The Performance Characteristics of a Permeation Membrane Device for the Preparation of Dilute Standard Gas Mixtures

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The performance chracteristics of the permeation membrane device for the preparation of dilute standard gas mixtures developed by us was investigated in detail from the practical standpoint. By selecting a silicone-rubber and a TFE Teflon for CO or CH_4, and NO or SO_2, respectively, the steady permeation state was rapidly attained. The small quantities of the gases permeating through the membranes were precisely determined within a relative standard deviation of 1% based on a pressure-differential method. It was confirmed that the permeation rates were reproducible after repeated membrane-temperature, gas-pressure, and gas-cycle changes during an experimental period of more than five months. By changing the gas pressure and the membrane temperature, and by introducing 1—2 $\mathrm{l\,min^{-1}}$ of a diluent gas, N_2 or air, standard gas mixtures containing 0.5—10 ppm of CO or CH_4 and 0.05—0.7 ppm of NO or SO_2 were easily obtained. The standard gases concerning CO, CH_4, and NO were compared with those in cylinders prepared by the weighing method, and for SO_2 the concentration of the gas was checked by the West-Gaeke method. A good agreement in concentration was observed for CO, CH_4, and SO_2; the discrepancy found for NO was explained in terms of the decrease in the NO concentration in the cylinder.

For the accurate determination of the concentrations of gaseous pollutants at ppm and ppb levels, standard reference materials are needed to calibrate the air-monitoring instruments. Accurate gas mixtures in cylinders at 10 ppm levels have been prepared by the weighing method for various gases.[1)] However, mixtures of nitrogen dioxide (NO_2) or sulfur dioxide (SO_2) change greatly in concentration with the time because of their adsorption or reaction with the cylinder wall. Permeation tubes for the condensable gases were proposed by O'Keeffe and Ortman,[2)] and their performance characteristics have been widely investigated.[3—10)] Unfortunately, several months or more are required to calibrate the low gas-permeation rates of the tubes by means of standard gravimetric methods at a constant, strictly controlled temperature. Dietz *et al.* recently proposed a rapid calibration method using the pressure-differential technique to measure microgram quantities of gas permeating through the plastic membrane or diffusion devices.[11,12)] The device using the membrane can also be applied to non-condensable gases, such as nitrogen monooxide (NO), carbon monooxide (CO), and methane (CH_4). However, the performance characteristics of the device in the preparation of dilute standard gas mixtures have not yet been reported. We have previously studied the performance characteristics of a commercial apparatus based on the permeation method and have pointed out some of its defects from the standpoint of practical value.[13)] The permeability of gaseous pollutants through various kinds of plastic membranes has, therefore, been investigated.[14)] It was shown that various kinds of standard gas mixtures, ranging widely in concentration, can be prepared by selecting an appropriate combination of pure pollutant gas and membrane, together with an appropriate gas pressure and membrane temperature.

We wish to report here the performance characteristics of the permeation membrane device we have developed with regard to the following subjects: precision in the measurement of a gas-permeation rate, the dependence of the rate on the gas pressure or the membrane temperature,[13)] the long-term stability of the rate under many temperature changes,[8)] the procedure and the length of time to reach a steady permeation rate,[10)] and, especially, whether or not the gas-permeation phenomenon will change because of the different conditions of the membrane in the measurement of the permeation rates of gas and in the preparation of dilute gas mixtures. Silicone-rubber and TFE Teflon membranes are used for CO or CH_4, and for NO or SO_2, respectively, since their permeation rates and the length of time to reach steady permeation rates have been suggested to be favorable for the precise and rapid preparation of very dilute gas mixtures.[14)] Moreover, the concentrations of the dilute gases are examined by using analyzers and standard gas mixtures in cylinders for CO, CH_4, and NO, because it is important to compare the standard gases prepared by the permeation device with those in cylinders prepared by the weighing method. For SO_2, the concentration is determined by the West-Gaeke method because of the lack of reliable dilute standard gas mixtures in cylinders. The results are also discussed with respect to the development of a practical type of the permeation device.

