

CHAPTER 18

PROPERTIES DETERMINING MASS TRANSFER IN POLYMERIC SYSTEMS

Permeation and dissolution are the main processes determined by diffusive mass transfer. Permeation of polymers by small molecules depends on their solubility and diffusivity. For both quantities reasonable estimations are possible if some basic data of the permeating molecules (e.g. critical temperature and collision diameter) and of the polymer (structure, glass transition temperature, crystallinity) are known. For the estimation of the permeability of thin layers (films) an additive quantity, the *permachor*, is available.

Dissolution of polymers is controlled by processes of diffusion and convection. The rate of diffusion may be estimated from the intrinsic properties of the polymer and the Reynolds number of the dissolving liquid.

Introduction

In this chapter the diffusive mass transfer, as observed in practical applications of polymeric systems will be discussed. Three categories will be considered.

First of all, the permeation of simple gases through thin layers of polymers, as occurs in protective coatings and in packaging films, will be treated. This category is the most widely studied; for simple gases (such as hydrogen, air, oxygen, carbon dioxide) the permeation rules are relatively simple. Generally the knowledge within this category is well-rounded, though not yet complete, as far as the full understanding of the diffusive mechanism is concerned.

The second category is that of the mass transfer of heavier organic vapours and liquids as occurs in polymeric constructions such as plastic containers and bottles. In this case the situation is more complicated; very often there is stronger interaction between penetrant and polymer. The performance of useful and repeatable experiments and the acquiring of quantitative knowledge can be very difficult.

The last category of mass transfer problems is the dissolution of polymers by liquids. The study of this category is still in its infancy.

We shall discuss these three categories in succession.

A. PERMEATION OF SIMPLE GASES

For simple gases a general relationship between the three main permeation properties P (permeability), S (solubility) and D (diffusivity) is almost exactly valid:

$$P = S \cdot D \quad (18.1)$$

This means that permeation is a sequential process, starting with solution of the gas on the outer surface of the polymer (where equilibrium nearly exists), followed by slow inward diffusion ("reaction with pre-established equilibrium"). For all three physical quantities P , S and D , the temperature dependence can be described by a Van't Hoff-Arrhenius equation:

$$S(T) = S_0 \exp(-\Delta H_s/RT) \quad (18.2)$$

$$D(T) = D_0 \exp(-E_D/RT) \quad (18.3)$$

$$P(T) = P_0 \exp(-E_p/RT) \quad (18.4)$$

where ΔH_s = molar heat of sorption

E_D = activation energy of diffusion

E_p = apparent activation energy of permeation

As a consequence of equation (18.1), we also have

$$P_0 = S_0 \cdot D_0 \quad (18.5)$$

$$E_p = \Delta H_s + E_D \quad (18.6)$$

With $\log x = 1/2.3 \cdot \ln x = 0.435 \ln x$ and $0.435/298 = 1.46 \cdot 10^{-3}$, the equations (18.2–4) may be written in the following way:

$$\log S(T) = \log S_0 - 0.435 \cdot \Delta H_s/RT \quad (18.2a)$$

$$\log D(T) = \log D_0 - 0.435 \cdot E_D/RT \quad (18.3a)$$

$$\log P(T) = \log P_0 - 0.435 \cdot E_p/RT \quad (18.4a)$$

and:

$$\log S(298) = \log S_0 - 1.46 \cdot 10^{-3} \cdot \Delta H_s/R \quad (18.2b)$$

$$\log D(298) = \log D_0 - 1.46 \cdot 10^{-3} \cdot E_D/R \quad (18.3b)$$

$$\log P(298) = \log P_0 - 1.46 \cdot 10^{-3} \cdot E_p/R \quad (18.4b)$$

where $\Delta H_s/R$, E_D/R and E_p/R have the dimension of a temperature (K). By means of the equations (18.2–4) the six basic parameters S_0 , D_0 , P_0 , H_s , E_D and E_p can be derived from measurements of $S(T)$, $D(T)$ and $P(T)$ at different temperatures.

We shall first of all consider the main characteristic physical data of simple gases; then solubility, diffusivity and permeability will be separately discussed; finally some useful inter-conversion ratios will be given.

1. Main characteristic physical data of simple gases in connection with solubility and diffusive transport

In simple gases the molecular interactions are small. As a consequence some “model-laws” may successfully be applied, e.g. the “laws” of Van der Waals, Trouton and Lennard-Jones. *Van der Waals’ law* is an extension of the law of Boyle-Gay Lussac, with corrections for the weak interaction and the proper volume of the gas molecules. For simple gases it is a fair approximation of the P - V - T -behaviour. It reads:

$$(p - a/V^2)(V - b) = RT$$

where a and b are the Van der Waals constants. The critical pressure, temperature and volume can be calculated as an expression in a , b and R .

Trouton’s law is the relationship between the boiling temperature and the molar heat of vapourisation; it reads:

$$\Delta H_v = 10.0RT_b$$

Deviations are observed as soon as stronger (polar) interaction plays a part.

The *Lennard-Jones equation* for the potential energy at high compression reads:

$$\phi(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$$

where $\phi(r)$ = molecular interaction energy as a function of the separation distance

r = separation distance

ϵ = potential energy constant

σ = potential length constant

ϵ and σ are the Lennard-Jones scaling factors.

Division of ϵ by the Boltzmann constant k gives the *Lennard-Jones temperature* ϵ/k , expressed in K (elvin).

The constant σ may be considered as the collision diameter of the molecule.

In table 18.1 a survey of the most important physical data of simple gases is given.

2. Solubility

S is the amount of substance (gas) per unit volume of solvent (polymer) in equilibrium with a unit partial pressure, as expressed in the equation:

$$c = Sp(\text{Henry's law})$$

For simple gases S is usually given in $\text{cm}^3(\text{STP})$ per cm^3 polymer per bar; the conversion into S.I units is easy:

$$1 \text{ cm}^3(\text{STP})/\text{cm}^3 \cdot \text{bar} = 10^{-5} \text{ m}^3(\text{STP})/\text{m}^3 \cdot \text{Pa}$$

N.B. For organic vapours the solubility is normally expressed in weight per weight of polymer at equilibrium vapour pressure. In order to convert this into $\text{cm}^3(\text{STP})/\text{cm}^3 \cdot \text{bar}$ one has to multiply by

TABLE 18.1
Some physical data of simple gases

Gas	T_b [K]	T_{cr} [K]	ϵ/k [K]	ΔH_b [kJ mol ⁻¹]	$\frac{\Delta H_b}{RT_b}$	σ [10 ⁻² nm]	σ^2 [10 ⁻³ (nm) ²]
He	4.3	5.3	10.2	0.36	10.0	0.255	6.6
{ H ₂	20	33	60	1.66	10.0	0.283	8.0
{ Ne	27	44.5	33	2.70	10.0	0.282	7.9
{ N ₂	77	126	71	6.47	10.1	0.380	14.4
{ CO	82	133	92	6.75	9.9	0.369	13.6
{ Ar	87.5	151	93	7.3	10.0	0.354	12.5
{ O ₂	90	155	107	7.5	10.0	0.347	12.0
{ CH ₄	112	191	149	9.4	10.0	0.376	14.1
{ Kr	121	209	179	10.1	10.0	0.366	13.4
{ Xe	164	290	231	13.7	10.0	0.405	16.4
{ C ₂ H ₄	175	283	225	14.4	10.1	0.416	17.4
{ C ₂ H ₆	185	305	216	15.6	10.1	0.444	19.7
{ CO ₂	195	304	195	16.2	(10)	0.394	15.4
H ₂ S	212	373	301	(19.3)	(11)	0.362	13.2
C ₃ H ₈	231	370	237	19.0	9.8	0.512	26.3
NH ₃	240	406	558	23.3	11.6	0.290	8.4
{ (CH ₃) ₂ O	250	500	395	22.6	10.9	0.431	18.6
{ SO ₂	263	431	335	24.8	11.3	0.411	17.0
C ₄ H ₁₀	272	425	331	24.3	10.7	0.469	22.0
{ CH ₂ Cl ₂	313	510	356	31.6	12.1	0.490	24.0
{ (CH ₃) ₂ CO	329	509	560	31.9	11.7	0.460	21.2
CH ₃ OH	338	513	482	39.2	13.9	0.363	13.2
C ₆ H ₆	353	562	412	34.0	11.6	0.535	18.9
H ₂ O	373	647	809	41.0	13.3	0.264	7.0

the factor:

$$\frac{22,400 \times \rho(\text{polymer})}{M(\text{vapour}) \times p(\text{vapour})}$$

where 22,400 is the STP molar volume of vapour (in cm³/mol) (M expressed in g/mol).

The *solubility* of gases in polymers is not so easy to determine, since the solubilities of simple gases in polymers are low. The most accurate procedure is to establish sorption equilibrium between polymer and gas at known pressure and temperature, followed by desorption and measurement of the quantity of gas desorbed.

For fairly soluble organic vapours the determination of S is easier; a sample of polymer of known weight is kept at a fixed temperature and pressure in contact with the vapour and the weight increase is measured, usually by means of a quartz spiral.

A survey of the numerical data of the solubilities of the most important simple gases in polymers at room temperature is given in table 18.2.

It is evident that for a given gas the solubilities in the different polymers do not show large variations. The nature of the gas, however, is important. Taking the solubility of nitrogen as 1, that of oxygen is *roughly* 2, that of carbon dioxide 25 and that of hydrogen 0.75 (see later Table 18.6 on page 555).

TABLE 18.2

Solubility of simple gases in polymers ($S(298)$ in $\text{cm}^3(\text{STP})/\text{cm}^3 \cdot \text{bar} =$

	$10^{-5} \text{cm}^3(\text{STP})/(\text{cm}^3 \cdot \text{Pa})^1$				Heat of solution (ΔH_s in kJ/mol)			
	N ₂	O ₂	CO ₂	H ₂	N ₂	O	CO ₂	H ₂
<i>Elastomers</i>								
polybutadiene	0.045	0.097	1.00	0.033	4.2	1.3	-8.8	6.2
cis-1,4-polyisoprene (natural rubber)	0.055	0.112	0.90	0.037	2.1	-4.2	-12.5	-
polychloroprene	0.036	0.075	0.83	0.026	-	-	-9.6	6.2
styrene-butadiene rubber	0.048	0.094	0.92	0.031	0.3	2.3	-	-
butadiene-acrylonitrile rubber 80/20	0.038	0.078	1.13	0.030	5.8	2.0	-9.2	4.1
butadiene-acrylonitrile rubber 73/27	0.032	0.068	1.24	0.027	4.1	2.0	-10.8	4.1
butadiene-acrylonitrile rubber 68/32	0.031	0.065	1.30	0.023	4.6	0.8	-12.5	5.2
butadiene-acrylonitrile rubber 61/39	0.028	0.054	1.49	0.022	4	4.6	4.6	5.0
poly(dimethyl butadiene)	0.046	0.114	0.91	0.033	3.8	0.8	-6.6	2.0
polyisobutylene (butyl rubber)	0.055	0.122	0.68	0.036	1.7	-5.0	-8.8	2.5
polyurethane rubber	0.025	0.048	(1.50)	0.018	-	-	-	-
silicone rubber	0.081	0.126	0.43	0.047	-	-	-	-
<i>Semicrystalline polymers</i>								
polyethylene H.D.	0.025	0.047	0.35	-	2.1	-1.7	-5.3	-
polyethylene L.D.	0.025	0.065	0.46	-	7.9	2.5	0.4	-
trans-1,4-polyisoprene (Gutta-percha)	0.056	0.102	0.97	0.038	-	-	-	-
poly(tetrafluoroethylene)	-	-	0.19	-	-5.4	-7.2	-14.7	-
polyoxymethylene	0.025	0.054	0.42	-	-	-	-	-
poly(2,6-diphenyl-1,4-phenylene oxide)	0.043	0.1	1.34	-	-	-	-	-
poly(ethylene terephthalate)	0.039	0.069	1.3	-	-11.4	-13.0	-31.4	-
<i>Glassy polymers</i>								
polystyrene	-	0.055	0.65	-	-	-	-	-
poly(vinyl chloride)	0.024	0.029	0.48	0.026	7.1	1.3	-7.9	0
poly(vinyl acetate)	0.02	0.04	-	0.023	-	-4.6	-24.5	10.3
poly(bisphenol A-carbonate)	0.028	0.095	1.78	0.022	-	-12.9	-21.7	-

¹ Van Amerongen (1950, 1964) and Polymer Handbook.

A simple linear relationship has been found by Van Amerongen (1950, 1964) between the solubility of various gases in rubber and their boiling points or their critical temperatures. The solubility of these simple gases in natural rubber is shown in fig. 18.1.

The drawn lines can be described by the following expressions (S in $\text{cm}^3/\text{cm}^3 \cdot \text{Pa}$):

$$\log S(298) \approx -7.0 + 0.0074 T_{\text{cr}}$$

$$\log S(298) \approx -7.0 + 0.0123 T_{\text{b}} \quad (18.7)$$

$$\log S(298) \approx -7.0 + 0.010 \epsilon/k$$

The last expression is possibly the most accurate one, as was demonstrated by Michaels and Bixler (1961).

The nature of the polymer slightly affects the solubility and is probably related to the solubility parameter of the polymer. For amorphous elastomers without strong polar groups (and even for amorphous polymers in general!) the expression (18.7c) may be used as a first approximation (with an accuracy of ± 0.25).

Van Amerongen found a pronounced selective effect of the polarity of the polymer on gas solubility in butadiene-acrylonitrile copolymers. As the acrylonitrile content of the copolymer increases, the solubility of carbon dioxide increases, whereas that of hydrogen, nitrogen and oxygen decreases.

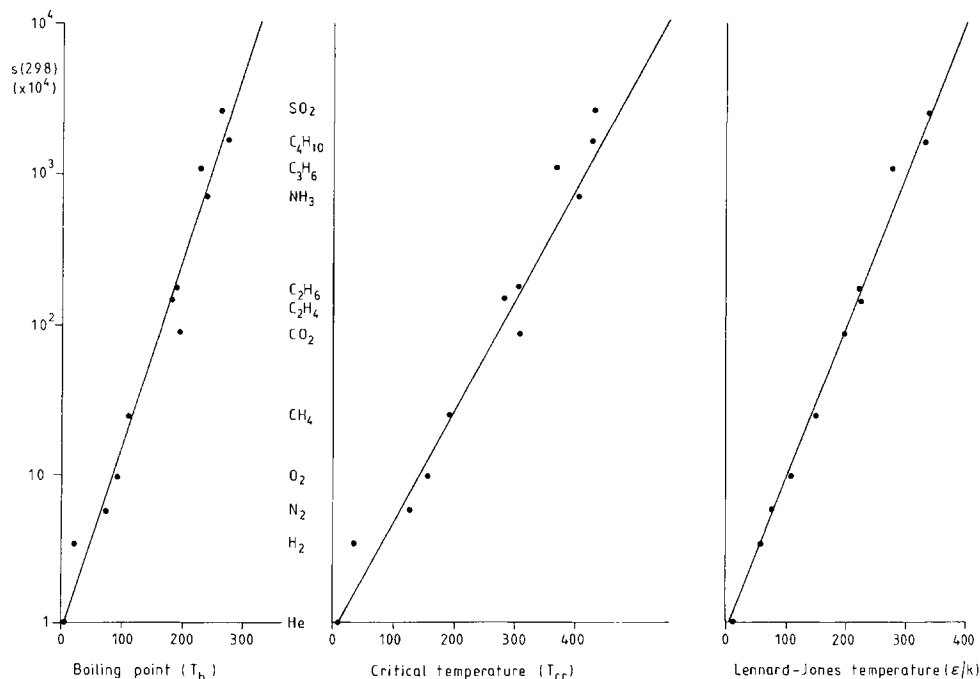


Fig. 18.1. The solubility $S(298)$ of different gases in natural rubber as a function of the boiling point, the critical temperature and the Lennard-Jones temperature.

$$S(298) \text{ is expressed in } \frac{\text{cm}^3(\text{STP})}{\text{cm}^3 \cdot \text{Pa}} \times 10^{-7}$$

The temperature dependence of the solubility obeys the *Clausius–Clapeyron equation*:

$$\frac{\Delta H_s}{R} = - \frac{d \ln S}{d\left(\frac{1}{T}\right)}$$

where ΔH_s = heat of solution, expressed in J/mol.

