DIFFUSION OF METHANE THROUGH
A PALLADIUM MEMBRANE.

by

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Though the diffusion of gases through metals has
been studied by many, no investigators have, however, extended
their work to the diffusion of hydrocarbons through palladium.
As hydrogen readily diffuses through this metal and as this
phenomenon is made use of in the oil industry for the purpose
of determining the percentage of hydrogen in cracked gases,
and also, as it has been found recently that the Platinum
metals readily absorb hydrocarbons, it was thought that an
investigation of the ability of methane to diffuse through
palladium would be of value.

The phenomenon of diffusion is considered analagous
to those of conduction of heat and electricity. That is, the
rate of diffusion varies directly as the pressure gradient; and
indirectly as the resistance to the flow. The resistance is
dependant on the character of the material and varies directly
as the thickness of the material. The general equation
governing diffusion is $N = -D \frac{dn}{dz} dt dx dy$ where $N = \text{number of}$
molecules diffusing through a given area $dx dy$ in a time $dt$.
In this equation $\frac{dn}{dz}$ is the rate of change in the number of
molecules of the gas (i.e., the concentration) along the $Z$-axis
normal to the $xy$ plane. $D$ is the coefficient of diffusion.
The concentration gradient $\frac{dn}{dz}$ is the cause of the process of diffusion and is proportional to the partial pressure gradient $\frac{dp}{dz}$ of the gas through the membrane. The sign is a negative sign since the transfer is from higher values of $N$ to lower ones. As the thickness of the foil is constant the expression $\frac{dn}{dz}$ becomes $\frac{P_1 - P_2}{\Delta z}$ where $(P_1 - P_2)$ is pressure difference on the two sides of the foil and $\Delta z$ is the thickness of the foil. Hence the rate of diffusion in this case is proportional to the pressure difference divided by the thickness of the membrane. Obviously the constant "D" depends on the rate at which molecules can move across the area $dx\,dy$ as a result of the pressure gradient of their partial pressure $p$. This, as with all pressure phenomena, is, obviously, caused by the heat motions, and the problem merely devolves itself into one of determining the net number of molecules moving across a given area under a concentration gradient due to their proper heat motions. Our aim is, then, to find the coefficient of diffusion "D" for a number of different temperatures and show the variation by means of a graph.

It has been suggested that the mechanism of diffusion of gases through a metal diaphragm is such that the gas condenses on and forms a solution with the metal on the high pressure side and the gas evaporates from the metal gas solution on the low pressure side of the membrane.

The method developed and described in this paper has for its object the determination of the rate of diffusion of
methane through palladium under varying conditions of pressure of the gas, temperature and thickness of palladium.

**Apparatus.**

The necessary apparatus required that the gas of which the diffusion was to be measured should diffuse through a known area of the metal under a known pressure and at a known temperature.

All tubing and vessels, except the diffusion chamber, are of "Pyrex" laboratory glass.

**Apparatus for Measuring Gas Diffused.**

Fig. I represents the general hookup of the apparatus. "A" is a metal diffusion chamber of our own design, (to be described later).

That part of the apparatus which is attached to the right end of "A" is for the purpose of measuring the amount of gas which diffuses through the foil inside the chamber. The pure methane enters the chamber "A" at the left end and any of the gas which has diffused through the membrane comes out at the right end where its pressure is measured. This part of the apparatus was previously evacuated to a pressure of about 1 x 10^{-3} mm. of mercury. The small differences in pressure due to the gas diffusing through the foil are measured on a McLeod Gauge "B". "C", a bulb of known volume and "D" a manometer are both used for determining the volume of this part of the apparatus. The tube "E" goes to a "Genco Megavac..."
Suction Pump" in series with a "Pfeiffer Wetzlar" mercury diffusion pump.

**Measuring Volume of Apparatus.**

The volume of bulb "C" was determined in the same manner as volume of McLeod Gauge was found, (to be described later). The bulb was then sealed to the apparatus as shown in the diagram. The manometer "D" was especially constructed for this job. A levelling bulb is attached to the bottom of the manometer so that the mercury level in the left side of the manometer may be kept at the same height for all pressures in the apparatus. Hence, if the level of the mercury in the McLeod gauge is kept at a fixed point the volume of the apparatus will be fixed. To obtain the value of this volume dry air is admitted leaving stopcock at "G" open. The next step is to close this stopcock and open stopcock "d" and evacuate. "d" is then closed and "C" opened and the mercury levels in the McLeod Gauge and left side of manometer "D" are raised to their respective reference marks "a" and "b", the pressure in the apparatus being noted on manometer "D". We can now calculate the volume by the application of the perfect gas law.

