Transport of Gases through Porous Membranes & New Data on Sorption Coefficient & Permeability Coefficient for the Transport of Nitrogen, Carbon Dioxide & Ethylene through Unglazed Porcelain

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Mechanism of gaseous transport through membranes has been discussed. The thermodynamic theory has been compared with the non-equilibrium statistical theory. The previous experimental data have been examined from the viewpoints |of these theories. New data on sorption coefficient and permeability coefficient are reported. The data have been examined to provide insight into transport mechanism.

TRANSPORT through membrane is a complex phenomenon[1]. Membrane has a complex texture and a complicated net work of capillaries. The capillaries may be of different sizes. The measured rate of transport through membranes gives only a statistical value. Transport is considerably affected by membrane-permeant interaction and permeant-permeant interaction. Liquid-phase[2-5] transport is easy to measure but the theoretical interpretation in terms of molecular mechanism is rather difficult. However, this is not the situation for gaseous transport[6-11]. From this angle, thermoosmotic measurements on gaseous transport are of considerable value. Fortunately, such data are available although these have not been subjected to detailed analysis from the above angle. In this paper, we propose to examine various modes of transport and to compare the results with thermodynamics of irreversible processes and the kinetic theory of the phenomenon. Since, kinetic theory arguments are usually based on equilibrium distribution function, the theory would be reformulated in terms of non-equilibrium distribution function. We shall put greater emphasis on thermoosmosis and Knudsen flow.

Theoretical

(i) *Mode of gaseous transport* — If there are no (i) membrane-permeant, (ii) permeant-permeant interactions and further the membrane contains capillaries parallel to the direction of the flux vector, and (iii) the pore size of the membrane is comparable to the mean free path (λ), Knudsen flow would occur. If the diameter of the capillary $d > \lambda$, viscous flow would occur. Such a neat situation would seldom occur in practice. Following complex situations may arise:
(i) Some of the channels may have pore size greater than λ while some of these may have smaller pore-size. In that case, part of the transport would be due to Knudsen flow and part of it would be due to viscous flow; (ii) $d > \lambda$ but sorption of the permeant on the membrane may occur; (iii) $d \sim \lambda$ but

sorption may also occur; (iv) surface migration of the permeant may occur; and (v) stronger membrane interaction such as complexation may occur.

(ii) *Non-equilibrium thermodynamics of thermo-osmosis* — Non-equilibrium thermodynamic treatment of thermo-osmosis of gases[6-9] and gaseous mixtures[10,11] are available in the literature. The thermodynamics of irreversible processes[12] helps in spotting appropriate thermodynamic fluxes J and forces X for the phenomena. Thus, we obtain the following phenomenological equations

$$J_m = L_{11}X_1 + L_{12}X_2 \qquad ...(1)$$
$$J_Q = L_{21}X_1 + L_{22}X_2 \qquad ...(2)$$

where J_m is the mass flux per unit area per unit time through the membrane and J_Q is the heat flux per unit area per unit time through the membrane. L_{11}, L_{12}, L_{21} and L_{22} are the phenomenological coefficients. Further, on account of Onsager reciprocity relation $L_{12} = L_{21}$ and using thermodynamics of irreversible processes we can show that $X_1 = -v'\Delta P/T$ and $X_2 = -\Delta T/T^2$, where v' is the specific volume and T is the mean temperature.

For the steady state when $J_m = 0$, we have

$$\Delta P/\Delta T = -Q^*/v'T \qquad ...(3)$$

where Q^* is the ratio of L_{21} and L_{11}. It represents the heat flow per unit mass flow when ΔT is
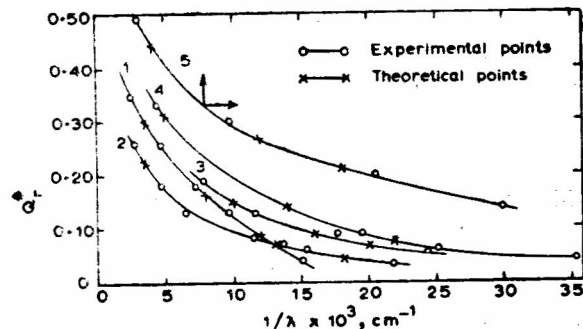

