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Parametric Analysis of the Propagation of Uncertainties in Sorption Measurements Made with a Pressure-Decay Apparatus*

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ABSTRACT

The general formulation for the propagation of statistical uncertainties is presented for the dual volume pressure decay method of measuring sorption capacity in polymers and other solid sorbents. These relationships are then used to determine the percent uncertainty in the calculated sorption coefficient (or capacity) with respect to ranges of values for several parameters that relate to choices in equipment design and operating conditions, and properties of the sorbent. These parameters include the ratio of system volumes, the relative volume of the sorbent, the accuracy and resolution of the sensors, the operating pressure, and the nominal sorption capacity of the sorbent. This analysis provides guidance for determining the uncertainty in the calculated sorption capacity and minimizing that uncertainty within whatever logistical and resource constraints may exist.

INTRODUCTION

This report examines the quantitative effects due to choices in design parameters, equipment specifications, and operating conditions on the uncertainty in the calculated sorption coefficient using the pressure decay method. There are several methods for directly determining mass sorption in polymers and other solid materials. The direct methods primarily include gravimetric (1) (quartz spring or microbalance), surface acoustic wave (2), and pressure

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decay techniques (3). Indirect methods that rely on a permeation model and the transient response of a transport measurement (4) are also used.

Pressure decay methods are very convenient and accessible to investigators with limited resources. There have been reports for several decades on designs for this sort of equipment, and useful design rules of thumb (5) have been passed along. When designing an apparatus to measure sorption, care must be given to apparatus dimensions and operating parameters.

In this report we limit our analysis to a dual volume, single transducer design, and to a specific method of determining system volumes. The overall uncertainty is determined using an accepted formulation for propagation of statistical uncertainties for a function of several variables (6, 7). We have tried to identify all the main causes of systematic uncertainty and estimate the magnitude of their effects realistically. This analysis can provide guidance for choices of equipment and design modifications in order to obtain the most accuracy, within whatever constraints may exist. Constraints may include available sample size, equipment budget, modification to an existing apparatus, space requirements, and operating conditions.

EXPERIMENTAL

The general experimental procedure is known as the "pressure decay technique." We determine the change in moles in the total system volume (unoccupied by solid materials) by measuring changes in both pressure and temperature. The pressure (P) and temperature (T) measurements are converted to gas density using an accurate equation-of-state correlation for the gas in question. The sorption coefficient can be determined from this quantity. The sorption coefficient is the number of sorbed moles normalized by the sample's volume and the gas pressure (fugacity) at equilibrium.

System Description

The apparatus is shown schematically in Fig. 1. The reservoir volume is V_1 and includes all the tubing and dead volumes between the two closed valves on either side of the reservoir. V_2 is the nominal volume of the sample cell. V_b is a solid volume used to modify the effective ratio of V_2 over V_1. V_b is known to high accuracy. It also may be the calibration volume ($V_{b'}$) used to determine the volumes of V_1 and V_2 in the procedure outlined later in this report. A dead volume V_d, contributed by the valve between the reservoir and the cell when open, is also considered. V_s is the volume of the sample determined by the methodology outlined later.

The usual operating procedure is initially to evacuate the cell volume containing the sample. An aliquot of gas is allowed to equilibrate in the reservoir

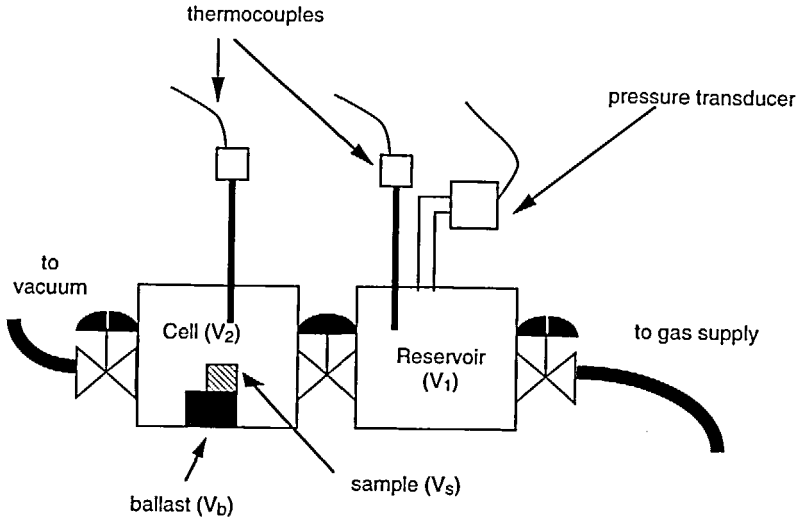


FIG. 1 Schematic of single transducer pressure decay apparatus.

volume. The initial P_i and T_i are measured. The cell is isolated from the vacuum, and the valve between it and the reservoir is opened. Again the pressure and temperature are carefully measured over time. The final P_f is defined when no further pressure decay is observed. At this point there are two separate ways further experiments can proceed: zero-initial-condition or titration.

Zero-Initial-Condition. The valve between the cell and reservoir is closed and the cell and sample are evacuated. The residual gas in the reservoir is allowed to reequilibrate with or without further addition of gas. When the sample has fully desorbed and the gas in the reservoir has reequilibrated, the experiment proceeds as described above.

Titration. The valve between the cell and reservoir is closed. Gas is allowed to re-equilibrate after it is either added to or subtracted from the reservoir. Then the valve between cell and reservoir is reopened and the experiment proceeds again as described above.