Let \( V \) = volume of apparatus
Let \( C \) = volume of bulb
Let \( P_1 \) = pressure in bulb "C" = atomospheric pressure
Let \( P_2 \) = pressure in bulb "C" and apparatus
Then

\[ P_2(V + C) = P_1C \]
\[ P_2V + P_2C = P_1C \]
\[ P_2V = C(P_1 - P_2) \]

\[ V = \frac{C(P_1 - P_2)}{P_2} \]

In every case when we measure the difference of pressure in volume \( V \), due to the methane diffusing through the membrane, we must be sure that the mercury level in the manometer is at "b". Hence knowing the volume of the apparatus and the change in pressure at a known time, we may calculate the amount of methane which diffuses through unit area of metal, in unit time. The volume of the bulb "C" is excluded from the volume of the apparatus so as to increase the sensitivity.

**Apparatus for Methane Supply.**

That part of the apparatus connected to the left end of the diffusion chamber "A" is for the supply of pure methane to the high pressure side of the palladium foil. The gas was prepared by Schorlemmer's method. (C. Schorlemmer, Chemical News, Vol. 29, P. 7.). An intimate mixture of anhydrous sodium acetate with more than twice its weight of dry calcium hydroxide and sodium carbonate is heated in florence flask "F". The gas thus obtained always contains some acetone which is easily removed by passing it through a solution of sodium acid sulphite. The methane is then passed through sodium hydroxide solution to remove any carbon dioxide that might be evolved. Cuprous
chloride solution was used to take out any carbon monoxide which might be present. The cuprous chloride (Mahin: Quantitative Analysis) was prepared by dissolving 17 grams of cupric oxide and 3 grams of finely divided copper in 200 c.c. of a mixture of equal volumes of concentrated hydrochloric acid and water, stirring until the solid matter dissolved and placing it in the woulff bottle having bundles of copper wire reaching from top to bottom.

The methane is stored in a gas reservoir "G" which was made by cutting the bottom off a "winchester" with a hot wire, and placing it upright in a pneumatic trough containing distilled water. The "winchester" is fitted with a two-hole rubber cork. The gas from the purifying train goes through a stopcock and enters the reservoir through the one hole forcing the level of the water down and leaves by the other hole which is connected by rubber tubing to stopcock "f".

The apparatus from "f" is made completely of pyrex glass so that it will be air tight. This consists of two sulphuric acid towers "H" to remove water and unsaturated hydrocarbons and a P₂O₅ tube to remove the last traces of moisture. The P₂O₅ tube is connected to the diffusion chamber "A" and to the left side of manometer "J" which is to measure the pressure of the methane on the high pressure side of the diaphragm. The right side of the manometer is connected to a vacuum pump through a stopcock. The left side of the manometer is also connected to the vacuum pump through a stopcock "g".
To get the methane into chamber "A" we close stopcock "f", open "g" and evacuate. "g" is then closed and "f" opened to admit methane from the reservoir "G". This process is repeated several times to remove last traces of air which may remain in the apparatus.

The diffusion chamber is enclosed within an electric resistance furnace especially constructed for the purpose, the temperature being regulated by means of a variable resistance rheostat.

**McLeod Gauge: (see Fig. I).**

The capillary tubing for the tip was first picked. This was to be of uniform bore to cancel surface tension effect in pressure readings. Lengths of about 80 cms. were available. The tubing was cleaned and dried and a piece of rubber tubing attached to one end. A thread of mercury (about 5 cms.) was sucked in at its length measured with a cathotometer at several points along the tube. A piece was found in which the small variations in length of thread indicated a uniform bore. This was given a more thorough examination and the most uniform 15 cm. portion was taken for the tip leaving a 30 cm. length for the manometer.

Into the 15 cm. portion was sucked a thread of mercury (about 1 cm.) its length from the centre of meniscus on either end being measured accurately with a cathotometer for several places along the tube. The mercury was then run into a watch glass and weighed. By calculations using data obtained from the
International Critical Tables it was seen that if the mercury was flat on the ends the same volume of mercury would occupy a thread length from the centre of the meniscus on each end. Then, from these values and knowing the temperature and weight of the thread, the average cross-sectional area of the capillary tube could be calculated. This value was then checked by a similar consideration of a thread about 14 cms. long.

