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LIQUID DIFFUSION IN POROUS MEDIA,
WITH SPECIFIC REFERENCE TO THE
ATHABASCA TAR SANDS

by

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ABSTRACT

The velocity of diffusion of the bitumin from sections of 'Tar Sands' has been measured in a specially designed diffusion cell. The solvent used in this case was benzene. The diffusion constant was found to be $D = 2.39 \times 10^{-5} / \text{ft}^2/\text{hr.}$

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I - INTRODUCTION

In chemical engineering a large number of unit processes depend on the diffusion of material through fluid films. Some of these operations are drying, rectification, gas absorption, extraction, and crystallization. This thesis will discuss the theoretical basis of diffusion with special reference to diffusion through a porous body; it will mention previous work based on this theory; and it will endeavour to fit into this theory data obtained by experimental methods from the solvent extraction of bitumen from the Tar Sands of the Athabasca region of northern Alberta.

II - THEORY OF DIFFUSION

General

The operation of diffusion involves the transfer of material through fluid films from one phase to another. The many operations which make use of the general principles of diffusion are classified for study as in the following table¹ which correlates the phase contacted and the contacting phase in the nine possible cases obtained from the three states of

matter - gas, liquid, and solid.

<u>TABLE 1</u>			
<u>Case No.</u>	<u>Phase Contacted</u>	<u>Contacting Phase</u>	<u>Example</u>
1	Gas	Gas	None; gases are completely miscible
2	Gas	Liquid	Absorption, butane by petroleum solvents
3	Gas	Solid	Adsorption, gas respirators
4	Liquid	Gas	Steam stripping
5	Liquid	Liquid	Extraction, petroleum with H_2SO_4
6	Liquid	Solid	Percolation decolorizing of sugar solution
7	Solid	Gas	Drying of wood or brick by hot air
8	Solid	Liquid	Leaching of sugar beets
9	Solid	Solid	None; transfer rates are slow

This paper is principally interested in case eight in which a solid phase is treated with a liquid phase.

In the distribution of a substance between two materials a distribution equilibrium is set up. In the case of a porous solid impregnated with a solution which is being removed by a less concentrated external surrounding solution the internal solution will come to an equilibrium with the external solution. This factor sets the limit on the quantity of external solution required for the extraction process.

The time element is another important factor. The rate of transfer of material will be proportional to the surface of contact between the phases.

There are two main mechanisms of transfer; one is actual bulk motion (convection) and the other is true molecular diffusion as a result of concentration gradient. These two mechanisms operate simultaneously; transfer by molecular diffusion goes on through the film from the interface while convection goes on in the main body.

It is generally assumed that phases in contact are at equilibrium at the interface although there is only limited data for this assumption in the interaction of solids and liquids. This paper will show some evidence that the principle mechanism of transfer between solid and liquid is molecular diffusion controlled by the difference in concentration of the solute in the liquid at the interface and the solute in the porous solid. Surface film resistance is assumed small and is neglected.

3

Mathematical Analysis

The general theory of diffusion is based upon analogy to the flow of heat through solid media, as is exemplified in the classical treatments of Fourier and also of Lord Kelvin in the Encyclopedia.

There are two states of flow by diffusion - the stationary and the non-stationary states. This analysis will be based on non-stationary, unidirectional diffusion in a slab of thickness $2R$.

Certain definite physical conditions pertaining to the porous solid under discussion will be assumed. In actual practice these conditions will be maintained as far as possible

within the bounds of experiment. The conditions are as follows:

1. Diffusion takes place through both faces and along one axis only.
2. The thickness of the solid is uniform.
3. There is a uniform concentration of solute in the solid at the beginning of the experiment.
4. The solvent is maintained at constant concentration throughout the experiment.
5. The diffusion coefficient is constant.
6. The temperature is constant.
7. The transfer of material at the surface of the solid is sufficiently rapid not to interfere with the internal diffusion process.
8. The porous solid is rigid and inert.

The mathematical conditions for diffusion within parallel boundaries are:

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

$$(ii) \quad \text{at } t=0, C=f(x) \text{ for } 0 \leq x \leq 2R.$$

$$(iii) \quad C=0 \text{ at } x=0 \text{ and } x=2R \text{ for all } t.$$

Condition (i) is the differential form of Fick's law of diffusion. D is the diffusion coefficient whose dimensions are area, and is a constant for a specified system for a constant time set of conditions.