Experimental

Apparatus. The apparatus used here is shown schematically in Fig. 1. It consists of a test cell (C), a vacuum system, a differential pressure transducer (VG), and gas-feed systems for a pure pollutant gas and a diluent gas. A flat plastic membrane (M, with an effective area for permeation of 3.14 $\mathrm{cm^2}$) is held between two metal flanges and sealed with Viton-O-rings. Thin stainless steel screens are inserted between the membrane and the flanges in order to avoid the deformation of the membrane. One flange is connected to the pollutant gas source, and the other one, to the fixed-volume system (the shaded part) and the diluent-gas source. The cell is placed in a constant-temperature water bath (TB) controlled within ±0.05 °C (Riko-Kagaku Co., Model UH-1000E). The vacuum system is of Pyrex glass tubes, and the stopcocks (1—11) are made of glass and Teflon (Young Co.) in order to avoid the adsorption of the pollutant gases on the grease of the usual vacuum cocks. The system can be evacuated below 5×10^{-6} mmHg (1 mmHg = 133.32 Pa) by means of an oil-diffusion pump (DP), an oil-rotary pump (RP), and a liquid-nitrogen trap. The volume of the shaded part was determined to be 215 ± 2 cm^3 by using the known volume of the glass vessel (H, 1188 ± 8 cm^3). The pressure transducer is composed of an MKS Baratron 310 AH sensor head and an 170 M-7A electronic unit, measuring the pressure range from 3×10^{-5} to 1 mmHg within a 1% accuracy. The pure pollutant gas is introduced to the cell through the 1 cock, the Hg bubbler (B), and the 2 cock. The pressure is precisely read by the Hg manometer (P). The diluent gas (very purified nitrogen or air) passes through the 4 cock, the upper compartment of the cell, and the 5 cock, and is then introduced into an analyzer. The flow rate of the diluent gas is controlled by a mass-flow-rate controller (F, Ohkura Electronic Co., Model MFC-1), which is usually calibrated by means of a soap-bubble flow-meter.

Operational Procedures. Measurement of the Gas-permeation Rate: All the systems, including the cell and membrane are usually conditioned until vacuum readings of less than 5×10^{-6} mmHg are obtained, and a very low baseline drift of the shaded-part pressure with no feed gases is checked by means of the transducer. Following the baseline determination, the pollutant gas is introduced at the pressure of p_1, while simultaneously the pressure build-up (h) of the shaded part is recorded. The permeation test is carried out about four times, the time needed to reach the permeation-rate equilibrium.

Preparation of Dilute Gas Mixtures and Measurements of the Concentration: After a sufficient evacuation of the system, the diluent gas is introduced into the cell at an appropriate flow rate and is led to an analyzer. The pollutant gas is then introduced into the lower compartment of the cell in the same manner described above.

The concentrations of CO and CH_4 in the prepared dilute gases are determined by means of a total hydrocarbon analyzer(Beckmann Co., Model 6800 FID gas chromatograph equipped with a convertor of CO to CH_4). Standard gas mixtures in cylinders (7.79 ppm CH_4 in air and 9.60 ppm CO in air), prepared by the weighing method, are used for the calibration of the analyzer. An NO chemiluminescent analyzer (Bendix Co., Model 8101-B) is used for the measurements of NO in the diluent gas. The standard gas mixture in a cylinder (8.4 ppm of NO in nitrogen) is diluted to 1.68 ppm by using a STEC Model SGD-75 (Standard Technology Co.) for the calibration of the analyzer. A very purified air is used to adjust the analyzer to zero. The concentration of SO_2 is determined according to the West-Gaeke method.[15,16] The gas-flow rate of 0.5—1.5 l min^{-1} passing through the scrubber of SO_2 is controlled by means of mass-flow-rate air sampler (Milab Co., Model 69).