For the smallest gas molecules dissolving in elastomers ΔH_s is positive (endothermic effect); for the larger gas molecules the reverse is true (exothermic effect). The process is exothermic if the sorption energy evolved exceeds the energy needed to make a hole of molecular size in the polymer.

Van Amerongen measured the heat effects of various gases in several elastomers. He found that ΔH_s of elastomers also mainly depends on the boiling points (or the Lennard-Jones temperatures) of the gas and is hardly dependent of the nature of the polymer. A representative expression is:

$$10^{-3} \Delta H_s / R = 1.0 - 0.010 \epsilon / k \pm 0.5 \quad (18.8)$$

By means of the equations 18.7c, 18.8 and 18.2b an expression for S_0 can be derived:

$$\log S_0 = -5.5 - 0.005 \epsilon / k \pm 0.8 \quad (18.9)$$

The equations 18.7–9 are valid for elastomers (and for polymers in the rubbery state). As was already mentioned earlier: no *systematic* correlation with the polymer structure could be demonstrated (it is small anyhow).

For *glassy amorphous* polymers analogous expressions could be derived from the experimental data in the literature. The numerical values of the constants in the equations are somewhat lower, and also the accuracy is lower (this is probably due to the fact that the physical structure of the glassy state strongly depends on the processing of the polymer).

It seems useful to summarize the derived expressions for the three main parameters of the solubility: $S(298)$, S_0 and $\Delta H_s/R$.

For *rubbers (elastomers)* the equations are:

$\log S(298) = -7.0 + 0.010 \epsilon / k \pm 0.25$	(18.7a)
$10^{-3} \Delta H_s / R = 1.0 - 0.010 \epsilon / k \pm 0.5$	(18.8a)
$\log S_0 = -5.5 - 0.005 \epsilon / k \pm 0.8$	(18.9a)

and for *glassy polymers*:

$\log S(298) = -7.4 + 0.010 \epsilon / k \pm 0.6$	(18.7b)
$10^{-3} \Delta H_s / R = +0.5 - 0.010 \epsilon / k \pm 1.2$	(18.8b)
$\log S_0 = -6.65 - 0.005 \epsilon / k \pm 1.8$	(18.9b)

For *all types* of amorphous polymers:

$$\log S(T) = \log S_0 - 0.435 \cdot \Delta H_s / RT = \log S(298) - 0.435 \frac{\Delta H_s}{R} \left(\frac{1}{T} - \frac{1}{298} \right) \quad (18.2a-b)$$

For fully *crystalline polymers* the solubility of gases is nearly zero; for *semi-crystalline polymers* it depends on the degree of crystallinity. Michaels and Bixler (1961) demonstrated that the following simple rule is valid for a considerable number of gases:

$$S(298) \approx S_a(298)(1 - x_c) \quad (18.10)$$

where x_c is the degree of crystallinity and S_a the solubility in the amorphous state.

Our conclusion is, that the three parameters of the solution (sorption) process of simple gases can be estimated from three hall-marks of the polymer-gas combination: the Lennard-Jones temperature of the gas (ϵ/k), and the glass transition temperature (T_g) and the degree of crystallinity (x_c) of the polymer.

Example 18.1 gives an illustration of a calculation; table 18.3 shows a comparison of calculated versus experimental values.

Example 18.1

Estimate the solubility and the heat of solution (sorption) of oxygen in poly(ethylene terephthalate) (PETP), both in the quenched amorphous glassy state and in the semi-crystalline state ($x_c = 0.45$).

Solution

PETP has a T_g of 345 K; so at room temperature the amorphous matrix is in the *glassy state*. We apply eq. 18.7b; substituting $\epsilon/k = 107$ gives:

$$\log S_a(298) = -7.4 + 1.07 \pm 0.6 = -6.33 \pm 0.6.$$

So the value of $S_a(298)$ will be 5.6×10^{-7} , with a margin between $1.2 \cdot 10^{-7}$ and $18.5 \cdot 10^{-7}$. The experimental value in the literature is $9.9 \cdot 10^{-7}$, in fair agreement (Polymer Handbook).

For the *semi-crystalline state* we find:

$$S_{sc}(298) = S_a(298)(1 - x_c) = 5.6 \cdot 10^{-7} \times 0.55 = 3.1 \cdot 10^{-7}$$

with a margin between $12.5 \cdot 10^{-7}$ and $0.8 \cdot 10^{-7}$. The experimental value is $7.4 \cdot 10^{-7}$, in fair agreement.

For the value of ΔH_s we use equation (18.8b):

$$10^{-3} \cdot \Delta H_s / R = 0.5 - 1.07 \pm 1.2 = -0.57 \pm 1.2$$

so that $\Delta H_s \cdot 10^{-3} = -4.8 \pm 10$ with a margin between -14.8 and 5.2 . The experimental value in the literature is -11.6 kJ/mol. This value determines the temperature dependence of $S(T)$ in the semi-crystalline state. The *heat effect* per mol PETP will be $\Delta H_s(1 - x_c) = -2.5 \pm 5.5$ kJ per mol PETP.

3. Diffusivity

The Diffusivity or Diffusion coefficient (D) is the amount of matter (m) passing per second through a unit area, under the influence of a unit gradient of concentration (the

TABLE 18.3
Calculated versus experimental data of $\log S(298)$ and $\Delta H_s/R$

Data	↓Polymer	Gas →	He		H ₂		N ₂		O ₂		CO ₂	
			$\epsilon/k = 10$		$\epsilon/k = 60$		$\epsilon/k = 71$		$\epsilon/k = 107$		$\epsilon/k = 195$	
			calc.	exp.	calc.	exp.	calc.	exp.	calc.	exp.	calc.	exp.
$\log S(298)$	Silicon rubber	$T_g = 146$		-6.37		-6.24		-6.70		-5.51		-
	Butyl rubber	200		-6.81		-6.45		-6.26		-5.92		-5.17
	Natural rubber	213	$\frac{-6.9}{\pm 0.25}$	-6.67	$\frac{-6.40}{\pm 0.25}$	-6.43	$\frac{-6.29}{\pm 0.25}$	-6.53	$\frac{-5.93}{\pm 0.25}$	-5.99	$\frac{-5.05}{\pm 0.25}$	-5.04
	Neopren rubber	230		-7.15		-6.59		-6.44		-6.13		-5.07
	PVAc	$T_g = 306$		-6.98		-6.58		-6.70		-6.20		-5.00
	PETP	345		-7.10		-6.40		-6.33		-6.00		(-4.53)
	PVC	360	$\frac{-7.3}{\pm 0.6}$	-7.26	$\frac{-6.80}{\pm 0.6}$	-6.59	$\frac{-6.69}{\pm 0.6}$	-6.63	$\frac{6.33}{\pm 0.6}$	-6.54	$\frac{-5.45}{\pm 0.6}$	-5.35
	PC	423		-7.88		(-5.86)		-6.80		-6.30		-5.91
	Silicon rubber	$T_g = 146$		-		-		0.80		-		-
	Butyl rubber	200		0.90		0.40		0.21		-0.60		-1.06
$\Delta H_s/R \times 10^{-3}$	Natural rubber	213	$\frac{0.9}{\pm 0.5}$	-	$\frac{0.40}{\pm 0.5}$	-	$\frac{0.29}{\pm 0.5}$	0.25	$\frac{0.07}{\pm 0.5}$	-0.51	$\frac{-1.05}{\pm 0.5}$	-1.50
	Neoprene rubber	230		-		0.75		-		0.28		-1.15
	PVAc	$T_g = 306$		1.06		1.23		-0.81		-0.55		-
	PETP	345		0.13		-		(-2.88)		-1.40		-2.9
	PVC	360	$\frac{0.4}{\pm 1.2}$	1.10	$\frac{-0.10}{\pm 1.2}$	0	$\frac{-0.21}{\pm 1.2}$	0.84	$\frac{-0.57}{\pm 1.2}$	0.16	$\frac{-1.45}{\pm 1.2}$	-0.95
	PC	423				0.21		-1.35		-1.55		-2.61

“driving force”), as expressed in the equation (Fick’s Law):

$$\frac{dm}{dt} = DA \left(\frac{dc}{dx} \right) \quad (18.11)$$

The dimension of D in m^2/s or, more usual in the literature: cm^2/s .

If D is only dependent of temperature (and thus not on concentration or time), the diffusion process is called Fickian. Simple gases show *Fickian diffusion*.

The *diffusivity* can be determined directly either from sorption or from permeation experiments.

In the first case the reduced sorption ($c(t)/(c_\infty - c_0)$) is plotted versus the square root of the sorption time and D is calculated from the equation:

$$D = \frac{\pi}{16} \delta^2 K^2$$

where δ = film thickness and K is the slope of the reduced sorption curve.

TABLE 18.4

Diffusivity of simple gases in polymers Values of $D(298)$ in $10^{-6} \text{ cm}^2/\text{s}$; D_0 in cm^2/s ; E_D/R in 10^3 K .

Polymers	Diffusing gas			
	N ₂			O ₂
	$D(298)$	D_0	E_D/R	$D(298)$
<i>Elastomers</i>				
polybutadiene	1.1	0.22	3.6	1.5
cis-1,4-polyisoprene (natural rubber)	1.1	2.6	4.35	1.6
polychloroprene (Neoprene)	0.29	9.3	5.15	0.43
styrene-butadiene rubber	1.1	0.55	3.9	1.4
butadiene-acrylonitrile rubber 80/20	0.50	0.88	4.25	0.79
butadiene-acrylonitrile rubber 73/27	0.25	10.7	5.2	0.43
butadiene-acrylonitrile rubber 68/32	0.15	56	5.85	0.28
butadiene-acrylonitrile rubber 61/39	0.07	131	6.35	0.14
poly(dimethyl butadiene)	0.08	105	6.2	0.14
polyisobutylene (butyl rubber)	0.05	34	6.05	0.08
polyurethane rubber	0.14	55	5.35	0.24
silicone rubber	15	0.0012	1.35	25
<i>Semicrystalline polymers</i>				
polyethylene H.D.	0.10	3.3	4.5	0.17
polyethylene L.D.	0.35	5.15	4.95	0.46
trans-1,4-polyisoprene (Gutta-percha)	0.50	8	4.9	0.70
poly(tetrafluoroethylene)	0.10	0.015	3.55	0.15
polyoxymethylene	0.021	1.34	5.35	0.037
poly(2,6-diphenyl-1,4-phenylene oxide)	0.43	11.2×10^{-5}	1.0	0.72
poly(ethylene terephthalate)	0.0014	0.058	5.25	0.0036
<i>Glassy polymers</i>				
polystyrene	0.06	0.125	4.25	0.11
poly(vinyl chloride)	0.004	295	7.45	0.012
poly(vinyl acetate)	0.03	30	6.15	0.05
poly(ethyl methacrylate)	0.025	0.68	5.1	0.11
poly(bisphenol-A-carbonate)	0.015	0.0335	4.35	0.021

In the second case D can be calculated from the *permeation time lag* by means of the equation:

$$D = \frac{1}{6} \frac{\delta^2}{\Theta}$$

where Θ is the time lag in seconds obtained by extrapolating the linear part of the pressure-versus-time graph to zero pressure.

Indirectly D can be determined by measuring the permeability and solubility, and applying eq. (18.1).

For simple gases the interactions with polymers are weak, with the result that the diffusion coefficient is independent of the concentration of the penetrant. In this case the penetrant molecules act effectively as "probes of variable size" which can be used to investigate the polymer structure.

In general, diffusion of gases may be regarded as a thermally activated process,

		CO ₂			H ₂		
D_0	E_D/R	$D(198)$	D_0	E_D/R	$D(198)$	D_0	E_D/R
0.15	3.4	1.05	0.24	3.65	9.6	0.053	2.55
1.94	4.15	1.1	3.7	4.45	10.2	0.26	3.0
3.1	4.7	0.27	20	5.4	4.3	0.28	3.3
0.23	3.55	1.0	0.90	4.05	9.9	0.056	2.55
0.69	4.05	0.43	2.4	4.6	6.4	0.23	3.1
2.4	4.6	0.19	13.5	5.35	4.5	0.52	3.45
9.9	5.15	0.11	67	6.0	3.85	0.52	3.5
13.6	5.45	0.038	260	6.7	2.45	0.92	3.8
20	5.55	0.063	160	6.4	3.9	1.3	3.75
43	5.95	0.06	36	6.0	1.5	1.36	4.05
7	5.1	0.09	42	5.9	2.6	0.98	3.8
0.0007	1.1	15	0.0012	1.35	75	0.0028	1.1
0.43	4.4	0.12	0.19	4.25	—	—	—
4.48	4.8	0.37	1.85	4.6	—	—	—
4.0	4.6	0.47	7.8	4.9	5.0	1.9	3.8
0.0017	3.15	0.10	0.00093	3.4	—	—	—
0.22	4.65	0.024	0.20	4.75	—	—	—
6.75×10^{-5}	1.15	0.39	9×10^{-6}	0.9	—	—	—
0.38	5.5	0.0015	0.75	5.95	—	—	—
0.125	4.15	0.06	0.128	4.35	4.4	0.0036	2.0
42.5	6.55	0.0025	500	7.75	0.50	5.9	4.15
6.31	5.55	—	—	—	2.1	0.013	2.6
0.039	3.8	0.030	0.021	3.95	—	—	—
0.0087	3.85	0.005	0.018	4.5	0.64	0.0028	2.5

expressed by an equation of the Arrhenius type:

$$D = D_0 \exp(-E_D/RT) \quad (18.3)$$

where D_0 and E_D are constants for the particular gas and polymer.

All the known data on the diffusivity of gases in various polymers were collected by Stannett (1968).

Table 18.4 gives a survey of the data of the most important simple gases. It is evident that the diffusivities – in contradistinction to the solubilities – of a given gas in different polymers show large variations; also the nature of the gas plays an important part.

The activation energy of diffusion (E_D) is the most dominant parameter in the diffusion process; it is the energy needed to enable the dissolved molecule to jump into another “hole”. It is clear that larger holes are necessary for the diffusion of larger gas molecules; hence the activation energy will be larger for the diffusion of bigger molecules and the diffusivity will be smaller. This is indeed found to be true in all cases.

The available data show a somewhat scattered correlation between the energy of activation and the diameter of the gas molecule, varying between the first and the second power of the molecular diameter of the penetrant molecule. In our experience the best correlation is obtained if E_D is assumed to be proportional to second power of the collision diameter (see Fig. 18.2, where the data of table 18.1 for the collision diameters are used).

If nitrogen is taken as the standard gas for comparison, we can use the product

$$(\sigma_{N_2}/\sigma_x)^2 \times 10^{-3} E_D/R = p \quad (18.12)$$

as a characteristic parameter for the polymer, for which a correlation may be found with other parameters of the polymer. In the parameter p the influence of the diffusing gas (via its collision diameter) on E_D is “neutralised”.