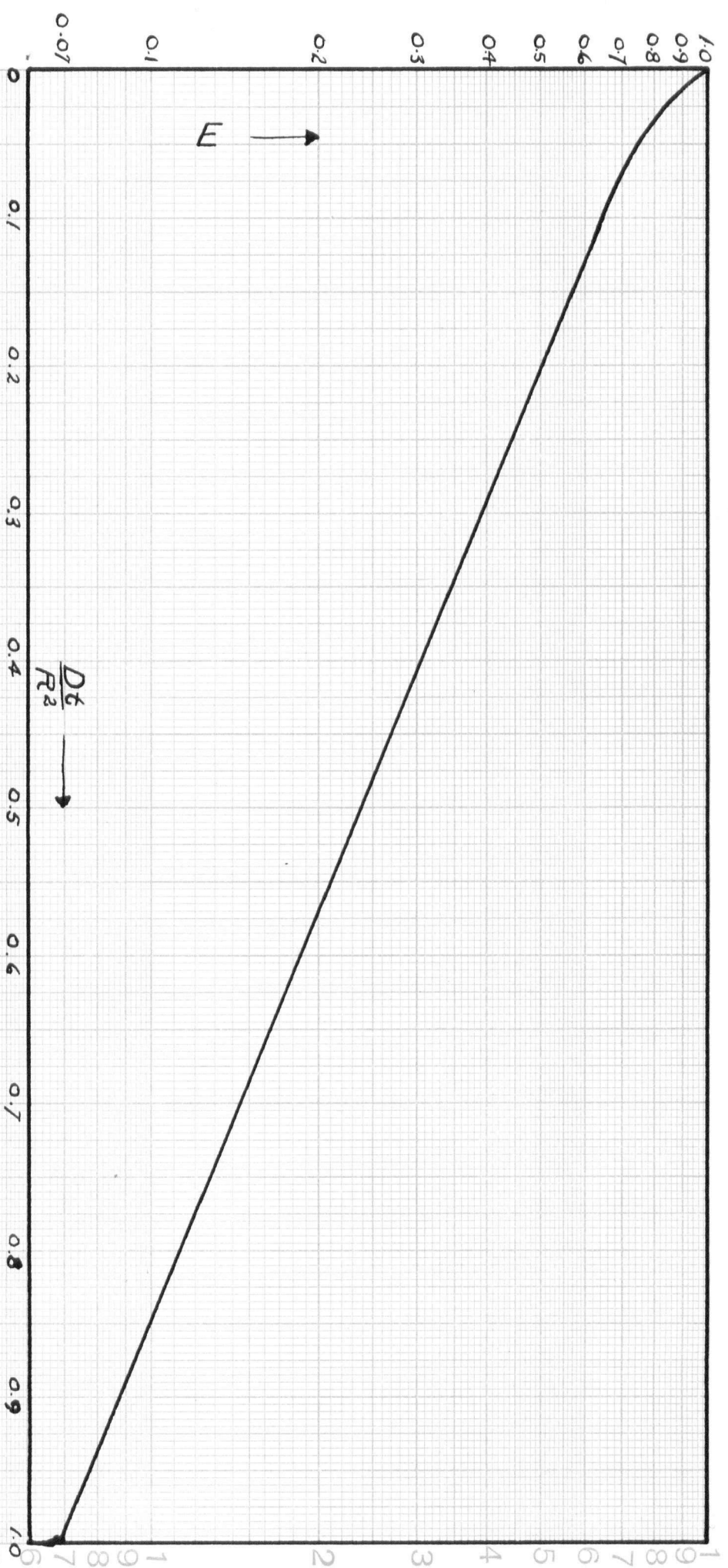


FIGURE 1

FRACTION UNEXTRACTED VS DIMENSIONLESS RATIO $\frac{D_t}{R_2}$

$$E = \frac{8}{\pi^2} \left[\exp\left(-\frac{D_t^2 t}{4R_2^2}\right) + \frac{1}{9} \exp\left(-\frac{9D_t^2 t}{4R_2^2}\right) + \frac{1}{25} \exp\left(-\frac{25D_t^2 t}{4R_2^2}\right) + \dots \right]$$

The solution under these conditions for the amount of solute left in a porous solid at any time t is

$$Q_1 = \frac{4C_0}{\pi} \int_0^{2R} \sum_{m=0}^{\infty} \frac{1}{(2m+1)} \frac{\sin(2m+1)\pi x}{2R} \exp\left[-\frac{D(2m+1)^2\pi^2 t}{4R^2}\right] dx \quad \text{Equation 1}$$

Upon integration this gives

$$Q_1 = \frac{16RC_0}{\pi^2} \sum_{m=0}^{\infty} \frac{1}{(2m+1)^2} \exp\left[-\frac{D(2m+1)^2\pi^2 t}{4R^2}\right] \quad \text{Equation 2}$$

The corresponding equation for the amount of solute removed in any time t is

$$Q_2 = 2RC_0 \left[1 - \frac{8}{\pi^2} \sum_{m=0}^{\infty} \frac{1}{(2m+1)^2} \exp\left[-\frac{D(2m+1)^2\pi^2 t}{4R^2}\right] \right] \quad \text{Equation 3}$$

The fraction E of the extractable solute left unextracted at any time t is

$$E = \frac{Q_1}{2RC_0} = \frac{8}{\pi^2} \sum_{m=0}^{\infty} \frac{1}{(2m+1)^2} \exp\left[-\frac{D(2m+1)^2\pi^2 t}{4R^2}\right] \quad \text{Equation 4}$$

This equation may be expanded into the rapidly converging series

$$E = \frac{8}{\pi^2} \left[\exp\left(-\frac{D\pi^2 t}{4R^2}\right) + \frac{1}{9} \exp\left(-\frac{9D\pi^2 t}{4R^2}\right) + \frac{1}{25} \exp\left(-\frac{25D\pi^2 t}{4R^2}\right) + \dots \right] \quad \text{Equation 5}$$

Sherwood has solved Equation 5 for a number of values of the dimensionless quantity $\frac{Dt}{R^2}$ which are presented in Table 2 and plotted on semi-log paper as Figure 1. The curve so represented is a straight line except for values of E above 0.7.

