

310. *Solution and Diffusion of Gases in Polystyrene at High Pressures.*

By D. M. NEWITT and K. E. WEALE.

The solubilities of hydrogen and nitrogen in polystyrene have been found to be proportional to the pressure in the range 80—300 atmospheres, and the solubility constants have been determined at temperatures up to 190°.

The diffusion constants of the same gases in polystyrene, at high pressure, have been measured in the range 20—190°, and found to increase exponentially with temperature.

A few diffusion and solubility constants have been obtained for carbon dioxide and ethylene; and the rate of desorption of hydrogen and nitrogen from polystyrene has been studied.

THE existing data on the solution and diffusion of gases in organic high polymers were summarised by Barrer ("Diffusion in and through Solids", Cambridge Univ. Press) in 1941. These data are almost entirely confined to the permeability of thin membranes of natural rubber or synthetic elastomers to gases, and were obtained by study of the rates of permeation at pressures of the order of 1 atm.

Since 1941, important contributions to the subject have been made by Barrer (*Trans. Faraday Soc.*, 1942, **38**, 322; 1947, **43**, 3), Reitlinger, (*J. Gen. Chem. U.S.S.R.*, 1944, **14**, 420; translated in *Rubber Chem. Tech.*, 1946, **19**, 385), Doty (*J. Chem. Physics*, 1946, **14**, 244), and van Amerongen (*J. Appl. Physics*, 1946, **17**, 972; *J. Polymer Sci.*, 1947, **2**, 381).

Barrer's summary confirms the view of Graham (1866) and later workers that permeation is a three-stage process of sorption, diffusion, and desorption of the diffusing gas. It also confirms, as Wroblewski (1879) had originally suggested, that the process obeys Fick's law, according to which the permeation rate is proportional to the concentration gradient across the diffusion medium; *i.e.*,

$$P = -D \, dc/dx \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where P is the permeability, D the diffusion constant or diffusivity, and dc/dx the concentration gradient.

Equation (1) refers to the state of steady flow through a membrane. The equivalent form appropriate to a non-stationary state of flow, as studied in the present work (*i.e.*, accumulation of diffusing matter at a given point in a medium as a function of time), is

$$dc/dt = D \cdot d^2c/dx^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

It is clear that the applicability of (1) and (2) is conditional on a solubility equilibrium existing at the gas-solid interface, *i.e.*, on diffusion in the solid being the rate-controlling process.

The processes of sorption and diffusion are expressed quantitatively in terms of two constants, namely, the diffusion constant, D (cm.²/sec.⁻¹), and the solubility constant, s (c.c. of gas/g. of polymer/atm.). The permeability constant, P , which is derived from D and s , is not used in the present work. Because the density of polystyrene is nearly 1·00, the values of s obtained are comparable with values for other gas-polymer systems given in the literature, but expressed in terms of c.c. of gas/c.c. of polymer.

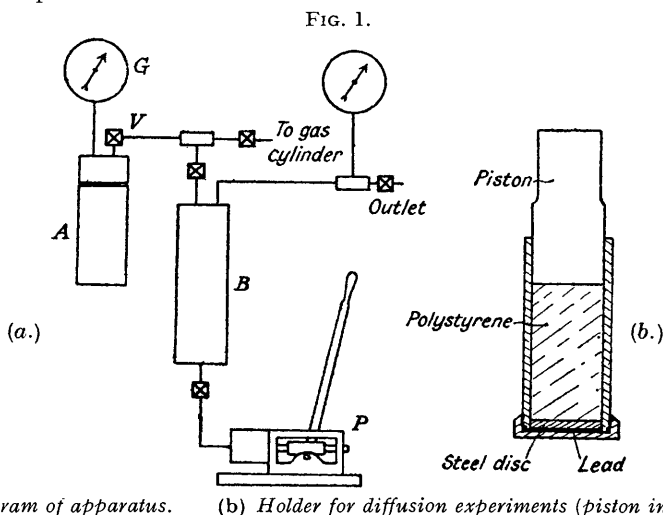
(a) *The Solubility of Gases in Polystyrene.*

Experimental.—The principle used in the determinations was measurement of the pressure drop, due to gas sorption by the polymer, in a closed system of known volume at constant temperature. The apparatus (Fig. 1) consisted of a stainless-steel pressure vessel, A (capacity about 250 c.c.), the cover of which screwed in to give a metal-to-metal seating. Holes drilled through the cover connected to a gas inlet valve, V , and through copper pressure tubing to a Bourdon pressure gauge, G . The pressure line from A communicated through a T with the gas supply, and with B , a stainless-steel cylinder in which gas could be compressed to the desired pressure by means of the hand-operated mercury pump, P .

