

THE HEAT OF WETTING OF SILICA GEL BY PETROLEUM HYDROCARBONS

Thesis by

Richard Werner Stenzel

In partial fulfillment of the requirements
for the degree of Master of Science

California Institute of Technology

Pasadena, California

1930

THE HEAT OF WETTING OF SILICA GEL BY PETROLEUM HYDROCARBONS

In a study of the retention of crude oil by oil sands, it becomes of interest to know what particular kinds of petroleum substances are most likely to resist removal by ordinary production methods. As a starting point for laboratory investigations, the oil sands may be considered as an agglomerate of fine grains under pressure; a picture which is probably not oversimplified. Such a porous structure has of course capillary properties and undoubtedly will give rise to selective adsorption phenomena. It is the purpose of this investigation to consider the possibilities of arriving at some quantitative conclusion about such adsorption processes. For the sake of further simplicity, only silica-oil systems will here be considered.

In order to determine the retentivity by silica of the various petroleum constituents, their selective adsorption might conceivably be directly measured. However the experimental difficulties are considerable, due principally to the lack of sufficiently sensitive analytical methods for the hydrocarbons. If in some way the free energy of wetting of these constituents by silica particles could be determined, then the problem would be fairly on its way to solution.

A survey of the literature shows that little has been done in the study of the capillary characteristics of hydrocarbons of the type largely present in petroleum. Numerous adsorption measurements have been made on the gaseous hydrocarbons using such porous substances as activated carbon and silica gel, but these capillary condensation

phenomena are not of particular interest in this study. The higher members of the series have been very largely neglected. Gaudechon¹ has published some values of the heats of wetting of pentane and hexane on a silica "dite amorphe". Recently Bartell and Miller² have published the "adhesion tensions" of various crude oils against silica, having developed a method which promises to put the study of the capillary characteristics of solid-liquid systems on a more quantitative basis than was previously possible.

The heat of wetting of a powder by a liquid has been suggested^{3,4} as being a good measure of its adsorption characteristics. That is, the liquid with the higher heat of wetting will be more strongly adsorbed. While this seems to be true in general, it is by no means universal, and can give no really quantitative values as has been pointed out by Bartell and Ying Fu⁵ in their work on the heats of wetting of carbon and silica gel by various substances.

However, because of the fact that such heat of wetting data may be useful in making free energy of wetting calculations; because of the directness of the method; and because of the scarcity of such data in the literature, it was decided to work at the problem from this angle.

I. PRELIMINARY INVESTIGATIONS

During the preliminary work it was thought desirable to use finely ground quartz, so that an estimate of surface area might be made. Accordingly, an attempt was made to measure the heat effect when kerosene and a quartz powder finer than 200-mesh were brought together. However the heat effects, though positive, were discouragingly small, even when large amounts of the quartz were mixed with just sufficient oil for thorough wetting. For a silica which had been dried in a current of dry air at 1000°C for several hours, these heat effects were of the order of 0.05 calorie per gram, corresponding to 10^{-4} cal/cm² of surface. This is about one-tenth the effect estimated by Parks⁶ for the heat of wetting of silica in water. It is significant that with the exception of these data of Parks there are no other available for which the surface area of the adsorbent was reasonably accurately known. Koehler and Mathews⁷, for example, found no measurable heat evolved when finely divided lead sulfate is immersed in saturated lead sulfate solution, even with surface areas as high as 32,000 cm²/gm.

It was obvious then that in order to measure a heat effect with powdered quartz, the ordinary calorimetric methods would need to be considerably modified. A highly sensitive thermocouple and an "aneroid" system of calorimetry would be necessary. This experimental work was not undertaken because of insufficient time.

The use of powdered quartz thus being eliminated, it was thought expedient to try silica gel as a substitute. The most recent views as to the nature of this material are that it is essentially an

aggregate of capillary pores, offering a large surface per unit weight^{8,9}. This type of capillary structure may not be greatly different from a porous oil sand, and consequently considerations based on a study of silica gel may be applicable to such a system. As a first step then, it was decided to study the heat of wetting of silica gel by various hydrocarbons.