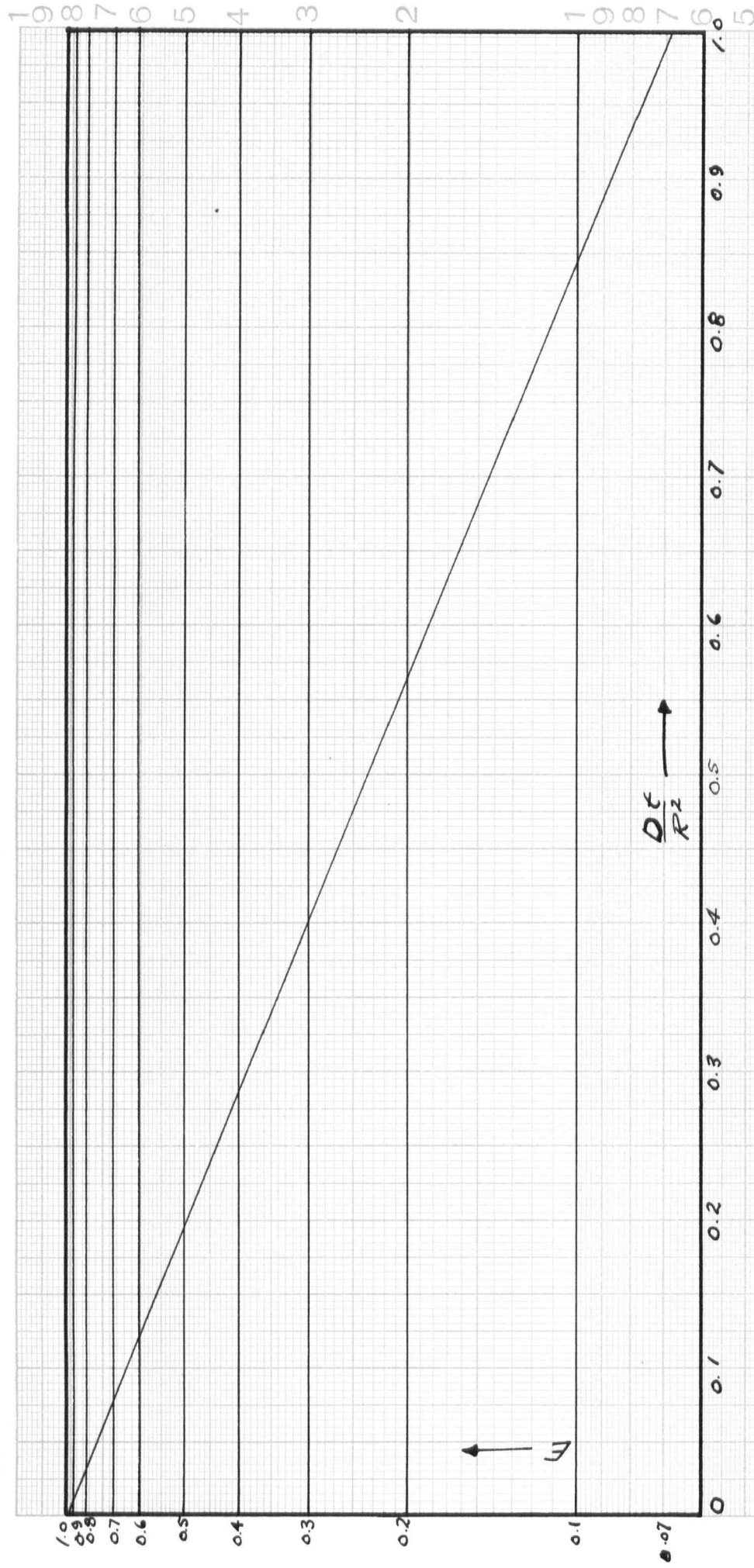


FIGURE 2

FRACTION UNEXTRACTED VS DIMENSIONLESS RATIO $\frac{D\xi}{R^2}$

$$E = \frac{8}{\pi^2} \left[\exp\left(-\frac{D\xi^2 t}{4R^2}\right) + \frac{1}{9} \exp\left(-\frac{9D\xi^2 t}{4R^2}\right) + \frac{1}{25} \exp\left(-\frac{25D\xi^2 t}{4R^2}\right) + \dots \right]$$

E IS ON SPECIAL SCALE PROPOSED BY SHERWOOD

TABLE 2

<u>E</u>		<u>E</u>	
0.000	1.000	0.200	0.496
0.005	0.909	0.300	0.387
0.010	0.885	0.500	0.237
0.025	0.822	0.600	0.184
0.050	0.748	0.700	0.144
0.100	0.642	1.000	0.069
0.150	0.564		

Equation 5 is replotted as Figure 2 according to a scale suggested by Sherwood whereby the scale of E is compressed so as to straighten out the curved portion. Accordingly any extraction data falling on a straight line on Sherwood's special paper shows that the mechanism of transfer is molecular diffusion following as it does Fick's law of diffusion within parallel boundaries for specified conditions.

III - PREVIOUS WORK BY OTHER INVESTIGATORS

The investigation of diffusion in Athabasca Tar Sands has been studied by Hopper who found the value of the diffusion coefficient for the tar-sand in carbon tetrachloride to be 4.25×10^{-5} ft.² per hour at 25°C.

A theoretical study of the mechanism of diffusion has been carried out by March and Weaver who derived an equation for the diffusion of a non-electrolyte out of a porous mass based on an integration of Fick's law equation, and presented data on the diffusion of area from a gel structure into a layer

8
of water. Barrer has presented a monograph on diffusion both from a theoretical and an experimental viewpoint which has already been made use of in this paper.

9
Newman has applied the theory of diffusion to the drying of solids. 10 11
Tuttle and Sherwood applied the diffusion theory to the drying of wood. A special feature of Sherwood's discussion is the introduction of a plotting paper used to compare experimental data with theoretical curves.

12 13,14
Friedman and Kraemer and Friedman investigated the structure of gels by measuring the rate of diffusion of solutions of non-electrolytes into and out of the gels, and showed that the movement of the non-electrolytes was a process of pure diffusion governed by the laws of molecular diffusion.
15,16
Cady and Williams extended the theory of molecular diffusion into a gel to diffusion into a porous solid such as wood.

17
In the field of extraction Boucher, Brier, and Osburn carried out experimental work on semi-batch and continuous counter-current extraction of porous plates saturated with soybean oil. The extraction, using as solvents perchlorethylene and a carbon tetrachloride-ethylene dichloride mixture was found to be one of pure molecular diffusion. Osburn and 18
Katz expanded the diffusion theory of solvent extraction from a porous solid to include the structure of the solid, and proved that the comparison of extraction data for different materials can be made only when details of the structure of the solids are compared. 19
King, Katz, and Brier confirmed the application of the theory of molecular diffusion to the

extraction of oil from a uniform, porous, inorganic solid, but found that the theory did not conform for the extraction of oil from soybean flakes. The structure of the soybean flakes was considered as the cause of the divergence from theory.

IV - THE ATHABASCA TAR SANDS

Composition

One of the world's largest reserves of bituminous materials is the Athabasca Tar Sands of northern Alberta. Tar-
²⁰sands are colloidal systems of bitumen (which itself is a colloidal solution of asphalt in hydrocarbon oils), water, and
²¹mineral matter. A breakdown of the sands reveals that the sandstone texture ranges from coarse to fine silt 80% of which will pass through a 150 mesh screen. The bitumen content ranges from 8 to 20%, averaging 15 to 18%. An average sample is as follows: bitumen soluble in CS_2 - 18.5%, sand - 80.2%, water - 1.3%, S.G. - 1.75 at $25^{\circ}C/25^{\circ}C$. The bitumen is a heavy, dark brown, viscous oil, S.G. - 1.010 to 1.035 at $25^{\circ}C/25^{\circ}C$, with a sulphur content of 4.5 to 5%. A further description of the bi-
²²tumen by Kriebel and Seyer represents the bitumen as of a type between the Trinidad and Bermudez asphalts with respect to its resinous and oily constituents, and completely soluble in carbon disulphide and carbon tetrachloride, and 98% soluble in benzene.

