considerations given above, an experiment has been made.

A quartz tube, 21 mm in diameter, was inserted into an oven to a depth of 20 cm. In its closed end a 160-mg mixture of three alkaline-earth carbonate powders was placed in a platinum crucible and heated at a constant rate of 1.6 K min^{-1}. The distance between sample and pressure meter was 28 cm, the pressure meter being an ionization gauge. The mixture consisted of 36 mole percent $CaCO_3$, 34% $SrCO_3$ and 30% $BaCO_3$, thoroughly homogenized, and was completely dissociated in the experiment.

The measured value of the pump resistance, R_1, including a piece of tube and a stopcock with a large bore, was 0.95 ± 0.06 dm^{-3} sec. The calculated value of the ratio p_S/p_M, as given by eqn (8), is in the temperature range of interest (800–1000 K) between 2.16 and 2.41. In the evaluation of the experimental results a mean value 2.29 has been used as multiplication factor of p_M. The calibration of the gauge has been inspected, and proved to be correct within 10%.

The pressure–temperature relation above the sample is shown in Fig. 2. It was established in a separate experiment that the three peak temperatures of the mixture were equal to those of the individual components. It is seen that the separation between the dissociation range of $CaCO_3$ and the two others is almost complete, whereas a fairly broad overlap occurs between the $SrCO_3$ and $BaCO_3$ components.

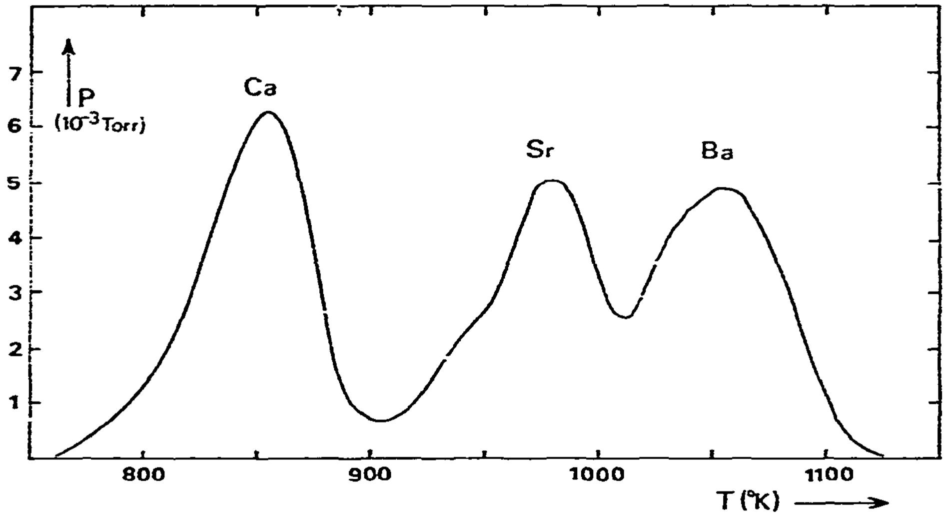

Fig. 2. Pressure above dissociating mixture of alkaline-earth carbonates as function of temperature. Mole ratio 36% $CaCO_3$, 34% $SrCO_3$, 30% $BaCO_3$. Weight 160 mg, $dT/dt = 1.6$ K min^{-1}.

In comparing the curve with Table 1 it can be seen that in this experiment the peak pressures are about a factor 3 above the calculated Knudsen limit.

Due to the approximate linearity of the system the areas under the different peaks must be proportional to the mole content of the components in the mixture, assuming there is no interaction between them during their decomposition. The molecular ratio of the components, given by analysing the curve of Fig. 2, is shown in Table 2. The experimental uncertainty stems from the uncertain interpretation of the overlap areas around 1000 K. Table 2 shows that the experimental results are in fair agreement with the molar ratio of the components in the carbonate mixture.

TABLE 2

MOLE PERCENT CARBONATES IN MIXTURE

	$CaCO_3$	$SrCO_3$	$BaCO_3$
Experimental	37	30–33	33–30
Expected	36	34	30

6. CONCLUSION

In the foregoing sections an analysis has been given of the conditions to be fulfilled in order to obtain maximum information from evolved gas detection (EGD) experiments at low pressures.

Firstly, in order to make a reliable determination of the pressure just above the dissociating sample, it is necessary to carry out the measurements in the range of molecular flow of the gas in the equipment used. This means that the pressure should not much exceed the Knudsen limit, which is about $1\text{–}3\times 10^{-3}$ Torr for general vacuum equipment. This pressure condition implies that there is an upper limit for the product of the rate of heating, dT/dt, and the mass M_c of the compound to be decomposed: $dT/dt \cdot M_c \leqslant C$. In this relation C depends only on the properties of the vacuum pump and the dimensions of the equipment, and of course on the compound considered. For a typical example of dissociation of $BaCO_3$ a value $C \simeq 10^{-3}$ g K sec^{-1} has been calculated.

It has been shown that the necessary determination of the vacuum pump resistance and the calibration of the pressure gauge used can be made with the EGD equipment itself. One only needs the Knudsen formula for the resistance of a tube with circular cross-section.

Finally the quantitative aspects of the method are briefly illustrated by the example in Section 5, concerning the dissociation of a mixture of three alkaline-earth carbonate powders.

In the foregoing sections attention has been focused on the EGD thermal analysis technique. However, the considerations made should be applied to the related DTA and TG technique as well, if operated at low gas pressures. The authors think that much of the scatter in literature data concerning the dissociation of carbonates and other compounds at low pressures is caused by uncertainties in the pressure measurements, which makes the reaction systems studied poorly defined. A few experiments, sustaining this point of view, will be given in a subsequent paper.

In conclusion, it can be stated that the EGD technique, applied at lower gas pressures, can be considered as a quantitative and relatively precise thermal analysis method, which is moreover rather simple. This fact makes it a useful tool in investigations of the kinetics of heterogeneous reactions at these pressures.

ACKNOWLEDGEMENT

The authors are indebted to Mr. F. H. R. Almer for helpful discussions.

REFERENCES

1 K. H. Stern and E. L. Weise, *High Temperature Properties and Decomposition of Inorganic Salts*, Vol. 2, Nat. Bur. Standards, Washington D. C., NSR DS-NBS 30, 1969.
2 T. L. Webb and J. E. Krüger, in R. C. Mackenzie (Ed.), *Differential Thermal Analysis*, Vol 1, Academic Press, London, 1970, p. 303.
3 M. D. Judd and M. I. Pope, in R. F. Shwenker and P. D. Garn (Eds.), *Proc. 2nd Conf. Thermal Analysis*, Vol. 2, Academic Press, New York, 1969, p. 1423.
4 M. D. Judd and M. I. Pope, *J. Appl. Chem.* (*London*), 19 (1969) 191.
5 M. D. Judd and M. I. Pope, *J. Appl. Chem.* (*London*), 20 (1970) 69.
6 M. D. Judd and M. I. Pope, *J. Appl. Chem.* (*London*), 20 (1970) 384.
7 M. D. Judd and M. I. Pope, *J. Appl. Chem. Biotechnol.* (*London*), 21 (1971) 149.
8 M. D. Judd and M. I. Pope, *J. Appl. Chem. Biotechnol.* (*London*), 21 (1971) 285.
9 S. Dushman, in J. M. Lafferty (Ed.), *Scientific Foundations of Vacuum Technique*, John Wiley and Sons, New York, 1961, Ch. I.
10 A. E. Barrington, *High Vacuum Engineering*, Prentice Hall, 1964, Ch. 4.
11 J. J. Lander, *J. Amer. Chem. Soc.*, 73 (1951) 5794.