SOME FUNDAMENTAL PROPERTIES OF ASPHALTS

Thesis by

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Asphalts and similar bitumens are extensively used as waterproofing materials and as protective coatings on metal structures, such as pipe lines. Practical experience has thus far governed the selection of the type of bitumen to be used for a specific purpose; but preferences so dictated have been subject to change, and are not quite consistent within locale or industry. Undoubtedly the lack of fundamental knowledge regarding bituminous substances contributes to the diversity of practice. To make available more information of certain fundamental properties of certain of these materials was the purpose of this research, which was conducted as a project of the Asphalt Institute.

Investigation of basic physical and chemical characteristics of bitumens has received but scant attention compared to the total amount of experimental work performed with them. Most investigations have been concerned with matters of immediate practical importance, having to do with production problems, the establishment of empirical standards and tests, and technical difficulties related to specific applications. Asphalts have been avoided by scientists as a subject of academic research because they are materials of indefinite composition, with properties depending upon the crude base stock and upon their subsequent treatment. In view of the great economic importance of the industry, a correlation of basic characteristics to behavior under empirical tests will be of benefit.

Difficulties encountered with asphalts and pitches in service present a picture of some complexity. Saturated roofings blister, metals covered with asphalts corrode, and pavements disintegrate.

Since the greater number of the manifold applications of asphaltic products have to do more or less directly with the exclusion of moisture, knowledge of the essential behavior of asphalts in the presence of water and other components of the application should be of value. If this behavior can be related to other properties of the material, a direct basis will be obtained for the design of a product for a specific use.

Materials Used

Samples of asphalts and coal tar pitches were obtained through the courtesy of the Union Oil Company at Wilmington, California, and of the Shell Development Company at Emeryville, California.

Code numbers assigned to the various materials are given below:

Code No.	Description	Pen. at 77° 100 g, 5 sec.*	Softening Point, °F.**
1	San Joaquin valley steam-blown asphalt	5	174
2	" " " " " "	2	165
3	" " " " " "	0	204
D-3100-4	Steam-blown asphalt from crude source A	15	159
D-3100-5	" " " " " " "	45	126
D-3100-6	" " " " " " "	7	189
E-5198-1	" " " " " " "	1	234
E-5198-2	" " " " " " "	25	140
E-5198-3	" " " " " " "	30	135
M-1	Steam-distilled from Panuco crude, Mexico	7	190
M-2	" " " " " "	12	176
M-3	" " " " " "	20	158
M-4	" " " " " "	34	142
M-5	" " " " " "	46	137
11	California air-blown asphalt	24	166
12	" " " "	19	188
D-3100-1	Air-blown asphalt from crude source A	20	169
D-3100-2	" " " " " " "	20	190

Code No.		Pen. at 77° 100 g, 5 sec.	Softening Point, °F.
D-3100-3	Air-blown asphalt from crude source A	18	215
E-5198-4	" " " " " " "	20	235
E-5198-5	" " " " " " "	22	152
21	Filled air-blown California asphalt	19	210
22	" " " " "	3	244
31	Coal tar pitch	24	140-150
32	" " "	2	160-170
33	" " "	2	180-190
41	Coal tar enamel	2	180-195
51	New Type coal tar pitch	2	214

* Penetration. - The distance a standard needle vertically penetrates a sample of the material when the needle is loaded with 100 grams for 5 seconds at 77°F.

** Softening Point. - The temperature at which a steel ball will sink through a plug of asphalt held in a brass ring of suitable diameter.

Transport of Water through Bitumens

It is reasoned, from a knowledge of the conditions under which asphalts fail to exclude water, that transport through the protective layer may be accomplished in one or more of three ways:

1. Penetration through microscopic cracks or pin-holes by the action of surface forces;
2. Electrosmosis, as a result of electrical potential differences across the coating; and
3. Diffusion under the influence of aqueous tension gradients.

Partial investigations of each of these three have been conducted.

-ooOoo-

Wetting Angles

A liquid in contact with a solid assumes a surface form which permits a static balance of the surface forces existing in the interfaces which join. From Figure 1 it is seen that a force balance at point A gives the equation

$$T_S = T_L \cos \theta + T_{SL}$$

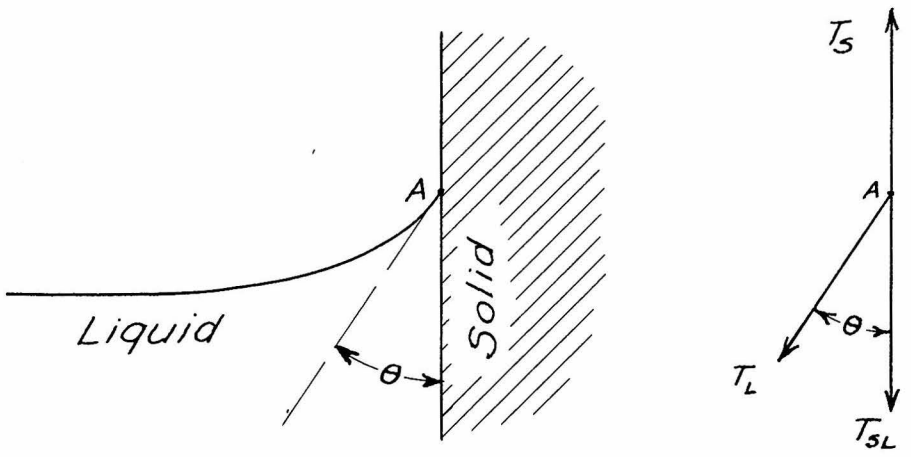


Figure 1.

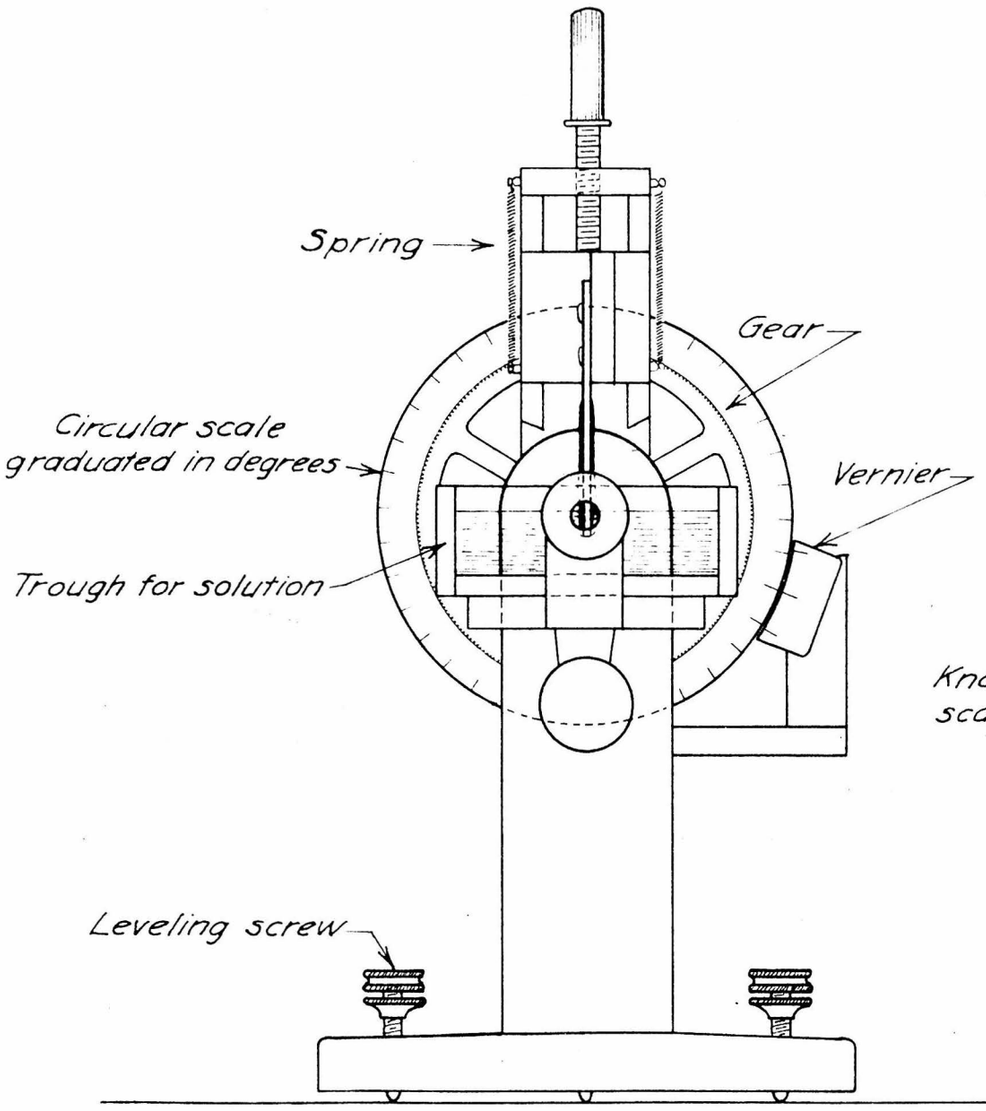
A knowledge of the magnitude of θ, the contact angle, is sufficient for a qualitative measure of the attraction of the surface of the solid for the liquid. If θ is 0, the liquid tends to spread indefinitely in a thin film over the surface of the solid; and if θ is 180°, the liquid will not wet the solid at all. Since the single quantity θ is in the case of solids more easily measured than the surface and interfacial tensions, it is used as an index to the tendency for water to move into cracks or pin-holes.

Method and apparatus: - Several methods of measuring contact angles have been developed and used. Talmud and Liebman[1] used with success a microscopic method for determining the dimensions of drops of liquid on a flat plate, and calculating therefrom the contact angle. Ablett[2] constructed a cylinder, coated with the solid to be studied, which could be rotated in a trough containing the liquid. His procedure was to rotate the cylinder at a constant speed, and raise the level of the liquid until the surface was horizontal up to the point of contact with the cylinder. Measurement of the liquid level in relation to the cylinder afforded data for calculation of the contact angle. Adam and Jessop[3], and subsequently Nietz[4] used a method whereby a coated plate was tilted while in the liquid until the meniscus became horizontal to the point of contact. Since this method was reported to be as reliable as any, it was selected in preference to the others because of the ease with which it could be applied to asphalts.