Reagents: All the reagents used in the West-Gaeke method were obtained from the Tokyo Kasei Co. and were used without further purification except for pararosaniline dye. TFE (tetrafluoro ethylene) Teflon and silicone-rubber membranes were obtained from the Nitto Rika Co. and the Toray Silicone Co. respectively. The pure pollutant gases in the cylinders were from the Takachiho Kagaku Co., for CH_4 (99.999%), CO (99.999%), and NO(99.8%), and from the Matheson Co. for SO_2 (99.98%).

Theoretical

According to Fick's gas-diffusion theory, q (the permeation rate of gas through a flat plastic membrane with a thickness of l and a certain area of A) is expressed as follows:[17,18]

$$q = DS(p_1-p_2)(A/l) \qquad (1)$$

where D is the diffusion constant, S, the solubility coefficient, and p_1 and p_2, the partial pressures at the lower and upper compartments of the cell in Fig. 1 respectively. The permeability coefficient, P, is the product of D and S:

$$P = D \times S \qquad (2)$$

The temperature dependence of the P, D, and S parameters follows an Arrhenius relationship:

$$\begin{aligned} P &= P_0 \exp(-E_p/RT) \\ &= D_0 \exp(-E_d/RT)\cdot S_0 \exp(H_s/RT) \qquad (3) \end{aligned}$$

where E_p and E_d are the activation energies for permeation and diffusion respectively, and H_s, the heat of solution.

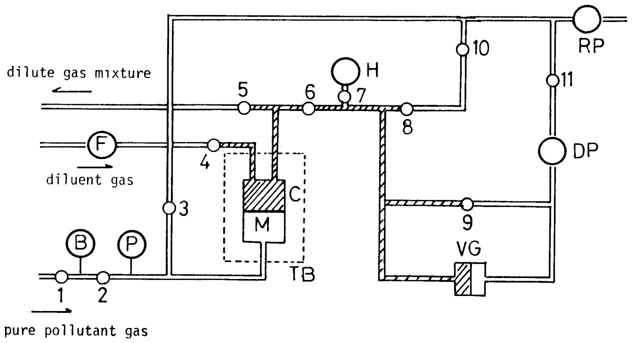

Fig. 1. Schematic diagram of permeation membrane device. M: Flat plastic membrane, C: cell, TB: constant temperature bath, B: Hg bubbler, P: Hg manometer, F: flow rate controller, H: known volume glass vessel, VG: pressure transducer, DP: diffusion pump, RP: rotary pump, 1—11: stopcocks.

TABLE 1. LAG-TIMES IN GAS-PERMEATION PROCEDURE FOR SILICONE-RUBBER-CO AND CH_4 AND TEFLON-NO AND SO_2 AT A GAS PRESSURE OF ABOUT 70 cmHg

Membrane temp	Gas			
	CO	CH_4	NO	SO_2
30.0 °C	2.93 min	3.28 min	4.58 min	38.2 min
45.0 °C	2.43	2.48	2.64	18.9
55.0 °C	2.06	2.30	2.18	11.3

Results and Discussion

Procedure and the Length of Time to Reach a Steady State of the Permeation. The permeation procedures (time *vs.* the pressure build-up, h, of the known volume part) found for the silicone rubber (thickness l=1080 μm)-CO or CH_4 and for the Teflon (l=200 μm)-NO or SO_2 were in good accordance with the Ficksian-type permeation.[14] In Table 1, the so-called lag-time, θ, in the permeation procedure is listed for each combination of gases and membranes. Apparently the time becomes shorter with an increase in the membrane temperature. About three times as long as the lag-time is the length of time needed to reach steady

TABLE 2. GAS-PERMEATION RATES AND THEIR STANDARD DEVIATIONS FOR SILICONE-RUBBER–CO AND CH_4 AND TEFLON–NO AND SO_2 AT A GAS PRESSURE OF ABOUT 70 cmHg

Membrane temp	Gas			
	CO[a]	CH_4[a]	NO[b]	SO_2[b]
30.0 °C	3.55±0.02	8.58±0.03	3.03±0.01	3.73±0.05
45.0 °C	4.20±0.03	10.1±0.04	4.46±0.06	5.98±0.07
55.0 °C	4.57±0.03	10.6±0.05	5.75±0.03	7.11±0.11

a) Permeation rate [cm^3(STP) $min^{-1} \times 10^{-3}$].
b) Permeation rate [cm^3(STP) $min^{-1} \times 10^{-4}$].

