

## **“A COMPUTER - AIDED EXPERIMENTAL SETUP FOR STUDYING SORPTION AND DESORPTION KINETICS”**

By

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### **ABSTRACT**

The details of a computer-aided experimental setup are reported in this communication. This set-up produces high-quality data which can be utilized in studying sorption and desorption kinetics.

### **1. INTRODUCTION**

Diffusion is a mechanism by which mass-transfer takes place. As a transport process, diffusion plays an important role in almost every branch of Chemical Engineering.

The interest in diffusion of liquids, vapors and gases in polymers originates from an academic standpoint as well as from industrial needs. Extremely accurate diffusion data are needed in order to subject existing theories of diffusion to critical testing. On the industrial side, diffusion plays an important role in separations employing polymeric membranes, dyeing of textile fibers, surface coating, etc. Moreover, mass-transfer is perhaps most prominent in the formation of polymers, where the rate of polymerization can be controlled or strongly

influenced by molecular diffusion of monomers, initiators, long chain free radicals, dead polymer chains, or low molecular weight condensation products (Vrentas and Duda, 1979).

The measurement of the diffusivity of vapors in polymeric membranes can be accomplished either by the desorption or the sorption technique. The former yields a value of the diffusion coefficient which is close to  $D_0$ , whereas the latter could yield the dependence of diffusivity on concentration.

The quartz-spring balance described by MacBain and Baker (1926) has been widely used for studying diffusion in polymeric membranes and powders. However, the quality of the data obtained through such an arrangement is usually not high.

The advent of micro-computers and digital weighing and pressure control equipment made it possible to build a computer-aided experimental setup which can be operated in either the desorption or the sorption mode and produces very high quality data.

## 2. 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, Datametrics valve controller, electrometer, electronic manometer, pressure transducer, Brooks servo valve, an HP 3421A data acquisition system, a Sargent-Welch temperature controller (Model ST) and Unitron 2200 (Apple II plus compatible) microcomputer with 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 water flows at constant temperature. Temperature fluctuation is about  $\pm 0.01$  °C. In order to avoid

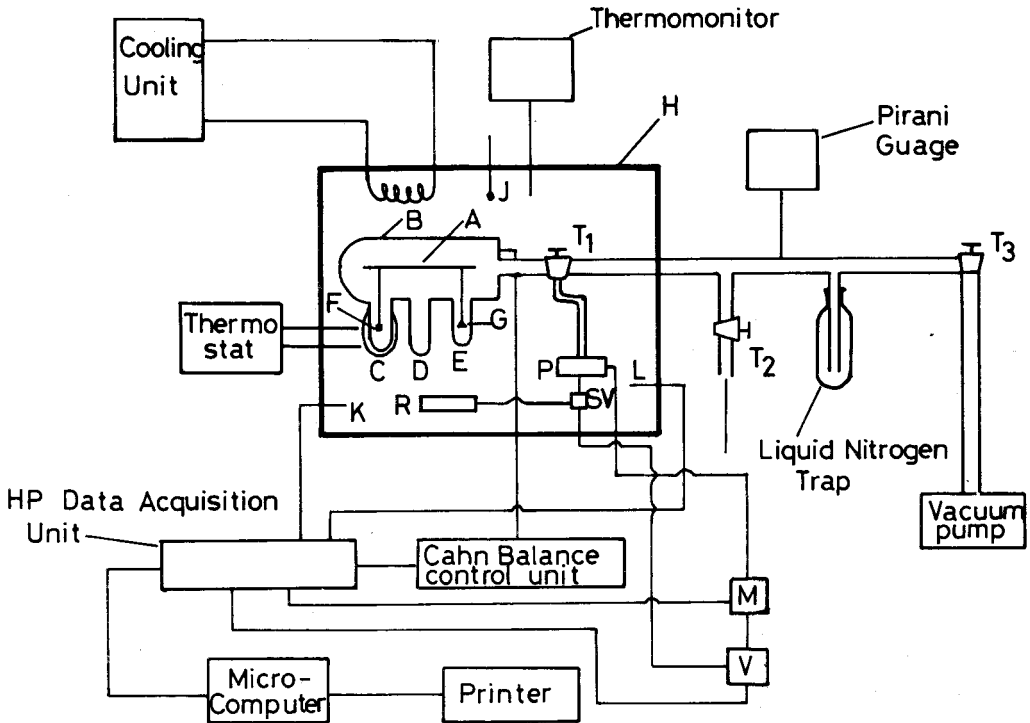


Figure 1 : A Flow Diagram of the Experimental Setup.

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 a household electric 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 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 (P), and a servo valve (SV).

