Part I.   CATAPHORESIS IN ROTATING ELECTRIC FIELDS.

Part II.   THE VARIATION IN THE SURFACE TENSION OF
GAS-SATURATED PETROLEUM WITH THE
PRESSURE OF SATURATION.

Thesis by

Charles Albert Swartz

In Partial Fulfillment of the Requirements for the

Degree of Doctor of Philosophy

California Institute of Technology

Pasadena, California

1931

Part I.   CATAPHORESIS IN ROTATING ELECTRIC FIELDS

Introduction

The alternating field method of measuring cataph-
oresis of colloid particles in the ultramicroscope, first
introduced by Cotton and Mouton,[1] has not come into gen-
eral use for this purpose although it possesses the dis-
tinct advantage of measuring instantaneous mobilities of
individual particles. This is undoubtedly due to the
fact that the interpretations of such measurements have
been open to question since the particles cannot have
the uniform velocities, always assumed in cataphoretic
theories, when in A.C. fields. They must have different
velocities in different parts of their paths.

For example, Blüh[2] found that the apparent
mobility of silver particles in water increased with the
frequency--an unexplainable result.[3] It was a question
whether the diffuse double layer could be out of phase
with the particle and thus noticeably influence the
measurements.

The advantages of the A.C. method can be pre-
served and most of the objectionable features removed by
using a rotating field[4] produced by applying a two phase

A.C. source to four electrodes placed at the corners of a square in a cataphoretic cell. Over a small area in the center of the square, the field thus produced will be practically uniform, constant in magnitude, and rotating with a constant angular velocity. This rotating field will cause each particle in this small area to describe the circumference of a circle with each rotation of the field. The greater the mobility of the particle the larger will be the circle which it will be able to traverse, and its speed will be given simply by the product of the circumference of the orbit by the frequency applied. Particles with constant mobility thus will move at constant speed, and the double layer or ionic cloud generally assumed to surround all colloid particles will reach the same kind of dynamic equilibrium as it would if the particle were moving in a straight line.

In the cell here developed, the electrodes were spaced sufficiently far apart so that the entire field of view in the high power microscope was small enough to fulfill the requirement of being a small area. On looking into the microscope, one finds the entire field of view filled with small circles or toroids of light.

Theory

In the small section of the cell under observa-

tion, the electrostatic field will be that due to the superposition of the two fields arising from the alternating potentials applied separately to the two opposite sets of electrodes, and its x and y components given as functions of time will be

$$X = F \cos \omega t$$
$$Y = F \sin \omega t.$$

Here F is the maximum value of the field strength, in the small region under consideration, due to the potential applied across one of the two sets of electrodes. The total resultant field is a uniform electric field of constant strength F rotating with the constant angular velocity ω.

In order to find the motion of a particle suspended in the liquid and acted upon by such a rotating field, some assumptions must be made from both the electrical and the hydrodynamic standpoints in order to make the problem soluble and yet represent the facts fairly accurately. It is, therefore, assumed that the force acting on the particle due to the electric field is directly proportional to the field strength and that the equations of motion of the particle are

$$A \frac{d^2x}{dt^2} + B \frac{dx}{dt} = kX = kF \cos \omega t \qquad (1)$$

$$A \frac{d^2 y}{dt^2} + B \frac{dy}{dt} = kY = kF \sin \omega t$$

where A and B are constants. A represents the effect of
the inertia of the particle and B represents the viscous
drag of the liquid surrounding the particle. Solving
these equations, neglecting the constant terms, and intro-
ducing the initial condition that the velocity is zero when
t = 0 we get

$$x = R_o \cos \delta \sin (\omega t - \delta) + R_o \cos \delta \sin \delta \, e^{-\omega t/\tan \delta}$$

$$y = - R_o \cos \delta \cos (\omega t - \delta) - R_o \sin^2 \delta \, e^{-\omega t/\tan \delta}$$

(2)

where $R_o = kF/B\omega$ and $\delta = \tan^{-1} \omega A/B$.

Omitting the last or transient term in each of
these equations, the path of the particle is seen to be
a circle of radius $R = R_o \cos \delta$. The velocity of the
particle is

$$R\omega = kF \cos \delta /B$$

whereas, in cataphoretic measurements in a straight line
it would be V = kF/B as seen from equations (1) and these
two will agree within the limits of accuracy of our ex-
periment if $\cos \delta$ is sufficiently near to unity. Now δ
is the angle by which the velocity vector of the particle
lags behind the electric field vector. One would expect

it to be quite small because for colloid particles one
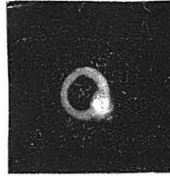would expect A to be very small compared to B.   Fortu-

Fig. 1.   Initial position and final path of oil
particle.   Diameter of particle 2 × 10^{-4}
cm, field 225 volts/cm, frequency 21.5
r.p.s.

