Use of a Microcomputer with a Gas Permeation Apparatus

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Synopsis

Hardware and software for collecting and storing the data of gas permeation in polymer membranes from the vacuum detector and various sensors have been developed for the GP-IB microcomputer online system. The system uses BASIC language programs. In comparison to manual inputs and calculations, the programs allow reductions in the time required for data treatment and in the standard deviation for a determination and, moreover, an improvement in the reproducibility of the results.

INTRODUCTION

Detailed information about the permeation of gases in polymers is essential not only for quantifying transport processes but also for relating the terms of diffusion models to polymer structure in a quantitative manner.

In a popular method[1] for obtaining the transport coefficients, the two reservoirs are divided by a polymer membrane. To one side, a gas at constant pressure is introduced. The gas diffuses through the membrane to the other side where the gas desorbs into the downstream reservoir. The pressure of gas $p(t)$ at time t tends over sufficiently large times to be a linear asymptote. The intercept of $p(t)$ on the t-axis yields the time lag from which the diffusion coefficient can be easily obtained.[2] From the slope of the linear asymptote, the permeation coefficients of the gas in the membrane can be also obtained.

In the earliest method of determining the time lag, the linear asymptote line was drawn by using a ruler on the curve recorded by the recorder.[3] But this method led to large or serious errors. Later, attempts toward reducing the error for the permeation method came with the use of a calculator to treat the data. Here the measurement of heights of the permeation curve was carried out by using calipers and the entry of the data into the calculator was done by hand.[4] Thus, the analysis was still a tedious process and also still erroneous. In the next step, a digital printer was connected to a pressure gauge through an analog to digital (A/D) converter. Downstream pressure changes were printed at regular time intervals with a precision of 0.01 s. A slope and intercept of the linear asymptote were calculated by the least square method through 30–50 experimental points by manual input. The precision of the slope and the time lag became greater, but the data input was time-consuming and prone to error.[5]

The final method of automation consists of using a GP-IB interface which connects a microcomputer with an A/D converter to sample the 1000–2000

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pressure change data and the many accompanying data detected by many sensors directly. Then, all the data were saved on a disk for data treatment by a standardized method using a BASIC program which can be easily mastered. Thus, flexibility is provided for at the analysis level. The data from these systems tend to be very accurate and can detect delicate changes in membrane structure, such as hysterysis or relaxation.

This paper describes both the hardware and software of a permeation measuring facility that exploits the advantages of such a system using a microcomputer.

HARDWARE DESCRIPTION

Permeation Apparatus. The permeation apparatus is shown schematically in Figure 1. Two pirani tubes were attached, one to each side of the permeation cell. The upper side pirani was operated by a simple bridge circuit which sent a signal to a computer at the instant gas was introduced to the cell. To measure the pressure change from a high vacuum at the lower side of the cell, another pirani tube was operated by a highly sensitive, constant temperature type circuit which was developed by our laboratory. Each pirani was set in a separate air bath in which the temperature was detected by a three-lead-type platinum resistance sensor.

There are a number of vacuum detectors in this apparatus. An MKS Baratron Capacitance calibrates the pirani gauge: an ion gauge detects the maximum vacuum reached just before the experiment, and a silicone diffusion type pressure sensor detects the pressure introduced upstream. Besides the intended pressure change data, it becomes more convenient to input automatically from these sensors to the online microcomputer.

Block Diagram of Data Collecting System. The full configuration of the microcomputer presently being used consists of:

(1) PC-8001 Microcomputer (NEC) with 64 kbytes of memory,

(2) PC-8011 Interface Unit (NEC),

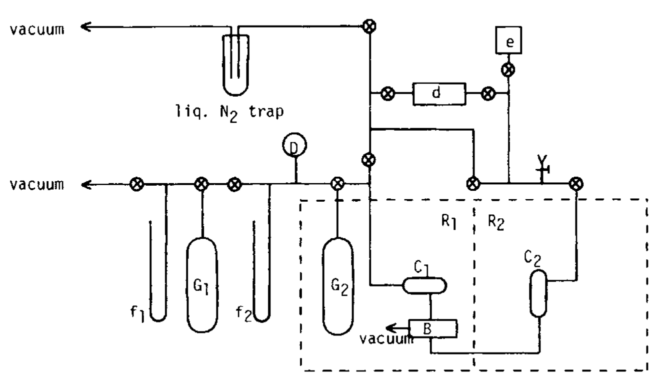

Fig. 1. Block diagram of permeation apparatus: (A_2, A_2) thermostat; (B) permeation cell; (f_1, f_2) mercury manometer; (G_1, G_2) gas cylinder. Sensors: (R_1, R_2) three lead type Pt resistance (R_{10}, R_1 for cell box temperature; R_{20}, R_2 for Pirani box temperature); (D) LX1600A (V_r, V_{r0} for upstream pressure); (e) ion gauge (p_I for monitoring vacuum degree of system); (C_1) Pirani guage for start signal; (C_2) Pirani gauge (v_0, v_n for downstream pressure change); (d) MKS Baratron Manometer (p_B for calibrating pirani gauge).

(3) Digital multimeter (TR6841, Takeda Riken) with an attached GP-IB adapter (TR1163),

(4) Channel selector with start signal circuit (newly devised),

(5) Two 5-in. floppy disk drives (one for the program master disk and one for data collection),

(6) Printer, xy-plotter, and monitor.

Figure 2 shows how this can be done.

GP-IB (IEEE-488). Most measuring instruments can now be obtained with the GP-IB interface which allows a microcomputer to output and/or input to the instrument.[6] This combination of computer and instrument leads to a very powerful experimental tool.[7] The permeation experiment, as well as other experiments, needs many additional data inputs as described above. It would be necessary to connect individually a GP-IB/A/D-converter system with each sensor, but this system would be very expensive. To avoid this problem, we made a multichannel system from one GP-IB system by connecting the lead relays with the I/O port of the microcomputer. As we can use the GP-IB port to send data to the computer, the multipurpose I/O port of the PC-8011 interface was employed here as the communication port.

Channel Selector. The user port of the PC-8011 is a 12-bit parallel input/output port, all of which can be used here as management lines. The channel select mode of operation is set by this user output port line. Twelve bits of the output data lines were connected to the lead relays, as shown in Figure 3. These relays act upon orders of the microcomputer with a BASIC program which is shown in Figure 4 as a flow chart (program A). At first all relays are opened. Then one intended relay is closed to connect to the digital multimeter. The digital multimeter takes in the signal of a sensor and converts the data from analog to digital. Then the digital data are sent to the microcomputer through the GP-IB interface. The program allows either the repetition of the data input from the same sensor or the change to another sensor by selecting the condition.

Start Signal Circuit. The upper pirani gauge in Figure 1 is operated by a simple bridge circuit which opens or closes a relay through a comparator circuit. This signal is further gated by a flip-flop circuit. Then the start signal is inputed to one of the input ports of the PC-8011 interface unit, as shown in Figure 3.

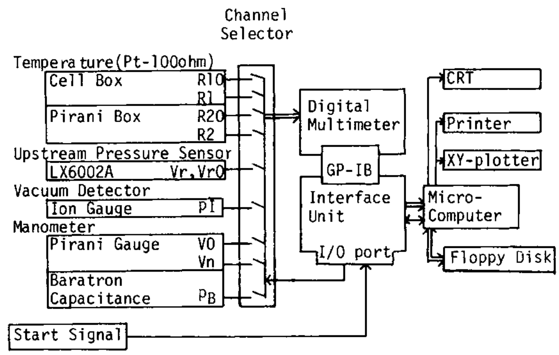

Fig. 2. Layout of online data logging.

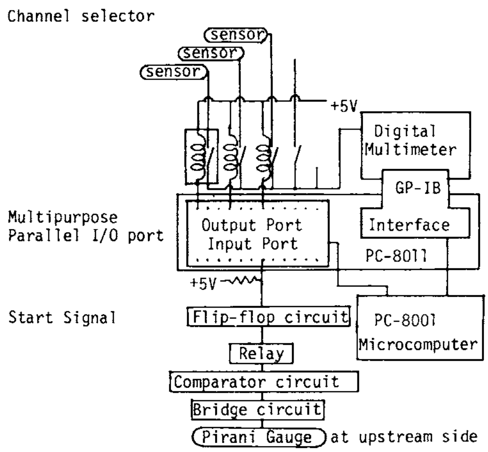

Fig. 3. Block diagram of channel select and start signal circuit.