We limit ourselves to the analysis of uncertainties with respect to the zero-initial-condition approach. The real-time temperature and pressure measurements in the sample cell and reservoir volume are used to calculate the gas densities (and fugacities) with the 32-term modified Benedict–Webb–Rubin (MBWR) equation of state (EOS) and tabulated parameters for each gas (8, 9). To facilitate the analytical approach that follows, we calculate the gas

density with the EOS form containing the compressibility factor (z). The MBWR-EOS can be used to calculate z. The gas densities, the absolute volumes of the reservoir and the sample cell, and the sample volumes are used to determine the mass balance and the amount of gas sorbed by the sample.

Measuring the Apparatus and Sample Volumes

In our practice the volumes of the reservoir (V_1) and the sample cell (V_2) are determined using a calibration gas (He) and a disk (or disks) of known volume (V_b). The calibration procedure involves two steps.

First, the pressure in volume V_1 is equilibrated and measured while isolated from the evacuated volume V_2, and then again after V_2 is connected to V_1. Several sequences of these initial and final pressure measurements can be made. The molar gas densities are calculated for each measurement, and the final density (ρ_f) can be plotted versus the initial value (ρ_i). The slope is proportional to $V_1/(V_1 + V_2 + V_d)$.

Second, the calibration disk is inserted in volume V_2 and the procedure is repeated. In this case the slope of ρ_f against ρ_i is proportional to $V_1/(V_1 + V_2 + V_d - V_b)$. A third set of measurements with a different calibration volume ($V_{b'}$) is used to estimate V_d.

The volume V_s of the sample is measured in the same way using He. Henry's law coefficient of He is small in polymers, and He is unlikely to self-associate or have any specific interactions with the polymer molecule. Therefore we use He to probe the sample volume, realizing that it will provide a result approaching the skeletal volume. The sample is inserted in the cell, which may or may not still contain a calibration disk, and the procedure is repeated. In this case the slope of ρ_f against ρ_i is proportional to $V_1/(V_1 + V_2 + V_d - V_s - V_b)$. The uncertainty of this method is included in the following analysis.

Calculations: General Material Balance

Pressure decay is analyzed by a simple mass balance. This mass balance can be applied at any point in time if one is interested in tracking the transient response, or just at the initial and final conditions for the equilibrium data. The overall mass balance is given as follows (variables are defined in a list at the end of the regular text):

Initial moles in cell volume:

$$\rho_{ci}(V_2 - V_b - V_s) + m_i$$

Initial moles in reservoir volume:

$$\rho_{ri}(V_1)$$

Final moles in cell compartment:

$$\rho_{cf}(V_2 - V_b - V_s + 0.5V_d) + m_f$$

Final moles in reservoir compartment:

$$\rho_{rf}(V_1 + 0.5V_d)$$

We have assigned half of the dead volume, from the valve between the cell and reservoir, to each of those volumes. Collecting terms and dividing through by V_1, we have the following general mass balance suitable for both single and dual transducer systems, and both zero-initial-condition and titration operating methods:

$$(\rho_{cf} - \rho_{ci})(a - b) + (\rho_{rf} - \rho_{ri}) + 0.5d(\rho_{cf} + \rho_{rf}) + \frac{\Delta m}{V_1} = 0 \quad (1)$$

For the zero-initial-condition method and a single transducer system, the following substitutions can be made directly: $m_i \approx 0 \therefore m_f = \Delta m = CV_s$ and $\rho_{cf} = \rho_{rf}$, where C is the sorption capacity of the polymer at the particular P and T. Dividing by ρ_{rf}, defining ρ_{ri}/ρ_{rf} as r, and rearranging terms leads to

$$a - b + 1 - r + \frac{C}{\rho_{rf}} b + \left[(b - a)\frac{\rho_{ci}}{\rho_{rf}} + d\right] = 0 \quad (2)$$

The term in brackets can be considered a dimensionless lumped error term ϵ'' that is likely dominated by d. Making this substitution yields

$$a - b + 1 - r + \frac{C}{\rho_{rf}} b + \epsilon'' = 0 \quad (3)$$

Using the general relationship for gas density as $\rho = P/(zRT)$, the term C/ρ_{rf} can be expanded and Eq. (3) can be solved for C in terms of known variables:

$$C = \frac{(r - \epsilon'' + b - a - 1)P_f}{bRz_fT_f} \quad (4)$$

Additionally, the term C/ρ_{rf} can also be converted to a term containing the solubility parameter S:

$$\frac{C}{\rho_f} = \frac{Cz_fRT_f}{P_f} \quad \text{and} \quad \frac{CR}{P_f} = S\frac{P_{STP}}{T_{STP}} = SM$$

where M is a numerical constant that makes the units conversions and contains P_{STP}/T_{STP}.

Thus, for a single transducer system, using the zero-initial-condition method, a general relationship for S is given by

$$S = \frac{r - \epsilon'' + b - a - 1}{bz_f T_f M} \tag{5}$$

Calculations: Derivations for the Propagation of Uncertainties

Equation (5) is a reasonable starting point for investigating the parametric sensitivity of the uncertainty in S with respect to equipment design and operating parameters. The uncertainty, dS, in S is given by

$$dS = \sqrt{\left(\frac{\partial S}{\partial r}\,dr\right)^2 + \left(\frac{\partial S}{\partial \epsilon''}\,d\epsilon''\right)^2 + \left(\frac{\partial S}{\partial b}\,db\right)^2 + \left(\frac{\partial S}{\partial a}\,da\right)^2 + \left(\frac{\partial S}{\partial z_f}\,dz_f\right)^2 + \left(\frac{\partial S}{\partial T_f}\,dT_f\right)^2}$$

if the ratios a and b are determined in a fashion such that they are independent and uncorrelated. The partial derivatives would be calculated using Eq. (5). But by our experimental procedure the ratios a and b would be correlated because the calculation of b depends on the prior value determined for a. We therefore use an alternative expression for S in terms of the independent measurements of P's and T's.