Products

²³

The work of the Fuel Testing Division of the Canadian

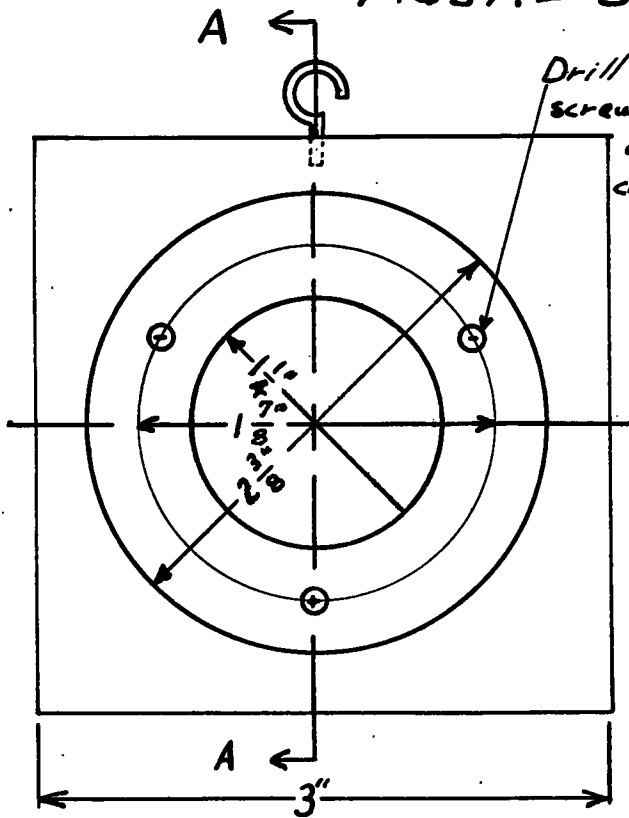
Department of Mines has shown that the crude bitumen can be treated by either the Dubbs or Cross process - the latter yielding as high as 40% by volume of gasoline with 28% fuel oil and 32% coke. Hydrogenation tests show an extremely high yield of gasoline. The refined asphalt is satisfactory and tests show that the oxidized pitch can serve as a briquet binder.

Extraction of Bitumen

The separation of the bitumen from the sand is a problem in colloidal chemistry. Until the summer of 1945 when it was destroyed by fire, a plant operated at Fort McMurray followed the procedure of open-pit mining of the tar-sand, separation of the bitumen from the sand by agitation with hot water, and subsequent cracking for gasoline and residual products. This type of separation has been described by Knight,²⁴ Clark and Pasternack,²⁵ and Clark.^{26,27,28,29} The principal problem to the open-pit mining of tar-sand is one of sand handling and disposal.

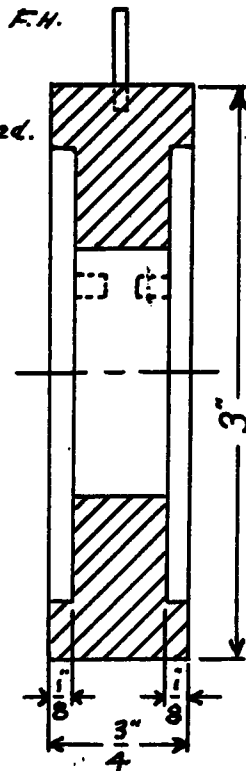
Another possible method of separation is extraction in situ as in the oil-field water drive, the Frasch process for sulphur, and in the production of common salt from brine wells.³⁰ Ellis has investigated a method of extraction in situ using steam although a patent on this process had been filed³¹ as early as September, 1927, by J.J. Rimmer. With the use of more volatile solvents, in order to prevent excessive loss, the greatest consideration would be the geological formations to be tapped. A comprehensive treatment of the flow of

FIGURE 3 - CELL

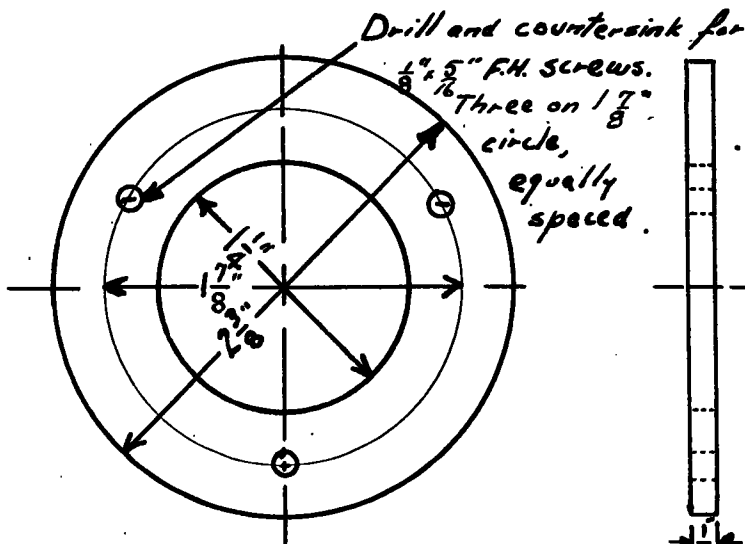


CELL ELEVATION

Drill and tap for $\frac{1}{8} \times \frac{5}{16}$ F.H. screws. Six - three on each side on $1 \frac{7}{8}$ " circle, equally spaced.

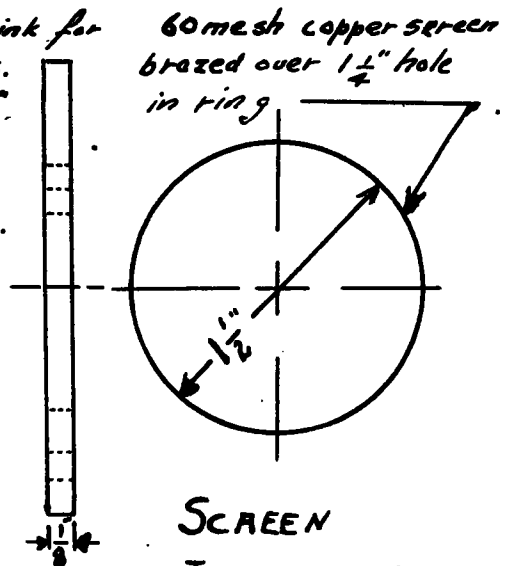


SECTION A-A



RING

Four required, two fitted with screens.

