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Solubility and Diffusion of Sulfur in Polymeric Materials

Abstract: Radiotracer techniques were used to study the sorption of sulfur vapor by silicone and epoxy polymers and to obtain information on the diffusion of sulfur in these materials. Sulfur was found to enter silicone polymers solely by a physical solution process which obeys Henry's law. The heat of solution is large (−0.43 eV) and at room temperature the solubility coefficient is at least five orders of magnitude greater than for many fully gaseous solutes, a result which fits an empirical rule relating the solubility coefficient of a given solute to its boiling point. Sorption of sulfur by a flexibilized anhydride-cured diglycidyletherbisphenol-A (DGEBA) epoxy is somewhat more complicated and appears to involve a double process of physical solution and chemical reaction. The rapid diffusion of sulfur in silicone rubber necessitated measurements of the diffusion coefficient D by a vacuum desorption technique. The activation energy Q and pre-exponential constant D_0 are found to be 0.74 eV and 4×10^5 cm^2/s, respectively. Corresponding values for the epoxy, as determined by a steady state permeation method, are 1.06 eV and 3×10^5 cm^2/s. These relatively large activation energies and pre-exponential factors are thought to reflect the large size of the S_8 molecule. Near room temperature, the difference in the activation energies causes sulfur diffusion to occur at least four orders of magnitude more slowly in the epoxy, which makes this material much more attractive for encapsulation applications requiring an effective diffusion barrier to elemental sulfur present as a pollutant of the atmosphere.

Introduction

Elemental sulfur is present in most atmospheric environments at trace levels, usually well below one part per billion. At such low levels, it may appear at first sight that sulfur interaction with polymeric materials would be slight indeed. In this paper, we show, however, that sulfur vapor has a substantial heat of solution in several polymeric materials and can be sorbed by them to concentration levels one hundred thousand times larger than in the surrounding atmosphere. Because of this, both the solubility and the diffusivity of elemental sulfur in polymeric materials become of considerable interest, particularly when applications are considered that demand strict levels of hermeticity against reactive atmospheric contaminants.

Currently available information on the subject of the permeation of gases and vapors through polymers is for the most part restricted to permeants which boil below room temperature and are completely gaseous at the measurement temperature [1]. The methods commonly used for solubility and diffusion measurements are usually unsuitable for substances of low volatility such as sulfur, whose partial pressure at room temperature is only 1.3×10^{-4} Pascals (10^{-6} torr). The use of tracer techniques [2, 3] is one method by which these limitations can be overcome. In the present study, use has been made of various sorption, desorption, and permeation measurements, all of which are based on the use of a source of sulfur containing a small fraction of the radiotracer S^{35}. This isotope, which is a β-emitter with a half-life of 87 days, provides nanogram sensitivity for the detection of sulfur by standard liquid scintillation counting methods. The materials investigated were a) poly(dimethylsiloxane) rubber, filled 50 percent by weight with iron oxide, b) a vinyl crosslinked silicone gel, and c) a flexibilized anhydride-cured epoxy of the DGEBA (diglycidyletherbisphenol-A) type. For brevity these are referred to simply as the silicone rubber, the silicone gel, and the epoxy material, respectively.

Theoretical considerations

Experiments described below indicate that the sorption of sulfur consists, either in whole or in part, of a process of physical solution which can be treated thermodynamically by one or more reversible reactions between elemental sulfur in the vapor phase and elemental sulfur in solution in the polymeric host material. For this situation, we may write in general that the sulfur concentration in solution (expressed as a weight percentage, X) is a unique function of the sulfur vapor pressure p and the temperature T:

$$X = f(p, T). \qquad (1)$$

It is implicit in Eq. (1) that a sample which contains less sulfur than the equilibrium content for a given pressure and temperature will sorb sulfur until the equilibrium level is reached, and conversely that a sample with a higher sulfur content will desorb sulfur until equilibrium is reached. An example of the approach to a unique solubility level from both a subsaturated and a supersaturated condition is illustrated in Fig. 1. (Note also from Fig. 1 that sorption is much slower than desorption. The reason for this is that in our work sorption is a source-limited process governed by the evaporation rate of the small radioactive source.)

While measurements of the type shown in Fig. 1 justify the existence of a unique functional relationship between X, p, and T, the specific form of this relationship depends on unknown details of the solution process and specifically on whether the molecular species existing in the vapor enters into solution without dissociation. It has been shown by vapor density measurements [4] that at temperatures of current interest the molecular species present in the vapor is S_8. Accordingly, the simplest examples of solution equilibria, wherein a single species in the vapor is taken to be in equilibrium with a single molecular species in solution, can be represented by the equation

$$S_8 \text{ (vapor)} \rightleftarrows n\, S_{8/n} \text{ (solution)}, \tag{2}$$

where n is 1, 2, 4, or 8 if the dissolved species is S_8, S_4, S_2, or S, respectively. Application of the mass-action principle to Eq. (2) leads to the following solubility relationship:

$$X = C\, p^{1/n} \exp\left(-\Delta h_s / nkT\right), \tag{3}$$

where C is a constant, Δh_s is the heat (enthalpy) of solution per molecule of sulfur vapor, k is Boltzmann's constant, and T is the absolute temperature. Equation (3) shows that Henry's law (X proportional to p at constant T) is obeyed only in the event that solution occurs without dissociation.

In the above, we have considered only cases in which a single molecular species is present in solution. It is also possible to imagine more complicated situations in which a mixture of several molecular species is present. In such cases the experimentally determined exponent governing the pressure dependence of the solute concentration does not, in general, correspond to an integral value of the parameter n. Fortunately, it appears that such complications are largely irrelevant in the present work, and that n has a value close to unity, corresponding to conformity with Henry's law. When Henry's law is obeyed, it is appropriate to define a solubility coefficient $H(T)$ as the solubility per unit vapor pressure of the solute. Thus we have

$$X = H(T)\, p. \tag{4}$$

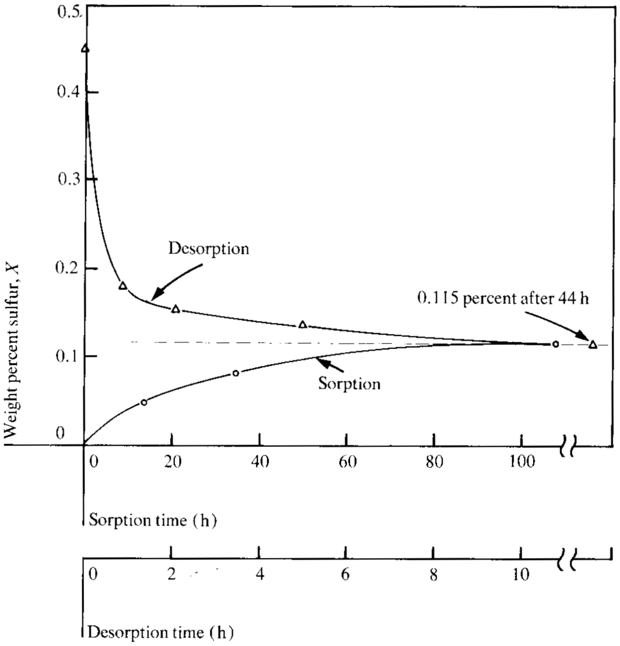

Figure 1 Illustration of the approach to a unique equilibrium solubility by sorption of sulfur from a subsaturated state and by desorption from a supersaturated state. The equilibrium solubility of 0.115 weight percent sulfur is for the silicone gel at 130°C (403 K) and a sulfur source at 91°C (364 K).

By comparison with Eq. (3) for the case $n = 1$ it is evident that

$$H(T) = C \exp\left(-\Delta h_s / kT\right). \tag{5}$$

An important special case of Eq. (3) occurs when X becomes the saturation solubility X_{sat} as a consequence of p becoming $\bar{p}$, the equilibrium vapor pressure at the temperature in question. For the current purpose $\bar{p}$ is given with adequate accuracy by the expression

$$\bar{p} = \bar{p}_0 \exp\left(-\Delta h_{\text{vap}} / kT\right), \tag{6}$$

where Δh_{vap} is the heat of vaporization and $\bar{p}_0$ is a constant. Inserting Eq. (6) into Eq. (3) and replacing X with X_{sat}, we obtain

$$X_{\text{sat}} = B \exp\left[-\left(\Delta h_{\text{vap}} + \Delta h_s\right)\right] / nkT, \tag{7}$$

where $B \equiv C(\bar{p}_0)^{\frac{1}{n}}$. Experiments involving the use of Eqs. (3) and (7) are described later in this paper.