In fig. 18.3 the parameter p is plotted versus T_g , as an index of the molecular stiffness of the polymer. The data show a considerable scattering, but the general course is unmistakable (Van Krevelen, 1972).

The drawn curves correspond to the following equations: for elastomers (rubbery polymers) with $T_g < 298$ K:

$$p = 7.5 - 2.5 \cdot 10^{-4} (298 - T_g)^2 \quad (18.12a)$$

for glassy amorphous polymers (with $T_g > 298$ K):

$$p = 7.5 - 2.5 \cdot 10^{-4} (T_g - 298)^{3/2} \quad (18.12b)$$

The factors $(298 - T_g)$ and $(T_g - 298)$ are the “thermal distances” of T_g from room temperature for rubbers and glasses respectively. The influence of these “thermal distances” is probably connected with the *fractional free volume* of the polymer; in rubbery amorphous polymers this f.f.v. increases with decreasing T_g , in glassy amorphous polymers the f.f.v. increases with increasing T_g (increasing formation of micro-voids), hence lowering of the activation energy.

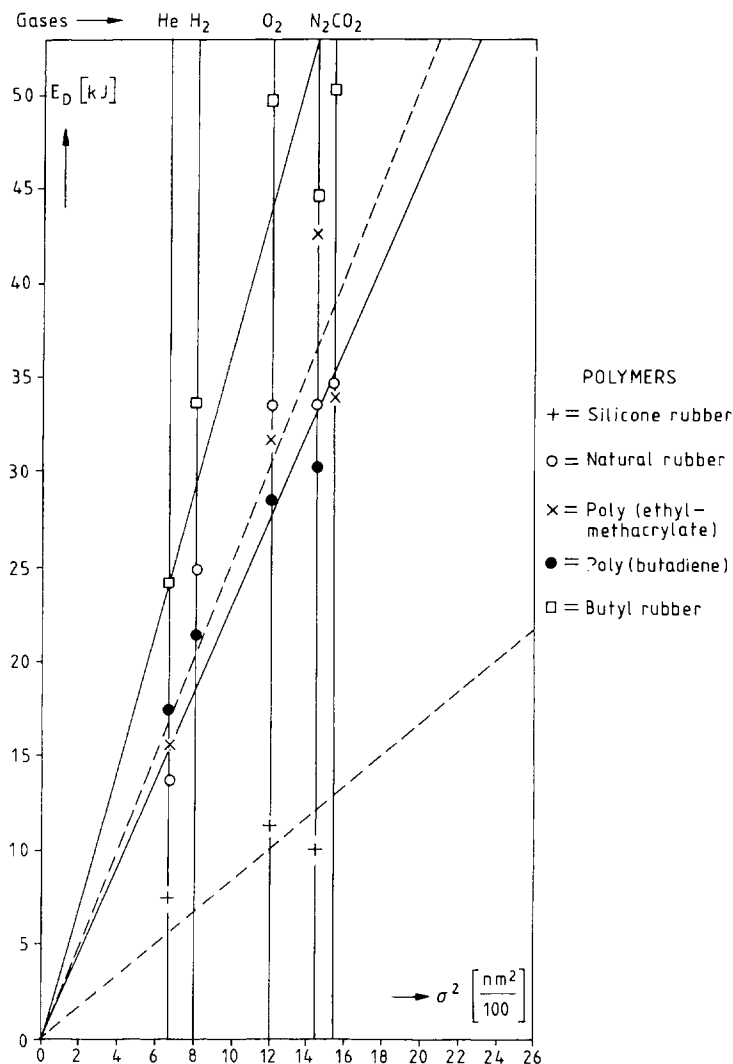


Fig. 18.2. Activation energy of diffusion versus mean square collision diameter.

The second important parameter of the diffusion process is the “constant” D_0 . Here we are favoured by the existence of a lucky correlation of D_0 with E_D .

If the values of $\log D_0$ are plotted versus E_D , a remarkably simple relationship is observed, as is shown in fig. 18.4 for elastomers. For the amorphous glassy polymers the correlation is less accurate but shows a similar tendency, as is clear from fig. 18.5.

So if for a certain gas–polymer combination the activation energy, E_D , is known, the diffusivity can be calculated. Formulae to be used are:

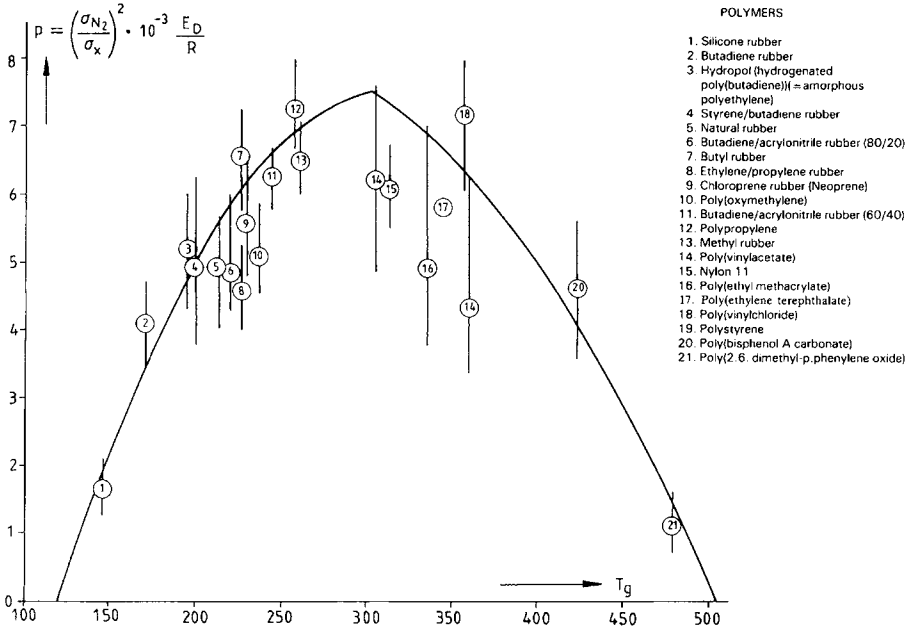


Fig. 18.3. Activation energy of diffusion as a function of T_g .

for elastomers:

$$\log D_0 = \frac{E_D \times 10^{-3}}{R} - 4.0 \quad (18.13a)$$

for glassy polymers:

$$\log D_0 \approx \frac{E_D \times 10^{-3}}{R} - 5.0 \quad (18.13b)$$

Expressions (18.13a) and (18.13b) are interesting examples of the so-called *compensation effect* (partial offset of the effect of higher E_D by higher D_0).

With useful equations for E_D/R (18.12a–b) and for D_0 (18.13a–b) at our disposal it is possible to calculate the diffusivity at room temperature $D(298)$ and at arbitrary temperature $D(T)$ by means of the equations 18.3b and 18.3a:

$$\log D(298) = \log D_0 - 1.46 \cdot 10^{-3} E_D/R \quad (18.3b)$$

$$\log D(T) = \log D_0 - 435/T \cdot 10^{-3} E_D/R \quad (18.3a)$$

As a consequence of the compensation effect mentioned earlier, the scattering of the E_D/R data is less harmful than might be expected. Some examples of estimations of $\log D(298)$ in comparison with experimental values are given in table 18.5.

Crystallization of polymers tends to decrease the volume of amorphous material available for the diffusion; crystalline regions obstruct the movement of the molecules and increase the average length of the paths they have to travel.

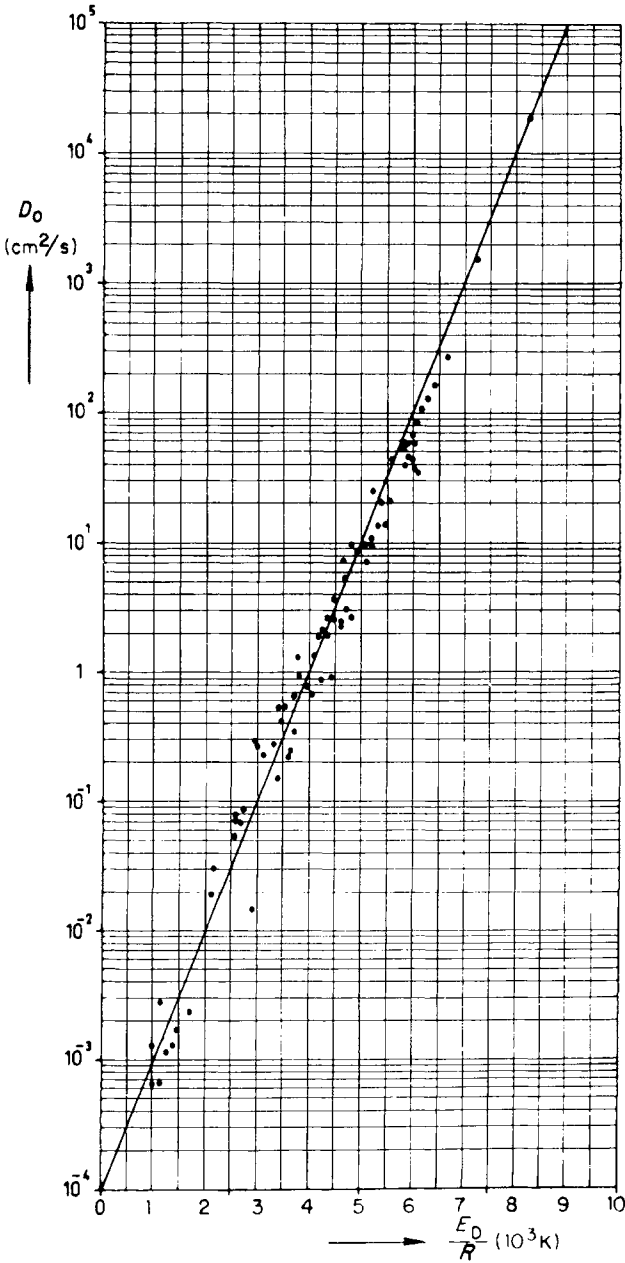


Fig. 18.4. $D_0 - E_D$ relationship for elastomers.

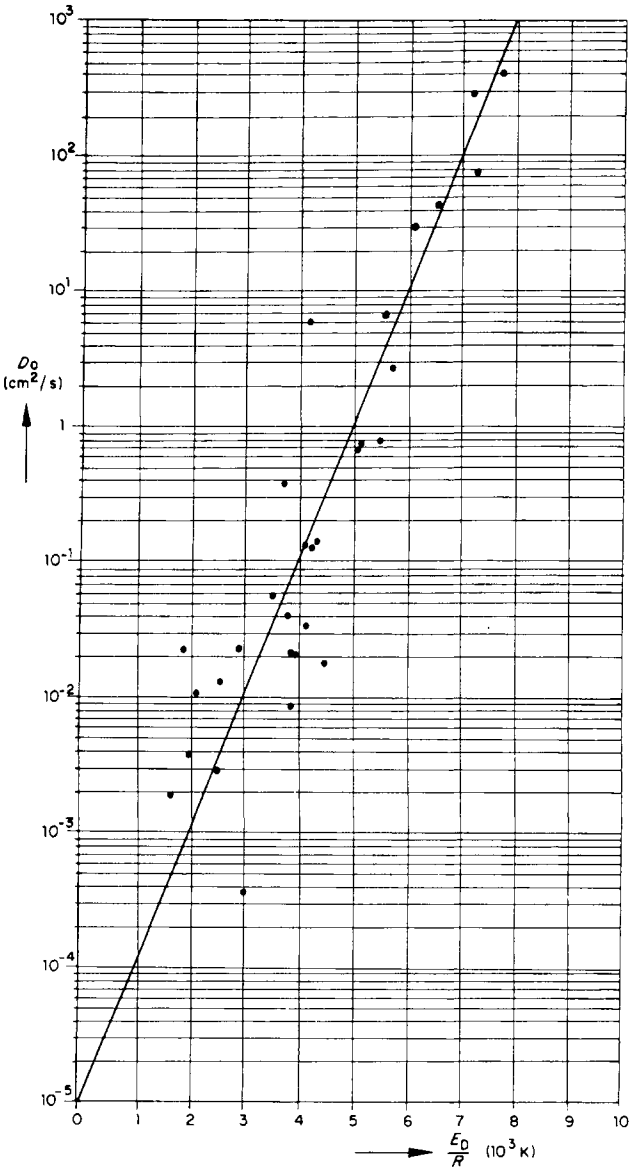


Fig. 18.5. $D_0 - E_D$ relationship for glassy polymers.

As a first approximation the following equation for (semi-)crystalline polymers

$$D = D_a(1 - x_c) \tag{18.14}$$

may be used, where x_c = degree of crystallinity.

This equation has been experimentally verified by Michaels et al. (1963) for the diffusion of several gases in poly(ethylene terephthalate).

TABLE 18.5
Calculated and experimental values of $\log D(298)$

Polymer↓	Gas→ T_g	He $\sigma = 25.5(\text{nm})$		H ₂ $\sigma = 28.3$		O ₂ $\sigma = 34.7$		N ₂ $\sigma = 38.0$		CO ₂ $\sigma = 39.4$	
		calc.	exp.	calc.	exp.	calc.	exp.	calc.	exp.	calc.	exp.
Silicone rubber	146	-4.36	-4.20	-4.45	-4.33	-4.50	-4.87	-4.78	-5.07	-4.85	-4.82
Butadiene rubber (poly-butadiene)	171	-4.77	-4.80	-5.27	-5.02	-5.53	-5.83	-5.73	-5.96	-5.85	-5.98
Butyl-rubber (poly-isobutene cpl)	200	-5.03	-5.23	-5.75	-5.58	-5.91	-7.1	-6.30	-7.37	-6.52	-7.24
Natural rubber (poly-cis-isoprene)	213	-5.14	-4.67	-5.45	-	-6.10	-5.66	-6.55	-5.93	-6.70	-5.90
Neoprene rubber (poly-chloroprene)	230	-5.30	-	-5.50	-5.35	-6.35	-6.37	-6.60	-6.54	-7.0	-6.57
Methyl rubber (poly-dimethyl butadiene)	262	-5.70	-	-5.80	-5.41	-6.70	-6.85	-7.16	-7.10	-7.5	-7.2
Polyvinyl acetate	306	-6.5	-6.0	-6.9	-5.6	-7.8	-7.3	-8.4	-7.5	-8.5	-
Polyethylene terephthalate	345	-6.4	-5.5	-6.7	-	-7.6	-8.3	-8.1	-8.7	-8.3	-9.1
polyvinyl chloride	360	-6.3	-5.6	-6.6	-7.3	-7.4	-7.9	-7.9	-8.4	-8.1	-8.6
Poly-bisphenol carbonate	423	-5.8	-	-6.0	-7.2	-6.5	-7.6	-6.8	-7.7	-6.9	-8.3

Our final conclusion is, that the three determining parameters of the diffusion process of simple gases can be estimated from three hall-marks of the polymer-gas combination: the (collision) diameter of the gas (σ) and the glass transition temperature (T_g) and the degree of crystallinity (x_c) of the polymer.