II. APPARATUS

1. Calorimeter. The method of calorimetry was similar to that used by Patrick and Grimm⁸ in their experiments on the heat of wetting of silica gel by various substances. Fig. 1 is a diagrammatic representation. It consists of a 100-ml. Dewar flask over which was fitted a hard rubber cover, the latter painted with bakelite to prevent reaction with the hydrocarbon vapors. In this cover were mounted a Beckmann thermometer, a nichrome wire heater, and a stirrup which served at once as a stirrer and as a holder for the glass bulbs in which the silica gel had been sealed. A pointed wire permanently fixed to the cover served as a means of breaking the glass bulbs. The heater had a resistance of 1.644 ohms and was connected to a number of dry cells in parallel. This size of Dewar flask is somewhat small to accommodate all the apparatus needed, but it was found expedient to limit its capacity so that the sample of oil required would not be excessive. The usual charge of oil actually was 35 ml. Due to the small dimensions it was also found that intermittent manual stirring was sufficient to keep the temperature equalized and mechanical stirring equipment could be dispensed with.

In some of the earlier experiments there was also used in place of the glass bulbs a copper flask which had a cover with a sliding fit, so that the silica gel could be dumped into the liquid merely by lifting the whole and then pushing out the bottom portion. This arrangement had the advantage of a metallic conductor to equalize the temperature of the oil and silica gel, but the sliding fit was gradually abraded by the action of the hard silica particles and with substances of high vapor pressure was then found to leak slightly.

2. Silica Gel. This was a commercial silica gel powder which was purified by repeated washings with hydrochloric acid and finally with distilled water until free from chlorides. It was then air dried and sifted through a 40-mesh screen. The extremely fine particles had of course been removed by the decantation process so that only the grainy material was left. This was then placed in a furnace and dried for 3-4 hours in a current of dry air at a temperature of 250-300°C. About 500 g. of the material was prepared in this way, 50 grams at a time; then the whole placed in a large bottle, thoroughly mixed by shaking, and then distributed to ten 100-ml. conical flasks which were tightly stoppered and placed in a desiccated cabinet. This cabinet was so arranged that the gel could be transferred from these flasks to the glass bulbs without exposure to the laboratory atmosphere. In this way it is believed that the charges used in the experiments were very nearly identical in composition.

An analysis of the gel showed a water content of 4.5% and impurities 0.075%. The latter are not considered of significance for the purposes of these experiments.

3. Hydrocarbons. The samples of benzene, n-hexane, n-decane, cyclohexane, and n-butyl mercaptan were all C.P. products from the Eastman Kodak Laboratories. The benzene and hexane were dried with calcium chloride and redistilled, and the decane dried with phosphoric anhydride and also redistilled. The n-butyl mercaptan was used as received.

The sample of hexylene was prepared by mixing $2\frac{1}{2}$ parts of 60% sulfuric acid with 1 part of hexyl alcohol and distilling the mixture. The crude hexylene was then shaken with dilute NaOH to remove any sulfur dioxide which had been formed during the distillation. The aqueous layer was then separated and the hexylene washed with distilled water, shaken with calcium chloride, and redistilled. The fraction which was used in these experiments had a one-degree boiling range (66-67°C at 740 mm) and probably did not contain more than two of the hexylene isomers.

III. EXPERIMENTAL PROCEDURE AND RESULTS

In order to make the heat of wetting determinations, about 1 gram of the silica gel was transferred to the glass bulbs in the atmosphere of the desiccated cabinet, then the neck of the bulb sealed off and the latter placed in the cradle. It was of course weighed before and after filling. The cover of the calorimeter was then put into place, the thermometer inserted, and the whole placed in an air bath, the temperature of which was automatically regulated to within 0.1°C at about 29.5°C . This was the lowest temperature that could conveniently be held in the thermostat, and since the temperature coefficient of the heat of wetting is probably nearly equal to zero¹⁰ this temperature was used throughout.