nately, there is a simple experimental method of deter-
mining cos δ with just the accuracy required, for on put-
ting t = 0 in equations (2), it is found that the initial
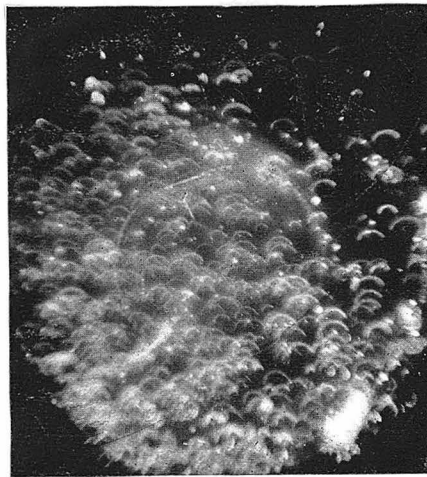

Fig. 2.   Arcs of circular paths showing parti-
cles all of same sign but varying
mobility.

position of the particle is at a distance R_0 from the cen-
ter of the final circle of radius R.   Long exposure micro-

photographs can then be taken in which the rotating field is not applied until the exposure is partly completed. The result is that the initial position and the final circle of the particle are recorded upon the plate from which R and R_O can be measured, whence $\cos \delta = R/R_O$.

Fig. 1 is an example of such a photograph for a particle of mineral oil in water. It is seen that the initial position lies almost exactly in the path of the final circle. From this and several other such photographs, it can be concluded that $\cos \delta = 1$ within the limits of experimental error.

If particles of opposite sign should exist in the same sol, these could be detected by exposing the photograph for only a fraction of a period of revolution. Since particles of opposite sign must rotate in the same direction as the field but 180° apart in phase, they will produce arcs of circles curved in opposite directions. Fig. 2 is a photograph taken in this manner of a mineral oil emulsion with particles ranging in size from 10^{-6} to 10^{-5} cm.

Apparatus

The apparatus consists essentially of three parts, the ultramicroscope and light source, the quartz cell (Fig. 3) containing the sol and electrodes, and the machine for

producing the two phase A.C. potential (Fig. 4).

The quartz cell, with its mounting and the high power oil-immersion objective are the special equipment made by Zeiss for colloidal work, and were adapted with slight modification for this purpose. The light source, used in connection with a cardioid condenser, consists of a pointolite lamp for visual observation and a carbon arc passing from 15 to 75 amperes for photographic work.
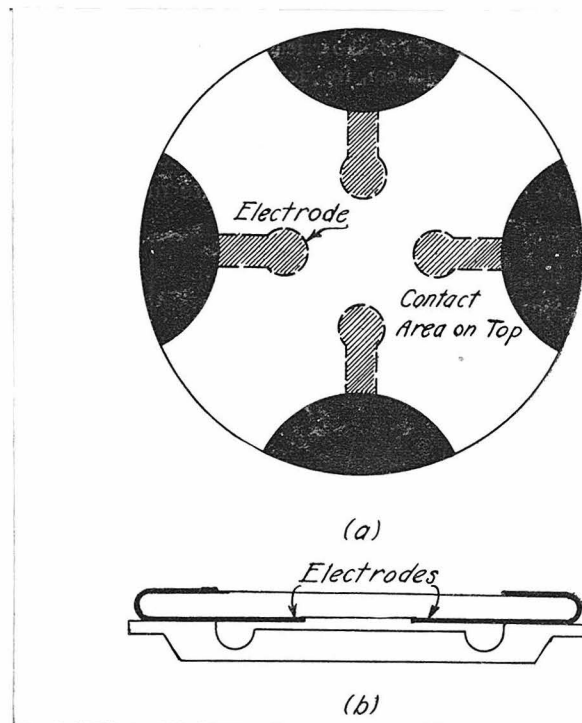

Fig. 3 a.   Quartz cover glass with gold elec-
trodes to produce rotating field.

Fig. 3 b.   Cross-section of cataphoretic cell
with cover glass.

The electrodes in the cell were formed by paint-
ing the proper design (Fig. 3a) on the under side of the
cover glass with the gold paint used for decorating china
and then heating in a furnace to 750°C. The cover glass
with electrodes made in this way may be cleaned in hot
cleaning solution without injury. Connection to the elec-
trodes was made by strips of the gold paint which extend
around the edge of the cover glass and connect to other
painted areas on top. It was found necessary to grind
the edges of the cover glass round and polish them in
order to insure electrical connection. To these painted
sections on top, connection is made directly by four
spring clips which also serve to hold the cover glass
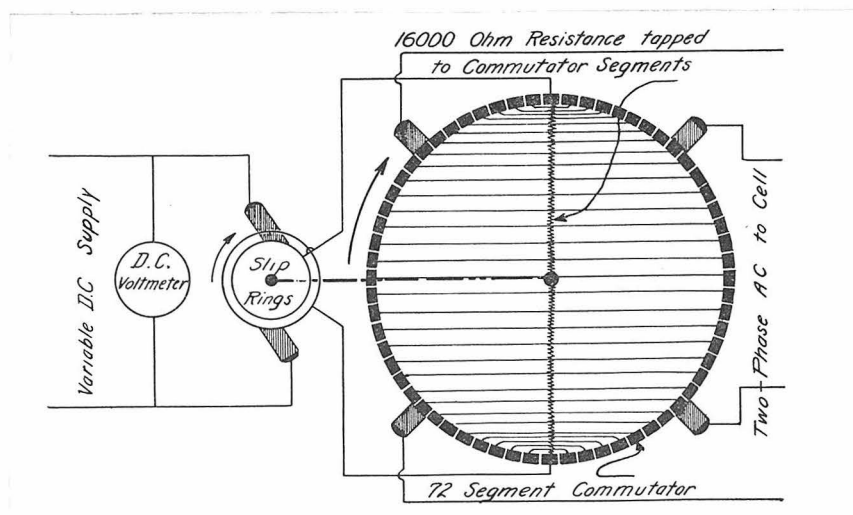firmly in place against the lower half of the cell.

