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Free Energies of Wetting of Minerals, I

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Özet: Bitümlü kaplamalardaki agregatı teşkil eden minerallerin soyulmaya karşı mukavemetlerine göre sınıflandırılması için termodinamik bir metod takib edilmiştir. Bu metod su buharı ve benzen buharının toz halindeki mineral tarafından adsorpsiyonunun denel olarak incelenmesi ve bu suretle elde edilen adsorpsiyon izotermelerinden mineralin su ve benzen tarafından ıslanma serbest enerjilerinin hesaplanmasına dayanmaktadır. Bu serbest enerjiler arasındaki fark mineralin soyulmaya karşı mukavemetini karakterize eder.

Kalsit-su ve kalsit-benzen sistemleri bu metcddle incelenmiş, 25°C. de kalsitin su ile ıslanma serbest enerjisi -261 ± 8 erg. cm.⁻² ve benzenle ıslanma serbest enerjisi -155 ± 4 erg. cm.⁻² bulunmuştur.

Bu sonuçlar literatürde kuartz için verilen değerlerle karşılaştırılınca kuartzın soyulmaya karşı olan meylinin kalsitten çok daha fazla olduğu anlaşılmaktadır.

1. Introduction

This is an introductory paper presenting the background and first experimental results of our investigations undertaken to throw some light onto the adhesion problem encountered in the construction of bituminous roads.

The stability of a compacted bituminous road mixture decreases appreciably when subjected to the action of water. The extent of this decrease which is an important factor in road engineering depends upon the type of aggregate used. For instance, quartz is known to be worse than limestone as an aggregate. It is generally accepted that this is a result of stripping i.e. displacement of bitumen film by water at the aggregate surface.

To asses the tendency of a given aggregate to stripping various laboratory tests have been suggested. Reviews of these tests can be found in the recent publications of Highway Re-

search Board^[1] and Permanent International Association of Road Congresses^[2]. In a large group of these tests the bituminous mixture is brought in contact with water under specified conditions and either the apparent stripping or the decrease of stability is measured, or some other properties which are considered to be related to the sensitivity of mixture to the action of water are determined. However, there is no theoretical justification to believe that the results of any one of these tests correctly represents the behaviour of the bituminous mixture concerned in actual practice.

In a second group, the field conditions are imitated in the laboratory and the mixtures are examined for adhesion failure^[3] or tested to determine the loss of tensile strength^[4]. Although the tests of this group give reliable information as to the behaviour of mixtures in the field, it would of course be desirable to have a scientific basis to decide on the film retaining properties of aggregates. Such an approach would involve investigating the fundamentals of stripping. In this way it would also be possible to have a better understanding of the causes of stripping and the steps to be taken for its prevention.

Some attempts of this kind in which interfacial tensions are considered have already been made. For instance, Hallberg^[5] has treated the process of stripping taking place in the capillary structure of the bituminous mixtures and shown that the quantity called the adhesion tension $\gamma_{sw} - \gamma_{sb}$ where γ_{sw} and γ_{sb} are solid-water and solid-binder interfacial tensions, respectively, is the driving force of adhesion i.e. the reverse process of stripping. This quantity has in fact a fundamental importance. It is the free energy change accompanying stripping. Therefore, it should measure the competition between water and binder for covering the aggregate surface and define the state of equilibrium whenever attained. This free energy change corresponds to the displacement of binder in the capillaries and its joining the bulk of the binder.

Lee and Nicholas^[3] virtually use a smaller free energy of the form $\gamma_{sw} - \gamma_{sb} - \gamma_{wb}$, where γ_{wb} is the water-binder interfacial tension, in similar treatments. This corresponds to an extreme case of displacement of a thin binder film covered with water on one side and formation of a drop of binder or its joining the bulk of the binder. This may take place in the voids or at the free surface of the pavements containing low viscosity binders.

The other extreme is the case of displacement of binder without changing its initial shape. The free energy change of this type of stripping which is likely to take place in the case of very stiff binders is even bigger than that used by Hallberg and given by $\gamma_{sw} - \gamma_{sb} + \gamma_{wb}$ which is a form of Dupré expression.

Before going any further, we would like to make a remark which follows from these considerations that the binders of high viscosity should be more resistant to stripping than liquid binders. This is actually what is observed in practice. The same conclusion drawn from somewhat different considerations was also stated by Hallberg^[5].

