The Diffusion of Gaseous Hydrocarbons through Rubber Membranes[1]

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IT MUST be understood that the following paper on the investigation of the diffusion of hydrocarbons through rubber membranes is a preliminary report. The research is by no means finished.

The investigation grew out of a desire to discover some method whereby the isoparaffins of petroleum might be isolated in a higher state of purity than has heretofore been found possible. This problem, which has intrigued chemists for the last 40 years, is one whose solution would have far-reaching effects on industry as we know it today. Ellis states that should it be found possible to separate the isoparaffins of petroleum, a new field would open up which would rival in importance the chemistry of ring compounds and increase the value of petroleum to such an extent that a substitute fuel would have to be found for internal combustion engines.

A study of scientific literature revealed that practically no work has been done on the diffusion of isoparaffins through rubber membranes, though Baxter and Beckham, of the Colorado School of Mines, published in 1933 a paper on "Diffusion as an aid to the analysis of gaseous hydrocarbon mixtures"(*1*). Their investigation involved the diffusion of hydrocarbons through a small orifice, the diameter of which was large in comparison with the mean free path of the molecules. An extension of the Maxwell diffusion equation was made to apply to a mixture of gases diffusing through the orifice against atmospheric pressure at a constant temperature. By using the diffusion method in combination with the absorption and slow combustion equipment, they were able to arrive at a closer approximation of the content of hydrocarbon mixtures than had previously been possible. However, their work does nothing toward solving the problem of purifying the isoparaffins.

Several months were spent in developing a piece of efficient apparatus which could be quickly and easily taken apart so that a new membrane might be inserted.

The first pieces of apparatus were made almost entirely of glass, and were for the purpose of determining whether the liquid hydrocarbons in the gaseous state could be made to diffuse through the membranes. Such an apparatus was found impractical because of the extreme difficulty encountered in constructing it so that pressures of several atmospheres might be reached without danger of breakage. Other difficulties were the maintenance of a diaphragm of uniform area, the support of the diaphragm against pressure in a manner to prevent any additional diffusional effect, and especially the maintenance of a tight connection between the bomb and the receiving flask.

In order to prevent leakage, it was necessary that a very tight joint be constructed between the bomb and the receiving flask, which, of course, involved a rather crushing pressure on the rim of the glass. Several accidents turned us in favor of metallic apparatus.

The apparatus which is now in use consists of a bomb made of six inches of 3-inch steel pipe which gives it a volume of 700 cc. Attached to the bomb near the top is a pressure gage and an outlet tube of copper fitted with a stopcock for evacuation purposes. A $5\frac{1}{2}$-inch disc of machined steel has been welded to the end of the cylinder so that a seat is formed for the diaphragm. There are six equally spaced holes near the edge to take care of $5/16$-inch machine bolts.

The detachable section of the head of the bomb is made of a similar disc of steel which is machined to set down into the part of the head which is welded on the pipe in such a manner that the diaphragm is between two rings of steel $1/2$ inch wide. The nuts may be tightened until the bomb is leakproof to hydrocarbons except as they diffuse through the diaphragm which has an effective area of 44 sq. cm.

When in use the bomb is placed in an air bath which is heated by a resistance coil. The temperature is controlled by a De Khotinsky thermoregulator to

within 1°C. A small electric fan is located in the upper part of the air bath in order that the hot air may be circulated in a manner to keep all parts of the bath at the same temperature.

The delivery tube from the bomb leads to a graduated receiving flask which is evacuated and cooled in order that the difference in pressures in the bomb and in the receiving flask might be as great as possible.

In actual practice it was found that the maximum temperature at which a rubber diaphragm of the type obtained from the E. I. du Pont Company could be used was 140°C. At this temperature the diaphragm would last for about 24 hours before it began to fuse against the support. At 130°C. the diaphragms may be used for several days.

Since it has been quite definitely established that the structure of rubber undergoes a change when subjected to stretching (2), it is necessary that a series of diffusions be carried out in such a manner that the diaphragm is not distorted because of the pressure exerted on it. It thus became imperative that the diaphragm be supported. The detachable head of the bomb is so constructed that when it is placed down on the diaphragm and the pressure within the bomb increased, the diaphragm is against a screen of nickel-chromium gauze. Should we desire to investigate the difference in the diffusion of hydrocarbons through rubber whose structure is changed because of stretching, we have merely to remove the gauze in order to let the pressure expand the diaphragm.

