

The Diffusion of Gases in Oils

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INTRODUCTION

The use by the petroleum industry of the method of "repressuring", by forcing gases into an oil formation, in order to increase the recovery of petroleum, has become of great importance during recent years. A more intimate knowledge of the nature of the changes taking place during the process of repressuring is desirable in order to make the most efficient use of this method. It is desirable to know, among other things, the extent to which gas will be redissolved by the oil during repressuring, and this involves a knowledge of the rate at which the gas will diffuse through the oil in the formation. The research which is described in part herein was undertaken, in order to furnish some information on this and other related problems.

The mechanism of the diffusion of various solutes through aqueous solutions was considered first by Parrot in 1815. Graham (A) made the first real investigation of the subject in 1850, and Fick (B) later proposed that "the quantity of salt which diffuses through a given area is proportional to the difference between the concentrations of two areas infinitely near one another." Subsequent investigations have demonstrated the validity of Fick's proposition (C).

Some measurements are on record of the rate of diffusion of a few gases in water and aqueous solutions and in alcohol. (D) However, no information has been found which will furnish a reliable basis for predictions as to the extent to which gases will diffuse through oils

(A) References at end

and oil sands, especially at high pressures.

For practical purposes it is most important to know how gases diffuse through oil sands, but it seemed desirable to start with the simpler case of a homogeneous liquid. In this article a theoretical foundation is laid for the work and the apparatus is described which has been evolved for making the desired measurements. Only such experimental data is presented as is needed to demonstrate the method and the principles involved in a consideration of the diffusion process.

THEORETICAL PART

A reasonably complete mathematical treatment of the process of diffusion under experimental conditions involves the consideration of factors which may not be significant as far as the immediate practical application of the results is concerned. Nevertheless, it appears desirable to present at this time a treatment sufficiently complete to serve as a substantial foundation for any expansion of this research in the near future.

Assuming the proposition of Fick (B), we may write

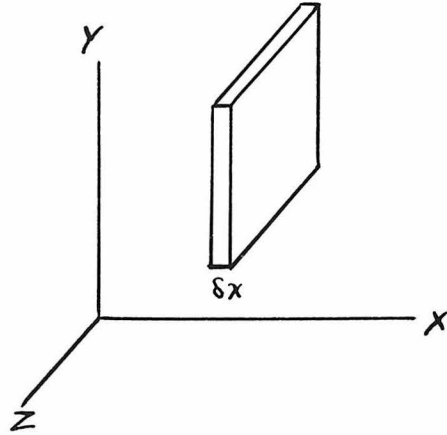
$$\frac{\partial Q}{\partial t} = -D A \frac{\partial c}{\partial x} \quad (1)$$

Where Q = quantity of solute past a given point
 A = area at right angles to direction of flow
 c = concentration
 x = distance in direction of flow
 t = time
 D = diffusion constant

If c.g.s. units are used, this equation defines the absolute diffusion

constant. Its dimensions are square centimeters per second.

From this equation a second important equation may be deduced, giving the change of concentration with time at any point. Let us



consider a thin slab of liquid of area A and thickness δx . Assume the concentration gradient to be zero in the Y and Z directions. If the average concentration in the body of liquid is C , the concentration at the left-hand face will

be $C - \frac{1}{2} \frac{\partial c}{\partial x} \delta x$ and at the right-hand face will be $C + \frac{1}{2} \frac{\partial c}{\partial x} \delta x$.

Since $\frac{\partial Q}{\partial t} = -DA \frac{\partial c}{\partial x}$, the rate of flow of solute through the left-hand face will be $\left(\frac{\partial Q}{\partial t}\right)_1 = -DA \frac{\partial}{\partial x} \left(C - \frac{1}{2} \frac{\partial c}{\partial x} \delta x\right)$, and the rate of

flow of solute through the right hand face will be $\left(\frac{\partial Q}{\partial t}\right)_2 = -DA \frac{\partial}{\partial x} \left(C + \frac{1}{2} \frac{\partial c}{\partial x} \delta x\right)$.

The first of these values minus the second will be the rate at which solute is accumulated in the slab.

$$\left(\frac{\partial Q}{\partial t}\right)_1 - \left(\frac{\partial Q}{\partial t}\right)_2 = DA \frac{\partial}{\partial x} \left(\frac{\partial c}{\partial x}\right) \delta x = DA \frac{\partial^2 c}{\partial x^2} \delta x$$

The rate of increase of concentration is equal to this value divided by the volume of the slab, which is $A \delta x$. Hence

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \quad (2)$$

Under experimental conditions, a gas is caused to diffuse into a body of liquid in the form of a cylinder, with the surface of the liquid perpendicular to the axis of the cylinder. We wish to know the rate at which the gas will be absorbed by the liquid, and how the gas will distribute itself in the body of the liquid. It is found desirable to solve the problem for two cases: first, the cylinder of li-

liquid is of infinite length; and second, the cylinder if of finite length.

Case I

Cylinder of liquid of infinite length

We will let x be the distance from the surface of the liquid. We are interested only in the cases where the initial concentration is uniform. We will let the initial concentration be C_0 . Also we are considering only cases in which the pressure of gas on the surface of the liquid is kept constant during the experiment, and we furthermore assume that the layer of liquid immediately under the surface is always saturated. The saturation concentration ~~may be~~ ^{may be} (in cc of gas per cc of solution) represented by C_s . These conditions may be embodied in the equations

$$C = C_0 \text{ at } t = 0 \text{ for all values of } x \tag{3}$$

$$C = C_s \text{ at } x = 0 \text{ for all values of } t \tag{4}$$

The mathematical procedure for the solution of equation (2) was first worked out by Fourier in connection with the treatment of the problem of the flow of heat, and may be found in mathematical text-books, esp. Ingersoll and Zobel (E). The solution subject to the given conditions is:

$$\frac{C - C_0}{C_s - C_0} = 1 - \frac{2}{\sqrt{\pi}} \int_0^{\frac{x}{\sqrt{Dt}}} e^{-\beta^2} d\beta \tag{5}$$

In most of the experimental work, C_0 is 0, in which case the left side of the equation becomes C/C_s and represents the fraction of the saturation concentration or the degree of saturation at any point in the liquid. The integral is of the form known as the probability integral, and values for it may be found in mathematical tables. A

plot of this equation (letting $C_0 = 0$) is given in Fig. 1. This curve will be referred to as the "Diffusion Concentration Curve."

If we differentiate equation (5) with respect to x we obtain

$$\frac{\partial c}{\partial x} = - \frac{2 C_s}{\sqrt{\pi}} \cdot \frac{1}{2\sqrt{Dt}} e^{-\frac{x^2}{4Dt}} \quad (6)$$

Substituting in equation (1)

$$\frac{\partial Q}{\partial t} = C_s A \sqrt{\frac{D}{\pi t}} e^{-\frac{x^2}{4Dt}} \quad (7)$$

This represents the rate of transfer of solute past a given boundary.

We may find the rate at which gas passes into the liquid by letting $x = 0$ in this equation. We obtain

$$\left(\frac{\partial Q}{\partial t} \right)_{x=0} = C_s A \sqrt{\frac{D}{\pi t}} \quad (8)$$

The total amount of gas in solution is found by integrating this equation

$$Q = 2 C_s A \sqrt{\frac{Dt}{\pi}} + M$$

If we understand by Q the amount of gas which has entered the solution since the beginning of the diffusion process (that is the total gas in solution minus any which was there at the start of the diffusion process) it is evident that $Q = 0$ when $T = 0$, and hence the integration constant M is 0. Hence we may write

$$Q = 2 C_s A \sqrt{\frac{Dt}{\pi}} \quad (9)$$

The derivation of these equations implies certain assumption, as follows: (a), equation (1) assumes that the diffusion constant does not change with the concentration of the solution; (b), condition (4) assumes, in case we are dealing with a gas diffusing into a liquid, that

the layer of liquid immediately under the surface is always saturated, that is, that a surface film does not retard the passage of gas into the liquid; (c), that the gas moves through the liquid only by diffusion.

- a. The first assumption cannot be more than an approximation. Experiments have been made, as will be shown later, in an attempt to find to what extent the rate of diffusion is influenced by the concentration.
- b. With regard to the second assumption, if there is present a surface film which retards the passage of the gas into the liquid, the retardation would be more serious in the early part of a run, when the gas is diffusing away from the surface rapidly, and would have relatively less effect later in the run when the gas is diffusing more slowly. Thus the rate of solution would be slower near the beginning of a run than the rate demanded by equation (8), but at a later time would show an increase toward the theoretical value. If the form of equation (9) is experimentally verified, it will prove that the second assumption is substantially true.
- c. The third assumption is not accurately true, even in the absence of convection currents. For when the gas dissolves in the liquid, the volume of the solution is greater than the volume of the original liquid. This expansion is of the order of 1%-4% at saturation in our experiments, with methane at pressures up to 300 lbs. per sq. in., and would be greater at higher pressures; therefore it is well for us to consider what will be the effect of this factor.

All of the effects of this expansion may be accounted for in terms of a transfer of solute due to a motion of the liquid away from the origin (surface). The fact that solute is transferred due to this expansion of the liquid will cause a slight distortion of the diffusion concentration curve (Fig. 1). An attempt to take this effect into account in a rigorous mathematical treatment leads to very complicated equations, which have not been solved. However, assuming that the distortion of the diffusion

concentration curve is small, we may calculate the rate of transference of solute by diffusion and by motion of the liquid. We will define the rate of transference of solute as the summation of each infinitesimal quantity of solute times the rate at which it moves.

If C is the concentration, the quantity of solute in any slab of liquid parallel to the surface, of area A and thickness δx , is $C A \delta x$. If this portion of solute moves at the rate $\frac{dx}{dt}$, the rate of transference of this portion of solute is $C A \delta x \frac{dx}{dt}$. The rate of transference of all of the solute is the summation of this over all of the δx slabs. That is,

$$T = \sum_{x=0}^{x=\infty} C A \frac{dx}{dt} \delta x \quad (10)$$

where T is the rate of transference.