The value of a (V_2'/V_1) is obtained by assuming measurements in which the cell is occupied only by a control volume V_b, as previously described. The number of moles are conserved,

$$r_a \equiv \frac{\rho_i}{\rho_f} = \frac{P_i T_f z_f}{P_f T_i z_i} = a + 1 + \epsilon'' \tag{6}$$

Similarly, to determine b (V_s/V_1), measurements are also made with He, which is assumed to not be significantly adsorbed by the sample. The number of moles are conserved so

$$r_b \equiv \frac{\rho_i}{\rho_f} = \frac{P_i T_f z_f}{P_f T_i z_i} = a - b + 1 + \epsilon'' \tag{7}$$

and

$$b = 1 + a - r_b + \epsilon'' = r_a - r_b + (\epsilon_b'' - \epsilon_a'') \tag{8}$$

The P's and T's are independent measurements made in the separate experiments (either to determine a or b) and the z's are calculated by the EOS. Therefore r_a and r_b are independent and uncorrelated. We therefore substitute for a and b into Eq. (5) using Eqs. (6) and (8) and make the further assumption

that $\epsilon'' \approx \epsilon''_a \approx \epsilon''_b$ (justified by the fact that in all measurements d has the same value and $\rho_{ci} \approx 0$). This results in the expression

$$S = \frac{(r - r_b)}{z_f T_f M(r_a - r_b)} \tag{9}$$

The uncertainty dS in S is now given by

$$dS = \sqrt{\left(\frac{\partial S}{\partial r}\,dr\right)^2 + \left(\frac{\partial S}{\partial r_b}\,dr_b\right)^2 + \left(\frac{\partial S}{\partial r_a}\,dr_a\right)^2 + \left(\frac{\partial S}{\partial z_f}\,dz_f\right)^2 + \left(\frac{\partial S}{\partial T_f}\,dT_f\right)^2}$$

with the partial derivatives determined from Eq. (9).

The dT's and dP's are based on the instrument specifications, and the dz's are based on the accuracy of the EOS (using the values and uncertainties of T and P). We calculated the dz's numerically. We next need to define the uncertainties dr, dr_a, and dr_b.

To develop the uncertainty in r, we use the following expression based on measured quantities:

$$r = \frac{P_i T_f z_f}{P_f T_i z_i} \tag{10}$$

Now, the uncertainty in r is given by

$$dr = \sqrt{\left(\frac{\partial r}{\partial P_i}\,dP_i\right)^2 + \left(\frac{\partial r}{\partial P_f}\,dP_f\right)^2 + \left(\frac{\partial r}{\partial T_i}\,dT_i\right)^2 + \left(\frac{\partial r}{\partial T_f}\,dT_f\right)^2 + \left(\frac{\partial r}{\partial z_i}\,dz_i\right)^2 + \left(\frac{\partial r}{\partial z_f}\,dz_f\right)^2}$$

For this sensitivity analysis we need to calculate a nominal value for P_f (in actual practice it would be measured). This is done by combining Eq. (10) and the following expression for r in terms of S and the other system parameters (obtained by rearranging Eq. 5):

$$r = Sbz_f T_f M + a - b + 1 + \epsilon''$$

therefore

$$P_f = \frac{P_i T_f z_f}{T_i z_i} \frac{1}{Sbz_f T_f M + a - b + 1 + \epsilon''} \tag{11}$$

The partial derivatives for r are obtained from Eq. (10), and Eq. (11) is used to calculate a nominal value for P_f.

The uncertainty in r_a is given by

$$dr_a = \sqrt{\left(\frac{\partial r_a}{\partial P_i}\,dP_i\right)^2 + \left(\frac{\partial r_a}{\partial P_f}\,dP_f\right)^2 + \left(\frac{\partial r_a}{\partial T_i}\,dT_i\right)^2 + \left(\frac{\partial r_a}{\partial T_f}\,dT_f\right)^2 + \left(\frac{\partial r_a}{\partial z_i}\,dz_i\right)^2 + \left(\frac{\partial r_a}{\partial z_f}\,dz_f\right)^2}$$

and the partial derivatives of r_a are obtained by using the middle set of terms in Eq. (6). The nominal final pressure is determined from the specified a, T's, and P_i, using

$$P_f = \frac{P_i T_f z_f}{T_i z_i} \cdot \frac{1}{a + 1 + \epsilon''} \tag{12}$$

Similary, the uncertainty in r_b is defined as

$$dr_b = \sqrt{\left(\frac{\partial r_b}{\partial P_i}\,dP_i\right)^2 + \left(\frac{\partial r_b}{\partial P_f}\,dP_f\right)^2 + \left(\frac{\partial r_b}{\partial T_i}\,dT_i\right)^2 + \left(\frac{\partial r_b}{\partial T_f}\,dT_f\right)^2 + \left(\frac{\partial r_b}{\partial z_i}\,dz_i\right)^2 + \left(\frac{\partial r_b}{\partial z_f}\,dz_f\right)^2}$$

and the partial derivatives are obtained from the middle set of terms in Eq. (7) with P_f defined as a function of the specified T's, P_i, b, and a, as in Eq. (13):

$$P_f = \frac{P_i T_f z_f}{T_i z_i} \cdot \frac{1}{a - b + 1 + \epsilon''} \tag{13}$$