Fig. 4. Two-phase A.C. potential generator
allowing independent variation of
voltage and frequency.

In this cell, it is found that the size of cir-
cles described by the colloids, and therefore the veloc-
ity of the particles, is not a function of the depth of
the particle in the cell as is usually found in thin
cells. This is due to the fact that the edges are free
(Fig. 3b) and the endosmose can, therefore, move the en-
tire layer of liquid in the center as a whole without
causing pressures which will give rise to reverse currents.
Blüh[2] made tests which seemed to show that endosmose could
be entirely damped out by using a cell as thin as ours.
Our results, however, indicate that the endosmose is only
reduced and not entirely eliminated. In use, the cell
thickness was about 10μ.

A specially constructed machine was used for pro-
ducing the A.C. potential its principle being illustrated
in Fig. 4. Thirty-six coils, each of proper resistance,
were wound non-inductively on an old D.C. generator arma-
ture shaft from which the iron core and windings had been
removed. The coils were connected as shown to the
seventy-two segments of the commutator so that, as one
proceeds from segment to segment around the periphery,
the resistance between the two diametrically opposite seg-
ments is a sine function of the angle. The coils were of
No. 30 "advance" wire and in series they totaled 16000
ohms. When a D.C. potential supply is connected in series

with them by means of slip rings and when the shaft is rotated at uniform speed, any number of sine function potentials may be obtained in any desired phase relation to each other by the use of sets of brushes properly spaced about the comutator. Two sets were placed 90° apart for the two phase. The advantage of this construction is that both the voltage and frequency of the A.C. potentials produced are variable over wide ranges and entirely independently of each other.

Results and Discussion

If we calculate the mobility of particles as explained above, we get results in agreement with other observers. For instance, using a silver sol made by the Bredig method we find the mobility to vary between 2×10^{-4} and 4×10^{-4} cm^2/volt · sec. which is practically the same range of mobility as given in Bancroft's "Applied Colloid Chemistry" for silver particles in water.[5]

In order to test the effect of a variable speed on the diffuse electric double layer assumed to surround the particle, several photographs of the same particle have been taken on the same plate, first with the rotating field, then with a straight alternating field obtained by disconnecting one of the phases composing the circular field. In the first case, the path is circular and the

speed of the particle is constant; in the second case, the path is a straight line vibration and the speed varies over wide limits. All photographs thus taken show that the amplitude of the straight line vibration is just equal to the diameter of the corresponding circle. This indicates that the distorting effect of the variation in speed on the distribution of the diffuse double layer and the consequent variation of the effective force on the particle due to the field is very small if it exists at all. A sample of such a photograph is reproduced in Fig. 5. Furthermore, when several photographs are taken on the same plate of the same particle moving in circles with constant frequency but with different field strengths and consequently with different speeds, the diameters of the orbits are in the same ratio as the applied voltages, showing again that the variation in speed has no effect on the double layer, at least for the frequencies and voltages used.

According to the tests described in this paper, the rotating field method must give correct values for the mobilities of the colloid particles. The single phase A.C. method, should also give correct values, since it agrees with that of the rotating field. Why, then, did Blüh[2] using the A.C. method find an increase in his measured

mobilities with increasing frequencies. Using the same sol,--Bredig silver in distilled water,--as he used, we repeated and checked his results. However, the test which he made to show that endosmose was entirely eliminated did not seem conclusive. His peculiar results can be easily explained if we assume that there was some endosmose in his cell and that this motion was opposite in direction to the cataphoretic motion of his particles. Since the inertia of the liquid is relatively large, its oscillatory motion, due to endosmose which tends to reduce the motion of the silver particles, would become less and less noticeable as the frequency increased. Consequently, at low frequencies the measured mobility would be too low, but it would approach the true mobility as the frequency increased. Thus, the measured mobility would increase with frequency. If this explanation be correct, then similar experiments using a colloid of sign opposite to that of silver should give a decrease rather than an increase in measured mobility with increasing frequency. This was tried out with a sol of Bredig copper in distilled water, and the result was a definite decrease in mobility with increasing frequency as was expected. Thus Blüh's increase in mobility with frequency can be explained if the endosmose was not entirely eliminated from his cell as he assumed.

