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A system for studying gas–solid reaction kinetics in controlled atmospheres

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Abstract

A system has been developed to allow the automatic measurement of weight change in controlled atmospheres. In this work we report the design and use of an automated balance system which allows rapid acquisition of data and real-time display of weight change in a closed reaction vessel as a function of time. The apparatus is used to study the kinetics of gas–solid reactions and the decomposition of inclusion compounds having volatile guests.

INTRODUCTION

A system which allows measurement of weight change with time in hermetically controlled atmospheres can be applied to a variety of pursuits [1–9]. Our interest lies mainly in the study of the kinetics of formation and decomposition of inclusion compounds as gas–solid reactions. These studies had previously been conducted using a McBain balance, where weight gain was determined by measuring the extension of a silica spring by means of a cathetometer [10]. However, this technique is not suitable for rapid reactions, which require many measurements over a relatively short period of time.

Some modern electronic balances are equipped with data transfer interfaces which allow fast, automatic monitoring of mass by a microcomputer. The problem with weighing in controlled atmospheres is that such balances cannot withstand reduced pressures or corrosive gases. Several devices have been described whereby a sample in a sealed reaction chamber can be linked to an external balance by means of free magnetic suspension [3,7,8,11]. In such systems a sample pan is attached to a permanent magnet

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(or an electromagnet) which is coupled across the vessel wall to an external electromagnet suspended from an analytical balance. This coupling is effected by maintaining the equilibrium between the upward electromagnetic and downward gravitational forces acting on the permanent magnet. Electronic feedback of the position of the permanent magnet is used to control the current through the electromagnet in order to balance the forces. Position feedback can be achieved by means of capacitive [3,7,15,16], inductive [8,11,13,14] or optical [11,17,18] sensing. In our system we have decided to use the last-named method, which requires the least complex circuitry. The additional design constraint of optical passage across the system boundary is easily overcome.

DESCRIPTION OF APPARATUS

The system consists essentially of a reaction vessel connected to a vacuum pump, a conventional laboratory balance (Mettler PM460 Deltarange), a feedback control circuit and a microcomputer (Fig. 1).

The reaction vessel can be evacuated and thermostated, and the pressure and temperature can be monitored by means of a manometer and a thermocouple respectively. Reactant liquid can be introduced via the inlet port and allowed to equilibrate to its temperature-dependent vapour pressure. An aluminium sample pan is connected by means of a thin brass rod to the PTFE screen, which is in turn connected to the permanent magnet. The head of the vessel is permanently clamped; the rest of the chamber is mounted on a stand, allowing it to be raised into the head and lowered for sample loading.

The electromagnet is suspended from the electronic balance and its position above the vessel head is adjustable for optimal performance. The balance is interfaced with an IBM-compatible microcomputer and the data-logging software was written in TURBO PASCAL [12]. The computer program allows entry of the duration period of the experiment, the expected maximum mass gain and the time interval required between readings. During the experiment, data are simultaneously written to the computer's hard disk and graphically displayed on the monitor in the form of a plot of mass gain or loss as a function of time.

The circuit (Fig. 2) is a voltage controlled current source, the voltage level being a function of the light intensity striking photodiode D_1. The light from the 6 V bulb is collimated by a lens with a 2 cm focal length. The resulting quasi-parallel light beam passes over the top edge of the conical PTFE screen and strikes the large area silicon photodiode. A photocurrent is produced which is a linear function of the light intensity. The photodiode is reverse biased and connected to a transimpedance amplifier (U1A), which ensures that the photodiode is operating in a short-circuit mode, thereby producing a current proportional to the incident irradiance.