It must be noted that the quantity $\gamma_{sw} - \gamma_{sb}$ is the mean of the two extreme values of the free energy change and, therefore, the best measure of the resistance to stripping in intermediate cases. Moreover, if a standard binder is chosen whatever the type of stripping is, $\gamma_{sw} - \gamma_{sb}$ is the part of the free energy change which characterizes the aggregate as far as stripping is concerned.

On the experimental side, investigations have also been made to determine the so called adhesion tension. The measurements of the angle of contact between the binder-water interface and the aggregate surface,^{[2], [5], [6]} and the determinations of the capillary pressure of this interface in a column of powdered aggregate^[5] are among this kind of studies.

In the former case, it has been concluded that the contact angle depends on the degree of polish of the solid surface^[6] and the direction of movement of the binder-water interface on this surface^[5] even in the case of highly polished surfaces and fluid binders. In other words, the angle of contact exhibits a hysteresis presumably due to unknown friction forces which upset the true equilibrium at the intersection of the interfaces. It follows that such measurements are not likely to give any reproducible results.

In the latter case, by modifying the technique used by Bartell et al^[7], Hallberg^[5] investigated the movement of binder-water interface in a mass of powdered aggregate using liquid binders and determined $\gamma_{sw} - \gamma_{sb}$ by measuring the minimum hydrostatic pressure required to make this interface move. Ne-

vertheless, Hallberg's experimental results indicate that the adhesion tension measured by this method also depends on the direction of movement of the interface as in the contact angle method. When water was the advancing liquid, he was able to obtain some positive adhesion tension values characteristic for each aggregate. When the movement was reversed, however, the measured adhesion tensions were even negative and numerically equal to $-\gamma_{wb}$ almost irrespective of the aggregate. For this reason, the concepts of "passive" and "active" adhesion have been introduced^[4]. These results clearly show that the interface could not be moved in the capillaries reversibly, in the thermodynamical sense, in these experiments. Therefore, it is doubtful whether the results obtained, even when water was the advancing liquid, correspond to true equilibrium states. On the other hand, we believe that the aggregate-binder-water system will in fact ultimately come to a true equilibrium in the pavement under the mechanical action of traffic in actual practice. It follows, therefore, that the prediction of field behaviour requires some experimental results obtained on the systems which are in true equilibrium. It is not certain whether Hallberg's capillary pressure method has a great advantage over the contact angle method as far as this requirement is concerned.

We have found that the method of vapour adsorption used by Boyd and Livingstone^[8] and Harkins et al.^{[9],[10]} to estimate the free energies of wetting of solids by liquids should meet this requirement. Indeed, it has been observed that the physical adsorption of vapours on solids is thermodynamically reversible^[11]. The only complication is a hysteresis exhibited at the higher pressures due to capillary condensation if the adsorbent is highly porous. However, it is expected that this would not be the case with mineral aggregates to be investigated.

It will be shown below that $\gamma_{sw} - \gamma_{sb}$ is equal to the difference between the free energy of wetting of the aggregate by water and that by the binder. Although the former can be estimated by vapour adsorption, it is not possible to estimate the latter by this method since the binders are not readily volatile. Therefore, we attempted to make an alternative approach by replacing the binder by a pure volatile hydrocarbon. Although the binders contain not only hydrocarbons but also certain amount of non-hydrocarbon constituents, we were justified in

doing so since the main purpose of our investigations was to obtain some relative data to classify the aggregates according to their tendencies to stripping, rather than to classify the binders. The effect of these constituents, which are more polar or polarizable than hydrocarbons, on γ_{sb} is by no means unimportant. When the absolute value of $\gamma_{sw} - \gamma_{sb}$ is required it is also necessary to have some other experimental data to evaluate this effect. We intend to tackle this problem in the future.

Considering the fact that the technique of adsorption measurements is highly elaborate, we realize that this method can hardly be used as a routine test. For this reason we have directed our work to investigate the possibility of classification of minerals which frequently occur in road aggregates according to their $\gamma_{sw} - \gamma_{sb}$ values. Once these data are available, it would also be possible to classify aggregates by mineralogical examination.