Probably the most important result of this research is the observation that the mobility of individual particles as measured by the diameter of their orbits is not constant with time but fluctuates considerably. These
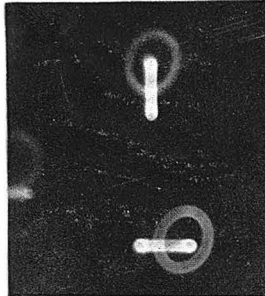

Fig. 5. Paths of an oil particle in the ro-
tating field and in each of the com-
ponent A.C. fields. (Four exposures)

fluctuations take place so rapidly that it is impossible to make quantitative visual measurements upon them. However, many hours of observation of the phenomena have yielded the following facts:

1. Each particle has one definite size of orbit or speed in which it is most frequently observed. This orbit will be called the perferred orbit. It is the same order of magnitude for all particles from the smallest to the largest found in a mechanically stirred oil emulsion, though it is slightly larger for the larger particles in agreement with Mooney's[6] results.

2. Particles are very rarely found in orbits

larger than their preferred orbits—almost all of the fluctuations take place between the preferred orbit and zero. The fluctuations are apparently quite random.

3. The amount and rapidity of these fluctuations depends upon the size of the particles in much the same way as the Brownian motion depends upon the size. They are hardly perceptible in particles larger than 10^{-4} cm diameter while the finest particles observable in the ultramicroscope fluctuate so violently that they seldom stay in any circle for one revolution.

4. The same type of fluctuation is found in all sols observed. Emulsions of mineral oil, olive oil and turpentine in distilled water; Bredigs sols of copper and silver in distilled water; and Zigmondy's nuclear gold sol[7] have been tried.

Why does the mobility fluctuate? Fluctuations in the charge on the particle seems the most reasonable explanation but how can a particle suddenly lose such a large charge. Calculations show that the change in charge necessary to produce some of the fluctuations observed must be at the very least several hundred electrons. It may be that the charge on all colloid particles is always fluctuating, or it may be that the strong electric field with the aid of an occasional heavy impact due to Brownian motion carries away some of the adsorbed layer

of ions causing fluctuations in charge only while the colloid mobility is being observed. At present we cannot answer this question.

REFERENCES

1. Cotton and Mouton, Compt. Rend. 138, 1584, 1692 (1904).

2. Bluh, Ann. d. Physik 78, 177 (1925).

3. Bluh, Ann. d Physik 79, 143 (1926); 80, 181 (1926).

4. Cotton and Mouton, in Compt. Rend. 138, 1584 (1904) suggested the possibility of using colloid particles in a rotating field as a kind of oscilloscope to analyze three-phase potentials.

5. Bancroft, Applied Colloid Chemistry, p. 258.

6. Mooney, Phys. Rev. 23,396 (1924).

7. Rinde, Diss. Upsala, p. 25 (1928).

Part II.   THE VARIATION IN THE SURFACE TENSION OF
             GAS-SATURATED PETROLEUM WITH PRESSURE
             OF SATURATION.

Introduction

The purpose of this research was to determine
quantitatively how the surface tension of petroleum, sat-
urated with gas under pressure, varies with the pressure
of saturation. Such data are of practical importance to
the oil industry for it is a well known fact that with
present methods of obtaining oil from the ground only a
small portion of the total amount of oil in the sands is
recovered. Since surface tension effects the rate of
flow of oil through sands and consequently the amount of
oil to be recovered, it seemed worth while to know how
the surface tension varies with the amount of gas in so-
lution, especially since by pumping gas into a well, the
amount of gas in solution can be artificially varied at
will.

Method

Of the many methods of measuring surface tension
the capillary rise method was selected as the most suit-
able. It is very simple and direct yet sufficiently

accurate for the purpose at hand. Furthermore, since
the measurements must be made inside a chamber under
very high pressure it is important that no moving parts
be required to be operated from the outside. With this
method it is only necessary to make observations through
a glass window of the chamber.

The suitability of the method is further en-
hanced by the fact that the angle of contact of all the
oils used is zero. This fact was determined by filling
a small piece of glass tubing to overflowing with the
liquid so that the upper surface was convex. Into this
convex surface was dipped a small glass filament so that
capillarity drew the liquid upward around the filament.
The angle of contact of this liquid with the glass of
the filament could then be easily observed with a micro-
scope and seen to be zero.

The surface tension is given by the formula

$$T = \frac{(h + \frac{a}{3}) \, da}{2}$$

where

$\quad\quad$ T $\;=\;$ surface tension

$\quad\quad$ h $\;=\;$ height of lowest part of
$\quad\quad\quad\quad\;\;$ meniscus above the level
$\quad\quad\quad\quad\;\;$ of the liquid

$\quad\quad$ a $\;=\;$ radius of capillary tube

d = density of the liquid

The height h is corrected by adding the quantity $\frac{a}{3}$ to account for the weight of liquid above the lowest part of the meniscus. h was determined by means of a cathetometer graduated in millimeters and which could be read to tenth millimeters by means of the vernier. To get h it is not only necessary to be able to set the cathetometer on the meniscus but also on the surface of the main body of liquid. Since the liquid is viewed through a glass window and since the surface tension pulls the edge of the liquid upward on the inside surface of the window it is impossible to set the cathetometer directly on the surface. This difficulty was overcome by arranging a pointer so that it could be lowered by a screw motion until the point just touched the surface as indicated by the sudden jump of the liquid upward around the pointer due to capillarity. When the liquid was removed the cathetometer could be set on the end of the pointer to get the required level.