One end of the tip was sealed and a bell blown on the other end in readiness for attachment to the gauge globe. To make the gauge globe a piece of pyrex tubing about 3 cms. in diameter was obtained, the end of which was pulled down and sealed to the capillary tip. The other end was then pulled down and pulled out to a tube smaller in diameter than that to which it was to be sealed and broken off. The mouth of the globe thus formed (represented by A in Fig. I) was inserted into the pyrex tubing and sealed. The purpose of this mouth was to afford an accurate cut-off. A hole was blown in the tube in such a way that the centre of the hole was at the end of the mouth and a piece of pyrex tubing sealed into the hole, to which is later attached the manometer. The centre of the hole must be at the end of the mouth, otherwise it will not cut off properly.

To obtain the volume of the globe, we clean, dry, and weigh. Boiled, distilled water is used to calculate volume. The problem was to get the liquid down into the capillary tip. To accomplish this the gauge was partially filled with water,
suction applied to pump the air out of the capillary and then released letting the water flow down the capillary tube. The remainder of the gauge was filled with distilled water and immersed in a constant temperature bath (40°C) for a couple of hours to ensure the water within the globe being 40°C. This was carried out at 40°C so that when the globe was removed the water inside would contract and none would be spilled. The gauge was dried and weighed.

Our next step was to estimate the volume of the air cone at the sealed end of the capillary tip. The height of the cone was measured with a cathotometer and knowing the height and the area of its base we were able to calculate its volume.

The next task was to put etchings on the capillary tip such that the pressure readings at these marks multiplied by a simple factor would give us the true pressure. Multiplying factors of $10^{-4}$, $.5 \times 10^{-3}$, and $10^{-3}$ were chosen. The product of the gauge volume and this factor gives the volume in the capillary tip above the etching. From this value was subtracted the volume of the air cone. Knowing the cross-sectional area of the tube the length of capillary corresponding to this volume was calculated. Then setting the travelling crosshair of the cathotometer at the base of the cone it was moved the exact distance of the above calculated length. At this point a piece of paper was glued around the tube, care being taken to have the edge of the paper come directly under the crosshair. This was done for each of the three compression
ratios. A thin layer of wax was spread around tube at each paper strip. The gauge was then set in a lathe and the wax scratched along the edge of the paper with a fine steel point. Hydrofluoric acid was then applied to the scratch with a fine cotton thread and allowed to remain a few minutes, after which the wax, acid and paper were washed off leaving a very fine scratch around the capillary.

The rest of the McLeod gauge was made as per diagram.

**Diffusion Chamber.**

Fig. II is a diagram of the diffusion chamber which is of our own design, although the original idea was obtained from a consideration of one used by LaRose and Johnson, (Journ. Am. Chem. Soc., Vol. 46, P. 1377, June 1924).

The chamber itself is constructed of steel and is made in two parts "A" and "B" which screw together. The part "B", into which we place the palladium foil "E", is well machined so that it will sit snugly on the seat. A recess is cut out of the seat and a porcelain plate of same width and depth is placed in it. This porcelain plate serves to support the diaphragm against the pressure but is so porous that it will not inhibit diffusion. The effective area through which the gas diffuses is the area of the recess. This area is found by measuring the average diameter with a cathotometer.

The other part of the chamber "B" screws down into the first part and holds the membrane firmly in place. The end of "B", which screws down next to the foil, has a groove cut in
it so that it will fit down snugly over a soft copper ring which is placed next to the foil and acts as a gasket, preventing leaking at this spot. This groove is of a larger radius of curvature than that of the ring so that when the two parts are tightly screwed together the soft copper will squeeze out and fill up the groove making an air tight joint. The side of the ring next to the diaphragm is flat. In the screwing up process the part "A" slips on the copper ring and hence the ring also serves the purpose of preventing the foil from being cut, torn, or buckled by coming in contact with the moving part "A". Before each assembling the ring must be heated to red heat and quenched in cold water to soften the copper.

The inside of the chamber was copper plated in order to prevent the methane at the high temperatures employed from reacting with the steel, also to prevent gases and hydrocarbons dissolved in the steel from being evaporated into the chamber.