It is useful to summarize the whole set of equations, available for the estimation of the diffusion parameters:

for *rubbers* (elastomers):

$$10^{-3} \cdot \frac{E_D}{R} = \left(\frac{\sigma_x}{\sigma_{N_2}} \right)^2 \{7.5 - 2.5 \cdot 10^{-4} (298 - T_g)^2\} \pm 0.6 \quad (18.12a)$$

(= p , see fig. 18.3)

$$\log D_0 = 10^{-3} E_D / R - 4.0 \pm 0.4 \quad (18.13a)$$

for *glassy amorphous* polymers:

$$10^{-3} \cdot \frac{E_D}{R} = \left(\frac{\sigma_x}{\sigma_{N_2}} \right)^2 \{7.5 - 2.5 \cdot 10^{-4} (T_g - 298)^{3/2}\} \pm 1.0 \quad (18.12b)$$

(= p , see fig. 18.3)

$$\log D_0 = 10^{-3} \cdot E_D / R - 5.0 \pm 0.8 \quad (18.13b)$$

for *semi-crystalline* polymers:

$$D_{sc} = D_a (1 - x_c) \quad (18.14)$$

for *all polymers*:

$$\log D(298) = \log D_0 - 1.46 \cdot 10^{-3} \cdot \frac{E_D}{R} = -4.0 - 0.46 \cdot 10^{-3} \frac{E_D}{R} \quad (18.15)$$

$$\log D(T) = \log D_0 - \frac{435}{T} \cdot 10^{-3} \frac{E_D}{R} = \log D(298) - 0.435 \cdot \frac{E_D}{R} \left(\frac{1}{T} - \frac{1}{298} \right) \quad (18.16)$$

Example 18.2

Estimate the diffusivity at 298 K and the activation energy of diffusion for oxygen in PETP, both in the glassy and in the semi-crystalline state.

Solution

For the derivation of E_D we use fig. 18.3, where we find at $T_g = 345$ K: $p = 6.75$. So

$$\frac{E_D}{R} \cdot 10^{-3} = \left(\frac{\sigma_{O_2}}{\sigma_{N_2}} \right) \cdot p = 0.83 \cdot (6.75 \pm 1.5) = 5.6 \pm 1.25,$$

which gives: $E_D \cdot 10^{-3} = 46.5 \pm 10.5$ kJ/mol. Two experimental values are mentioned in the literature, viz 46.1 and 48.5, so in good agreement with our estimation.

Equation 18.13b will be used for the estimation of $\log D_0$:

$$\log D_0 = -5.0 + E_D/R \cdot 10^{-3} \pm 0.8 = 0.6 \pm 0.8.$$

By means of eq. 18.15 we then find $D(298)$:

$\log D(298) = \log D_0 - 1.46 \cdot 10^{-3} E_D/R \pm 0.8 = -7.6 \pm 0.8$ so $D_a(298) = 2.5 \cdot 10^{-8}$, with a margin between $0.4 \cdot 10^{-8}$ and $16 \cdot 10^{-8}$. Two experimental values are available in the literature: $0.23 \cdot 10^{-8}$ and $0.5 \cdot 10^{-8}$ cm²/s. Our estimated value is a fairly good approximation.

Finally we find for the semi-crystalline state:

$D_{sc}(298) = D_a(1 - 0.45) = 1.4 \cdot 10^{-8}$ with a margin of $0.25 \cdot 10^{-8}$ to $9 \cdot 10^{-8}$. The literature gives $0.35 \cdot 10^{-8}$. Also in this case a fair estimation.

All literature data refer to the Polymer Handbook.

4. Permeability

The Permeability or permeation coefficient (P) is the amount of substance passing through a polymer film of unit thickness, per unit area, per second and at a unit pressure difference. Here we shall use the cm as unit of length and the Pa(scal) as unit of pressure, so that the dimension of P becomes: cm³(STP) · cm/cm² · s · Pa (=cm² · s⁻¹ · Pa⁻¹).

In the literature many units are used which easily leads to confusion and errors in computation[†].

For practical purposes the permeability is the most important of the permeation properties. Since methods of estimation of solubility and diffusivity are available, estimation of permeability is possible by means of equation (18.4).

As an illustration, fig. 18.6 shows the permeability of nitrogen (at room temperature) for a great variety of polymers (elastomers, semicrystalline polymers and glassy polymers). It can be seen that the values of P vary by a factor of nearly a million if silicone rubber on the one hand is compared with poly(vinylidene chloride) on the other!

Values of $P(298)$, P_0 and E_p/R can be calculated by application of the equations 18.1, 18.5 and 18.6, using the corresponding values of S and D .

[†] The following multiplication factors need to be applied in the conversion:

P expressed in:	do., abbreviated	Multiplication Factor
cm ³ (STP) · cm/cm ² · s · mm H _g	cm ² /s · mm H _g	7.5×10^{-3}
cm ³ (STP) · cm/cm ² · s · cm H _g	cm ² /s · cm H _g	7.5×10^{-4}
cm ³ (STP) · cm/cm ² · s · atm	cm ² /s · atm	0.99×10^{-5}
cm ³ (STP) · mil/100 in ² · day · atm		4.5×10^{-16}
cm ³ (STP) · cm/cm ² · s · bar	cm ² /s · bar	10^{-5}
cm ³ (STP) · cm/cm ² · s · Pa	cm ² /s · Pa	1
m ³ (STP) · m/m ² · s · Pa	m ² /s · Pa	10^4

where cm³(STP) is the amount of gas in cm³ at standard temperature and pressure (273 K, 1 bar).

Fig. 18.6. Permeability of polymers for nitrogen (units: $10^{-8} \text{ cm}^2/\text{s} \cdot \text{bar} = 10^{-13} \text{ cm}^2/\text{s} \cdot \text{Pa}$).

By analogy with equations 18.12a–16, (see page 552) the following empirical correlations could be derived from the available experimental permeability data:

for *rubbers*:

$$\log P_0 = -10.1 + 10^{-3} E_p / R \pm 0.25 \quad (18.17a)$$

$$\log P(298) = -10.1 - 0.46 \cdot 10^{-3} E_p / R \pm 0.25 \quad (18.18a)$$

for *glassy polymers*:

$$\log P_0 = -11.25 + 10^{-3} E_p / R \pm 0.75 \quad (18.17b)$$

$$\log P(298) = -11.25 - 0.46 \cdot 10^{-3} E_p / R \quad (18.18b)$$

for *semi-crystalline polymers*:

$$P_{sc} = S_{sc} D_{sc} = S_a D_a (1 - x_c)^2 = P_a (1 - x_c)^2 \quad (18.19)$$

for *all polymers*:

$$\log P(T) = \log P(298) - 0.435 \frac{E_p}{R} \left(\frac{1}{T} - \frac{1}{298} \right) \quad (18.20)$$

$$E_p / R = \Delta H_s / R + E_D / R \quad (18.6)$$

5. Relationships between the permeation parameters of different gases

Stannett and Szwarc (1955), Rogers et al. (1956) and Frisch (1963) have shown that simple relationships exist between the ratios of the permeability constants for either a series of gases through two polymers or the ratio between two gases through a series of polymers. If we take nitrogen as the standard gas, the permeabilities of the other gases can be calculated by a simple factor which is given in table 18.6.

TABLE 18.6
Relative values of permeability parameters (Rules of thumb)

Gas	P	D	S	E_p	E_D	σ^2	σ^{-2}
N ₂ (=1)	1	1	1	1	1	1	1
CO	1.2	1.1	1.1	1	1	0.95	1.05
CH ₄	3.4	0.7	4.9	(1)	(1)	0.98	1.02
O ₂	3.8	1.7	2.2	0.86	0.90	0.83	1.2
He	15	60	0.25	0.62	0.45	0.45	2.2
H ₂	22.5	30	0.75	0.70	0.65	0.55	1.8
CO ₂	24	1	24	0.75	1.03	1.0	1
H ₂ O (550)	(550)	5	—	0.75	0.75	0.94	1.06

A similar relationship as for the permeabilities is valid for the diffusivities and for the solubilities, although here the range in actual values is less impressive than with the permeability constants. These ratios are also given in table 18.6.

Finally, even the activation energies of diffusion and permeation can be estimated in this way, as was already quantitatively described by the relationship $E_D \sim \sigma^2$. We may conclude that if two of the three quantities D , S and P are known (or can be estimated) for nitrogen in a given polymer, those for the other gases can be estimated very quickly and rather accurately.

5. The Permachor; An additive molar function for the estimation of the permeability.

Recently Salame (1986) introduced a new physical parameter for which he coined the name (specific) Permachor (π). It is defined by the equation

$$P(298) = P^*(298) \exp(-s\pi) \quad (18.21)$$

or

$$\pi = -\frac{1}{s} \ln \frac{P(298)}{P^*(298)} = -\frac{2.3}{s} \log \frac{P(298)}{P^*(298)} \quad (18.22)$$

where $P(298)$ = permeability of an arbitrary simple gas in an arbitrary polymer

$P^*(298)$ = permeability of the same gas in a chosen standard polymer

s = a scaling factor, to be described below

As a *standard gas* nitrogen is used by preference, but in principle any other simple gas may be used, since the permeabilities of the different gases have a constant ratio determined by the collision diameter of the gas molecules (Table 18.1).

As a *standard polymer* Salame selected natural rubber, for several reasons. First of all it is a generally available polymer with a well defined chemical composition: poly(cis-isoprene). Furthermore it is – on the scale of permeabilities – rather representative for the “average” elastomer (with a relatively high permeability). This implies that *for natural rubber π is by definition zero*. Furthermore the value of $\log P^*$ of nitrogen in natural rubber at 298 K equals -12 ± 0.3 . Salame chose as a second fixed point on the π -scale a very “impermeable” polymer, viz. poly(vinylidene chloride (Saran®)), which has a $\log P(298)$ value of -17 ± 0.5 ; the assigned π -value for it is 100 (by analogy with the centigrade scale).

Since a linear relationship between $\log P(298)$ and π is implied in the definition of π , a graphical representation can be made in which the two fixed points are connected by a straight line. If $\log P(298)$ of a polymer is known, the value of π can be read from this graph. As an illustration fig. 18.7, gives the position of a number of polymers; numerical values are given in table 18.7. The scaling factor s is, as a matter of fact, determined by the choice of the second fixed point of the π -scale. For the gases N_2 , O_2 and CO_2 s has a value of 0.12 at 298 K.

By its definition π is proportional to the *negative logarithm* of a relative permeability. In this respect π is comparable to the p_H of solutions: the higher the p_H , the lower the acidity.

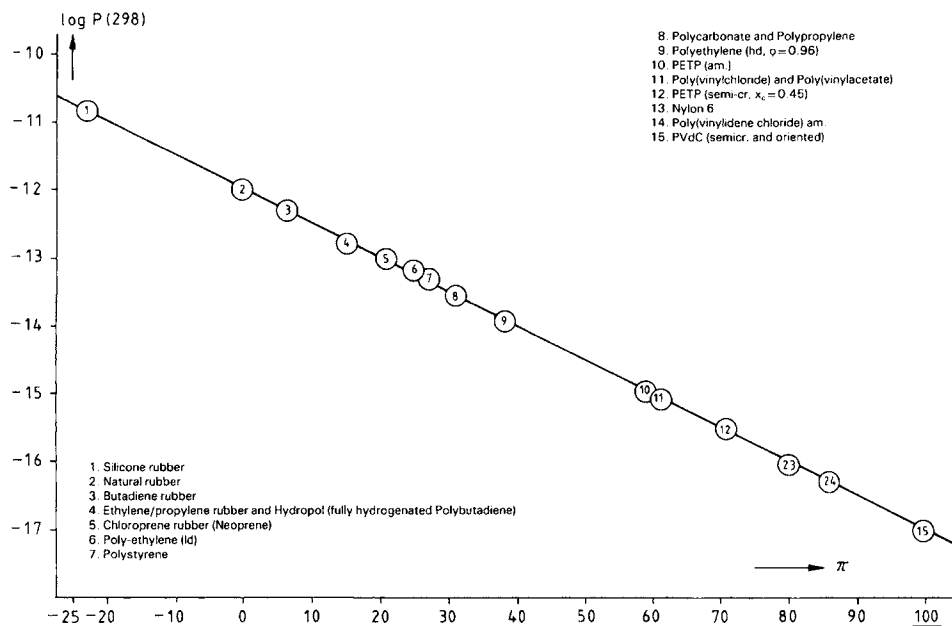


Fig. 18.7. Logarithm of Permeability versus specific Permachor.

In the same way we have: the higher the π , the lower the permeability, and the higher the “barrier effect”.

Salame found that the product $N \times \pi$, the *Molar Permachor* (Π) is an additive function:

$$N \times \pi = \Pi = \sum_i (N_i \cdot \Pi_i) \quad (18.23)$$

where N = number of characteristic groups per structural unit

Π_i = increment of the group i

Table 18.8 gives the list of group contributions to the molar permachor.

The numerical value of π being known, the permeability at room temperature can be estimated from the equation:

$$\log P(298) = \log P^*(298) - \frac{s \cdot \pi}{2.3} \quad (18.22a)$$

For permeation of nitrogen $\log P^*(298) = -12$ and $s = 0.122$, so that in that case the equation reduces to:

$$\log P(298) = -12 - 0.053 \pi \quad (18.24)$$

A disadvantage of the permachor method is that in case of different gases a set of values for $P^*(298)$ and for s should be known. It must be advised therefore to calculate first of all $\log P(298)$ for nitrogen (taking this gas as the standard gas) and then to apply the relative

TABLE 18.7

Values of π for different polymers (Salame, 1986)

Polymer	π
Elastomers	Silicone rubber
	Butyl rubber
	Natural rubber (poly-cis-isoprene)
	Butadiene rubber (poly-butadiene)
	Poly-(methyl pentene)
	Neoprene rubber (Poly-chloroprene)
Glassy amorphous polymers	Hydropol (hydrogenated p. butadiene)
	Polystyrene
	Poly(bisphenol)(carbonate)
	Poly(vinylfluoride)(quenched)
	Poly(ethylene terephthalate) am.
	Poly(vinyl acetate)
	Poly(vinyl chloride)
	Poly(vinylidene chloride) am.
Semi-crystalline polymers	Poly(acrylonitrile)
	Poly(ethylene) 1d ($a = 0.57$)
	Poly(propylene) ($a = 0.40$)
	Poly(ethylene) hd ($a = 0.26$)
	Poly(vinyl fluoride) ($a = 0.60$)
	Poly(ethylene terephthalate) ($a = 0.7$)
	Do. ($a = 0.55$)
	Nylon 66 ($a = 0.6$)
	Nylon 6 ($a = 0.4$)
	Poly(vinylidene chloride) (or.cr.)
	Poly(vinyl alcohol) (dry, $a = 0.3$)

P -values given in table 18.6 in order to estimate the P -value of the relevant gas. For other temperatures the permeability can be estimated by means of equation 18.20. For this E_p must be known ($=\Delta H_s + E_D$).

The π -values calculated by means of the Molar Permachor are valid for amorphous polymers. For semi-crystalline and oriented polymer films a correction must be made. Salame recommends for semi-crystalline polymers the following expression:

$$\pi_{sc} \approx \pi_a - 18 \ln a \approx \pi_a - 41.5 \log(1 - x_c) \quad (18.25)$$

where a = volume fraction amorphous and x_c = crystallinity. For oriented crystalline polymer films Salame gives the expression:



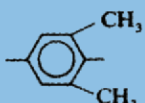
$$P_{\text{oriented,sc}} = P_{sc} \times 1/\tau_0 \quad (18.26)$$

where τ_0 = "tortuosity" of crystallites $\approx 1.13/a^{1/2}$.