RESULTS

Our purpose here is to illustrate the percent uncertainty in the value of the sorption coefficient that results from combinations of the nominal values for the parameters listed in Table 1. S is included since the uncertainty calculation is dependent on the magnitude of the sorption response. Table 2 lists the nominal values used in calculations if the parameter is not varied. Table 3

TABLE 1
Parameters and Ranges

Parameter	Significance	Low value	High value
a	Ratio of effective cell volume to the reservoir volume	0.25	1.5
P_i	Initial pressure in cell (kPa)	250.00	3500.00
S	Nominal sorption coefficient of the material being tested ($cm^3 \cdot cm^{-3} \cdot Pa^{-1} \times 10^5$)	0.05	1
b	Ratio of sample volume to reservoir volume	0.005	0.50

TABLE 2
Nominal Parameter Values

Parameter	Units	Nominal value
P_i	kPa	1723.0
a	—	0.5
S	$cm^3 \cdot cm^{-3} \cdot Pa^{-1} \times 10^5$	0.25
ϵ''	—	1×10^{-7}
Z	—	1.0
$T_i = T_f$	K	293.0
b	—	0.025

lists the values used for the measurement uncertainties. These are expressed as a linear function of the parameter. We refer to the constant part of the uncertainty as the resolution, and the uncertainty that is a percentage of reading as the linear part. Not all the parameters' uncertainties have contributions from both parts. A program was written to analyze the uncertainties using the LabView* software. This allows the calculation routine to also be integrated directly into the real-time data acquisition and analysis.

We have primarily plotted the results of the parametric analysis as percent uncertainty in the calculated sorption coefficient against the volume ratio b—(sample volume)/(reservoir volume.) One other parameter is varied on the plots while all others are kept at their nominal values from Table 2.

Calculations

Figure 2 shows the effect of changing the volume ratio a—(effective cell volume)/(reservoir volume.) The lines of constant a terminate at the point where the cell volume would not be large enough to accommodate the sample. Decreasing the volume of the cell containing a given sample volume will lead to less uncertainty. The change in density due to sorption is a greater fraction of the total measured change in gas density. This decreases the amount of uncertainty. The change in uncertainty is nonlinear with respect to the system parameters. For the case presented in Fig. 2, a sample with a volume 33% or greater of the reservoir's (and cell's) should result in a calculated sorption coefficient with ~10% uncertainty.

* Such identification is not intended to imply recommendation or endorsement by the National Institute of Standards and Technology, nor is it intended to imply that the software indentified is necessarily the best available for the purpose.

TABLE 3
Measurement Uncertainties

Measurement	Linear (percent of reading)	Resolution
Temperature	N/A	$\pm 1°C$
Pressure	0.12	± 0.002 kPa
Z	0.1	N/A
ϵ''	N/A	$\pm 1 \times 10^{-6}$

Figure 3 presents the effect on S's uncertainty from changing its nominal value, and Fig. 4 provides a more detailed view for two values of b. As expected, both the sample size and its sorption capacity greatly influence the accuracy of the measurement. The uncertainty in C, the sorption capacity, is exactly the same as the uncertainty in S.

Figure 5 shows that S's uncertainty is relatively independent of the initial pressure (there are small differences insignificant on the scale of the graphic). This is due to the basis of the uncertainty in pressure measurement. The

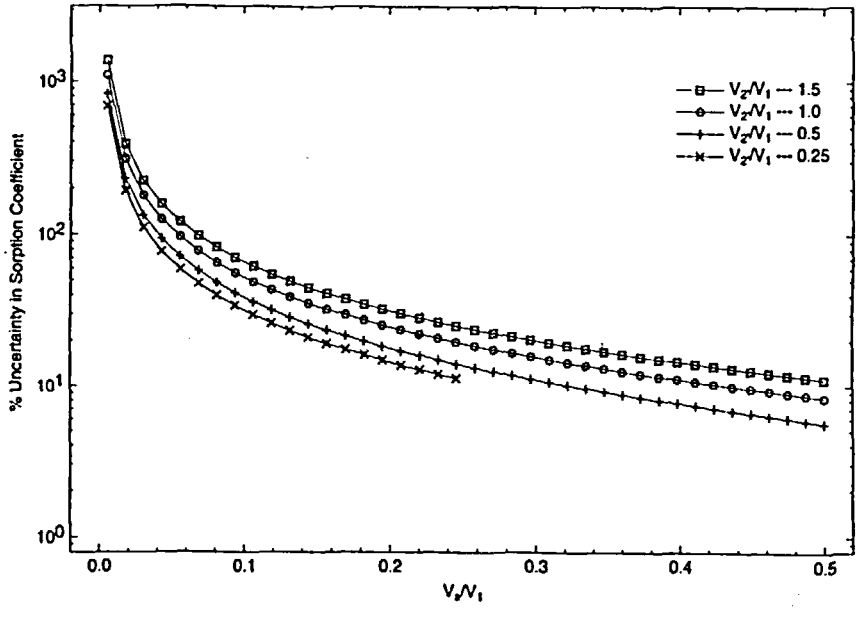


FIG. 2 Uncertainty (%) in sorption coefficient, S, against V_s/V_1 (b) for various values of V_2'/V_1 (a).