A precision mercury thermometer J and two thermocouples enable one to read the temperature at various points of the chamber. Normally, a fluctuation of  $\pm 0.3$  °C is observed.

The data acquisition equipment consists of an HP 3421 A data acquisition unit, a microcomputer and a printer. An analog output of a 1 mV from the electrobalance and 10 V output from the electronic manometer are fed into the data acquisition unit where they are digitized and sent to the microcomputer. The two thermocouples K and L are connected to the data acquisition unit.

The printer provides a hard copy of the weight change of the specimen, resulting from desorption or sorption as explained later, averaged over a selected time interval. The temperatures read by the thermocouples K and L are also averaged over the same interval.

### 3. MAJOR COMPONENTS OF THE SETUP

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Quantity	Item
One	Cahn 2000 electrorecording balance purchased from CAHN Instruments Company, California, U.S.A.
One	Valve controller, Model 1404 purchased from Datametrics, Mass., U.S.A.
One	Electronic Manometer, Model 1400 purchased from Datametrics, Mass., U.S.A.
One	Pressure Transducer, Model 590A purchased from Datametrics, Mass., U.S.A.
One	Brooks servo valve, purchased from Brooks Instruments Co., U.S.A.
One	Sargent-Welch Thermomonitor, Model ST purchased from Sargent-Welch, U.S.A.
One	Hewlett-Packard Model 3421A data acquisition/control unit, purchased from Hewlett-Packard.
One	Haake circulating bath, purchased from Fisher Scientific, Toronto, Ontario, Canada.
One	RMT refrigeration unit, purchased from Brinkmann Instrument Co., Toronto, Ontario, Canada.
One	Unitron 2200 microcomputer (Apple II Plus compatible). The computer is fitted with an IEEE card for parallel interfacing and a clock card.
One	Dot matrix printer.
One	Edwards high vacuum pump.

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## 4. EXPERIMENTAL PROCEDURE

Rectangular specimen of the polymer form with a hole at the top are cut. The size and hence the weight of the sample depends on the system under consideration. Care was taken to have a sample weight which enables one to operate below the 100 mg range limit of the microbalance. At this point, different procedures are adopted for sorption and desorption.

### 4.1 Desorption

Each of the samples prepared earlier are then immersed in a test tube containing the penetrant under investigation. This tube is already kept in a water bath at constant temperature. This is continued until equilibrium is attained. The time required for this equilibrium depends on the polymer-penetrant system; in most of the cases it does not exceed 24 hours. The equilibrium uptake of the penetrant is checked by periodically weighing the polymer film on a Mettler balance.

To start the desorption experiment, temperatures are set at the required level and the electrobalance is calibrated according to the procedures described by the manufacturer.

The polymer film is removed from the liquid and is sandwiched between two filter papers. This ensures the removal of the excess liquid from the surface of the polymer film. Thus a reproducible initial surface concentration of the penetrant can be achieved. The film is then suspended on the balance. The time between the removal of the film from the liquid and the suspension of the film on the balance should not exceed 10 to 15 seconds. The balance is immediately opened to the vacuum system at a pressure of 0.01 mmHg and desorption kinetics are followed by monitoring the weight loss with time using the microcomputer.

### 4.2 Sorption

Each of the samples prepared earlier is hung on the balance and vacuum is turned on for 24 hours to insure dryness of the sample.

The penetrant under investigation is placed in the glass reservoir (R). The reservoir is then placed in liquid nitrogen for about 2 hours until it completely freezes. Following that, the reservoir is connected back to the system and the system is evacuated.

Sufficient time is allowed for the penetrant in the reservoir to attain the temperature of the experiment. The valve controller is set at the required pressure.

The weight gain is monitored on the microcomputer until equilibrium is reached.

## 5. THEORY

Since the experiment setup is capable of being operated in the sorption as well as the desorption modes, the theoretical equations pertaining to each mode will be covered in this section.

### 5.1 Desorption

Figure 2 illustrates the polymer film under consideration. The film extends from  $-\ell$  to  $+\ell$  in the  $x$ -direction.