The volume of the system was determined by measuring in a gas burette the successive volumes of gas released when a pressure of 2—3 atm. (measured by a large mercury-in-glass manometer) was reduced by stages to 1 atm. Pressure-volume graphs were plotted, and separate runs gave results for the volume agreeing to $\pm 0\cdot15$ c.c.

The pressure vessel, containing a known weight of polystyrene (40—100 g.) cut into thin discs, was contained in a cylindrical electrically-heated jacket, the space between the two being filled with asbestos wool. Under these conditions, a temperature steady to 1° could be maintained by running the heating jacket at a constant current. For each determination the vessel was kept at a steady temperature for an hour before admission of gas.

The compressed gas was admitted through V in about 30 seconds, V was closed, and the initial pressure reading was taken one minute later. Blank experiments showed that a constant reading could not be obtained until after this interval, presumably because of the time necessary for attainment of thermal equilibrium. In a typical experiment, the pressure fell slowly for 6—8 hours and then remained constant. Usually the pressure was allowed to reach a constant value overnight, though longer periods were required at temperatures below 130° .



Discussion.—The gas solubility at the equilibrium pressure and temperature was calculated from the pressure drop and the free volume of the system. In the absence of compressibility data for polystyrene, the volume occupied was calculated on the basis of a density of 1.05 g./c.c. Correction factors at different temperatures for the non-ideal behaviour of the gases were taken from PV tables.

The effect of pressure on solubility was examined chiefly at 170° because of the more rapid attainment of equilibrium at this relatively high temperature. It was not possible to obtain higher pressures of ethylene or carbon dioxide than 92.5 and 51 atm. , respectively, with the apparatus described.

The data obtained are given in Tables I and II, and shown graphically in Fig. 2. In Table I, solubility (s) is recorded in terms of c.c. (measured at N.T.P.) per g., and in Table II, the solubility constant (s) is in the units given on p. 1541.

The variation of solubility (corrected for deviations from the ideal-gas law) with pressure is found to obey Henry's law for nitrogen at 170° , hydrogen at 170° and 72° , and ethylene at 170° . Because carbon dioxide could not be used above 50 atm. pressure, it remains uncertain whether the two values found are those for true equilibrium, and whether Henry's law holds for this gas. The corresponding solubility constants (s) are:—

Gas.	Temp.	s .	Gas.	Temp.	s .
Hydrogen.....	170°	0.037	Nitrogen.....	170°	0.0275
„.....	72	0.060	Ethylene.....	„	0.105

Solubility constants, calculated from individual solubility values, were determined for hydrogen and nitrogen over a wide temperature range. No value for nitrogen could be found below 74° as it attained equilibrium much more slowly than hydrogen. The values of s for both gases below 120° are not as great as would be expected from the trend of values between 120° and 190° . This may be due to incomplete attainment of equilibrium or to a discontinuity in the solubility-temperature curve, occurring in the softening range of the thermoplastic (95 — 115°). Experiments on the desorption of gas from previously saturated pieces of polystyrene (described later) indicate minimum values for s at 20° to be 0.05 and 0.025 for hydrogen and nitrogen, respectively.

FIG. 2.

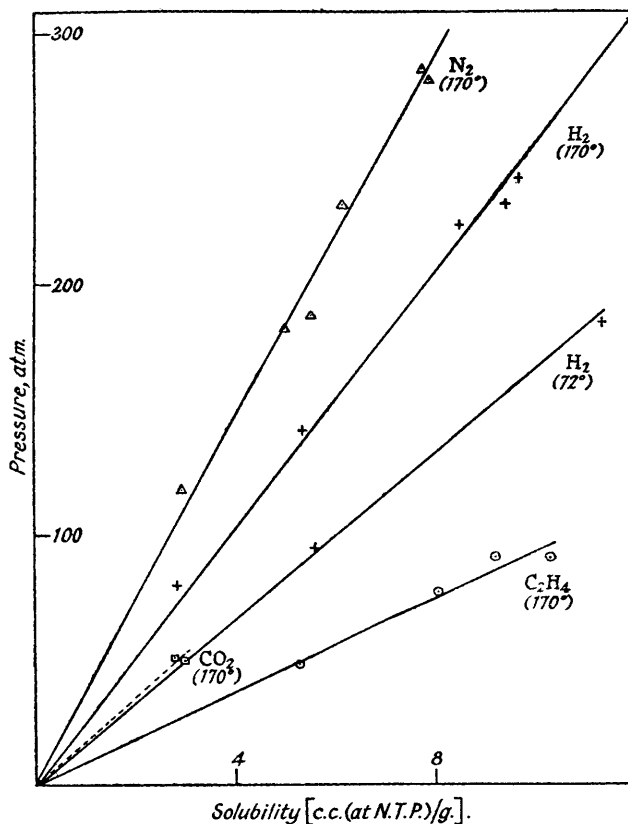


TABLE I.