In all measurements the meniscus was always allowed to come to the same point on the capillary tube and at the conclusion of the experiment the radius "a" was determined by breaking the tube at this point and measuring it directly. In this way any error due to variation in the inside radius of the tube along its

length was completely avoided.

Since the density d varies considerably with the saturation pressure it is necessary to make a separate determination of d as a function of the pressure. For this purpose a bulb of known volume was suspended from a spring and immersed in the saturated liquid. By calibrating the spring with known weights and measuring the extension when the bulb was immersed in the liquid at various saturation pressures the density change could be easily calculated. By adding this change in density to the density at atmospheric pressure (as determined by a Mohr balance) the absolute value of the density as a function of the pressure is found.

Apparatus

A schematic diagram of the apparatus is shown in Figure 1. It consists essentially of two chambers, one for mixing the oil and gas to complete saturation and one for measuring the capillary rise. The mixing chamber is provided with a motor operated stirrer consisting of a paddle fastened to a rotating shaft extending through the top of the chamber to the outside through a large packing gland. The measuring chamber contains the capillary tube and pointer both visible through the glass window in front. The capillary tube and pointer are illuminated by

shining light in through the window from the front and re-
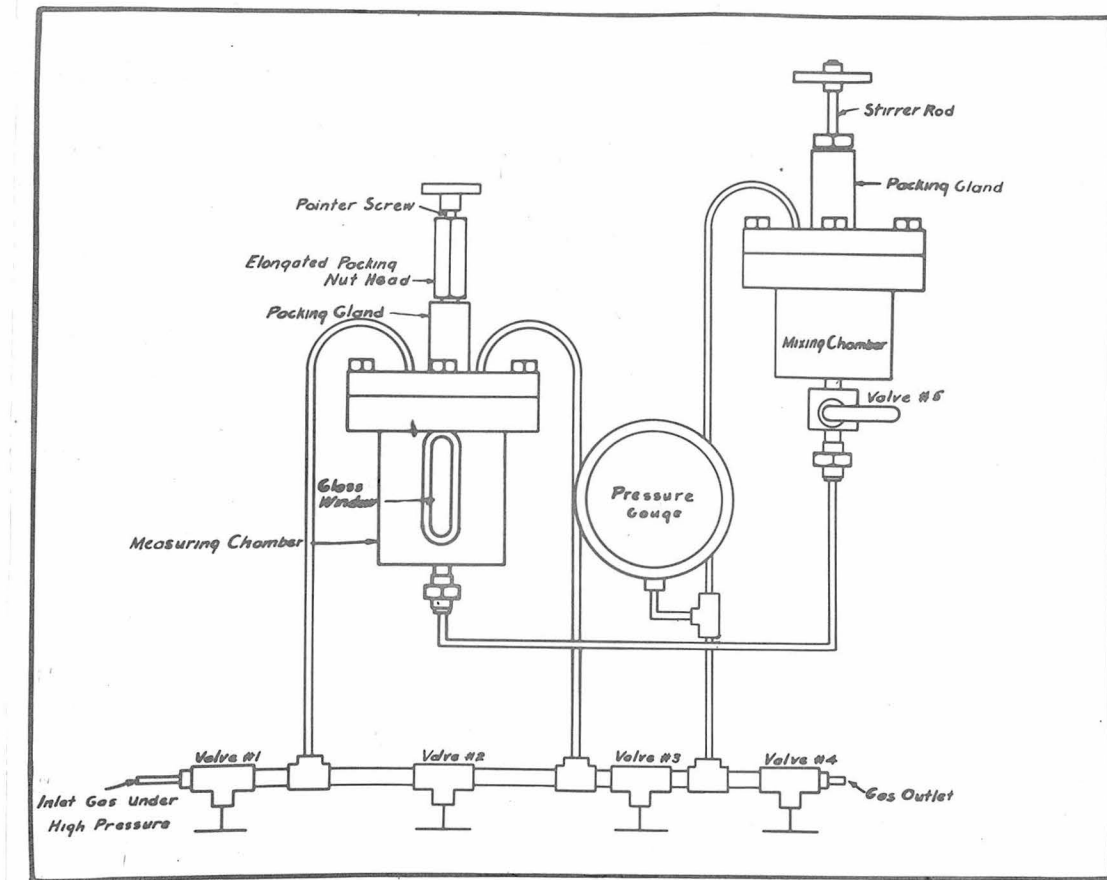flecting from a mirror placed in the back of the chamber.

Fig. 1.   Apparatus for measuring surface
tension under high pressure.

The pointer which is used as explained above to obtain the
level of the liquid in the chamber consists of a pointed
shaft extending through the top of the measuring chamber
through a packing gland.   The packing nut has an elon-
gated head with a hole through the center which is tapped
to fit the threads on the pointer screw.   Thus, by turn-

ing the pointer screw it may be raised or lowered through a range determined by the threaded portion of the packing nut head. The tops of both chambers are fastened rigidly to a wooden frame while the bottom portions are removable by taking out the bolts holding them to the top. The joint between the two parts of each chamber is made gas tight by means of a lead washer (made from 30 ampere fuse wire) fitting into V shaped grooves turned into the abutting surfaces.