To discuss the solubility quantitatively, information is required on the vapor pressure of sulfur and, specifically, on the parameters $\bar{p}_0$ and Δh_{vap} in Eq. (6). There is currently an unresolved discrepancy between the unpublished data of Abbott [5] and the data of other workers [6–8]. Between room temperature and the melting point the numerical relationships are, respectively,

$$p = 1.3 \times 10^{8} \exp\left(-0.81 / kT\right), \tag{8a}$$

$$p = 1.7 \times 10^{13} \exp\left(-0.99 / kT\right), \tag{8b}$$

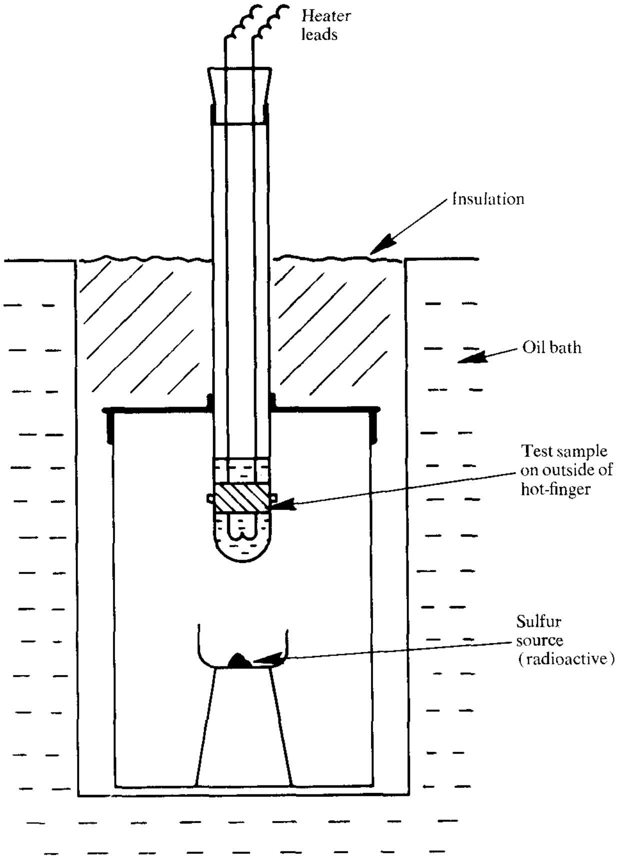

Figure 2 The "hot finger" sorption-desorption apparatus.

where p is the vapor pressure in pascals (Pa) and kT is expressed in eV. There is universal agreement on a vapor pressure close to 1.3×10^{-4} Pa (10^{-6} torr) at room temperature; however Abbott's value of Δh_{vap} is noticeably below that of the other workers. Fortunately, this discrepancy is not large enough to interfere seriously with the major conclusions of the present work.

Experimental methods

- *Radiochemical procedures*

Although the solubility and diffusion measurements involve different specific procedures to be described later, each of the techniques depends on the use of sulfur tagged with the radioisotope S^{35}. This enables the determination of minute quantities of sulfur by liquid scintillation counting. In this procedure, a sulfur sample is dissolved in a vial containing 20 ml of toluene activated with an organic scintillant compound. The weight of sulfur is then found from the counting rate measured with a liquid scintillation spectrometer, using a daily calibration factor which allows for the gradual decay of activity of the source material.

To prepare the radiotracer sulfur sources, a known weight of pure stable sulfur was dissolved in either toluene or benzene and tagged by addition of a quantity of the S^{35} tracer. After thorough mixing, a known small amount of the solution was pipetted off and diluted with Omnifluor-activated toluene to form a calibration standard. The bulk of the solution was then divided equally among several glass thimbles and evaporated to dryness under a hood. It was found necessary to bake such freshly prepared sources at 90°C (363 K), typically for a few days, before the sulfur residue attained a stable morphology and evaporation rate. Most of the work reported here was performed with 50 mg sources tagged to a level such that 1 μg of sulfur, when redissolved and counted in the liquid scintillation spectrometer, yielded a counting rate of about 10000 cpm. Since the background counting level was about 25 cpm, this arrangement provided a detection sensitivity in the region of 1 ng of sulfur. Tables giving a daily calibration factor (expressed as the counting rate per microgram of sulfur) were computed from the initial activity of the standard and the isotope half-life of 87.1 days. Confirmation of the computed calibration table was obtained by periodic checks of the calibration standard. The agreement obtained served as a check on the radiochemical purity of the isotope employed.

In tests described later, sulfur vapor that has permeated through a sample membrane is condensed directly in a standard counting vial. In the majority of solubility and diffusion measurements, however, the objective was to determine the weight percentage of sulfur contained in a sample after a known exposure to sulfur vapor. The simple and sensitive method used for determining the sulfur content is based on the finding that physically sorbed sulfur could be extracted from the polymeric samples by immersion in toluene at room temperature. The extraction from the silicones proceeded quite rapidly (in a matter of minutes), during which time appreciable swelling of the polymer was noted. On the other hand, extraction from the epoxy proceeded more slowly, to the extent that an overnight soak prior to counting became the usual procedure. In practice, the sampling procedure consists of taking a small piece (5 to 10 mg) of the total test specimen, weighing it, and then dropping it into a standard liquid scintillation vial filled with 20 ml of toluene. The activity built up in the liquid gives, via the calibration factor, the weight of sulfur extracted from the sample and hence permits calculation of the weight percentage X.

From various tests conducted on the silicone rubber, it was concluded that virtually complete removal of sorbed sulfur was possible by extraction with liquid toluene. The most important single piece of evidence was the observation of a simple proportionality between the sulfur content based on toluene extraction and the surface activity of a homogeneously doped sample, as measured with a proportional counter. Such a proportionality was not obtained with the epoxy material.

• *Hot-finger apparatus*

As indicated by Eq. (1), the sulfur solubility X depends on the two independent variables p and T, and therefore two types of experiment (isothermal and isobaric) are needed to establish the solubility relationship. In the isobaric case, the solubility is measured as a function of sample temperature while the vapor pressure p is kept constant. In the isothermal experiment the solubility is measured as a function of temperature under conditions where p is allowed to take on its equilibrium value $\bar{p}$ at each temperature of the sample. Both types of experiment can be accomplished with the simple "hot-finger" apparatus shown in Fig. 2. The essential feature of this arrangement is the ability to vary the sample temperature T independently of the sulfur source temperature T_s, which controls the sulfur vapor pressure. The hot-finger itself, which carries the test samples on its outer surface, is a pyrex test tube sealed with an epoxy compound into the screw cap of a glass jar containing the radioactive sulfur source. The hot-finger is filled to a depth of about 2 cm with a light silicone oil and is fitted with a heater, thermocouple and stirrer so that the test samples can be brought to a selected temperature above the jar temperature, which is determined by the temperature of the oil bath in which the assembly is immersed. For tests on samples available in sheet form, a sample strip is hooked onto small glass horns projecting from the hot-finger, so as to be held by slight tension against the curved surface of the hot-finger. For the silicone gel, which is naturally sticky, small individual dabs are simply applied to the surface of the hot-finger. Both arrangements give good thermal contact to the hot-finger, so that the sample temperature can be taken to be that of the inner thermocouple.