Solubility data for gases in polystyrene at high pressures and constant temperature.

Press. (atm.).	s.	Press. (atm.).	s.	Press. (atm.).	s.	Press. (atm.).	s.
Nitrogen at 170°		Hydrogen at 170°.		Hydrogen at 72°.		Ethylene at 170°.	
287	7.77	306.5	11.95	186	11.33	92.5	10.30
282.5	7.93	243	9.66	95	5.63	92.5	9.20
232	6.15	233	9.42			77.5	8.05
187	5.57	224.5	8.48	Carbon dioxide at 170°.		49	5.27
182	5.02	142	5.35	51	2.82		
118	2.95	80	2.89	50	3.04		

TABLE II.

Variation of solubility constant with temperature for nitrogen and hydrogen in polystyrene.

Temp.	s.	$\log_{10}s.$	$10^3/T.$	Temp.	s.	$\log_{10}s.$	$10^3/T.$
Nitrogen.				Hydrogen.			
191°	0.026	-1.585	2.155	186.5°	0.034	-1.467	2.177
170	0.0275	-1.561	2.257	170	0.037	-1.426	2.257
149	0.031	-1.509	2.370	142	0.042	-1.377	2.410
136	0.033	-1.482	2.445	126	0.047	-1.328	2.506
74	0.035	-1.456	2.882	72	0.060	-1.222	2.899
				49	0.061	-1.215	3.106
				17	0.065	-1.187	3.448

Although, in the works referred to in the introduction, Henry's law has been generally assumed to hold, there have been few independent determinations of sorption equilibria in

organic polymers. The only data recorded for gas-polymer systems at high pressures are those of Tamman and Bochow (*Z. anorg. Chem.*, 1928, **168**, 322), who measured the volumes of hydrogen evolved from different kinds of rubber saturated at 550 and 1150 kg./cm.². They found Henry's law to be approximately obeyed, with solubility constants of the order of 0.1 (c.c. of gas/c.c. of rubber).

The variation of the solubility constant with the nature of the gas, in polystyrene, is qualitatively similar to that found in rubber at ordinary temperature and pressure. Carbon dioxide and ethylene, having the highest critical temperatures, are most soluble. In rubber, however, the differences are much greater.

For both hydrogen and nitrogen, the solubility constants in polystyrene show a gradual decrease with increasing temperature. Plots of $\log_{10} s$ against $1/T$ in the range 130—190° are approximately straight lines, the equations to which are :

$$\begin{aligned} \text{For H}_2 & \dots \log_{10} s = -2.4 + 1900/4.6 T \\ \text{For N}_2 & \dots \log_{10} s = -2.4 + 1700/4.6 T \end{aligned}$$

of the form

$$\log_{10} s = \log_{10} s_0 - E_s/2.3 RT \dots \dots \dots (4)$$

in which E_s is the heat of solution in cal./mole; but as the solubility variation is not great, there is considerable experimental uncertainty.

From the relationships :—

$$\Delta G_0 = -RT \log_e s \dots \dots \dots (5)$$

$$\Delta G = E_s - T\Delta S \dots \dots \dots (6)$$

(in which ΔG is the free-energy change), the change in entropy, ΔS , accompanying solution of 1 mole of gas in polystyrene has been calculated as :

$$\begin{aligned} \text{for N}_2 & \dots \Delta S = (\text{approx.}) - 11 \text{ entropy units (cals./}^\circ\text{C.) per mole at 170}^\circ \\ \text{for H}_2 & \dots \Delta S = (\text{approx.}) - 10 \text{ ,, ,, ,, ,, } \end{aligned}$$

These compare with values of from -8.3 to -10.1 given by Barrer (*Trans. Faraday Soc.*, 1939, **35**, 628) for synthetic elastomers at lower temperatures. It is noteworthy that for water vapour dissolved in polyvinyl chloride-acetate, where specific interaction between polymer and solute undoubtedly occurs, Doty (*loc. cit.*) found $\Delta S = -20.8$. This high value was lowered to -3.6 on addition of 25% of plasticiser. (Doty's units refer to water-vapour pressure of 1 cm. Hg.)