In his 1986-paper Salame also gave a derivation of his equations of departure (18.30–31) from the basic permeation equations (18.1–6) which can be summarized as follows:

$$P(T) = S(T) \cdot D(T) = S_0 \cdot D_0 \cdot \exp. -(\Delta H_s + E_D) \quad (18.1-6)$$

TABLE 18.8
Group contributions to the molar permachor

Group	Π_i	Group	Π_i
$-\text{CH}_2-$	15	$-\text{CH}(\text{OH})-$	255
$-\text{CH}(\text{CH}_3)-$	15	$-\text{CH}(\text{CN})-$	wet 100 205
$-\text{CH}(\text{C}_6\text{H}_5)-$	39	$-\text{CHF}-$	85
$-\text{CH}(\text{i butyl})-$	-1	$-\text{CF}_2-$	120
$-\text{C}(\text{CH}_3)_2-$	-20	$-\text{CHCl}-$	108
$-\text{CH}=\text{CH}-$	-12	$-\text{CCl}_2-$	155
$-\text{CH}=\text{C}(\text{CH}_3)-$	-30	$-\text{CH}(\text{CH}_2\text{Cl})-$	50
$-\text{CH}=\text{C}(\text{Cl})-$	33	$-\text{Si}(\text{CH}_3)_2-$	-116
	-54	$-\text{O}-$	70
	60	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{O}- \end{array}$	102
	-44	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{O}-\text{C}-\text{O}- \end{array}$	24
		$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{NH}- \end{array}$	309
			wet 210

Salame substituted in this basic equation four empirical expressions which he derived from literature data, viz. for E_D , D_0 , ΔH_s and S_0 . In these expressions he used his parameter π as the characteristic datum of the polymer (instead of T_g , used as such in our treatment of Diffusivity given earlier).

Salame's four equations read as follows (using the S.I. units J and Pa):

Equation for:	a) Rubbers	b) Glasses	(18.27-30)
I E_D/R	$\left(\frac{\sigma_N}{\sigma_{N_2}}\right)^2 (3125 + 78\pi)$	$\left(\frac{\sigma_N}{\sigma_{N_2}}\right)^2 (2875 + 45\pi)$	
II $\log D_0$	$-4.0 + 10^{-3} \cdot E_D/R$	$-3.5 + 0.6 \cdot 10^{-3} E_D/R$	
III $\Delta H_s/R$	$1550 - 13.25\epsilon/k$	$450 - 13.25\epsilon/k$	
IV $\log S_0$	$-5.3 - 0.0057\epsilon/k - 0.013\pi$	$-6.5 - 0.0057\epsilon/k - 0.013\pi$	

Equation I is similar to our equation (18.12a/b) (but π is used for characterising the polymer instead of T_g); II is almost equal to (18.13a/b); III is nearly identical to (18.8a/b) and IV is an extension of (18.9a/b).

Salame then combined all terms containing π into a product $s \times \pi$ (giving so the full

expression of the exponent in eq. 18.21) and all terms not containing π into a quantity $A(T)$, which is identical to P^* .

Salame finally found (1987) that π is a linear function of $\log(e_{\text{coh}}/f_v)$, where e_{coh} = cohesive energy density and f_v = fractional free volume of the polymer.

Example 18.3

Estimate the permeability $P(298)$ for oxygen of two polymer films: one a neoprene rubber film, the other a PVC film.

Use two methods of estimation: one via the solubility and diffusivity ($P = SD$), the other via the permachor-method. For oxygen $\epsilon/k = 107$ and $(\sigma_{\text{O}_2}/\sigma_{\text{N}_2})^2 = 0.83$; for neoprene $T_g = 230$ K, for PVC $T_g = 360$ K.

Solution:

a) *estimation via S and D.*

Neoprene is a rubber, so we use the equations summarized on pages 541 and 552,

$$\begin{aligned}\log S(298) &= 0.010\epsilon/k - 7.0 \pm 0.25 = -5.93 \pm 0.25 \\ 10^{-3}E_D/R &= (\sigma_{\text{O}_2}/\sigma_{\text{N}_2})^2 \cdot p = 0.83 \times 6.2 = 5.5 \\ \log D_0 &= -4.0 + 10^{-3} \cdot E_D/R \pm 0.4 = 1.15 \pm 0.4. \\ \log D(298) &= \log D_0 - 1.46 \cdot 10^{-3} \cdot E_D/R \pm 0.4 = -6.35 \pm 0.4.\end{aligned}$$

So we get $\log P(298) = \log S(298) + \log D(298) = -6.35 - 5.93 \pm 0.6 = -12.28 \pm 0.6$ or $P(298) = 5.25 \cdot 10^{-13}$ with a margin of $1.3 \cdot 10^{-13}$ to $13 \cdot 10^{-13}$; the experimental value (Polymer Handbook) is $3 \cdot 10^{-13}$, in good agreement with our estimation.

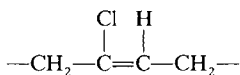
Polyvinyl chloride is an amorphous polymer in the glassy state. We use the equations summarized on pages 541 and 552 again.

$$\begin{aligned}\log S(298) &= 0.010\epsilon/k - 7.4 \pm 0.6 = -6.33 \pm 0.6 \\ 10^{-3}E_D/R &= (\sigma_{\text{O}_2}/\sigma_{\text{N}_2})^2 \cdot p = 0.83 \times 6.25 = 5.2 \pm 0.8. \\ \log D_0 &= -5.0 + 10^{-3} \cdot E_D/R \pm 0.8 = 0.2 \pm 0.8. \\ \log D(298) &= \log D_0 - 1.46 \cdot 10^{-3} \cdot E_D/R \pm 0.8 = -7.4 \pm 0.8\end{aligned}$$

So $\log P(298) = \log S(298) + \log D(298) = -6.33 - 7.4 = -13.73 \pm 1.4$ or $P(298) = 1.85 \cdot 10^{-14} [\text{Pa}^{-1}]$, with a margin between $0.7 \cdot 10^{-14}$ and $3.7 \cdot 10^{-14}$. The experimental value is $0.34 \cdot 10^{-14}$.

b) *estimation via the permachor (π)*

The structural formula of neoprene (poly-chloroprene) is



The contributions to the molar parachor are:

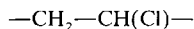
$$\begin{array}{rcl} 2 & \text{---CH}_2\text{---} & = 2 \times 15 = 30 \\ 1 & \text{---CH=C(Cl)---} & = 33 \\ \hline N = 3 & & \Pi = 63 \end{array}$$

The specific parachor then becomes: $\pi = \frac{\Pi}{N} = 63/3 = 21$. Now Salame's equation can be applied:

$$\log P(298) = \log P^*(298) - s \cdot \pi/2.3.$$

For the standard gas (nitrogen) in the standard polymer (natural rubber) we have: $\log P^*(298) = -12$ and $s = 0.12$. Substitution gives $\log P(298) = -12 - 0.12 \times 21/2.3 = -13.1$ or $P(298) = 8 \cdot 10^{-14}$, for nitrogen in neoprene; the experimental value (Polymer Handbook) is $9 \cdot 10^{-14}$, in good agreement. The conversion factor for P (from nitrogen to oxygen (table 18.6) is 3.8. So for oxygen in neoprene $P(298)$ becomes $3.4 \cdot 10^{-13}$. The experimental value (Polymer Handbook) is $3.0 \cdot 10^{-13}$, again in very good agreement.

For PVC the structural formula is:



Hence the contributions to the Molar Permachor are:

$$\begin{array}{rcl} 1 & -\text{CH}_2- & = 15 \\ 1 & -\text{CH}(\text{Cl})- & = 108 \\ \hline N = 2 & & \Pi = 123 \end{array}$$

So $\pi = \Pi/N = 123/2 = 61.5$.

For nitrogen in PVC we then find:

$$\log P(298) = -12 - 0.12 \times 61.5/2.3 = -15.2 \text{ or } P(298) = 6.3 \cdot 10^{-16}.$$

(experimental value $8.9 \cdot 10^{-16}$, Polymer Handbook).

So for oxygen in PVC the result is $6.3 \cdot 10^{-16} \times 3.8 = 2.4 \cdot 10^{-15}$;

This is to be compared with the experimental value $3.4 \cdot 10^{-15}$.

For a glassy polymer this is a very good agreement.

B. PERMEATIONS OF A MORE COMPLEX NATURE

Introduction

Until now we have considered the simplest case of more or less ideal permeation behaviour: Henry's law for sorption (sorbed penetrant randomly dispersed within the polymer) and Fick's first law for diffusion (diffusion coefficient independent of the concentration of the sorbed penetrant).

This ideal behaviour is observed in practice only when "permanent gases" are the penetrants and if the gas pressure is nearly atmospheric. In this case there are no strong polymer-penetrant interactions and no specific interactions between the penetrant molecules.

As soon as interactions become important, also other types of sorption are observed. Figure 18.8 gives a classification of sorption isotherms, proposed by Rogers (1965, 1985).

Type I is of course the ideal sorption behaviour according to Henry's law. As said before, it is observed in the sorption of permanent gases at moderate pressures.

Type II is the well-known sorption isotherm according to Langmuir. This type of isotherm will result when gases are sorbed at specific sites at higher pressure; the concentration of the sorbed substance will reach a "saturation capacity". This isotherm is also found when non-permanent gases at higher pressures are sorbed in glassy amorphous polymers having preëxisting micro-voids.

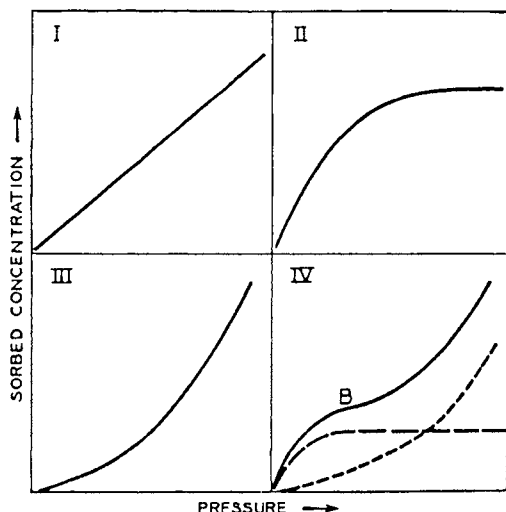


Fig. 18.8. Typical isotherm plots of sorbed concentration versus ambient vapour pressure. (I) Henry's law, $S = \text{a constant}$; (II) Langmuir equation; (III) Flory-Huggins equation; (IV) BET equation, site saturation at point B. (From C.E. Rogers, 1985).

Type III is the sorption isotherm of *Flory-Huggins*. Here the solubility coefficient increases continuously with pressure. It represents a preference for formation of penetrant pairs and clusters; it is observed when the penetrant acts as a swelling agent for the polymer without being a real solvent. An example is water in relatively hydrophobic polymers containing also some polar groups.

Type IV is the typical 2-stage isotherm according to *Brunauer, Emmett and Teller* (BET-isotherm) which may be considered as a combination of the other types (e.g. II at low with III at high pressure). This type is especially found if water is sorbed in hydrophilic polymers.

Types II – IV are coined as “anomalous sorption isotherms”. As a matter of fact the type of sorption isotherm has a profound effect on the permeation behaviour.

1. Partially immobilizing sorption (“dual-mode” model)

Precise studies of sorption of non-permanent gases in glassy polymers showed that the sorption isotherms do not follow Henry's law (see fig. 18.9a). A very good approximation of the isotherm (see fig. 18.9d) is:

$$C = Sp + \frac{C_H bp}{1 + bp} \quad (18.31)$$

Here

C = total concentration of sorbed penetrant

C_H^s = saturation capacity of Langmuir isotherm (in “holes”)

b = affinity coefficient of Langmuir isotherm

S = solubility

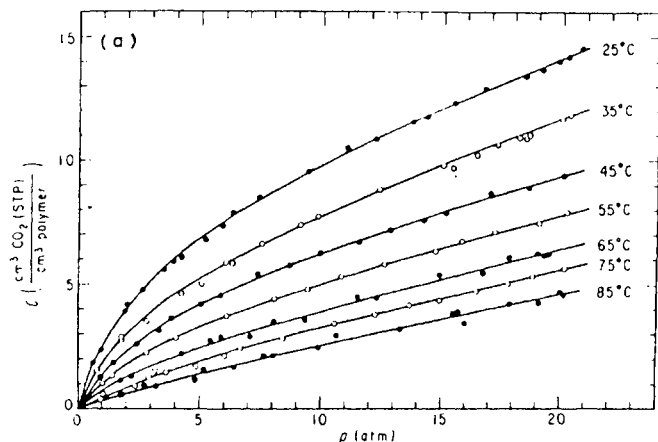


Fig. 18.9a. CO₂ sorption in PET below T_g . From Paul (1979); Courtesy of Verlag Chemie.

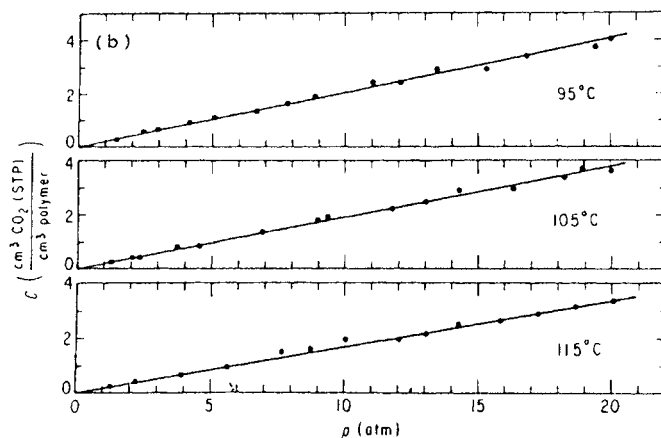


Fig. 18.9b. CO₂ sorption in PET above T_g . From Paul (1979); Courtesy of Verlag Chemie.

This equation has become known as the “dual sorption model”, because obviously two separate sorption mechanisms are operative for gases in glassy polymers. One mode (first term on the right in eq. 8.31) follows Henry’s law; the other mode (second term) follows a Langmuir form. This additional mode is attributed to sorption into micro-voids which apparently preëxist in the glassy state of the polymer (and only there!); it disappears above T_g (see fig. 18.9b).

The dual-sorption model was first suggested by Barrer et al. (1958) and Vieth et al. (1963/72), and developed by Petropoulos (1970) and especially by Paul and Koros et al. (1969/88).

Early investigations of the dual-sorption model started from the assumption that only the Henry’s law part of the sorbed gas contributed to the gas transport, whereas the Langmuir part would not contribute to it, due to immobilization. Then the transport flux

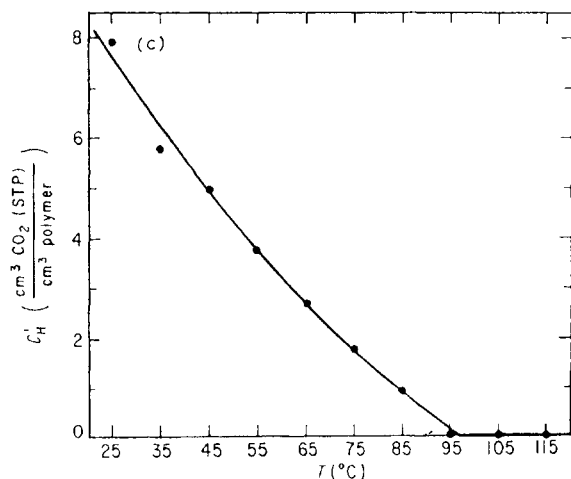


Fig. 18.9c. Effect of temperature on Langmuir capacity for CO_2 sorption in PET. From Paul (1979); Courtesy of Verlag Chemie.

