PERMEATION THROUGH ELASTOMERIC O-RING SEALS*

K. BREHM, K.H. ECKER,
H. KOWALEWSKY, H.-P. WEISE
Federal Institute for Materials Testing,
Berlin (West)

Abstract

PERMEATION THROUGH ELASTOMERIC O-RING SEALS.

Permeation of He, Ne, Ar, Kr, Xe and D_2 through O-ring seals of fluorocarbon rubber (e.g. Viton), ethylene-propylene rubber (EPDM) and silicone rubber (VMQ) has been measured at temperatures from 290 K up to the destruction of the materials, at about 600 to 700 K. Test gas pressures Δp up to 2 bar were applied. The quantity of the test gas that permeated was detected using high sensitivity quadrupole mass spectrometry. To investigate the influence of seal geometry, permeation through VMQ O-rings was measured as a function of their compression and compared with measurements of sheet geometry for the same material. The measured time dependence of the permeation gas flow is well described by theoretical predictions, when the flow through the O-ring is considered as the sum of flows through a number of rectangular slabs approximating the shape of the compressed O-ring. Equilibrium gas flow, the permeation coefficient, solubility, the diffusion coefficient, the activation energy of diffusion and the heat of solution are derived from the measurements and are compared with values given in the literature, where available. By extrapolating the results for rare gases He to Xe, permeation parameters for Rn are estimated for the three elastomers under investigation.

1. INTRODUCTION

The containment of radioactive gases, including fission products, in transport or storage casks is primarily determined by the construction of the sealing system and the choice of the sealing material. Permeation of gaseous radionuclides through the gasket is a major activity leakage factor when using elastomeric seals. Permeation parameters are usually derived from measurements of the gas flow Q through a seal as a function of time t after the application of a pressure gradient Δp of a test gas. In most cases, experimental data are given for the permeation of gas through a sheet and for temperatures up to 400 K. To permit a realistic estimate of the gas release from typical containment systems with O-ring seals at elevated temperatures, we have extended our previous flat-geometry permeation measurements [1] in three ways.

First, in order to relate parameters obtained from measurements using different seal geometries, we have measured Q(t) for silicone rubber O-rings of various compressions and compared it with measurements on a sheet of the same sealing

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material. Second, measurements were performed up to temperatures where the sealing failed in order to get an idea of the safety margins of a sealing system. Finally, from the range of test gases used (i.e. D_2, He, Ne, Ar, Kr and Xe), an attempt is made to give a rough estimate of permeation parameters for the radioactive gases tritium and radon, important for design considerations of casks for nuclear wastes.

2. EXPERIMENT

Figure 1 is a diagram of the apparatus used for permeation measurements. Sheet — as well as O-ring — samples up to an outer diameter of 16 cm are mounted in an all-metal, sealed permeation cell, which is held in an oven at a temperature in the range between 20 and 500°C. Test gases up to 2 bar are applied to one side of the permeation cell, while the other side is kept at high vacuum by turbomolecular pumps. A quadrupole mass spectrometer (QMS) is used to measure the partial pressure of the test gas on the high-vacuum side. This pressure is proportional to the flow of the permeating gas. A system of two throttle valves permits the handling of a wide range of gas flows with high detection sensitivity, while still maintaining the total pressure in the QMS below 10^{-6} mbar, necessary for reliable mass spectrometry. The system is calibrated with known gas flows through a capillary (for details, see Ref. [2]). The control of the measurement procedure, as well as the data acquisition and analysis, is fully automated using a personal computer with interfaces to the experiment based on the IEE-bus.

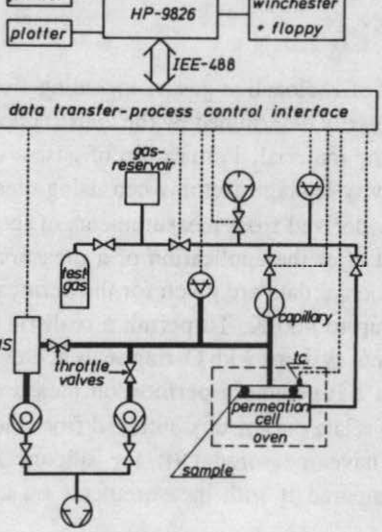

FIG. 1. Experimental setup for permeation measurements.