TABLE 3. PERMEABILITY COEFFICIENTS OBTAINED FOR SILICONE-RUBBER–CO AND CH_4 AND TEFLON–NO AND SO_2 [cm^3(STP)·cm/cm^2·s·cmHg]

Membrane temp	Gas			
	CO ($\times 10^{-8}$)	CH_4 ($\times 10^{-8}$)	NO ($\times 10^{-10}$)	SO_2 ($\times 10^{-10}$)
30.0 °C	2.92±0.02	7.06±0.04	4.63±0.08	6.26±0.18
45.0 °C	3.44±0.01	7.86±0.02	6.95±0.11	9.74±0.25
55.0 °C	3.76±0.03	8.36±0.05	8.97±0.15	13.2±0.30

permeation rates.[13] Even for SO_2 at 30.0 °C, the time of about two hours required for calibration is much shorter than that required using conventional gravimetric or volumetric procedures for usual SO_2 permeation tubes.[11] It should further be noted that, with regard to CO, CH_4, and NO, the time needed to reach the steady-permeation state is remarkably shortened in comparison with that estimated for the use of a commercial apparatus using a FEP Teflon membrane.[13]

Precision in Measurement, Repeatability, and Long-term Stability of Permeation Rates. The permeation rates (q) were calculated from the values of dh/dt at the steady-pressure build-up state and the volume employed. The values of q obtained for CO, CH_4, NO, and SO_2 at about 70 cmHg of p_1 are summarized in Table 2, together with the standard deviations. The very small quantities of gas permeating, less than 10^{-4} cm^3 min^{-1}, were precisely measured within a relative standard deviation of 1%. It is also confirmed that the values of q obtained under various gas pressures less than 70 cmHg changed linearly with the gas pressure of p_1 in Eq. 1. This suggests that the gas pressure in the upper compartment (p_2) is negligibly small compared to p_1 [Eq. 1 can, then, be rewritten as $q = DS(p_1)(A/l)$] and that P ($D \times S$) is constant regardless of the pressure changes.

In order to ascertain the repeatability of the permeation rates, the values of q at various gas pressures of p_1 were converted to the permeability coefficients (P) according to Eqs. 1 and 2. The values of P concerning CO, CH_4, NO, and SO_2 as well as the standard deviations are summarized in Table 3. Each value of P was derived by averaging all the values of P obtained periodically for more than five months at the membrane temperatures of 30.0, 45.0, and 55.0 °C. It has been ascertained that the permeation rates are reproducible within small deviations after repeated temperature, pressure, and gas cycles for a long experimental period.

The long-term stability of the device differs in meaning from that for the conventional permeation tubes of SO_2, NO_2, *etc.* In the former device, the gas permeating through the membrane is fed and removed in each experiment, while the liquefied gases are always stored in the tubes. It is, therefore, considered that the long-term stability of the device is also confirmed by the results on the repeatability. The excellent repeatability and the long-term stability arise from the better storage condition of the membranes than in the conventional permeation tubes; that is, the membranes are in contact with the pollutant gases only at use and, moreover, can be protected from moisture or air.