After the apparatus had been in the air bath for one hour, the calorimeter temperature was about 2 degrees below that of the bath. Temperature readings were now recorded, the charge being intermittently stirred. Usually 30 minutes was sufficient time to give a smooth temperature curve, and the glass bulb was broken by lifting into contact with the pointed wire. The temperature rise was usually about 0.5°C , and stirring was continued until temperature equilibrium had again been established. Then the heater was turned on and a quantity of heat approximately equal to that developed by the silica gel was introduced. By plotting the temperature-time curves, the actual temperature rise could be determined and from this could be calculated the heat capacity of the apparatus and the heat of wetting of the liquid by the silica gel. Previous calibration had shown that a simple graphical method could be used which would give the true temperature differences. Such an empirical method was necessary since the usual heat loss formulas

are hardly applicable to a Dewar flask type of calorimeter. The method of determining the heat capacity of each charge eliminated any uncertainties which would be introduced by the use of calculated heat capacities. It should perhaps be mentioned that the dry cells were short circuited for about a minute through a resistance equal to that of the calorimeter heater before the latter was turned on, so that no fluctuations of the current would occur due to polarization.

It was found that the heat effect of breaking the glass bulbs was about 0.1 cal., quite within the limit of experimental error. A typical set of data is tabulated below:

Run. No. 28a.	Sample: n-decane.	Silica Gel:
		1.3770
Heat Capacity		0.4338
Amps. 0.855	Final Temp. 2.442	<u>0.9432 g.</u>
Sec. 40.9	Initial Temp. 1.898	
Ohms 1.644	Temp. rise 0.544°C	
Cal. 11.8		

$$\text{Heat Capacity} = 11.8/0.544 = \underline{21.6 \text{ cal/}^\circ\text{C}}$$

Heat of Wetting	
Final Temp. 1.612	
Initial Temp. 1.062	
Temp. Rise 0.550°C	

$$\text{Heat of wetting} = (0.550)(21.6)/.943 = \underline{12.6 \text{ cal/}^\circ\text{gm.}}$$

The results obtained have been summarized in Table I. In comparing the values for water and benzene given by Bartell and by Patrick, the results of the present experiments are in closer accord with those of the latter. The absolute values of the heats of wetting depend of course on the degree of hydration of the silica gel used. However, the relative values should not differ greatly. If the heat of wetting of water is considered as 100%, then the value for benzene is 58.2%, 57.8%,

and 88.5% for the author's, Patrick's, and Bartell's values respectively. The values for the other substances cannot be checked as there are no data available in the literature.

The values marked with a * were the results of the initial heat of wetting on the particular substance used, the same sample of liquid being used in the subsequent tests of that group. The bracketed values (in all cases the initial values) were not included in the "average" values shown in the next column.

TABLE I

<u>Substance</u>	<u>Run No.</u>	<u>Q</u> <u>cal/g</u>	<u>Final Ave.</u>	<u>Bartell</u> ⁹	<u>Patrick</u> ⁸
Water	21 a	25.5*	25.6	24.3	19.2
	b	<u>25.8</u>			
Benzene (undried)	17 a	(17.0)*	13.1		
	b	(17.3)*			
	c	12.8			
	d	<u>13.5</u>			
Benzene (dried) and redis- tilled)	23 a	15.3*	14.9	21.5	11.1
	b	14.7			
	c	<u>14.7</u>			
n-Hexane (undried)	26 a	(16.6)*	12.4		
	b	12.0			
	c	<u>12.9</u>			
n-Hexane (dried and redis- tilled)	27 a	13.7*	13.3		
	c	<u>12.9</u>			
Hexylene	18 b	(19.2)*	11.9		
	c	12.0			
	d	<u>11.8</u>			
Hexylene (dried and redis- tilled)	24 a	12.9*	12.7		
	25 a	12.6			
	b	<u>12.6</u>			
n-Decane (dried and redis- tilled)	28 a	12.6*	12.5		
	b	12.5			
	c	<u>12.3</u>			
n-Butyl Mercaptan	30	24.6*	24.6		

The final average values showing the heats of wetting of the dried substances by silica gel are shown graphically in Fig. 2.

IV. DISCUSSION

A study of Table I reveals some interesting results. Water, of course, shows the highest heat of wetting of the substances studied. The mercaptan shows a surprisingly high value, nearly equal to that of water itself. The hydrocarbons fall into a group at about half the value of the heat of wetting of water, not differing greatly among themselves.