We will calculate first the transference by diffusion, which will be indicated by T_0 . Now

$$C A \frac{dx}{dt} = \left(\frac{\partial Q}{\partial t} \right)_x$$

Therefore

$$T_0 = \sum \frac{\partial Q}{\partial t} \delta x$$

or, if δx becomes an infinitesimal,

$$T_0 = \int_0^{\infty} \frac{\partial Q}{\partial t} dx$$

Equation (7) gives us the value of $\frac{\partial Q}{\partial t}$ due to diffusion. Substituting this in the above equation

$$T_0 = \int_0^{\infty} C_s A \sqrt{\frac{D}{\pi t}} e^{-\frac{x^2}{4Dt}} dx$$

$$T_D = C_s A \sqrt{\frac{D}{\pi t}} \cdot 2 \sqrt{Dt} \int_0^{\infty} e^{-\frac{x^2}{4Dt}} d\left(\frac{x}{2\sqrt{Dt}}\right)$$

$$= \frac{2 C_s A D}{\sqrt{\pi}} \cdot \frac{\sqrt{\pi}}{2} = C_s A D$$

It is interesting to note that the transference by diffusion will be constant throughout a run, since the expression does not involve t . This is easy to appreciate, for early in a run there will but it will be moving rapidly, while late in a run there will be much gas in solution, be only a small amount of gas in solution, but moving slowly.

The expansion of a given liquid when a given gas is dissolved in it has been found in our experiments to be proportional to the amount of gas dissolved. We will let ϵ be the increase in volume of the liquid when one cubic centimeter of gas is dissolved in it. The motion, dx , of a portion of the liquid at the point x in the time dt , due to the expansion of the liquid, will be $\frac{\epsilon}{A}$ multiplied by the amount of solute retained during the time dt in all of the liquid from the origin to the point x . The amount of gas entering the liquid is $C_s A \sqrt{\frac{D}{\pi t}} dt$ (equation 8). The amount flowing past the point x is $C_s A \sqrt{\frac{D}{\pi t}} e^{-\frac{x^2}{4Dt}} dt$ (equation 7). Hence the amount retained in the liquid up to the point x is $C_s A \sqrt{\frac{D}{\pi t}} (1 - e^{-\frac{x^2}{4Dt}}) dt$. Therefore $dx = \epsilon C_s A \sqrt{\frac{D}{\pi t}} (1 - e^{-\frac{x^2}{4Dt}}) dt$. Substituting the value of obtained from this equation in equation (10), we get

$$T_E = \sum_{x=0}^{x=\infty} C A \epsilon C_s \sqrt{\frac{D}{\pi t}} (1 - e^{-\frac{x^2}{4Dt}}) \delta x$$

where T_E is the rate of transference by expansion of the liquid. If δx is taken as an infinitesimal,

$$T_E = \epsilon C_s A \sqrt{\frac{D}{\pi t}} \int_0^{\infty} C (1 - e^{-\frac{x^2}{4Dt}}) dx$$

It will serve our purpose to evaluate this expression only for the case

where the initial concentration of solute, C_0 , is 0. Substituting equation (5), with C_0 0, in the above equation,

$$T_E = \epsilon C_s^2 A \sqrt{\frac{D}{\pi t}} \int_0^\infty \left\{ 1 - \frac{2}{\sqrt{\pi}} \int_0^{\frac{x}{2\sqrt{Dt}}} e^{-\beta^2} d\beta \right\} \left\{ 1 - e^{-\frac{x^2}{4Dt}} \right\} dx$$

Since the value of the definite integral is independent of the variable, we may write

$$T_E = 2 \epsilon C_s^2 A D \frac{1}{\sqrt{\pi}} \int_0^\infty \left\{ 1 - \frac{2}{\sqrt{\pi}} \int_0^\alpha e^{-\beta^2} d\beta \right\} \left\{ 1 - e^{-\alpha^2} \right\} d\alpha$$

Values for the integral representing the concentration can be obtained from tables (or from Fig. 1), and so we can plot the entire expression under the α -integral as a function of α and evaluate the integral from the area. The curve for this function is tangent to the α -axis at the origin, which means that transference by expansion is unimportant near the surface, rises to a maximum where C/C_s is about 31%, and then decreases and rapidly approaches the α -axis as an asymptote.

The value of the integral is found to be 0.1205. Hence

$$T_E = \frac{2 \times 0.1205}{\sqrt{\pi}} \epsilon C_s^2 A D = 0.136 \epsilon C_s^2 A D$$

It is seen that the rate of transference due to expansion of the liquid, as well as the transference by diffusion, will be constant throughout a run.

In order to obtain some idea of the relative importance of T_E and T_D , we may divide one by the other

$$\frac{T_E}{T_D} = 0.136 \epsilon C_s$$

The quantities ϵ and C_s are known experimentally for all of our runs.

In the experiment to be described in detail later in this article, namely the one with isopentane and methane at a partial pressure of $192\frac{1}{2}$ lbs. per sq. in. and at 30°C , the value of ϵC_s (which indicates the relative expansion at saturation) is 0.0291, and T_E is therefore only 0.39% of T_D . This ratio varies in other runs with methane up to 300 lbs. per sq. in. (in which the initial concentration was zero) from less than 0.1% up to about 0.5%.

This ratio of T_E to T_D has been calculated on the basis of the assumption that the distortion of the diffusion concentration curve can be neglected. A small distortion of the concentration curve could not have any very great effect upon the value of this ratio. Furthermore, the transference by expansion of the liquid is so small compared to the transference by diffusion that the distortion of the concentration curve cannot be very great, and so would affect the ratio only by an amount in the nature of a second order correction.

In the absence of a rigorous mathematical treatment it is not possible to say just how much the observed diffusion constant as determined by equation (9) will be affected by this expansion, but it seems probable that the observed value will be too high by a fraction similar in magnitude to the ratio of T_E to T_D . Actually we have seen that the transference due to expansions is very small near the surface, whereas the maximum diffusion is near the surface. And since the diffusion constant is experimentally determined by the rate at which gas diffuses through the surface layer, it may be that the error will be even less than T_E/T_D . We feel that T_E/T_D is an upper limit for the error due to this effect, and since it is less than 0.5% we have neglected it in all of our results thus far.

In case the initial concentration is not zero, T_E becomes in-

finite for a cylinder of infinite length (bearing in mind always that we calculate transference from the surface as the origin.) But it is evident that the transportation of the solute beyond the region where diffusion is significant would not influence the determination. The transference due to expansion in the region where diffusion is important will be greater than in the former case, but in none of our experiments will this effect be very large.

Case II

Cylinder of liquid of finite length

We will let l_0 be the initial length of the cylinder of liquid. At any later time, due to the expansion of the liquid, the length will be $l_0 + \frac{\epsilon Q}{A}$. At the end of the column of liquid there will be no flow, and hence no concentration gradient. Hence in Case II equation (2) should be solved subject to the condition

$$\frac{\partial c}{\partial x} = 0 \quad \text{at} \quad x = l_0 + \frac{\epsilon Q}{A} \quad (11)$$

as well as conditions (3) and (4) under Case I.

Because of the correction term due to the expansion of the liquid, the equations soon become hopelessly complicated, and no solution has been found. The next best thing is to modify condition (11) by ignoring the expansion of the liquid and write

$$\frac{\partial c}{\partial x} = 0 \quad \text{at} \quad x = l' \quad (12)$$

We shall consider later what value should be given to l' .

As before, the solution may be found in mathematical works. Concentration is given by the equation.

$$\frac{C-C_0}{C_s-C_0} = 1 + \frac{4}{\pi} \sum_{m=1}^{m=\infty} \frac{(-1)^m}{(2m-1)} e^{-D\left(\frac{2m-1}{2l'}\right)^2 \pi^2 t} \sin\left[(2m-1) \frac{\pi x}{2l'}\right] \quad (13)$$

When t is large, that is late in a run, all terms of the summation beyond the first can be neglected. We may then express the concentration at a given time by

$$\frac{C-C_0}{C_s-C_0} = 1 - B \sin \frac{\pi x}{2l'}$$

where the term B includes the constants and the function of t . By integrating the concentration throughout the cell and equating the result to Q , an expression for B may be obtained. For the case that $C_0 = 0$, the resulting equation is

$$\frac{C}{C_s} = 1 - \frac{\pi}{2} \left(1 - \frac{Q}{Q_s}\right) \sin \frac{\pi x}{2l'}$$

where Q_s is the quantity of gas dissolved in the liquid at saturation. This equation is a very close approximation of (13) even when the liquid is only 50% saturated.

The quantity of solute which has entered the liquid during a run is

$$Q = C_s A \int_0^{l'} \left(\frac{C-C_0}{C_s-C_0}\right) dx$$

Multiplying both sides of equation (13) by $C_s A dx$ and integrating from 0 to l' , we get

$$Q = C_s A l' \left[1 - \frac{8}{\pi^2} \sum_{m=1}^{m=\infty} e^{-D\left(\frac{2m-1}{2l'}\right)^2 \pi^2 t} \left(\frac{1}{2m-1}\right)^2 \right] \quad (14)$$

When t is very small, so that the gas behaves as though it were diffusing into an infinite column of liquid, equation (14) reduces to

$$Q = 2 C_s A \sqrt{\frac{Dt}{\pi}}$$

which is identical with equation (9) under Case I. When this equation is compared with equation (14), it is found, by making calculations according to both equations, that (14) differs from (9) by only 0.02% even when the amount of gas dissolved in the liquid is 30% of the amount necessary to saturate the liquid, by 0.25% when the liquid is 50% saturated, and by only 4.7% even when the saturation is 70%. On the other hand, as t increases, the summation in (14) converges more and more rapidly, until finally it is possible to neglect all terms beyond the first, in which case we get

$$Q = C_s A l' \left[1 - \frac{g}{\pi^2} e^{-\pi^2 t \left(\frac{\pi}{2l'} \right)^2} \right] \quad (15)$$

This approximation involves an error of only 0.20% when the saturation is 50% and decreases rapidly as the saturation increases. Hence we can fairly accurately describe the course of a diffusion run by equation (9) from 0 to 50% saturation and equation (15) from 50% to 100%.