Fig. 1 — Dependence of reduced heat of transport of (1) oxygen, (2) nitrogen, (3) carbon dioxide, (4) ethylene and (5) hydrogen sulphide on mean free path

maintained zero. Experimental measurements of thermoosmotic pressure for several gases have been made and reliable data is available in literature. It is also observed that Eq. (1) and (2) are valid for a very large even up to $\Delta T \sim 120°$.

Eq. (3) is valid so long as (i) linear laws (1) and (2) are valid, (ii) Onsager reciprocity relation is valid and (iii) Gibbs equation is valid even outside equilibrium. Condition (iii) is basic and outweighs condition (i) and (ii). It is more likely to be true in the case of membrane phenomenon, since, in experiments the two chambers separated by the membrane are maintained at two different fixed temperatures. In all probability local equilibrium is established in the two chambers at least when the steady state is attained. In other words, mean free time is much smaller than the observation, time.

The thermodynamics of irreversible processes by itself cannot give an insight into the mechanism of transport through membranes. Neither it can enable one to predict the limit explicitly up to which it would be valid. Accordingly, we shall use statistical mechanical arguments to understand the phenomena.

(iii) *Non-equilibrium statistical theory of thermo-osmosis*[13] — We consider an orifice of a membrane of negligible thickness, the diameter of which is comparable to mean free path. Number of molecules passing through the orifice would be equal to the number of molecules striking the orifice. We consider the direction of the x-coordinate perpendicular to the hole. The polar angle θ is to be counted from the x-axis. Let Φ be the azimuthal angle. The number of molecules per unit volume with velocities between v and $v+dv$ in the solid angle dw in the direction (θ, Φ) is given by $n.f.v^2.dv.dw$, where n is the number density, i.e. the total number of molecules per unit volume and f is the Maxwell velocity distribution function which at equilibrium[13] is given by:

$$f° = (m/2\pi kT)^{3/2} \exp. (-\tfrac{1}{2}mv^2/kt) \qquad ...(4)$$

The number of molecules, $Z_v dv$ passing through the hole per unit area and per unit time with velocities between v and $v+dv$ would be given by

$$Z_v dv = \int_{\Phi=0}^{2\pi} \int_{\theta=0}^{\pi/2} v_x n f v^2 \, dv \, dw \qquad ...(5)$$

Since $v_x = v \cos \theta$ and $dw = \sin \theta d\theta d\Phi$, we have

$$Z_v dv = \int_{\Phi=0}^{2\pi} \int_{\theta=0}^{\pi/2} n v^3 f \cos \theta \sin \theta d\theta d\Phi dv \qquad ...(6)$$

where $f°$ is related to total number of molecules N_0 by Maxwell-Boltzmann distribution law as follows:

$$dN/N_0 = 4\pi f v^2 dv \qquad ...(7)$$

On integrating Eq. (6) between appropriate limits, we have

$$Z_v dv = \pi n f v^3 dv \qquad ...(8)$$

Now, the total number of molecules striking the orifice per unit time whose velocities lie between 0

to ∞ would be given by:

$$\frac{dn}{dt} = \int_0^\infty Z_v dv = \int_0^\infty \pi n f v^3 dv \qquad ...(9)$$

$$= \tfrac{1}{4}n\bar{v} \quad \text{if } f = f° \qquad ...(10)$$

where

$$\bar{v} = \frac{\int_0^\infty v dN}{N_0} = \frac{\int_0^\infty N_0 f v^3 dv}{N_0} = \int_0^\infty f v^3 dv = \sqrt{\frac{8kT}{\pi m}} \qquad ...(11)$$

When we consider two chambers separated by an orifice, whose diameter is comparable to mean free path and further when the two compartments are maintained at temperatures T_1 and T_2, we get

$$\frac{P_1}{\sqrt{T_1}} = \frac{P_2}{\sqrt{T_2}} \qquad ...(12)$$

where P_1 and P_2 are the pressures in the two chambers in the steady state.