• *Permeation apparatus*

The first procedure developed for diffusion measurements made use of the permeation apparatus shown in Fig. 3. A specimen membrane (typically 0.5 mm thick and 3 cm in diameter) is clamped in a Teflon collar assembly, each half of which is threaded to receive a standard liquid scintillation vial. The exposed area of the sample is a central circular region with an area of about 2 cm^2. The lower vial (the source bottle of Fig. 3) contains the radioactive source, while the upper vial serves as the collection bottle to receive the sulfur vapor that permeates through the membrane. The assembly is placed in a tubular copper receptacle and is heated by an oil bath to bring the membrane and the sulfur source to the desired test temperature. To insure that the sulfur vapor pressure in the collection bottle is always less than that in the source bottle (and hence that there is a vapor pressure differential across the membrane), the projecting end of the collection bottle is cooled by an air jet. Sampling is performed on an intermittent basis by periodically withdrawing the collar and vial assembly from the oil bath, cooling to room temperature, and performing the following operations:

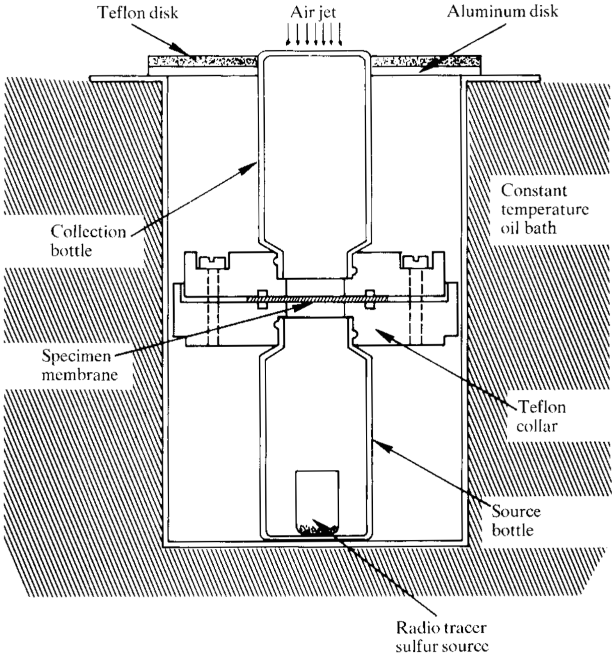

Figure 3 The arrangement for permeation tests.

1. The source bottle is unscrewed from the collar, capped, and temporarily set aside.
2. The collection bottle is unscrewed and the standard quantity of 20 ml of Omnifluor-activated toluene added to it to dissolve the condensed sulfur, the amount of which is then determined by liquid scintillation counting. This quantity may then be used to calculate the mean permeation rate for the prior test interval. Alternatively, when added to all previous increments, we obtain the cumulative amount of sulfur, Q_t, that has permeated through the sample since the beginning of the test.
3. The surface activity of the membrane is measured on both the entrance and the exit faces, using a gas-filled proportional counter.
4. Following completion of these measurements, the same source bottle and a new collection bottle are fitted to the collar, and the test is resumed for the next selected interval.

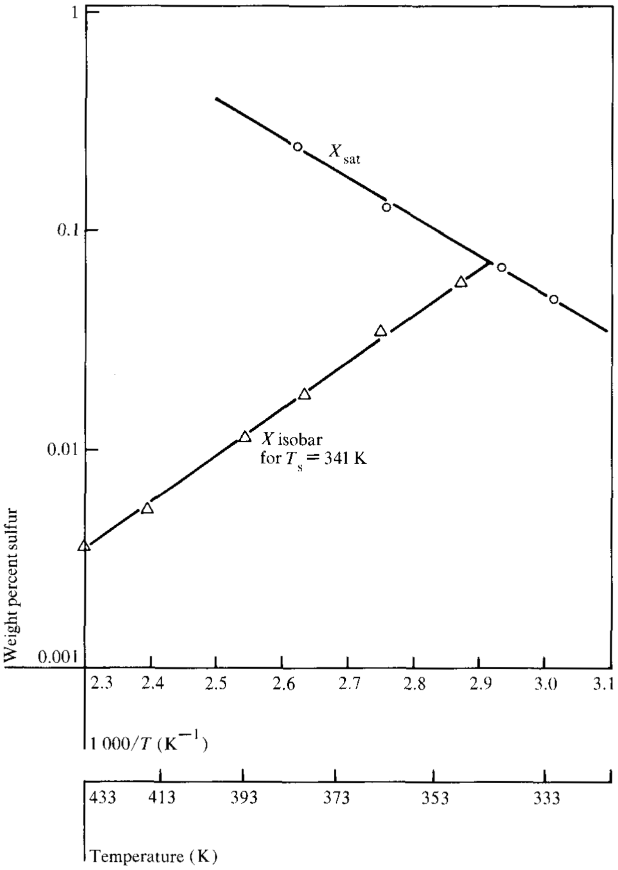

Figure 4 Solubility data for sulfur in silicone rubber. The isobaric data were obtained with the sulfur source at 68°C (341 K).

Two comments should be made about the surface activity measurements mentioned in step 3 above. First, the measurements are made without removing the membrane from the Teflon collar, to avoid possible difficulties associated with breaking and remaking the seal between the membrane and the collar. To insure that stray activity from the Teflon collar is not included in the count of surface activity, metal shields are positioned in and around the throat of the collar prior to each measurement. Second, the objective of the proportional counter measurements is to obtain a relative measure of the sulfur concentration at the two surfaces of the membrane. Strictly, however, the observed counting rate is proportional to the integral

$$\int_0^a C(z) \exp(-\mu z) dz,$$

where $C(z)$ is the sulfur concentration at depth z below the surface of a membrane of thickness a, and μ is the linear absorption coefficient for the electrons emitted by S^{35} atoms. The value of μ was obtained for a number of polymers by measuring the fractional reduction in counting rate that occurs when a thin, nondoped membrane is interposed between a doped (radioactive) membrane and the window of the proportional counter. The general result is that for the materials of current interest, the characteristic absorption length $1/\mu$ is about 10^{-3} cm. This is many times smaller than the membrane thickness customarily used, and at steady state the variation of sulfur concentration over this distance is small. Consequently, the ratio of the two surface activities, A_1/A_2, gives, to a very good approximation, the ratio of the sulfur surface concentrations, C_1/C_2.

Experimental results

- *Solubility results for the silicones*

In a typical sorption experiment, the temperature of the hot-finger is first adjusted to be a degree or so hotter than the selected temperature of the sulfur source. This is a precaution to avoid the possibility of condensation of free sulfur on the surface of the sample. Sorption is then allowed to proceed until equilibrium is established. The progress toward equilibrium may be followed by periodic sampling. (With the small sulfur sources used in the present study, sorption is a relatively lengthy process which proceeds at a rate determined by the evaporation capability of the source.) Once saturation has been achieved, the temperature of the hot finger may be raised in a series of steps and the equilibrium sulfur content found at each step. In experiments of this type, it was always found that an increase in the temperature of the hot finger caused the solubility to decrease, i.e., the new solubility level was approached by a desorption of sulfur from the sample. (An example of this behavior is shown in Fig. 1.) Since the temperature of the hot finger does not sensibly affect the temperature of the sulfur source, a set of such measurements yields an isobaric solubility curve.

Data for the silicone rubber, taken with a source temperature T_s of 68°C (341 K), are shown in Fig. 4. It is clearly evident that the isobaric solubility decreases with increasing temperature. On the other hand, Fig. 4 also shows the results of complementary experiments on the variation of X_{sat} with temperature. These data were obtained under isothermal conditions by raising the temperature of the sample and source together. In contrast to the situation at constant pressure, the isothermal solubility is seen to increase with increasing temperature. Clearly, this behavior must reflect the fact that the sulfur vapor pressure rises rapidly enough with temperature to override the decrease in solubility that occurs at constant pressure. Figure 5 shows that the silicone gel behaves in an entirely parallel fashion to the silicone rubber, but exhibits a solubility approximately four times higher for the same conditions of temperature and pressure. The actual magnitudes of the observed solubilities (typically hundredths to tenths of one weight percent) correspond to a number of molecules per unit volume in solution which is typically 10^5 times larger than the number of sulfur molecules per unit volume in the vapor.