2. Theoretical

By Gibbsian methods of approach, it has been shown by Bangham et al.^[12], Inness et al.^[13] and Boyd et al.^[8] that the free energy of immersion of a solid surface of unit area in the saturated vapour is calculable from vapour adsorption data. The formulae given by these authors are derivable from each other^[9]. The equation for ΔG , the free energy of immersion, due to Boyd and Livingstone^[8] reads

$$\Delta G = -\frac{RT}{M\Sigma} \int_0^{P_0} \frac{q}{P} dP \quad \dots\dots\dots(1)$$

where q is the mass of vapour adsorbed by the solid of unit mass at pressure P ; R , T , M , Σ and P_0 are the gas constant, absolute temperature, molecular weight of the vapour, specific surface of the solid and the saturation pressure, respectively. Boyd et al.^[8] and Harkins et al.^{[9],[10]} determined the adsorption of various vapours by various powdered solids at pressures from 0 to P_0 and calculated ΔG for each system by eqn. (1) or its equivalent.

Here, we would like to present an independent and simpler derivation of eqn. (1) and to discuss its meaning more rigorously.

The differential free energy change at constant temperature T on transferring saturated vapour onto the solid surface of unit area in equilibrium with the vapour at pressure P is

$$\frac{\partial \Delta G}{\partial n} = \mu - \mu_0 \quad \dots \dots \dots (2).$$

where ΔG is the free energy change, n is the number of moles of vapour transferred, μ_0 is the chemical potential of the saturated vapour and μ is that of the vapour at pressure P . If the vapour is an ideal gas, then

$$\mu = \mu_0 + RT \ln P/P_0 \quad \dots \dots \dots (3).$$

Let n_0 be the number of moles of vapour adsorbed when $P=P_0$. From eqns. (2) and (3) we obtain the integral free energy change on transferring saturated vapour onto the solid surface in vacuum until the equilibrium pressure equals to the saturation pressure :

$$\Delta G = RT \int_0^{n_0} \ln P/P_0 \, dn \quad \dots \dots \dots (4).$$

On the assumption, which has also been made by Boyd et al. and other authors mentioned above, that the limit of n/P at $P=0$ is finite, changing the integration variable we obtain from eqn.(4)

$$\Delta G = -RT \int_0^{P_0} \frac{n}{P} \, dP \quad \dots \dots \dots (5).$$

which leads to eqn. (1) and can be put into a more convenient form as follows:

$$\Delta G = -\frac{RT}{M\Sigma} \int_0^1 \frac{q}{P/P_0} \, d(P/P_0) \quad \dots \dots \dots (6).$$

ΔG given by eqn.(1) is the free energy change accompanying the above mentioned process which is terminated when the equilibrium pressure equals to P_0 . When the adsorbent used is a mass of non-porous fine powder, before this final stage is reached, as a result of capillary condensation starting to take place in the contact zones of particles, all the voids in it

should theoretically be filled with the liquid if the solid is wettable by the latter. There are also experimental evidences for this^{[14], [15]}. It follows, therefore, that in such cases

$$\Delta G = \gamma_{sl} - \gamma_{so} \dots \dots \dots (7).$$

where γ_{sl} is the solid liquid interfacial tension and γ_{so} is the surface tension of the solid in vacuum. In other words, ΔG calculated should be the free energy of immersion of a solid surface of unit area in the bulk liquid, which we call the "free energy of wetting". This point of view was also put forward by Bartell et al. in the case of porous solids^[16] and recently applied to compressed powders of a non-porous solid^[17] in a similar treatment. Its validity should not depend on the degree of compression and equally be applicable to powders of non-porous solids which are not compressed at all.

It appears that the adsorption isotherms have not been extended experimentally to actual saturation in the works of Boyd et al.^[8] and Harkins et al.^{[9], [10]}. In spite of the fact that the solids investigated are wettable, these authors assume that no capillary condensation takes place even at the highest experimental pressure and calculate ΔG by an extrapolation to saturation pressure. Consequently, they identify ΔG with the free energy of immersion in saturated vapour and make a correction to obtain $\gamma_{sl} - \gamma_{so}$. This correction amounts to subtracting the surface tension of the liquid from ΔG in the case of solids showing zero contact angles. The extrapolation is made over a short pressure range. But the adsorption isotherms in this region are very steep. In our opinion, the above mentioned assumption on one hand and this extrapolation on the other introduce uncertainties into the free energy of wetting determined in this way. It has been shown by Carman and Raal^[18] and Craig, Van Voorhis and Barf III^[17] that by using a compressed powder as adsorbent an adsorption isotherm of type IV is obtained instead of usual type II and, therefore, the isotherm can be extrapolated to saturation with certainty. At the same time, however, a hysteresis is observed. For these reasons, using loose powders, we paid particular attention to actually reach the saturation in our work and calculate the free energy of wetting directly from eqn.(6).