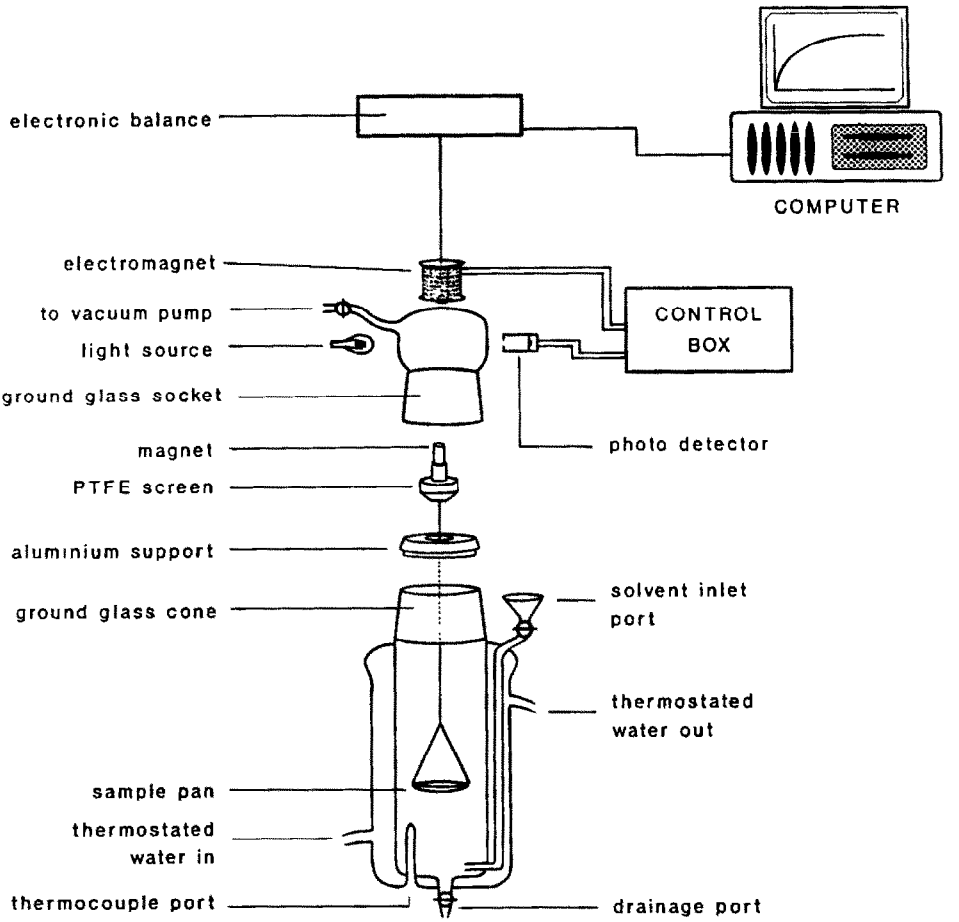

Fig. 1. Schematic diagram showing the principal features of the balance system.

The output voltage $V_P = -R_F I_P$, where R_F is the feedback resistance and I_P is the photodiode current. The voltage V_P then feeds into a phase-lead amplifier U1D that ensures stability of the control loop by compensating for lags in the system. The levitating magnet experiences a low frequency oscillation if C_4 is removed; the optimum value for C_4 can be empirically selected for stability. The transfer function of the phase-lead amplifier is given by

$$\frac{V_C}{V_P} = \frac{-R_4(1 + j\omega R_3 C_4)}{R_3(1 + j\omega R_4 C_3)} \tag{1}$$

where $j\omega R_3 C_4$ and $j\omega R_4 C_3$ are complex numbers. The transfer function may also be expressed in terms of the complex frequency s as