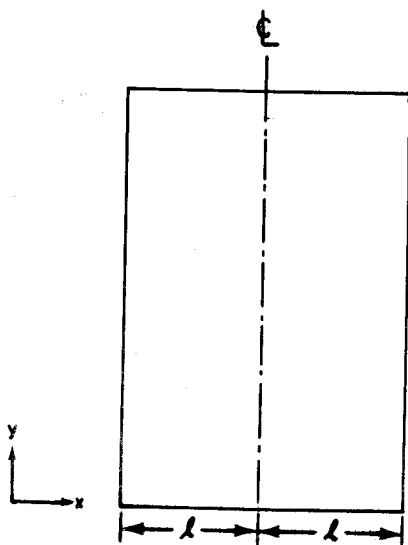


Figure 2 : Polymer Film

Fick's Second Law

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left[ D \frac{\partial C}{\partial x} \right] \quad (1)$$

is employed with the following conditions :

- (i) due to symmetry  $\frac{\partial C}{\partial x} = 0$  at  $x = 0$  and all  $t$
- (ii)  $C = 0$  at  $x = \pm \ell$  and  $t > 0$
- (iii)  $C = C_0$  at  $t = 0$  and at all  $x$

Application of the boundary and initial conditions mentioned earlier, combined with the orthogonality property of the cosine functions leads to the following relations for  $\lambda$  and  $C$  :

$$\lambda = (2n + 1) \frac{\pi}{2\ell} \quad (2)$$

$$C = \sum_{n=0}^{\infty} \left[ \frac{4C_0 (-1)^n}{(2n + 1)\pi} \cos \left[ (2n + 1) \frac{\pi x}{2\ell} \right] \right] \exp - \left[ (2n + 1) \frac{\pi}{2\ell} \right]^2 Dt \quad (3)$$

The quantity of liquid remaining in the polymer film per unit area,  $Q_t$ , is given by

$$Q_t = 2 \int_t^{\infty} D \frac{\partial C}{\partial x} \Big|_{x=\ell} dt = \sum_{n=0}^{\infty} \left[ \frac{4C_0}{\ell [(2n+1)(\pi/2)\ell]^2} \right] \exp - \left[ (2n+1) \frac{\pi}{2\ell} \right]^2 Dt \quad (4)$$

Since this series converges very rapidly, one can proceed using only one term. This term represents the system in the later stages of desorption.

$$Q_t \approx \left[ \frac{16 C_o \ell}{\pi^2} \right] \exp - \left[ \left[ \frac{\pi}{2 \ell} \right]^2 Dt \right] \quad (5)$$

Initially, the amount of liquid contained in the polymer film is denoted by  $Q_o$ ; where

$$Q_o = \frac{16 C_o \ell}{\pi^2} \quad (6)$$

If  $M_o$ ,  $M_t$  and  $M_\infty$  denote the weight of the dry film and the liquid contained in the film per unit area at times  $t$  and  $\infty$ , respectively, then

$$Q_t = M_t - M_\infty \quad (7)$$

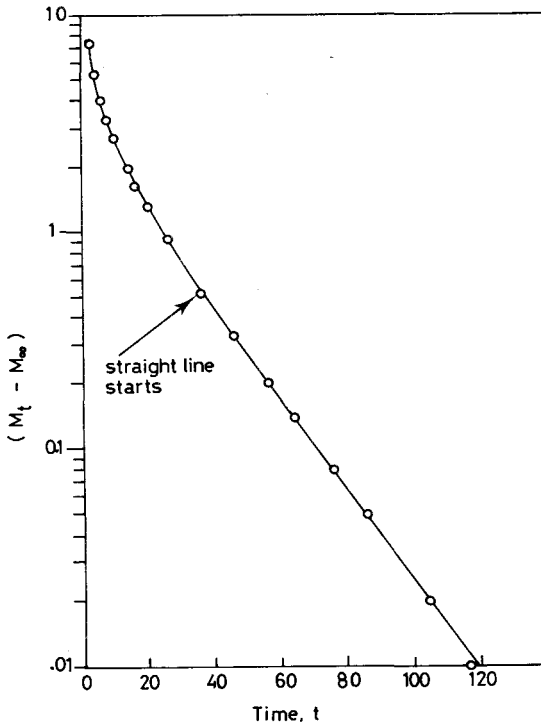
$$Q_o = M_o - M_\infty \quad (8)$$

combining equations (5) and (6) yields

$$(Q_t / Q_o) = \exp - \left[ \left[ \frac{\pi}{2 \ell} \right]^2 Dt \right] \quad (9)$$

Therefore, a plot of  $\ln(Q_t/Q_o)$  versus  $t$  yields a straight line whose slope allows the determination of  $D$ . A typical plot for the desorption of chloroform from low density polyethylene (Salem et al. 1989) is shown in Figure 3.





**Figure 3 : Typical Plot for the Desorption of Chloroform from Low Density Polyethylene at 25°C.**

## 5.2 Sorption

In a sorption experiment the dry polymer film is hung on the balance. Vapor is then admitted into the balance chamber. The chamber is kept at a controlled pressure. The increase in the weight of the polymer film is monitored with time.