The question now arises as to what value should be used for l' in equations (14) or (15). The length of the column of liquid when the solution is saturated may be as much as 4% greater than the initial length, and since D depends upon the square of l' , we are dealing with a factor which may influence D by as much as 8% (and of course much more is higher pressures or other gases were used.) Equation (14) of course is not accurate, since we neglected the effect of expansion in the derivation. We can only hope that the expansion will not seriously affect the distribution of concentration or the course of the diffusion process. The line of reasoning given under Case I shows that no considerable error is introduced in the early part of the run, provided the correct value of l' is used.

In the first part of the run, (14) reduces to an equation which

does not contain l' , and hence it makes no difference what value is used for l' . Even at 70% saturation, since equation (14) differs only moderately from (9), a considerable error in l' will only slightly affect the result. Hence it is only rather near the end of a run that the accurate determination of l' is important. Near the end of a run, the length of the cylinder of liquid will be near the value which it will have when saturation is complete. The gas must be diffusing throughout the entire length of the column of liquid under these conditions, so it would seem that close to the end of the run l' can be given the value $l_0 + \frac{\epsilon Q_s}{A}$. Since l' can be given any value early in a run, and since it approaches the saturation value of l as its determination becomes more significant, it would seem that we would not introduce any serious error by giving it the value $l_0 + \frac{\epsilon Q_s}{A}$ in equations (14) and (15), Q_s being the amount of gas in solution at saturation. We will call $l_0 + \frac{\epsilon Q_s}{A}$ simply l , remembering that it represents the length of the column of saturated solution.

For purposes of calculating D , equations (9) and (15) may be written in different forms. Since $Q_s = C_s A l$, equation (9) gives

$$D = \frac{\pi}{4} \left(\frac{q}{Q_s} \right)^2 \frac{l^2}{t} \quad (16)$$

($\frac{q}{Q_s}$ between 0 and 50%)

Equation (15) gives

$$D = \left[-\log_{10} \left(1 - \frac{q}{Q_s} \right) - 0.0912 \right] \times 0.9332 \frac{l^2}{t} \quad (17)$$

($\frac{q}{Q_s}$ 50% - 100%)

MATERIALS AND APPARATUS

Materials

The liquids used in the experiments described in this article were iso-pentane, a gasoline fraction approximating heptane in properties, and a high-boiling gasoline fraction. The iso-pentane was obtained by repeated fractionation of casing-head gasoline. ^{Since} the only compound in gasoline boiling very near to iso-pentane is pentane, with a boiling point 9°C higher, it is possible to obtain a fairly pure product by this method. The material used had a boiling range of $27.3^{\circ} - 28.2^{\circ}\text{C}$ corr. to 760 mm.

In order to obtain the heptane fraction, a quantity of commercial gasoline was fractionated three times. The portion boiling between 90°C and 105°C was treated with fuming nitric acid. This treatment was probably sufficient to remove completely any unsaturated and benzenoid compounds, and to partially destroy the naphthenes. The remaining oil was washed with H_2SO_4 , water, and NaOH , dried over CaCl_2 , and fractionated several more times, until a product was obtained with a boiling range of $97.5^{\circ} - 99.0^{\circ}\text{C}$ (corr. to 760 mm.) *Density at $30^{\circ}\text{C} = 0.7095$; index of refraction at 23° for sodium D line = 1.4013.* The values for pure heptane are: b.p. 97.5 , density 0.6752, index of refraction at 23°C 1.3867. From a consideration of these properties it seems likely that the product contained about 60% by volume of heptane, the remainder being mostly naphthenes, for example methyl cyclohexane.

The high-boiling gasoline fraction was purified from a $170^{\circ} - 180^{\circ}\text{C}$ cut in a manner similar to the heptane fraction. It probably consists almost entirely of naphthenes. The properties are: b.p. $79.4^{\circ} - 88.5^{\circ}\text{C}$ at 38 mm., density 0.7894 g. per cc at 30° ; index of

refraction 1.4399 at 30°. The gas used was methane, obtained from dry natural gas from Southern California fields. The samples of natural gas used contained between 85% and 90% of methane. The methane was purified by allowing it to stand for a half hour or more at a pressure of 500-1000 lbs. per sq. in. in a cell filled with activated charcoal. Each time after using the charcoal cell it is evacuated for an hour or more accompanied by heating. The temperature of heating used in most of our work was a little over 100°C, but we are at present using about 200°C. The charcoal is renewed three or four times a year.

The methane obtained by this method was analysed occasionally by the simple process of passing a known volume into a liquid-air trap and then applying a vacuum to the trap for a suitable length of time. All of the probable constituents of the gas except methane and nitrogen are completely retained in the trap, and may be measured by the pressure which they exert after removing the liquid air. The condensible fraction was never found to be over 2%, and was usually about 1.5%. The condensible fraction doubtless consists principally of ethane. The gas from Southern California fields is known to contain very little nitrogen. *Furthermore, the nitrogen,* by virtue of having a solubility less than that of methane, would in part counteract the effect of the ethane, which has a greater solubility.

Apparatus

The plan adopted for the determination of diffusion rates is to place the liquid in a cylindrical cell, admit gas to the cell until the desired pressure is reached, and then keep this pressure as nearly constant as practical by adding more gas from time to time to replace that

which diffuses into the liquid. The volume of gas which has been added is determined, and this, together with the times at which the additions were made, constitute the data for the calculation of diffusion constants.

Fig. 2 shows diagrammatically the apparatus which we are now using for the making of these measurements. The apparatus was remodeled recently, and hence the one used for the measurements described in this article was not identical with that shown in the diagram, but the changes did not involve any new principles. Attention will be called in the description to any changes of significance. The absorption cell (Fig. 2) is made of brass with walls $5\frac{1}{2}$ mm thick, and has an inside diameter of 35.54 mm and an inside length of 102 mm. The cell is closed by a brass plate which bolts on to a flange around the top of the cell. Into the plate and the flange are cut matched grooves 2.4 mm deep. A lead gasket is cast to fit these grooves, and serves to make the cell gas-tight in a very satisfactory manner. The top plate is fitted with an outlet valve, a connection to flexible copper tubing through which the gas is admitted to the cell, and a $3\frac{1}{2}$ " 500 lb. Crosby test gauge. This test gauge was calibrated from time to time against a dead-weight tester. A copper shield in front of the inlet prevents the incoming gas from causing agitation of the surface of the liquid.

The flexible copper tubing connects the cell to the outlet of the control valve. The control valve is sensitive enough to allow the gas to be admitted a fraction of a cc at a time if necessary, even with a differential pressure of several hundred pounds. The packing on the low pressure side must be practically leak-proof. Leakage of 1 cc a day with a back pressure of 300 lbs. is the maximum that could be tolerated. Raw-hide disks were previously used, but we are now using metallic packing moistened with a very small amount of mercury. The mercury

allows the valve stem to move easily. This same packing arrangement is being used on an apparatus which we have constructed for work at 2500 lbs., and shows no detectable leakage. The valve is fitted with an 8" lever, which allows it to be opened very gradually, and also allows it to be closed until the gas just ceases to pass, thus avoiding undue pressure in closing.

A 6", 1000 lb. gauge with a stainless-steel tube constitutes the reservoir from which the gas is admitted to the cell. The readings of the gauge may be used to measure the quantity of gas which it contains, and hence the quantity which has been admitted to the cell. In order to obtain volumes of gas from gauge readings, a calibration is carried out by filling the gauge with gas and then sampling it out with a very accurate gas pipette, while the gauge readings are recorded. From this data tables are made up giving the total volume of gas delivered when the gauge drops from its maximum reading down to any other reading. The actual volume of the gauge, plus the connecting tubing as far as the valve, is about 24 cc, so that a drop of one pound on the gauge corresponds to about 1.6 cc. Readings are taken to $\frac{1}{2}$ lb.

Before rebuilding the apparatus, we used for a reservoir an 8" Ashton bronze-tube gauge, reading from 300 to 600 lbs. The volume of this gauge was a little over 100 cc. Readings were made to $\frac{1}{6}$ lb., corresponding to about 1.2 cc. In spite of the fact that the gauge was only of the ordinary type intended for industrial use, remarkably good results were obtained. Two calibrations ~~were~~ made a week apart, covering a range of 1000 cc, showed an average irregular deviation of ^{1.9}~~1.9~~ cc, with no definite trend to the deviations. Two other calibrations 3 days apart, covering a range of 850 cc, showed an average irregular deviation of 1.5 cc. Again, two calibrations made two days apart, cover-

ing 1800 cc, or all of the range ordinarily used in the experiments, showed a trend of about 0.05% plus an average irregular deviation of 1.1 cc. The irregular deviations very rarely exceeded 5 cc. The gauge was calibrated every 2-4 months. Over these intervals of time, some definite change was always noted, sometimes in the direction of larger volumes, sometimes of smaller. The maximum difference was about 5%, with the difference between successive calibration never exceeding 2%. Interpolations between successive calibrations were made on the basis of the time interval between calibrations.

The apparatus thus far described is enclosed in an air thermostat, 2'x2 $\frac{1}{2}$ 'x4', constructed of a commercial insulating board. The thermostat regulator, shown in detail in Fig. 3, makes use of a bimetallic strip 14' by $\frac{1}{8}$ ". The bimetallic strip responds to temperature changes much more quickly than would a tube of mercury, and this is quite essential for the successful operation of an air thermostat. The electrical contact in the regulator circuit is between a platinum point and a drop of mercury. A rotating platinum point and a platinum plate were first tried, but were not as successful as the present arrangement. The mercury is covered with oil in order to diminish contamination of its surface, and is also surrounded by a dust shield. A coil of wire fastened to the end of the strip and dipping into a cup of oil serves to damp out vibrations of the strip. A 1-mfd. condenser and a 2000 ohm leak in parallel with the contact serve to eliminate sparking. Two dry cells furnish the current to actuate a relay. This regulator is reliable to 0.05°C over long periods of time, and when properly adjusted will keep the temperature within 0.01° of the desired value. The drop of mercury must be renewed about once a month.

A fan in the box, driven by a motor outside of the box, provides

a vigorous circulation of air, which is very important in an air thermostat. The heating coil is suspended in front of the fan.

The temperature chosen for most of our work was 30°C , and since the temperature in the room in summer is often over 30° , the thermostat is equipped with a copper cooling coil, also suspended in front of the fan. In one of the windows of the room there has been arranged a piece of burlap with water trickling over it, and this supplies water which even on the hottest days is not over 22° . When this water is pumped through the cooling coil the box is easily kept at 30° .