Into the ends of the chamber were screwed copper pipes "C" and "D" for purposes of leading the methane to and from the chamber. Copper tubing was used here for the same reason that copper plating was applied to the inside of the diffusion chamber. Water cooling jackets were placed around each pipe to keep the outer ends from getting warm enough to melt the "Dekhotinsky" used for sealing the glass tubing to the metal. It was necessary to have the tubes silver soldered to the chamber in order to make these joints air tight. Ordinary soft solder would not be suitable here because at the
temperatures employed the zinc in the solder would oxidize and vaporize and the presence of these fumes within the chamber would alter the pressure and upset the readings. A similar reason applies for not using "Shellac", white lead or "Smooth-On" which are ordinarily used for making threaded joints air tight.

To the outer end of tube "C" is soldered a "T" joint in such a manner that one opening of the "T" is in line with the copper pipe. Through this a resistance thermometer "L" is placed so that its bulb is within a few millimeters of the diaphragm. The thermometer is sealed in with "Dekhotinsky" cement. To the other opening in the "T" is sealed the pyrex tube coming from the methane supply.

To the outer end of pipe "D" is sealed the pyrex tube which goes to the McLeod Gauge, etc.

The chamber itself was enclosed in an electric resistance furnace especially designed for this job.

A great deal of difficulty was encountered in this part of the apparatus in getting rid of leaks. Much time and experimenting was necessary before the ingenious devices to prevent leaking, as described above, were devised. It was also very difficult to obtain air tight joints between the metal and the glass using "Dekhotinsky" cement for sealing.
Calibration of Apparatus.

Volume of Bulb "C".

Weight of bulb + water = 278.6122
Weight of bulb = 57.4943
Weight of water = 221.1179

Temperature of water = 40°C

Volume of 1 gram of water at 40°C = 1.00782 c.c.
Volume of 221.1179 grams of water at 40°C
= (221.1179) (1.00782)
= 222.847 cu. cms. = Vol. of Bulb

Area of Recess.

Average diameter of recess = 2.898 cms.
Area of recess = \(\frac{(3.1416)(2.898)^2}{4}\)
= 6.59611 sq. cms.

Thickness of Membrane.

The average thickness of the palladium membrane measured with a micrometer = .0043 in. = .0109 cms.

Calibration of McLeod Gauge.

Volume of Bulb

Weight of Bulb + water = 166.6760
Weight of Bulb = 84.4618
Weight of Water = 82.2142

Temperature of water in bulb = 40°C

Volume of 1 gram of water at 40°C =
= (82.2142) (1.00782)
= 82.8571 c.c. = Vol. of gauge.
Diameter of Capillary Tip.

Length of thread at 24.2°C
(Corrected for meniscus) = 14.560 cms.

1 gram of mercury at 24.2°C = 73.8763 cu.mm.
Weight of mercury thread = 1.1912 grams.

Volume of thread = (1.1912)(73.8763)
= 88.0015 cu.mm.

But the volume of thread = (Area)(Length)
= \( \frac{3.1416 D^2}{4} \times 14.560 \) cms.

Hence Diameter "D" = \( \frac{88.0015 \times 4}{145.6 \times 3.1416} \)
= .8773 mm.

Cross-sectional area = \( \frac{88.0015}{145.6} \) = .60442 sq. mm.

Calculations for Etching on Tip.

The travelling crosshair of the cathometer was set at a point up from the base of the air cone equivalent to the volume of the air cone. This point was used as zero point.
To obtain a compression ratio of \( 10^{-3} \) the volume in Capillary must be: \( (82857.1 \text{ cu.mm.})(10^{-3}) = 82.8571 \text{ cu mm.} \)

Length of capillary corresponding to
\( 82.8571 \text{ cu. mm.} = \frac{82.8571}{.60442} \)
= 137.089 mm.
= 13.7089 cms.
Length of capillary for a compression ratio of 
\[ 0.5 \times 10^{-3} = \frac{(82857.1)(0.5 \times 10^{-3})}{0.60442} \]
\[ = 6.85445 \text{ cms.} \]
Length of capillary for a compression ratio of \(10^{-4}\)
\[ = \frac{(82857.1)(10^{-4})}{0.60442} = 1.37089 \text{ cms.} \]