The maximum uncertainty was found with respect to the SO_2–Teflon system, as can be seen from Tables 2 and 3. The precision of the temperature control of the membrane and the laboratory is considered to be an important factor in this experiment, affecting the uncertainty in the determination of q or P. The magnitude of the activation energy for permeation, E_p, is associated with the required level of the membrane-temperature control, as is suggested by Eq. 3. The values of E_p concerning CO, CH_4, NO, and SO_2 were found to be 2.0, 1.3, 5.1, and 5.9 kcal mol^{-1} (1 kcal mol^{-1}=4.184 kJ mol^{-1}), in that order, from the plots of log P *versus* the reciprocal temperature of the membrane shown in Table 3. The value for SO_2–TFE Teflon agreed well with that of 6.5 kcal mol^{-1} reported by Felder.[19] If an error of less than a 1% in the measurement of P is desired, the temperature should be maintained within ±0.36 and ±0.18 °C when the values of E_p are 5.0 and 10.0 kcal mol^{-1} respectively. The temperature control within 0.05 °C in our experiment is too much to realize less than a 1% relative standard deviation. The uncertainty can, then, be attributed to the deviation of the ambient temperature of our laboratory (±1.0 °C during 1 h). The largest uncertainty in P observed for SO_2 is related to the result shown in Table 1 that the time required to determine the permeation rate of SO_2 is much longer than those required for the other gases.

Preparation of Dilute Standard Gas Mixtures and Measurements of the Concentration. *CO and CH_4 Standard Gas Mixtures*: The flow rate of a diluent air (Q) was precisely measured at each experiment by means of a soap-bubble flow-meter. The air was mixed with the small quantity of CO or CH_4 (q) permeating through the silicone-rubber in the cell. The dilute gas thus prepared was then introduced into the gas chromatograph and was analyzed at intervals of 5 min. It was confirmed that the steady state of the observed concentration was achieved at the second sampling time (10 min), which is in accordance with the results shown in Table 1. The concentration of CO or CH_4 was maintained for more than four hours, long enough to calibrate the analyzer. Concentrations of CO or CH_4 ranging 0.5 to 10 ppm were easily realized by only changing the gas pressure from about 10 to 76 cmHg. The change in the membrane temperature

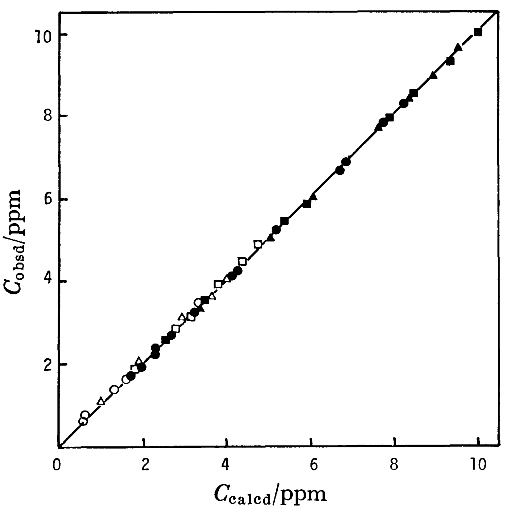

Fig. 2. Comparison of C_{calcd} with C_{obsd} for CO (unfilled symbols) and CH_4 (filled symbols)-silicone rubber. The membrane temperature were 30.0 °C (○), 45.0 °C (△), and 55.0 °C (□).

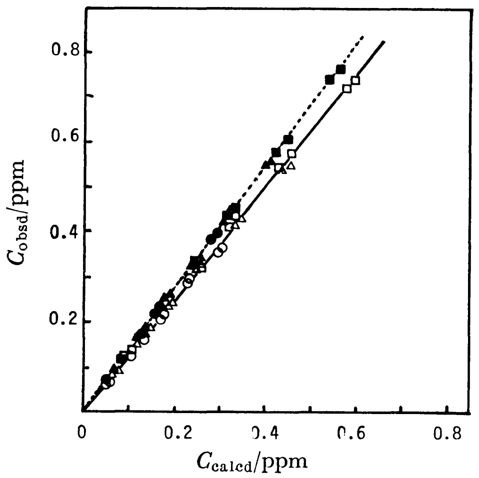

Fig. 3. Comparison of C_{calcd} with C_{obsd} for NO–Teflon at temperatures of 30.0 °C (○), 45.0 °C (△), and 55.0 °C (□). The filled symbols were obtained about two months later when the unfilled symbols were done.