SOFTWARE DESCRIPTION

The hardware connecting the PC-8001 to the GP-IB multimeter was kept to a minimum in order that cost and the potential for failure be reduced. Instead, most of the data collection (and control) are done by means of software. The BASIC software programs, designed and developed in our laboratory specifically for this system, were written in N-Basic (Trademark of NEC). This BASIC language allows for easy modifications and is sufficiently fast for use with the GP-IB unit. The software programs fall into the two categories of data collection and data treatment.

Data Collection Routines. The following data collecting routines are presently in use:

(a) A first program for initializing the GP-IB/microcomputer interface. This routine prepares the interface for data collection by clearing all registers in the microcomputer.

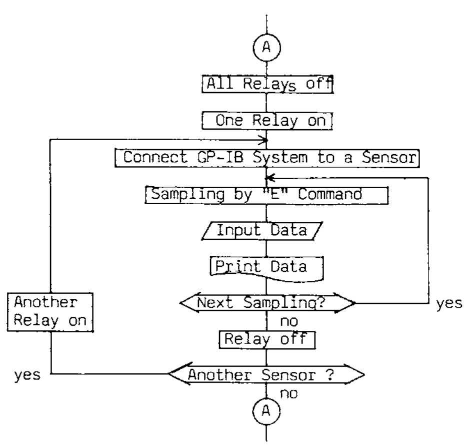

Fig. 4. Flow chart for "Input Data" subroutine program.

(b) A program which monitors the various detectors (sensors) and displays their current values using program A as a subroutine.

(c) The data collection routine itself. After monitoring temperature and vacuum detectors, the program enters a waiting loop. At the time when the start signal comes, the program escapes from the waiting loop, the time is set at 00:00:00, and at the same time the first data are input. The program enters another waiting loop until the next prescribed sampling time. This program collects on a continual basis from the lower side another waiting loop until the next prescribed sampling time. This program collects on a continual basis from the lower side pirani gauge about 1000 points at time intervals specified by the experimenter. Present data collection intervals can vary from 1 s to any interval.

The flow chart drawn in Figure 5 shows an outline of the data collection program. This program is activated by inputing the experiment number. The actual data are not processed at the time of data collection, but are preserved in a data disk for reduction. Disk space is kept to a minimum by converting the sensor values to integer and by not storing times. These times can be recreated in the output and in the calculation routine.

Data Treatment Routine. Data treatment consists of reading the raw data as stored in disk by the program and manipulating them in some predetermined fashion to produce the required results. In the case of permeation experiments the required results are (1) time lag (TL), (2) apparent diffusion coefficient (D_a), (3) apparent permeation coefficient (P_a), (4) apparent solubility coefficient (S_s), and (5) solubility ($C = S_a p$).

Factors which must be taken into account for the calculation above are cell and pirani box temperatures (T_1, T_2) and the upstream pressure (p_2).

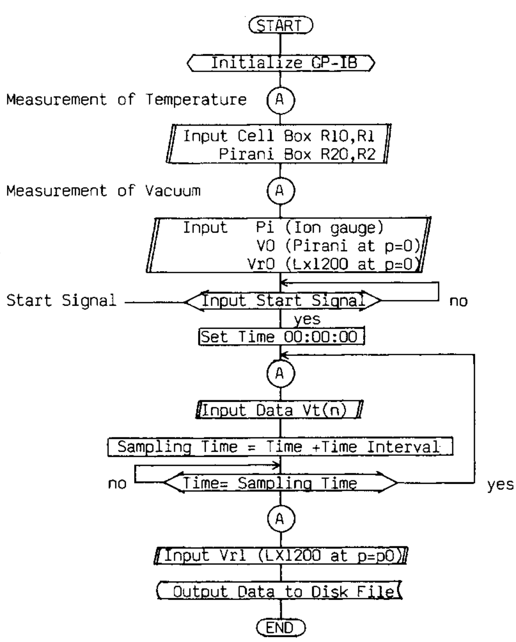

Fig. 5. Flow chart for "Collect Data" program.