The mixing chamber is at a higher level than the measuring chamber so that after the oil is thoroughly saturated in the former it may be allowed to run into the latter when valve #5 is opened. This valve is a specially constructed leak-proof steel stopcock. The copper tubing connecting the two chambers is easily removable for cleaning purposes by taking apart the two unions shown in the figure.

There are two connections by means of copper tubing through the top of the measuring chamber. The tube leading to the left side of the chamber in the figure connects on the inside to the top of the capillary tube, while the tube on the right merely opens into the inside of the chamber. By this arrangement, as long as valve #2 is open, the pressure above the meniscus in the capillary tube is the same as in the surrounding chamber. Between

successive measurements, however, it is necessary to force out the liquid remaining in the capillary tube and this may be done by closing valve #2 and opening valve #1 thus admitting gas through the capillary tube. It is of course always necessary to have a reservoir of gas under high pressure so that it may be admitted through valve #1.

The first apparatus made was constructed entirely of brass and was used only up to a maximum pressure of 400 pounds. When it was found desirable however to go to a pressure of 2000 pounds the apparatus was reconstructed and the two chambers made of steel. In each case the window opening in the measuring chamber was two and one half by one half inch. In the low pressure apparatus the glass window was plate glass 1/4 inch thick and in the high pressure apparatus it was 1/2 inch thick. These were sealed in place with sealing wax against the inside of the chamber and the sealing wax was painted over with Duco paint to prevent the dissolving of the sealing wax in the oil. The values #1-4 and the nipples and tees connecting them were in each case ordinary 1/8 inch brass pipe stock.

The procedure followed in making a set of measurements on the capillary rise with a given sample of oil and gas is as follows.

The mixing chamber is filled with the oil and the capillary tube is cleaned thoroughly by allowing benzene to flow through it. The capillary tube is made easily

removable by sealing it into a nut which screws into the
end of the copper tube making connection to the capillary.
The first measurement is taken at atmospheric pressure by
leaving valves #2, 3, and 4 open and allowing the oil to
run into the measuring chamber by opening valve #5.
Enough oil is run into the chamber to just bring the menis-
cus in the capillary tube up to the marked position on the
tube. The cathetometer is then set on the meniscus for
the first reading and the pointer is screwed down until it
touches the surface of the liquid in the chamber. The oil
is then forced back into the mixing chamber by closing
valves #3 and 4, opening valve #5 and then gradually ad-
mitting gas through valve #1. With the end of the pointer
now clearly visible the cathetometer may be set on the
point to get the second reading and the height h is the
difference between this and the first cathetometer reading.
When all the oil is forced back into the mixing chamber
valve #5 is closed and valve #3 is opened and gas allowed
to flow in through valve #1 until the next desired pressure
is reached as indicated by the pressure gauge. The stirrer
is now put in operation and the oil and gas mixed until
saturated. The saturation point is reached when the pres-
sure read on the gauge ceases to drop, value #1 being
closed. Valves #3 and 5 are now opened and the saturated
oil allowed to run into the measuring chamber for the

second set of readings. This process is repeated again at
the next higher saturation pressure and for the desired
number of succeeding higher pressures.

When the apparatus was first put into operation
the level of the meniscus was found to be very unstable,
oscillating up and down for no apparent reason. The
trouble was soon found to be due to very slight currents
of gas flowing in the copper connecting tubing. This tub-
ing had a small inside diameter of 1/8 inch so that its
resistance to flow was considerable and any slight cur-
rents would set up pressure gradients which tended to
raise or depress the meniscus. Such trouble would be
caused for instance by a slight leak in the packing around
the stem of valve #2. The difficulty was eliminated by
making a very small hole in the tubing which connects to
the capillary tube inside the measuring chamber. The hole
was located just above the top of the capillary tube so
that there was definite connection between the gas just
above the meniscus and the gas in the surrounding chamber
thus eliminating the possibility of a pressure gradient
between these two bodies of gas. The resistance to flow
of gas through the hole, however, was large enough so
that it was easily possible to expel the liquid from the
capillary between measurements as explained above.

It is very desirable that the inside of the

capillary tube be thoroughly wet near the meniscus to make
sure that the final rest position is one of true equilib-
rium. This may be accomplished by causing the liquid to
rise too high in the tube and allowing it to slowly settle
back into equilibrium. This excessive rise may easily be
brought about by suddenly opening and closing valve #4
(valves #2 and 3 being open) thus allowing a small amount
of gas to rush out and set up currents in the connecting
tubes which cause the meniscus to rise.

The first apparatus constructed which was used up
to pressures of 400 pounds was not thermostated and the
temperature variation during a set of measurements on a
given sample of gas and oil amounted to perhaps one or two
degrees in some cases. The later apparatus, however, which
was used for pressures up to 2000 pounds was enclosed in an
air thermostated box so that the temperature variation in
the apparatus could not exceed a small fraction of a degree.
The constant temperature used was 31°C.