The material for the diaphragms was furnished by

FIGURE 1.—APPARATUS

the E. I. du Pont Company of Wilmington, Delaware. Two sets of diaphragms were given to us. One set consisted of rubber sheets of the following dimensions and composition: 10 sheets $5\frac{1}{2}$ by 6 by 0.05 inches; 10 sheets $5\frac{1}{2}$ by 6 by 0.125 inches; 10 sheets $5\frac{1}{2}$ by 6 by 0.187 inches. Rubber (smoked sheets), 100; zinc oxide, 5; P-33 Black, 92.1; stearic acid, 2; Neozone D, 2; Thionex, 2.5; sulfur, 0.4.

The second set of diaphragms was a duplicate set in neoprene instead of rubber. The composition is: Neoprene type E, 100; magnesia, 10; FF wood rosin, 3; P-33 Black, 60; Neozone D, 2; zinc oxide, 10. Both stocks contain an equal volume loading. That is to say, the rubber and the neoprene are diluted to the same extent. Neozone D is a du Pont antioxidant and is chemically phenyl-*b*-naphthylamine. Thionex is a du Pont accelerator and chemically is tetramethyl-thiuram-monosulfide. Theoretically it will contain 46.1 per cent sulfur. P-33 Black referred to is a soft or nonreinforcing carbon black. Wood rosins are graded according to their color. The initials *FF* in the neoprene formula refer only to the color of the wood rosin used.

The sulfur content of the neoprene will be from 0.5 to 1 per cent. The rubber compound was cured in a mold in a hydraulic press for 40 minutes at a steam pressure of 40 pounds and a temperature of 141.5°C. The neoprene compound was vulcanized for the same time, but at a pressure of 60 pounds and a temperature of 153.0°C.

A characteristic of rubber which must be taken into account is that of swelling, a property which shows itself when rubber is placed in practically any hydrocarbon such as benzene, gasoline, etc. Though just how the molecules of vulcanized rubber are interrelated is not known, the phenomena of swelling and elasticity indicate that there is a strong attraction between them which sets up a complicated three-dimensional network which in effect forms a single giant molecule, except for the uncombined vulcanizing ingredients.

Scott has shown that the swelling is due to two different processes (3). If we plot the increase in volume against time we get a curve which rises rapidly at first and then more slowly. The initial rapid rise is thought to be due to a physical saturation of the rubber, while the slower rise is due to chemical action.

After being in gasoline for three days, the rubber obtained from the du Pont Company increased in thickness by 40 per cent while the neoprene increased in thickness only 10 per cent.

The hydrocarbons used in this investigation were obtained from the Eastman Kodak Company and the Texas Company. The normal heptane and octane were made synthetically and are of a high degree of purity, while the hexane, cyclohexane, and methylcyclohexane were prepared from petroleum. The 2,2,4-trimethylpentane was obtained from petroleum also.

In running a diffusion on a particular hydrocarbon, the procedure was as follows: 40 cc. of the hydrocarbon to be determined were placed in a beaker within the
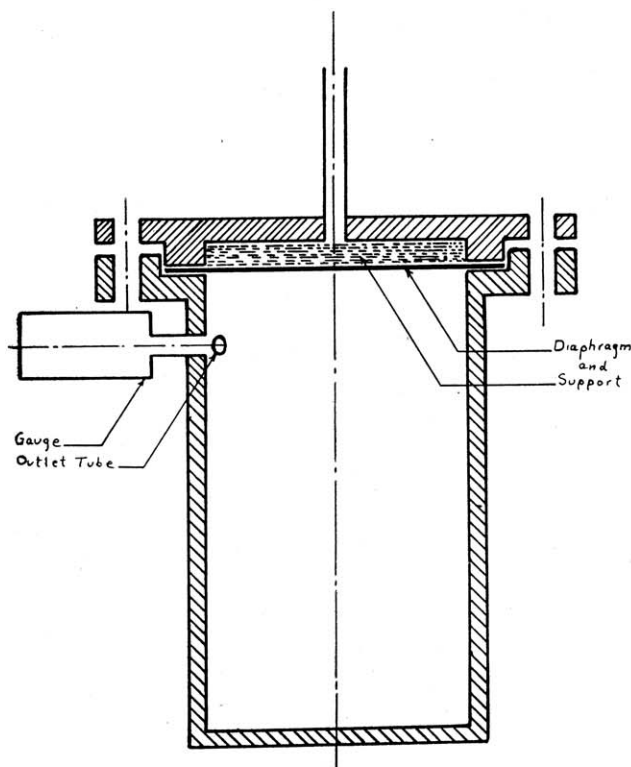
bomb. The detachable part of the head was placed down over the diaphragm and bolted into place. It was found that gaskets were not necessary since the pressure exerted by the parts of the head against the diaphragm was distributed evenly and there was no cutting into the rubber. The bomb was placed in the air bath and the receiving flask connected. First the receiving flask was evacuated and then the bomb. The evacuation is for the purpose of increasing the difference in pressures and also to remove the layer of air which would be above the hydrocarbon.