If ΔG_w and ΔG_b are the free energies of wetting of the same solid by water and hydrocarbon, respectively, determined in this manner, it follows from eqn.(7) that the adhesion tension is given by

$$\gamma_{sw} - \gamma_{sb} = \Delta G_w - \Delta G_b \dots\dots\dots (8).$$

3. Experimental

We have investigated the systems calcite water and calcite-benzene at 25.0°C.

(a) Materials

The calcite mineral used was clear and colourless which occurs in Selçuk near İzmir. It was washed, dried crushed, ground and sieved through a Tyler No. 325 sieve.

The water was twice distilled and boiled vigorously just before introducing into the adsorption apparatus.

"Analar" benzene was purified by one fractional distillation and five recrystallizations. After drying with P_2O_5 its refractive index was found to be 1.5010 at 20°C. against 1.5011 given by Allen, Everett and Penny^[19]. It was stored over sodium wire and used for adsorption experiments.

(b) Apparatus

The experimental method is similar to that used by Tompa^[20] for measuring the vapour pressures of solutions. It differs, however, from the latter in that a mercury manometer is used instead of a Bourdon gauge and that all the vapour lines and the manometer are immersed in the thermostat instead of being heated electrically to avoid condensation. The apparatus is shown in Fig. 1. The bulb A which is attached to the apparatus by means of a mercury sealed joint contains the adsorbent. B is a calibrated capillary tubing of 2 mm. bore which contains the liquid. C is a mercury manometer. The right hand limb of the manometer is provided with a fine glass needle bent downwards to indicate a reference level. This part of the apparatus is separated from the rest by a mercury cut-off D and immersed in a water thermostat at 25°C. The mercury in C and D can be raised and lowered by means of reservoirs E_1 and E_2 via air

traps F_1 , F_2 and taps T_1 , T_2 , respectively. The bulbs G and H and the P_2O_5 tube form the distillation train. I is the vacuum mains.

The vacuum train consisted of a rotary pump, a P_2O_5 tube, a single stage Hickman type oil diffusion pump operating with silicone oil and a cold trap containing dry ice-acetone mixture. All the glass parts were made of Pyrex. Hard rubber grease was used for all taps and joints except that of bulb A. The

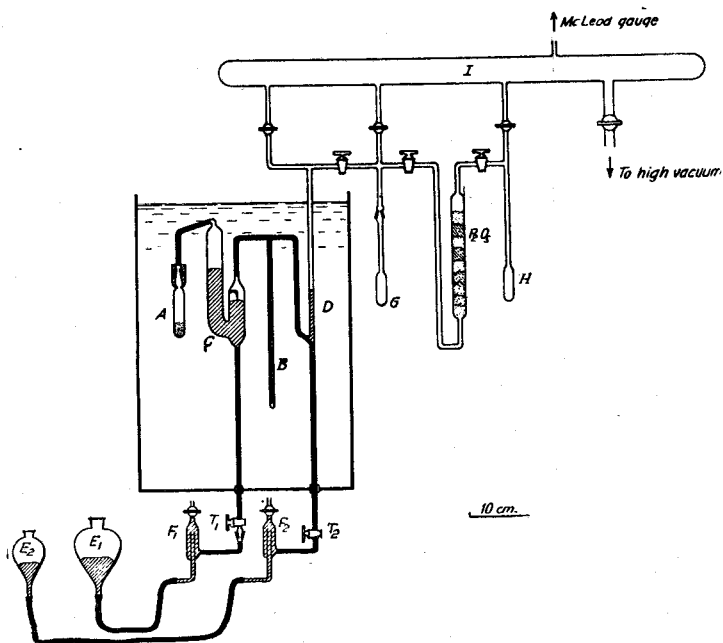


Fig. 1. Adsorption Apparatus

thermostat was fitted with a glass window for observation. The variation of thermostat temperature was not more than $\pm 0.002^\circ\text{C}$. over a period of several hours. A cathetometer reading to 0.01 mm. was used for measuring the level of the liquid in B as well as those of mercury in manometer C.