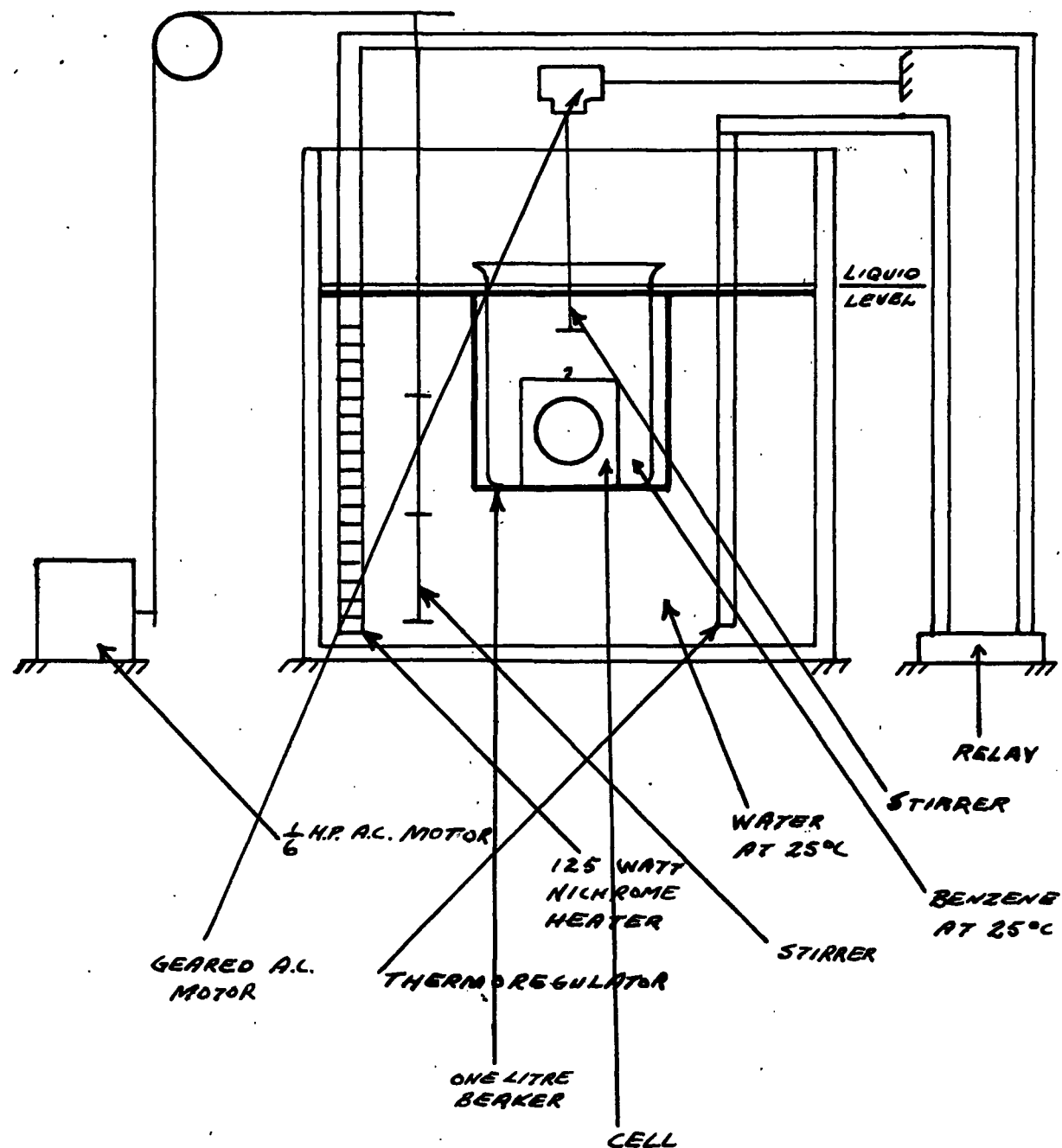


SCREEN

Two required.

FIGURE 4

LAYOUT OF APPARATUS



homogeneous fluids through porous media by Muskat pays considerable attention to this point.

V - EXPERIMENTAL PROCEDURE

General

In carrying out the experimental work on this project frequent reference was made to the previous work of Hopper.³³ The experimental setup as diagrammatically shown in Figure 4 follows his pattern, and at his suggestion benzene was used as the solvent in the extraction of the tar-sands.

Diffusion Cell

The cell (Figure 3) was a simple parallelepiped of cast aluminium constructed to give a cylinder of tar-sand with the ends exposed for diffusion, as required to follow the preceding diffusion theory. The end exposure was effected by using a fine-mesh, removeable screen over the ends which held the sand in place while permitting contact with the solvent. The bare rings and the screened rings used were machined from duraluminum.

Preparation of the Cell

The cell was laid flat on a small piece of steel plate with a set of bare rings in place, and a one inch length of $1\frac{1}{2}$ inch pipe placed on top. Warm tar-sand was tamped into the cell until the level was up in the pipe when a one inch length of loosely fitting round stock was placed on top of the tar-sand. The whole was placed in a vise, tightened up, and

left for 5 or 6 hours.

After removing the cell from the vise the pipe was taken off, and the excess tar-sand cut off flush with the outside face of the cell. The bare rings were removed, the screened rings put in place, and the cell and tar-sand weighed. From the known weight of the empty cell the weight of the tar-sand contained was obtained by subtraction.