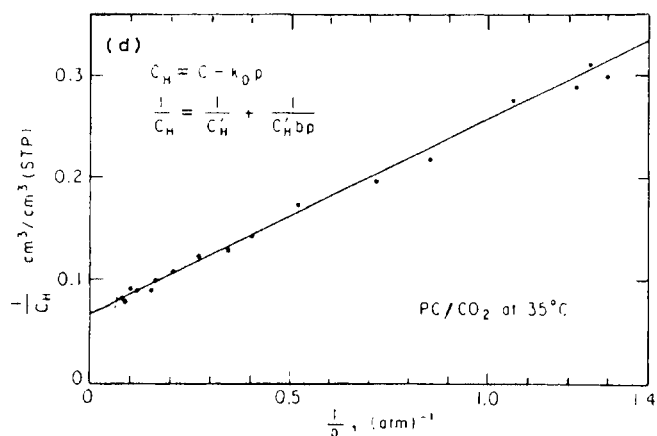


Fig. 18.9d. A graphical test to show how well C_H is described by the Langmuir isotherm. From Koros, Paul and Rocha (1976); Courtesy of John Wiley & Sons, Inc.

would be

$$J = -D \frac{dC_D}{dx} \quad (18.32)$$

where $C_D = S \cdot p$ (random dispersed)

However, Petropoulos (1970) speculated that the Langmuir part might have a certain mobility and proposed a more general form of Fick's law:

$$J = -D_D \frac{dC_D}{dx} - D_H \frac{dC_H}{dx} \quad (18.33)$$

where C_H = concentration of the gas held in “holes” (micro-voids)

D_D and D_H are separate diffusion coefficients of the two species (randomly dispersed and holes).

This form is actually that used by Koros and Paul (1978).

Equation (18.33) can be solved for the boundary conditions of transient permeation. The set of equations then obtained is given in table 18.9. These equations (18.34–18.37) enable us to derive S , C_H^s and b from experimental sorption isotherms, and the values of D_D and D_H from transient permeation experiments.

The equations contain a number of dimensionless groups:

$\frac{D_D \Theta}{L^2}$, a “model numeric” (see Chapter 3) ;

$$\left. \begin{aligned} \alpha &= \frac{b}{S} \\ K &= \frac{C_H^s \cdot b}{S} \end{aligned} \right\} \text{“intrinsic numerics of the polymer/gas combination ;”}$$

$F = \frac{D_H}{D_D}$, a “resultant numeric”, expressing an experimental result .

Figures 18.10a-b show an example of a calculated (and experimentally confirmed) behaviour of the diffusional time lag (Θ) and the permeability (P) in dimensionless form, as a function of the dimensionless variable bp ; K is held constant at a (realistic) value 10.

If $F = 0$, there is *total immobilization* of the penetrant population in the microvoids; if $F = 1$ there is *no immobilization* at all. In practice F has values in the neighbourhood of 0.1 (see fig. 18.10c).

Table 18.9 also gives a formula for the “effective diffusivity” at varying F , K and αC_D . Fig. 8.10d shows its graphical representation.

The available experimental data on the dual-mode sorption and mobility parameters have been summarized in table 18.10. Their number is too small to derive correlations with the chemical structure; only some tentative conclusions can be drawn. D_D and S may be estimated along similar rules as D and S in section I of this Chapter. From table 18.10 we may conclude that the values of α and F are of the order of 0.4 and 0.15, respectively. The parameter C_H^s remains as the great “unknown”. Barbari, Koros and Paul (1988) suggested that C_H^s probably will be proportional to the fractional volume of the holes; as a measure for it we may take the fractional unrelaxed volume of the glassy state: $f_H(V_g - V_1)/V_g$.

If for $V_g(T)$ and $V_1(T)$ the values derived in Chapter 4 are substituted (equations (4.26)), we obtain:

$$f_H = \frac{V_g(T) - V_1(T)}{V_g(T)} = 0.33(T_g - T) \cdot 10^{-3} \quad (18.38)$$

Barbari, Koros and Paul derived as full expression for C_H^s :

$$C_H^s = \frac{22,400}{V_p} \cdot f_H \quad (18.39)$$

TABLE 18.9
Main formulae of the dual-mode model of permeation*

Experiment	To measure:	To find:	Formula of dual mode model to be used:	Eq.	Limiting case in simplest (ideal) model
Sorption isotherm $C = f(p)$	C, p	S, b and $\frac{C_H^s}{C_D}$ calculate α and C_D	$C = Sp + \frac{C_H^s bp}{1 + bp} = C_D + C_H = C_D \left[1 + \frac{K}{1 + \alpha C_D} \right]$	(18.34)	$C = Sp$
Transient permeation $P = f(p)$	P	$D_D \approx D$ $\frac{FK}{C_H}$ calculate C_H and D_H	$P = SD_D \left[1 + \frac{FK}{1 + bp} \right] \xrightarrow{bp \rightarrow 0} SD_D [1 + FK] = SD_D + bC_H^s D_H$	(18.35)	$P = SD$
Diffusion time lag $\Theta = f(D)$	D	$\frac{D_D}{FK, K}$ calculate FK, K	$\frac{\Theta D_D}{L^2} = \frac{1}{6} [1 + f(F, K, b, p)] \xrightarrow{bp \rightarrow 0} \frac{\Theta D_D}{L^2} = \frac{1}{6} \left[\frac{1 + K}{1 + FK} \right]$	(18.36)	$\frac{\Theta D}{L^2} = \frac{1}{6}$
Effective diffusivity $D_{eff} = f(p, C, F)$	D_{eff}	$\frac{D_D, F, K}{D_0}$ calculate D_0	$D_{eff} = D_D \left[\frac{1 + \frac{FK}{(1 + \alpha C_D)^2}}{\frac{K}{1 + \frac{FK}{(1 + \alpha C_D)^2}}} \right] \xrightarrow{\alpha C_D \rightarrow 0} D_0 = D_D \left[\frac{1 + FK}{1 + K} \right]$	(18.37)	$D_{eff} = D = D_0$

* Index D means: (randomly) dispersed; index H means: in; holes (microvoids).

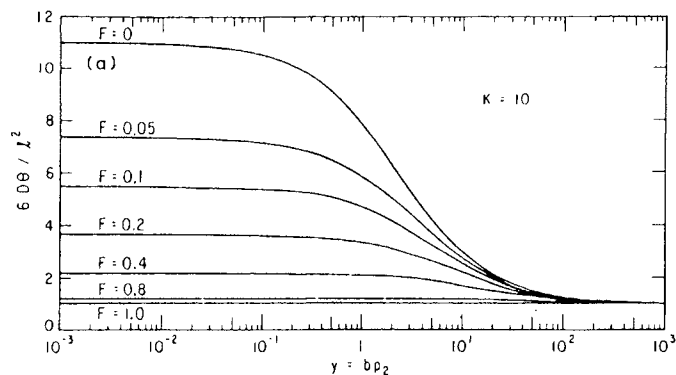


Fig. 18.10a. Time lag predicted from assumption that D is constant. From Paul & Koros (1976); Courtesy of John Wiley & Sons, Inc.

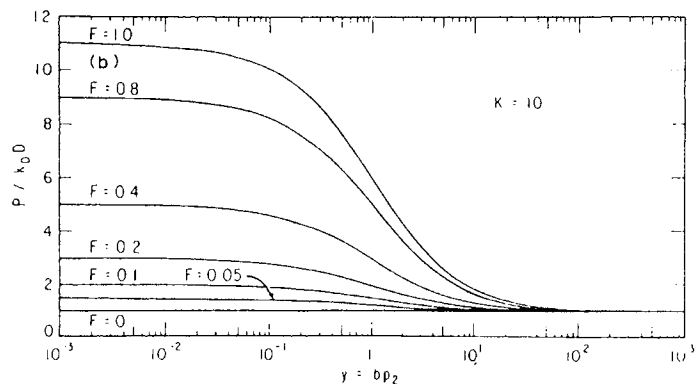


Fig. 18.10b. Permeability predicted from assumption that D is constant. From Paul & Koros (1976); Courtesy of John Wiley & Sons, Inc.

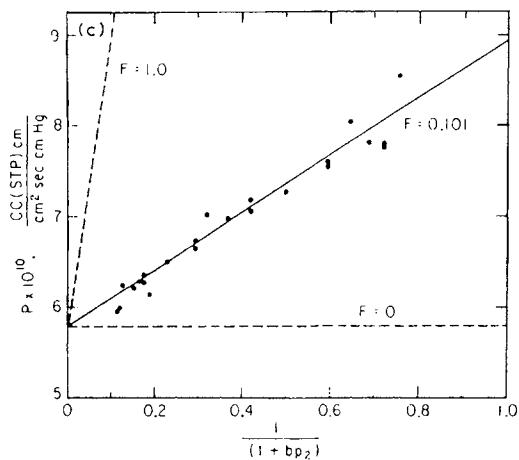


Fig. 18.10c. Permeability plotted in accordance with the partial immobilization model with D constant. From Koros, Paul & Rocha, (1976); Courtesy of John Wiley & Sons, Inc.

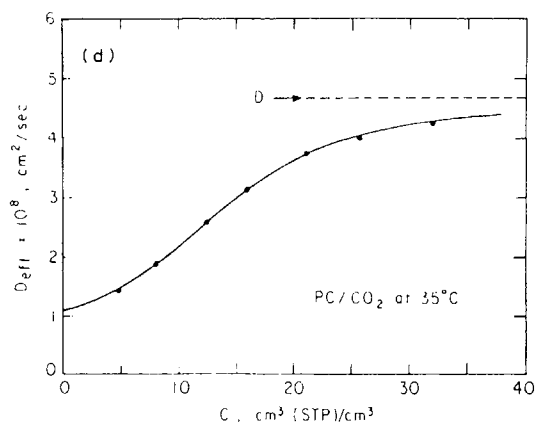


Fig. 18.10d. Concentration dependence of the effective diffusion coefficient. From Koros, Paul & Rocha (1976); Courtesy of John Wiley & Sons, Inc.

where

$$\frac{22,400}{V_p} = \frac{\text{Molar Volume (STP) of penetrant in gaseous state}}{\text{Molar Volume of penetrant in sorbed state (in "holes")}}$$

For permanent gases V_p will be of the order of the molar volume in the gaseous state, so that C_H^s will be small (of the order of 0.05); also the values of K and FK will consequently be very small.

For vapours whose critical temperature is higher than room temperature, however, V_p will be almost equal to the molar volume in the liquid state (capillary condensation) and C_H^s becomes:

$$C_H^s = 7.5(T_g - T)/V_p \quad (18.39a)$$

CO_2 is a typical "border case" ($T_{cr} = 304 \text{ K}$). For the V_p of CO_2 an average value for V_p of 55 can be calculated from the experimental data of $C_H^s(\text{CO}_2)$ for different glassy polymers (table 18.10); this is of the order of the critical molar volume of CO_2 .

An estimation of all the dual mode parameters is therefore possible in cases where no experimental data are available.

The dual-mode model proved rather successful to describe the isotherms and permeabilities at higher pressures.

Barrer (1984) suggested a further refinement of the dual-mode mobility model, including diffusive movements from the Henry's law mode to the Langmuir mode and the reverse; then four kinds of diffusion steps are basically possible. Barrer derived the flux expression based on the gradients of concentration for each kind of diffusion step. This leads to rather complicated equations, of which Sada (1987, 1988) proved that they describe the experimental results still better than the original dual-mode model. This, however, is not surprising, since two extra adaptable parameters are introduced.

The "gas-polymer-matrix model"

Another model for the sorption and transport of gases in glassy polymers at super-atmospheric pressures is the gas-polymer-matrix model, proposed by Raucher and Sefcik (1983). The premise of this model is that the penetrant molecules exist in the glassy polymer as a *single* population and that the observed pressure dependence of the mobility is *completely* due to gas-polymer interactions. In the mathematical representation of this model the following expressions for sorption and transport are used:

$$\left. \begin{aligned} C &= \sigma_0 \cdot p \cdot \exp(-\alpha C) \\ D &= D_0 \cdot \exp(\beta C) \\ p &= \sigma_0 \cdot D_0 \cdot \exp(-\alpha C) \cdot \exp(\beta C) \end{aligned} \right\} \quad (18.40)$$

where

σ_0 and D_0 are the infinite dilution solubility and diffusion coefficients, respectively α and β are constants describing the effect of gas-polymer interactions on changes in solubility and mobility, respectively.

Also this model describes the experimental data very properly.

A comparison of the two models ("dual-mode" and "matrix") was made by Barbari, Koros and Paul (1988) on the basis of their experimental data. They state that both models give a good description of the experiments; yet the dual mode model has their preference, since it has simple physical interpretations of the parameters and can be related rather well to gas and polymer characteristics. The parameters of the matrix model do, however, not follow any consistent trend.

Although the dual-mode model seems to be favoured at this moment, the relative validity of the two models is not yet firmly established. Quoting Rogers (1985) we may conclude, that "it must be realised that both models are only approximations which require estimation of a number of parameters".

2. Moisture absorption and transport

The behaviour of water in polymers presents a special case, due to the nature of the water molecule. This molecule is relatively small and has a strong tendency towards hydrogen bond formation in its own liquid and solid state as well as with other polar groups. In polar polymers both equilibrium sorption and diffusivity are strongly influenced by these interactions, but also in less polar polymers anomalies, e.g. association of sorbed water molecules, may occur ("clustering").

Equilibrium sorption of water (solubility) is described by the different isotherms of the Brunauer–Emmett–Teller classification.

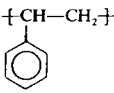
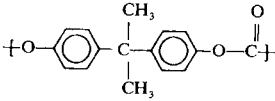
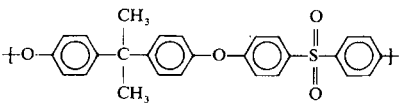
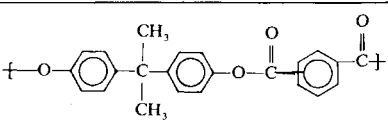
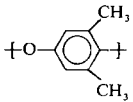
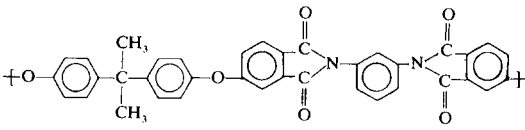
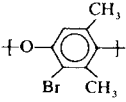
In most hydrophilic polymers, such as cellulose and proteins, each polar group interacts strongly with only one water molecule. In hydrophobic polymers such as polyolefins, on the other hand, Henry's law is obeyed over the complete range of relative pressures and only minute quantities of water are sorbed.

The more polar groups are present in the polymer matrix, the higher its sorptive affinity for water will be. However, the accessibility of the polar groups, the relative strength of the water–water versus the water–polymer bonds and the degree of crystallinity of the

TABLE 18.10

Dual mode sorption and mobility data of glassy amorphous polymers (values at 35°C)

Data from Sada et al. (1987); Chern et al. (1987); Barbari, Koros and Paul (1988)

Polymer	Structural formula	T_g		ρ g/cm ³	Gases
		°C	K		
Polystyrene PS		100	373	1.05	CO ₂ CH ₄ N ₂
Polycarbonate PC Lexan®		150	423	1.20	CO ₂ CH ₄ N ₂
Polysulfone PSF		186	451	1.24	CO ₂ CH ₄ N ₂
Polyarylate PAR Ardel 100®		190	463	1.21	CO ₂ CH ₄ N ₂
Poly oxide PDMPPO PPO®		210	483	1.06	CO ₂ CH ₄ N ₂
Polyetherimide PEI Ultem®		215	488	1.28	CO ₂ CH ₄ N ₂
Brominated PPO (91% aryl substitution)		262	535	1.38	CO ₂ CH ₄ N ₂

polymer matrix are very important factors, which explain the fact that no simple correlation between number of polar groups and solubility exists. For instance, well-defined crystallites are inaccessible to water, but on the surfaces of the crystallites the polar groups will "react with water".