The charcoal cell completes the equipment for the diffusion measurements. This cell is similar in construction to the diffusion cell, but somewhat larger. It is surrounded by a cooling coil and an electrical resistance heater. At one end there is an outlet going to the supply tank of gas and another to the vacuum pump, while at the other end an outlet communicates through a valve to the reservoir gauge.

The increase in volume of the liquid when the gas is dissolved in it must be known for the correct interpretation of the results. This was obtained in an apparatus similar in principle to one used by Mills and Heithecker (F), but constructed of glass. Two glass bulbs, a lower one of 25 cc volume and an upper one of 15 cc volume are joined by a graduated tube 0.472 cm. in diameter and 13 cm. in length. An outlet goes from the upper bulb to one side and downward, and to this is fastened a high-pressure rubber hose, which communicates with a gauge and with the supply of methane.

The apparatus is filled with oil until it comes up a little distance into the narrow tube connecting the two bulbs. The apparatus is evacuated, and the height of the oil read on the scale. Gas is then admitted and the apparatus is inverted repeatedly until the gauge shows

no further decrease of pressure. The height of the oil is read again, and from this data the increase of volume can be calculated. The apparatus has withstood a pressure of 170 lbs. per sq. in. Readings are taken at three or more successively increasing pressures. The increase in the height of the oil at 150 lb. is usually 2-4 cm. By using care to secure uniform drainage conditions, and by keeping the apparatus thoroughly thermostated, readings can be obtained which are consistent to 0.03 cm.

EXPERIMENTAL RESULTS

In the section entitled "Theoretical Part," a general equation (14) was obtained expressing the quantity of gas dissolved in the liquid as a function of time, which should be valid throughout the entire course of an absorption run. Equations (16) and (17) were shown to be close approximations to (14) valid respectively for the first half and last half of a run. The diffusion constant is most easily determined by continuing an absorption run until the liquid is not over 50% saturated, and applying equation (16). However, it seemed worth while to carry one absorption run very near to completion and thereby subject the absorption equations to a more rigorous test. The liquid chosen for this purpose was iso-pentane, because it has a high diffusion constant which can consequently be more accurately determined.

The diffusion cell was partly filled with 28.69 grams of iso-pentane (47.02 cc at 30°C) A brass plug was suspended in the top of the cell to reduce the gas space to a suitable volume. The apparatus was assembled and brought to 30°, and the methane admitted to the cell until the gauge read 200. In this run, as in all others, no attempt was made to remove the air from the cell, because if the air in the gas phase is in equilibrium with air dissolved in the liquid, which we may assume is approximately the case, this equilibrium will be only slightly affected while the methane diffuses into the oil. A careful consideration of the extent to which this equilibrium would be disturbed has shown that any error due to this cause is negligible. After making necessary correction for error in the gauge and partial pressures of air and iso-pentane vapor, the partial pressure of the methane in this run was found to be 192 $\frac{1}{2}$ lbs. per sq. in.

During the course of the run the guage was usually allowed to drop to about 198 ; gas would then be admitted until the reading was 200, and the time and the reading of the reservoir guage recorded. More gas would then be admitted until the gauge read 202 (or as far above 200 as it had previously fallen below 200) and the apparatus would then be allowed to stand until the pressure had again fallen to 198. It has been determined experimentally that if the fluctuations of pressure are allowed to become as great as 15 lbs., instead of the limits of 3-10 lbs. usually observed in our experiments, no effect upon the rate of absorption of the gas can be detected. Hence we may assume that when the pressure fluctuates regularly between 198 and 202 lbs., the gas diffuses substantially as though the pressure were constant at 200 lbs.

Table I gives the experimental results. The first column gives the time interval in hours from the beginning of the run. The time required to bring the pressure in the cell up to the operating pressure is usually about 10 seconds; zero time is considered to be at the middle of this interval. The last value, for which time is indicated as ∞ , was obtained by removing the cell from its support and shaking it vigorously until no more gas could be dissolved at the pressure of the run.

The second column shows the volume equivalents of the reservoir gauge readings, obtained by use of the calibration tables. All gas volumes are in cc of gas at 1 atm. pressure and 30°C.

The exact amount of gas which must be admitted to the cell in order to raise the pressure to the desired value before any gas dissolves cannot be directly determined. The gas may be admitted very rapidly up to the run pressure, and the reservoir gauge read immediately, but even this reading would have no significance, for effects due to the head of

Table I

Methane and Iso-pentane at 192½ lbs./sq. in.

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---------|------------------|-------|-------|-----------------------|-------------------|----------|--|
| t (hrs) | Volume Equiv. | Q' | Q | Q/Q _s % | Dx10 ⁵ | Q (Calc) | Q _{calc} -Q _{exp} |
| 0.038 | 387.5 | 13.0 | 13.5 | 2.64 | 10 | 16.8 | 3.3 |
| 0.085 | 395.9 | 21.4 | 22.2 | 4.37 | 12 | 25.0 | 2.8 |
| 0.150 | 404.9 | 30.4 | 31.5 | 6.20 | 13.5 | 33.2 | 1.7 |
| 0.227 | 411.0 | 36.5 | 37.8 | 7.44 | 12.8 | 40.8 | 3.0 |
| 0.332 | 419.6 | 65.1 | 46.8 | 9.23 | 13.5 | 49.4 | 2.6 |
| 0.433 | 428.2 | 53.7 | 55.9 | 10.36 | 13.3 | 56.5 | 0.7 |
| 0.547 | 434.5 | 60.0 | 62.2 | 11.86 | 13.45 | 63.5 | 1.3 |
| 0.683 | 443.0 | 68.5 | 70.0 | 13.35 | 13.63 | 71.0 | 1.0 |
| 0.850 | 449.7 | 75.2 | 78.0 | 14.87 | 13.61 | 79.1 | 1.1 |
| 1.017 | 457.1 | 82.6 | 85.6 | 16.32 | 13.71 | 86.5 | 0.9 |
| 1.183 | 464.3 | 89.8 | 93.1 | 17.75 | 13.93 | 93.3 | 0.2 |
| 1.393 | 473.0 | 98.5 | 102.1 | 19.47 | 14.23 | 101.3 | -0.8 |
| 1.573 | 480.3 | 105.8 | 109.7 | 20.92 | 14.57 | 107.6 | -2.1 |
| 1.822 | 487.8 | 113.5 | 117.7 | 22.44 | 14.46 | 115.8 | -1.9 |
| 2.067 | 495.0 | 1205. | 124.9 | 23.82 | 14.37 | 123.3 | -1.6 |
| 2.300 | 502.3 | 127.8 | 132.5 | 25.27 | 14.53 | 130.1 | -2.4 |
| 2.53 | 508.4 | 132.9 | 138.8 | 26.47 | 14.47 | 136.5 | -2.3 |
| 2.80 | 514.6 | 140.1 | 145.3 | 27.71 | 14.35 | 143.5 | -1.8 |
| 3.07 | 523.4 | 148.9 | 154.4 | 29.44 | 14.79 | 150.2 | -4.2 |
| 3.35 | 528.8 | 153.8 | 159.5 | 30.42 | 14.45 | 156.9 | -2.6 |
| 3.63 | 533.3 | 158.9 | 164.7 | 31.41 | 14.21 | 163.5 | -1.2 |
| 3.97 | 539.3 | 164.8 | 170.9 | 32.58 | 14.00 | 170.9 | 0 |
| 4.32 | 545.4 | 170.9 | 177.2 | 33.77 | 13.82 | 177.9 | 0.7 |
| 4.68 | 553.8 | 179.3 | 185.9 | 35.45 | 14.05 | 185.6 | -0.3 |
| 5.10 | 562.3 | 187.8 | 194.7 | 37.13 | 14.15 | 193.7 | -1.0 |
| 5.53 | 570.6 | 196.1 | 203.3 | 38.77 | 14.22 | 201.7 | -1.6 |
| 5.95 | 577.8 | 203.3 | 210.8 | 40.20 | 14.21 | 209.2 | -1.6 |
| 6.35 | 585.1 | 210.6 | 218.3 | 41.63 | 14.28 | 216.1 | -2.2 |
| 7.05 | 595.9 | 221.4 | 229.6 | 43.78 | 14.23 | 227.7 | -1.9 |
| 7.70 | 604.3 | 229.8 | 238.3 | 45.44 | 14.03 | 238.0 | -0.3 |
| 8.30 | 615.0 | 240.5 | 249.3 | 47.54 | 14.07 | 248.6 | -0.7 |
| 9.08 | 624.5 | 250.0 | 259.2 | 49.43 | 14.08 | 258.5 | -0.7 |
| 9.73 | 631.7 | 257.2 | 266.7 | 50.86 | 13.90 | 267.6 | 0.9 |
| 10.48 | 642.0 | 267.5 | 277.3 | 52.88 | 13.99 | 277.4 | 0.1 |
| 11.10 | 651.1 | 276.6 | 286.8 | 54.69 | 14.16 | 285.2 | -1.6 |
| 11.77 | 657.9 | 283.4 | 293.8 | 56.03 | 14.05 | 293.6 | -0.2 |
| 12.52 | 666.3 | 291.8 | 302.5 | 57.68 | 14.03 | 302.1 | -0.4 |
| 13.17 | 672.0 | 297.5 | 308.5 | 58.83 | 13.91 | 309.5 | 1.0 |
| 13.92 | 679.9 | 305.4 | 316.6 | 60.37 | 13.90 | 317.6 | 1.0 |
| 14.68 | 687.8 | 313.3 | 324.8 | 61.94 | 13.92 | 325.7 | 0.9 |
| 15.38 | 695.7 | 321.2 | 338.0 | 63.50 | 14.02 | 332.8 | -0.2 |
| 16.33 | 702.4 | 327.9 | 340.0 | 64.84 | 13.82 | 342.0 | 2.0 |
| 17.02 | 709.1 | 334.6 | 346.9 | 66.15 | 13.87 | 348.5 | 1.6 |
| 17.92 | 717.0 | 342.5 | 355.1 | 67.71 | 13.89 | 356.3 | 1.2 |
| 18.78 | 724.8 | 350.3 | 363.2 | 69.26 | 13.96 | 363.7 | 0.5 |