Eq. (12) is equivalent to Eq. (3). In deriving Eq. (12) we have made use of the equilibrium distribution function $f°$ and strictly speaking Eq. (12) should not be valid for non-equilibrium situations. However, on account of conservation of momentum,

$$\int f v^3 dv = \int f° v^3 dv \qquad ...(13)$$

Eq. (13) would be valid in the steady state and hence, should be valid for a very large range as is found to be the case experimentally.

The energy transferred U^* per unit mass through the hole would be given by:

$$U^* = \frac{N(\overline{\tfrac{1}{2}mv^2})}{M} = \frac{N}{M} \int_0^\infty \tfrac{1}{2}mv^2 Z_v dv \Big/ \int_0^\infty Z_v dv = 2RT/M \qquad ...(14)$$

where $\overline{\tfrac{1}{2}mv^2}$ is the mean energy of the molecules passing through the hole, N is the Avogadro's number and M is the molecular mass. By definition, heat of transfer Q^* would be given by

$$Q^* = U^* - h \qquad ...(15)$$

where h is the specific enthalpy.

If we consider a monoatomic gas or if we consider that translational energy is exclusively transferred,

$$h = E + PV = 3/2RT + RT = 5/2RT \qquad ...(16)$$

so that

$$Q^* = (2 - 5/2)\frac{RT}{M} = -1/2 \frac{RT}{M} \qquad ...(17)$$

On account of the law of conservation of energy, Eq. (14) would be expected to remain valid in the steady state.

Using the above theory, J_m, the mass flowing per unit area per unit time, would be given by

$$J_m = \tfrac{1}{4}mn \sqrt{\frac{8RT}{\pi m}} \qquad ...(18)$$

where $mn = \rho = M/V$

so that

$$J_m = MP \sqrt{\frac{1}{2\pi MRT}} \qquad ...(19)$$

If there are two chambers at temperatures T_1 and T_2 and pressures P_1 and P_2 and separated by a membrane, the mass flow J_m would be given by

$$J_m = \frac{M}{\sqrt{2\pi RM}}\left[\frac{P_1}{\sqrt{T_1}} - \frac{P_2}{\sqrt{T_2}}\right] \qquad ...(20)$$

The mean temperature T is given by

$$T = (T_1+T_2)/2 \qquad ...(21)$$

and

$$\Delta T = T_1 - T_2 \qquad ...(22)$$

On making proper substitutions in Eq. (20) we have

$$J_m = \frac{M}{\sqrt{2\pi RM}}\left[\frac{(P+\Delta P/2)}{(T+\Delta T/2)^{1/2}} - \frac{(P-\Delta P/2)}{(T-\Delta T/2)^{1/2}}\right] \quad ...(23)$$

which yields on expansion and neglecting higher powers of ΔP and ΔT,

$$J_m = \frac{MP}{\sqrt{2\pi RTM}}\left[\frac{\Delta P}{P} - \frac{\Delta T}{2T}\right] \qquad ...(24)$$

On comparing Eq. (24) with the thermodynamic relation, viz.

$$J_m = L_{11}\left(-\frac{v'\Delta P}{T}\right) + L_{12}\left(-\frac{\Delta T}{T^2}\right) \qquad ...(25)$$

we get

$$L_{11} = -\frac{M^2 P}{R\sqrt{2\pi MRT}} \qquad ...(26)$$

and

$$L_{12} = \frac{MPT}{2\sqrt{2\pi MRT}} \qquad ...(27)$$

So that

$$\frac{L_{12}}{L_{11}} = -\frac{RT}{2M} \qquad ...(28)$$

Therefore, Eq. (28) is identical with Eq. (17).