Polystyrene resembles the rubber-like organic polymers in that gas solubilities in it are of much the same order of magnitude as in organic liquids. As with the elastomers, there is no evidence for any chemical or other specific interaction between polystyrene and the gases employed, which are presumably held in solution by van der Waals type forces.

(b) *The Diffusion Constants of Gases in Polystyrene at High Pressures.*

Experimental.—The determination of D by observation of the rate of membrane permeation is clearly not possible at pressure differences much above 1 atm. The method is also restricted to temperatures below the softening point of the plastic.

It was first proposed to calculate D from high-pressure experiments in which the rate of fall of pressure during sorption was observed. This proved impracticable and a method was developed analogous to the determination of the diffusion constant of a coloured substance by observation of the position of the colour boundary. Three variants of the method were used.

(i) *The axial diffusion method.* In this method, used at temperatures above 120°, gas at known pressure and temperature was allowed to penetrate axially through one of the plane faces of a cylinder of polystyrene, for a known time. The polymer cylinder was contained in the cylindrical steel holder shown in section in Fig. 1, and was machined to be a close sliding fit. The bottom of the holder was closed by a brass cap which was obturated by a lead disc.

Before the experiment, the holder containing the polystyrene was heated to *ca.* 150° in an oil-bath, and pressure was applied to the piston in a hydraulic press. This produced a gas-tight joint between the polystyrene and the holder. The piston was then removed, and the holder enclosed in the pressure-vessel of the solubility apparatus, which was raised to the required constant temperature. Compressed gas was admitted and allowed to diffuse into the exposed surface for a predetermined time (1 or 2 hours for hydrogen, overnight for nitrogen, carbon dioxide, and ethylene). The pressure was then quickly reduced to 1 atm. (in about 30 secs.), and the holder removed from the pressure vessel.

The polystyrene cylinder, on removal, consisted of a glass-clear lower portion and a cloudy, aerated upper portion into which gas had diffused. In successful experiments, the boundary between the two regions was sharp, consisting of a plane of small bubbles at right angles to the axis of the cylinder. Control experiments showed that, under these conditions, bubbles of gas were formed on pressure-release at pressures of the order of 2—3 atm. In the calculations, the diffusion limit was taken to be the point at which the gas concentration corresponded to 2 atm. pressure. The depth of diffusion, x , is the difference between the original length of the clear cylinder (dimensions approximately 1" diameter by 2½" long) and the length of the clear portion of the part-expanded cylinder.

D was calculated as follows : Assuming Fick's law (equation 2), we have

$$C_{xt} = C_s \left(1 - \frac{2}{\sqrt{\pi}} \int_0^\beta e^{-y^2} \cdot dy \right) \dots \dots \dots (7)$$

for diffusion normal to the plane surface of a "semi-infinite" solid. Here C_{xt} is the gas concentration x cm. below the surface t secs. after diffusion commences; C_s is the gas concentration at the surface; and $\beta = x/2\sqrt{Dt}$, where D is the diffusion constant in $\text{cm.}^2 \text{sec.}^{-1}$.

C_{xt} was taken, as stated above, to correspond to 2 atm. pressure and, as already shown, actual pressures could be used instead of concentrations; x is the depth of diffusion measured as described above.

Equation (7) may be rewritten as
$$C_{xt} = C_s(1 - \text{erf } y) \dots \dots \dots (8)$$

where erf y is the Gaussian error function; erf y was obtained from (8), the corresponding value of β found from tables and D computed.

(ii) *The modified axial diffusion method.* Below 120° bubbles did not form readily in the polystyrene on release of pressure because of its increased viscosity. It was then necessary to modify the method by heating the holder and polystyrene in an oil-bath to 140—150° (time taken, about 10 mins.), after pressure release, in order to develop the bubble structure. D was calculated as in the first method.

This modification was successful with nitrogen, but few values for D_{H_2} below 120° were obtained by its use. Most of the experiments with hydrogen were spoiled by gas-leakage between the polystyrene cylinder and the steel holder.

(iii) *The radial diffusion method.* This was used to obtain values of D_{H_2} below 80°. At these temperatures, the thermoplastic is rigid and the holder could be dispensed with. A cylinder of polystyrene, machined to the same dimensions as those used in the other experiments, was placed in the pressure vessel, and compressed hydrogen was allowed to diffuse into the flat and curved surfaces. After pressure release, the cylinder was pushed into the steel holder, and the bubble structure developed by heating in an oil-bath.