Table I (cont)

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|--------|------------------|-------|-------|-----------------------|-------------------|---------|--|
| t(hrs) | Volume Equiv. | Q' | Q | Q/Q _s % | Dx10 ⁵ | Q(Calc) | Q _{calc} -Q _{exp} |
| 19.68 | 732.6 | 358.1 | 371.3 | 70.80 | 14.02 | 371.0 | -0.3 |
| 20.55 | 739.2 | 364.5 | 377.9 | 72.06 | 14.01 | 377.8 | -0.1 |
| 21.55 | 744.8 | 370.3 | 383.9 | 73.21 | 13.89 | 385.2 | 1.3 |
| 22.53 | 751.4 | 376.9 | 390.8 | 74.52 | 13.88 | 392.1 | 1.3 |
| 23.47 | 756.9 | 382.4 | 396.5 | 75.61 | 13.83 | 398.3 | 1.8 |
| 24.55 | 763.6 | 389.1 | 403.4 | 76.93 | 13.83 | 405.2 | 1.8 |
| 25.62 | 769.2 | 394.7 | 409.2 | 78.03 | 13.77 | 411.6 | 2.4 |
| 26.80 | 774.8 | 400.3 | 415.1 | 79.16 | 13.70 | 418.1 | 3.0 |
| 28.22 | 781.4 | 406.9 | 421.9 | 80.45 | 13.63 | 425.8 | 3.9 |
| 29.83 | 789.0 | 414.5 | 429.8 | 81.96 | 13.61 | 433.7 | 3.9 |
| 31.92 | 797.9 | 423.4 | 439.0 | 83.71 | 13.59 | 443.0 | 4.0 |
| 34.13 | 807.8 | 433.5 | 449.5 | 85.72 | 13.75 | 451.7 | 2.2 |
| 36.18 | 814.4 | 439.9 | 456.1 | 86.98 | 13.66 | 459.2 | 3.1 |
| 38.33 | 821.0 | 446.5 | 463.0 | 88.29 | 13.64 | 466.0 | 3.0 |
| 40.75 | 827.8 | 453.5 | 470.2 | 89.66 | 13.66 | 472.9 | 2.7 |
| 43.20 | 834.5 | 460.0 | 477.0 | 90.96 | 13.73 | 479.0 | 2.0 |
| 46.17 | 841.3 | 466.8 | 484.0 | 92.30 | 13.78 | 485.4 | 1.4 |
| 49.37 | 846.9 | 472.4 | 489.8 | 93.40 | 13.73 | 491.4 | 1.6 |
| 53.25 | 852.6 | 478.1 | 495.7 | 94.53 | 13.68 | 497.4 | 1.7 |
| 57.83 | 859.5 | 485.0 | 502.9 | 95.90 | 13.93 | 503.1 | 0.2 |
| 63.50 | 865.4 | 490.9 | 509.0 | 97.06 | 14.12 | 508.5 | -0.5 |
| 70.17 | 870.2 | 495.7 | 514.0 | 98.02 | 14.38 | 513.2 | -0.8 |
| 82.00 | 874.8 | 500.4 | 518.8 | 98.93 | 14.27 | 518.1 | -0.7 |
| ∞ | 880.3 | 505.8 | 524.4 | | | | |
| | | | | Average | 14.00 | | 1.5 |

of compression render invalid any readings for at least minute. The rate of absorption at the beginning of the run is of course very high, and so several cubic centimeters of gas are absorbed in the first minute.

In spite of this difficulty, we may plot the total amount of gas admitted to the cell against \sqrt{t} , and we should have a straight line if equation (16) is valid. Or, more conveniently still, we may merely plot against \sqrt{t} the values of column 2 of table I, which differ from the actual volumes of gas admitted by some constant quantity corresponding to the reading of the reservoir gauge before the start of the run.

The plot of \sqrt{t} against the values of column 2 was found to give a fairly straight line for the first part of the run, and this verifies the form of equation (16). Actually there appears to be a slight downward curvature of the line, but this is doubtless due to some abnormal experimental condition. For in similar plots of some 40 other successful experiments, the lines obtained very rarely showed any definite curvature. The extent of this deviation from a straight line will be evident in the subsequent discussion.

If this straight line be extrapolated to zero time, a value of 374.5 cc is obtained. When this number is subtracted from the values of column 2, it gives the values of column 3, which correspond to the volume of gas admitted after the start of the run. In other words, 374.5 cc is the equivalent of the reservoir reading which would be obtained if the cell were filled just to a pressure of $192\frac{1}{2}$ lbs. per sq. in. but without any gas diffusing into the oil. That the result obtained by extrapolation does have this significance is shown by the following observations. If the reservoir gauge is read before admitting any gas to the cell, the difference between the volume equivalent

of this reading and the result obtained by the extrapolation should give the volume of gas actually required to bring the cell to pressure. In different runs in which the height of the liquid is the same, and other conditions are constant, this volume of gas is quite closely the same, and when the height of liquid varies, this initial volume of gas varies with the height of the liquid in the expected manner.

The values of column 3 are not the volumes of gas actually dissolved by the oil, a correction being necessary because of the expansion of the liquid when the gas dissolves in it. Suppose that n cc of gas dissolve in the liquid. The volume of the liquid is increased, and hence the gas space is decreased, by the volume $n\epsilon$, where ϵ is the increase in volume in cc per cc of gas dissolved. The number of cc of gas, measured at one atmosphere, which would occupy this volume is $n\epsilon p$, where p is the pressure in atmosphere. (This assumes that the gas obeys the gas laws; the error involved in this assumption has been considered and has been found to be negligible up to 25 atmospheres.) The volume of gas which must now be admitted to the cell to restore the gas pressure to its original value, which we will call n' , is

$$n' = n - n\epsilon p \quad . \quad \text{Hence } n = \frac{n'}{1 - \epsilon p} \quad .$$

Therefore, in order to obtain the volumes of gas dissolved by the oil, we must divide the values of column 3 by $1 - \epsilon p$.

The data from which the values of ϵ were calculated is given in Table II.

The values ^{in Table II} for the volume of gas dissolved are calculated from solubility coefficients obtained from saturation values of the absorption runs, after first making preliminary corrections of these saturation values with approximate values of ϵ .

Table II

26.52 cc of iso-pentane

| Pressure interval (corr.) lbs./sq. in. | Increase of volume cc | Volume of gas dissolved cc | ϵ |
|---|--------------------------|-------------------------------|----------------|
| 0 - 42.5 | 0.172 | 65.6 | 0.00262 |
| 0 - 92.5 | 0.392 | 142.8 | 0.00274 |
| 0 - 126.7 | 0.531 | 195.6 | 0.00271 |
| 0 - 147.8 | 0.614 | 228.0 | <u>0.00269</u> |
| | | Weighted Average | .00270 |

33.89 cc of high gasoline fraction

| | | | |
|--------------|-------|------------------|----------------|
| 21.1 - 99.4 | 0.240 | 110 | 0.00218 |
| 21.1 - 122.0 | 0.309 | 142 | <u>0.00218</u> |
| | | Weighted Average | 0.00218 |

33.90 cc of heptane fraction

| | | | |
|-------------|-------|------------------|----------------|
| 21.1 - 70.5 | 0.200 | 87 | 0.00230 |
| 21.1 - 97.3 | 0.321 | 134 | <u>0.00240</u> |
| | | Weighted Average | 0.00237 |

The consistency of the results obtained indicates that the accuracy is more than adequate for making the small expansion corrections with a considerable degree of certainty. There is no evidence of a variation of ϵ with the pressure, so the use of these values at somewhat higher pressures is justifiable. Furthermore, results of Mills and Heithecker (F) obtained with natural gases and crude oils indicate that ϵ is constant up to 1000 lbs. per sq. in.

The pressure of the isopentane absorption run was 13.1 atm. The term $1-\epsilon p$ therefore becomes 0.9646 for this run. Returning to Table I, we obtain the values of column 4 by dividing this number into column 3. Column 5 is obtained by dividing column 4 by 524.4. The height of the

liquid at saturation is calculated to be 4.898 cm. The values of the absolute diffusion constant are obtained, by use of equation (16) and (17), from this data (changing time to seconds however.)

It will be seen that a very satisfactory constant is obtained. It shows a slight tendency to rise after the beginning of the run, and then to fall again, corresponding to the downward curvature, previously mentioned, of the line obtained by plotting column 2 against \sqrt{t} . Near the beginning of the run and near the end, small variations in Q produce a large change in D . The very excellent agreement of the values of D so near to complete saturation must be considered somewhat fortuitous. The average value of D between 15% and 90% is 14.00×10^{-5} . The magnitude of the deviation from the theoretical equation is made more evident by calculating values of Q from the average constant. These values are tabulated in column 7, and in the last column are given the differences from the experimental values of Q . The agreement is certainly within the limits of experimental error.

We may now examine the bearing of these results upon certain assumptions which are inherent in the calculations.

a. It has been assumed that the rate of diffusion is independent of the concentration. The proportionality between Q and \sqrt{t} involved in equation (16) would be obtained regardless of any effect that the solute might have on the properties of the solvent. In fact, it can be shown that the only requirement necessary to obtain this relationship is that the curve representing the distribution of solute under the surface should always have the same shape, regardless of what its shape might be, merely expanding in the x direction with increasing time. However, if the rate of diffusion is dependent in any considerable degree upon the concentration of the solution, different values

for D should be obtained in the first part and in the last part of a run which is carried near to saturation. For in the first part of the run the solute is diffusing through a solution with the concentration varying from saturation down to 0, while near the end of the run the concentration has a relatively high value at all points in the solution. In other words, the average concentration over the region where the diffusion process is going on is greater in the last part of the run than in the first part. The constancy of the values of D found in the iso-pentane experiment would seem to indicate that the concentration did not have any very great effect upon D. We should expect the effect, if any, to be in the direction of higher values of D for higher concentrations, whereas the slight trend which does appear in the experiment is in the opposite direction. More information on this point has been obtained in the experiments to be described presently.

b. Saturation of the surface layer at all times is assumed. As was pointed out previously, an increasing value of D would be obtained if the liquid immediately under the surface were not at all times completely saturated. The experimental results seem to be very good evidence that there is no appreciable retardation, under these experimental conditions, in the passage of the gas through the surface of the liquid.

c. It is assumed that no solute is transferred by convection. The tendency for convection to take place is greatly reduced by the fact that the solutions of methane in oils have lower densities than the pure oils. The density of the solution of methane in iso-pentane at $192\frac{1}{2}$ lbs. is calculated to be 2.7% less than the density of the pure liquid. By virtue of this fact, a stable density gradient is established. The careful thermostating of the apparatus reduces the tendency for convection currents to arise as a result of temperature differences. In

one or two cases, a temporary variation of the temperature by as much as 1° above or below 30° , although it rendered invalid any *gauge* readings taken at the time, nevertheless did not produce any apparent effect upon the rate of solution of the gas after the termination of the disturbance. The apparatus is heavy enough and mounted rigidly enough so that vibrations should not be serious. One of our preliminary experiments was made with CO_2 and kerosene. It gave a very high diffusion constant at first, decreasing greatly with time. The explanation of this is that the solution is heavier than the pure liquid, and hence *(this effect being most pronounced when there is only a little of the gas in solution, convection occurs)* The fact that the iso-pentane experiment agrees so well with the theoretical equations is an indication that there ~~were~~ no appreciable convection effects.