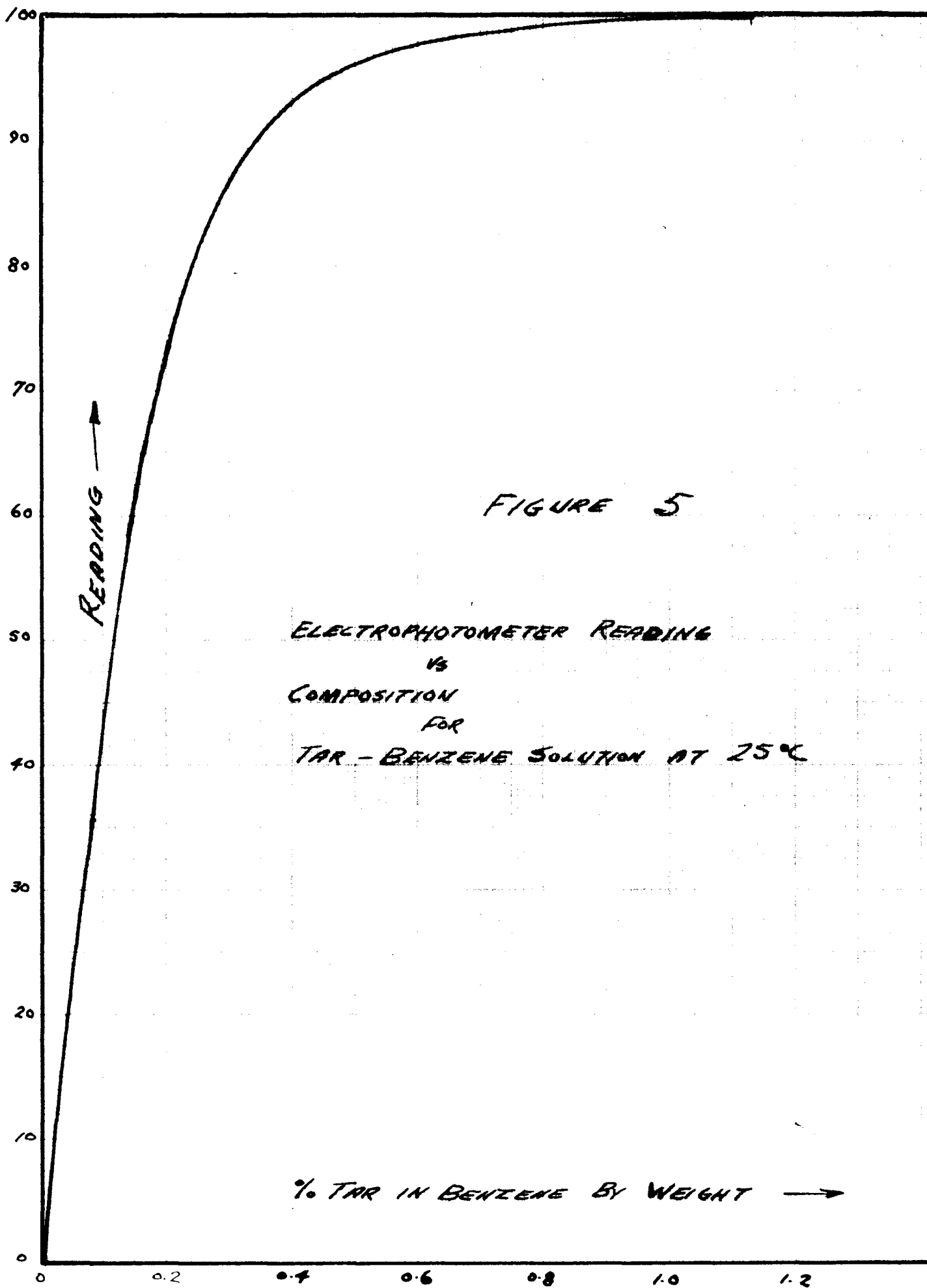
Diffusion Bath

This bath was simply a one litre beaker suspended in the constant temperature water-bath so that the level of the liquid in the two baths was the same. The solvent in the bath was kept barely in motion by a slow-moving propellor so that there was no impact of the solvent against the face of the tar-sand yet the transfer of material away from the surface was sufficiently rapid not to interfere with the internal diffusion process. The temperature of the diffusion bath was maintained at $25^{\circ}\text{C} \pm 0.10^{\circ}$

Diffusion and Extraction Procedure

The loaded cell was placed centrally in the diffusion bath and held there by a wire brace so that no motion of the cell was permitted. Active diffusion was timed from the moment of insertion of the cell until the removal of the cell at the end of the run.

After removing the cell from the bath the partially extracted tar-sand was put in a tared paper Soxhlet thimble and extracted completely with clean solvent. The solution



resulting from the Soxhlet extraction was weighed in a tared container and analysed for tar content.

Similarly the solution from the controlled diffusion was analysed to get the weight of tar extracted from the sample.

The Soxhlet thimble containing the extracted sand was oven-dried at 110°C for at least two hours, cooled in a dessicator, and weighed quickly to avoid moisture pickup.

34 Since the solvent used does not dissolve all the tar a further Soxhlet extraction using carbon tetrachloride was carried out, the thimble again dried and weighed to give the amount of sand in the original sample.

Original Method of Analysis for Tar Content

35 In looking for a method of analysis the method of Hopper was discarded because of the closeness of the specific gravities of the tar and the benzene. It was decided that an electrophotometer would be used to measure the amount of light transmitted by solutions of various compositions. Standard solutions of known composition of tar and benzene were made up, and the amount of light penetrating each noted as a reading on the electrophotometer. The readings were plotted against percent tar as in Figure 5.

The curve in Figure 5 was used to analyse a number of samples obtained on test runs but failed to give the correct composition. The flaw in the analysis was traced to the fact that the tar used to make up the original standard solutions was obtained by complete extraction of a sample of tar-sand.

However, benzene, when extracting tar by diffusion on a time basis, first extracts the oily components, then the resins, and finally the asphaltenes. Consequently the curve obtained for a mixture of all the components of the tar was not correct when applied to a solution obtained by selective extraction. Because of the difficulty of making up a composite curve the electrophotometric method of analysis was discarded in favour of a simpler one.

Final Method of Analysis for Tar Content

An aliquot of the solution to be analysed was weighed in a tared flask, and the solvent removed by distillation over a water bath under a water pump vacuum. When all the solvent had been evaporated the flask was again weighed to get the weight of tar in the aliquot. From this the actual weight of tar in the solution was calculated.

VI - EXPERIMENTAL DATA AND TREATMENT

The following table gives a summary of the data obtained in the extraction of a number of samples from the Athabasca Tar Sands.