Barrie (1968) collected all the known data on water sorption. From these data it is possible to estimate the effect of the different structural groups on water sorption at different degrees of humidity. Table 18.11 presents the best possible approach to the sorptive capacity of polymers versus water, namely the amount of water per structural group at equilibrium, expressed as molar ratio. From these data the solubility (cm³ water

S	C_H^s	b	D_D	D_H	α	K	F	FK
$\text{cm}^3 \text{ STP}/\text{cm}^3$	$\text{cm}^3 \text{ STP}/\text{cm}^3$	bar^{-1}	$\text{cm}^2/\text{s} \times 10^8$	$\text{cm}^2/\text{s} \times 10^8$	$= b/S$	$= \alpha C_H^s$	$= D_H/D_D$	–
0.65	9.45	0.11	11.9	3.8	0.17	1.6	0.32	0.51
0.26	4.7	0.055	1.9	0.9	0.21	0.95	0.47	0.45
–	–	–	6	–	–	–	–	–
0.69	18.8	0.26	6.22	0.49	0.38	7.1	0.08	0.56
0.29	8.4	0.084	1.09	0.13	0.29	4.7	0.12	0.54
0.09	2.1	0.056	1.76	0.51	0.63	1.3	0.29	0.38
0.66	17.9	0.33	4.5	0.54	0.53	9.0	0.12	1.1
0.16	9.9	0.7	0.09	0.12	0.44	6.9	0.17	1.2
0.075	10.0	0.015	0.93	0.53	0.20	2.1	0.60	1.25
0.63	22.7	0.215	6.9	0.86	0.34	7.7	0.13	0.96
0.18	6.5	0.10	1.3	0.21	0.53	3.6	0.16	0.57
0.08	1.2	0.07	2.75	0.41	0.88	1.1	0.16	0.17
0.92	32.7	0.20	36.8	3.7	0.24	7.1	0.10	0.71
0.32	22.7	0.107	6.2	0.43	0.34	7.4	0.07	0.52
0.15	10.0	0.048	–	–	0.32	–	–	–
0.76	25.0	0.37	1.14	0.07	0.49	12	0.063	0.76
0.21	7.3	0.14	0.11	0.01	0.67	4.9	0.073	0.36
0.063	4.15	0.045	0.57	0.02	0.71	2.9	0.042	0.12
2.57	37.5	0.29	4.82	3.3	0.11	4.3	0.07	0.30
1.32	26.9	0.12	6.1	0.2	0.10	2.5	0.05	0.13
0.57	15.1	0.06	–	–	0.10	–	–	–

vapour (STP) per cm^3 of polymer) can be easily calculated. (The multiplication factor is $22.4 \times 10^3/V$, where V is the molar volume per structural polymer unit.)



The heat of sorption is of the order of 25 kJ/mol for non-polar polymers and 40 kJ/mol for polar polymers.

Example 18.4

Estimate the moisture content of nylon 6,6 at 25°C and a relative humidity of 0.7. The crystallinity is 70%.

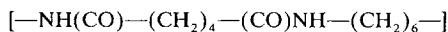
TABLE 18.11

Molar water content of polymers per structural group at different relative humidities at 25°C

Group	Relative humidity				
	0.3	0.5	0.7	0.9	1.0
$\left. \begin{array}{l} \text{—CH}_3 \\ \text{—CH}_2\text{—} \\ \text{—CH—} \end{array} \right\}$	(1.5×10^{-5})	(2.5×10^{-5})	(3.3×10^{-5})	(4.5×10^{-5})	(5×10^{-5})
	0.001	0.002	0.003	0.004	0.005
>C=O	0.025	0.055	(0.11)	(0.20)	(0.3)
—C(=O)O—	0.025	0.05	0.075	0.14	0.2
	0.006	0.01	0.02	0.06	0.1
—OH	0.35	0.5	0.75	1.5	2
—NH ₂	0.35	0.5	0.75	(1.5)	(2)
—NH ₃ [⊕]			2.8	5.3	
—COOH	0.2	0.3	0.6	1.0	1.3
—COO [−]	1.1	2.1	4.2		
—C(=O)NH—	0.35	0.5	0.75	1.5	2
—Cl	0.003	0.006	0.015	0.06	(0.1)
—CN	0.015	0.02	0.065	0.22	(0.3)

Solution

The structural unit is



From table 18.11 it is evident that the sorptive capacity of the CH₂ groups may be neglected. So we have two CONH groups per structural unit with a molar water content (at a relative humidity of 0.7) of

$$2 \times 0.75 = 1.5 \text{ mole/structural unit.}$$

The molar weight of the structural unit is 226.3, so that $1.5 \times 18 \text{ g}$ water is absorbed on 226.3 g of polymer or 12 grams per 100 g. Taking the crystallinity into account and using formula (18.10) we get for the solubility of the (semi-) crystalline polymer:

$$0.3 \times 12 = 3.6 \text{ grams per 100 g polymer.}$$

This is in good agreement with the experimental value (4 g/100 g).

Also the diffusivity of water in polymers is highly dependent on the polymer–water interaction.

When a polymer contains many hydrogen-bonding groups (cellulose, poly(vinyl alcohol), proteins, etc., and to a lesser extent synthetic polyamides) the diffusivity increases with the water content. This is explained by the strong localization of the initially sorbed water over a limited number of sites, whereas at higher water contents the polymer matrix will swell and the sorbed water will be more and more mobile. As a good approximation the following expression can be used:

$$\log D = \log D_{w=0} + 0.08w \quad (18.41)$$

where w = water content in weight per cent.

Compared with the nonhydrophilic polymers the diffusivity as such is greatly retarded by the strong interaction forces: instead of (18.13a-b) one now finds the relationship:

for water in hydrophilic polymers

$$\log D_0 \approx \frac{E_D \times 10^{-3}}{R} - 7 \quad (18.42)$$

with E_D expressed in J/mol.

The other extreme is formed by the less hydrophilic polymers such as polyethers and polymethacrylates. Here the diffusivity markedly decreases with increasing water content. This is explained by the increasing “clustering” of water in the polymer (at polar “centres” or in microcavities) so as to render part of the water comparatively immobile. In this case the influence of water can be approximated by the expression:

$$\log D = \log D_{w=0} - 0.08w \quad (18.43)$$

where w = water content in weight per cent.

Furthermore the relationship between D_0 and E_D is the same as for other simple gases.

The third case is that of really hydrophobic polymers, such as polyolefins and certain polyesters. Here the solubility is very low (thermodynamically “ideal” behaviour) and the diffusivity is independent of the water content. Water vapour then diffuses in exactly the same way as the other simple gases.

It will be clear that the diffusive transport (permeability) of water in and through polymers is of extreme importance, since all our clothes are made of polymeric materials and water vapour transport is one of the principal factors of physiological comfort.

3. Diffusion of organic vapours

The diffusion behaviour of organic vapours is much more complicated than that of simple gases. Normally the interaction is much stronger, so that the diffusion coefficient becomes dependent on the concentration of the penetrant:

$$D = D_{c=0} f(c) \quad (18.44)$$

Empirical equations for $f(c)$ are:

$$\left. \begin{aligned} f(c) &= \exp(\alpha c) & c &= \text{concentration} \\ f(c) &= \exp(\beta \phi) & \phi &= \text{volume fraction} \\ f(c) &= \exp(\gamma a) & a &= \text{activity} \end{aligned} \right\} \text{ of penetrant} \quad (18.45)$$

α , β and γ are temperature-dependent constants.

Usually the concentration dependence of D is reduced as the temperature is raised. The general equation for D then becomes:

$$D = D_0 \exp(-E_{D,0}/RT) f(c) \quad (18.46)$$

If for a small temperature range a mean activation energy E_D is defined by

$$D = D_0 \exp(E_D/RT)$$

we get from the last two equations:

$$E_D = E_{D,0} - \left[R \frac{\partial \ln f(c)}{\partial (1/T)} \right] \quad (18.47)$$

So the apparent activation energy is also concentration-dependent! If $f(c)$ is a monotonically increasing function, E_D will decrease continuously with increasing c . If $f(c)$ is a monotonically decreasing function, E_D increases continuously with c .

For the diffusion of benzene in natural rubber the apparent activation energy decreases from 48 kJ/mol at $c=0$ to 35 kJ/mol at a volume fraction of 0.08. $E_{D,0}$ shows a discontinuity at transition temperatures.

For organic vapours the correlation $E_D \sim d^2$ which was found for simple gases cannot be used any longer. Zhurkov and Ryskin (1954) and Duda and Vrentas (1968) correlated the energy of activation E_D with the molar volume of the diffusing molecules (V_D). Their results are reproduced in fig. 18.11 and show that there is a linear correlation between E_D and V_D at very low concentrations of the diffusate (where the polymer does not show any swelling).

4. Diffusion of liquids

Diffusion coefficients of organic liquids in rubber have been determined by Southern and Thomas (1967), who followed the kinetics of mass uptake of a rubber sheet immersed in the liquid. Anomalies in the mass uptake–time relation were found and are due to stresses set up in the sheet during swelling and to their variation as swelling proceeds. These anomalies could be eliminated by the use of specimens constrained laterally by bonding to metal plates, which maintains boundary conditions constant during swelling. At liquid concentrations used (up to volume fractions of 0.8 for the best swelling agents!) the diffusion coefficient was shown to depend on the liquid viscosity rather than on the compatibility of rubber and liquid. Fig. 8.12 shows the relationship found, which might have a more general significance.

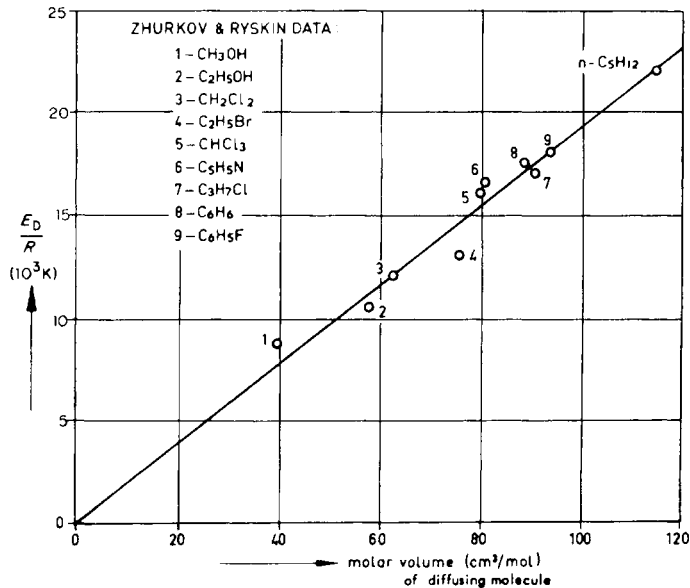


Fig. 18.11. Correlation of activation energy for diffusion in polystyrene with molar volume for temperature range $T_g < T$.

5. Self-diffusion

Self-diffusion is the exchange of molecules in a homogeneous material by a kind of internal flow. It has a direct bearing on *tackiness*, which depends on interpretation by diffusion of polymer molecules at the interface; this effect is well known in elastomers.

Bueche et al. (1952) derived that the coefficient for self-diffusion of poly(n-butyl

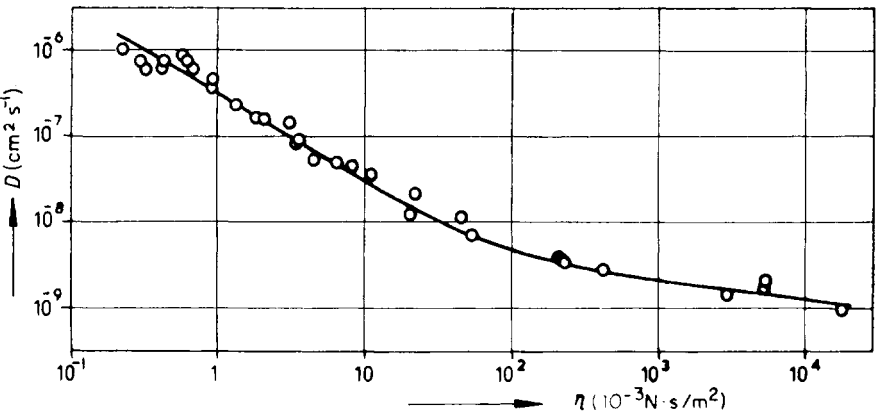


Fig. 18.12. Relation between diffusion coefficient D and liquid viscosity η for various liquids in natural rubber at 25°C (after Southern and Thomas, 1967).

acrylate) is inversely proportional to the bulk viscosity of this polymer¹. Also in the natural rubber–polyisoprene diffusion system a clear connection appears to exist between diffusion coefficient and bulk viscosity.

The energy of activation for self-diffusion of polymers is almost exactly equal to that of viscous flow, as was demonstrated by Bueche et al. Van Amerongen (1964) suggested that the activation energy for self-diffusion of low-molecular-weight material increases with molecular weight, levelling off above a molecular weight corresponding to that of a polymer chain section capable of making independent diffusion jumps. The limiting value would be the same as that of the activation energy for viscous flow.

6. General description of polymer–penetrant system

Hopfenberg and Frisch (1969) succeeded in describing all observed behavioural features for a given polymer–penetrant system in a diagram of temperature versus penetrant activity, which seems to be of general significance for amorphous polymers. It is reproduced in fig. 18.13.

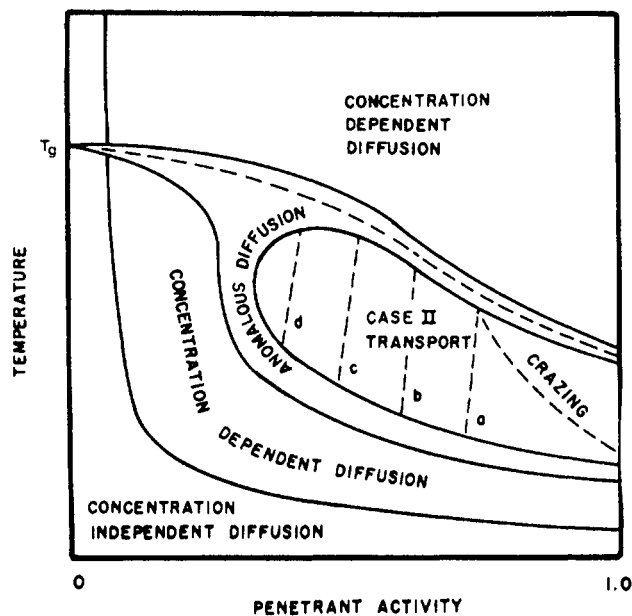


Fig. 18.13. Transport features in the various regions of the temperature–penetrant activity plane. Lines a, b, c, d are lines of constant activation energy. $E_{act_a} > E_{act_b} > E_{act_c} > E_{act_d}$ (after Hopfenberg and Frisch, 1969).

¹ The following expression may be used as a good approximation:

$$D\eta \approx CkT \quad (18.48)$$

where k is the Boltzmann constant ($1.38 \times 10^{-23} \text{ J} \cdot \text{K}^{-1}$) and $C \approx 10^9 \text{ m}^{-1}$.

Concentration-independent diffusion only occurs at low temperatures and/or low penetrant “activities”. At high penetrant activities over a range of temperatures well below T_g the transport of penetrant into the polymer is accompanied by solvent crazing or cracking: the osmotic stresses produced by the penetrant are sufficiently large to cause local fracture of the material.