The holder prevented expansion radially, the increase in volume due to bubble formation being taken up by length-wise expansion. After cooling, sections were cut through the cylinder near the middle, *i.e.*, where the flow is radial, so that the radius of the glass-clear core, to which the gas had not penetrated, could be measured.

D was calculated as follows (Barrer, *op. cit.*, p. 32) : For a circular cylinder of radius $r = a$ as diffusion medium, with a constant surface concentration of gas C_s , and with the medium initially free of solute, the solution of the appropriate Fick diffusion equation can be given in terms of Bessel's function of the first kind and zero order $J_0(x)$ and its differential $J_0'(x)$ [= $-J_1(x)$]. The solution is

$$C_{rt} = C_s \left(1 + \frac{2}{a} \sum \frac{1}{\alpha_n} \cdot \frac{J_0(\alpha_n r)}{J_0(\alpha_n a)} \cdot e^{-D\alpha_n^2 t} \right) \dots \dots \dots (9)$$

where r is the radius of the clear core to which no gas has penetrated, and α_n is the n th root of the equation

$$J_0(\alpha_n a) = 0 \dots \dots \dots (10)$$

TABLE III.

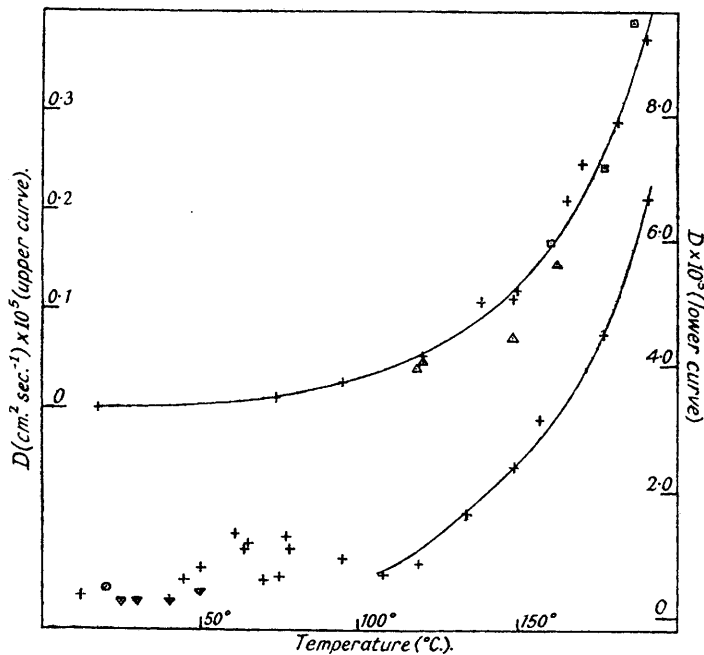
Diffusion constants for nitrogen, carbon dioxide, ethylene, and hydrogen in polystyrene.

Nitrogen.					Hydrogen.				
Temp. (atm.).	$D \times 10^5$.	$\log_{10} D$.	$10^3/T$.	Method.*	Temp. (atm.).	$D \times 10^5$.	$\log_{10} D$.	$10^3/T$.	Method.*
190°	270	0.363	-5.400	2.160	191°	108	6.68	-4.175	2.155
181	280	0.293	-5.533	2.203	177	205	4.50	-4.347	2.222
170	280	0.25	-5.602	2.257	157	108	3.15	-4.502	2.326
160	282	0.169	-5.772	2.309	149	108	2.41	-4.618	2.370
149	110	0.11	-5.959	2.370	134	106	1.66	-4.780	2.457
148	200	0.119	-5.925	2.375	119	14	0.90	-5.046	2.551
138	272	0.106	-5.975	2.433	108	95	0.68	-5.168	2.625
120	206	0.052	-6.284	2.545	95	80	0.96	-5.018	2.717
95	160	0.027	-6.569	2.717	75	31	0.65	-5.187	2.874
74	205	0.01	-7.0	2.882	40	62	0.29	-5.538	3.195
18	134	~0.0004	-8.5	3.436	78	88	1.10	-4.959	2.849
					77	94	1.3	-4.886	2.857
					70	104	0.59	-5.229	2.915
					65	43	1.2	-4.921	2.959
186	50	0.39	-5.409	2.179	64	108	1.1	-4.959	2.967
177	40	0.245	-5.612	2.222	61	98	1.35	-4.870	2.994
165	40	0.211	-5.676	2.283	50	102	0.8	-5.097	3.096
					45	96	0.6	-5.222	3.145
					12	96	0.35	-5.456	3.509
Ethylene.									
210	65	0.644	-5.191	2.070					
162	56	0.147	-5.833	2.299					
148	52	0.071	-6.148	2.375					
120	54	0.048	-6.319	2.545					
118	53	0.042	-6.377	2.558					

* (i) = Axial diffusion method; (ii) = modified axial diffusion method; (iii) = radial diffusion method.

