A Generalized Correlation of Gas Permeation Constants

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Polymeric materials are being increasingly used for separating gases. When determining the best polymer, it becomes highly important to know the permeation constant for the gases to be separated. To date there has been no correlation available to estimate easily these constants.

It is the purpose of this note to present a generalized correlation for estimating gas permeation constant in a polymeric membrane from the properties of the gas and the glass transition temperature of the polymer.

The gas permeation constant P is defined as the product of the diffusion coefficient D and the solubility constant (Henry's law constant) H such that

$$P = D \cdot H \tag{1}$$

On the basis of the two parameter (ϵ, σ) corresponding state theory, the reduced diffusion coefficient D^* can be written as (Hirschfelder et al., 1954)

$$D^* = D \frac{m^{1/2}}{\sigma\ \epsilon^{1/2}} \tag{2}$$

The reduced Henry's law constant from the dimensional analysis has the following expression:

$$H^* = H \cdot \frac{\epsilon}{\sigma^3} \tag{3}$$

Combining Equations (1), (2), and (3), the reduced gas permeation constant P^* is obtained.

$$P^* = D^*\ H^* = DH \frac{m^{1/2}\ \epsilon^{1/2}}{\sigma^4} \tag{4}$$

The molecular parameters (ϵ, σ) are not readily available. This difficulty, however, can be easily overcome if the following functional relationship between the molecular parameters and macroscopic properties is assumed:

1. The critical temperature T_c is proportional to the energy parameter ϵ.
2. The critical volume to the cube of the collision diameter σ.

In so doing, the reduced diffusion coefficient in terms of M, T_c, and V_c is

$$D_R = DM^{1/2}\ T_c^{-1/2}\ V_c^{-1/3} \tag{5}$$

The reduced Henry's law constant becomes

$$H_R = H\ T_c\ V_c^{-1} \tag{6}$$

By combining Equations (5) and (6), the reduced gas permeation constant P_R is obtained

$$P_R = P \frac{T_c^{1/2}\ M^{1/2}}{V_c^{4/3}} \tag{7}$$

The permeation constant can be described by the Arrhenius equation (Michael and Bixler, 1961). It implies that the logarithm of the reduced permeation constant should be a linear function of the reciprocal reduced temperature

$$\log P_R = \log \left(P \frac{T_c^{1/2}\ M^{1/2}}{V_c^{4/3}} \right) = A + \frac{B}{T_R} \tag{8}$$

where $T_R = \dfrac{T}{T_c - T_g}$ and T_g is the glass transition temperature of the polymer.

To verify Equation (8), the available literature data of gas permeation constants in polydimethyl silicone (GE Permselective Membrane Bulletin), polycarbonate, natural rubber, polystyrene and polyvinyl chloride (Stern, 1966), polyethylene and polybutadiene (Stannett and Szarc, 1955) were used. The correlation result is shown in Figure 1 and the glass transition temperature of these polymeric materials is compiled in Table 1. The critical constants of gases were taken from Kobe and Lynn (1953).

In the consideration of a generalized correlation covering a wide range of permeation constants in various polymeric membrane, Equation (8) seems to correlate the data rather well. The accuracy of the correlation is of course not high, but it is very useful for estimating gas permeation constant in a membrane using only the properties of the gas in addition to the glass transition temperature of the membrane.

It is important to point out that one of the fundamental premises in this correlation—as defined in Equation (1)—is the validity of a limited gas solubility in a membrane which can be described by Henry's law. This may explain why some of the gases, for example, C_2H_2, shows substantial deviation from the correlation line.

The permeation constant of acetylene (C_2H_2) in polydimethylsilicone is 2200 × 10^{-9} cm^3(STP) cm/s cm^2 cm Hg. This is an order of magnitude higher than that of C_2H_4 (115 × 10^{-9}) or C_2H_6 (210 × 10^{-9}). On the other hand, the reduced diffusion coefficient for C_2H_2 and C_2H_6 in natural rubber are about the same (Michaels and Bixler, 1961). It is reasonable to assume that their diffusion coefficients are also similar to polydimethylsilicone. Therefore, the high solubility of C_2H_2 in dimethylsilicone may be outside the region of Henry's law.