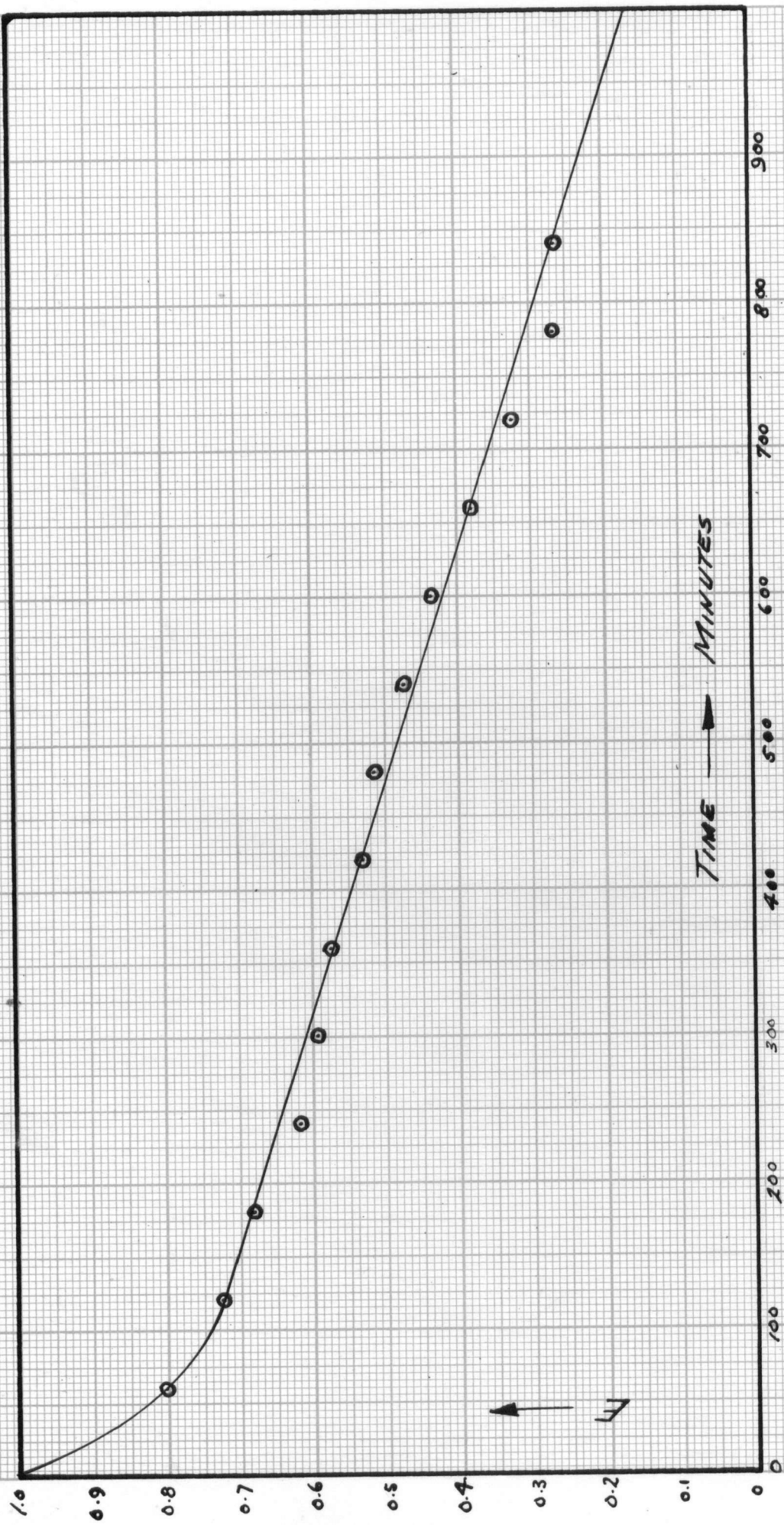
TABLE 4

Run No.	Wt. of Sample	Wt. of Sand	Wt. of Tar	% Tar	Extractable Tar		"E" Fraction not ext.	Time
					Tar ex-tracted	Tar not ext.		
1	30.933g	25.647g	5.286g	17.1	1.020g	4.161g	0.803	60 min.
2	29.951	25.354	4.597	15.7	1.221	3.223	0.726	120
3	31.751	26.001	5.750	18.1	1.712	3.698	0.684	180
4	30.183	25.127	5.056	16.7	1.812	2.941	0.619	240
5	30.526	25.335	5.191	17.0	1.823	2.649	0.593	300
6	30.651	25.537	5.114	16.7	1.970	2.746	0.583	360
7	30.074	25.494	4.580	15.2	2.143	2.442	0.532	420
8	30.119	25.386	4.733	15.7	2.334	2.460	0.513	480
9	30.229	25.409	4.820	16.0	2.390	2.150	0.473	540
10	31.276	25.837	5.439	17.4	3.110	2.408	0.437	600
11	30.558	25.576	4.982	16.3	2.784	1.703	0.380	660
12	30.169	25.423	4.746	15.8	3.201	1.535	0.325	720
13	30.342	25.462	4.880	16.1	3.472	1.265	0.267	780
14	30.061	25.176	4.885	16.3	3.478	1.241	0.263	840

16.4%

Average

The fraction of extractable tar not extracted was calculated as nearly as possible on the basis of the amount of tar which a suitably large amount of the solvent benzene could remove over an infinitely long period of time, and without regard for the equilibrium value of extractable tar which would be of negligible dimensions in any case.