$$T(s) = \frac{-C_4\,(s + 1/R_3 C_4)}{C_3\,(s + 1/R_4 C_3)} \tag{2}$$

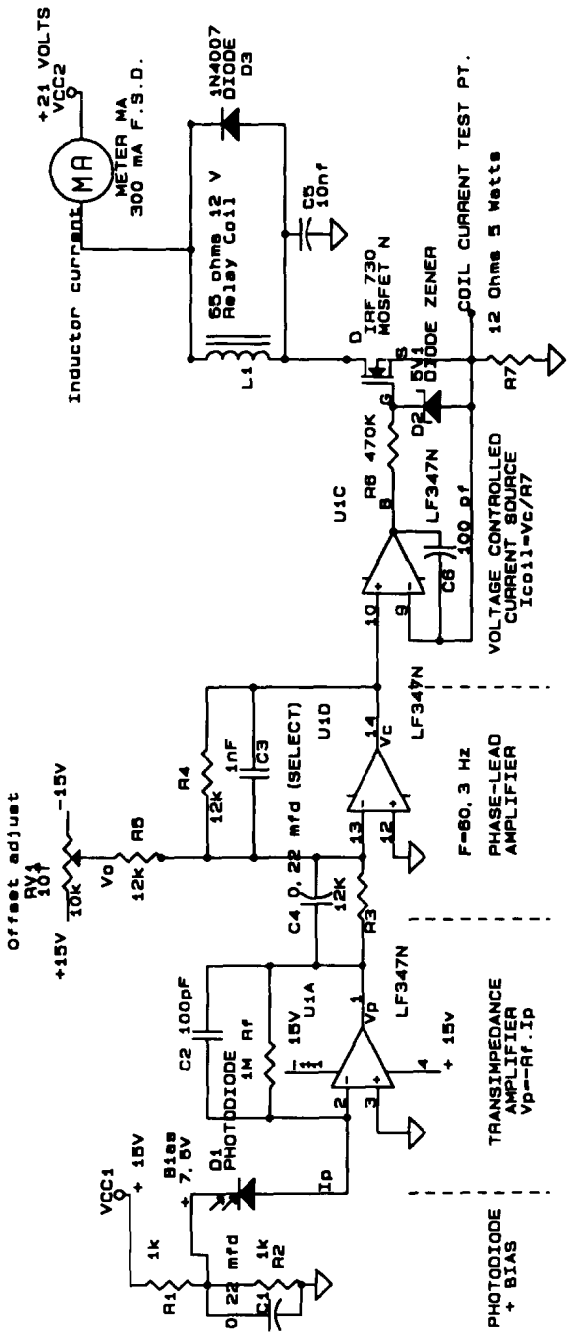

Fig. 2. Diagram of the feedback control circuit.

Equation 2 indicates that $1/R_4C_3$ is a pole of $T(s)$ and that $1/R_3C_4$ is a zero. With the values shown, the first break-point frequency (f_1) is 60.3 Hz. A second break-point ($f_2 = 13.3$ kHz) is due to a pole created by C_3 and R_4. The ten-turn potentiometer (RV_1) and the resistor R_4 are used to set the current through the coil L_1 when the PTFE screen blocks 50% of the light projected at the photodiode. The length of the magnet protruding from the levitating cone must be optimised to ensure that the barrier blocks the correct amount of light, at the same time making sure that the gap between the permanent magnet and the electromagnet permits stable levitation to take place. These two adjustments are critical but, once set, need no further attention. The output of U1D is given as

$$V_C = R_4(V_o/R_5 + R_f I_D/R_3) \tag{3}$$

where V_o = offset from potentiometer VR_1 and $R_f I_D$ = voltage due to photodiode current = V_P. But $R_4 = R_5 = R_3$, therefore

$$V_c = V_o + V_P \tag{4}$$

The voltage V_C at pin 10 of U1C is identical to the voltage at pin 9, which is the voltage across resistor R_7 (proportional to the current). The action of the negative feedback loop, comprising the MOSFET transistor, R_7 and the operational amplifier, ensures that I_{coil} is directly proportional to V_c. This section therefore acts as a voltage controlled current source, i.e.

$I_{R_7} = V_c/R_7 = I_{L_1}$ = coil current

The 5.1 V zener diode protects the MOSFET transistor from excessive gate–source voltage and the capacitor C_5 is used to suppress a high frequency oscillation due to the inductance of L_1. The 6 V power supply is fitted with a slow start circuit feature to prolong the life of the lamp and to ensure a more controlled and gradual attraction between the electromagnet and the permanent magnet. When the levitating cone is in the rest position and the lamp is turned on, the current passing through the electromagnet is at a maximum because there is no interruption of the light beam. There is therefore a powerful initial force of attraction that lifts the permanent magnet off its resting platform. Once it reaches the correct height and interrupts the light beam, the electronic feedback takes control and levitation of the permanent magnet is automatically maintained.

The balance has a weighing range of 410 g and features subtractive taring with a readability of 1 mg. The electromagnet weighs approximately 78 g and the tare weight of the levitating system (comprising the permanent magnet, PTFE screen, brass connecting rod and the sample pan) is 25.2 g. An additional weight of up to 16 g can be supported by the electromagnet. The gap between the electromagnet and the permanent magnet is maintained at between 3 and 7 mm. Since we have used a compensating beam balance for which there is no perceptable vertical displacement of the