was found to be less effective than that of the pressure, which reflects the very small value of E_p obtained for CO or CH_4. The observed CO or CH_4 concentrations of the dilute gas mixtures (C_{obsd}) are plotted against the calculated ones ($C_{calcd}=q/q+Q=q/Q$) in Fig. 2. By the use of the least squares method, $C_{obsd}/C_{calcd}=0.998$ and the correlation coefficient $r=0.999$ for CO and $C_{obsd}/C_{calcd}=1.01$ and $r=0.999$ for CH_4 were obtained. As has previously been pointed out, the CO or CH_4 concentrations of the dilute gas mixtures in cylinders scarcely changed with the time because of their low adsorbilities and reactivities. It is generally accepted that standard gas mixtures containing such low concentrations of CO or CH_4 prepared by the weighing method are reliable. The excellent agreement of C_{obsd} with C_{calcd} for both gases thus supports the validity of the gas-permeation rates determined here.

NO Standard Gas Mixtures: A very purified nitrogen was used as a diluent gas. By introducing less than 1 l min^{-1} of N_2, dilute gas mixtures containing 0.05—0.7 ppm NO were generated at various gas pressures and at various membrane temperatures. The steady state of the concentration of NO was reached within 20 min at the lowest temperature of 30.0 °C and was maintained more than four hours as well as both CO and CH_4. The concentrations observed by the NO analyzer (C_{obsd}) are plotted against the calculated concentration (C_{calcd}) in Fig. 3. While the correlation coefficient, r, was found to be 0.999 by the least-squares method, a large discrepancy between C_{obsd} and C_{calcd} ($C_{obsd}/C_{calcd}=1.26$) appeared. The same experiment was, therefore, performed about two months later by using the same standard cylinder gas for the span calibration of the NO analyzer. The results obtained are depicted by the dotted line in Fig. 3. The linearity ($r=0.999$) was confirmed to be good, but the C_{obsd}/C_{calcd} ratio increased from 1.26 to 1.37. This can be explained as being due to the decrease in the NO concentration in the cylinder, taking into consideration the fact that the permeability coefficient, P or q, is constant within 2% for 6 months, as has been mentioned above. NO probably adsorbs or reacts with the cylinder wall or an impurity gas such as oxygen and so decreases in concentration.[1] However, it is necessary to rule out the possibility that the discrepancy may result from the change in the quantity of gas permeating through the membrane on account of the different environmental conditions of the Teflon membrane; the determination of the permeation rate was carried out *in vacuo*, but the preparation of the dilute gas mixture was done in a diluent gas (N_2) flowing in the upper compartment of the test cell.

The values of the diffusion constant under the two environmental conditions of the membrane were, therefore, determined and were compared each other, since the diffusion constant is the factor governing the process of the permeation. The diffusion constant, D_v, in the evacuated condition can be calculated from the lag-time, θ, in Table 1 according to the following equation:

$$D_v = l^2/6\theta \tag{4}$$

The lag-time, θ, in the case of the preparation of the dilute gas mixtures can also be obtained by analyzing the change in the concentration of NO with the time.[13,20] The diffusion constants, D_d, in N_2 flowing thus were calculated according to Eq. 4. The values of both D_v and D_d, determined at the temperatures of 30.0, 45.0, and 55.0 °C, are summarized in Table 4(a). It is found that D_d agrees well with D_v within in the limits of experimental error. The possibility mentioned before can thus be excluded; the large discrepancy between C_{obsd} and C_{calcd} is attributable to the decrease of NO in the cylinder.

SO_2 Standard Gas Mixtures: A diluent nitrogen was introduced into the cell at the flow-rate of 1—2.5 l min^{-1}. As soon as the pure SO_2 was fed into the cell, the gas sampler began to operate. In Fig. 4, the observed concentration of SO_2 at the steady-permeation rate determined by the West-Gaeke method (C_{obsd}) is plotted against the calculated values (C_{calcd}).