Since the gases used in this work were available only
at the relatively low pressures of from 250 to 900 pounds
it was necessary to construct an apparatus for compressing
this gas up to the necessary high pressure. A diagram of
this apparatus is shown in Figure 2. It consists of two
cylinders containing mercury and which are connected at
their bottom ends by a small pipe. The low pressure gas is

admitted into the right hand cylinder through valve #3
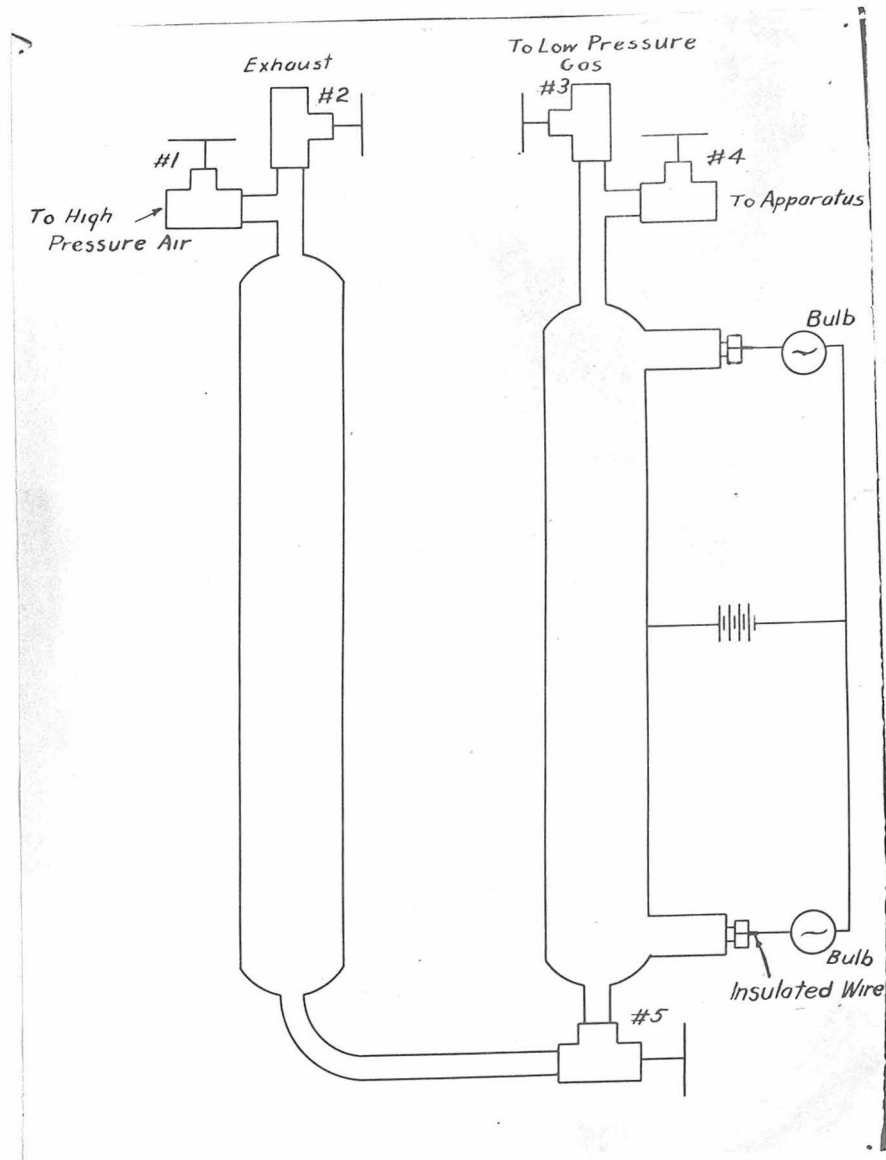thus forcing the mercury over into the left hand cylinder

Fig. 2. Apparatus for compressing gas.

with valve #2 open. Valves #2 and 3 are now closed and
valve #1 which connects to a tank of air at very high

pressure is opened and the mercury forced back into the right hand cylinder compressing the gas therein which may be released into the main apparatus through valve #4. This process may be repeated until the maximum pressure is reached.

The tank of high pressure air which furnishes the motive power was obtained from the liquid air plant compressor at about 3500 pounds pressure. Valve #5 was used for controlling accurately the flow of the mercury from one cylinder to the other. The level of the mercury in the right hand cylinder was indicated at its extreme positions by the flash light bulbs connected as shown to insulated wires leading into the cylinder which could make contact with the mercury on the inside.