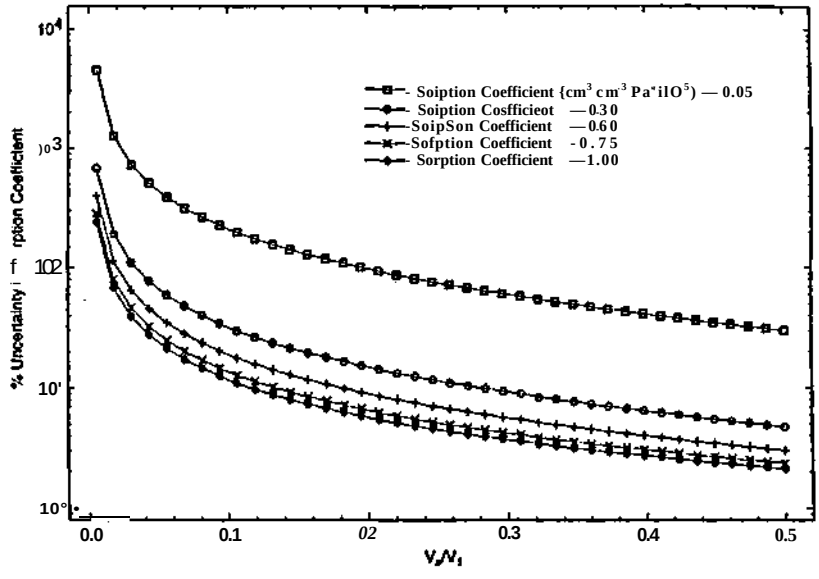
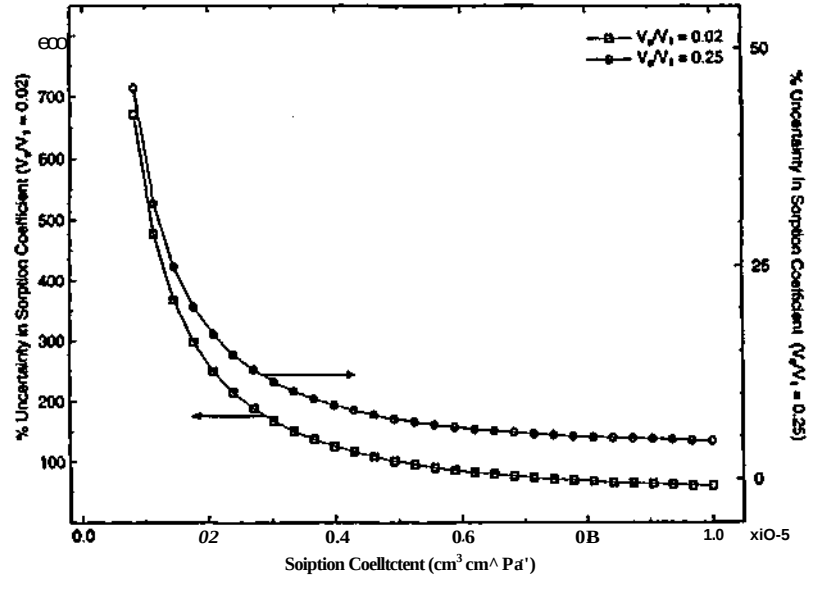


FIG. 3 Uncertainty (%) in sorption coefficient, 5, against V_s/V_l *(b)* for various nominal values of *S.*



HO. 4 Uncertainty *(%)* in sorption coefficient 5 against *S,* for two values of VJV_U 0.02 and 0.25.

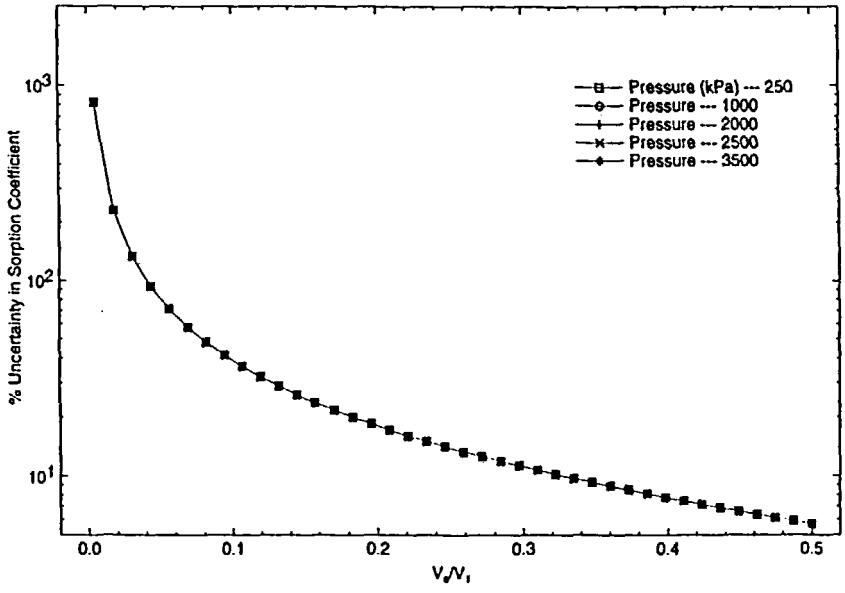


FIG. 5 Uncertainty (%) in sorption coefficient, S, against V_s/V_1 (b) for various values of initial pressure P_i.

largest uncertainty is a percentage of the reading, which is inherent in the transducer. So, as the magnitude of the initial pressure increases, the uncertainty increases proportionally. Since the magnitude of the solubility response increases as the pressure increases, the percentage uncertainty of the solubility coefficient stays relatively constant as illustrated in Fig. 5.