TIME - MINUTES

FIGURE 6

FRACTION UNEXTRACTED VS TIME
TAR-SAND BENZENE SYSTEM AT 25°C

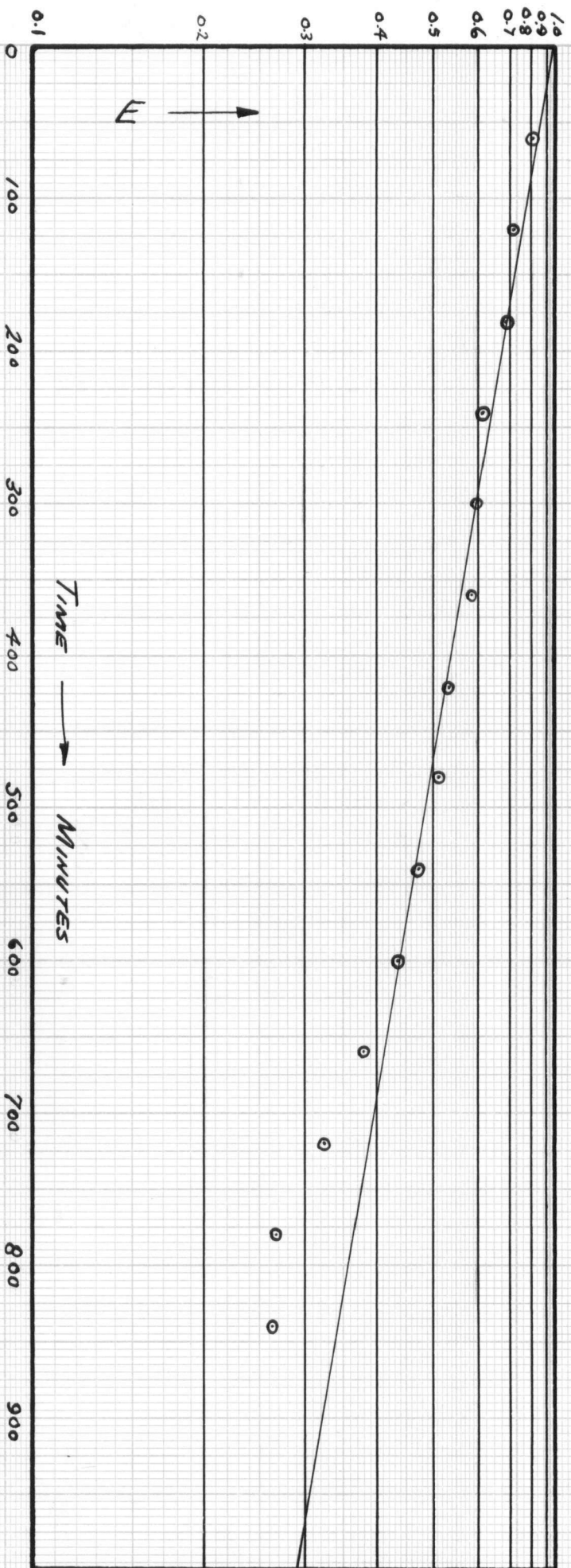


FIGURE 7

FRACTION UNEXTRACTED VS TIME

F IS ON SPECIAL SCALE PROPOSED BY SHERWOOD

The fraction of extractable tar unextracted was plotted against time in Figure 6. Following Sherwood the fraction E was again plotted against time on semilog paper using the compressed scale for E as in Figure 7.

The resulting curve closely approaches a straight line deviating only at the upper limit of time. The deviation might be explained as a consequence of the departure from the original physical conditions for true diffusion which would occur as the tar concentration of the solvent increases with elapsed time.

According to the diffusion theory which has been presented the data obtained indicates that the mechanism involved in the extraction of tar-sand by benzene is one of true molecular diffusion.

From Figure 7 choose $E = 0.5$ for which $t = 477$ min.

From Figure 2 $E = 0.5$ gives $D = 0.195$

$$R = 3/8 \text{ inch}$$

$$D = 0.195 \times \left(\frac{3}{8} \times \frac{1}{12}\right)^2 \times \frac{60}{477} = 2.39 \times 10^{-5} \text{ ft}^2 \text{ per hour.}$$

This is the value of the diffusion coefficient at 25°C for the extraction of bitumen from Athabasca Tar Sands using benzene as a solvent.

VII - CONCLUSIONS

The data which has been presented serves to indicate that the extraction of the bitumen from the Athabasca Tar Sands involves the mechanism of true molecular diffusion following as

it does so closely the theoretical curve of Figure 2.

NOMENCLATURE

x, y, z	-	rectangular coordinates
A	-	surface area in square feet
t	-	time in hours
D	-	diffusion coefficient in square feet per hour
R	-	half thickness of slab in feet
C	-	concentration in pounds per cubic foot at any time t
C_0	-	concentration in pounds per cubic foot at time $t = 0$
Q_1	-	weight in pounds of solute left in porous solid at any time t
Q_2	-	weight in pounds of solute removed at any time t
E	-	fraction of extractable solute left unextracted at any time t

BIBLIOGRAPHY

1. Walker, Lewis, McAdam, and Gilliland - "Principles of Chemical Engineering", p.424 McGraw-Hill (1937)
2. Hopper, D.A. - Master's Thesis - "Liquid Diffusion in Porous Media, Referring in Particular to the Athabasca Tar Sands", (1945)
3. Barrer, R.M., "Diffusion In and Through Solids", pp. ix, xi, 13, 17, Cambridge University Press (1941)
4. Sherwood, T.K., Ind. and Eng. Chem., 21, 12-16, (1929)
5. Sherwood, T.K., ibid.
6. Hopper, D.A., Loc. sit.
7. March, H., and Weaver, W., Phys. Rev., 31, 1072-1081 (1928)
8. Barrer, R.M., Loc. sit.
9. Newman, A.B., T.A.I.Ch.E., 27, 310-333 (1933)
10. Tuttle, F.J., J. Franklin Inst., 200, 609-614 (1925)
11. Sherwood, T.K., Loc. sit.
12. Friedman, L., and Kraemer, E.O., J.A.C.S., 52, 1295-1304 (1930)
13. Friedman, L., Ibid., 52, 1305-1310 (1930)
14. Friedman, L., Ibid., 52, 1311-1314 (1930)
15. Cady, L.C., and Williams, J.W., Chem. Rev., 14, 171-217 (1934)
16. Cady, L.C., and Williams, J.W., J. Phys. Chem., 39, 87-102 (1935)
17. Boucher, D.F., Brier, J.C., and Osburn, J.O., T.A.I.Ch.E., 38, 967-991 (1942)
18. Osburn, J.O., and Katz, D.L., T.A.I.Ch.E., 40, 511-531 (1944)
19. King, C.O., Katz, D.L., and Brier, J.C., T.A.I.Ch. E., 40, 533-556 (1944)
20. Clark, K.A., Can. Min. and Met. Bulletin, 212, 1385-1395 (1930)
21. Egloff, G., and Morrell, J.C., T.A.I.Ch.E., 18, 347-357 (1926)

22. Kriebble, V.K., and Seyer, W.F., J.A.C.S., 43, 1337-1349, (1921)
23. Ells, S.C., Mining Mag., 54, 329-341 (1936)
24. Knight, C., Can. Patent Office Record, 278,861; 278,862. (1928)
25. Clark, K.A., and Pasternack, D.S., Ind. and Eng. Chem., 24, 1410-1416 (1932)
26. Clark, K.A., Can. Min. and Met. Bulletin, 212, 1385-1395 (1930)
27. Clark, K.A., Nature, 127, 199 (1931)
28. Clark, K.A., Nat. Petroleum News, 27, 3032-3036 (1935)
29. Clark, K.A., T. Can. Inst. of Min. and Met., 47, 257-274 (1940)
30. Ells, S.C., Can. Dept. of Mines, Report 719, 28-42 (1930)
31. Rimmer, J.J., Can. Patent Office Record, 278,618 (1928)
32. Muskat, M., "The Flow of Homogeneous Fluids Through Porous Media", McGraw-Hill (1937)
33. Hopper, D.A., Loc. sit.
34. Kriebble, V.K., and Seyer, W.F., Loc. sit.
35. Hopper, D.A., Loc. sit, p. 11
36. Sherwood, T.K., Loc. sit.