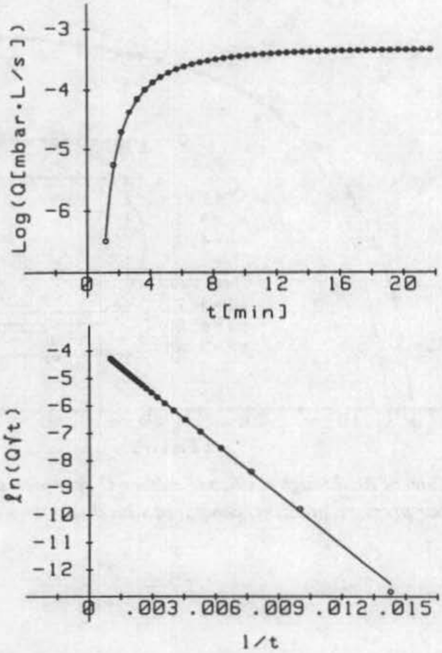

FIG. 2. Permeation gas flow of Ar through a silicone rubber sheet as a function of time and compared with theory.

3. RESULTS AND DISCUSSION

Figure 2(a) shows the gas flow Q as a function of time t for a typical permeation experiment on a silicone rubber sheet. The initial rising part of the curve can be well described by the 'Holstein approximation' [3]:

$$Q(t) = Q_\infty \, (2d/\sqrt{\pi D t}) \, \exp(-d^2/(4\,Dt)) \text{ for } t < 0.4\, d^2/D \tag{1}$$

The equilibrium gas flow (i.e. the asymptotic value for $t \rightarrow \infty$) is represented by the constant factor

$$Q_\infty = A \cdot P \cdot \Delta p/d \tag{2}$$

Here A is the surface area of the sheet, d its thickness and p is the difference of partial pressures of the test gas on the two sides of the sample. P and D are permeation and diffusion coefficients which are coupled by

$$P = \alpha \cdot D \tag{3}$$

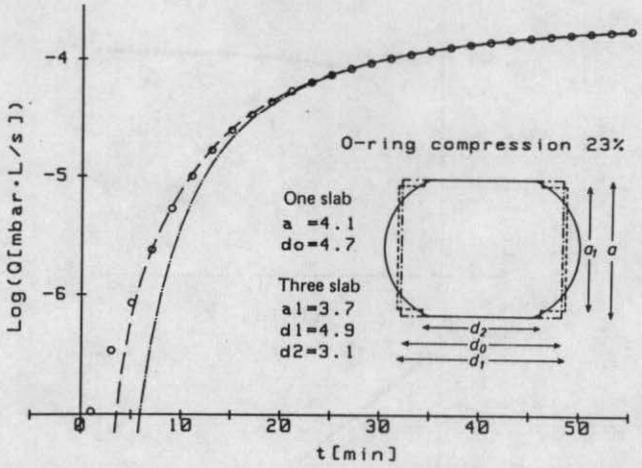

FIG. 3. Permeation gas flow of Ar through a silicone rubber O-ring with dimensions 153×5.33 mm, compression 23% and 1 bar pressure gradient, compared with theory (—·—·— one slab; --- three slab approximation).

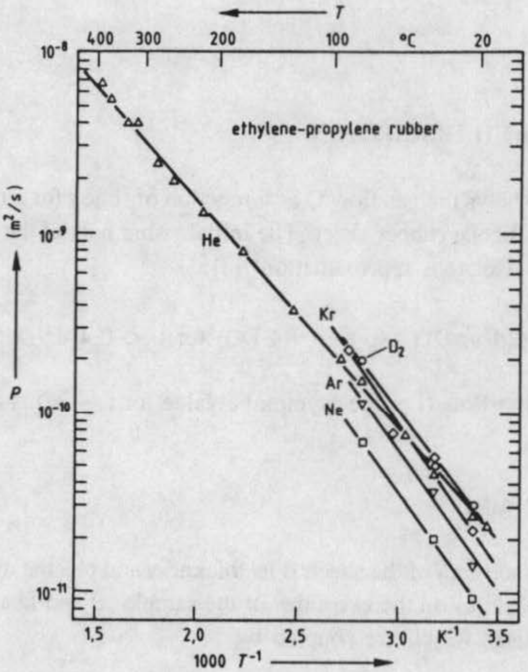

FIG. 4. Permeation coefficients as functions of temperature for EPDM.

