

A Computer-Aided Experimental Setup for Studying Sorption Kinetics

INTRODUCTION

Diffusion is a mass transport process by which molecules are transferred between different parts of a mixture as a result of random molecular motion. Diffusion phenomena play a very important role in many processes such as in separations employing polymer films and molecular sieves, heterogeneous chemical reactions, dyeing of textile fibers, and surface coatings, etc.

The most important parameter in a diffusion process is the diffusion coefficient. Many different methods can be used to determine the diffusion coefficient of a mixture. Although the quartz-spring balance described by McBain and Bakr¹ has been widely used in sorption studies of gas (vapor)-solid systems, its operation involves too much human interference and labor, and it is not convenient for sorption kinetics studies. Many investigators have used the analog output of the electronic balance in sorption studies. Human interference is still required to transfer analog recording data into numerical numbers. In this communication, we describe a computer-aided experimental setup and its application in measuring diffusion coefficients of vapor-solid systems based on the mathematical description of the diffusion process.

EXPERIMENTAL SETUP

A block diagram of the experimental setup is shown in Figure 1. It consists of a Cahn 2000 electrorecording balance, a vacuum system, a Datametrics valve controller, an electronic manometer, a pressure transducer, a Brooks servo valve, an HP 3421A data acquisition system, a Sargent-Welch temperature controller (Model ST), and a PRSM V20-12 (IBM compatible) microcomputer installed with a HP-1B interface card and a printer.

The Cahn 2000 balance consists of a control unit and a weighing unit, A. This weighing unit is enclosed in a glass vacuum bottle, B, having a vacuum outlet and three hangdown glass tubes, C, D, and E. The polymer film F and the counterweight stirrup G are suspended on the

balance beam by means of hangdown wires and metal loops attached to the beam. The glass tube C enclosing the polymer sample has a glass jacket through which the heat-carrying liquid flows at constant temperature. Temperature fluctuation is about $\pm 0.05^\circ\text{C}$. In order to avoid condensation, the whole weighing unit was fitted inside a metal box, H. The temperature of this box is controlled by a Sargent-Welch thermomonitor. Heating and cooling of the box is carried out by an infrared bulb and an RMT cooling unit, respectively. The weighing unit is connected to the glass vacuum line through a cap. The vacuum line consists of a vacuum pump, liquid nitrogen traps, Pirani gauge, and three taps T_1 , T_2 , and T_3 . The weighing unit is evacuated by opening tap T_1 , whereas tap T_2 serves as a vent and tap T_3 connects the system to the vacuum pump.

The pressure control loop consists of a valve controller (V), an electronic manometer (M), a pressure transducer (R), and a servo valve (SV).

A thermocouple is embedded inside the glass vacuum bottle B and the head of the couple is only 1-3 mm from the solid sample. This assures an accurate and sensitive measurement of the sample temperature.

The data acquisition system consists of an HP 3421A data acquisition unit, a microcomputer equipped with a HP-IB interface card, and a printer (optional). An analog output of 1 MV reflecting the sample weight from the electrobalance and a 10 MV output, indicating the pressure of the vapor phase from the electronic manometer, are fed into the data acquisition unit where they are digitized. The two thermocouples measuring the temperatures of both the sample and the chamber are also connected to the data acquisition unit.

A computer software is developed in BASIC to transfer the digitized output from the data acquisition unit to the computer through the interface card. The program then prints the values of all the system variables (temperature, sample weight, and pressure) as a function of time on the computer screen. The kinetic data are also written at different frequencies for the different stages of the sorption kinetics into a magnetic diskette. A hard copy of the data can also be obtained from the printer if required.

The ready to use data stored on the diskette can be loaded into any data manipulation software (such as lotus-123, supercalc, etc.) and analyzed based on the governing diffusion equations as discussed in the next section.