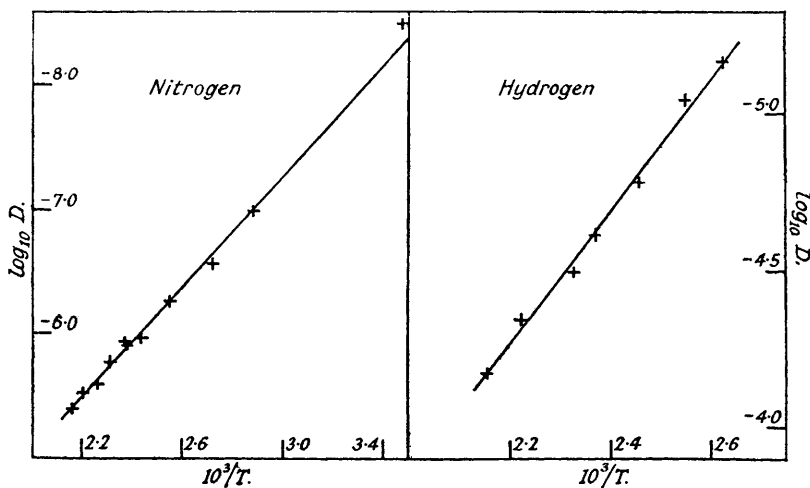
The first three roots of (10) are $a_1 = 2.405/a$, $a_2 = 5.520/a$, $a_3 = 8.654/a$, and these were found to be sufficient. Evaluation of (9) using these roots, gave for each case an equation in three exponential terms which was solved graphically for D . The units used were cm. and secs. with pressures substituted for concentrations in the same way as for the other methods.

FIG. 3.



The upper curve shows the N_2 diffusion constants (+), with the values for CO_2 (□) and C_2H_4 (Δ) plotted on the same axes. The lower curve shows the H_2 diffusion constants (+). The points ○ and ▽ represent values taken from the work of Reillinger, and of Thomas and Gent respectively.

FIG. 4.



Values found by the radial diffusion method are slightly less accurate than the others because of the greater uncertainty in the radius measurement involved. The results are given in Table III, where D is in the units $cm.^2 sec.^{-1}$, and shown in Figs. 3 and 4.

Discussion.—The values of D are comparable with those given in the literature for diffusion of gases in rubbers and in organic liquids. The values for hydrogen are much greater, at a given

temperature, than those for nitrogen, whilst the few values obtained for the other two gases approximate to those for nitrogen. The values of D for all the gases increase steeply with temperature.

The diffusion constants of gases in various liquid and solid substances, *e.g.*, organic liquids, glasses, silica, rubber, and synthetic rubbers, have been shown (see Barrer, *op. cit.*) to increase exponentially with absolute temperature, according to the relation

$$D = D_0 e^{-E_D/RT} \quad \dots \quad (13)$$

where D_0 is a constant and E_D is the heat of activation of diffusion in cal./mole.

The graphs of $\log_{10}D$ against $1/T$ show that this relation holds for nitrogen in polystyrene and for hydrogen in polystyrene over the temperature range 108—191°, at high gas pressures.

The equations derived from these straight lines are :

$$\text{For nitrogen : } D = 0.21e^{-10,100/RT}; \log_{10}D = -0.67 - 10,100/2.3RT$$

$$\text{For hydrogen : } D = 2.04e^{-9,600/RT}; \log_{10}D = 0.31 - 9,600/2.3RT$$

As may be seen from the tables, the pressure used in the experiments varied over a fairly wide range, without noticeably affecting the diffusion constants.

The equations above can be compared with those given by Barrer (*op. cit.*) and van Amerongen (1946, *loc. cit.*) for diffusion of nitrogen and hydrogen in rubbers. In the latter, E_D varies between 5100 and 9900 for hydrogen, and between 7200 and 12,400 for nitrogen. The values of D_0 vary between 0.053 and 54.4 for hydrogen, and between 0.22 and 105 for nitrogen.