(c) Preliminaries

The dead space above the mercury in the left hand side of the manometer was calibrated at 25°C . This was achieved as follows: When A, B, and C were empty, the air trap F_1 was

replaced by a capillary tubing dipping into a bowl of mercury. The apparatus was evacuated and, by opening the tap T_1 , some mercury was admitted into the manometer so that it just touched the tip of the glass needle in the right hand side. Then the bowl was weighed. Subsequently, admitting more and more mercury and resetting the point by letting some air into the right hand side of the manometer, and finally filling all the dead space in this way, the bowl was reweighed and the mercury level in the left hand side above that in the right was measured each time. From these results it was possible to draw a calibration curve relating the dead volume to the mercury level in the left.

After thoroughly heating and evacuating down to 10^{-5} mm. as much of the apparatus as possible, the mercury in C was raised and the purities of water and benzene used were checked as follows: A sample of benzene was put into G and thoroughly degassed and dried by successive freezing in dry ice-acetone mixture, pumping and distilling to and from bulb H through P_2O_5 and finally into B as described by Baxendale, Enüstün and Stern^[21]. The mercury in D was raised and the vapour pressure at 25°C . was measured on the manometer C. Then, a small fraction of the benzene was distilled at this temperature into A by lowering the mercury in C. After raising it again no difference was observed between the vapour pressure of the fraction distilled and that of the residue. Thus the sample purified and introduced into the apparatus in the manner described proved to be pure enough not to fractionate. Similar experiments were made with a sample of freshly boiled bidistilled water and the same result was obtained. In the latter case bulb G was replaced by a couple of bulbs and the sample was degassed by freezing, pumping and distilling from one bulb to the other several times and finally distilled into B.

Moreover, the thermometer used was calibrated against the vapour pressure of benzene measured in this manner using Smith's^[22] empirical equation which is in perfect agreement with the data of Baxendale et al.^[21] at 25°C . Using this calibration, an agreement was obtained between the vapour pressure of water measured similarly and the data given in the literature^[23] within the experimental errors, as further evidence for purity.

Experiments in the manner described below were also car-

ried out without any adsorbent to see whether the vapours concerned were adsorbed appreciably by the glass apparatus. We found, in confirmity with the results of Lambert, Roberts, Robinson and Wilkinson^[24], that there was no adsorption in the case of benzene. However, we observed appreciable adsorption in the case of water and established the adsorption characteristic experimentally at 25°C from zero to saturation pressure to be used for corrections.

(d) Procedure

The procedure of actual adsorption experiments was as follows: 5 grams of powdered calcite sample were introduced into A. By lowering the mercury in C and D, it was pumped down to 10^{-5} mm. at 100°C. for several days. The mercury in C was then raised and some benzene was distilled into B in the manner described above. While the benzene was frozen by dry ice-acetone mixture, the mercury in D was also raised. The thermostat was filled with water and brought to 25°C. After the attainment of thermal equilibrium, the mercury in the left hand arm of D was set to the mark previously engraved on the glass tubing. The mercury in the right hand limb of C was also set to the point accurately as described by one of us elsewhere^[25]. The liquid level in B was then measured. During this measurement we had to be sure that there was no liquid anywhere outside the liquid column in B. However, in the course of the time, condensation of vapour in other places was inevitable. For this reason, before the measurement, a few millimeters below the meniscus the capillary tubing B was cooled by a local stream of cold water until all the condensates were collected in B as indicated by a sudden rise of mercury in the right hand limb of C. 45 minutes later actual measurement was taken. In this way we were able to obtain reproducible results.

Then, by cooling the liquid meniscus in B as just described to avoid condensation and lowering the mercury in C gradually, some vapour was let into A by bubbling through the mercury. The mercury in C was raised and reset to the point. The liquid level in B was then measured again. From the difference between the t_w° readings we calculated the amount of vapour transferred to the adsorption bulb A.

After the attainment of equilibrium, which took less than 24 hours, the pressure difference was measured on the manometer and the temperature recorded. Making the usual corrections on the pressure difference and subtracting it from the saturation pressure P_0 previously measured, the equilibrium pressure P in A was obtained.