To discuss the results of Figs. 4 and 5 in quantitative terms we observe first that the data plots are all linear in terms of log X versus $1/T$, in a manner consistent with Eqs. (3) and (7). Both solubility isobars are given by an empirical expression of the type

$$X = A \exp(0.43/kT). \tag{9}$$

By comparing this expression with Eq. (3) we conclude that

$$\Delta h_s/n = -0.43 \text{ eV}. \tag{10}$$

On the other hand, from Fig. 4 we find that X_{sat} for silicone rubber (and nearly so for the gel) varies with temperature through the factor $\exp(-0.35/kT)$, so that by comparison with Eq. (7) we have

$$(\Delta h_{vap} + \Delta h_s)/n = 0.35 \text{ eV}. \tag{11}$$

Combining Eqs. (10) and (11) we obtain

$$\Delta h_{vap}/n = 0.78 \text{ eV}. \tag{12}$$

Turning now to the vapor pressure results, Eqs. (8) give

$$\Delta h_{vap} = 0.81 \text{ to } 0.99 \text{ eV}. \tag{13}$$

Hence, by comparison of Eqs. (12) and (13) we obtain the important result

$$n \approx 1, \tag{14}$$

which indicates substantial conformity to Henry's law. Inserting the value $n = 1$ in Eqs. (3) and (10) we obtain the solubility relation

$$X = Cp \exp(-\Delta h_s/kT), \tag{15}$$

where the heat of solution Δh_s has the value -0.43 eV. The magnitude and sign of Δh_s correspond to a substantial evolution of heat when sulfur vapor dissolves in either of the silicone polymers. To obtain the numerical form of Eq. (15), we first find from Fig. 4 that the empirical parameter A in Eq. (9) has the value 3×10^{-8} for silicone rubber. This must be equated [cf. Eq. (15)] to a Cp of 68°C, since the experiments of Fig. 3 were performed with a source temperature of 68°C. Adopting a value of p (68°C) $= 1.3 \times 10^{-2}$ Pa, we find that $C = 2.3 \times 10^{-6}$ Pa^{-1}. Thus the solubility of sulfur in silicone rubber is found to be

$$X = 2.3 \times 10^{-6}\, p \exp(0.43/kT), \tag{16}$$

where X is in weight percent, p is in Pa, and kT is in eV.

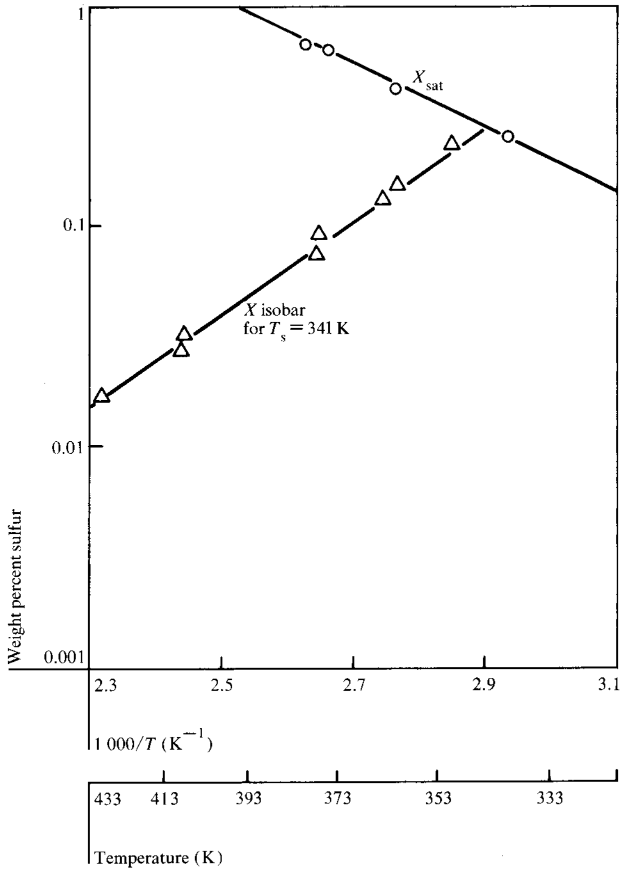

Figure 5 Solubility data for sulfur in the silicone gel. The isobaric data were obtained with the sulfur source at 68°C (341 K).

A similar expression also applies to the silicone gel, provided the pre-exponential factor is increased by a factor of four.

- *Solubility results for the epoxy material*

Although toluene extraction appears to give virtually complete removal of sorbed sulfur from the silicone polymers, this was not the case for the epoxy material. The first indication of incomplete extraction was obtained from observations that linked the sorption of sulfur to a yellow discoloration of the sample which toluene extraction failed to remove entirely. To investigate the matter further, surface activity measurements were made on a number of specially prepared samples to obtain a relative indication of their sulfur content before and after extraction. If we denote the sulfur content of a uniformly doped sample before and after extraction by X_T and $X_{T'}$ (weight percent), respectively, and its corresponding surface activities by A and A', then

$$X_T/X_{T'} = A/A'. \tag{17}$$

If toluene extracted a weight of sulfur Δw from a sample of weight W, then

$$X_T - X_{T'} = 100\ \Delta w/W, \tag{18}$$

and hence, using Eq. (17), we have

$$X_{T'} = 100 \left(\frac{A'}{A - A'}\right)\left(\frac{\Delta w}{W}\right). \tag{19}$$

The following example illustrates the type of behavior observed. By slow source-limited sorption, a sample weighing 39 mg was uniformly doped with sulfur to a (nonsaturation) level which, in a certain reference counting geometry, gave a surface activity A of 1359 cpm. Extraction with liquid toluene removed 25 μg of sulfur from the sample and reduced the surface activity to 1090 cpm. Using Eqs. (17)-(19) we found that toluene removed only 0.067 weight percent of sulfur out of a starting amount of 0.34 weight percent, i.e., only one-fifth of the total amount.

After this type of experiment, several attempts were made to extract the sulfur that the normal procedure failed to recover. Longer soaking times, warming the toluene, and multiple extractions were all tried, without improvement. As a next step, toluene extraction was tried in a Soxhlet (distillation-type) apparatus for a period of several days, again without any significant improvement in the yield of sulfur recovered. Finally, samples were extracted with carbon disulfide in place of toluene, again without increase in the yield of sulfur recovered.

Taken together, these experiments appeared to demonstrate in a clear-cut manner that the sulfur sorbed by the epoxy polymer exists in not one but two distinct states. One of these states is relatively freely bound and susceptible to toluene extraction, while the other is a much more tightly bound state, from which recovery is not obtained. A working hypothesis that appears to fit the solubility results in a natural way is that the extractable component X_E corresponds to sulfur held in physical solution, while the nonextractable component X_B has become fixed by a chemical reaction which presumably involves decomposition of the S_8 molecule. Using the terms introduced above, we note for future reference that the total sulfur content X_T is given by

$$X_T = X_E + X_B. \tag{20}$$

Before proceeding to the solubility data, it is appropriate to introduce one other important observation made in connection with the toluene extraction procedure. This concerns the effect of residual sample activity due to bound sulfur on the counting rate measured by the liquid scintillation spectrometer. As explained previously, the normal sampling procedure for sulfur is to add a small snippet taken from the main specimen to a standard liquid scintillation vial containing 20 ml of toluene sensitized with the organic scintillant compound Omnifluor. In the case of the silicones, where essentially all the sorbed sulfur enters the toluene and the residual activity of the sample itself drops to negligible values, it makes no difference in the counting rate whether the sample piece is left in the vial or not. In the case of the epoxy, however, activity from the unextracted bound sulfur contributes to the measured counting rate to an appreciable extent unless the sample is removed from the vial.

The reason for this is that polymeric materials of the type considered here have a small but finite absorption length for the electrons emitted by the decay of S^{35} atoms. Consequently, bound sulfur atoms present in a near-surface layer of the polymer can induce scintillation events in the surrounding liquid, over and above those produced by the sulfur which has actually been extracted from the sample. The existence of such an effect was clearly established from the decrease and subsequent restoration of the counting rate upon removal and replacement of an extracted sample. Because of this effect, it is obviously necessary for the determination of X_E to remove the sample piece from the vial in order to obtain the correct counting rate corresponding to the amount of sulfur actually extracted. However, once this measurement has been made, a useful elaboration of the procedure is to cut up the removed sample into the smallest possible fragments and return these to the vial. As the fragment size is made smaller, and absorption effects become less marked, the enhancement in the counting rate associated with the presence of the sample becomes greater. In the limit, as the fragment size becomes negligibly small with respect to the absorption length $1/\mu$ (μ is the linear absorption coefficient), the counting rate tends to that which would have been obtained if all the sulfur had been extracted from the sample.

In the measurements described below, we have made use of an "apparent sulfur content," X_A, which is derived from the total counting rate obtained after a chopped-up sample is returned to the vial used for the initial extraction. In view of the preceding discussion, we may write

$$X_A = X_E + \beta X_B, \tag{21}$$

where X_B is the bound sulfur content and β is an absorption parameter which increases with the degree of pulverization of the sample and which tends to a maximum value of one [at which point X_A becomes identical to X_T, cf. Eq. (20)].