Comparison with Experimental Data

We have seen above that for a Knudsen gas in the limit $\lambda \to \infty$ the heat of transport is given by $-RT/2M$ from kinetic theory[14] when only translation degree of freedom of permeating molecules is considered. The measurements of thermo-osmotic pressure of earlier workers[15] are in a range which can not be extrapolated to $\lambda \to \infty$ and hence a comparison with kinetic theory results can not be made although frequent guesses have been made.

Rastogi and coworkers[9] have measured thermo-osmotic pressure of gases at several mean pressures. It has been suggested[9] that $\Delta P/\Delta T$ can be related to mean free path by the following relation:

$$\frac{\Delta P}{\Delta T} = \frac{P}{2T} \cdot \frac{\lambda^2}{\alpha + \beta\lambda + \Upsilon\lambda^2} \qquad ...(29)$$

and hence reduced heat of transport is given by

$$Q_r^* = \frac{Q^*}{-RT} = \frac{\lambda^2}{\alpha + \beta\lambda + \Upsilon\lambda^2} \qquad ...(30)$$

Thus, when $\lambda \to \infty$, $Q_r^* \to 1$, if $\Upsilon = 1$, the observed value of heat of transport would be equal to that predicted for Knudsen gas.

Since pressure is related to mean free path by the relation

$$\lambda = 3\eta RT/P\bar{v}M \qquad ...(31)$$

where η = viscosity coefficient.

It is easy to obtain the values of Q_r^* for various values of λ. These are plotted in Fig. 1. Since extrapolation to $\lambda \to \infty$ is not possible under the present circumstances, following procedure was adopted. The values of α, β, Υ were found by the method of least squares. These are given in Table 1. The theoretical curves are compared with the experimental curves in Fig. 1.

The functional dependence of Q_r^* on $1/\lambda$ is in agreement with the dusty-gas model of Manson and coworkers[16].

The values of $[Q_r^*]_{\lambda \to \infty}$, given in Table 1, are less than 1 showing that the flow through the membrane is not purely Knudsen flow. The discrepancy may be due to the fact that collisions of the permeating molecule with the walls of the membrane are not elastic. The reason for the discrepancy may be one out of the following: (i) The membranes may have some pores greater than mean free path and some comparable to mean free path; (ii) the sorption of the permeant may take place on the membrane; and (iii) surface migration of the permeant may take place on the membrane.

We would now report data on sorption coefficient of CO_2, N_2 and C_2H_4 to examine to what extent the above factors are responsible using the membrane for which heat of transport data are available. In the pressure range investigated (1·6-18·4 cm Hg) mean free path of the gases would range between 10^{-4} and 10^{-5} cm.

Materials and Methods

Unglazed porcelain (thickness = 0·4 cm and area of cross-section = 3·14 cm^2) was used as the membrane. The permeability of gases was measured by using the set-up described in Fig. 2.

The two chambers A and B are connected to each other by unglazed porcelain membrane C. A differential manometer M_1 is in communication with both compartments and the pressure in one of

TABLE 1 — HEATS OF TRANSPORT OF GASES AND CONSTANTS OF EQ. (29)