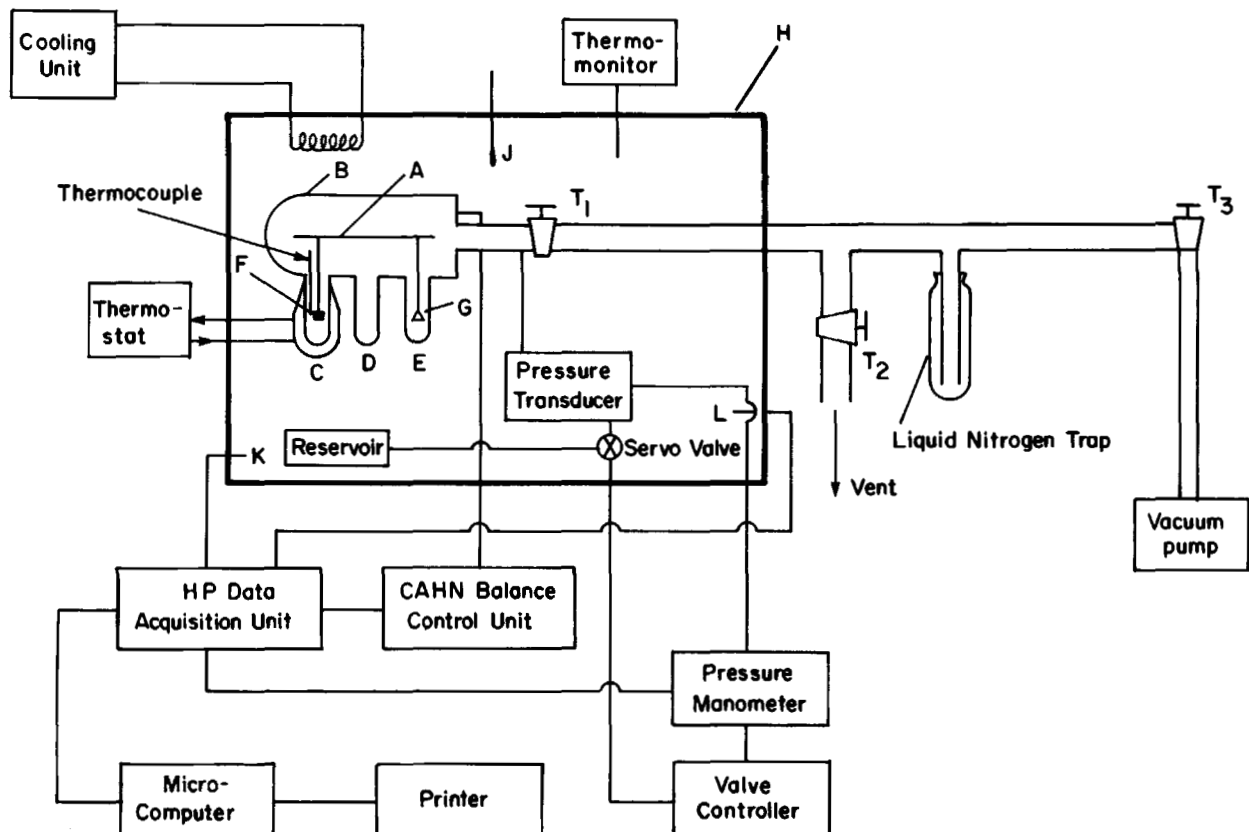


Figure 1 Schematic of the experimental setup.

This setup can be used to measure both adsorption and desorption kinetics of a gas–solid system. (The data of sorption equilibrium are obtained at the same time.) In the case of adsorption, the vapor phase pressure can be kept constant by the valve controller. This is very important in validating the assumption of constant surface concentration especially at lower pressures which is required by a simpler solution of the diffusion equation.

In the case of desorption, a saturated sample is suspended on the balance at time 0 and the vapor phase pressure is kept at 0.01 mm Hg by continuous pumping.

The weight gain or loss as a function of time can be acquired in a time interval as short as 3 s. The computer will end the data acquisition automatically when sorption equilibrium is reached (when the weight change of the sample is less than 1×10^{-4} mg/10 min). To obtain a set of kinetic data on the computer spreadsheet for a vapor–solid system using the present setup, the only thing one needs to do is loading the sample at time zero.¹

MATHEMATICAL FORMULATION OF VAPOR–SOLID DIFFUSION AND EXPERIMENTAL DESIGN

It is well known that if the diffusion process in a gas–solid system is Fickian, very simple approximate solutions of

the diffusion equation can be obtained in both the initial (short time) region and in the approach to equilibrium (long time) region.

For a thin film extending from $-l$ to l in the x direction, the following relations can be obtained² for the long time region:

$$\ln \left(\frac{M_\infty - M_t}{M_\infty} \right) = \left[\frac{\pi^2 D}{4l^2} \right] t \quad (1)$$

For the short time region, one obtains

$$\frac{M_t}{M_\infty} = \left[(2/l) \sqrt{D/\pi} \right] t^{1/2} \quad (2)$$

where M_t and M_∞ are the amount of diffusing substance gained by (in case of adsorption) or removed from (in case of desorption) the solid film at time t and at equilibrium, respectively. For the diffusion of organic molecules in rubbery polymeric materials, Fickian diffusion kinetics can be expected. Figure 2 shows some typical sorption curves obtained by the present setup for the system n -