There are no comparable data for gas diffusion in polystyrene or similar long-chain thermoplastics. The recorded data for D_{H_2} in polystyrene (none for D_{N_2} have been found) appear in Fig. 3. They consist of a value determined by Reitlinger (*loc. cit.*), at 20°, and three derived from data of Thomas and Gent (*Proc. Physical Soc.*, 1945, **57**, 324), which are of uncertain accuracy because the thickness of the films used could not be exactly measured.

The "non-specific activated diffusion" characteristic of gas flow in rubber-like high polymers is now generally assumed to proceed by the following mechanism. Gas molecules dissolve in the surface layer of the polymer and move about inside by jumping into "holes" in their immediate neighbourhoods. These "holes" are constantly forming and disappearing as a result of the random thermal motion of segments of the long-chain molecules. When a concentration gradient exists, the net effect is a drift of gas molecules into regions of low concentration. Capillary flow occurs only as a result of mechanical injury or imperfection.

According to this view E_D is chiefly the energy of "hole" formation. For polystyrene, E_D is greater for nitrogen than for hydrogen. This relation has been found for the rubber-like polymers and is attributed to a molecule of larger diameter requiring a slightly larger "hole" for its passage. Barrer points out that viscous flow of long-chain polymers probably proceeds by a similar mechanism, and that the energies of activation for viscous flow of rubbers are of the same order (10 k.-cals./mole) as E_D .

This view of diffusion is obviously applicable to polystyrene, as the polymer is a non-crystalline disordered tangle ("sub-microscopic felt") of long-chain molecules.

Ferry (*J. Amer. Chem. Soc.*, 1942, **64**, 1330) has estimated an activation energy of 12 k.-cals. for viscous flow of polystyrene. Also, as would be anticipated from the above view of the diffusion process, Reitlinger found his value of D_{H_2} at 20° to be independent of the average chain length of the polystyrene used.

The Constant D_0 .—Several attempts have been made to relate D_0 , which varies widely among different media, to more fundamental quantities, such as molecular dimensions, but with little success. Barrer (1942, *loc. cit.*) and van Amerongen (1946, *loc. cit.*) (see also Doty, *loc. cit.*) have pointed out that for rubber and synthetic elastomers an approximately linear relation exists between $\log D_0$ and E_D . The diffusing gases carbon dioxide, nitrogen, and oxygen fall on one line, while hydrogen, which diffuses more quickly, falls on another line. A similar empirical relation may hold for thermoplastics, but insufficient data are available to confirm this.

The diffusion constants of hydrogen in polystyrene below 108° are greater than would be expected from the trend at higher temperatures, and the plot of $\log_{10}D$ against $1/T$ departs from linearity below this temperature. This is not attributable to the lesser accuracy of the results of the radial diffusion method (compare the results of Thomas and Gent, and of Reitlinger).

The values of D_{N_2} obey the exponential relation very well down to 74°. At 18° the value of D_{N_2} should, according to this, be very small—of the order of 1×10^{-9} cm.² sec.⁻¹. An experiment at this temperature, by the modified axial diffusion method, resulted in a gas penetration of ~ 1 mm. in 66½ hours at 134 atm. pressure, giving a value of the expected order for D .

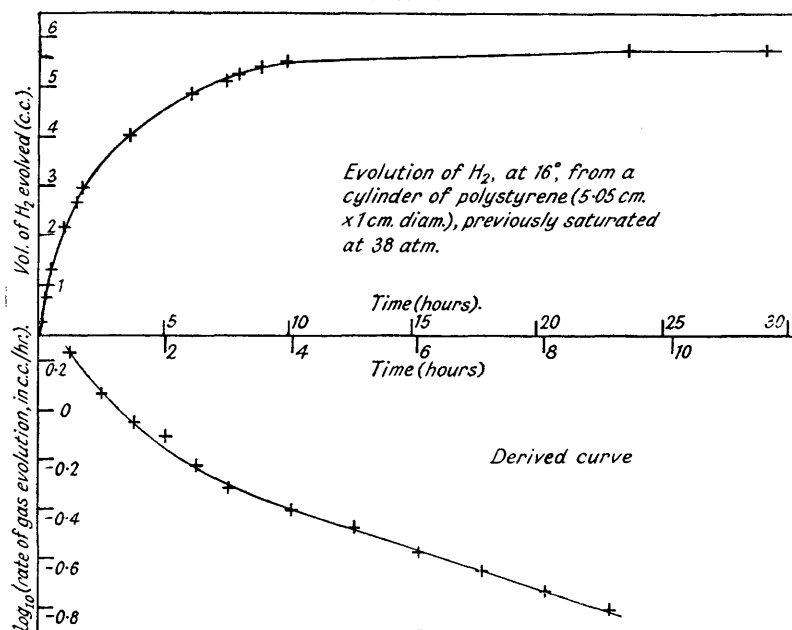
The desorption experiments (see Section c), indicate a value for hydrogen of $D = 1.0 \times 10^{-5}$ cm.² sec.⁻¹ at room temperature, in fair agreement with the other experimental values. For nitrogen, however, the rate of desorption corresponds to $D = 0.1 \times 10^{-5}$, which is much greater than the other values.