By subtracting the amount of vapour in the dead space calculated from the dead volume, the equilibrium pressure and the equation of state of benzene vapour^[19] from the amount of vapour transferred to A and dividing by the amount of adsorbent taken we obtained q i.e. the mass of vapour in grams adsorbed by one gram of adsorbent. In this way, by transferring more and more vapour to the adsorption bulb A we covered all the pressure range almost up to saturation. Then, reversing the process and condensing more and more vapour back into B, we also obtained some desorption points.

The adsorbent was then renewed and similar experiments were carried out with water. In this case the rate of equilibration was on the whole much lower. It took several days to obtain a constant pressure. Moreover, in the higher pressure range pressure vs. time curves exhibited more or less prominent minima before the equilibria were reached. The pressure range explored in this case did in fact contain the saturation point. In order to determine the minimum amount of vapour transferred to give rise to an equilibrium pressure equal to P_0 we used a different technique, in addition to pressure measurements, which proved to be more accurate than the latter in the vicinity of saturation. Namely, we observed the disappearance of a small amount of dew produced by cooling a small area on the upper part of the left hand limb of C by pouring a few ccs. of water at 23°C. through a pipette under same conditions. Just before the saturation only a small increase in q could reduce the rate of disappearance appreciably. By increasing q in small increments the time of disappearance gradually increased to a few minutes, then sharply to several hours indicating the attainment of saturation. In this way, we were able to determine the minimum q at saturation with an accuracy of ± 0.6 percent.

The adsorption isotherms obtained in this manner are shown in Fig. 2 by plotting q against P/P_0 .

(e) Errors.

In order to test the reproducibility in pressure measurements, readings were taken with different amounts of mercury in the manometer when both sides were under vacuum. Similar readings were also taken while measuring the vapour pressures of water and benzene as described above. The results agreed within each three series of measurements within ± 0.05 mm., ± 0.02 mm. of this maximum deviation was due to the cathetometer and the remaining apparently due to optical disturbances. By repeated readings at zero pressure difference when the mercury was set to the point, we could estimate the contribution of these disturbances to correct the readings taken under similar conditions. Thus, the accuracy of readings in the vicinity of zero pressure difference could be made ± 0.02 mm..

It can be shown that the error in P/P_0 is given by $\pm [(1 - P/P_0)^2 (\delta P_0/P_0)^2 + (\delta \Delta P/P_0)^2]^{1/2}$ where δP_0 is the error in P_0 and $\delta \Delta P$ is that in the pressure difference measured. Therefore, it follows from the foregoing explanation that in the case of water the maximum error involved in P/P_0 in the intermediate pressure range is $\pm [4 \times 10^{-6} (1 - P/P_0)^2 + 4 \times 10^{-6}]^{1/2}$, in the vicinity of $P/P_0 = 1$ is $\pm [0 + 10^{-6}]^{1/2}$ and in the vicinity of $P/P_0 = 0$ is $\pm [10^{-6} + 10^{-3}]^{1/2}$. In the case of benzene the corresponding errors are $\pm [2.5 \times 10^{-7} (1 - P/P_0)^2 + 2.5 \times 10^{-7}]^{1/2}$, $\pm [0 + 4 \times 10^{-8}]^{1/2}$ and $\pm [4 \times 10^{-8} + 4 \times 10^{-8}]^{1/2}$, respectively. The first terms in these brackets are the systematic errors in P/P_0 due to the determination of P_0 which are involved in all the experimental points. The second terms are the errors due to the measurements of pressure differences. The error of the latter kind involved in an experimental point is independent of those in other points.

The maximum experimental error in determining q was due to level measurements and similarly estimated to be ± 0.00003 .

4. Discussion and Results.

It will be seen from Fig. 2 that the adsorption and desorption points in the higher pressure range fall in the same isotherms in both systems within the experimental errors. We can conclude, therefore, that the systems investigated do not exhibit hysteresis. However, an unusual kind of hysteresis is observed

in the case of water. Namely, the desorption points tend to fall below the adsorption isotherm as the pressure decreases. We have also observed on a different sample that when adsorption is extended as far as to saturation and followed by desorption down to zero pressure, re-adsorption experiments give points lying significantly below the adsorption isotherm obtained in the first run. This behaviour as well as the negative hysteresis just mentioned is perhaps a result of a decrease in the specific surface of the adsorbent due to the growth of calcite crystals in the presence of bulk water at saturation.