Between these two extremes there are a series of transitions. The so-called “Case II” transport (Alfrey et al., 1966) or “partial penetrant stress controlled transport” is characterized by an activation energy which increases with the penetrant activity. It is a highly activated process (80–200 kJ/mol) and is confined to temperatures in the vicinity of and below the effective T_g of the system (dashed line in the figure)

The region of “Case II” sorption (relaxation-controlled transport) is separated from the Fickian diffusion region by a region where both relaxation and diffusion mechanisms are operative, giving rise to diffusional anomalies; time-dependent or anomalous diffusion.

Next to it is the concentration-dependent Fickian diffusion zone which is characteristic of many small organic molecules of moderate to high activity at temperatures above or sufficiently below the effective T_g of the system.

Outstanding work of more recent date was done by Vrentas and Duda. For this we have to refer to their contribution in the Encyclopedia of Polymer Science and Engineering (1986) and their papers since 1976. They introduced an important dimensionless quantity which is characteristic for polymer-solvent systems: the *Deborah number*.

It is defined in the following way:

$$(N_{\text{Deb}})_D = \frac{\lambda_m}{\Theta_D} = \frac{\text{Characteristic time of the fluid}}{\text{Characteristic time of diffusion}} \quad (18.49)$$

As an illustration one of their diagrams is reproduced here (see fig. 18.14).

Recently they found (1986) that there are at least two Fickian regions for polymer-solvent diffusion which can be observed by varying the time scale, keeping the other parameters (T , c and M) constant. A low-frequency region is a viscous Fickian diffusion region, and a high-frequency region is a rubberlike elastic Fickian diffusion region.

C. DISSOLUTION OF POLYMERS AS A CASE OF PERMEATION

The first phase of the process of polymer dissolution is the penetration of solvent molecules into the polymer structure. This results in a *quasi-induction period*, i.e. the time necessary to build up a swollen surface layer. The relationship between this “swelling time” Θ_{sw} and the thickness of the swollen surface layer δ is:

$$\Theta_{\text{sw}} = \frac{\delta^2}{6\bar{D}} \quad (18.50)$$

where \bar{D} is the mean diffusion coefficient of the penetrating molecule.

After this quasi-induction period a *steady state* may develop. During this steady state the volume-diffusion fluxes of the solvent and of the polymer will be equal. Then the *rate of*

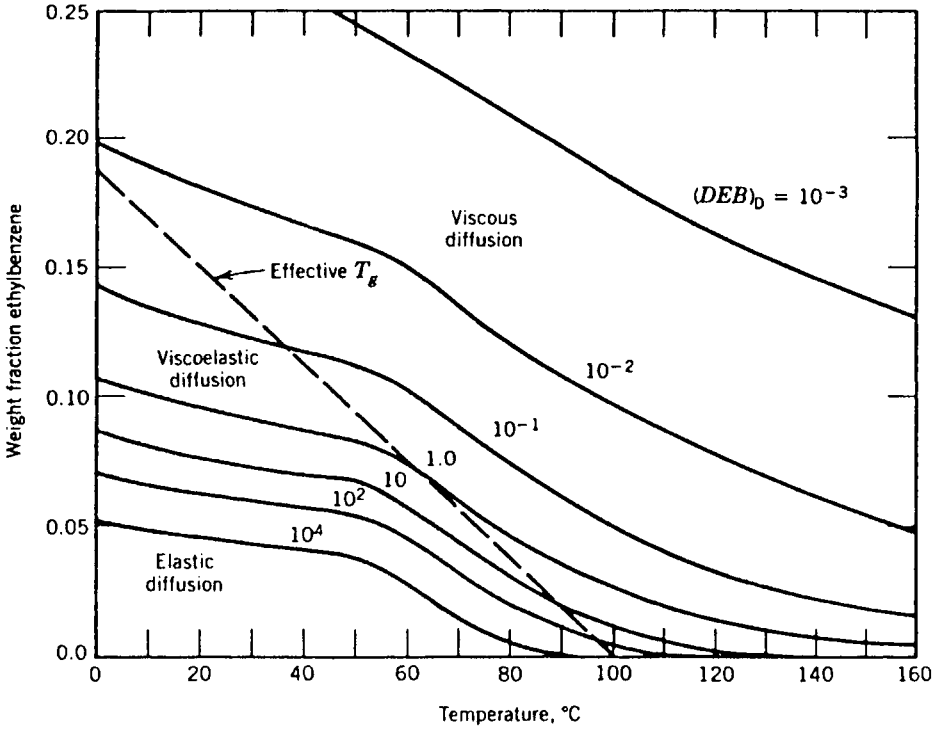


Fig. 18.14. Deborah number diagram for ethylbenzene-polystyrene system with $M = 3 \times 10^5$ and $L = 10^{-3}$ cm.

dissolution will be:

$$\dot{s} = \frac{\bar{D}}{\delta} \Delta\phi_s \tag{18.51}$$

where ϕ_s is the volume fraction of the solvent and $\Delta\phi_s$ is the total gradient in solvent concentration (expressed in volume fractions) between liquid and polymer surface.

If the dissolution takes place in pure solvent, $\Delta\phi_s$ is unity, so that (18.41) becomes:

$$\dot{s} = \frac{\bar{D}}{\delta} . \tag{18.52}$$

1. The diffusion layer

According to Ueberreiter (1968) the integral surface layer (δ) on glassy polymers is composed of four sublayers:

- δ_1 , the *hydrodynamic liquid layer*, which surrounds every solid in a moving liquid
- δ_2 , the *gel layer*, which contains swollen polymer material in a rubber-like state
- δ_3 , the *solid swollen layer*, in which the polymer is in the glassy state
- δ_4 , the *solid infiltration layer*, i.e. the channels and holes in the polymer filled with solvent molecules.

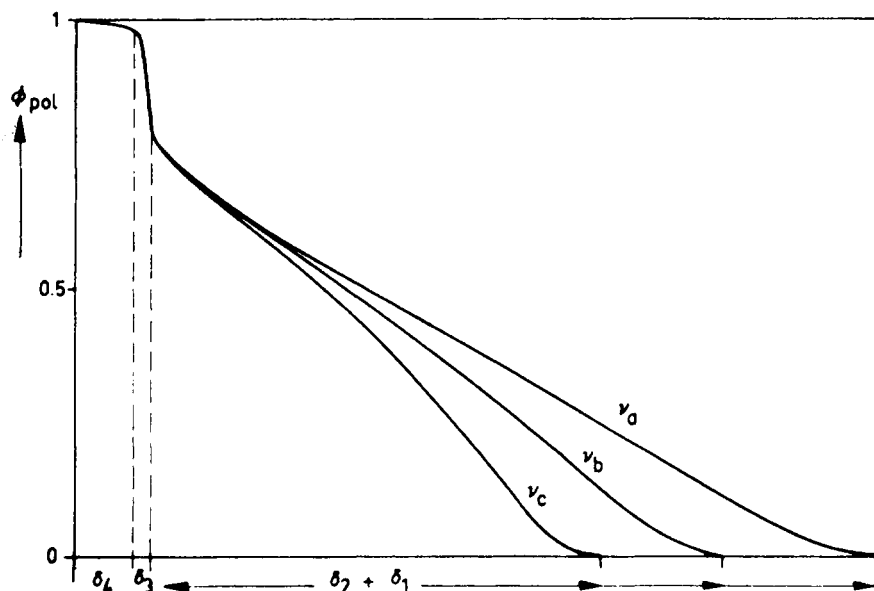


Fig. 18.15. Polymer concentration in the surface layer vs. layer thickness δ . δ_4 = infiltration layer; δ_3 = solid swollen layer; $\delta_2 + \delta_1$ = gel and liquid layer; v_{a-c} = frequency of the stirrer (Ueberreiter, 1968).

Fig. 18.15 gives an impression of the size of these sublayers and of the polymer concentration in them. Quantitatively, δ_1 and δ_2 are by far the most important sublayers. It is obvious that the thickness of the surface layer (δ) will be influenced by the degree of turbulence in the liquid. Since the latter is characterized by the Reynolds number ($N_{Re} = vL\rho/\eta$), one may expect a correlation between δ and N_{Re} . This has been found indeed, as is shown in fig. 18.16. Below the glass transition temperature the influence of

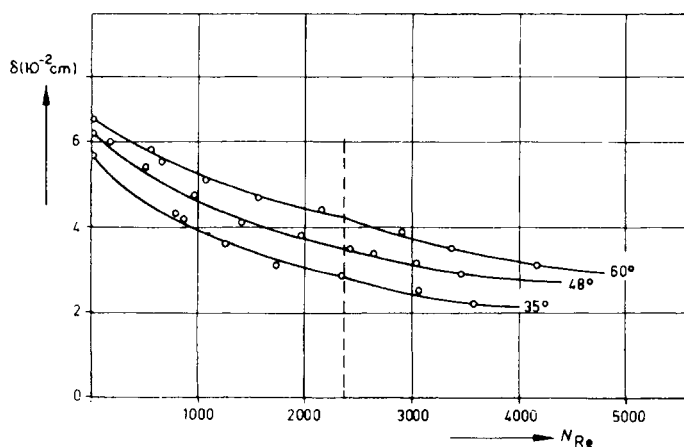


Fig. 18.16. Thickness of surface layer δ vs. Reynolds number, N_{Re} . Temperatures of dissolution are indicated (Ueberreiter and Kirchner, 1965).

the temperature on δ follows the relation:

$$\delta = \delta_0 \exp(-A/T) \quad (18.53)$$

and indicates a dependence of the stability of the gel layer on the viscosity within it; δ increases with temperature! The value of A is of the order of 1000 (K).

Finally, as can also be expected, δ is dependent on the molecular weight of the polymer. In the normal range of molecular weights a relationship of the form

$$\delta = kM^{1/2}$$

has been found. For molecular weights higher than 6×10^5 , δ increases rapidly, possibly due to increasing entanglement of the macromolecules.

The overall expression for δ (integral surface layer) for polymers of the "normal" molecular weight range becomes:

$$\delta(\text{cm}) \approx 0.35 \times 10^{-2} M^{1/2} \frac{\exp(-A/T)}{1 + 0.35 \times 10^{-3} N_{\text{Re}}} \quad (18.54)$$

δ itself is of the order of $10^{-2} - 10^{-1}$ cm at usual temperatures and molecular weights. Asmussen and Ueberreiter (1962) showed that the quantity

$$\frac{\text{layer thickness } (\delta)}{\text{coil diameter of polymer molecule } \langle h^2 \rangle^{1/2}} \quad (18.55)$$

is nearly constant ($\approx 1.2 \times 10^4$ at room temperature).

According to Chapter 9

$$\langle h^2 \rangle^{1/2} = \alpha M^{1/2} \left(\frac{K_{\Theta}}{\Phi_0} \right)^{1/3}$$

and $\Phi_0 \approx 2.5 \times 10^{23} \text{ mol}^{-1}$.

2. Diffusivity

Earlier (Ch. 18B.4) we have shown that the diffusion coefficient of liquid penetrants appears to be determined by the viscosity of the solvent (at room temperature) as a measure of molecular size. This conclusion is confirmed by experiments of Ueberreiter (1965) on plasticizers where \dot{s} and δ were measured simultaneously and \bar{D} could be calculated from (18.52).

3. Types of dissolution

Ueberreiter (1968) demonstrated that the state of a polymer influences the type of dissolution to a great extent.

If an amorphous polymer is dissolved at a sufficiently high temperature, viz. higher than the "flow temperature" (which is the limit of the rubbery state), the surface layer will consist of δ_1 only: the dissolution process is reduced to a simple mixing of two liquids.

If the polymer is in its rubber-elastic state, the surface layer will contain δ_1 and δ_2 . Solvent molecules are able to penetrate faster into the polymer matrix than the macromolecules can be disentangled and transported into the solution.

Most of the amorphous polymers are dissolved when they are in the glassy solid state. In this case the surface layer is "fully developed". The solid state of the polymer permits the existence of all four layers. The gel layer δ_2 is very important because it heals the cracks and holes which have been created by the penetrating front of dissolving macromolecules.

In some cases dissolution without a gel layer is found, especially at low temperatures. It appears that dissolution by stress cracking is the cause of this phenomenon. Cracks are observed which run into the polymer matrix, combine to form small blocks of the polymer, which leave the surface in a kind of eruption process. Large amounts of stored stress energy, frozen in the glass transition interval and concentrated along the wider channels and hole systems, seem to be responsible for this process. In the extreme case of the original sublayers only δ_1 remains. In this process no induction period exists.

Different from the dissolution of amorphous polymers is that of semi-crystalline ones. Dissolution of these polymers is much more difficult than that in the glassy state, as the enthalpy of melting has to be supplied by the solvent. Many solvents which are able to dissolve tactic but glassy polymers, are unable to dissolve the same polymer in the crystalline state. Asmussen et al. (1965) have found that the velocity of dissolution of crystalline polymers as a function of temperature closely resembles the velocity of crystallization versus temperature curves. Polymers formed at the highest rate of growth also dissolve at the highest rate.

Example 18.5

Estimate the rate of dissolution of polystyrene in toluene at 35°C (308 K)

a) at a very low Reynolds number ($N_{Re} \approx 0$), b) at a Reynolds number of 1000.

The molecular weight of polystyrene is 150,000; the diffusivity of toluene in polystyrene at 35°C is about $1.5 \times 10^{-6} \text{ cm}^2/\text{s}$.

Solution

We apply formula (18.54)

a) at $N_{Re} \approx 0$:

$$\begin{aligned}\delta &\approx 0.35 \times 10^{-2} \times (150,000)^{1/2} \times \exp(-1000/308) \\ &= 0.35 \times 10^{-2} \times 3.87 \times 10^2 \times 3.88 \times 10^{-2} = 5.25 \times 10^{-2} \text{ cm}.\end{aligned}$$

b) at $N_{Re} = 1000$:

$$\delta \approx 0.35 \times 10^{-2} \times 3.87 \times 10^2 \times \frac{3.88 \times 10^{-2}}{1 + 0.35} = 3.9 \times 10^{-2} \text{ cm}.$$

We check this value with formula (18.55).

From Chapter 9 we know that K_Θ of polystyrene is $0.08 \text{ cm}^3 \cdot \text{mol}^{1/2} \cdot \text{g}^{-3/2}$. So

$$\begin{aligned}\langle h^2 \rangle^{1/2} &= \alpha M^{1/2} \left(\frac{K_\Theta}{2.5 \times 10^{23}} \right)^{1/3} = \alpha \times 3.87 \times 10^2 \left(\frac{0.08}{2.5 \times 10^{23}} \right)^{1/3} \\ &= \alpha \cdot 3.87 \times 10^2 \times (0.32 \times 10^{-24})^{1/3} = \alpha \cdot 2.65 \times 10^{-6} \text{ cm}.\end{aligned}$$

Since $\alpha \approx 1.4$, we get

$$\delta \approx 1.2 \times 10^4 \langle h^2 \rangle^{1/2} = 1.2 \times 10^4 \times 1.4 \times 2.65 \times 10^{-6} \approx 4.5 \times 10^{-2} \text{ cm (at } 25^\circ\text{C)}$$

in good agreement.

The rate of dissolution is

$$\dot{s} = \frac{\bar{D}}{\delta} = \frac{1.5 \times 10^{-6}}{5.25 \times 10^{-2}} \approx 3 \times 10^{-5} \text{ cm/s at } N_{\text{Re}} \approx 0.$$

Ueberreiter and Kirchner (1965) measured a value of 5×10^{-5} cm/s. The agreement may be considered fair.

At $N_{\text{Re}} = 1000$

$$\dot{s} = \frac{\bar{D}}{\delta} = \frac{1.5 \times 10^{-6}}{3.9 \times 10^{-2}} \approx 4 \times 10^{-5} \text{ cm/s.}$$

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