In order to obtain more information as to the effect of the concentration upon the diffusion rate, so-called "split runs" were tried with the high gasoline fraction and with the heptane fraction. In these experiments, a diffusion run was made at one pressure, the liquid was then saturated at that pressure, and another diffusion run was made at a higher pressure.

In the case of the high gasoline fraction, the first run was made at $143\frac{1}{2}$ lbs. per sq. in., and then after saturating the liquid an absorption run was made at $287\frac{1}{2}$ lbs., or almost exactly twice the first pressure. Another experiment was then made in which the pressure was raised at once from 0 to $287\frac{1}{2}$. If the diffusion constant is not appreciably affected by the concentration, and if the solubility is proportional to the pressure, the rate of solution should be the same in the first two cases, and twice as great in the third.

In Fig. 4 the results of these runs are shown. Volumes of gas absorbed, calculated in the same way as column 4 of Table I, are plot-

ted against the square root of time in hours. The results of the two halves of the split run are seen to be in very good agreement, and the line for the single run at $287\frac{1}{2}$ lbs. has a slope twice as great as the line for the split run.

The absolute diffusion constant may be calculated from the slope of the line. The equation of the line is

$$Q = m\sqrt{t'}$$

where m is the slope and t' is the time in hours. From this and from the equation

$$Q = 2C_s A \sqrt{\frac{D}{\pi t}} \quad (t \text{ in seconds})$$

and the relationship $t = 3600 t'$, we get

$$D = \frac{\pi m^2}{14400 C_s^2 A^2} \quad (18)$$

Table III gives the results of this experiment. The slopes were determined carefully from a large scale plot. Actually, it was not necessary to obtain the slope from a plot of corrected values of Q . The identical result should be obtained by plotting uncorrected Q values, or by merely plotting the volume equivalents of the reservoir gauge readings, and then applying the correction factor to the slope of the line so obtained. The uncorrected slopes are designated as m' , while the corrected slopes are tabulated under m . In order to obtain the values of C_s , the expansion of the oil is calculated, and the final volume of the solution is divided into the volume of gas dissolved. C_s for the second half of the split run refers just to the gas dissolved

TABLE III

Methane and High Gasoline Fraction

| Pressure interval lbs./sq.in. | m' | m | C_s | C_s/p | C_s from average C_s/p | $D \times 10^5$ |
|-------------------------------------|------|------|-------|---------|----------------------------------|-----------------|
| 0 - $143\frac{1}{2}$ | 27.0 | 27.7 | 6.00 | 0.0418 | 5.93 | 4.97 |
| $143\frac{1}{2}$ - $287\frac{1}{2}$ | 26.5 | 27.8 | 5.98 | 0.0415 | 5.93 | 5.01 |
| 0 - $287\frac{1}{2}$ | 53.1 | 55.5 | 11.77 | 0.0409 | 11.87 | 4.98 |

above $143\frac{1}{2}$ lbs. When the values of C_s are divided by the pressure intervals, the values obtained are approximately constant, the differences being within the limits of experimental error. A weighted average of this ratio of C_s/p is used to calculate values of C_s for substitution in equation (18). The area of the cell, 9.879 cm^2 completes the data necessary for the calculation. The values of D are seen to agree very closely. Actually the experimental error is considerably greater than the differences which appear in the results.

The experiments with heptane fraction gave much poorer results. In this case an attempt was made to run at three successive pressures. It happened, accidentally, that saturation after each part of the split run was obtained at a slightly greater pressure than that of the preceding run, but when the results are properly calculated this makes no difference. Three duplicate runs were first made over the pressure interval from 0 - 300 lbs. These results are shown graphically in Fig. 5. In this graph the original volume equivalents of the gauge readings are used. It is from large-scale graphs of this sort that we ordinarily calculate the diffusion constants. The slopes of the three lines should of course be the same. The data for the second determination is obviously too limited and too irregular to give a reliable value for the

constant. This determination is included merely as an illustration of the erratic data which may sometimes be obtained when operating conditions are not ideal. In the large-scale plot the last three points were disregarded, which gives a much lower slope. The validity of the exclusion of these points may be open to question, but the matter is unimportant, since the determination can be given no weight anyway. The other two lines show somewhat greater divergence than is apparent in Fig. 5. The data on the split run is shown in Fig. 6. It is evident now that the parts of this split run were not continued long enough to give reliable results.

Table IV gives a summary of the results with heptane fraction. Columns m' and m are the uncorrected and corrected slopes, and C_s is calculated from an average solubility coefficient. It is seen that the value of D obtained for the first section of the split run is widely

Table IV
Methane and Heptane Fraction

| | Pressure interval Lbs./sq. in. | m' | m | C_s (Calc) | $D \times 10^5$ | Deviation from weighted average |
|-----|-----------------------------------|------|------|--------------|-----------------|---------------------------------|
| (1) | 0 - 300 | 91.1 | 95.5 | 15.63 | 8.31 | 1.3% |
| (2) | 0 - 300 | 90.9 | 95.3 | 15.63 | 8.26 | 0.7% |
| (3) | 0 - 300 | 87.6 | 93.0 | 15.63 | 7.69 | 6.2% |
| (A) | 0 - 135 | 37.4 | 38.3 | 7.03 | 6.56 | 20 % |
| (B) | 136 - 250 | 35.7 | 37.1 | 5.97 | 8.58 | 4.6% |
| (C) | 251 - 380 | 38.4 | 40.8 | 6.72 | 8.20 | 0 |

Weighted Average 8.2

divergent from the others; we are unable to account for this. In view of the fact that D depends upon the square of m , the agreement of the other values is about as good as could be expected under the conditions.

This run furnishes little additional evidence as to the effect of pressure upon the diffusion rate. Its inclusion serves to make apparent the experimental limitations of the method. Reliable values can be obtained for the diffusion constant, but in order that they may be reliable there must be obtained at least 25 pts. lying close to a straight line. As evidence that reliable values may be obtained we may consider the results of duplicate runs in which good lines were obtained. There are four other liquids for which pairs of satisfactory runs were obtained. In three of these pairs of runs, namely with kerosene, benzene, and cyclohexane, results were obtained which differed respectively by ~~0.8%~~^{1.6%}, ~~1.8%~~^{0.8%}, and 0%. A wide disagreement was found in the fourth case, but this was with a liquid giving a very low constant which was extremely difficult to measure.

From a consideration of the information furnished by the isopentane and high-gasoline-fraction runs, and what little evidence may be gleaned from the heptane fraction runs, we feel safe in saying that any effect which the concentration or pressure up to 300 lbs. per sq. in. may have upon the rate of diffusion of methane in light oils probably does not exceed 4%, and certainly does not exceed 8%.

In addition to the possible sources of error which have been discussed, there was another one present in our experiments which probably was not negligible. This was the effect of the impurities in the methane. Since ethane is more soluble in oils than is methane, a content of 1%-2% of ethane might be expected to give a rate of solution slightly higher than would be obtained with pure methane. However, the preparation of an adequate supply under pressure of methane of higher purity than that which we used is a difficult undertaking, and it seemed probably that the impure methane would give results accurate enough for the purpose for which the experiments were originally undertaken.

SUMMARY

An apparatus has been constructed which allows the determination of diffusion constants and solubilities of gases in liquid at pressures up to 400 lbs. per sq. in. Results obtained with methane and iso-pentane are found to be in good agreement with theoretical equations. An investigation of the extent to which the diffusion constant may be affected by pressure ~~or~~ by the concentration of the gas solution up to pressures of 300 lbs. per sq. in. did not reveal any effect, but, because of the limitations of the experiments which were performed, the most that we can say is that any effect which does exist probably does not exceed 4% for the case of methane and light oils. A consideration of the assumptions involved indicates that the method is capable of giving fairly reliable values of the true absolute diffusion constant, although the probable error may be as great as 4%.

I wish to express my thanks to the American Petroleum Institute for the financial support of this research, and to Dr. W. N. Lacey for his advice in the work. I wish to also acknowledge my appreciation for the co-operation of my co-workers, Nathan F. Scudder, Frederick P. Stapp, Earl S. Hill, and Bruce H. Sage.