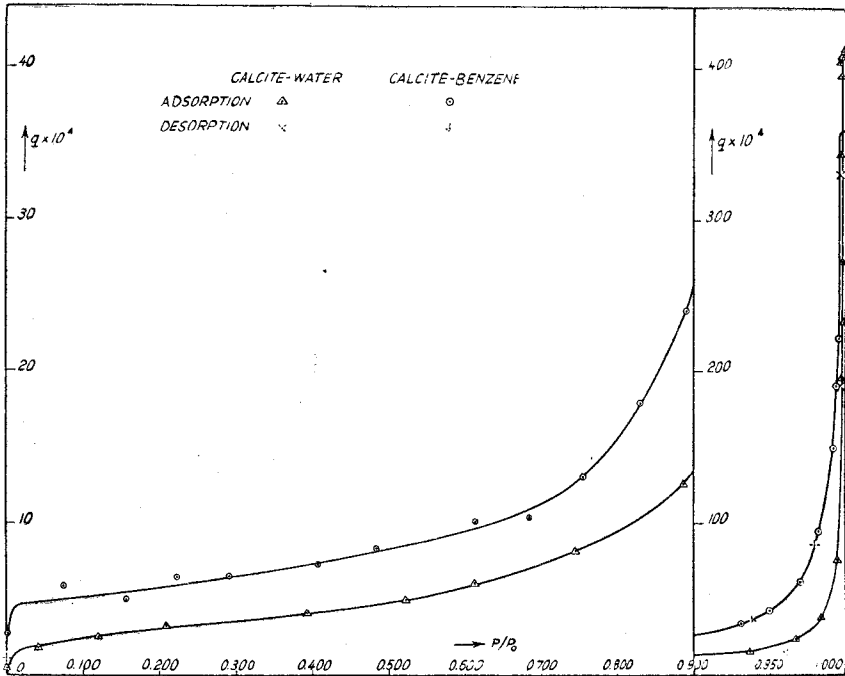


Fig. 2. Adsorption Isotherms at 25.0°C.

As seen in Fig. 2, the isotherms are very steep near the saturation and in the case of water adsorption the isotherm becomes vertical at $P/P_0 = 0.998$. At this stage the appearance of the adsorbent was decisively wet. Therefore, at least in this region, capillary condensation takes place. Similar conclusions were also arrived at by Emmett et al.^[14] and Higuti et al.^[15] in the case of other non-porous solids. The calculation of effective

radius of pores being filled at this relative pressure from the Kelvin equation gives 1.5 microns. As q exceeds a value of 0.04096 ± 0.00026 the saturation pressure is reached abruptly. When the volume of water collected as liquid on the adsorbent at this stage was compared with that of the voids, determined on another sample at the same state of compaction, we found that only 5 percent of the voids was filled. These observations lead us to conclude that although only a small fraction of the voids is actually filled at this point, the largest pores to be filled by capillary condensation is in 1.5 microns effective radius and that the remaining empty ones are so much larger that practically no capillary condensation takes place in them. This is equal to the statement that the filling of these large pores with bulk water does not contribute appreciably to the free energy. In other words, these empty pores are so large in dimensions that they constitute only a negligibly small fraction of the specific surface. We can safely assume, therefore, that practically all the solid surfaces are covered with bulk water at this point and that ΔG to be calculated accordingly from eqn.(6) is in fact the free energy of wetting as defined in Section 2.

In the case of benzene adsorption, the isotherm was not followed experimentally up to actual saturation. However, it is clear from the above discussion that the isotherm is expected to have the same general characteristics as in the case of water in the vicinity of saturation. On this assumption, we calculated P/P_0 where the isotherm would be a vertical line from the Kelvin equation using the effective pore radius given above and obtained a value of 0.996. This figure agrees very well with the experimental point at the highest pressure and the general trend of the isotherm in this region. We also calculated the minimum q at saturation from that observed in the case of water, on the assumption that the capillary volume to be filled with liquid would be the same in both cases. Thus, we extrapolated the experimental isotherm up to saturation by analogy to the water adsorption isotherm, as shown in Fig. 2.