TABLE 1. GLASS TRANSITION TEMPERATURE

Polymer	T_g, °K	Reference
Polydimethylsilicone	150.0	Boyer and Macromol, 1973
Polyethylene	237.0	Boyer and Macromol, 1973
Polystyrene	373.0	Boyer and Macromol, 1973
Polybutadiene	190.0	Boyer and Macromol, 1973
Natural rubber	201.0	Sharma et al., 1972
Polyvinylchloride	355.0	Wolstenholme, 1968
Polycarbonate	263.0	Sharma et al., 1972

NOTATION

A, B = constants in Equation (8)
D = diffusion coefficient, cm^2/s
H = Henry's law constant, cm^3(STP)/cm^3 polymer cm Hg

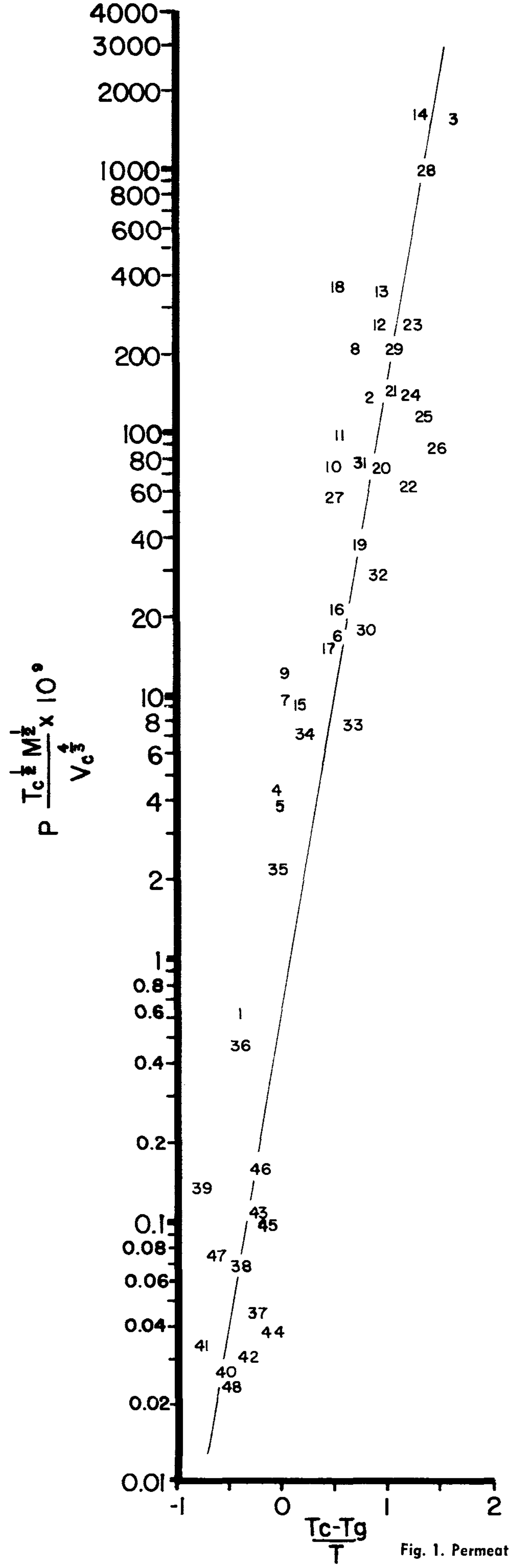

Fig. 1. Permeation constant correlation.