Two groups of values have been given for most of the hydrocarbons. In the first, the substance was used as received, and it can be seen that the initial value of the heat of wetting is in all cases much higher (30-50%) than the subsequent values when the same sample of hydrocarbon was used. This may be accounted for by the presence of some foreign substance, presumably dissolved water, which is preferentially adsorbed and thus gives a higher heat of wetting than does the dried substance. Since the solubility of water in hydrocarbons is of the order of 0.01% it can be seen how marked is the effect of even traces of foreign substances on the capillary activity. That the cause of these high initial values was probably dissolved water is evidenced by the uniform heats of wetting obtained when the substance was thoroughly dried before the experiment. A plot of the final values on the dried samples is shown in Fig. 2.

Considering first the case of the hydrocarbons hexane and decane, it is seen that the heat of wetting of the two substances is not greatly different. If we denote by Q the heat evolved (heat of wetting) when a solid of large surface area (such as silica gel) is immersed in a liquid (such as a hydrocarbon), by E_1 the total surface energy of the solid, and

by E_{12} the total energy of the solid-liquid interface, then, say for hexane,

$$Q' = E_1 - E_{12}'$$

and for decane,

$$Q'' = E_1 - E_{12}'' \quad (1)$$

Now for the paraffin hydrocarbons the work of Harkins and of Langmuir has shown that the total surface energy is quite independent of the length of the hydrocarbon chain. From this it might be inferred that the total energy of the hydrocarbon-silica gel interface is also nearly the same for the different members of the series since they are composed of non-polar molecules. In such a case clearly enough $Q' = Q''$ etc., and the heat of wetting of the various members of the paraffin series should not be expected to vary greatly. Such has indeed been found to be the case for the samples of hexane and decane used in these experiments.

With the aid of the Gibbs-Helmholtz equation an expression may be derived for the free energy change accompanying a wetting process. This quantity will be called the "free energy of wetting" j . It is clearly related to the surface tension as follows:

$$j = \sigma_1 - \sigma_{12}$$

Now by (1) we have

$$Q = E_1 - E_{12} = a \left[\left(\sigma_1 - T \frac{d\sigma_1}{dT} \right) - \left(\sigma_{12} - T \frac{d\sigma_{12}}{dT} \right) \right] \quad (2)$$

where a is the total surface area of the solid. Then for the free energy of wetting,

$$j = \sigma_1 - \sigma_{12} = \frac{Q}{a} + T \frac{d\sigma_1}{dT} - T \frac{d\sigma_{12}}{dT} \quad (3)$$

In order to make some predictions about the variation of j from one hydrocarbon to another, one might first consider a water-oil inter-

face since in such a system the surface and interfacial tensions are susceptible to direct measurement. If the process of wetting be conceived similar to the case of the silica gel-oil system, then the hypothetical free energy of wetting ($\underline{j} = \sigma_1 - \sigma_i$) and heat of wetting \underline{q} may readily be calculated. Then since the water and silica gel surfaces are of a similar nature, the behavior of the one may be used as a rough indication of the behavior of the other. Complete data are at present available only for a few of the paraffin hydrocarbons and the calculated values of \underline{j} and \underline{q} for these are shown in Table II. The values for benzene are shown for comparison. The surface tension of water at 20°C is taken as 72.8 ergs/cm².

TABLE II

Values of \underline{j} and \underline{q} for water-oil interface (ergs/cm²)

	σ_2	σ_i	\underline{j}	\underline{q} (calc)
n-Hexane	18.4	50.8	22.0	58.8
n-Heptane	20.1	51.0	21.8	
Octane	21.8	50.8	22.0	57.2
Benzene	28.9	35.0	37.8	65.4

Here σ_2 represents the surface tension of the oil and σ_i that of the oil-water interface. It is seen that the hypothetical heat of wetting \underline{q} is less for octane than for hexane, a trend which is shown also by the silica gel-hydrocarbon interface, as can be seen from the values for hexane and decane in Table I. The free energy of wetting \underline{j} shows no definite trend either to increase or decrease, and the prediction might be made that the silica gel-hydrocarbon interface would behave similarly.