The data obtained on the solubility of sulfur in the epoxy material are shown in Fig. 6. The isobar lines were obtained by first saturating a sample 0.015 cm thick at 76°C (349 K), and then raising the sample temperature while maintaining the sulfur source and ambient vapor pressure at their 76°C values. It is again evident that the isobaric solubility exhibits a marked decrease with increase of temperature, corresponding to a desorption of sulfur from the sample. The two isobars shown in Fig. 6 are for the extractable sulfur content X_E and the apparent sulfur content X_A (determined from the liquid scintillation counting rate in the presence of the chopped-up samples). For comparison, the two upper curves show that under saturation conditions where the temperature of the sulfur source is equal to the sample temperature, the previously noted desorption trend is reversed and both saturation solubilities $(X_E)_{sat}$ and $(X_A)_{sat}$ increase with temperature.

The behavior of X_E and $(X_E)_{sat}$ is reminiscent of that observed for the silicones and seems entirely consistent with the suggestion that these curves correspond to sulfur that enters into physical solution. Quantitatively, the X_E isobar of Fig. 6 corresponds to the equation

$$X_E = 3.7 \times 10^{-9} \exp (0.58/kT), \qquad (22)$$

whereas the saturation line is fitted by

$$(X_E)_{sat} = 3.5 \times 10^3 \exp (-0.25/kT). \qquad (23)$$

In terms of the thermodynamic analysis presented earlier for a physical-solution process, we deduce from Eqs. (22) and (23) a value for $\Delta h_{vap}/n$ of 0.83 eV, which fits the vapor pressure data of Eq. (8) with the value $n = 1$. We may thus conclude that a) X_E corresponds to sulfur in simple physical solution, b) Henry's law is obeyed, c) the solute species is the S_8 molecule, and d) the heat of solution of sulfur is −0.58 eV. Additionally, taking the value p (76°C) $= 2.6 \times 10^{-2}$ Pa, we find $C = 1.4 \times 10^{-7}$ Pa^{-1} and hence that the physical solubility X_E is given as a function of pressure and temperature by the expression

$$X_E = 1.4 \times 10^{-7}\, p \exp (0.58/kT), \qquad (24)$$

where X is in weight percent, p is in Pa, and kT is in eV. It may be noted that the present heat of solution, −0.58 eV, is similar in magnitude but noticeably larger than the value of −0.43 eV found for the silicones. As a consequence, it follows that for comparable conditions of pressure and temperature, the solubility levels of sulfur in the epoxy material are larger by a significant factor (typically 3 to 10 times) than in the silicones.

To conclude this section, we consider the information that Fig. 6 provides on the bound sulfur content X_B. To this end we use Eq. (21) in the form

$$X_A - X_E = \beta X_B. \qquad (25)$$

Inspection of the differences between the corresponding X_A and X_E curves (for both isobaric and saturation conditions) brings out the interesting fact that βX_B has an essentially constant value of 0.6 weight percent. While it is difficult to estimate the actual value of β which applies in the present case, it is reasonable to assume as a first step that the value of β is nearly the same for all specimens. It follows therefore that the bound sulfur level X_B was approximately the same for all conditions of temperature and pressure represented by Fig. 6. Since all of the samples of Fig. 6 are fully equilibrated, this result supports a very simple model wherein it is postulated that the epoxy material contains a certain definite concentration of reaction sites or chemical groupings at which sulfur atoms can become incorporated into the polymer structure. The nature of this grouping, and the extent to which its concentration may be controlled by changes in the formulation of the material, are interesting questions which, however, fall beyond the scope of the present work. The only additional information that can be deduced from Fig. 6 follows from the fact that β approaches one as the particle size of the chopped-up sample becomes comparable with the absorption length $1/\mu$, which is about 10^{-3} cm. A minimum estimate of $X_B \approx 0.6$ weight percent is obtained by assuming $\beta \approx 1$. This value has been used in connection with the permeation measurements discussed below.

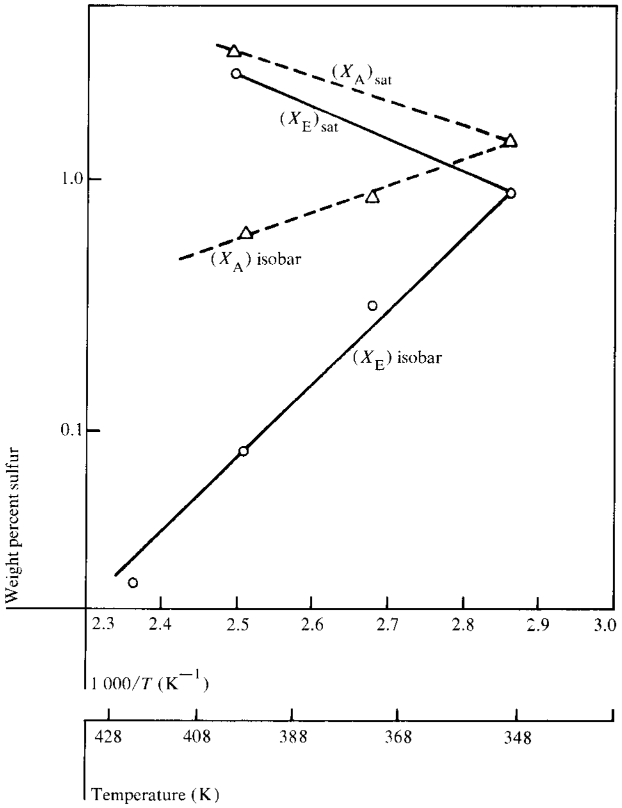

Figure 6 Solubility results for sulfur in the epoxy material. The quantity X_E refers to the extractable sulfur content, identified with physically dissolved sulfur. The quantity X_A is the apparent sulfur content $X_E + \beta X_B$, defined in the text. The isobars are for a sulfur source held at 76°C (349 K).

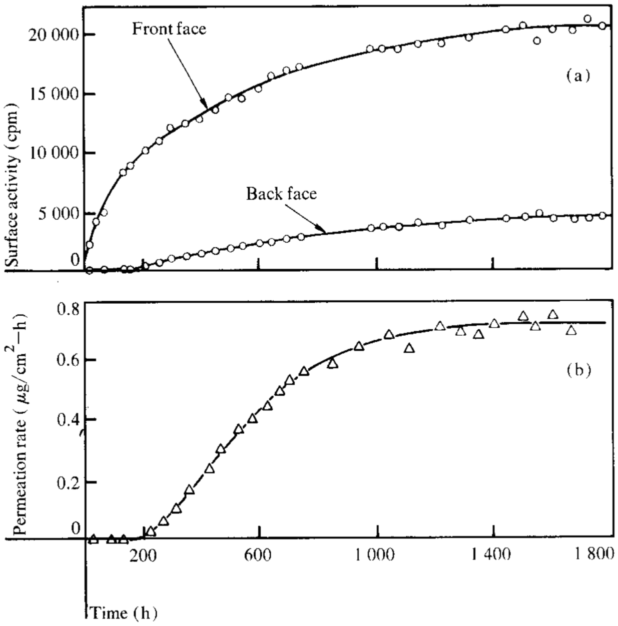

Figure 7 Permeation of sulfur through a 0.5 mm thick membrane of the epoxy material at 88°C (361 K). (a) Variation of the activity on the front and the back surfaces of the membrane; (b) the corresponding permeation rate data. The surface activity data have been corrected for the decay in activity that occurred during the run, which occupied an interval corresponding to 0.8 of the half-life of the S^{35} isotope.

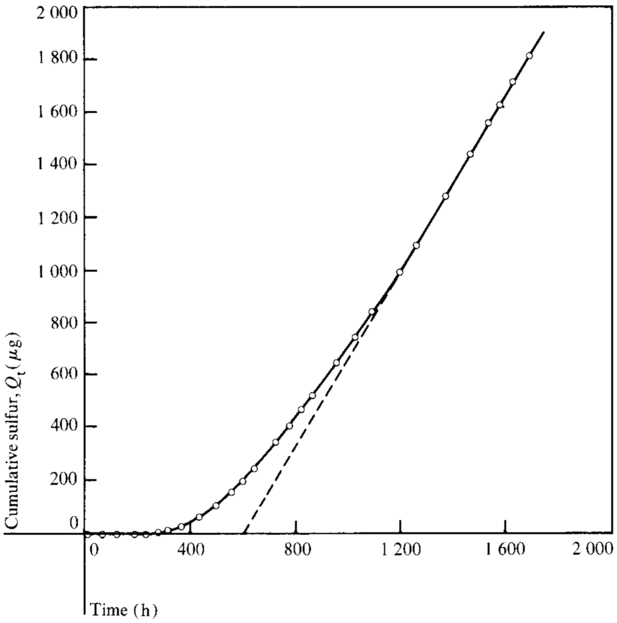

Figure 8 The permeation rate data of Fig. 7 replotted in the form of the cumulative quantity Q_t versus time.

