Gas Solubility in Polymers: Errors Selective for Helium

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WHEN measuring the solubility of sparingly soluble gases in polymers, using the desorption method of Meares[1] and of Draisbach *et al.*,[2] we have observed an effect for helium which can lead to large overestimates of the solubility of this gas. The desorption curve for helium from certain polymers in Pyrex glass apparatus was unusual in the quantity of gas evolved, and the time required for a given fractional desorption was much longer than expected from the dimensions of the polymer sample and the diffusion coefficient of helium in it. It was suspected that, simultaneously with solution in the polymer, helium had dissolved in the glass walls of the apparatus from which it was gradually released during the desorption process.

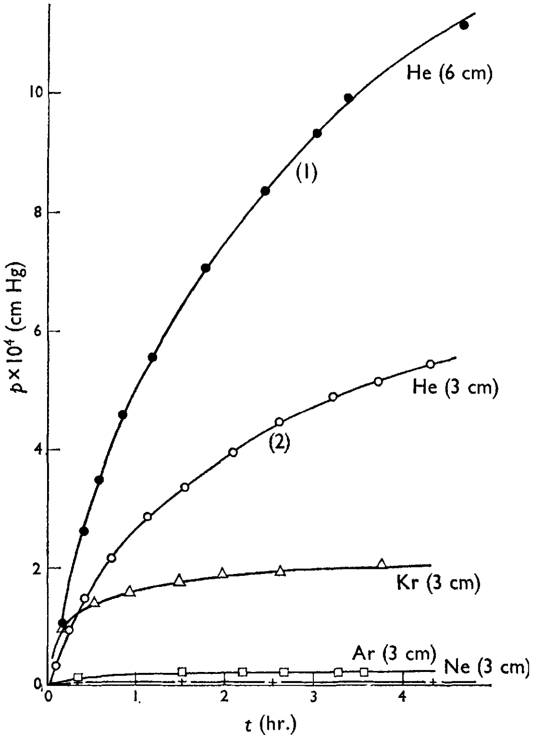

FIGURE 1. *Release of inert gases from Pyrex glass at* ~23°C.

To test this possibility a series of experiments was conducted by admitting, in turn and at 3 cm. pressure of Hg, each of various gases, into a McLeod gauge. For helium a run at 6 cm. pressure was also made. A given gas was left for about 15 hours at room temperature (~23°C) and then the gauge was outgassed for between 3·0 and 4·0 minutes, by which time the pressure in it was reduced to about 10^{-5} torr. The subsequent pressure rise was next measured for each gas as a function of time. Figure 1 shows the desorption curves for He, Ne, Ar, and Kr and demonstrates a slow release of He, nearly doubled when the initial pressure was doubled, and a lesser release of Kr, but very little evolution of Ne or Ar. These effects were interpreted in the following way.

The diffusion and solution of gases in glass have been studied by several authors,[3-7] some results near room temperature being given in the Table, extrapolated where necessary. In the diffusion problem of our experiments, one can treat the glass as a semi-infinite medium bounded on one side by the plane at $x = 0$. The boundary conditions for the concentration C are:

$$C = C_1 \text{ at } x = 0 \text{ for } 0 < t < t_0$$
$$C = 0 \text{ at } t = 0 \text{ for } 0 < x < \infty.$$

The solution of Fick's equation, $\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2}$ for these boundary conditions, and at the time $t = t_0$, is[8]

$$C(x) = C_1\left(1 - erf\,\frac{x}{2\sqrt{Dt_0}}\right) \qquad (1)$$

On expanding the error function as a series, for small enough values of $\frac{x}{2\sqrt{Dt_0}}$, equation 1 gives as an approximation

$$C'(x) = C_1\left(1 - \frac{x}{(\pi Dt_0)^{\frac{1}{2}}}\right) \qquad (2)$$

for the concentration distribution at $t = t_0$. At this time taken as the new zero, as indicated in paragraph 2 above, the gas is pumped away for a short period t_1 and desorption commences. The solution now appropriate is[9]

$$C(x) = \frac{1}{2\sqrt{\pi Dt}}\int_0^{\infty} C'(x)\left\{exp - \frac{(x - x')^2}{4Dt} - exp - \frac{(x + x')^2}{4Dt}\right\}dx \qquad (3)$$

On substitution of equation 2 and integration, equation 3 gives

$$C(x) = C_1 \, erf \, \frac{x}{2\sqrt{Dt}} - C_1 \frac{x}{(\pi D t_0)^{\frac{1}{2}}} \tag{4}$$

Per unit area of surface the flux is then

$$- D\left(\frac{\partial C}{\partial(-x)}\right)_{x=0} = \frac{D^{\frac{1}{2}}C_1}{(\pi t)^{\frac{1}{2}}} - \frac{D^{\frac{1}{2}}C_1}{(\pi t_0)^{\frac{1}{2}}} \tag{5}$$

and the corresponding amount, M, of substance desorbed per unit area during the time interval $(t-t_1)$ is given by

$$\frac{M}{(t^{\frac{1}{2}} - t_1^{\frac{1}{2}})} = C_1\left(\frac{D}{\pi}\right)^{\frac{1}{2}} \left[2 - \frac{(t^{\frac{1}{2}} + t_1^{\frac{1}{2}})}{t_0^{\frac{1}{2}}}\right] \tag{6}$$

or

$$\frac{M}{(t - t_1)} = C_1\left(\frac{D}{\pi}\right)^{\frac{1}{2}} \left[\frac{2}{(t^{\frac{1}{2}} + t_1^{\frac{1}{2}})} - \frac{1}{t_0^{\frac{1}{2}}}\right] \tag{7}$$

M can be related to the pressure p by

$$M = \frac{V}{A} \cdot \frac{p}{76} \cdot \frac{273}{296} \tag{8}$$

where V and A are the volume and internal surface of the McLeod gauge respectively, and so plots of $p/(t^{\frac{1}{2}} - t_1^{\frac{1}{2}})$ against $(t^{\frac{1}{2}} + t_1^{\frac{1}{2}})$ or $p/(t - t_1)$ against $(t^{\frac{1}{2}} + t_1^{\frac{1}{2}})^{-1}$ should be straight lines. Figures 2(a) and 2(b) show that the desorption curve of helium initially follows such a relationship satisfactorily, apart from a deviation for very short times.