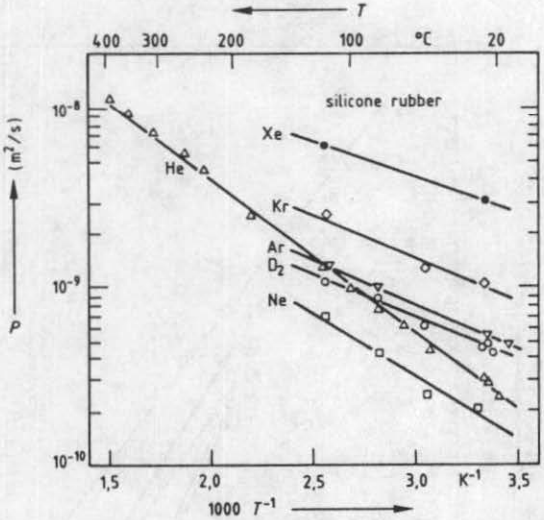

FIG. 5. Permeation coefficients as functions of temperature for silicone rubber.

with α being the solubility of the gas in the sealing material. Rewriting Eq. (1), a linear relationship between $\ln (Q(t)\sqrt{t})$ and $1/t$ can be obtained:

$$\ln (Q(t)\sqrt{t}) = \ln (Q_\infty \, 2d/\sqrt{\pi D}) - d^2/4Dt \qquad (4)$$

For flat samples, the coefficients P, for permeation, and D, for diffusion, are determined by a least squares fit (Fig. 2(b)) of this relation to the experimental data points, with $t < 0.4\, d^2/D$. Since Q usually changes by several orders of magnitude during the early stages of an experiment, for the determination of D, in particular, a fit to (4) is preferred to a fit to (1), which would emphasize data points at high values of Q at long times. In such cases, where the equilibrium permeation flow Q_∞ was actually reached (i.e. for times $t \gg 0.4\, d^2/D$), P is determined from the experimental Q_∞ using Eq. (2).

For samples with O-ring geometry, the shapes of the experimental permeation curves Q(t) deviate from the theoretical predictions for flat geometry (Eq. (1)). At short times, especially, a considerable deviation is observed (as depicted in Fig. 3) for the case of a silicone rubber O-ring compressed by 23%. The dashed-dotted line in Fig. 3 is a fit of the data points to Eq. (1) and can be considered as a first-step approximation which assumes the compressed O-ring to be of rectangular shape. When inserting the diffusion coefficient D from the flat geometry measurements of the same material into the 'fitting' parameter $d/\sqrt{D}$, an effective thickness d_0 for this zero-order approximation can be derived. It is noted that for the present investigation

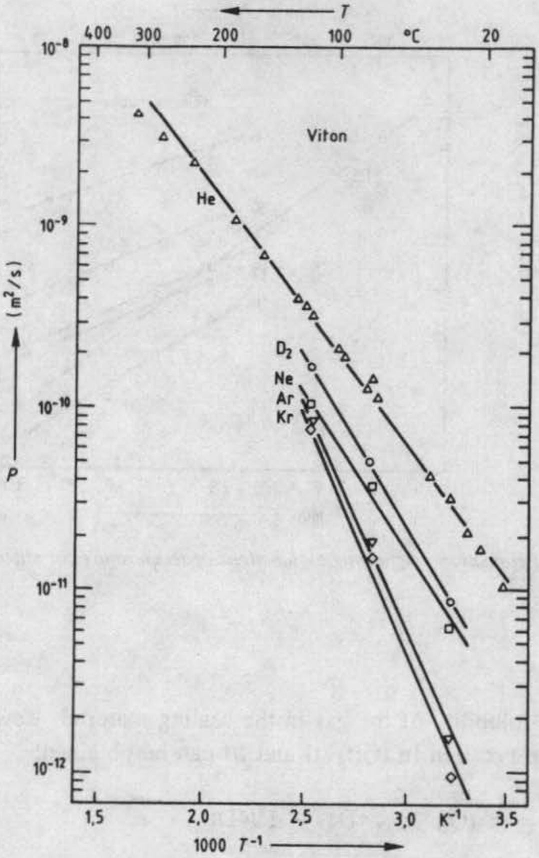

FIG. 6. Permeation coefficients as functions of temperature for Viton.

of silicone rubber O-rings compressed by 17–34%, the values of d_0 are smaller, by 10–20% as compared with the 'nominal thickness', i.e. the width of a rectangle with the same area as the cross-section of the uncompressed O-ring.

As a second step, the gas flow through the O-ring as the sum of flows through rectangular slabs can be considered. The broken line in Fig. 3 is a fit to the experimental data, assuming three slabs, and is a satisfactory description of the experiment. The insert in Fig. 3 shows the slab dimensions obtained from the fit compared with the theoretical shape of the compressed O-ring, which has been calculated from the theory of elasticity [4]. For experiments on rings compressed in the range of 17–34%, a similar good approximation of the theoretical O-ring shape is achieved by the three-slab model. Thus, together with previous flat geometry measurements of Viton and ethylene-propylene rubber (EPDM) (Eq. (1)), we are now able to deduce permeation data from O-ring measurements within this range of compressions.