	GAS	*POLYMER*	*REFERENCE*
1	He	Polydimethyl Silicone	GE Membrane
2	NH_3	(Silicone Rubber)	" "
3	H_2O	" "	" "
4	CO	" "	" "
5	N_2	" "	" "
6	NO	" "	" "
7	O_2	" "	" "
8	H_2S	" "	" "
9	Ar	" "	" "
10	CO_2	" "	" "
11	N_2O	" "	" "
12	NO_2	" "	" "
13	SO_2	" "	" "
14	CS_2	" "	" "
15	CH_4	" "	" "
16	C_2H_6	" "	" "
17	C_2H_4	" "	" "
18	C_2H_2	" "	" "
19	C_3H_8	" "	" "
20	nC_4H_{10}	" "	" "
21	nC_5H_{12}	" "	" "
22	nC_6H_{14}	" "	" "
23	CH_3OH	" "	" "
24	ACETONE	" "	" "
25	BENZENE	" "	" "
26	TOLUENE	" "	" "
27	Xe	" "	" "
28	CCl_4	" "	" "
29	CCl_3F	" "	" "
30	CCl_2F_2	" "	" "
31	$CClHF_2$	" "	" "
32	$CClFCClF_2$	" "	" "
33	$CClF_2CF_3$	" "	" "
34	CH_4	" "	Stern, S.A. 1966
35	N_2	" "	"
36	He	" "	"
37	CH_4	Polycarbonate	"
38	N_2	"	"
39	He	"	"
40	CH_4	Polystyrene	"
41	N_2	"	"
42	N_2	Polyethylene	Stannett V and Szarc M 1955
43	O_2	"	"
44	O_2	Polybutadiene	"
45	N_2	"	"
46	N_2	Natural Rubber	Stern, S.A. 1966
47	He	"	"
48	CH_4	Polyvinylchloride	"

P = gas permeation constant defined in Equation (1) $\frac{\text{cm}^3\ (\text{STP})\ \text{cm}}{\text{s cm}^2\ \text{cm Hg}}$
m = mass of the molecule
σ = collision diameter, cm
ϵ = energy parameter, erg
M = molecular weight, g/g-mole
T = temperature, °K
T_c = critical temperature, °K
T_g = glass transition temperature, °K
V_c = critical volume, cm^3/g-mole

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Application of Khodorov's and Li's Entrainment Equations to Rotary Coke Calciners

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Two entrainment equations for rotary cylinders are available in the literature (Khodorove, 1961; Li, 1974). Pysiak (1965) has applied the equation of Khodorov (1961) to an aluminum salt rotary calciner. In this study the two equations were combined and used to derive a specific entrainment equation in order to predict the yield of petroleum coke from a rotary calciner. Entrainment is an important factor affecting the calcined coke yield, cost of elimination of entrained fines, and reactions occurring in the gas phase inside the kiln. Therefore, the entrainment equation is very important for studying the operation and design of a calciner. It is essential for the coke calciner simulation study (Li and Friday, 1974).

COMBINATION OF KHODOROV'S AND LI'S EQUATIONS

Khodorov (1961) presents an entrainment equation

$$\frac{C_g}{\rho} \propto \frac{U^3 \mu^{3/2}}{d^{3/2} D^{3/4} \overline{D}_s^3\, n} \tag{1}$$

where n is obtained by fitting a linear equation, $\ln[\ln(1/m)] = a + n \ln(D_s)$. Equation (1) can be expressed as

$$W = \frac{\pi}{4} D^2 (1 - X) C_g U = K \frac{U^4 \mu^{3/2} \rho D^2 (1 - X)}{d^{3/2} D^{3/4} \overline{D}_s^3\, n} \tag{2}$$

Li (1974) shows

$$dW/dL \propto ND\sqrt{V} \tag{3}$$

and

$$W = K_1 L (DNFS^{-1} \theta^{1/2})^{1/2} \tag{3a}$$

Khodorov conducted his experiment at constant rotation speed of 1.5 rev./min. and constant degree of fullness X of 0.1. When X is constant, $\sqrt{V}$ will be proportional to D. Under these conditions, Equation (3) can be written as

$$W = K_1 L D^2 \tag{4}$$

Equating Equations (2) and (4), and substituting $X = 0.1$, we obtain