Experimental

We have made a series of measurements of O_2 sorption into polysulfone (PSf) powder. Our intention was to be able to use very small volumes of sample and, to that end, we constructed an experimental apparatus with very small volumes (reservoir volume ~3.45 cm^3 and cell volume ~2.96 cm^3). Table 4 presents the parameter values for our experimental apparatus, and Table 5 lists the instrument measurement uncertainties based on manufacturer's specifications and our own analysis.

The measurements are listed in Table 6. The sorption capacity is plotted in Fig. 6 with a linear fit. The average sorption coefficient S is 0.278×10^{-5} $cm^3 \cdot cm^{-3} \cdot Pa^{-1}$ ($\pm 0.031 \times 10^{-5}$.) The good linear fit and apparent reproducibility of the data suggest that the value of S is accurate within $\pm 22\%$

TABLE 4
Nominal Parameter Values for Measurements of O_2 Sorption into PSf

Parameter	Units	Nominal value
a	—	0.7749
S	$cm^3 \cdot cm^{-3} \cdot Pa^{-1} \times 10^5$	Calculated from data
ϵ''	—	1×10^{-7}
Z	—	Calculated from data
b	—	0.0456
V_S	cm^3	0.1570

TABLE 5
Instrument Uncertainties for Measurements of O_2 Sorption into PSf

Measurement	Linear (percent of reading)	Resolution
Temperature	N/A	±1°C
Pressure	0.10	±0.344 kPa
Z	0.1	N/A
ϵ''	N/A	$\pm 1 \times 10^{-6}$

TABLE 6
Measurements of O_2 Sorption into PSf

T_i (K)	T_f (K)	P_i (kPa)	P_f (kPa)	S ($cm^3 \cdot cm^{-3} \cdot Pa^{-1} \times 10^5$)	C ($mol/cm^3 \times 10^4$)	Uncertainty, %S or C
292.0	292.2	417.4	240.1	0.247	0.26	106
291.7	291.7	675.8	388.5	0.280	0.49	85
291.6	292.2	719.9	414.8	0.286	0.53	83
291.7	291.5	1165.8	670.7	0.285	0.85	83
290.6	290.3	1171.8	674.0	0.283	0.85	85
291.5	291.6	1242.2	714.9	0.310	0.99	76
289.6	289.5	1842.4	1061.2	0.328	1.55	73
290.9	290.8	1956.4	1128.7	0.264	1.33	91
291.7	292.0	2006.1	1158.8	0.281	1.45	85
290.4	290.6	2015.1	1163.6	0.281	1.46	85
291.1	291.5	2128.6	1232.8	0.210	1.15	116

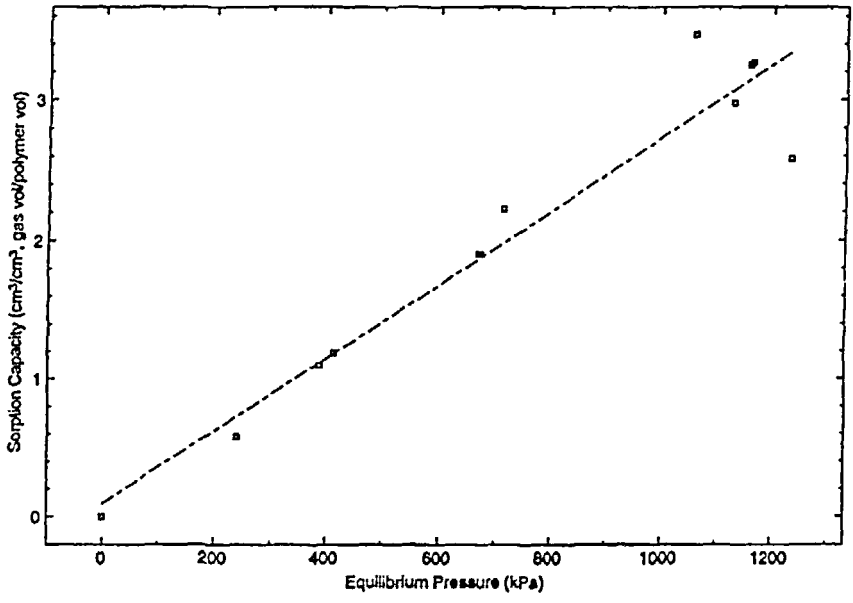


FIG. 6 Sorption capacity (cm^3/cm^3, gas volume at STP/polymer volume) of O_2 in polysulfone powder at ~291 K.

(based on 2σ.) But with the parameter values in Tables 4 and 5, the uncertainty in these calculated values are actually 70–120%.

A further example of the implications of uncertainty analysis in pressure-decay measurements is taken from Koros and Paul (5). Their paper presented the advantage gained by decreasing the reservoir volume of their apparatus. Two sets of measurements for N_2 sorption into polycarbonate (PC) at 308 K were taken. Greatly diminished scatter in the set with the smaller reservoir volume supported their position. We scanned and digitized the data from the original plots. Both sets of data are presented in Fig. 7. The data scatter was the greatest at the higher pressures for the larger reservoir volume case.

We chose one data point from both cases to illustrate the uncertainty analysis. Table 7 presents the parameters and results. We used the values listed in Table 8 for the instrument and analysis uncertainties. Most of the latter are the same as we have used to analyze our own experiments. However, the resolution of the pressure reading was based on the uncertainty of the zero point of a voltmeter described in their paper and the full range of their reported pressures.