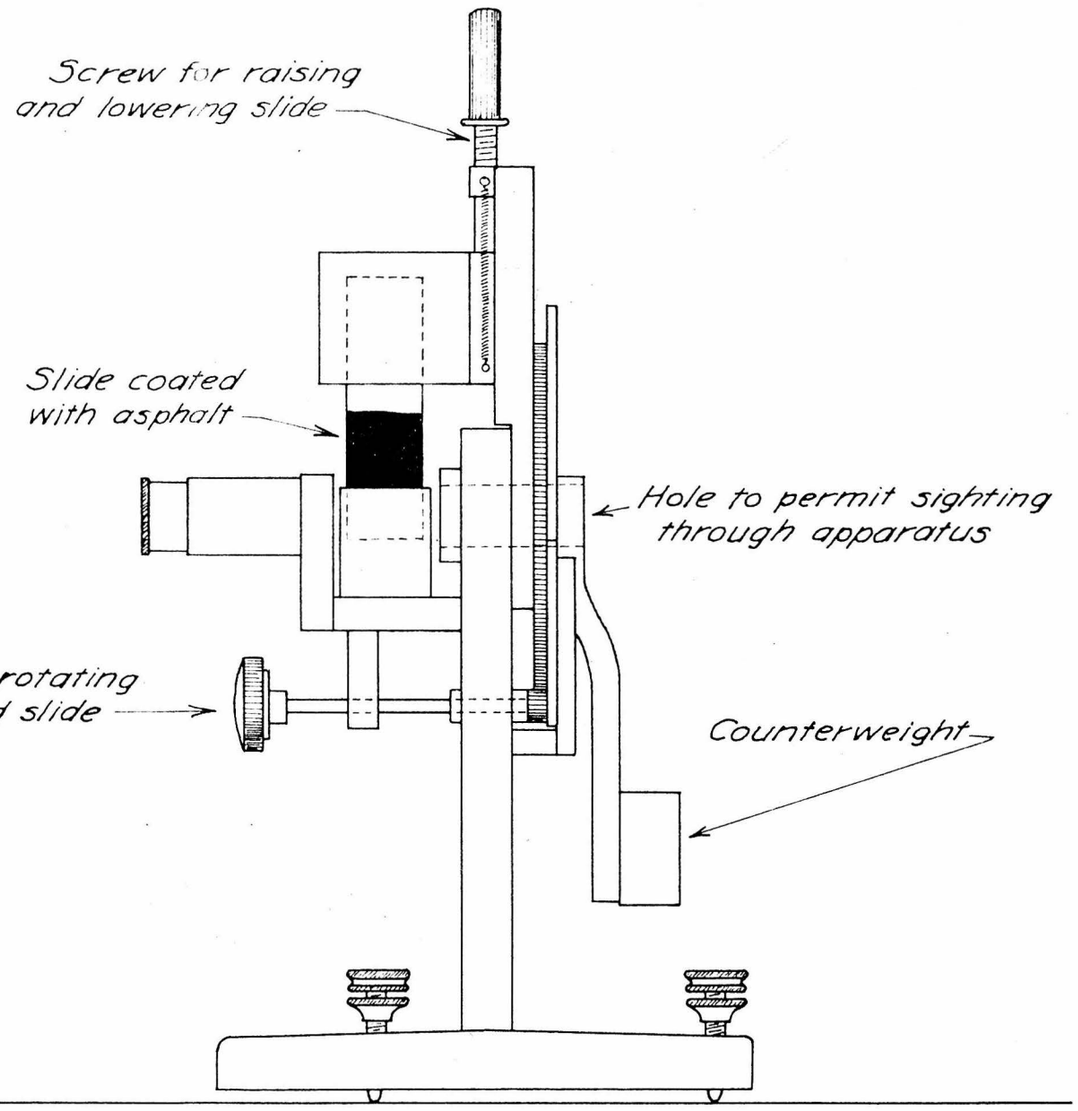
A tilting plate apparatus, shown in Figure 2, was constructed. It consists of a rigid stand which supports a rectangular trough

CONTACT ANGLE APPARATUS

Scale - Half Size



FRONT VIEW



SIDE VIEW

Figure 2

fitted with plane glass sides. By means of an accurately machined slide and a screw, a microscope slide coated with asphalt may be moved in or out of the liquid. An eye-piece is used to provide an enlarged view of the junction between the surface of the liquid and the asphalt coating. The assembly which holds the slide may be rotated about the optical axis of the system, and the degrees of rotation may be read on an affixed graduated scale.

Theoretically, if a plate is immersed in a liquid, the true contact angle should be observed if time enough is provided for the attainment of equilibrium. However, the time required is so long that it is almost impossible to measure the angle under conditions of true equilibrium. Investigators report that equilibrium angles are not even approximated after periods of waiting as long as 24 hours or more[5].

It becomes necessary, then, to measure contact angles more or less dynamically, and to correct for the lag in approach to equilibrium. Angles have been commonly observed to be larger when the solid is immersed in the liquid than when it is being withdrawn. Such a phenomenon suggests a "hysteresis" effect which Adam[6] ascribes to friction between the surfaces. Some controversy has arisen in regard to the cause of the lag, but the derivation of the equilibrium contact angle from immersion and receding angles is quite generally accepted as explained by Adam.

Let F = the force of "friction" which just prevents relative motion of the phases.

θ_i = immersion contact angle.

θ_r = receding contact angle

T_S = surface tension of the solid

T_L = surface tension of the liquid

T_{SL} = interfacial tension between solid and liquid

θ = equilibrium contact angle

At equilibrium there is no force of friction, so

$$T_S - T_{SL} = T_L \cos \theta \qquad (1)$$

When the plate is immersed

$$T_S - T_{SL} = T_L \cos \theta_i + F \qquad (2)$$

And when the plate is withdrawn

$$T_S - T_{SL} = T_L \cos \theta_r - F \qquad (3)$$

Adding (2) and (3),

$$2(T_S - T_{SL}) = T_L(\cos \theta_i + \cos \theta_r)$$

Substituting in (1),

$$\cos \theta = \frac{\cos \theta_i + \cos \theta_r}{2}$$

According to restrictions placed on this derivation originally, it is valid only in case there is no motion of one phase relative to the other at the instant of measurement. However, Ablett[2] has shown that if receding and immersion angles are determined at the same rate of relative motion of phases, the relationship still holds.

With the apparatus used in this research, the juncture of liquid and solid was caused to occur at the axis of rotation of the slide assembly when the meniscus is horizontal. Careful manipulation then results in a condition quite close to static at the time when the angle is read. However, readings made while the slide was slowly

moved in or out of the liquid gave results which checked the others within the expected error of the static determinations.

The slides were coated with asphalt by dipping into molten asphalt, allowing to drain, and then to cool in air.

Experimental Results: - To test the reproducibility of the readings on contact angles, three independent sets of determinations were made on six of the asphalts. The maximum discrepancy between any two of the determinations for one type of asphalt was found to be 1.75°, and the general agreement was much better than that. The data indicated that if a reasonable number of independent measurements on the same sample are made, the average ought to be consistent with respect to measurements on other samples within 1°.

At the outset there was some question whether the angles measured were of the correct absolute value. Slides were coated with paraffin wax, and contact angles determined for fresh distilled water on paraffin. The average of the values obtained was 108°, which agrees quite well with the 105° reported by Adam and Jessop[3], and the value of 109° ± 30' reported by Nietz[4].

Care was taken to maintain a clean fresh surface on the liquid by frequent cleaning of the vessel, flushing with fresh solution before each reading, and sweeping the surface with a paraffined float. No discrepancies were noted which could be attributed to the presence of a contaminating surface film, an observation also reported by Nietz[4].

The dependence of the angle of contact on the pH of the solution

was investigated. To eliminate variation in ionic strength between solutions of different pH values, Clark and Lubs buffers were prepared and brought to equal ionic strength with NaCl. The surface tensions of the resulting solutions were measured with a Du Nuoy tensiometer, and the pH values were determined with a glass electrode pH meter. Data obtained are as follows:

Table I

pH	0.99	1.93	4.96	7.16	10.99
T, dynes/cm.	62.6	62.3	57.9	57.6	59.4
Material					
1	85	79	75	86	82
2	81	80	55 (?)	85	79
3	84	74	75	77	80
11	97	95	96	94	95
12	97	96	95	95	96
21	101	96	97	99	100
22	87	86	95	93	90
31	50	44	53	40	21
32	58	56	55	55	31
33	64	57	62	52	54
41	67	66	66	60	51

Each value recorded in the table is an average of at least four readings on each of two or more slides coated with asphalt.

There seems to be no significant variation in wetting angles over the pH range of these buffers, except for the two coal-tar pitch samples 31 and 32.

In order to obtain some data covering the behavior of wetting angles in acids, bases, and salts, solutions of HCl, KOH, and $CaCl_2$ were prepared. $CaCl_2$ was selected because it afforded a large range of surface tension of solution, and it was thought desirable to discover whether the surface tension of the solution would have a marked effect on the contact angle. Data for these solutions are given in Table II.

Table II

Concentration	H_2O	0.05 N HCl	1.29 N HCl	0.5 N KOH	1.13 N KOH	0.04 N $CaCl_2$	0.1 N $CaCl_2$	20.0 N $CaCl_2$
T	72.0	72.6	72.4	73.8	75.1	56.0	61.0	105.0
Sample								
1	89	83	90	66				95
2	82	88	86	68	42	80		100
3	78	82	86	63	40	80	73	96
11	97	98	93	80	69		96	107
12	100	99	92	77	74	93	97	108
21	100	99	100	83	80	98	99	110
22	97	97	92	78	73	96	98	108
31	74	68	59	31	28			70
32	73	72	63	25	28			66
33	73	75	67	20	24			68
41	76	76	65	21	24			81

A marked decrease in the wetting angle was observed in all cases in KOH, although the concentration required to produce the decrease is less for coal tars than for asphalts. The slight increase in angles for the coal tar pitches in 1.3 N KOH may not be real because of the difficulty of measuring small angles.

Coal tar pitches, in contrast to the asphalts, showed a definite decrease in wetting angle in HCl solutions.

The contact angles in $CaCl_2$ solutions appeared to have no marked relationship to the concentration, excepting that for 20.0 N $CaCl_2$ the angles are larger for asphalts, and in general slightly smaller for the coal tar pitches. Apparently the solution-asphalt interfacial tension increases with concentration slightly, and the solution-coal tar pitch interfacial tension decreases somewhat. The changes are, however, not significant, since an angle around 90° would have to change appreciably to indicate a substantial change in interfacial tension.

Discussion of Results: - Water and aqueous solutions, being polar, would be expected to have greatest affinity for polar surfaces. On this basis the surface polarity of the classes of materials may be ranked in the following order of decreasing polarity: coal tar pitch > steam-blown asphalts > air-blown asphalts. It is questionable, however, to make this a conjecture concerning the average chemical constitutions, since there is evidence that, for instance, the oily portion of air-blown asphalts exudes, or "blooms" on the surface, making the surface characteristics a function of the dispersing phase.

To illustrate the application of contact angle data, the levels to which water will rise in asphalt and coal tar pitch coatings will be computed. If we assume a vertical circularly-cylindrical hole of radius r in a thick coating, the height to which a liquid of density d and surface tension T will rise is given by the equation

$$h = \frac{2T \cos \theta}{dgr}$$

As a specific example take r = 0.1 mm.

Material No.	Contact angle, θ	Height, h, cm.
1	88	0.50
2	82	2.04
3	78	3.06
11	97	-1.80
12	100	-2.56
21	100	-2.56
22	98	-2.04
31	74	4.06
32	73	4.30
33	73	4.30
41	76	3.56

Water will not penetrate the air-blown asphalts, but will penetrate the steam-blown asphalts and coal tar pitches to a height of several centimeters. Similar calculations could be made for cracks.

This investigation was carried out on fresh or comparatively fresh surfaces. It is conceivable that weathered asphalts would show a substantially lower contact angle, since water-soluble constituents are formed. However, the surfaces in a crack in a coating would remain relatively fresh for some time, since the principal effect of weathering is due to photochemical action. An interesting supplement

to these measurements would be a study of the effect of weathering on the wetting angles.

Electrosmosis

Electrosmosis experiments were conducted by Charles Best, Asphalt Institute Research Assistant, 1936-37. The results indicated that water transport through asphalts by means of electrical potential differences is nil.

Diffusion

If a constant aqueous tension gradient is maintained across a sheet of material, the weight, w, of water diffused through in time, t, under steady state conditions will be given by Fick's law of diffusion:

$$w = \frac{K A t \Delta P}{L}$$

where A = area of diffusion path.