This is more difficult of verification, since neither the surface tension of silica gel and its interfacial tension against a liquid nor their respective temperature coefficients, as required by equation (3), may easily be measured.

In order to arrive at some quantitative values of \underline{j} for the silica gel-hydrocarbon interface, the method of Bartell and Ying Fu⁹ may be followed, and the free energy of wetting calculated from the heat of wetting. Without detailing the method, it may be stated that the following assumptions are involved:

1. That the energy changes which occur when silica gel is immersed in a liquid are essentially due to a replacement of a solid surface by a solid-liquid interface; a process to which the usual thermodynamic relations of plane surfaces may be applied.

2. In the relation

$$\sigma_1 - \sigma_{12} = k \sigma_2$$

where σ_1 is the surface tension of the solid, σ_2 that of the liquid, and σ_{12} that of the interface solid-liquid; that the constant \underline{k} is independent of the temperature.

3. That in the wetting process, the same amount of surface per gram is covered by each of the liquids used.

The first assumption is quite reasonable, since it is in harmony with the generally accepted view of the nature of porous materials. The third is not unreasonable since the liquids used all give a zero contact angle with silica, and would consequently be expected to penetrate to equal extent. The second assumption is not factually justified since there are no data available for solid-liquid interfaces which would serve to indicate the nature of the variation, if any. However, since

calculations based upon this assumption yield results which are not unreasonable, it may be considered valid as a first approximation until further experimental data are available.

The calculation of absolute values of \underline{j} as was done by Bartell and his co-workers will not be undertaken here, since additional assumptions involving other experiments would be necessary, and since the purpose of this study is served as well by relative as by absolute values. Thus since water of all the substances here considered shows the greatest activity toward silica gel, it will be used as a standard of comparison, all other values being relative to water as 100%.

On the basis of the above assumptions, equation (3) now becomes:

$$j = \frac{Q}{a \left(1 - \frac{T}{\sigma_2} \frac{d\sigma_2}{dT}\right)} = \frac{q}{\left(1 - \frac{T}{\sigma_2} \frac{d\sigma_2}{dT}\right)}$$

Thus if \underline{j} for water is considered as 100, \underline{a} takes the value of 6.65×10^6 . The values of \underline{j} for the other substances may then be calculated if the temperature coefficients of the surface tension of the liquids are known. The results of such calculations are shown in Table III. The values are for a temperature of 20°C.

TABLE III

	Q cal/g	σ_2 ergs/cm ²	$\frac{d\sigma_2}{dT}$ ergs/cm ² /deg	\underline{j} %
Water	25.6	72.8	-0.151	100.0
n-Hexane	13.3	18.4	.106	31.0
n-Heptane	(13.1)	20.1	.102	33.1
Octane	(12.9)	21.8	.097	35.2
n-Decane	12.5	(25.3)	(.085)	39.6
Benzene	14.9	28.9	.136	39.1

The values in brackets are not empirical data, but were taken from a smooth curve drawn through the plots of the other values. The values of \underline{j} thus calculated have been plotted in Fig. 3 and show a linear rise with increasing molecular weight of the hydrocarbons. This is in accord with the general experience that for similar substances, those of high molecular weight are more readily adsorbed. The assumptions as given above are thus partially justified, although the analogy to the water-oil interface apparently breaks down in this case.

The substances other than the paraffin hydrocarbons may now be considered. As has been seen, the heats of wetting of the unsaturated hydrocarbon (hexylene) and the aromatic hydrocarbon (benzene) are of the same order of magnitude as those of the paraffins. Their free energy of wetting is then primarily dependent upon their surface tension temperature coefficient as was the case with the paraffins. For benzene the value of \underline{j} has been given in Table III, and can be seen to be considerably higher than that of the corresponding saturated hydrocarbon (hexane). For the hexylene and the mercaptan there are not sufficient data in the literature to make the necessary calculations, and it will be necessary to await further experimentation before the values can be found. The high heat of wetting value of the mercaptan, however, is noteworthy, and indicates high capillary activity.

