

able importance of electron transit-time in high-frequency phenomena in gaseous discharge tubes has already been indicated by, among others, Armstrong¹ and Schumann⁴. The anode of the hard tube, in this mechanism, is replaced by the plasma of the discharge, and the resonator by the oscillating sheet of plasma. Semi-quantitative agreement, with appropriate modifications of the theory for hard tubes, can be obtained if allowance is made for the fact that the boundary between the double space-charge sheath round the filament and the plasma is diffuse^{5,6}.

There are outstanding problems, some of which were referred to by Armstrong, which cannot obviously be accounted for in the present picture; but there appears to be no serious inconsistency between the relatively simple considerations advanced here, and the experimental data for oscillations of small amplitude, provided that the introduction of probes into the plasma does not modify fundamentally the natural oscillatory phenomena.

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¹ Armstrong, E. B., *Nature*, **160**, 713 (1947).

² Webster, J. *App. Phys.*, **10**, 864 (1939).

³ Merrill and Webb, *Phys. Rev.*, **55**, 1191 (1939).

⁴ Schumann, Z. *Phys.*, **121**, 7 (1942).

⁵ Tonks and Langmuir, *Phys. Rev.*, **33**, 954 (1929).

⁶ Druyvesteyn and Warmoltz, *Physica*, **4**, 51 (1937).

Thermo-osmosis of Gases through a Membrane

THERMO-OSMOSIS may be defined as the passage of a fluid through a membrane against the hydrostatic pressure, due to a temperature gradient. It was first observed by Lippmann¹ in the passage of water through membranes of gelatine, etc. The fact that temperature gradients are able to give rise to a flow of matter is shown also by such varied phenomena as the thermal effusion of a gas through a porous diaphragm, the fountain effect in helium II, and also (in multicomponent systems) by thermal diffusion and the Soret effect.

The phenomenon observed by Lippmann was complicated by the presence of electrolytes² and was not a pure thermo-osmosis. I have sought to discover such an effect by investigating the passage of a gas through a non-porous membrane in which it is slightly soluble. The experimental difficulty is the maintenance of an appreciable difference of temperature across a membrane thin enough to allow the passage of the gas at an observable rate. This was achieved by loosely pressing a rubber disk, 0.1 mm. thick, between two aluminium plates, sealed with 'Pycene' at the periphery. At the centre of each plate there was a small hole which allowed the thin layer of gas between the rubber and the metal to communicate with a vacuum system. The whole apparatus was supported in the dividing wall between two thermostat tanks, so that each metal plate was held at a constant temperature.

At a temperature difference of 5–10° C., it was found that carbon dioxide passed through the membrane at an appreciable rate and could be made to circulate continuously through a bubbler in an external circuit. The system is thus a heat engine, although of very low efficiency relative to the heat passing through the membrane by conduction. With

no external circuit, the carbon dioxide passed through the membrane until a stationary pressure difference had been built up which was just sufficient to prevent any further flow. This pressure difference was measured for as long as a week and was entirely constant. Similar results were obtained with hydrogen, except that the flow was *in the reverse direction*, being in this case from warm to cold. The flow was also much slower and the final pressure difference was only about 30 per cent of that obtained with carbon dioxide and of opposite sign (cf. thermal effusion in a porous diaphragm where the flow is always from cold to warm).

It was shown by de Groot³ that the following equation is applicable to thermal effusion and also to the fountain effect in helium II:

$$\frac{dp}{dT} = \frac{-Q^*}{VT} \quad (1)$$

Here dp is the stationary pressure difference due to a temperature difference dT , V is the molar volume of the migrating fluid, and Q^* is a non-classical heat effect, called the 'heat of transport'. The equation is not obtained from classical thermodynamics, since the system is not in equilibrium, but is derived on the basis of Onsager's reciprocity theorem in irreversible processes⁴.

The preliminary experimental results indicate that this equation is satisfied also in the present effect. For a perfect gas, substituting $pV = RT$, the equation may be integrated over the finite temperature difference between the two surfaces of the rubber:

$$\log \frac{p_1}{p_2} = \frac{Q^*}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad (2)$$

The results for carbon dioxide are given in the accompanying table and are in agreement with this equation, as shown by the constancy in the calculated value of Q^* . This value, however, is certainly too low, due to the fact that the temperatures, as measured by means of thermocouples in the aluminium plates, were not the true temperatures at the surfaces of the rubber membrane. Attempts are now being made to overcome this difficulty and also to extend the range of temperatures and pressures.

Pressure (mm. Hg)		Temp. (° Abs.)		Q^* (cal./mole)
p_1	p_2	T_1	T_2	
792.10	781.56	305.0	297.2	-310
788.73	782.57	306.7	302.0	-308
466.62	463.15	306.6	302.1	-306
252.61	248.57	307.5	298.0	-309

It is of interest that three processes so diverse in their kinetic mechanism may all obey the same thermodynamic expression. It remains to be seen whether the thermo-osmosis is entirely due to the effect of temperature on the solubility of the gas in the rubber, or whether there is also a thermal diffusion process inside the membrane.

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¹ Lippmann, *C.R. Acad. Sci., Paris*, **145**, 104, 105 (1907).

² Aubert, *Ann. Chim. Phys.*, **26**, 145, 551 (1912). Also, Freundlich, "Colloid and Capillary Chemistry", 272 (1926).

³ de Groot, *J. de Phys. et Le Radium*, **8**, 188 (1947); *Physica*, **13**, 555 (1947). Also Derjaguin and Sidorenkov, *C.R. Acad. Sci., U.R.S.S.*, **32**, 622 (1941). For review see Hutchison, Nixon and Denbigh, *Trans. Farad. Soc.*, Discussion No. 3, 86 (1948).

⁴ Onsager, *Phys. Rev.*, **37**, 405 (1931); **38**, 2265 (1931).