Gas	$\alpha \times 10^7$ (cm^2)	$\beta \times 10^4$ (cm^2)	Υ	$-[Q^*]^{obs}_{\lambda-8}$ (cal/g)	$-[Q^*]^{ideal}_{\lambda \to 8}$ (cal/g)	ΔH (cal/g)	$[Q_r^*]_{\lambda \to 8}$
O_2	0·510	0·969	2·221	4·52	10·04	5·52	0·45
N_2	0·398	3·963	2·457	4·79	11·69	6·90	0·41
CO_2	0·245	1·194	2·743	2·65	7·37	4·72	0·36
C_2H_4	0·175	1·306	2·126	5·40	11·48	6·08	0·47
H_2S	0·064	2·832	1·668	5·57	9·28	3·71	0·60
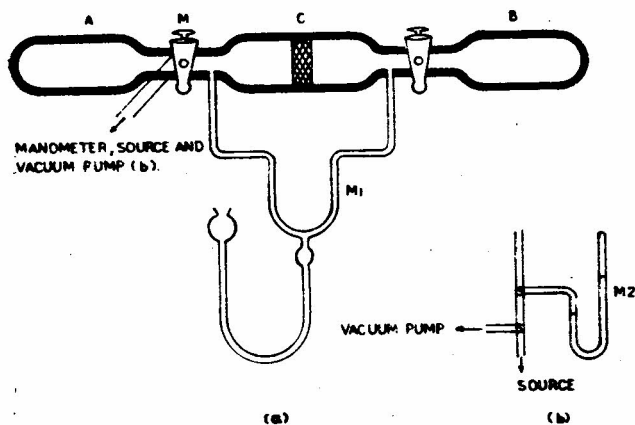
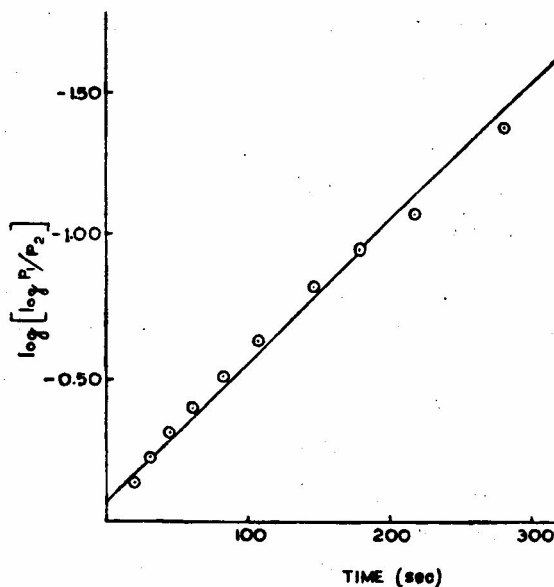Fig. 2 — Experimental set-up for measuring permeability of gases

Fig. 3 — Plot of log [log P_1/P_2] against time for nitrogen

TABLE 2 — COEFFICIENTS OF PERMEABILITY, DIFFUSION AND SORPTION OF GASES

Gas	Permeability $K \times 10^3$ (cc cm/cm²/ sec/atm)	Diffusion coefficient $D \times 10^3$ (cm²/sec)	Sorption coefficient (cc/cm³/atm)
N_2	1.88 ± 0.09	0.33 ± 0.006	5.8 ± 0.36
CO_2	2.44 ± 0.11	0.32 ± 0.005	7.7 ± 0.50
C_2H_4	2.50 ± 0.12	0.34 ± 0.006	6.6 ± 0.45

the chamber is noted with the help of another manometer M_2.

Initially, the whole assembly was evacuated and the gas under study was subsequently introduced. The cell was again evacuated and filled with the gas. The process of evacuation and filling the cell was repeated several times to ensure complete removal of air. Now, the gas was allowed to enter in one of the chambers through the stopcock M. The pressure was noted with the help of manometer M_2. Pressure difference on the two sides of the membrane was then created. The pressure difference ΔP, and the pressure in the first chamber decreased with time. This was measured at different time intervals and was plotted against time. The diffusion coefficient (D) and sorption coefficient (σ) characterizing the solubility of the gas in the membrane were determined using the procedure of Barrer[17]. These are related to permeability K as follows[18]:

$$K = D\sigma \qquad \ldots(32)$$

where the permeability is defined by

$$K = -J_m/\partial P/\partial x \qquad \ldots(33)$$

where $\partial P/\partial x$ is the pressure gradient. Permeability coefficient (K) is numerically equal to the volume of gas passing through unit crossectional area of the membrane at unit pressure gradient during one second. Following equation due to Denbigh and Raumann was used for the determination of the permeability coefficient K.