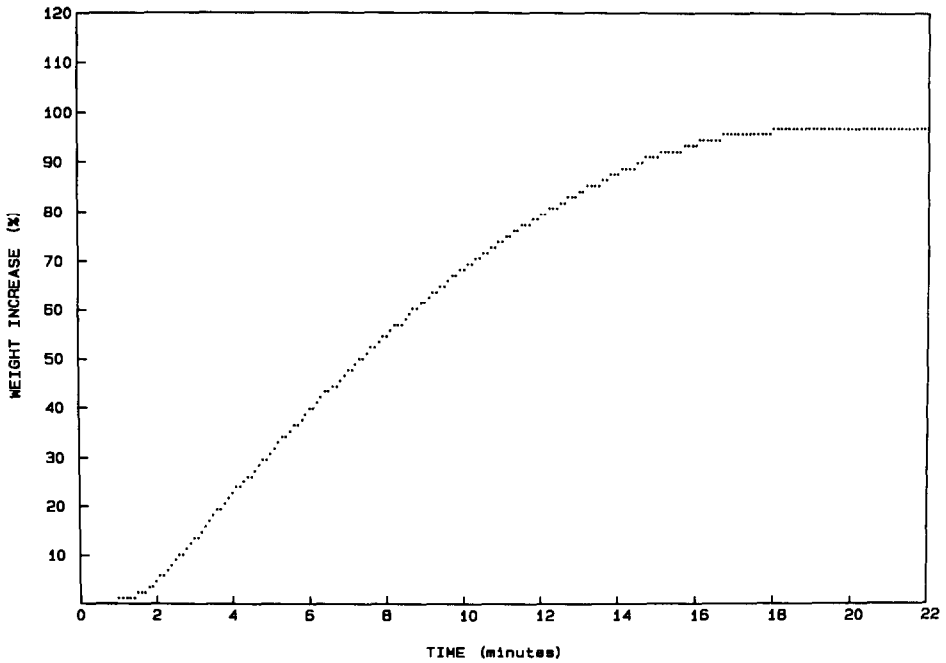

Fig. 3. Absorption isotherm of acetone by 9,10-dihydroxy-9,10-diphenyl-9,10-dihydroanthracene at 21°C.

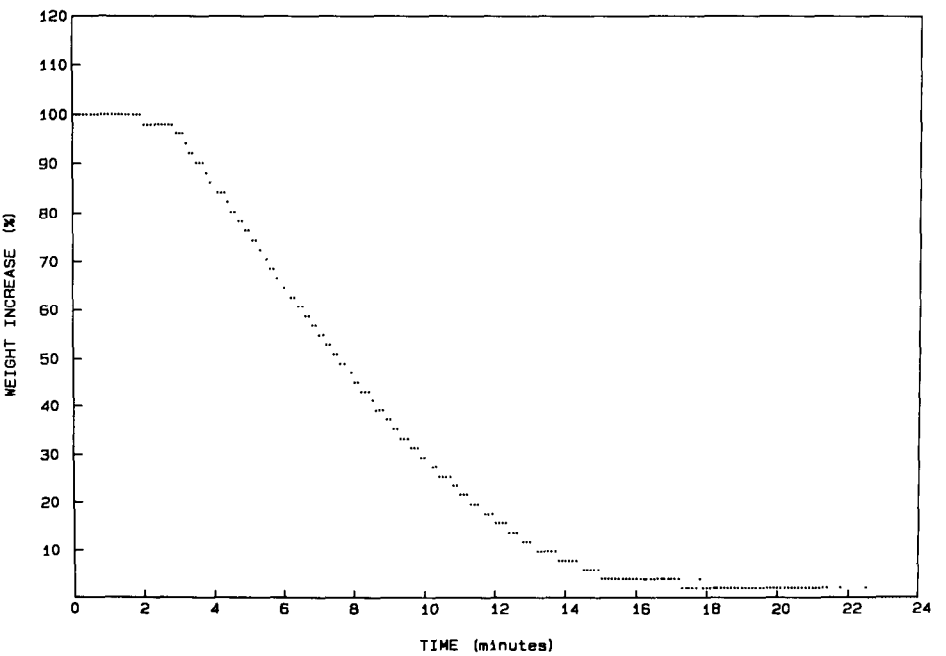

Fig. 4. Desorption isotherm of acetone by 9,10-dihydroxy-9,10-diphenyl-9,10-dihydroanthracene at 18°C.

weighing mechanism, fluctuating forces due to elastic deformation of the electric lead (double strand of 0.1 mm diameter copper wire) to the electromagnet are eliminated.

Once in operation, the levitating system quickly gains sufficient stability to allow accurate mass readings, restricted only by the detection limit of our analytical balance.

APPLICATION

In our studies we typically use 100–500 mg of host sample and expect a stoichiometric mass increase in the range 30–200 mg of absorbed guest. This is well within the capabilities of the free suspension system.

Figures 3 and 4 show the absorption and desorption curves of acetone by 9,10-dihydroxy-9,10-diphenyl-9,10-dihydroanthracene at 21 and 18°C respectively. The advantage of the system is that many data points can be obtained even though absorption and desorption are rapid. This is particularly important in the initial stages of the reaction. Interpretation of the kinetic results for this particular host–guest system is currently under consideration and will be published elsewhere.

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