A possible explanation for these discrepancies might be that below the softening range of the polymer some form of gas flow, through extremely small cracks or mechanical imperfections, contributes to diffusion. (Visible internal cracks and fracture surfaces are present in pieces of polystyrene, which have been saturated with gas at pressures of the order of 300 atm., and have been released from pressure at temperatures below the softening point.) The small hydrogen molecule might be able to diffuse through these, even when the medium was under high compressive stress, whereas this mode of flow would only become possible for the relatively large nitrogen molecule when the medium was under tensile or "bursting" stress, as in the desorption experiments. The available evidence is too slight to confirm or reject this tentative hypothesis.

(c) *Desorption of Gas from Polystyrene saturated at High Pressure.*

Experimental.—Three experiments with hydrogen and one with nitrogen were carried out. In each case, a machined cylinder of polystyrene was saturated with compressed gas at room temperature. It was necessary, for experimental reasons, to use different pressures for the two gases. After pressure

FIG. 5.



release, the saturated cylinder was placed, with the least possible delay (*ca.* 2–5 mins.), under a mercury-filled gas burette. For each cylinder (see example in Fig. 5), a curve of gas volume evolved (V c.c.) against time (t) was obtained. Tangents were drawn to the volume–time curve at selected points and the rates of evolution at various values of t were calculated from their slopes. Graphs of \log_{10} (rate of evolution) against t were constructed.

Discussion.—Euringer (*Z. Physik*, 1935, **96**, 37) has shown that, for radial diffusion of gas out of a saturated cylinder, the Fick diffusion equation has a particular solution which may be written

$$\log_e q = \log_e 2cD/r + \log_e (\exp. - 5.8 Dt/r^2 + \exp. - 30.5 Dt/r^2 + \dots) \quad (11)$$

where q is the rate of gas evolution from the curved surface (in c.c./cm.² per sec.), c is the initial gas concentration (c.c. at N.T.P./c.c. medium), r is the cylinder radius (cm.), t is the time of desorption (secs.), and D is the diffusion constant (cm.² sec.⁻¹).

The assumptions made in deriving (11) are: (a) That at the commencement of desorption, the gas is uniformly distributed throughout the medium. (b) That the rate-controlling stage of the desorption process is Fick-law diffusion of the gas in the medium. (c) That the gas concentration at the surface of the medium is zero.

At high t , depending on the value of D/r^2 , the series rapidly converges so that (11) reduces to

$$\log_e q = \log_e 2cD/r - 5.8 Dt/r^2 \quad \dots \quad (12)$$

The derived curves of \log_{10} (rate of evolution) against t are all of the expected shape, showing asymptotic approach to a straight line as t increases. This is characteristic of desorption in which the rate-controlling process is Fick-law diffusion within the medium, and, in theory, D may be calculated from the slope ($= -5.8 D/r^2$) of the straight portion of the derived curve. From the experiment with nitrogen and the experiments with hydrogen dissolved at 57 and 54 atm., the "end effect" (due to desorption from the plane surfaces) makes it possible to say only that the diffusion constants are of the order of

$$\left. \begin{array}{l} 1 \times 10^{-5} \text{ for H}_2 \\ 0.1 \times 10^{-5} \text{ for N}_2 \end{array} \right\} \text{ at room temperature.}$$

The experiment with hydrogen dissolved at 38 atm. (Fig. 5) was made using a thinner cylinder, in which the "end effect" was much smaller. From this experiment, D_{H_2} at 16° can be fairly accurately estimated at 1.0×10^{-5} cm.² sec.⁻¹.

In three cases, the polystyrene was heated in an attempt to expel residual gas. The total volume of gas evolved gives a minimum value for s at room temperature of 0.05 for hydrogen and 0.025 for nitrogen.

We wish to thank Messrs. B.X. Plastics Ltd. for supplies of polystyrene, and for financial assistance to one of us (K. E. W.), which enabled this work to be carried out.

DEPARTMENT OF CHEMICAL ENGINEERING AND APPLIED CHEMISTRY,
IMPERIAL COLLEGE, S.W.7.

[Received, October 29th, 1947.]