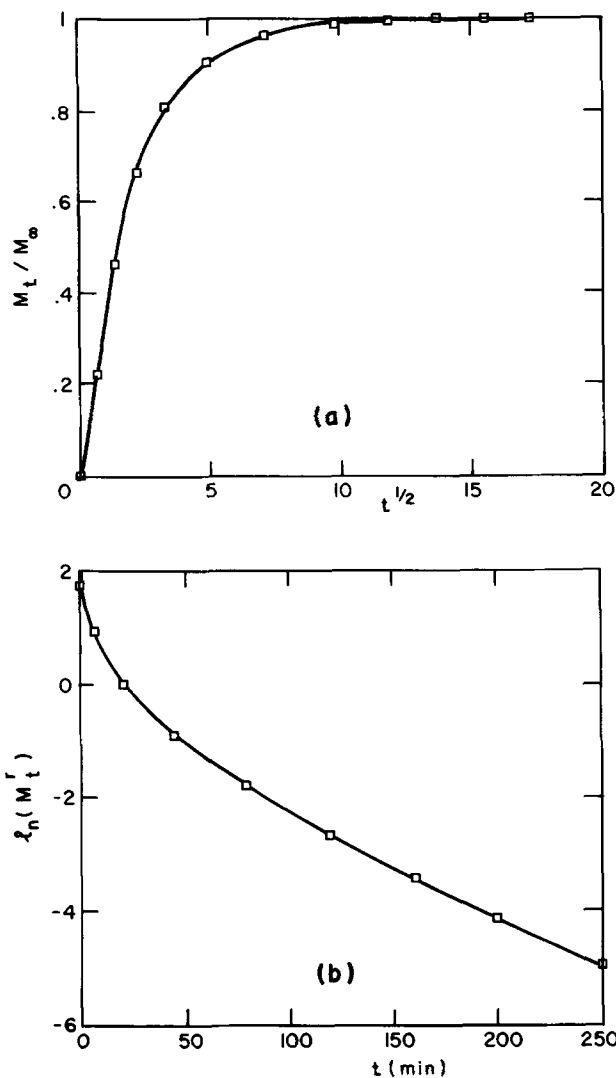


Figure 2 Kinetic curves for the desorption of *n*-hexane from a 0.015 mm LDPE film at 25°C. The straight line in the short time region of (a) indicates a major feature of Fickian diffusion. The straight line in the long time region of (b) enables the accurate determination of the diffusivity. The squares in the figures denote the data points acquired by the computer.

hexane-LDPE, where (M'_t) is the amount of diffusing substance still remaining in the film at time t . The straight lines in both the (M'_t) vs. t and the (M_t/M_∞) vs. $t^{1/2}$ plots can be used to obtain the diffusion coefficient of the system. It is to be noted, however, that the values of the diffusivity obtained by applying eq. (1) to desorption data at zero final concentration and that of eq. (2) to adsorption data may be different when the diffusivity is concentration-dependent. This is because the former gives essentially the diffusivity at zero concentration (D_0), whereas

the latter usually provides a concentration dependent diffusivity.

In the case of the desorption experiment in which a saturated polymer film is introduced in the balance at time 0, the value of M_∞ may be subjected to certain uncertainty as a result of the existence of excess liquid on the external surface of the film and vapor-phase pressure fluctuations. This will result in some uncertainty in applying eq. (1) to determine the diffusivity. If, however, a quantity (M'_t) as defined above, is used, then eq. (1) becomes

$$\ln M'_t = -(\pi^2 D / 4l^2)t + \ln M_\infty \quad (3)$$

where

$$M'_t = M_\infty - M_t \quad (4)$$

In a desorption measurement using a gravimetric technique, the value of (M'_t) is the difference between the sample weight at time t (W_t) and the sample weight at equilibrium (W_∞). In the measurement of D_0 , W_∞ is the weight of the dry film. Therefore, M'_t can be determined alternatively by the following equation:

$$M'_t = W_t - W_\infty \quad (5)$$

The quantity W_∞ can be determined very accurately and easily. Therefore, the diffusion coefficient can be determined by $\partial \ln M'_t / \partial t$ value of the approach-to-equilibrium desorption curve without involving M_∞ .

Although both eqs. (1) and (2) can be used to determine the diffusion coefficient of a gas-solid system, the use of eq. (1) is more reliable for the following reasons.

1. The initial sorption curve will definitely be affected by the temperature variation caused by the heat release (for adsorption) or heat absorption (in case of desorption), invalidating the isothermal condition which is usually assumed in the solutions of the diffusion equations. A temperature change from 2 to 10°C has been detected in some organic vapor-polymer system by the thermocouple placed very close to the sample.
2. The concentration of the vapor phase varies more drastically in the initial sorption region. This results in more errors, when using a constant surface concentration assumption.
3. In desorption runs with zero final concentration, the diffusion coefficient at zero concentration (D_0) can be obtained by applying eqs. (1) or (3) for the long time region data, obviating the use of M_∞ .

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