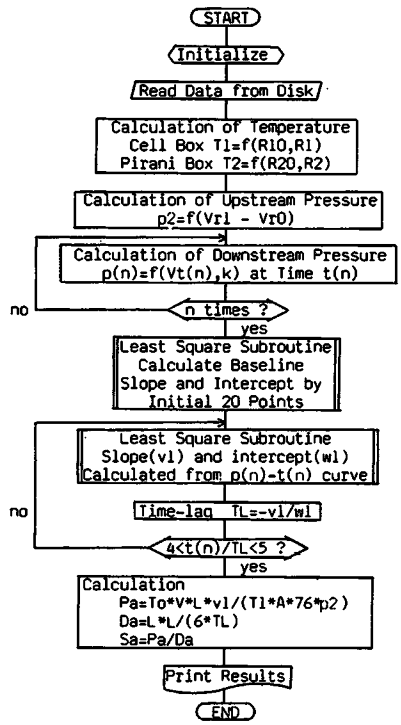

Fig. 6. Flow chart for "Calculation" program.

These values are converted from the values of resistance and voltage according to each corresponding equation in the program. Other factors are membrane area and thickness (A,L), and standard temperature (T_0). They are built into the program as constants.

The following data reduction routines are used:

(1) Reading the raw data from the appropriate file.

(2) Converting the values of resistance into temperature and voltage into pressure.

(3) Calculating the base line by the least square subroutine through the first 10–20 points.

(4) After calculating the base line, a slope (v_1) and intercept (w_1) of the linear asymptote line were calculated by the least square subroutine through 100–200 experimental points taken from a time interval 4.0–5.0 times the time lag. The precisions of the slope and of the time lag of the permeation curve using this method are greater than 0.1% and 0.5% respectively. The flow chart of this program is given in Figure 6.

Usually, the thicknesses of membranes were prepared so that the values of the time lag became to be 100–200 s. Then, the one measurement requires less than about 1500 s. The time of analysis per experiment is less than 10 min. If inputting the data by hand, it takes more than 1 h and leads to mistakes in striking the keys. In such a case, the precision of the slope and intercept of a permeation curve is not expected to be sufficient. This compares with the high effectiveness of using this online system.

Other Routines. There are many other programs which we have developed for convenience. For instance, once the raw data have been collected, they can be examined in order to establish how the permeation curve proceeds by a program which makes a high resolution plot of the permeation curve on the xy-plotter. Other programs are a program for calibrating the pirani gauge by the Baratron Capacitance Manometer, a program for making a new file for only the measuring conditions and the results of each series of experiments, a program for plotting results (for example, ln $D_a - 1/T$ or ln $P_a - p$) on the xy-plotter and so forth. The flow charts for these programs were omitted, but all the programs are available from the authors if desired.

The experimental data points obtained from the above system for the permeation of CO_2 in poly(vinyl acetate) membrane at 40°C and 22°C were compared with the analytical permeation curve calculated by a finit difference technique using the xy-plotter in our previous paper.[8]

References

1. R. M. Barrer and G. Skirrow, *J. Polym. Sci.*, **3**, 549 (1948).
2. J. Crank, *The Mathematics of Diffusion*, 2nd ed., Clarendon, New York, 1976.
3. K. Toi, K. Igarashi, and T. Tokuda, *J. Appl. Polym. Sci.*, **20**, 703 (1976).
4. K. Toi, K. Takeuchi, and T. Tokuda, *J. Polym. Sci., Polym. Phys. Ed.*, **18**, 189 (1980).
5. K. Toi, Y. Maeda, and T. Tokuda, *J. Membrane Sci.*, **13**, 15 (1983).
6. N. Collongs, *J. Phys. E: Sci. Instrum.*, **15**, 114 (1982).
7. V. Narasimhan, A. R. Telfer, R. Y.-M. Huang, and C. M. Burns, *J. Appl. Polym. Sci.*, **27** 3461 (1982).
8. K. Toi, Y. Maeda, and T. Tokuda, *J. Appl. Polym. Sci.*, **28**, 3589 (1983).

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