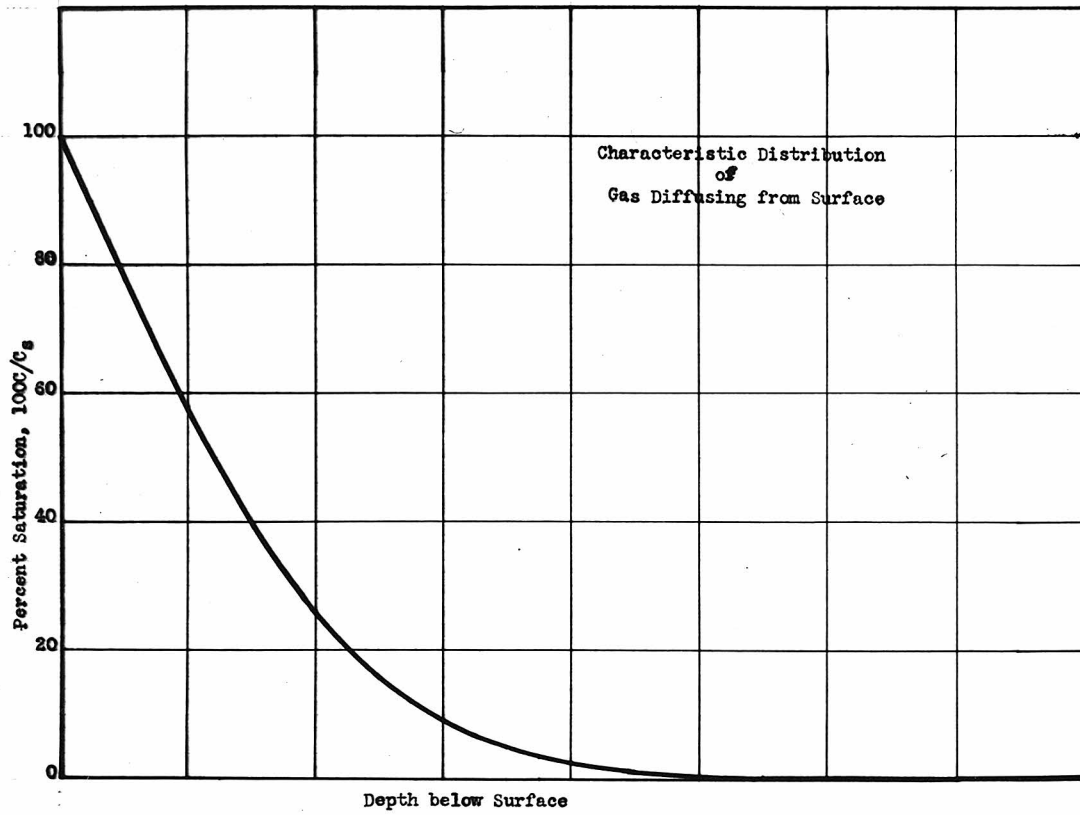


Figure 1.

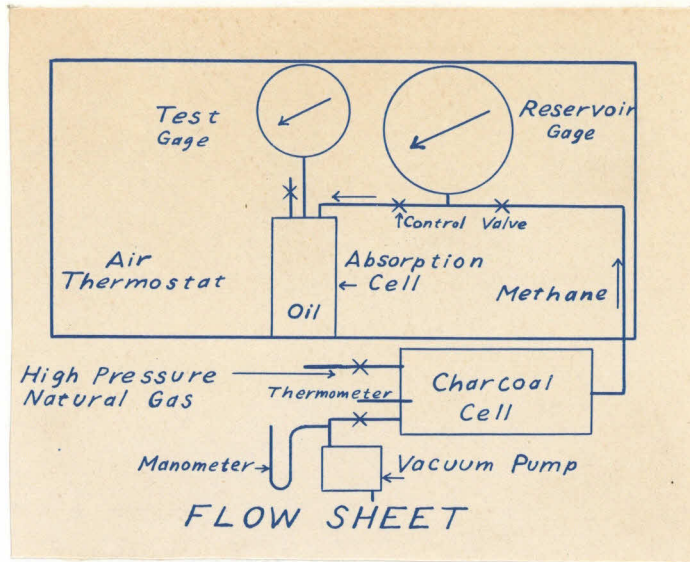
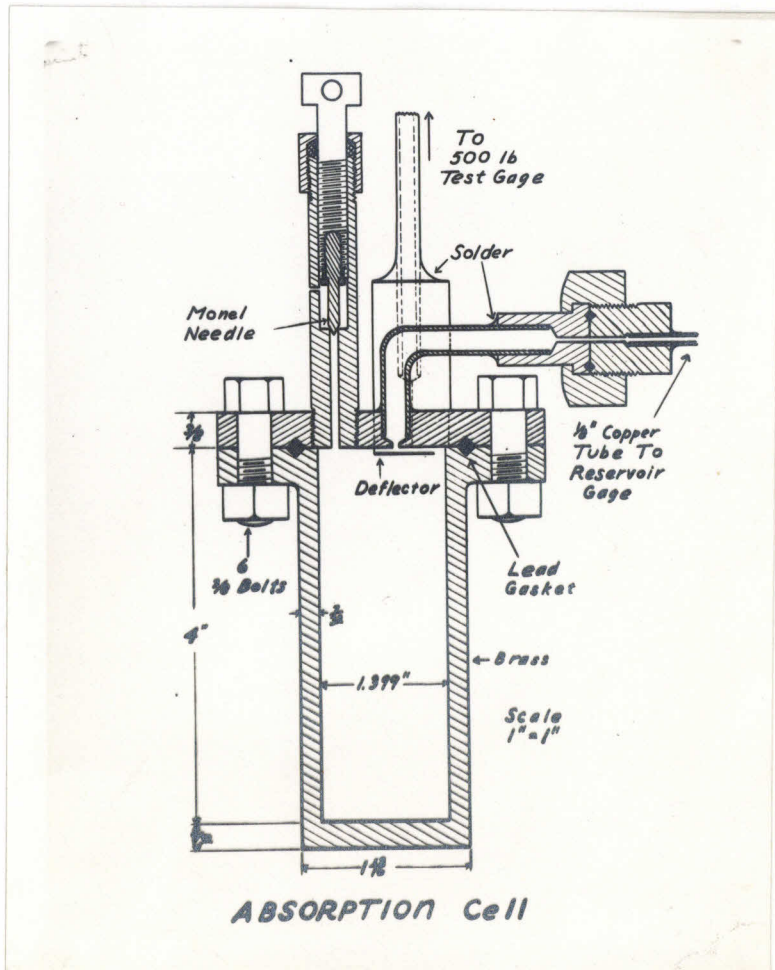