In considering the application of these results to the question of the selective adsorption in oil sands, final predictions must of course be deferred until free energies of wetting of the substances other than the paraffin hydrocarbons can be evaluated. The statements of Gurvich⁴, which seem to express the prevailing opinion, are to the effect that the order of adsorption of petroleum substances on siliceous adsorbents is as follows:

Paraffins < naphthenes < aromatics < unsaturateds < O,N,S compounds
He also states that of similar substances those of higher molecular weight are more strongly adsorbed. Both of these rules seem to be borne out by the results of the present work. However, his rule that the substances which show higher heats of wetting are more strongly adsorbed does not appear to be as applicable, since the heat of wetting does not in general parallel the free energy of wetting.

The results of the experimental work done thus far indicate that the heat of wetting offers a convenient means of determining the adsorption or displacement tendencies of liquids on solids when a few other readily determinable quantities are simultaneously measured.

This work was carried on as American Petroleum Institute Project 37, with funds made available by John D. Rockefeller and the Universal Oil Products Company. Grateful acknowledgement is made for this assistance and to Professors Lacey and Badger for their interest and helpful criticism.

FIG 1o
CALORIMETER

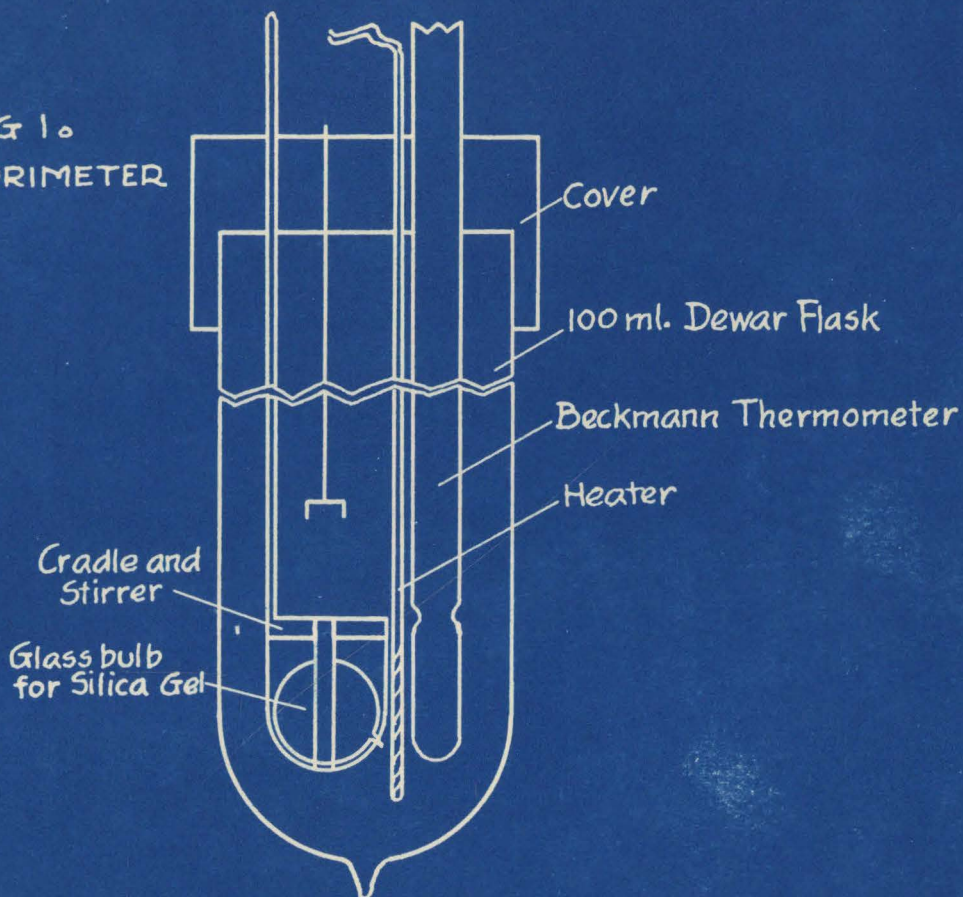


FIG 2o
HEATS OF WETTING
WITH SILICA GEL

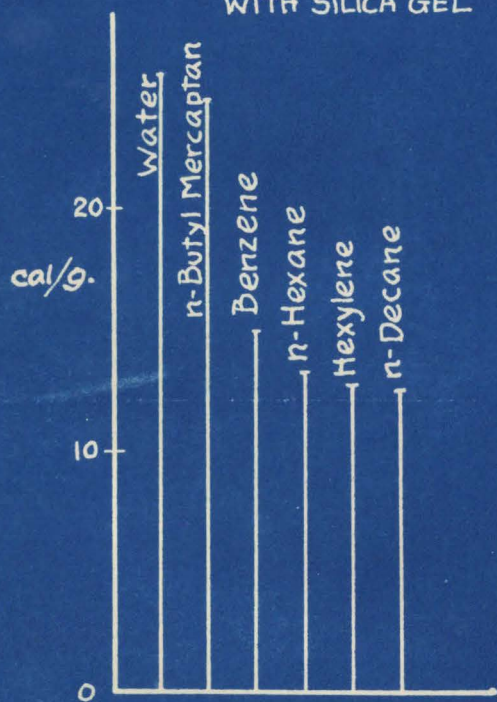
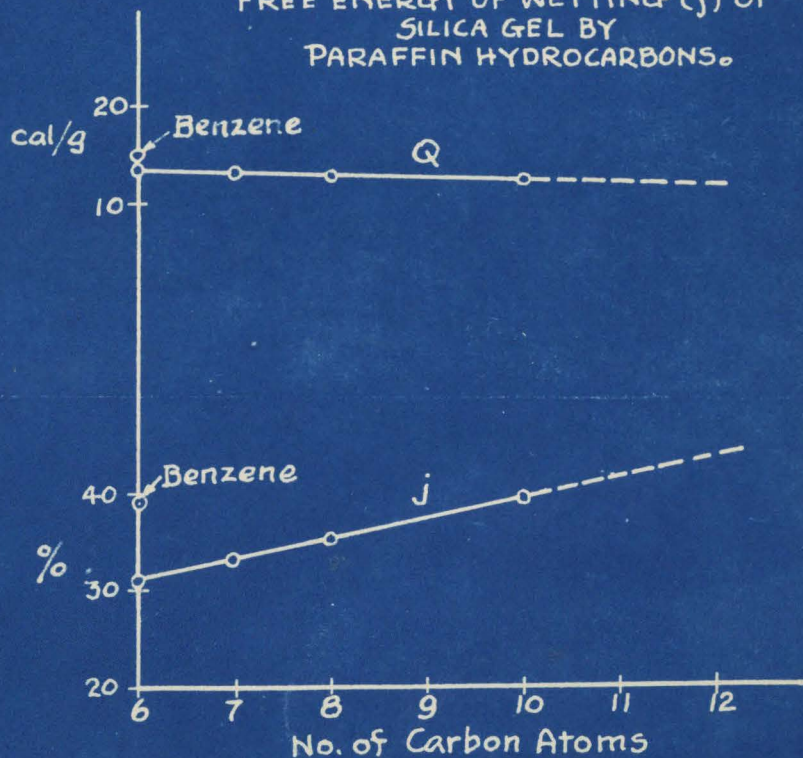


FIG 3o
HEAT OF WETTING (Q) and
FREE ENERGY OF WETTING (j) of
SILICA GEL BY
PARAFFIN HYDROCARBONS.



V. SUMMARY

1. Experimental values for the heats of wetting of silica gel by n-Hexane, n-Decane, Benzene, Hexylene, n-Butyl Mercaptan, and Water have been obtained. These are shown in Table I.

2. The heats of wetting for the paraffin hydrocarbons do not differ greatly, and even show a tendency to decrease with increasing molecular weight. Their free energies of wetting, however, as calculated by the method of Bartell and his co-workers⁹, show a definite increase for the higher molecular weights. This is shown in Fig. 2.

3. Heat of wetting data promise to offer a convenient method for determining the adsorption and displacement tendencies of petroleum substances on their sands.