The general conclusion of Koros and Paul (5) is consistent with the results from a propagation of uncertainties analysis. Our analysis shows that a four-

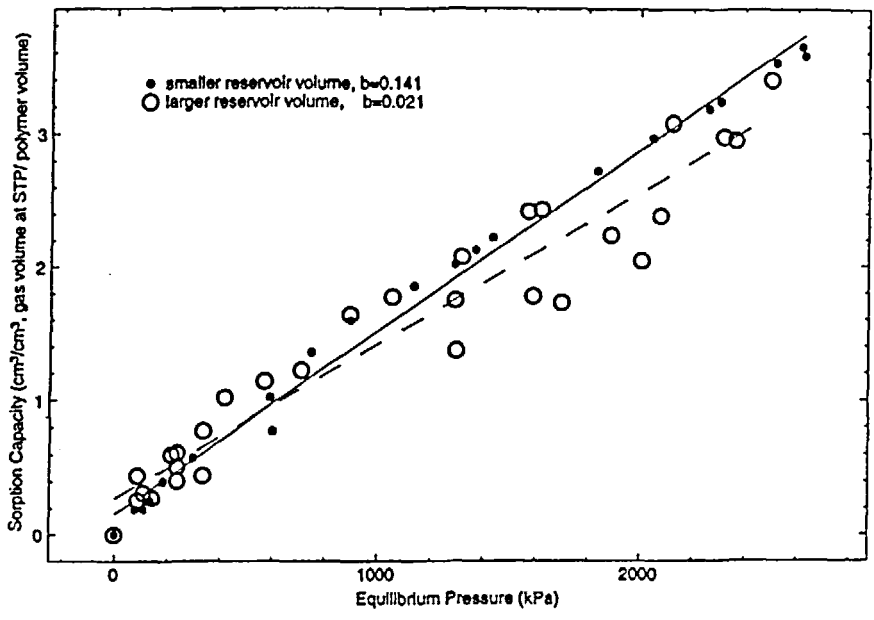


FIG. 7 Sorption capacity (cm^3/cm^3, gas volume at STP/polymer volume) of N_2 in polycarbonate at 308 K. Data taken from Ref. 5. Filled circles (solid line linear fit) are for $b = 0.141$ and open circles (dashed line linear fit) for $b = 0.021$.

TABLE 7
Parameters and Results for Analysis of N_2 Sorption in PC (s)

Variable	Smaller reservoir	Larger reservoir
a	0.828	0.120
b	0.141	0.021
S ($cm^3 \cdot cm^{-3} \cdot Pa^{-1} \times 10^5$)	0.145	0.145
C (cm^3/cm^3)	2.20	2.20
T (K)	308	308
P (kPa)	1519.9	1519.9
Maximum uncertainty in C ($\pm$ cm^3/cm^3) reported in original paper	0.07	0.45
% Uncertainty (from original paper)	3.2	22.5
% Uncertainty in C (calculated in this paper)	53	232

TABLE 8
Instrument and Analysis Uncertainties Used for N_2 Sorption in PC

Measurement	Linear (percent of reading)	Resolution
Temperature	N/A	±1°C
Pressure	0.12	±1.317 kPa
Z	0.1	N/A
ϵ''	N/A	$\pm 1 \times 10^{-6}$

fold increase in the accuracy of the experimental measurements should be obtained from the decrease in size of the reservoir.

DISCUSSION

The discerning reader will have noticed that the absolute magnitude of the uncertainty in the sorption coefficient (or capacities) calculated in this report can be quite high. An uncertainty of 1000% suggests that the experimenter would obtain very scattered data and that other researchers would likely obtain different results. High uncertainties are observed not only for the parametric analysis but also with the analysis of our own measurements on PSf and the measurements reported by Koros and Paul (5). Indeed, the latter authors had estimated their uncertainty to be an order of magnitude lower than our calculations indicate. A source of confusion is the difference between repeatability (and reproducibility), also known as "precision," and measurement uncertainty (7), often mistakenly referred to as "error." The difference between error and uncertainty is often forgotten. A measurement (after corrections) can unknowably be very close to the "true value," and thus have negligible error, even though it may have a large uncertainty. There are two general categories of uncertainties (7): type A—components of uncertainty arising from random effects—and type B—components of uncertainty arising from systematic effects. We have primarily used type B uncertainties in our calculations. Thus, the reproducibility of our measurements (Table 6) has a 2σ of 22% that is primarily due to the fact that the random effects were minimized (for example, by averaging P and T data for $\geq$4 hours even though equilibrium is reached within 20 minutes. But the overall uncertainty due to uncorrected systematic uncertainties (sensor calibration, resolution, slow drift, etc.) is 70–120%.

Our analysis of Koros and Paul's (5) results indicates that equipment and operating changes that will lower uncertainty can also increase the reproducibility of measurements and dramatically decrease data scatter. But it must be remembered that the absolute accuracy will remain based on the overall

propagation of uncertainties in how accurately each measured or calculated parameter can be specified.

With regard to the pressure-decay measurement technique, the uncertainty in the sorption coefficient can be very effectively improved by lowering the uncertainty in the temperature measurement. Table 9 lists the calculated effects for a single measurement of O_2 sorption in PSf. We have illustrated the effects of two doublings of the sample volume and of substantial improvements in the uncertainty of the temperature measurement. Note that the manufacturer's specifications for thermocouples are ± 2 K or, with special limits-of-error wire, ± 1 K.