The temperature is then raised to the desired point and readings taken over a period of from 24 to 48 hours. Time is then plotted against volume to show the relation between the pressure and the rate of diffusion.

Figure 2 shows the results of a series of diffusions with normal heptane and iso-octane using various diaphragms of rubber and neoprene.

Curve A represents the diffusion of normal heptane through the 0.05-inch diaphragm at a temperature of 110°C. and a pressure of 22.3 pounds. Curve B represents a similar diffusion with the temperature changed to 120°C. and the pressure to 30.7 pounds. Curve C is a third diffusion with the temperature raised to 130°C. and the pressure to 37.5 pounds.

A study of the curves shows that the rate of diffusion is directly proportional to the pressure. The slope of A is equal to 1.3 and the slope of B equals 1.8. Then

$$\frac{\text{Slope of A}}{\text{Slope of B}} = \frac{\text{pressure of A}}{\text{pressure of B}} \quad \frac{1.3}{1.8} = \frac{22.3}{30.7}$$
$$29.91 = 40.14$$

which is within experimental error.

Curve G represents the diffusion of normal heptane through the 0.187-inch diaphragm at a temperature of 119.7°C. and a pressure of 30.2 pounds. On measuring the increase in thickness of the diaphragm in curve B, it was found to have increased to a thickness of 0.07 inch while the diaphragm in curve G increased in thickness only to a very small degree. This was probably due to the fact that the thicker diaphragm requires a much longer time to expand. The slope for curve G is 0.7. Then

$$\frac{\text{Slope of B}}{\text{Slope of G}} = \frac{\text{thickness of G}}{\text{thickness of B}} \quad \frac{1.8}{0.7} = \frac{0.187}{0.07}$$
$$0.126 = 0.1309$$

which indicates that the rate of diffusion is inversely proportional to the thickness of the diaphragm.

Curve D represents the diffusion of iso-octane (2,2,4-trimethylpentane) through the same diaphragm as used in curve B. The slope of this curve is 1.6 at a temperature of 129.5°C. and a pressure of 29.3 pounds. The diffusion rate for normal heptane at a pressure of 29.3 pounds would be 1.72. This shows that at the same pressure normal heptane will diffuse at a greater rate

than iso-octane. Since the partial pressure of heptane is greater in a mixture of heptane and iso-octane than the partial pressure of iso-octane, it seems probable that a separation of the two might be obtained by diffusion through the diaphragm.
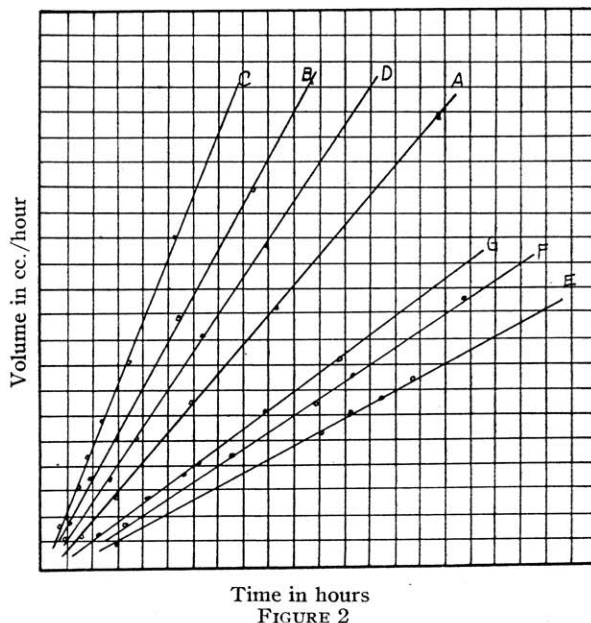

Time in hours
FIGURE 2

Curves E and F represent the diffusion of heptane through neoprene diaphragms of 0.05-inch thickness. The rate is proportional to the pressure, and is less than half the rate through rubber diaphragms of the same thickness.

We have shown, then, that the diffusion of hydrocarbons through rubber membranes fits the equation for the diffusion of gases through solids, which is as follows (4):

$$\frac{dm}{dt} = -K \frac{dp}{dz} dx dy \sigma_0$$

σ_0 = Density of gas at 0°C.
dm = Change in mass per time dt or the mass diffusing in time t
dp = Difference in the pressures in the bomb and in the receiving flask
dz = Thickness of the diaphragm
$dxdy$ = Area of the diaphragm.

Then K equals the permeability of the diaphragm.
The negative sign means merely that the mass in the bomb is decreasing.

LITERATURE CITED

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