L = length of diffusion path.

ΔP = partial pressure gradient over the length, L, of the path.

K = diffusion constant.

This relation applies to any steady state diffusion process if values of ΔP and L remain constant, and applies unrestrictedly to a case in which the partial pressure varies linearly along the diffusion path.

If hygroscopic materials are present in the diaphragm, or if adsorption of water occurs, the concentration of water as vapor in the membrane will not be linearly related to the vapor pressures in contact; and the linear diffusion law constants will be found to vary

with thickness of diaphragm and with vapor pressure gradient. A true description of the diffusion process under such complicating conditions may be obtained by the use of a more involved expression; but for practical purposes Fick's law is a convenient basis for calculation, since the quantities it involves are readily measurable. For any material, adequate information for the computation of diffusion rates may be derived from establishment of the variation of linear diffusion law constants with pressure gradients and with thickness of material.

Methods and Apparatus: - Measurement of the diffusion rate was accomplished by a simple and direct method. Constant aqueous tension gradients were maintained across a thin sheet of asphalt, and the amount of water transported through determined by weight as a function of time. The weight of water diffused through was obtained either by loss of weight of water from the high vapor-pressure side, or by gain in weight of a desiccant on the low vapor-pressure side.

The first determinations of diffusion rate were performed with a simple type of diffusion cell, consisting of a spun anodized aluminum cup with an alundum filter disc support for the diaphragm of asphalt, which was sealed over the mouth of the cup, as shown in Figure 3.

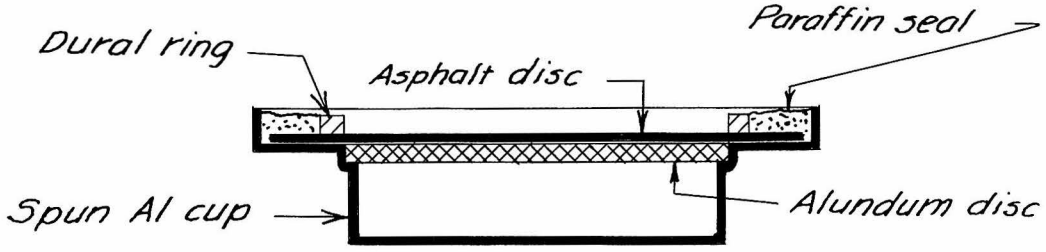


Figure 3. Diffusion Cell

The lower surface of the thin diaphragm was sealed around the edges to the cup by careful application of heat, and the diffusion area was restricted on the upper surface by centering on it a heated dural ring. The space between the lip of the cup and the dural ring was poured full of paraffin wax to help prevent leakage. Blank runs indicated that this was an effective seal.

Two types of experiments were conducted with the cups illustrated in Figure 3. In one case the base of the receptacle was partially filled with water before sealing the diaphragm in place, and the assembly placed in a desiccator in a constant temperature water bath. The cups were removed periodically and weighed. The other method was simply to reverse the position of water and drying agent, placing water in the desiccator, and the drying agent in the cup.

Diffusion of water through asphaltic materials proved to be relatively slow. The time required to establish an accurate steady-state rate of diffusion was great because of the errors involved in obtaining changes in weight as a small difference between two comparatively large figures which were in themselves subject to accidental changes incident to frequent handling. Results indicated the desirability of finding a method whereby smaller amounts of moisture could be determined with moderate precision.

A different type of cell, similar to the one used by Taylor, Herrmann, and Kemp,[7] was designed to avoid the objections found to the methods outlined above. In essence this new cell, shown in Figure 4, differs from the others only in that a quartz spring

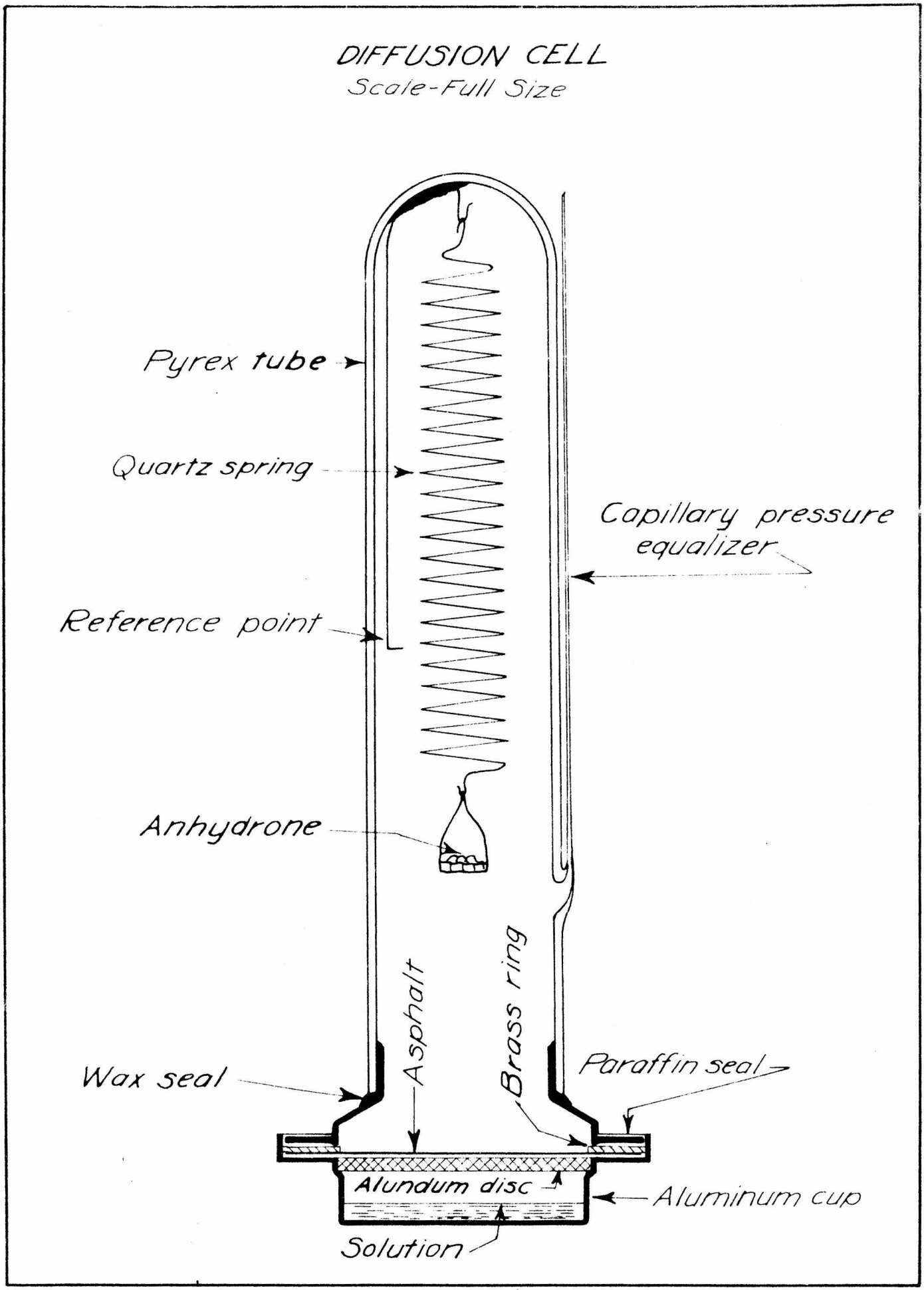

DIFFUSION CELL
Scale-Full Size
Pyrex tube
Quartz spring
Capillary pressure equalizer
Reference point
Anhydrone
Asphalt
Brass ring
Wax seal
Paraffin seal
Alundum disc
Aluminum cup
Solution

Figure 4.

balance for measuring changes in weight of the drying agent is added as a superstructure to the cup. Water passes from the cup at the bottom, through the diaphragm, and into the space above, where it is absorbed by $Mg(ClO_4)_2$ held on an aluminum foil pan supported by the calibrated fused quartz spring. With this cell, small amounts of water are easily detected without disturbing the system.

A solution for maintaining constant humidity was placed in the cup, an asphalt diaphragm sealed to an accurately turned and ground flat brass ring was placed over the mouth of the cup, and over this the inverted test tube containing the quartz spring supporting some anhydrone was sealed with a thick layer of paraffin. The assembled cells were placed in an air thermostat maintained within 0.2°C. of the desired temperature. The elongations of the springs were measured with a cathetometer without removing the cells from the thermostat.

It was found in some cases that the absorption of the water vapor initially present in the inverted test tube resulted in a pressure differential across the diaphragm sufficient to cause it to warp or to fracture. To avoid this a capillary tube was pulled out on the side of the cell. After assembling the cells, the capillaries were left open for three or four hours, and then sealed. In all cases where this procedure was followed there was no damage to the asphalt membrane as a result of pressure reduction.

Construction of Quartz Springs: - In order to construct these cells, it was necessary to make quartz springs, since none were readily

available on the market. A method and apparatus for making quartz helices with ease was developed.

After some experimentation, a machine for winding springs from pre-formed fibers was constructed. The essential details of the apparatus are shown in Figure 5.

Fibers were prepared by heating a section of a clear quartz rod in an oxy-hydrogen flame, and drawing the fused portion down to a fiber about 0.08 mm. in diameter. With a certain amount of practice to develop the technique, one is able to prepare fibers of the proper size and of relatively uniform diameter throughout their lengths.

To construct the spring, a fiber is run through the capillary feed, a hook is formed in the upper end with the aid of a torch, and affixed to the wire support. On a similar hook at the lower end of the fiber is placed a weight of about 0.5-1.0 grams to assist in keeping tension on the spring while it is formed on the silica mandrel. After the fiber is thus secured, the motor, adjusted to turn the mandrel at about 3-6 r.p.m., is started, and the torch with a gas-oxygen flame is swung around and directed on the fiber just above where it touches the mandrel. As the fiber softens and conforms to the shape of the quartz tube, the capillary feed and the torch are advanced by the screw on which they are mounted. Any desired pitch of helix may be obtained by varying the size of the pulley which drives the threaded shaft. Proper adjustment of the flame and of the speed of the motor will result in perfectly true helices. Since the translucent quartz tubing used for a mandrel has a slight taper as made, there is little