The first step in the evaluation of free energies of wetting from adsorption data is the estimation of specific surface Σ . We calculated Σ from the experimental points in the low pressure range up to $P/P_0 = 0.4$ by B.E.T. method^[26]. Using the data of water and benzene adsorptions separately, we obtained the

best agreement between the two values so calculated by assuming that the density of the adsorbed phase is equal to that of the solid adsorbate at the same temperature in both cases. By taking into account the limits of experimental errors given in Section 4, (e), thus we obtained $9200 \pm 810 \text{ cm}^2 \cdot \text{g}^{-1}$ from water adsorption and $9875 \pm 135 \text{ cm}^2 \cdot \text{g}^{-1}$ from benzene adsorption. We took the latter range as a basis for our subsequent calculations since it determines the specific surface more accurately.

The free energies of wetting were then calculated from eqn.(6) using the experimental points and the specific surface estimated. These calculations were made in two steps. The integral in eqn.(6) was calculated between the limits 0 and 0.3 in the first step. In this low pressure region the integral is rather sensitive to the curvature of the isotherm. On the other hand, the curves were not well defined by the experimental points in this region. We, therefore, integrated the multilayer adsorption equation^[26] according to eqn.(6) between the limits 0 and 0.3 using the parameters which had already been obtained in the determination of specific surface by B.E.T. method. In the second step we calculated the integral between the limits 0.3 and 1 graphically. Thus ΔG 's were calculated. The results of these calculations are given in Table 1 together with the maximum errors estimated. The greatest fractions of these errors are due to the determinations of q in the low and intermediate pressure ranges.

Table 1.

Free Energies of Wetting of Calcite at 25.0°C.

System	ΔG , erg cm ⁻² .
Calcite — Water	— 264 \pm 8
Calcite — Benzene	— 155 \pm 4

Since the vapours concerned are not ideal gases, eqn (6) should more correctly be written in terms of fugacities instead of pressures and ΔG 's be calculated accordingly. However, the fugacity corrections are negligible.

It follows from eqn.(8) and the figures in Table 1 that the adhesion tension for calcite is $\gamma_{sw} - \gamma_{sb} = -109 \text{ erg} \cdot \text{cm}^{-2}$ at 25.0°C. Water-benzene interfacial tension at this temperature

is $\gamma_{wb} = 34.7 \text{ erg. cm}^{-2}$.^[27] The free energy of displacement of benzene defined by the Dupré type equation (see Sec 1) is, therefore, negative: $\gamma_{sw} - \gamma_{sb} + \gamma_{wb} = -74 \text{ erg. cm}^{-2}$. This implies that an actual contact between calcite and benzene is unattainable in the presence of bulk water. Therefore, the experimental values of the contact angle observed on the same system by Reh binder et al.^[28] have no thermodynamical significance.

Boyd and Livingstone^[8] have estimated the free energy of wetting for the systems quartz-water from their own experimental data and vitreous silica-benzene from the data of Palmer and Clark^[29] and obtained -316 and -81 erg. cm^{-2} , respectively. If we can assume that the surface characteristics of vitreous silica are similar to those of crystalline quartz, the adhesion tension in the case of quartz-water-benzene is found to be $-235 \text{ erg. cm}^{-2}$. Comparing this figure with $-109 \text{ erg. cm}^{-2}$ obtained for the system calcite-water-benzene, we come to the conclusion that the tendency of quartz to stripping is twice as much as that of calcite. A qualitative observation well known to road engineers thus finds a scientific justification.

The results on some other minerals will be reported in due course.

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Summary

A thermodynamical method has been used to classify minerals which occur in aggregates used for bituminous pavements according to their resistance to stripping. This comprises investigating experimentally the adsorptions of water vapour and benzene vapour by the powdered mineral and calculating the free energies of wetting of the latter by water and benzene from the adsorption isotherms so obtained. The difference between these free energies is a measure of the resistance of mineral to stripping.

The systems calcite-water and calcite-benzene were investigated by this method. The free energies of wetting of calcite by

water and benzene were found to be -264 ± 8 and -155 ± 4 erg. cm⁻², respectively, at 25.0°C.

Comparing these figures with those given in the literature for quartz, it can be concluded that the tendency of quartz to stripping is much greater than that of calcite.

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