The corresponding intercepts on the ordinate of Figure 2(a) and the slopes of Figure 2(b) are found to be virtually identical, just as required by equations 6 and 7, and to be doubled in magnitude when the initial pressure was 6 cm. (curves 1) as compared with the value when this pressure was 3 cm. (curves 2), again as required by equations 6 and 7. The mean value of $p/(t^{\frac{1}{2}}-t_1^{\frac{1}{2}})$ was $5{\cdot}0 \times 10^{-5}$ when the solution of helium had occurred at 3 cm pressure. With D taken from the Table ($D = 7{\cdot}2_6 \times 10^{-9}$ cm.²sec.⁻¹), and with C_1 also estimated from this Table ($C_1 = 5{\cdot}2 \times 10^{-3} \times 3/76$ cm.³ at s.t.p. per cm.³ of glass), one may combine equations 6 or 7 with 8 and obtain $A/V = 3{\cdot}6$. Calculations based on the dimensions of the component parts of the McLeod gauge lead to a value of $A/V \sim 2{\cdot}2$. Thus the evidence of Figures 2(a) and 2(b) and the numerical value of A/V strongly support the explanation that solution of helium in Pyrex accounts for the high apparent solubilities of this gas in certain polymers.

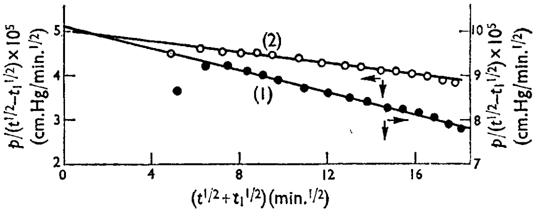

FIGURE 2(a) *Linear relation between* $p/(t^{\frac{1}{2}} - t_1^{\frac{1}{2}})$ *and* $(t^{\frac{1}{2}} + t_1^{\frac{1}{2}})$ *for helium.*

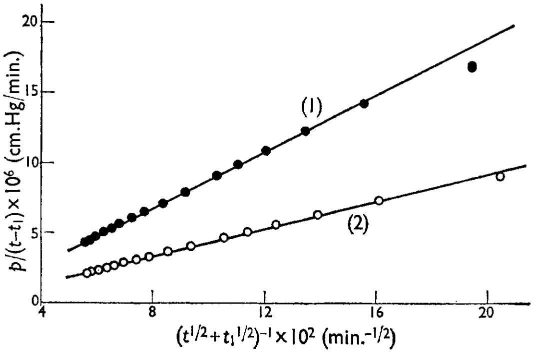

FIGURE 2(b) *Linear relation between* $p/(t-t_1)$ *and* $1/(t^{\frac{1}{2}} + t_1^{\frac{1}{2}})$ *for helium.*

TABLE

Gas	Temp. (°c)	Diffusion Coefficient, D(cm.²sec.⁻¹)	Solubility (cm.³ at s.t.p. at 1 atm. per cm.³ of glass)	Type of glass	Reference
He	27	$7{\cdot}7_4 \times 10^{-9}$	$6{\cdot}5 \times 10^{-3}$	Pyrex 7740	4
	23·3	$7{\cdot}2_6 \times 10^{-9}$	$5{\cdot}2 \times 10^{-3}$	Pyrex 7740	5
	25	$2{\cdot}0 \times 10^{-8}$	$1{\cdot}9 \times 10^{-2}$	Vitreous silica	7
Ne	25	5×10^{-12}	3×10^{-3}	Vitreous silica	7
H_2	25	5×10^{-12}	4×10^{-2}	Vitreous silica	7
O_2	25	10^{-20}	—	Vitreous silica	7
Ar	25	2×10^{-25}	—	Vitreous silica	7
N_2	25	2×10^{-25}	—	Vitreous silica	7

In view of the small diffusion coefficients in Pyrex of gases other than helium, any appreciable homogeneous diffusion of these other gases in the glass matrix is unlikely. But from Figure 1 an increase in the amount of desorbed gas is observed in the sequence Ne < Ar < Kr. The more condensable gases are thought to migrate to some extent down flaws and crevices at the glass surface giving entrained populations of molecules in the order of their condensabilities. The desorption curve of Kr rises very fast initially and then levels off after a short time. This suggests fairly rapid evolution of krypton from crevices at the glass surface but negligible amounts of krypton dissolved in glass. The magnitudes of the effects observed for these more condensable gases are not likely to lead to significant errors, especially since the more condensable the gas the greater its solubility in the polymer generally becomes.

In silica apparatus the behaviour noted above for helium in Pyrex will, according to the figures in the Table, be even more in evidence, but in soda glass apparatus as used by Meares[1] it would probably be negligible since molecule diffusion in soda glass is much slower than in Pyrex.

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