DEVICE FOR WINDING QUARTZ SPRINGS

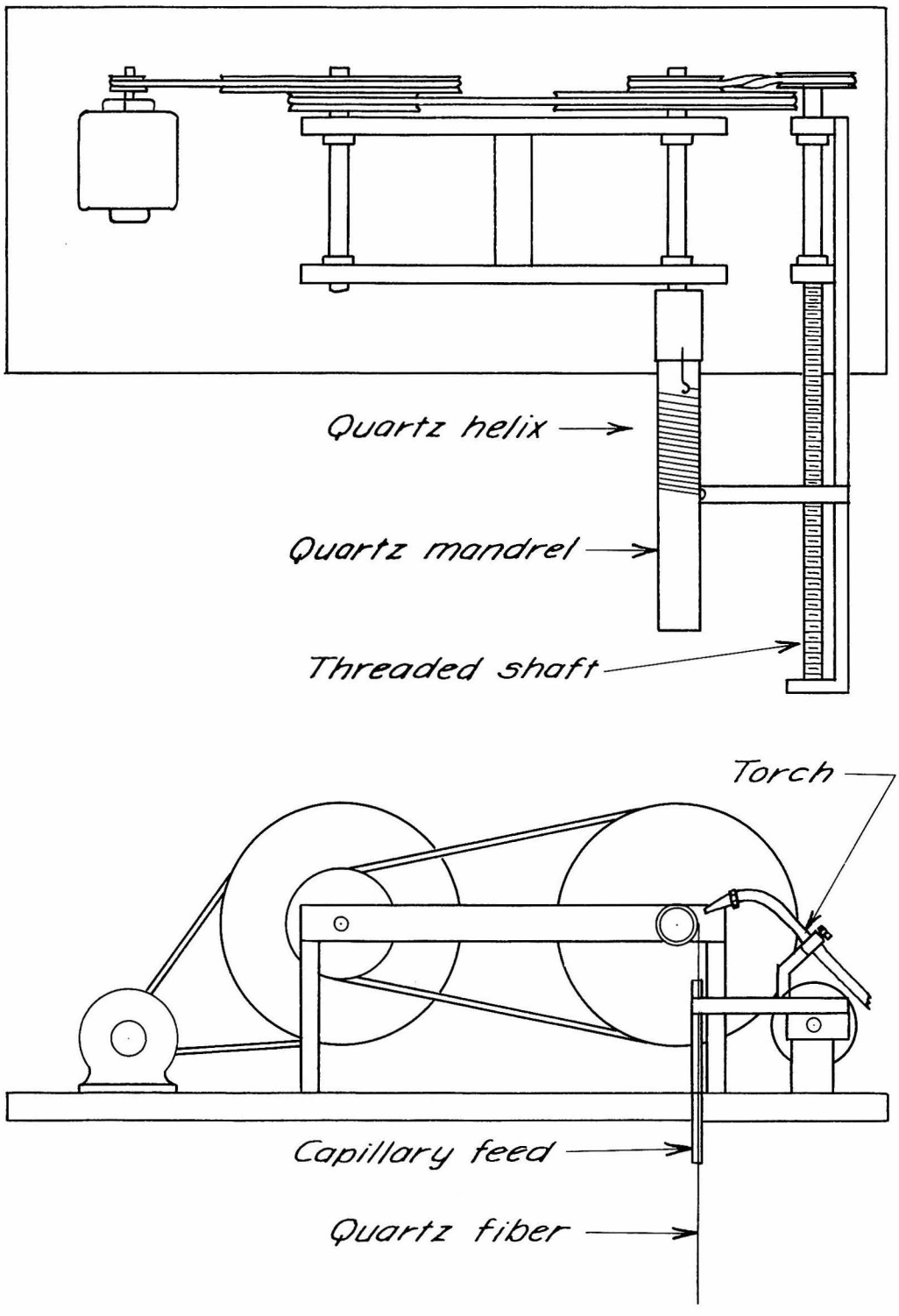


Figure 5.

difficulty with removing the springs after they are formed

The springs were calibrated by measuring the elongation with known weights on the foil pan. Over a wide range they followed Hooke's law within the errors of measurement. Sensitivities of the springs used varied between 0.5 and 2.5 milligrams per millimeter of deflection.

Preparation of Asphalt Diaphragms: - Some difficulty was at first experienced in preparing thin test sheets of asphalts and pitches. The extreme brittleness of some of the samples made necessary the development of methods and technique in manipulation; and depressions in the surfaces of the diaphragm invalidated measurements of the thickness.

Asphalt was known to contain water and entrapped non-condensible gases. From observation of its behavior on heating, and from the appearance of freshly fractured surfaces, it was decided that voids might appear in the test diaphragm unless steps were taken to remove air and water. Indeed, preliminary diffusion runs indicated that some such imperfection was present.

Removal of the air and water was accomplished by heating a small sample of the material to about 30°C. above the softening point in a flask in an oil bath, and applying suction with a water aspirator until bubbles ceased to form. This usually took about 30 to 45 minutes.

That this process removed the occluded gases was shown by results of "void tests" before and after the evacuation treatment. Figure 6 shows the apparatus for this test. A tube is filled with

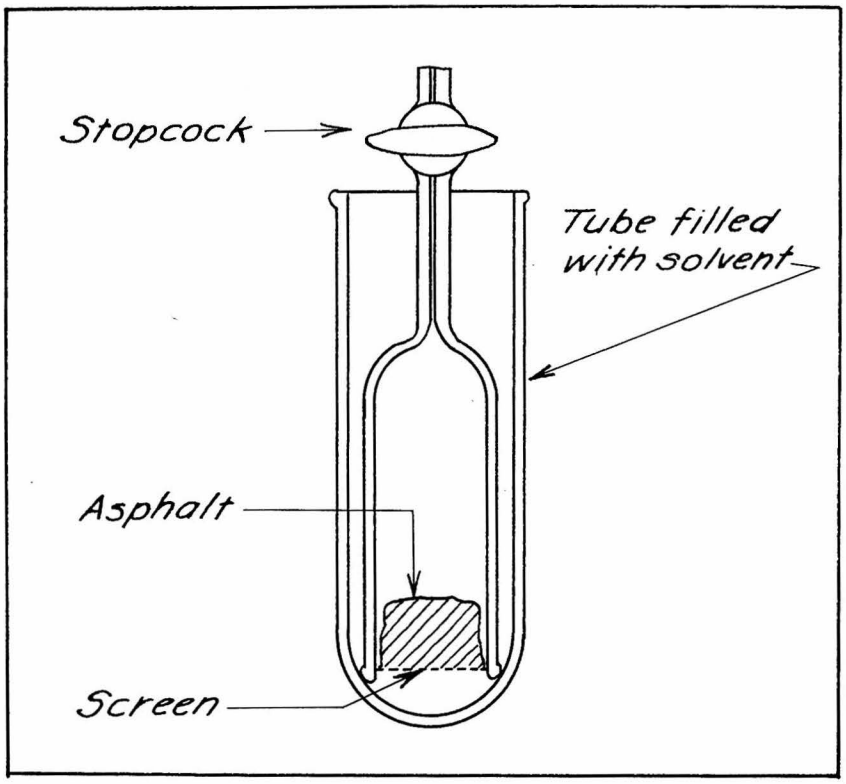


Figure 6. Void Test Apparatus.

a solvent, such as benzene for asphalts and carbon disulfide for coal tar pitches, and a second tube containing the sample on a screen is lowered into it. The solvent is allowed to rise in the inner tube until it reaches the stopcock, which is then closed. As the material on the screen is dispersed in the solvent, entrapped gases are set free, and they collect in the capillary tube at the top. Tests with a number of different samples as received indicated the presence of an appreciable quantity of "voids"; but evacuated samples subjected to the same procedure invariably showed an amount scarcely detectable.

It was thought that, because the properties of asphalts are subject to change on heating, the evacuation treatment might alter the material substantially. In order to determine whether this was

the case, it was thought advisable to select a property known to be variant with heating, and to measure the effect, if any, of the treatment on that property. Softening points, determined by the standard "ball and ring" method, were thought to be sufficiently indicative, and were selected as test characteristics because they are easily determined. Softening points measured before and after evacuation were the same within experimental error - two or three degrees Fahrenheit - and agreed within a like amount with softening points obtained by the same procedure in the laboratories of the corporations which provided the samples.

As an additional precaution before a great deal was done with the evacuated asphalt, diffusion runs were made with asphalts which had been subjected to various degrees of heating and evacuation. Some samples were heated under vacuum for periods appreciably longer than necessary to remove voids, and their diffusion constants determined. Since the values obtained were not significantly different from those determined for the same kind of asphalt which had been heated and evacuated for a minimum of time, it was concluded that the properties of the asphalts would change no more during heating and evacuation than the amount by which they vary from point to point in a batch of asphalt.

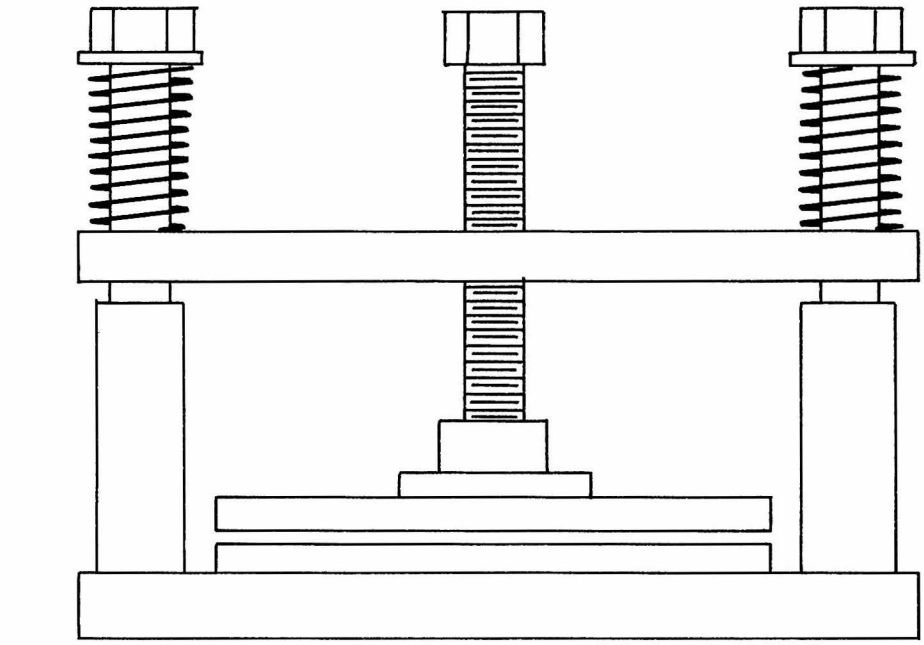
The samples after evacuation were cast, for convenience, into smooth pellets on warm mercury, each pellet containing enough for one diaphragm.

The method finally selected for forming satisfactory test sheets was to press each of the pellets to a definite thickness

between two flat amalgamated brass plates placed in an oven set a few degrees above the softening point of the asphalt. The apparatus with which this was accomplished (Figure 7) consists primarily of an arrangement whereby two springs may be used to force the two plates together while they are in the oven. By means of the bolt threaded through the uppermost cross-member, the springs may be compressed before the assembly is heated. The two brass plates, in order to insure that the two surfaces of the diaphragm would be parallel, were accurately turned flat, and then ground together before amalgamation. The thickness of the finished sheet was regulated by interposing pieces of flat brass stock, of equal thickness, between the plates at three points around the periphery. The apparatus was removed from the oven as soon as the plates were separated only by the thickness of the spacers.

A circular portion to use in the diffusion cells was cut from each diaphragm with a circular amalgamated brass knife edge, the diameter of which was accurately known. The temperature at which the cutting was done had to be controlled properly in order to obtain a disc without fracture. Since asphalts and pitches do not adhere to mercury, the discs were easily removed from the plate if the temperature was maintained above that at which the material became brittle. The diameter of the circular portion was very close to the internal diameter of the cutting edge, so the area of the disc was easily computed.

The thickness of each diaphragm used was measured, since they were found to be variable in thickness by a few percent.