Very often the variation in temperature of an apparatus during the course of a measurement is used to represent its uncertainty (in our apparatus ~0.1 K). This is actually more closely related to the reproducibility of the temperature measurements. The latter's overall uncertainty can only be specified after calibration against defined standards. A well-designed and operated experimental apparatus (protocol) can provide a set of data that is highly reproducable and has little scatter from a trend. Unfortunately, the absolute position of that data (or trend) may still have substantial uncertainty associated with it.

We have primarily concerned ourselves with the potential sources of bias in sorption measurements. We have not specifically addressed other sources of interference including leakage through valve seats and gaskets, and sorption on the chamber surfaces. We have assumed that the issue of leakage is controlled by the experimenter before beginning measurements. For example, in our own work we pressurize the entire apparatus with He at the highest anticipated pressure and calculate the density (from the measurements) for a week. The system is considered "leak tight" when there is no monotonic decay in density over that extended period. The question of gas sorption on internal surfaces is addressed by making volume calibration measurements with a variety of gases and at several temperatures. These provide us with a measure

TABLE 9
Effect of Decreasing Uncertainty of Temperature Measurement[a]

	Uncertainty in T ($\pm$K)			
	2.0	1.0	0.5	0.1
$b = V_s/V_1$	% Uncertainty in sorption capacity			
0.046	184	99	61	42
0.092	89	48	29	20
0.184	43	23	14	10

[a] $S \approx 0.25$ cm^3·cm^{-3}·Pa^{-1} $\times$ 10^{-5}, T_i and $T_f \approx 290.5$ K, $P_i \approx$ 2015 kPa, $a = 0.775$.

of the mass balance uncertainty due to sorption on the system walls and can be included (as appropriate) in the ϵ values.

CONCLUSIONS

We have illustrated a sensitivity analysis of the propagation of uncertainties for a specific zero-initial-condition, pressure-decay method of determining the sorption capacity of polymers. Application of this approach is useful in designing and specifying experimental equipment and procedures that maximize both the accuracy and reproducibility of the final calculated results. Alternative data analyses approaches and methods will yield somewhat different results, and we are currently studying these issues.

The results of our current parametric analysis indicate that, for materials with low sorption coefficients ($<0.5 \times 10^{-5}$ cm^3·cm^{-3}·Pa^{-1}), sample volumes ~40–50% of the reservoir volume and high accuracy temperature measurements will be required to achieve uncertainties on the order of 10–20% in the calculated sorption capacity. It is also possible that well-behaved literature data for sorption in materials with low capacity may still have significant uncertainties associated with them.

VARIABLES

V_1	volume of the reservoir (cm^3)
V_s	volume of the sample (cm^3)
V_b	volume of the ballast (cm^3)
V_d	dead volume from valve between cell and reservoir (cm^3)
V_2	volume of the cell (cm^3)
V_2'	$V_2 - V_b$
a	V_2'/V_1
b	V_s/V_1
d	V_d/V_1
P	pressure (kPa)
T	temperature (K)
ϵ	number of moles in the evacuated cell
ρ	gas density at P and T (mol/cm^3)
r	ρ_i/ρ_f
ϵ''	$\epsilon/(\rho_f V_1)$
M	a conversion factor, 370.95 (Pa/K)
m	gas sorbed in polymer (mol)
Δm	$m_f - m_i$
C	sorption capacity (mol/cm^3 polymer)

S sorption coefficient ($cm^3 \cdot cm^{-3} \cdot Pa^{-1}$) (gas volume at STP)/(polymer volume·pressure)
z compressibility factor for real gases
R gas constant (8314.4 $cm^3 \cdot kPa \cdot K^{-1} \cdot mol^{-1}$)

Subscripts

i initial condition
f final condition
c in the cell volume
r in the reservoir volume
a measurements made for determining ratio V_2'/V_1
b measurements made for determining ratio V_s/V_1
STP standard conditions, $T = 273.15$ K and $P = 101.325$ kPa

REFERENCES

1. Y. Kamiya, T. Hirose, K. Mizoguchi, and Y. Naito, *J. Polym. Sci., Polym. Phys. Ed., 24*, 1525 (1986).
2. C. L. Graves, G. C. Frye, D. M. Smith, C. J. Brinker, A. Datye, A. J. Ricco, and S. J. Martin, *Langmuir, 5*, 459 (1989).
3. R. M. Felder and G. S. Huvard, "Permeation, Diffusion, and Sorption of Gases and Vapors," in *Methods of Experimental Physics, Polymers: Physical Properties, Vol. 16, Part C* (R. A. Fava, Ed.), Academic Press, New York, NY, 1980.
4. J. Crank and G. S. Park, "Methods of Measurement," in *Diffusion in Polymers* (J. Crank and G. S. Park, Eds.), Academic Press, London, UK, 1968.
5. W. J. Koros and D. R. Paul, *J. Polym. Sci., Polym. Phys. Ed., 14*, 1903 (1976).
6. J. Andraos, *J. Chem. Educ., 73* (2), 150 (1996).
7. B. N. Taylor and C. E. Kuyatt, *Guidlines for Evaluating and Expressing the Uncertainty of NIST Measurement Results*, National Institute of Standards and Technology, Technical Note 1297, 1994.
8. D. G Friend and M.L. Huber, *Int. J. Thermophys., 15*, 1279 (1994).
9. B. A. Younglove, *J. Phys. Chem. Ref. Data, 11*, Suppl. 1 (1982).

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