- *Diffusion results for the epoxy material*

Diffusion experiments on the epoxy material were performed with the permeation apparatus described previously. Illustrative data are shown in Fig. 7. For subsequent discussion, the permeation rate data have been replotted in cumulative form in Fig. 8, which gives the total amount of sulfur passed through the membrane, Q_t, as a function of time. From an inspection of these figures, it may be noted that a) the experiment was conducted over a period of approximately 70 days (1700 hours); b) attainment of the steady state required in excess of 1000 h; c) the permeation rate exhibits a sigmoidal variation with time characteristic of diffusion-controlled behavior; d) the attainment of the steady state permeation rate in Fig. 7 corresponds in Fig. 8 to the cumulative curve becoming linear with time; e) the front surface activity rises slowly and continually during the run and does not level off until the steady state is achieved; and f) the buildup of the back surface activity lags behind that of the front surface in the manner expected of a diffusion-controlled process and finally levels off at a lower level indicative of a concentration gradient across the membrane. The time dependence of the surface activities during the approach to steady state means that the standard transient solution of the diffusion equation cannot be rigorously used for the determination of the diffusion coefficient *D*, and recourse must be made to the steady state measurements. For the epoxy material, there is also the additional complication of the reaction which converts a part of the total sulfur concentration to the bound form. Fortunately, in the case of the steady state data, it appears that this complexity can be handled by the adoption of a simple and reasonable assumption. This assumption is that at steady state there exists through the membrane a uniform background of bound sulfur on which is superposed a linear concentration profile of physically dissolved sulfur which alone provides the driving force for the steady state flux. This assumption follows naturally from the previously introduced idea of a chemical saturation level and the expectation that bound sulfur diffuses at a negligible rate compared with the physically dissolved fraction.

With this assumption, the analysis to obtain the diffusion coefficient *D* proceeds as follows. Fick's first law is written in the form

$$\bar{J} = D(\bar{C}_1 - \bar{C}_2)/a, \tag{26}$$

where $\bar{J}$ is the steady state permeation flux, a is the thickness of the membrane, and $\bar{C}_1$ and $\bar{C}_2$ are the steady state concentrations (per unit volume) of the physically dissolved sulfur at the entrance and exit faces of the membrane. Since $\bar{J}$ is found experimentally, the determination of D reduces to an evaluation of $\bar{C}_1$ and $\bar{C}_2$. In the absence of bound sulfur, these two quantities can be found uniquely from the ratio of the two surface activities, $\bar{A}_1$ and $\bar{A}_2$, and from the mean concentration $\bar{C}_m$ obtained by toluene extraction of the membrane in the final steady state condition. In the presence of a uniform concentration of bound sulfur C_B, however, we have the relations

$$\bar{A}_1/\bar{A}_2 = (\bar{C}_1 + C_B)/(\bar{C}_2 + C_B) \tag{27}$$

and

$$\bar{C}_m = \tfrac{1}{2}(\bar{C}_1 + \bar{C}_2). \tag{28}$$

Equations (27) and (28) contain three unknowns and hence do not themselves permit the evaluation of $\bar{C}_1$ and $\bar{C}_2$. To proceed, however, it was possible to use the approximate value of C_B corresponding to the earlier estimate $X_B \approx 0.6$ weight percent. [To avoid a negative value of $\bar{C}_2$, the assumed value of X_B had to be reduced to 0.4 weight percent for the 88°C (361 K) data.] In this way, steady state permeation data obtained at 67, 88, 109, and 127°C (340, 361, 382, and 400 K respectively) were reduced via Eqs. (26)-(28) to the diffusion coefficients shown in Fig. 9. The results for the epoxy material conform to an Arrhenius expression of the type

$$D = D_0 \exp(-Q/kT), \tag{29}$$

with the values 3×10^5 cm^2/s for D_0 and 1.06 eV for the activation energy Q.

It should be noted that the values of D shown in Fig. 9 are rather insensitive to the particular assumption made concerning the level of the bound sulfur concentration, C_B. This can be brought out by considering the difference in D values that are obtained with the two extreme and opposing assumptions that a) $\bar{C}_2 = 0$, which yields the smallest value of D, $D_{\min}$, and b) $C_B = 0$, which yields the largest value of D, $D_{\max}$. It is readily found with some algebraic manipulation of the preceding equations that

$$D_{\max}/D_{\min} = (\bar{A}_1 + \bar{A}_2)/(\bar{A}_1 - \bar{A}_2). \tag{30}$$

In the case of the 88°C (361 K) data shown in Fig. 7, we find, for example, that $D_{\max}/D_{\min} = 1.5$. This range is small enough to provide considerable reassurance that no major error was introduced in the data analysis by the approximate value assumed for C_B.

It is illuminating to compare this steady state determination of D with the approximate value computed from Fig. 8 using the relationship

$$D \approx a^2/6t_i, \tag{31}$$

where t_i is the intercept obtained by extrapolation of the linear portion of the cumulative curve. Equation (31) is an exact relationship for the simpler case of no chemical binding ($C_B = 0$) and the idealized boundary conditions $C_1 = C_2 = 0$ for $t < 0$ and $C_1 = C_1$, $C_2 = 0$ for $t > 0$. Despite the fact that these conditions clearly do not describe the present situation at all well, we find, for example, that the application of Eq. (31) to the data of Fig. 8 gives $D \approx 2.2 \times 10^{-10}$ cm^2/s, in surprisingly good agreement with the value $D = 5.5 \times 10^{-10}$ cm^2/s obtained from the steady state analysis.

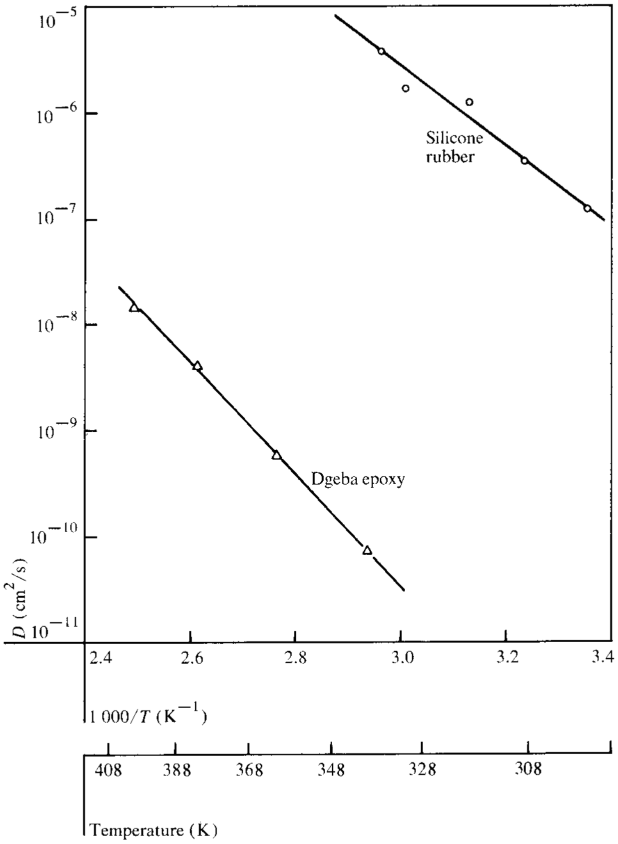

Figure 9 Temperature dependence of the diffusion coefficient of sulfur in two polymeric materials.