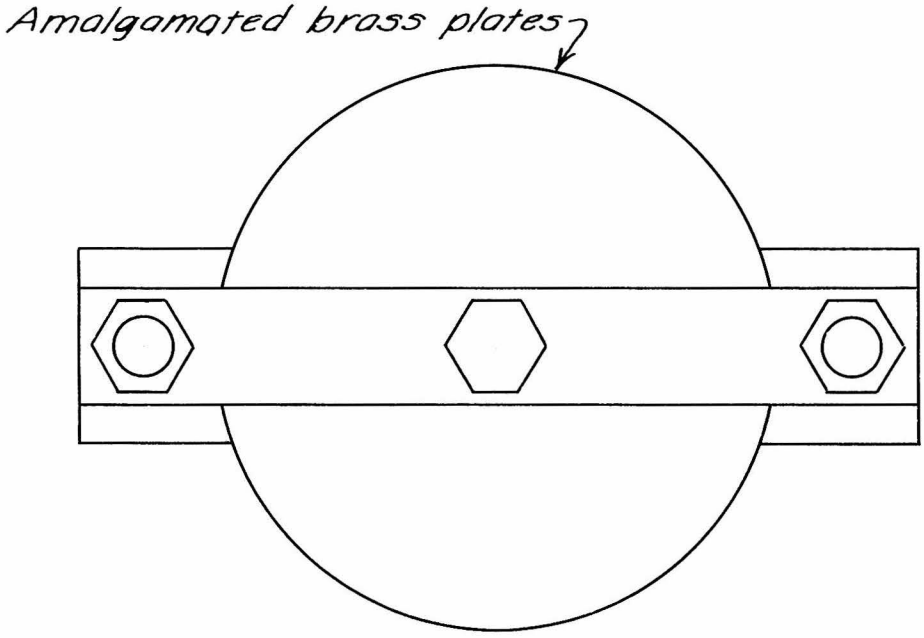


Figure 7. Diaphragm Press.

Densities on all the evacuated samples were obtained by a loss of weight in water method; and from the density of the asphalt and the weight and area of the disc the average thickness was computed. Whenever practicable this calculated value was checked by taking the average of a number of micrometer readings taken around the edge of the diaphragm. Usually the two independent measurements checked within one percent.

Variation of partial water vapor pressure: - A number of saturated solutions in contact with a definite phase of the solid solute are suitable for maintaining constant humidity. Some of these were utilized as a simple and direct means of obtaining different partial pressure differentials in measuring the effect of pressure gradient on the linear law diffusion constants. Solutions of $CaSO_4 \cdot 5H_2O$, NH_4Cl, $Ca(NO_3)_2 \cdot 4H_2O$, and $CaCl_2 \cdot 6H_2O$ were used to maintain aqueous tensions of 23.3, 18.8, 11.9 and 7.31 mm. Hg., respectively at 25°C.; and for measurements at 35°C. solutions of NH_4Cl, which have a vapor pressure of 34.2 mm. Hg., were utilized. Magnesium perchlorate was used in each case on the other side of the diaphragm.

An alternative method of measuring the diffusion rate under constantly varying vapor pressure gradients was originated, and apparatus for measuring it and equations for interpreting results developed.

If the water vapor available for diffusion is restricted in amount by having as the source a constant volume space containing only water vapor, as shown in Figure 8, the partial aqueous pressure

in the space may be related to the amount of water diffused through the membrane as described below.

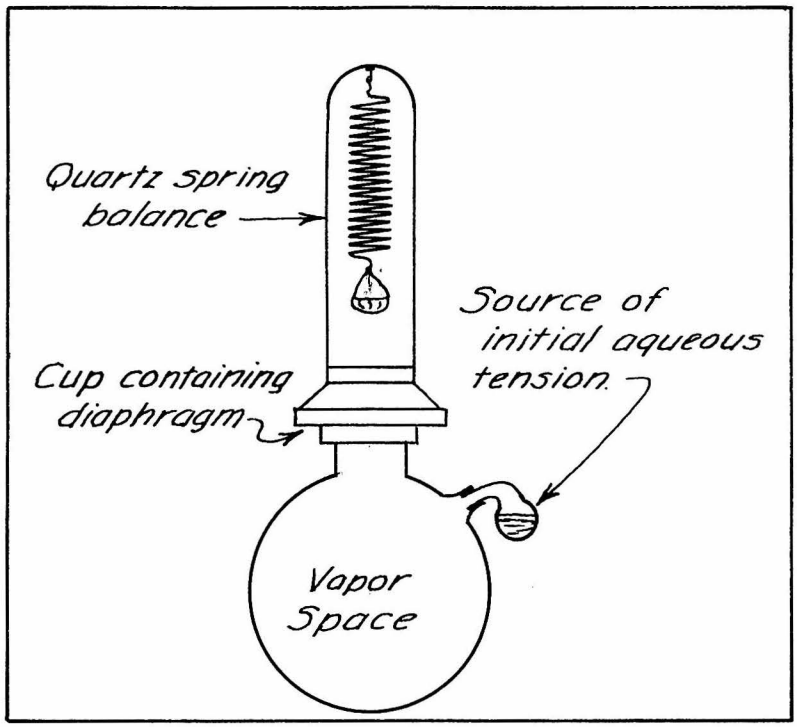


Figure 8. Variable Pressure Cell.

Let K = linear law diffusion constant

L = length of diffusion path

A = area of diffusion path

P = aqueous tension, mm. Hg.

t = time

V = volume of vapor space

w = weight diffused through at time t

m = wt. of water vapor in vapor space

n = conversion factor between vapor density and pressure = 1.03×10^{6} for water at 25°C

If the vapor space is so large that changes in aqueous tension within it occur slowly, it may be assumed that the unsteady-state diffusion takes place under conditions close to equilibrium. This is thought to be true because test diaphragms previously exposed to normal atmospheric humidity require only a few hours (12 to 15) for the establishment of equilibrium, as judged by the approach to linear diffusion rates, when placed between a partial pressure gradient of 23.3 mm. Hg. Then under conditions of slow change of vapor pressure in the vapor space, for an increment of weight dw,

$$dw = \frac{K\ A\ P}{L}\ dt$$

At any instant in the vapor space,

$$P = \frac{n\ m}{V}$$

At any time the amount of water absorbed by the drying agent on the spring will be the sum of that which has diffused through and that which has left the diaphragm because of a change in concentration within it as demanded by the constantly varying pressure gradient. Experiments on the absorption of water vapor by asphalts indicate that the moisture which could be lost by a diaphragm of the size used would be quite small. So if the amount of vapor diffused through is large compared to the loss of moisture from the diaphragm, we may for practical purposes neglect the latter. Then

$m = m_o - w$, where m_o is the weight of moisture initially present in the vapor space.

Also $P = P_o - \frac{w\,n}{V}$ where P_o is the initial aqueous tension in the vapor space.

$$dw = \frac{K\,A\,P_o}{L}\,dt - \frac{K\,A\,w\,n}{L\,V}\,dt$$

$$\frac{dw}{dt} = \frac{K\,A\,P_o}{L} - \frac{K\,A\,w\,n}{L\,V}$$

The quantity $\frac{dw}{dt}$ is the slope of the diffusion rate curve.

To express the equation in terms of K,

$$K = \frac{\frac{dw}{dt}}{\frac{A}{L}\left(P_o - \frac{w\,n}{V}\right)} = \frac{\frac{dw}{dt}}{\frac{A}{L}(P)}$$

All the quantities involved are constant for a given experiment or are readily obtainable from a plot of the time rate of increase in weight of the drying agent above the diaphragm.

The experimental procedure is to provide a source of constant humidity for the vapor space and to let equilibrium conditions for the initial aqueous tension to be established before the start of the variable pressure gradient experiment. When such equilibrium, as shown by a constant rate of diffusion, is reached, the supply of moisture is removed, and the vapor pressure from then on is allowed to vary with diffusion.

Experimental Results: - The method used was refined as far as was practical, but because of the nature of the materials a great deal of manipulation and a great deal of time were required to obtain a body of reliable data. It was necessary to prepare each test

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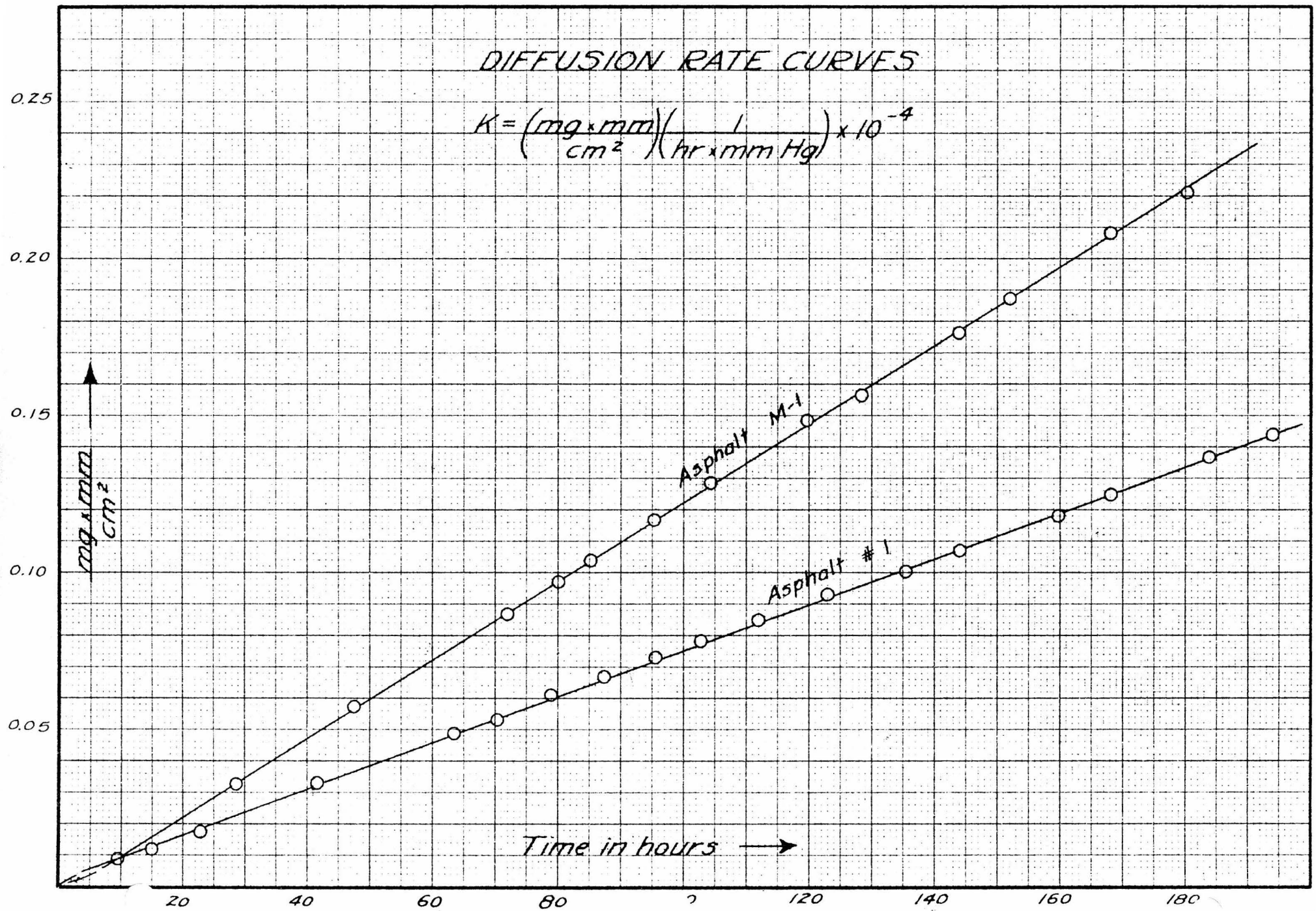

Figure 9.