Fig. 2



TEMPERATURE REGULATOR

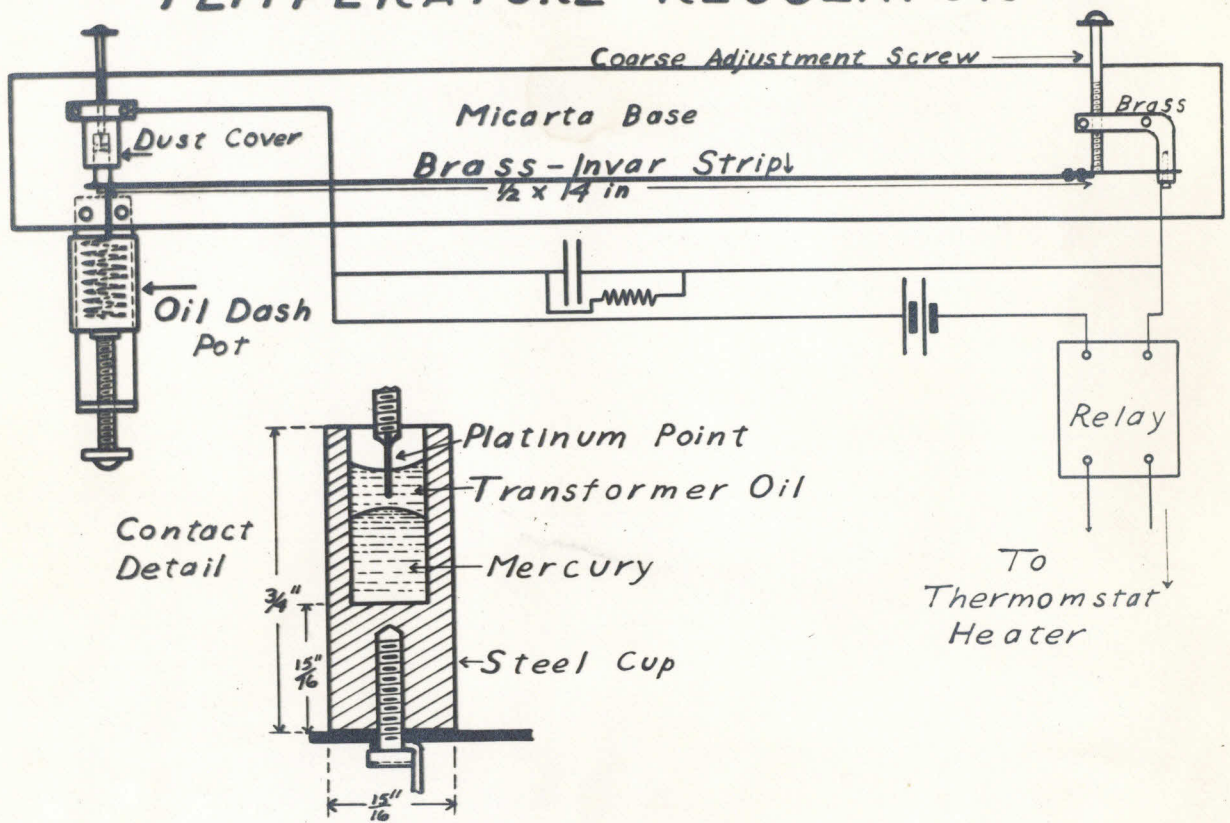


Fig. 3

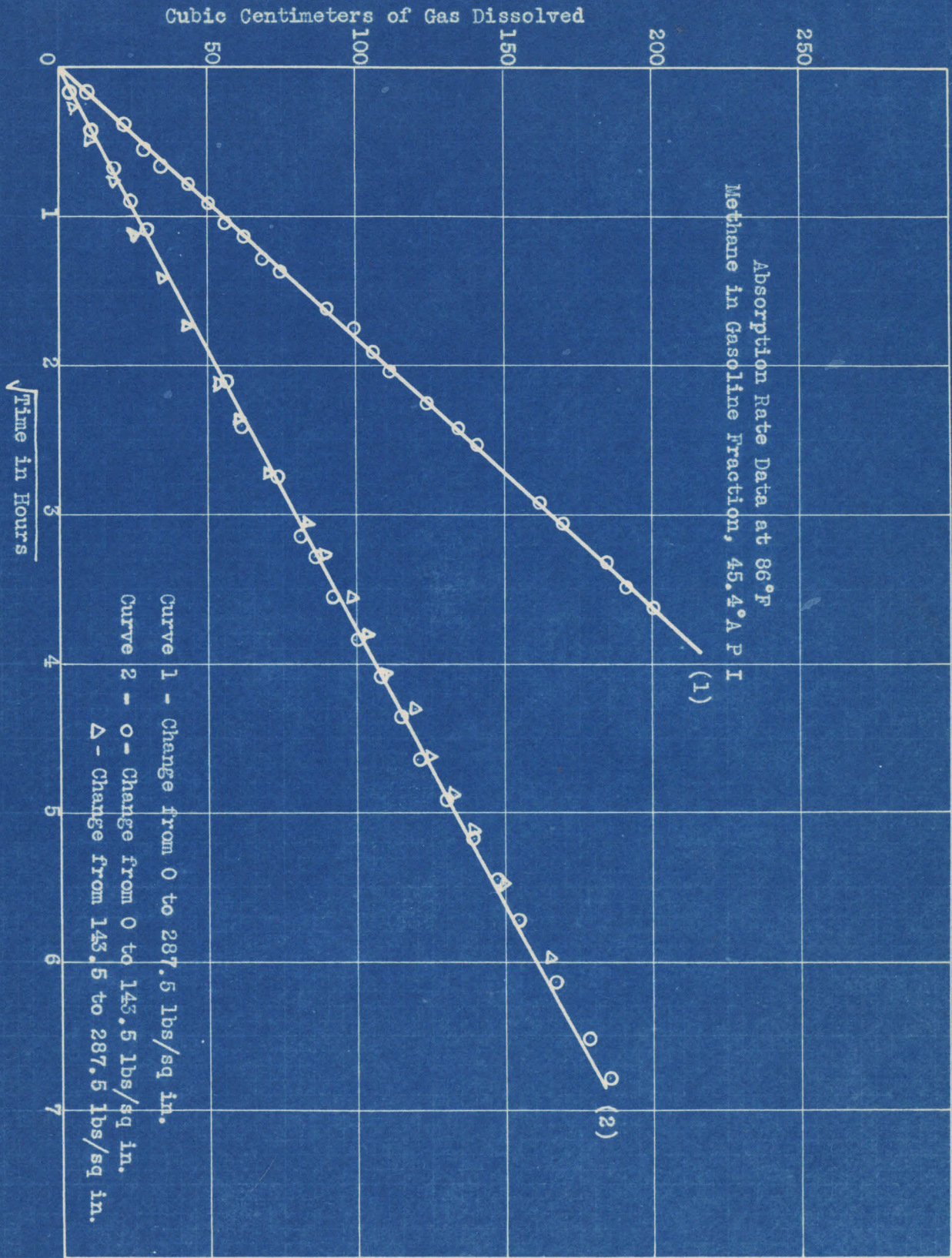


Fig. 4

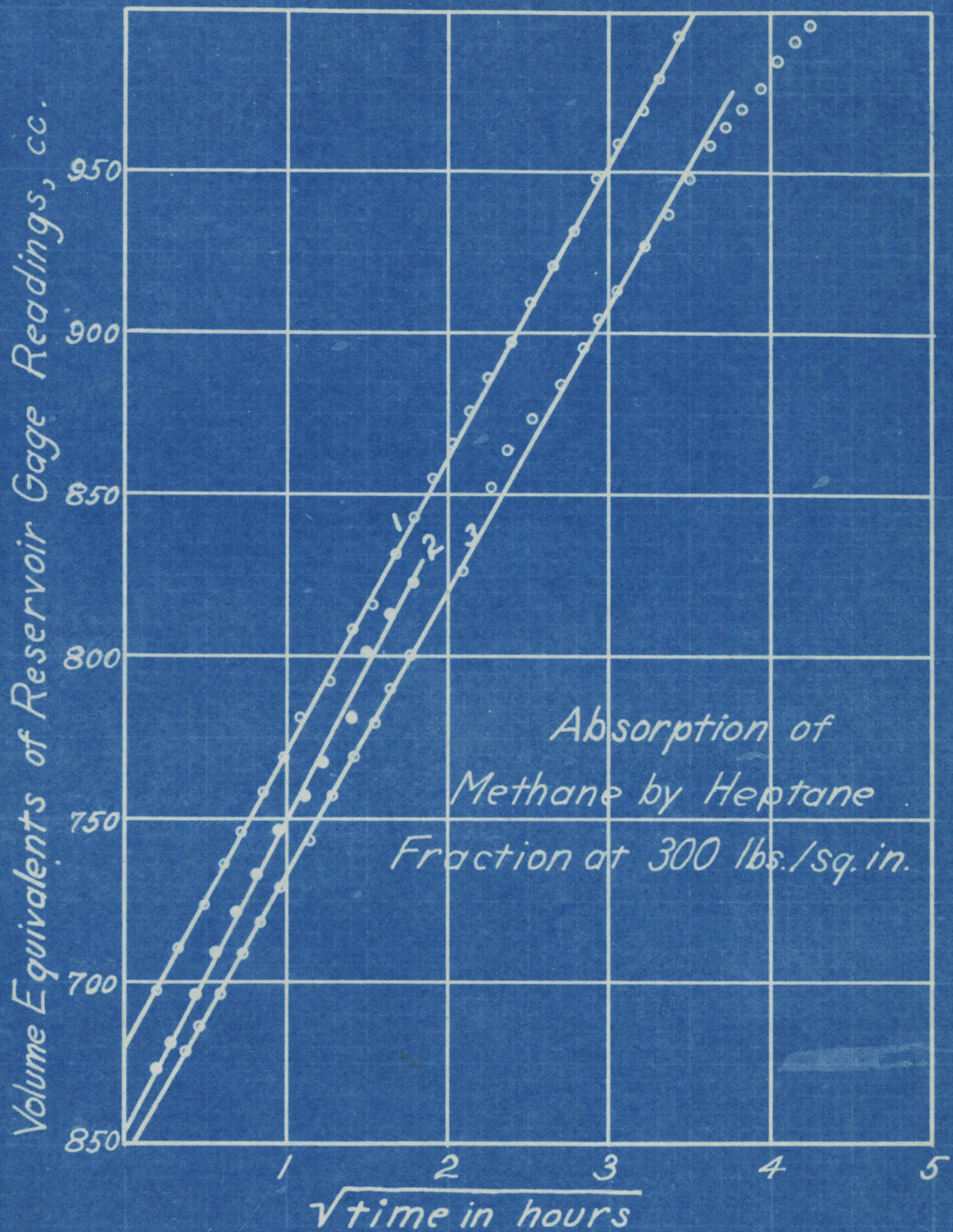


Figure 5

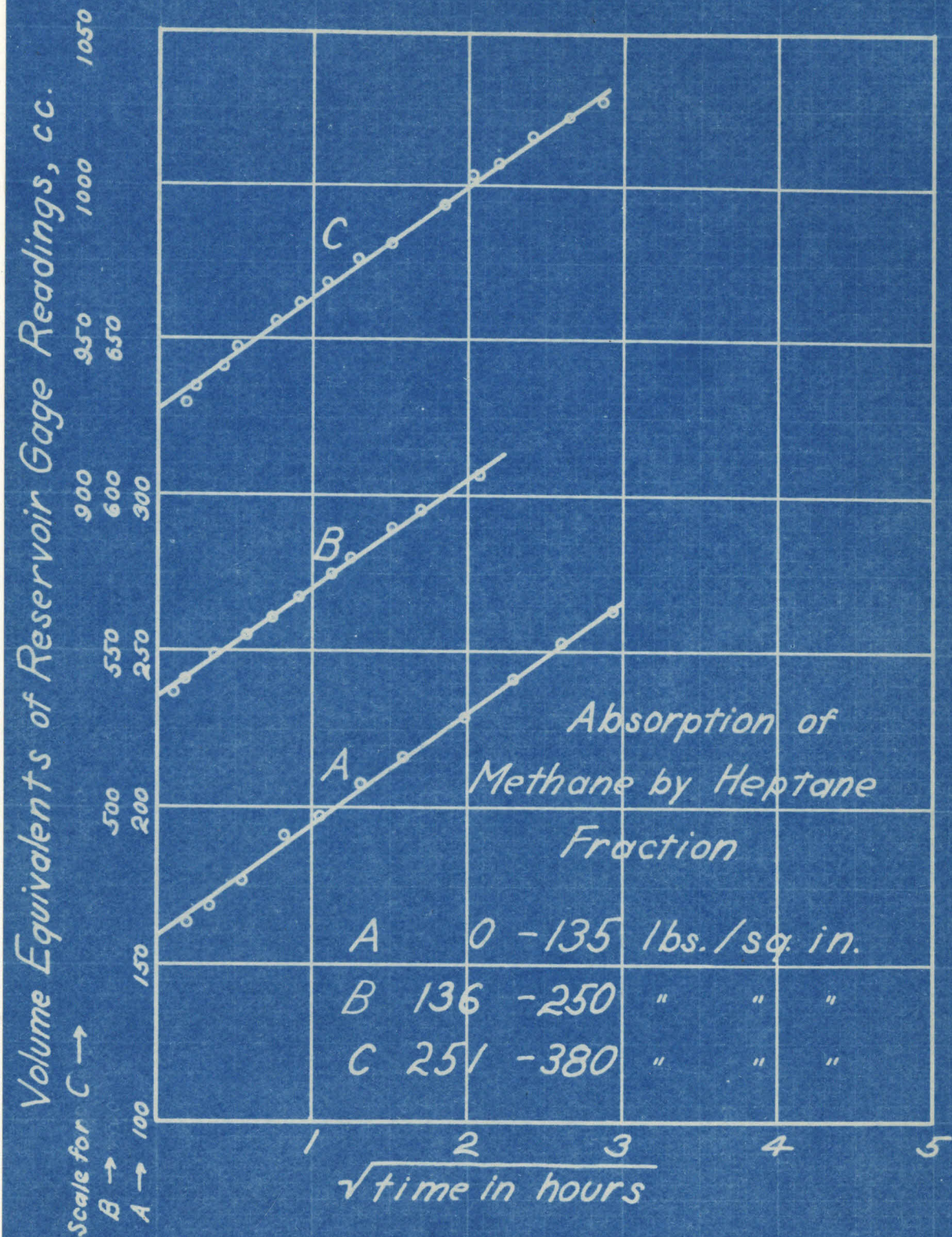


Figure 6.

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