- *Vacuum desorption measurements*

The first attempts to measure the diffusion constant of sulfur in silicone rubber were by permeation tests of the type described above. In this case, the approach to the steady state showed some interesting differences compared with Fig. 7. The surface activities on the front and the back faces were always essentially identical to each other, indicating that sorption and permeation proceeded without the appearance of an appreciable concentration gradient across the membrane. Furthermore, it was found that the steady-state permeation rate achieved with the membrane present was only slightly less than that obtained when the membrane was entirely removed. These observations clearly suggest that the diffusivity of sulfur in silicone rubber is so high that the membrane easily transmitted the maximum flux permitted by the source and collection arrangements, and hence was not required by the test conditions to develop a perceptible

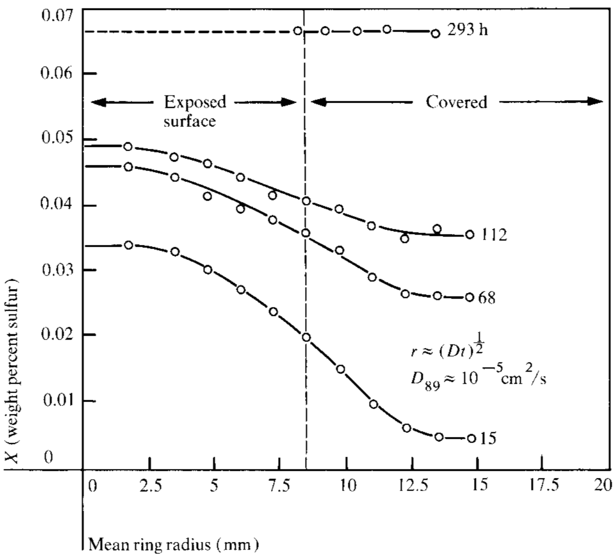

Figure 10 Radial diffusion of sulfur in circular membranes of silicone rubber at 89°C (362 K). Each profile was obtained by sectioning a membrane after the annealing time indicated.

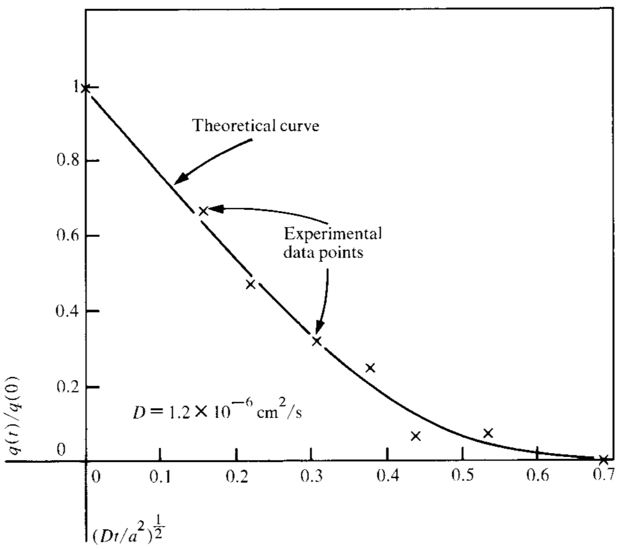

Figure 11 Vacuum desorption of sulfur from silicone rubber at 47°C (320 K). The experimental points fit the theoretical curve for diffusion-controlled desorption behavior and yield a diffusion coefficient of 1.2×10^{-6} cm^2/s.

concentration gradient. Under these conditions, the kinetics of the approach to steady state have nothing to do with the diffusivity of sulfur in the material but are determined instead by the rate of vaporization of the source.

This behavior also suggests that very appreciable lateral diffusion should occur into the outer clamped rim of the test membrane which is masked off from direct access to sulfur vapor by the Teflon collar. To look for the existence of a lateral or radial concentration gradient in the test membranes, a special tool was prepared with a set of concentric circular cutting edges that, in one operation, could section a membrane into a set of concentric rings for subsequent sulfur analysis by toluene extraction. Data obtained by this "lateral spread" procedure are shown in Fig. 10 for silicone rubber membranes annealed at 89°C for various lengths of time before sectioning. These measurements reveal that after as short a time as 15 h sulfur has diffused over a distance of at least 6 mm to reach the outside periphery of the membrane. As indicated in Fig. 10, these data indicate a diffusivity at 89°C of about 10^{-5} cm^2/s, which is about four orders of magnitude faster than for the epoxy material.

Because of the measurement difficulties introduced in the permeation tests by this much higher diffusivity, further efforts to obtain quantitative data on the diffusion of sulfur in silicone rubber were pursued by a different technique, namely, through the kinetics of the desorption of sulfur from previously charged samples. Although use of this technique avoids the particular source-limitation problem associated with the permeation apparatus, it is not possible to assert a priori that desorption must necessarily be a diffusion-limited process. For example, preliminary experiments showed that desorption into vacuum proceeds much more rapidly than into flowing air, indicating that a surface evaporation step is important in the latter case at least. Accordingly, it became clear that if the desorption technique was to be successful for diffusion measurements, the desorption must be into a vacuum and the experimental results must be shown to conform with the behavior expected for a diffusion-controlled process.

The mathematics of diffusion-controlled desorption from a parallel-sided slab have been considered by a number of workers, including Crank [9] and Henry [11]. The quantity of solute in the slab after time t, $q(t)$, expressed as a fraction of the initial amount $q(0)$, is given by the series solution

$$q(t)/q(0) = \frac{8}{\pi} \sum_{m=0}^{\infty} \frac{1}{(2\,m+1)^2} \times \exp\left[-D(2\,m+1)^2\,\pi^2 t/a^2\right], \qquad (32)$$

where D is the diffusion coefficient and a is the thickness of the slab. The required numerical computations have been performed to obtain values of $q(t)/q(0)$ as a function of the dimensionless parameter Dt/a^2. As shown by the solid line in Fig. 11, when $q(t)/q(0)$ is plotted against $(Dt/a^2)^{1/2}$, the desorption curve is essentially linear to somewhat below the level $q(t)/q(0) = 0.5$, and then it becomes progressively less steep.

Representative experimental data for the silicone rubber are also shown in Fig. 11. Each point was obtained by placing a small sheet sample (which had previously been uniformly charged with sulfur to a known level) inside a closed-end glass tube whose temperature could be controlled by immersion in a small oil bath. The sample was allowed to warm up to the test temperature with air at atmospheric pressure inside the tube, after which the vacuum valve was opened for a preselected time for desorption to occur. At the end of the interval, air was readmitted to the specimen chamber. The specimen was then quickly removed, cooled, and subjected to toluene extraction to find the remaining quantity of sulfur. To analyze the data, a preliminary plot of $q(t)/q(0)$ versus time was first prepared to establish the time $t_{0.5}$ at which $q(t)/q(0) = 0.5$. By reference to the theoretical curve (Fig. 11) it is seen that

$$(Dt_{0.5}/a^2)^{1/2} = 0.22, \tag{33}$$

so that D can be calculated from the experimental values of $t_{0.5}$ and a. This value of D, 1.2×10^{-6} cm^2/s for the data of Fig. 11, may then be used to convert all the experimental times to the form $(Dt/a^2)^{1/2}$ so that the shape of the experimental curve can be checked for a fit against the shape of the theoretical curve. The agreement obtained (Fig. 11) indicates that the desorption occurred under diffusion-controlled conditions.

A second check was to investigate the effect of changing the specimen thickness on the desorption kinetics. As indicated by Eq. (33), desorption from two samples of thicknesses a_1 and a_2 should obey the relationship

$$\frac{a_1}{a_2} = \left[\frac{(t_{0.5})_1}{(t_{0.5})_2}\right]^{\frac{1}{2}}. \tag{34}$$

A test of this relationship is provided by the data of Fig. 12. Here, the ratio a_1/a_2 has the value 3.5 whereas the right hand side of Eq. (34) has a value of 4.5. The agreement is not quite as good as might have been hoped for, but the nature of the discrepancy is in the direction of a stronger, rather than a weaker, dependence on thickness than is predicted by the theory. Since the effect of an interference from a surface reaction would be to lessen the dependence of the desorption rate on thickness, we conclude that the experiments provide a satisfactory confirmation that the experiments refer to diffusion-controlled conditions.

Data obtained by the vacuum desorption technique on the temperature dependence of D are included in Fig. 9. The D values range from about 10^{-7} cm^2/s at room temperature to an (extrapolated) value of 2×10^{-5} cm^2/s at 90°C. It is noteworthy that the latter value checks well with the estimate obtained by the lateral spread technique. As shown by Fig. 9, the data for sulfur diffusion in silicone rubber conform to the standard expression of Eq. (29), and yield the values 4×10^5 cm^2/s for the pre-exponential constant D_0 and 0.74 eV for the activation energy Q. It should be noticed that since the D_0 value is similar for both the silicone and the epoxy polymers, the much slower sulfur diffusion in the epoxy can be attributed wholly to the larger value of Q for that material.