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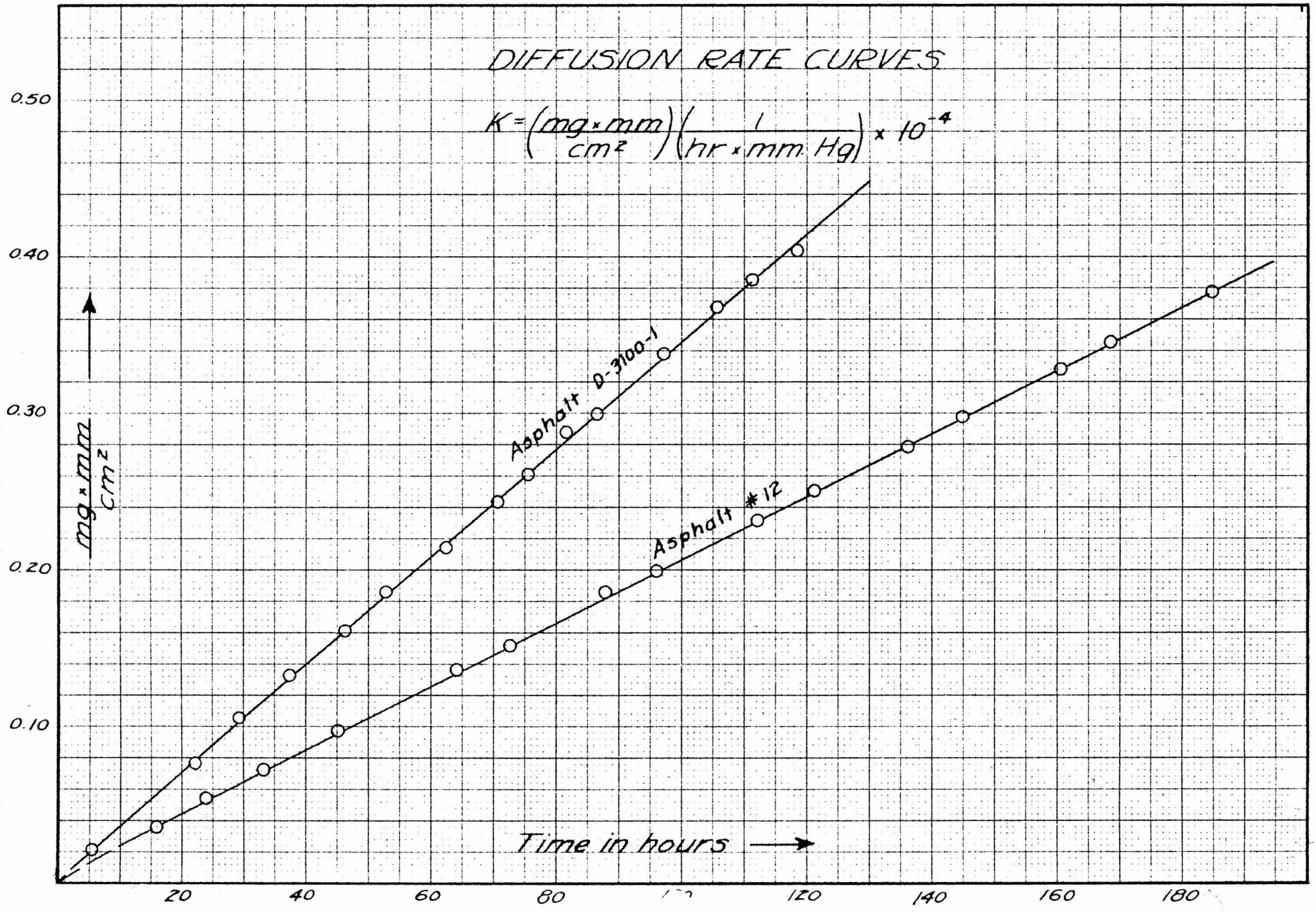


Figure 10.

diaphragm and to measure pertinent dimensions on each individually. The length of time needed for a single experiment to proceed to the point at which an accurate diffusion rate could be determined varied from 150 to 1500 hours, depending on the nature of the material.

From 12 to 20 observations were made on each diffusion cell during the course of each experiment, in order to obtain a sufficient number of experimental points to define with good precision the diffusion rate curves. Each run was made at least in triplicate to diminish possibilities of error. A total of over 5000 observations have been made during the work on diffusion.

The quartz spring balance diffusion cells were found to yield quite satisfactory data. Typical curves showing experimental results are given in Figures 9 and 10, where the centers of the circles represent experimental points and the size of the circles represent the probable error of the measurement. A similar curve was drawn for each membrane, the slope of the curve giving the diffusion constant.

Constants at 98% Humidity at 25°C.: - The greater portion of the diffusion measurements were made with a constant partial pressure gradient of 23.3 mm. Hg. The results of these experiments are given below in Table III. The figures recorded are the diffusion constants, expressed in the units of $\frac{\text{gms.}}{\text{cm. mm. hr.}}$, for each individual diaphragm.

Table III

Material No.	M.P.	Pen.	Diffusion Constant x 10^9	Average Constant x 10^9
1	174	5	4.02	4.00
			3.97	
2	165	2	4.05	
			4.05	4.05
			4.04	
3	204	0	3.07	3.07
D-3100-4	159	15	5.92	
			5.87	
			6.12	6.00
			6.03	
			6.08	
D-3100-5	126	45	9.27	9.27
			9.28	
D-3100-6	189	7	4.82	
			4.73	4.77
			4.76	
E-5198-1	234	1	3.50	3.50

Material No.	M.P.	Pen.	Diffusion Constant x 10^9	Average Constant x 10^9
E-5198-2	140	25	7.54	
			7.57	7.58
			7.63	
E-5198-3	135	30	8.39	8.40
			8.41	
M-1	190	7	5.40	
			5.38	5.39
			5.45	
			5.33	
M-2	176	12	6.05	5.95
			5.85	
M-3	158	20	6.92	
			6.72	6.93
			7.14	
M-4	142	34	7.74	
			7.70	7.81
			7.98	
11	166	24	9.35	
			9.43	9.30
			9.20	
			9.20	

Material No.	M.P.	pen.	Diffusion Constant x 10^9	Average Constant x 10^9
12	188	19	8.12	
			8.23	8.15
			8.10	
D-3100-1	169	20	8.27	
			8.15	8.22
			8.25	
D-3100-2	190	20	9.28	
			9.24	9.25
			9.25	
D-3100-3	215	18	9.25	
			9.31	9.31
			9.37	
21	210	19	8.80	
			8.73	8.79
			8.75	
			8.89	
22	244	3	3.66	3.66
			3.67	
31	140 - 150	24	3.43	3.37
			3.32	

Material No.	M.P.	Pen.	Diffusion Constant x 10^9	Average Constant x 10^9
32	160 - 170	2	2.16 2.15 2.12	2.14
33	180 - 190	2	1.4	1.4
41	180 - 195	2	0.434 0.437	0.435

The materials for which only one figure is given are extremely brittle at ordinary temperatures, and therefore very difficult to work with. The other two of the three diaphragms - and, indeed, others prepared - fractured. However, it is reasonably certain that the single values are nearly correct.

Diffusion Constants at Various Humidities: - Diffusion constants were evaluated for a number of the samples at different constant aqueous tension gradients. The results obtained are recorded in Table IV as average values of the triplicate runs. The agreement among the individual values is much the same as that in Table III.

Table IV

Vapor pressure, mm.			23.3	18.8	11.9	7.31
Material No.	M.P.	Pen				
1	174	5	4.00	3.88		
2	165	2	4.05	3.82		
3	204	0	3.07	3.02		
D-3100-4	159	15	6.00	6.55		
D-3100-6	189	7	4.77	4.93	5.04	
11	166	24	9.30	9.00	8.55 at 16.9 mm.	
12	188	19	8.15	7.65	7.50	
21	210	19	8.79	7.10		6.70
22	244	3	3.66	3.25		
D-3100-1	169	20	8.22	8.08	8.03	7.85
D-3100-2	190	20	9.25	8.99		8.40
31	140 - 150	24	3.37	3.82	4.08	
* 11	166	24	9.23	8.93	8.23	

* These values were obtained from the variable-pressure method described on pages 25-29.

Diffusion with Water in Contact: - Since in practice liquid water is often in contact with asphalt, it was thought important to establish whether the diffusion constant would be much different if liquid water were in contact with the diaphragm instead of water vapor. The results, given below, indicate that diffusion for liquid water is definitely faster, especially for steam-refined asphalts.

Table V

Material No.	K for liquid	K for vapor at 23.3 mm.
1	5.15	4.00
2	5.10	4.05
D-3100-4	6.60	5.97
D-3100-6	5.15	4.77
11	9.60	9.30
12	8.45	8.15
21	8.85	8.79
22	3.75	3.66
D-3100-1	8.32	8.22
D-3100-3	10.00	9.31

In order to arrive at some conception of the magnitude of change in diffusion constants with temperature, some experiments were conducted at 35° C., using saturated NH_4Cl to regulate the humidity. The results are compared below to constants for the same asphalts at 25°C. under equal relative humidities. (80.1%)

Table VI

Material No.	$K \times 10^9$ at 25°	$K \times 10^9$ at 35°
1	3.88	5.40
2	3.82	5.50
D-3100-4	6.55	7.55
11	9.40	10.50
12	7.65	10.10

Diffusion through Pipe Line Coating: - As a matter of practical interest, several portions of a pipe-line coating which had been in service were obtained. This material had been on a 12-inch hot line at the Los Angeles refinery of the Union Oil Company since 1927. Test specimens were used for the diffusion runs in the condition in which they were received. Values of K for several tests did not check, but all were in the region of 3×10^{-3} $\frac{gm}{cm.mm.hr.}$

The data reported, with the exception of those for the pipe-line coating, are for freshly prepared asphalt. Attempts were made to devise a method of weathering thin diaphragms in a Weather-O-Meter and subsequently measuring diffusion rates; but the temperatures reached during the artificial weathering made it thus far extremely difficult to devise a support for the asphalts in such a fashion that diffusion experiments could later be run with reasonable certainty.

Discussion of Results: - From the data obtained a number of interesting observations may be made concerning the dependence of the diffusion constants on various factors.

Type of Material. In general, air-blown asphalts offer the least resistance to the passage of water, and coal tar pitches the most. Constants for steam-refined asphalts are lower than those for the air-blown type, and higher than the constants for coal tar pitches.

Fillers. Diffusion through the filled products available was found to be slower than through an unfilled material corresponding to that from which the enamels were made. However, since only three materials containing mineral fillers were at hand, no generalities may yet be drawn.