$$\ln\left(\frac{P_2}{P_1}\right)_t = \left[\ln\left(\frac{P_2}{P_1}\right)_0 - \ln\left(\frac{P_2}{P_1}\right)_\infty\right]e^{-k't} + \ln\left(\frac{P_2}{P_1}\right)_\infty \qquad \ldots(34)$$

where P_1 and P_2 are the pressures in the first and second chambers respectively and t is the time in second. At infinity $P_2 = P_1$, Eq. (34) reduces to the following form:

$$\ln\left(\frac{P_2}{P_1}\right)_t = \ln\left(\frac{P_2}{P_1}\right)_0 e^{-k't} \qquad \ldots(35)$$

On plotting ln [ln(P_2/P_1)$_t$] against time, t, a linear curve is obtained. A typical curve is shown in Fig. 3. The coefficient k' was determined from the

slope of the curve. Knowing the value of k', the permeability coefficient K could easily be determined by Eq. (36)[6]

$$k' = \frac{4AKP}{nv_0 l} \qquad \ldots(36)$$

where A is the exposed area of each surface of the membrane in cm², p is the mean gas pressure in atm, l is the thickness of the membrane in cm, nv_0 is the total volume of gas in the apparatus in cm³ at n.t.p. and K is the permeability coefficient in cm²/sec/atm.

Diffusion coefficient was calculated from the intercept θ on the time-axis using the time-lag method described by Barrer[16] from the relation

$$D = l^2/6\theta \qquad \ldots(37)$$

where l is the thickness of the membrane. The results are given in Table 2.

When $\Delta T = 0$, we have from Eq. (20) and (25),

$$J_m = M/\sqrt{2\pi MRT} \times \Delta P \text{ and } J_m = L_{11}\left(-v. \frac{\Delta P}{T}\right).$$

Comparing it with Eq. (33) we have

$$K = \sqrt{M}/2\pi RT \times l \qquad \ldots(38)$$

Discussion

The observed values of $[Q^*]_{\lambda \to \infty}^{obs}$ in Table 1 do not agree with that predicted by Eq. (17). Denbigh

TABLE 3 — COMPARISON OF THEORETICAL AND EXPERIMENTAL VALUES OF PERMEABILITIES

Gas	$(L_{11}) \times 10^7$ (g sec deg/ cc/cm)	$K \times 10^6$ (sec)	
		Theoretical	Expl
N_2	50·4	5·32	0·23
CO_2	99·2	6·64	0·45
H_2S	67·4	5·84	—
C_2H_4	50·4	5·32	0·30
O_2	61·6	5·68	—

and Raumann[6] suggested that these are related by Eq. (39)

$$[Q^*]_{\lambda \to \infty}^{obs} = [Q^*]_{\lambda \to \infty}^{idel} + \Delta H \qquad \dots (39)$$

where ΔH = heat of sorption of the gas in the membrane. The values of ΔH calculated by Eq. (39) are given in Table 1. These are all positive, showing that heat is absorbed during sorption. However, it is known that physical adsorption is an exothermic process and hence it does not appear that Eq. (39) can account for the discrepancy.

In order to ascertain whether sorption actually takes place, permeability experiments were performed, the results of which are recorded in Table 2. The sorption does occur and the order of sorption-coefficient is similar in the case for all the gases studied. In spite of this, sorption mechanism is not acceptable, since this would require the reduced heat of transport to be greater than 1. What seems to be a greater probability is that there 'may be combination of viscous flow and Knudsen flow over which sorption may be superimposed. If latter is not very important, we would have

$$L_{11} = (L_{11})_{vis} + (L_{11})_{Knudsen} \qquad \dots (40)$$

so that

$$Q^* = \frac{L_{21}}{L_{11}} = \frac{L_{r1}}{(L_{11})_{vis} + (L_{11})_{Knudsen}} \qquad \dots (41)$$

and hence

$$Q_r^* < 1 \qquad \dots (42)$$

in agreement with experiment.

It would be instructive to compare kinetic theory results with experimental results.

The calculated values of L_{11} using Eq. (26) have been recorded in Table 3. Using the kinetic theory of effusion and Eq. (38), permeability K can be calculated. These are given in Table 3 along with the experimental values. The latter is smaller than the former. This is understandable since the ratio of available pore area to total membrane area would be much less than unity.

Acknowledgement

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