TABLE I. ACTIVATION ENERGIES OF DIFFUSION E_D AND HEATS OF SOLUTION H_S FOR GASES IN THREE ELASTOMERIC SEALING MATERIALS (kcal/mol)[a]

Gas	Silicone rubber		EPDM		Viton	
	E_D	H_S	E_D	H_S	E_D	H_S
He	2.3	1.6	4.9	1.1	5.5	1.7
Ne	2.4	0.81	5.0	2.1	7.3	1.3
D_2	2.6	−0.11	6.3	0.47	7.9	0.93
Ar	2.7	−0.24	7.3	0.39	11.5	0.43
Kr	2.9	−0.85	7.8	0.83	13.2	0.06
Xe	3.0	−1.2				

[a] 1 calorie = 4.184 J.

Permeation coefficients as functions of temperature are presented in Figs 4–6. Similar figures (not shown here) have been obtained for the diffusion coefficient D. Within the experimental error, most data lie on straight lines when log P or log D are plotted versus 1/T (Arrhenius plot). Thus, for the range investigated here, the classical relationship

$$P = D \cdot \alpha = D_0 \exp(-E_D/RT) \cdot \alpha_0 \exp(-H_S/RT) \tag{5}$$

holds with a single activation energy for diffusion E_D and one heat of solution H_S. Some deviations from this behaviour are observed for the helium measurements of Viton and EPDM above 200°C. Since in these cases we have also observed a change in the shapes of the permeation curves Q(t), it is at present not clear whether the deviation is due to a deformation of the O-ring seal or due to a change in the permeation process. Values of E_D and H_S, as derived from the slope of straight lines fitted to the data up to 200°C, are given in Table I. For the range of gases investigated here, in general a decrease in H_S and an increase in E_D are observed with increasing size of the gas molecules for all three elastomers.

In Fig. 7 the logarithm of the permeation coefficient has been related to the square of the gas molecular diameter, as taken from Ref. [5]. Similar to the findings of Hammon et al. [6] for rare gas permeation in a number of polymers, we also observe a good straight line fit for the Ne, Ar, Kr and Xe data while the points for He and D_2 are scattered. Extrapolating in Fig. 7 to Rn, approximate permeation coefficients of 8×10^{-9}, 8×10^{-11} and 2.5×10^{-14} m^2/s for Rn in silicone rubber, EPDM and Viton, respectively, were found.

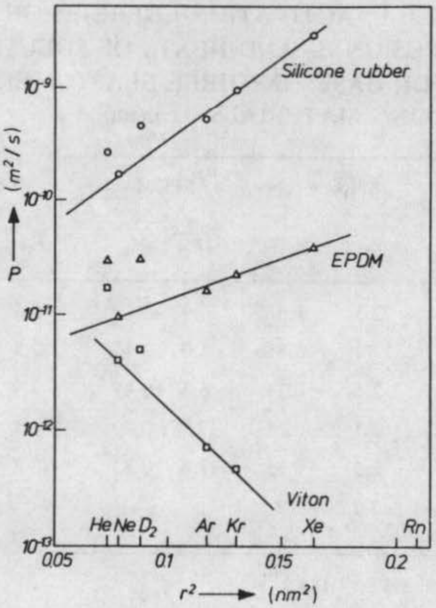

FIG. 7. Permeation coefficients as functions of the square of the gas molecular diameter.

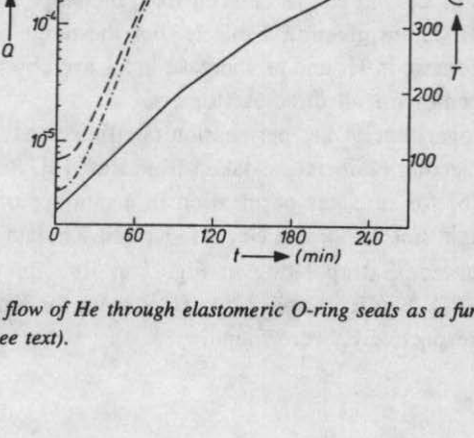

FIG. 8. Permeation gas flow of He through elastomeric O-ring seals as a function of time, during a heating-up experiment (see text).

To investigate the realistic behaviour of an elastomeric seal during a possible fire accident, the permeation gas flow for He as a function of time has been measured while the seal was heated up. Figure 8 shows typical experimental results, where the temperature increase with time (solid line) was chosen to simulate the temperature at the seal of a TN-1300 spent fuel cask in a fire at 800°C environment temperature [7]. The gas flows shown in Fig. 8 are normalized to a pressure gradient of 1 bar helium across the seal. However, during this particular experiment a gas mixture of 0.5 bar helium and 0.5 bar air was applied for a more realistic approach. The seals failed at temperatures of 380–400°C, corresponding to a fire duration of about 4 h.

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