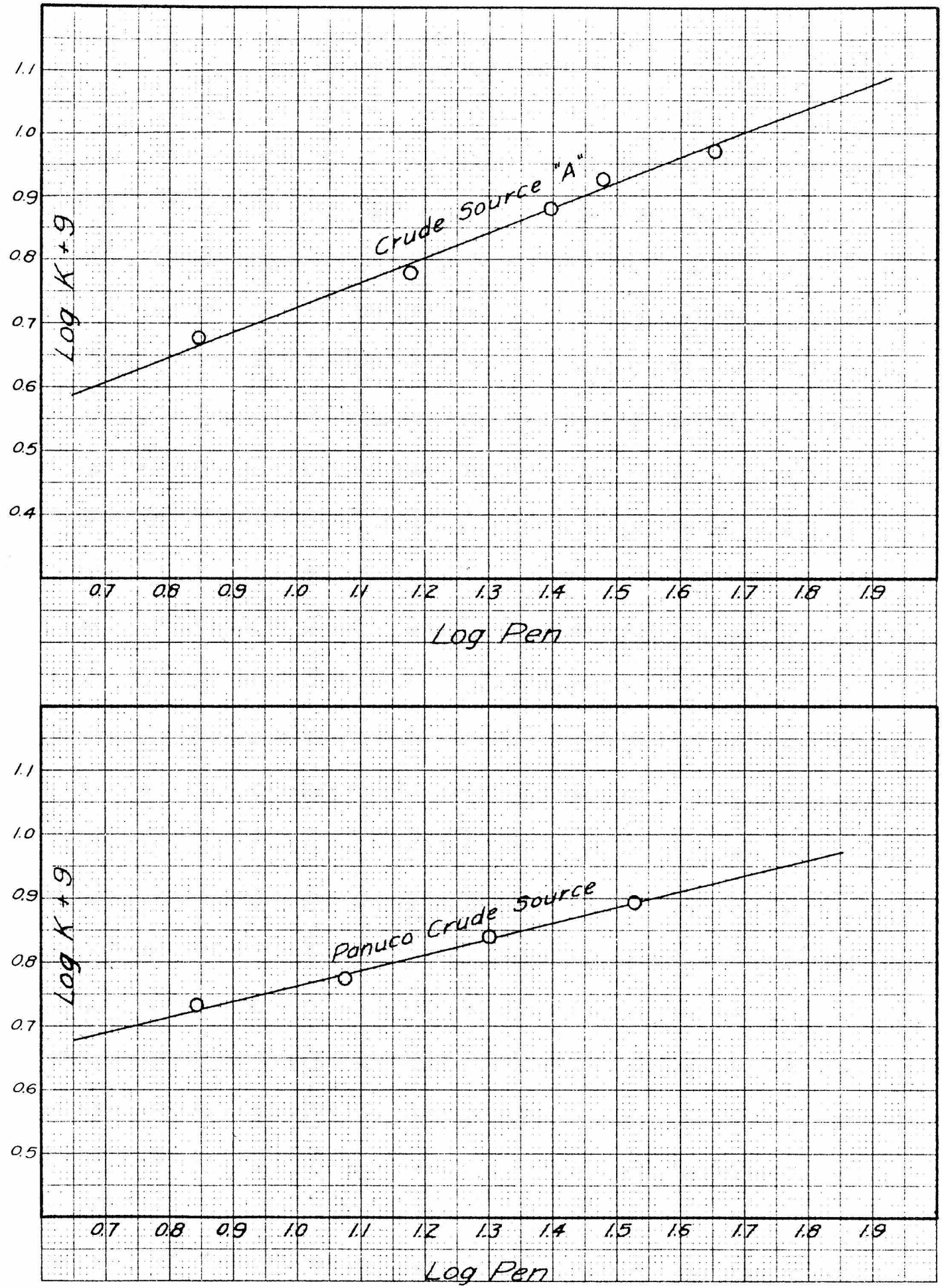
Temperature. The diffusion constant increases with temperature.

Viscosity. In an attempt to find correlations between diffusion rates and other properties of the materials studied, plots were made of K versus penetration for each type of bitumen. For the case of the air-blown asphalts there appeared to be no regularity to the values of K, but for the steam-refined asphalts the plot gave a curve of exponential form. When the data were plotted on a log-log scale, a straight line resulted for each series of steam-blown asphalts. Figure 11 is such a plot of log K versus log Pen.

The relationship between diffusion constant and penetration for the series of steam-blown asphalts from crude source "A" is described by the equation

$$\log K + \log 10^9 = 0.33 + 0.39 \log \text{Pen}$$

Figure 11. Correlation of Diffusion to Penetration.



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and for the asphalts steam distilled from Panuco crude,

$$\log K + \log 10^9 = 0.52 + 0.25 \log \text{Pen.}$$

A fundamental relationship[8] between the penetration and the viscosity of asphalts has been derived and generally accepted by workers in the field. The expression is

$$\eta = \frac{5.13 \times 10^9}{\text{Pen}^{1.93}} \text{ poises}$$

which holds for asphalts which are of the nature of Newtonian liquids, in that they exhibit viscous rather than plastic flow. Since coal tar pitches and steam-refined asphalts approach Newtonian behavior[9], we are justified in considering this equation for the case at hand.

Taking the logs of both sides of the above equation we have

$$\log \eta = \log (5.1 \times 10^9) - 1.93 \log \text{Pen.}$$

It is readily apparent that if the diffusion constants are a linear function of the penetration, they are also at least an approximately linear function of the absolute viscosity.

In order to discuss more freely the properties of asphalts, something must be said of their composition and structure. Asphalts are generally considered to be a colloidal dispersion of very high molecular weight hydrocarbons of an aromatic or hydro-aromatic nature in a mixture of resinous materials and oils.[9] If the dispersing phase is highly aromatic, the dispersion will be well peptized, and the viscosity will be a function of the oily phase and of the relative amounts of the two phases. If the amount of aromatic compounds is reduced, as by air-refining, wherein the aromatics become polymerized and become transferred to the dispersed phase, the peptizing ability

of the oil fraction is reduced, and plastic flow characteristics are developed. On the other hand, if steam-distilling is carried far enough, a point will be reached where an inversion of phases results,(10) and as that is approached the flow characteristics of the material are no longer simply related to those of the oil and resin fraction.

If these statements are assumed to be essentially fact, it may be deduced that diffusion through steam-refined asphalts is dependent on the properties of the dispersing phase, and that the principal effect of the colloidal micelles is to hinder the transport of the water molecules through the oily fraction. A condition imposed upon this, however, is that it applies only up to the point at which the supposed inversion of phases takes place. This condition is strengthened by the fact that the hardest asphalt from crude source "A" yielded a diffusion constant (Penetration 0) which on the log-log plot was quite far from the straight line through the other five points.

The two curves relating diffusion constants to penetration have different slopes by a substantial amount. The observation might be made that the two series of asphalts are quite different in temperature susceptibility, which is a function, in the last analysis, of the chemical nature of the constituents.

Vapor Pressure Gradient: - The data presented for the variation of diffusion rates with humidity gradients indicates fairly conclusively that there is noticeable digression from linear diffusion as represented by Fick's equation. This suggests the presence of water-soluble materials or of adsorption effects. Sufficient information is not

yet at hand from which to deduce the cause of deviation from simple diffusion.

However, to indicate directions of attack, it might be stated that if the distortion of the pressure gradient is due to the solution of water, it is probable that diffusion constants measured under conditions of humidity which are below those for saturated solutions of the hygroscopic materials will be independent of the vapor pressure in the range below that critical humidity. But if the vapor pressures of those solutions are low, the results will be experimentally indistinguishable from those expected for adsorption on surfaces, which would vary with vapor concentrations along a curve like an adsorption isotherm. An investigation of the concentration gradient by means of laminated diaphragm may shed some light on the problem.

Mechanism of Diffusion: - The concept of linear diffusion implies the transport of water as vapor through the interstices in the solid by means of molecular motion.(7) Concentrations of water vapor within the solid would then be somewhat less than the concentration in the adjacent vapor phase because of the space occupied by the solid, but would be directly proportional to the concentration gradient. For diffusional processes characterized by this mechanism Fick's law applies unrestrictedly.

Asphalts contain a number of polar molecules, such as oxygen and sulphur compounds, and it would be expected that these exhibit a certain affinity for water. This may conceivably affect the diffusion process in several ways.

When water vapor is adsorbed, energy is liberated, and the fugacity is lowered. Vapor then moves in to take the place of that adsorbed, and possibly a second layer becomes associated with the first layer adsorbed. These adsorbed layers may be subject to strong spreading forces, thereby providing a means of transport which may be much more rapid than by molecular motion through inter-molecular spaces.

Air-blown asphalts give evidence of structure[11], while steam-refined asphalts and coal tar pitches are nearly homogeneous. Movement of adsorbed water along the structure would explain the reason why diffusion through the air-blown type is more rapid than through the others.

When a molecule is adsorbed, energy in substantial amount is liberated; and likewise energy must be supplied to remove a molecule from an adsorbent. The quantities of energy so involved depend upon the state from which the molecule was adsorbed or the state to which it is returned, the heat requirement increasing with a decrease in pressure. Then a water molecule would be adsorbed from a high humidity at a low heat of condensation, and would be removed at low humidities only by the absorption of a higher heat of vaporization. Under isothermal conditions this would result in retarding escape from the low pressure side of the diaphragm, and would cause a shift of the concentration toward the low-pressure side until an energy balance was obtained. The effect would be to change the rate of diffusion with concentration gradient.

Applications of Diffusion Rate Data: - Wherever the exclusion of water is an important factor, it is of value to be able to calculate how much of a given protective agent must be used for provision of the most efficient protection under a given set of conditions. Although each problem possesses its own peculiarities, nevertheless a general type of approach may be indicated.

The only condition required for the transport of water through organic materials is a fugacity gradient across the material. Whether this differential is produced by a dry space on one side, by solution, by adsorption, or by chemical reaction, such as the corrosion of a metal pipe line, is of small consequence to the mechanics of the calculation.

Assume, for the sake of simplicity, that water is being transferred into a space initially free of water, the pressure of water vapor in the space being built up during the process.

At any instant the pressure, P_2, in the space will be represented by

$$P_2 = c \frac{W}{V}$$

where W = weight of water present in the space

= weight of water diffused through the material

V = volume of space

c = conversion factor between vapor density and pressure.

From the linear diffusion law, which will apply quite closely if proper diffusion constants are known,

$$W = \frac{K A t}{L} (P_1 - P_2)$$

where K = diffusion constant

A = area of the diffusion path

t = time

L = length of the diffusion path

P_1 = external aqueous tension (constant)

For an increment of time dt

$$P_1 - P_2 = \frac{L}{K\,A}\,\frac{dW}{dt}$$

Assuming it is desired to know the length of time required for the transport of a given amount of water to diffuse through a given thickness of coating, the derivation is as follows:

Since $P_2 = \frac{C}{V}\,W$

$$dP_2 = \frac{C}{V}\,dW$$

Also $dP_2 = -d(P_1 - P_2)$

and $dW = \frac{V}{c}\,dP_2$

Substituting,

$$P_1 - P_2 = \frac{L}{K\,A} \cdot \frac{V}{c} \cdot \frac{dP_2}{dt}$$

$$dt = \frac{VL}{K\,A\,c}\,\frac{dP_2}{P_1 - P_2}$$

$$dt = -\frac{VL}{K\,A\,c}\,\frac{d(P_1 - P_2)}{P_1 - P_2}$$

$$dt = -\frac{VL}{K\,A\,c}\,d\left[\ln\,(P_1 - P_2)\right]$$

Integrating,

$$t = -\frac{VL}{K\,A\,c}\,\ln\,(P_1 - P_2) + c$$

at $t = 0$, $P_2 = 0$, and $c = \frac{VL}{K A c} \ln P_1$

Then $t = - \frac{VL}{K A c} \left[\ln (P_1 - P_2) - \ln P_1 \right]$

$$t = \frac{VL}{K A c} \ln \frac{P_1}{P_1 - P_2}$$

$$\frac{K A c t}{VL} = \ln \frac{P_1}{P_1 - P_2}$$

$$e^{\frac{K A c t}{VL}} = \frac{P_1}{P_1 - P_2}$$

$$(P_1 - P_2) e^{\frac{K A c t}{VL}} = P_1$$

From which $P_2 = P_1 \left(1 - e^{\frac{K A c t}{VL}}\right)$

At any given time

$$W = \frac{P_2 V}{c} = \frac{V}{c} P_1 \left(1 - e^{\frac{K A c t}{VL}}\right)$$

$$\frac{W c}{P_1 V} - 1 = - e^{\frac{K A c t}{VL}}$$

$$\log \left(\frac{W c}{P_1 V} - 1 \right) = - 2.303 \frac{K A c t}{VL}$$

and $$t = - \frac{VL}{2.303 K A c} \log \left(\frac{W c}{P_1 V} - 1 \right)$$

From this expression may be calculated the inter-relation of t and W, or of W and L at constant t.