Table 4(a). Comparison of D_v with D_d for NO-Teflon

Diffusion constant	30.0 °C	45.0 °C	55.0 °C
D_v	2.42±0.16	3.47±0.11	4.69±0.32
D_d	2.02±0.10	3.41±0.46	4.50±0.17

D_v and D_d: cm^2/s $\times 10^{-8}$

Table 4(b). Comparison of D_v with D_d for SO_2-Teflon

Diffusion constant	30.0 °C	45.0 °C	55.0 °C
D_v	2.87±0.10	5.81±0.23	8.56±0.62
D_d	2.58±0.28	5.17±0.59	7.85±1.74

D_v and D_d: cm^2/s $\times 10^{-8}$

Although some scatter is found, C_{obsd} agrees well with C_{calcd} ($C_{obsd}/C_{calcd}=0.997$ and $r=0.995$). About 6% of the relative standard deviation in the observed concentration is considered to be due to the analytical method. Although the purification of the parasoaniline dye used here was performed and a freshly prepared parasoaniline stock solution was used, the relatively large and irreproducible blank values, ranging from 0.057 to 0.078 absorbance, were not satisfactorily decreased. A better quality of the dye and a more rigorously reproducible analytical procedure will be needed to decrease the experimental error.

The diffusion constants, D_v and D_d, were also compared in the same manner as with NO; the values are listed in Table 4(b). They agreed well with each other within the limits of experimental error. The large difference in D between NO and SO_2, shown in Tables 4(a) and 4(b), is particularly noteworthy. The activation energies for diffusion (E_d) were determined to be 8.7 kcal mol^{-1} and 5.8 kcal mol^{-1} for SO_2 and NO, in that order, while those for permeation (E_p) were similar in both NO and SO_2. This reflects the difference in the gas-permeation property between SO_2 and NO. The longer time needed to reach the steady-permeation rate for SO_2 and the more rapid decrease of it with an increase in the temperature are interpreted in terms of the magnitude of D and E_d.

In conclusion, the permeation membrane device using silicone-rubber and TFE Teflon membranes shows excellent performance characteristics in the preparation of dilute standard gas mixtures. The stable and reproducible permeation rates for long periods of time are useful for the examination of the changes in the concentration of the standard gases in cylinders with time. An important characteristics of the device is that the permeation rate, *i.e.*, the concentration of the gaseous pollutants in the mixture, can easily be changed by changing the gas pressure. The calibration line and/or curve of air-monitoring instruments can be obtained more easily and rapidly than with conventional calibration devices. The use of a gas pressure lower than 76 cmHg enables us to apply the device to such condensable gases as SO_2, NO_2, H_2S, NH_3, and so on, which are not suitable for study with the commercial permeation device because of their liquefaction at 2—5 atmospheric pressures. In addition, a portable type of permeation device is expensive to fabricate. The present device consists of only a cell including a membrane whose gas-permeation rates have been measured, a simple constant-temperature oven (the precision in control is about 0.3 °C because of the small values of E_p), a flow-rate controller for a diluent gas, a pressure gauge for a pollutant gas, and a vacuum pump.

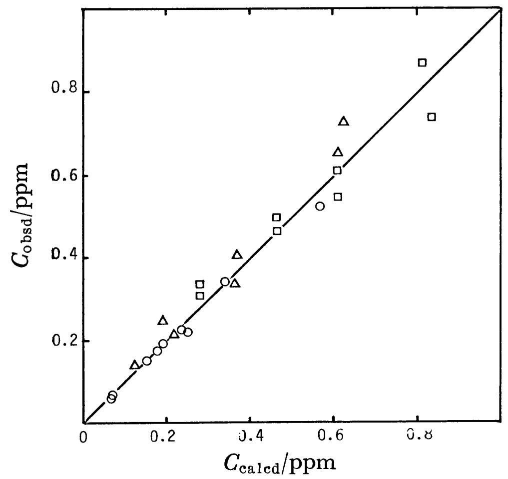

Fig. 4. Comparison of C_{calcd} with C_{obsd} for SO_2–Teflon at temperatures of 30.0 °C (○), 45.0 °C (△), and 55.0 °C (□).

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