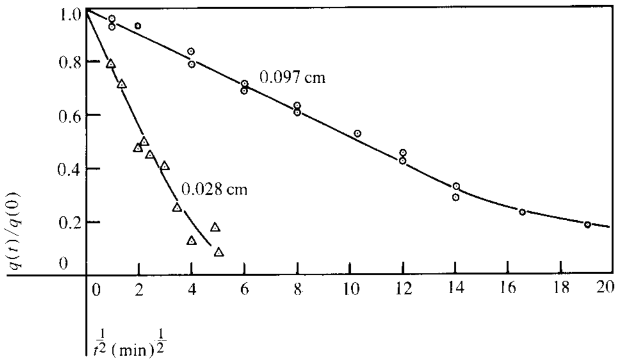

Figure 12 Room-temperature vacuum desorption of sulfur from two thicknesses of silicone rubber.

Discussion

The most significant aspect of the solubility measurements is the manner in which the physical solution behavior of sulfur vapor correlates with and extends data on a wide variety of gaseous solutes. Previous work in both silicone and natural rubbers [12, 13] has shown that Henry's law is obeyed by various gases ranging in complexity from monatomic helium to the hydrocarbon n-butane, C_4H_{10}. Thus, the observation that Henry's law is obeyed by S_8 vapor seems simply to add to a general body of evidence that physical solution usually occurs in polymers without dissociation of the solute molecule.

The current data provide quite a dramatic extension of several orders of magnitude in an empirical correlation between the solubility coefficient H and the boiling point of the solute T_b. With volumetric units of the type customarily used in the literature, the solubility coefficient at 25°C (298 K) for sulfur in silicone rubber is given by the present work as

$$\begin{aligned} H_{25} &= (4 \pm 2) \times 10^6 \text{ ml STP/cm}^3 \text{ atm, or} \\ H_{25} &= (40 \pm 20) \text{ ml STP/cm}^3 \text{ Pa} \end{aligned} \tag{35}$$

where the indicated uncertainty primarily reflects an uncertainty in the vapor pressure of sulfur. Previous data [12, 13] on the correlation between H_{25} and T_b, shown in Fig. 13, covered a range of less than four decades in H_{25} and were restricted to solute species with boiling points below room temperature. The present

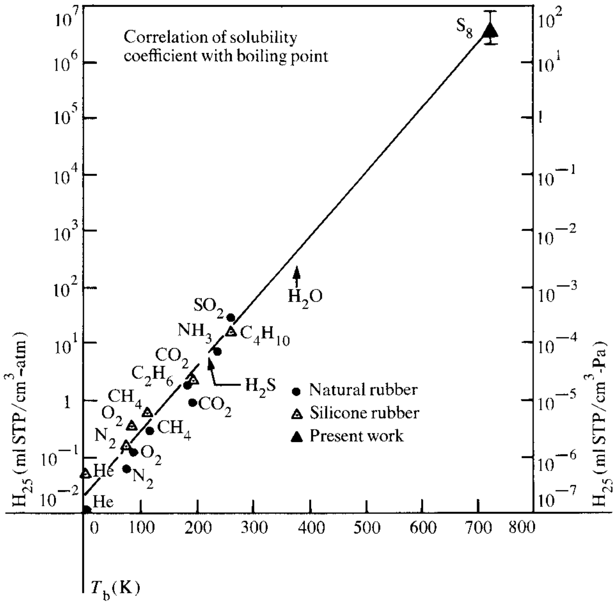

Figure 13 Correlation of the Henry's law solubility coefficient H_{25} (i.e., for 25°C) with the boiling point of the pure dissolving species. The current work provides the only point on this plot for a solute which boils above room temperature and extends previous work by five decades. Note the arrows for H_2S and H_2O, which indicate their predicted solubility coefficients.

work provides a point which more than doubles the range of this plot and which shows that the solubility coefficient for sulfur is orders of magnitude larger than for the other solutes. Although in the past the H_{25} solubility coefficient has been used to show a logarithmic correlation with T_b, it should be noted that the same correlation could be stated more simply in terms of a linear relation between Δh_s and T_b. In these terms, based on Fig. 13, an empirical rule for estimating the heat of solution of a given vapor species in both silicone and natural rubbers is

$$\Delta h_s(\text{eV}) = -6 \times 10^{-4} T_b. \tag{36}$$

Further, based on the single point afforded by the current work, the analogous expression for the epoxy material is

$$\Delta h_s(\text{eV}) = -8 \times 10^{-4} T_b. \tag{37}$$

Inasmuch as the boiling point of a given solute scales roughly with its heat of vaporization, Eqs. (36) and (37) also indicate that, for a given polymeric host, Δh_s scales roughly with Δh_{vap}.

In discussing the diffusion measurements, it may be remarked that the values obtained for both Q and D_0 at first appeared unusually large when compared with the general run of results for many gaseous species in a variety of polymers [13]. However, this was also the situation for the heat of solution where, as noted above, it proved possible to make a very satisfactory correlation with previous work. This provides encouragement for some speculation on the magnitude of D_0 and Q. It is suggested that the large values found for these quantities can be related to the large size of the diffusing entity, which is taken to be the S_8 molecule in view of the conformity to Henry's law. As noted by Stannett in his review [14], the activation energy for diffusion of a gas in a given polymer invariably increases with the molecular size of the gas. For some polymers the increase is quite dramatic. For example, in poly(vinyl acetate) Q increases from 0.22 to 0.87 eV as the molecular size of the diffusing gas increases from 20 to 40 nm. In natural rubber the same trend is present but is less marked, with Q changing from 0.17 to 0.35 eV for the same range of molecular size. It thus appears reasonable that the relatively large values of Q found for sulfur diffusion in the present work can be traced to the large size of the S_8 molecule. Since a correlation with size implies that the activation energy Q may be dominated by strain-energy considerations, it is also possible to rationalize by the same argument why the value of Q is larger for the harder and more rigid epoxy material than for the silicone rubber.

Turning to the parameter D_0, previous results with the simpler gases again show a definite correlation between the magnitude of D_0 and the magnitude of Q. In those few cases in which diffusion of a simple gas is associated with an activation energy as high as that for sulfur diffusion, the D_0 value also has the large magnitude reported here. For example, the diffusion of methane in poly(vinyl acetate) has a Q of 0.84 eV and a D_0 of 2×10^5 cm^2/s. What is implied by a strong correlation between D_0 and Q can be appreciated by writing the expression for D which is derived from chemical rate theory [15]:

$$D = [\alpha\lambda^2\nu_0 \exp(\Delta S_d/k)] \exp(-Q/kT). \tag{38}$$

Here α is a constant of order unity, λ is the jump distance of the diffusing species, ν_0 is the appropriate molecular vibration frequency, and ΔS_d is the entropy change associated with the transfer of the diffusing species from the equilibrium to the activated state. By comparison of Eqs. (29) and (38), we find

$$D_0 = \alpha\lambda^2\nu_0 \exp(\Delta S_d/k). \tag{39}$$

Of the parameters appearing in Eq. (39), α, ν_0, and λ cannot be expected to vary strongly with the size of the diffusing species. A strong correlation between Q and D_0 can therefore occur only if the size and character of the diffusing species not only affect the enthalpy of activation Q, but also affect in similar degree the entropy of activation ΔS_d. This result implies the physically reasonable conclusion that the jump of a large molecule requires the cooperative movement of a relatively large number of atoms.

To conclude, it is of interest to comment briefly on the implications of this work with respect to the use of polymeric materials in packaging technology. First of all, it appears that sulfur vapor is likely to exhibit a large heat of solution in a wide variety of polymeric materials. This means that the relatively low sulfur levels present in industrially polluted atmospheres tend to become concentrated to much higher levels in these materials. There is thus a potential danger if these materials are used to package a product which is susceptible to damage by sulfur. To assure a product of satisfactory lifetime, the polymer selected must have a low diffusivity for sulfur so that the ability to sorb and be permeated by sulfur is effectively "frozen out" of the material. From this point of view, the diffusion data of Fig. 9 demonstrate that the epoxy material represents an improvement of several orders of magnitude over the use of silicone rubber.

Acknowledgments

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