For thin membranes of asphalt the diffusion constant will not vary appreciably with change in pressure differential, so in that case the equation may be solved formally. If thick layers greater than about 0.25 mm. in thickness are to be used, variations in K with the quantity $(P_1 - P_2)$ may be taken into account if knowledge of the specific conditions is sufficiently precise to warrant it.

As a specific case for illustrating the calculation, the length of time required for a layer of water molecules two deep to be built up on the surface of a hydrophilic rock covered with asphalt will be estimated. Assuming a water molecule to be approximately an oblate spheroid of maximum and minimum radii of 1 and 2 Angstroms, respectively, consider the time required if that amount of water on the rock has a fugacity corresponding to 15 mm. Hg. The volume term, for the basis of estimation, may be considered to be that which will contain that amount of water as a vapor at a vapor pressure of 15 mm. This assumption will result in a longer calculated time than that actually obtaining if adsorption occurs, but will give an approximation much better than a conjecture.

Aggregates in a hot mix often have a coating of asphalt only 5 microns thick. Assume for convenience a thickness of 100 microns.

For an air-blown asphalt having a constant, K, of 10^{-8}, the calculated time is

$$t = - \frac{(2.36)(10^{-3})(10^{-2})}{(2.303)(10^{-8})(1)(10^{6})} \log \left[\frac{(3.75)(10^{-8})(10^{6})}{(27.76)(2.36)(10^{-3})} - 1 \right]$$

$t = 1.85 \times 10^{-4}$ hours, for a case in which P_1 is 23.76 mm. Hg.

Similar calculations could be made for other problems, such as the penetration of moisture into the organic fibers used in asphalt roofings, the corrosion rate of protected metals, and the like. If conditions are known, the computations will be an indication of the amount of protection against water which will be afforded by the material in question.

Surface and Interfacial Tensions

In a great many applications of asphalts as protective coatings, displacement of the asphalt by water occurs or is suspected to have occurred. As an instance, when coated pipe-lines corrode at a place where a crack in the coating has appeared, the corrosion is not limited to the region exposed by the rupture, but is quite general on either side under an apparently sound protective layer. Often deep pits are found some distance from the crack. A possible reason for this may be that water displaces the asphalt, thereby forming a channel along the surface of the metal in which water may move freely, providing a means by which extensive corrosion may take place.

By measurements of interfacial and surface tensions the free surface energy change accompanying the exchange of an asphalt-water and a metal-water interface for an asphalt-metal interface may be computed. The sign of this energy change will be an indication of the energetic possibility of such an exchange of interfaces. When correlated to the results of other simple experiments, such as

simple measurements of adhesion in the presence of water, information may be available from which to deduce whether the displacement takes place, or, if it does, whether it goes freely or only under mechanical shocks and stresses.

Experimental Methods and Results: - A constant temperature bath has been constructed and adopted for use with a Du Nuoy tensiometer.

Preliminary measurements of asphalts and pitches at various temperatures above the softening point have been made. Extrapolation of the results to room temperature, however, is found to be inexact for most of the materials because of the length of the extrapolation. The data taken indicate that at room temperature the surface tensions are approximately 40, 45 and 65 dynes per centimeter for air-blown asphalts, steam-blown asphalts, and coal tar pitches, respectively.

An indirect method of obtaining surface tensions of asphalts is the measurement of surface tensions of solutions of asphalts in benzene at known concentrations and extrapolating to 100% concentration. Typical results obtained are as follows:

Concentration of asphalt	Surface Tension Dynes per cm.
10 %	28.2
20	28.4
30	28.5
40	28.6
50	29.1
60	29.8

The 60% concentration represents practically the limit of the solubility in benzene.

Although this method has been used by other workers to estimate surface tensions, it may be seen from inspection of the above figures that an extrapolation from 60% to 100% is subject to a large probable error. The trend of the figures indicate that benzene is probably capillary active with respect to asphalt, so the greatest change in surface tension most likely occurs in the region of 100% asphalt, which is impossible to realize experimentally. It was concluded that for reasonably exact determinations this method is without merit.

The softening points of the materials at hand are too high to permit direct measurement of interfacial tensions between asphalts and water, so preliminary experiments were conducted on the determination of asphalt-water interfacial tensions by a method involving benzene solutions as in the method described above. Since the interfacial tensions were found to decrease with an increase in asphalt concentration of the benzene phase, it was decided that this procedure may be of value. Typical results are shown below.

Concentration of asphalt	Interfacial Tension Dynes per cm.
0 %	31.6
10	23.1
25	22.9
45	21.3
65	20.7

Chromatographic Analysis

Adsorption methods have been used to remove resins in one step of a selective solution procedure for splitting asphalts into three fractions; but no known attempt has been made to fractionate asphalts entirely by adsorption methods.

When a mixture of molecules of different kinds and sizes are passed through an active adsorbent, the molecules are separated, sometimes quite sharply, according to chemical nature and size. In many cases the separation can be effected quantitatively if the adsorbing material has the proper activity, and the solvent chosen for the mixture to be separated is not adsorbed more strongly than the compounds which are desired to be removed from the mixture.

Asphalts have thus far practically defied attempts at exhaustive organic analysis. However, even though the great number of individual compounds present may not easily be identified, it will be of consequence to a fuller understanding of asphaltic products if groups of similar compounds can be isolated and characterized as to amount and kind. The possibility was entertained that selective adsorption might offer a new and convenient method of fractionation of asphalts.

Experimental Method.

Fractionation by Adsorption: - Activated alumina, ground to 80 - 100 mesh in a ball-mill, was selected, since it gave the most promising results of any tried as the adsorbent to be used in fractionation of asphalts. A glass column, 16 mm. in diameter,

is packed to a height of 10 cm. with the alumina, and a measured portion of a solution of asphalt of known weight concentration in Xylene allowed to run through under suction. The column is then washed with additional Xylene to remove any unadsorbed material.

The packing is then pushed out, cut apart at the juncture between bands of different color, and each band agitated for a minute or two with benzene and a few drops of alcohol, the alcohol serving to displace the substance adsorbed. To reduce the amount of solvent required to wash the alumina free of the displaced fraction, each portion of the column packing is extracted in a Soxhlet extractor with the solvent mixture with which it had been agitated.

The solutions obtained from the extractions are each evaporated under vacuum in a tared flask, so that the weight of each fraction may be obtained.

Activation of Alumina: - The original alumina which was crushed in a ball-mill was used in preliminary work without any treatment to increase its activity. Spent alumina when reactivated by heating proved to be so active that no separation could be obtained with it until it had been thoroughly exposed to normal atmospheric conditions. When it had been so exposed, results obtained with it checked very well the original work.

Characterization of Fractions: - At this stage of the investigation molecular weights of the fractions are being determined. The procedure followed is that devised by Barger[13]. The principle on which it is based is that if droplets of two solutions of unequal

vapor pressure are placed in a capillary, one will grow at the expense of the other. This growth is observed by means of a microscope fitted with a micrometer eye-piece, and can be detected quite readily within a few minutes if the two droplets are much different osmotically. A solution of known weight concentration of an unknown compound may readily be compared to several solutions of known molal concentration of a known compound, and the molecular weight of the unknown obtained by trial. The capillaries used are approximately of the same size as those used for melting point determinations. Benzene is used as a solvent both for the unknown and for azobenzene, which is used as a reference compound. The droplets are placed in the capillary tubes by means of capillary pipettes.

Experimental Results.

Fractionation of asphalts: - The procedure developed effected a separation of asphalts into three distinct fractions. The upper 4 cm. of the packed column became brownish-black; the lower 6 cm. became a faint reddish color; and a solution having the appearance of a highly refined lubricating oil went completely through the column. Data for some of the asphalts are presented below.

Sample No.	wt. % top fraction	wt. % bottom fraction	wt. % unadsorbed	% recovery
D-3100-6	44.4	7.95	45.6	98.0
	44.7	7.50	45.6	97.8
	47.5	7.8	45.9	100.2*
D-3100-1	36.8	6.0	55.0	97.8
E -1	47.5	6.6	45.7	99.8
	49.5	6.6	44.4	100.5
	48.5	4.5	45.4	98.4

* Run with reactivated and conditioned alumina.

These data are uniformly quite satisfactory. It is thought that the deviations are due more to manipulative errors rather than to some failure of the method.

Molecular weights: - The technique of this micro-method of molecular weight determination has not yet been fully developed, but work with the two large fractions of the asphalts has yielded results which are felt to be exact within 5%. By trial the molecular weights of the two largest fractions obtained from asphalt No. D-3100-1 were found to be 1425 for the top fraction and 575 for the unadsorbed fraction.

Discussion: - The method of selective adsorption as applied to asphalts apparently holds some promise. Additional fractions might possibly

be detected by viewing the column under ultra-violet light, and re-fractionation might prove to effect further separation. The excellence of recovery of material from the alumina indicates that there is some probability that the procedure might be made quantitative.

Summary

1. An apparatus for the accurate measurement of angles of contact between asphalt surfaces and liquids was constructed.

Measurements show that the ease of wetting increases in the following order: filled air-blown asphalts, unfilled air-blown asphalts, steam-blown asphalts, coal-tar pitches. The angles assumed by water in contact with air-blown asphalts are greater than 90°, hence water does not tend to enter cracks in a fresh air-blown asphalt surface. For the other materials the angle is less than 90°, which indicates a tendency for water to penetrate under the action of surface forces.

Contact angles for all the materials are reduced in highly alkaline solutions, the reduction being most pronounced in the case of coal-tar pitches throughout the entire alkaline range.

The effect of $CaCl_2$ solutions and of HCl solutions on contact angles is very slight, excepting that the wetting angles for coal-tar pitch are noticeably reduced in HCl solutions.

2. A cell for measuring rates of diffusion with a probable over-all error of less than 3.5% was developed.

A method and an apparatus for the construction of quartz springs were devised.

Measurements of diffusion rates indicated that water transport is most rapid through air-blown asphalts, less rapid through steam-refined asphalts, and least rapid through coal-tar pitches. Diffusion constants were found to increase with temperature for all classes

of bitumens studied. Evidence that diffusion through these substances does not follow a simple diffusion law was discovered.

A correlation between diffusion constants and viscosity for steam-blown asphalts is presented.

Applications of diffusion rate data are indicated.

3. Preliminary measurements of surface tensions of asphalts and of interfacial tensions between asphalts and water were made. The method of determining the surface tension of asphalt at room temperatures by extrapolation from measurements with benzene solutions of asphalts was found to be invalid.

4. A method of fractionating asphalts by chromatographic analysis methods was developed, and evidence that the procedure might yield quantitative results was obtained.

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