The mathematical treatment of the sorption problem is similar to that given earlier for desorption except that the following conditions apply :

- (i)  $C = 0$  at  $t = 0$  and at all  $x$

(ii)  $C = C_0$  at  $x = \pm \ell$  and at  $t > 0$

(iii) due to symmetry  $\frac{\partial C}{\partial x} = 0$  at  $x = 0$  and at all  $t$

The following solution should be obtained

$$\frac{M_t}{M_\infty} = 2 \left[ \frac{Dt}{\ell^2} \right]^{1/2} \left[ \pi^{1/2} + 2 \sum_{n=1}^{\infty} (-1)^n \operatorname{erf} \frac{n \ell}{\sqrt{Dt}} \right] \quad (10)$$

Where  $M_t$  denotes the total amount of diffusing substance which has entered the sheet after time  $t$  and  $M_\infty$  the corresponding quantity after infinite time.

In the early stage of sorption and for a constant diffusion coefficient,  $D$ , one obtains

$$\frac{M_t}{M_\infty} = \frac{2}{\pi^{1/2}} \left[ \frac{Dt}{\ell^2} \right]^{1/2} \quad (11)$$

Plotting  $M_t / M_\infty$  versus  $t$  should yield a curve as that shown in Figure 4 which depicts a typical curve for the sorption of ethanol in cellulose acetate (Achkar, 1986). If sorption is Fickian, the initial part of the curve would be a straight line. In such case, the slope of the line would be :

$$\frac{2}{\pi^{1/2}} \left[ \frac{D}{\ell^2} \right]^{1/2}$$

The value of  $D$  obtained is an integral value. The differential value of  $D$  can be obtained by the procedure outlined by Crank (1979).

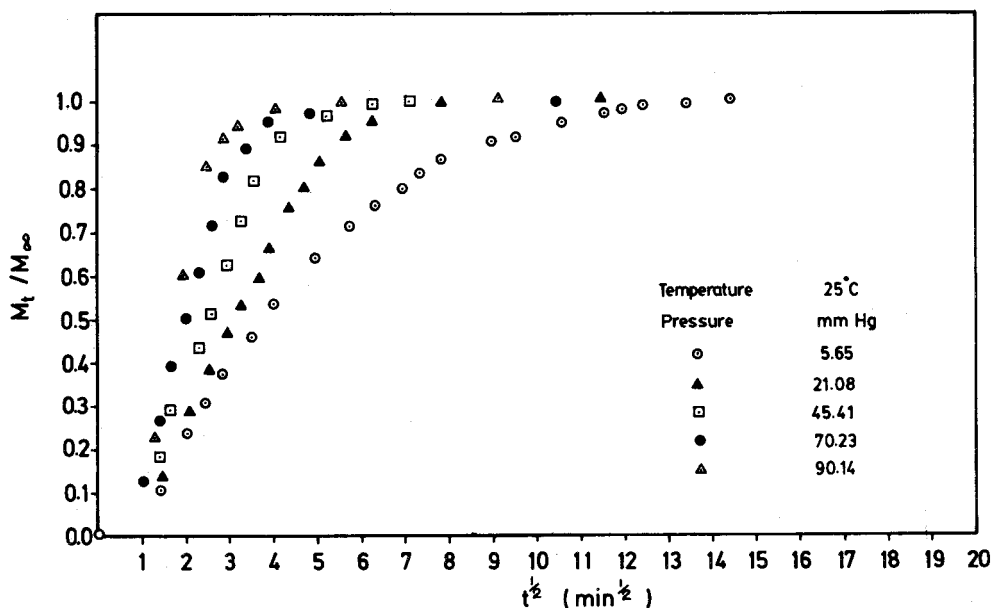


Figure 4 : Typical Plots for the Sorption of Ethanol in Cellulose Acetate at 25°C.

#### NOMENCLATURE

- C            Concentration (mg penetrant/mg polymer)  
 $C_0$         Initial concentration (mg penetrant/mg polymer)  
D            Diffusion coefficient,  $m^2$   
 $D_0$         Diffusion coefficient at zero penetrant concentration,  $m^2/s$   
 $\ell$          Thickness of the polymer film, m  
 $M_t$        Amount of penetrant sorbed at time t, mg  
 $M_\infty$       Amount of penetrant sorbed at equilibrium, mg  
 $Q_t$        Quantity of liquid remaining in the polymer film per unit area,  $mg/m^2$   
 $Q_0$        Initial quantity of liquid contained in the polymer film,  $mg/m^2$   
t            time, s

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