Results

The natural oils and gases used in these measurements were chosen from various oil fields throughout the country. Natural gases from Sugarland Texas, Seal Beach California, and Bartlesville Oklahoma were used as well as carbon dioxide and air. Crude petroleum from Sugarland Texas, Midwest Wyoming, Santa Fe Springs California, and Findlay Ohio as well as pure benzene were used as liquids. The results of the experiments are shown in the graphs of figures 3, 4, and 5. In these graphs each curve is des-

ignated by the names of the states from which that particu-
lar combination of gas and oil came. The first name indi-
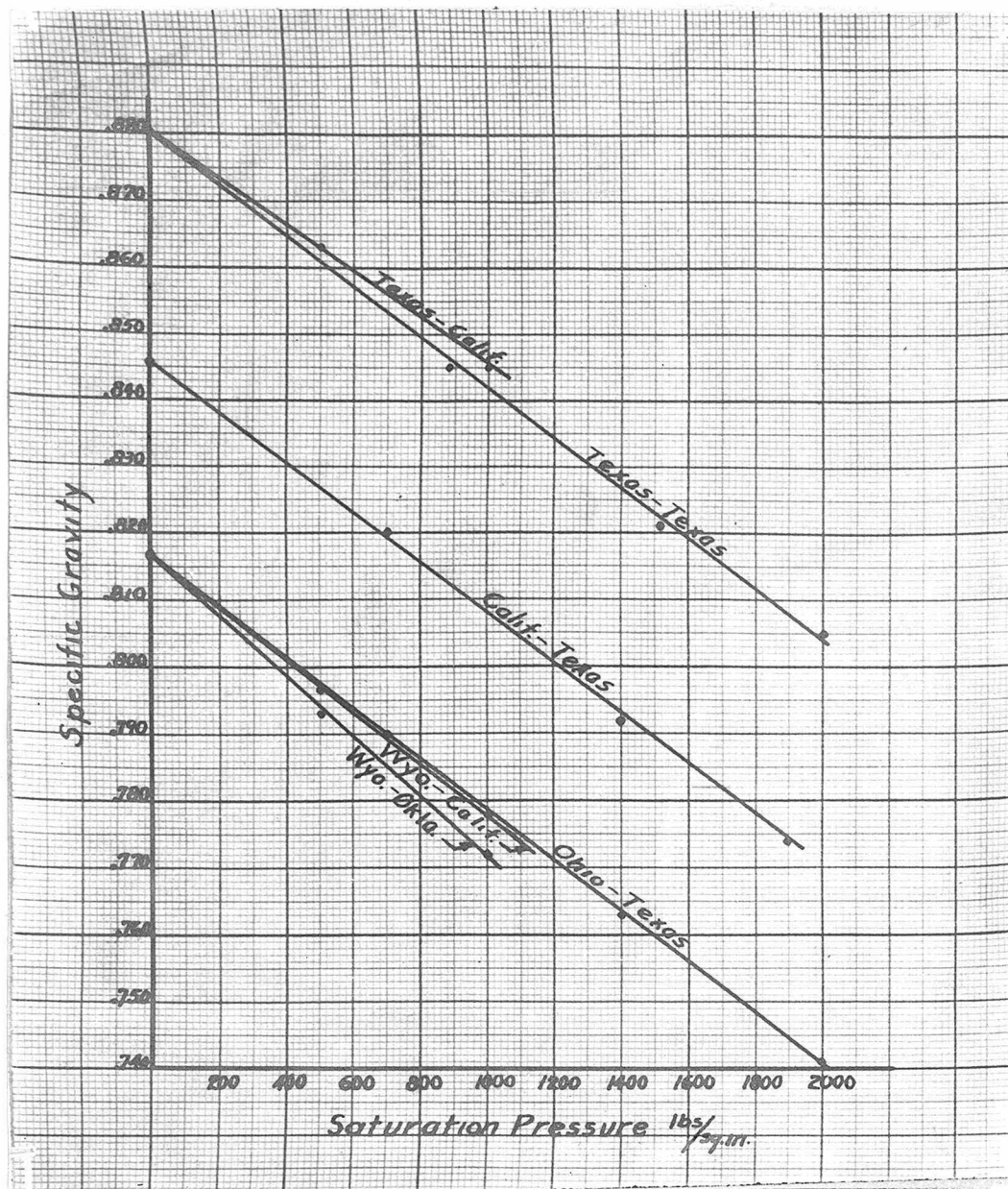cates the state from which the oil came and the second the

Fig. 3. Curves showing density of oil as
function of saturation pressure
for various oil-gas combinations.

state from which the gas came.

Figure 3 shows how the density varies with the saturation pressure for the various combinations of gas and oil used. It will be noted that no curves are shown for air or carbon dioxide. This is because the variation in density with these gases was so small as to be less than the experimental error known to exist in other parts of the experiment. For all combinations shown, however, it is seen that the variation with pressure is practically linear and of approximately the same amount.

Figures 4 and 5 show the variation in the actual surface tension with pressure of saturation. With air the decrease is very slow while with carbon dioxide it is very rapid, more rapid than with any of the natural gases used. With all gases except carbon dioxide the curves are slightly concave upward. In the case of carbon dioxide the curves are almost straight lines. This may be explained by the fact that carbon dioxide is the only pure gas used and in all other cases there may have occurred selective absorption of the various constituents of the gases or perhaps even successive condensation of some of the constituents. It is interesting that the curves for all the natural gases are of the same general shape and the relative decrease in surface tension of approximately the same amount.

The chemical analysis of only one of the natural
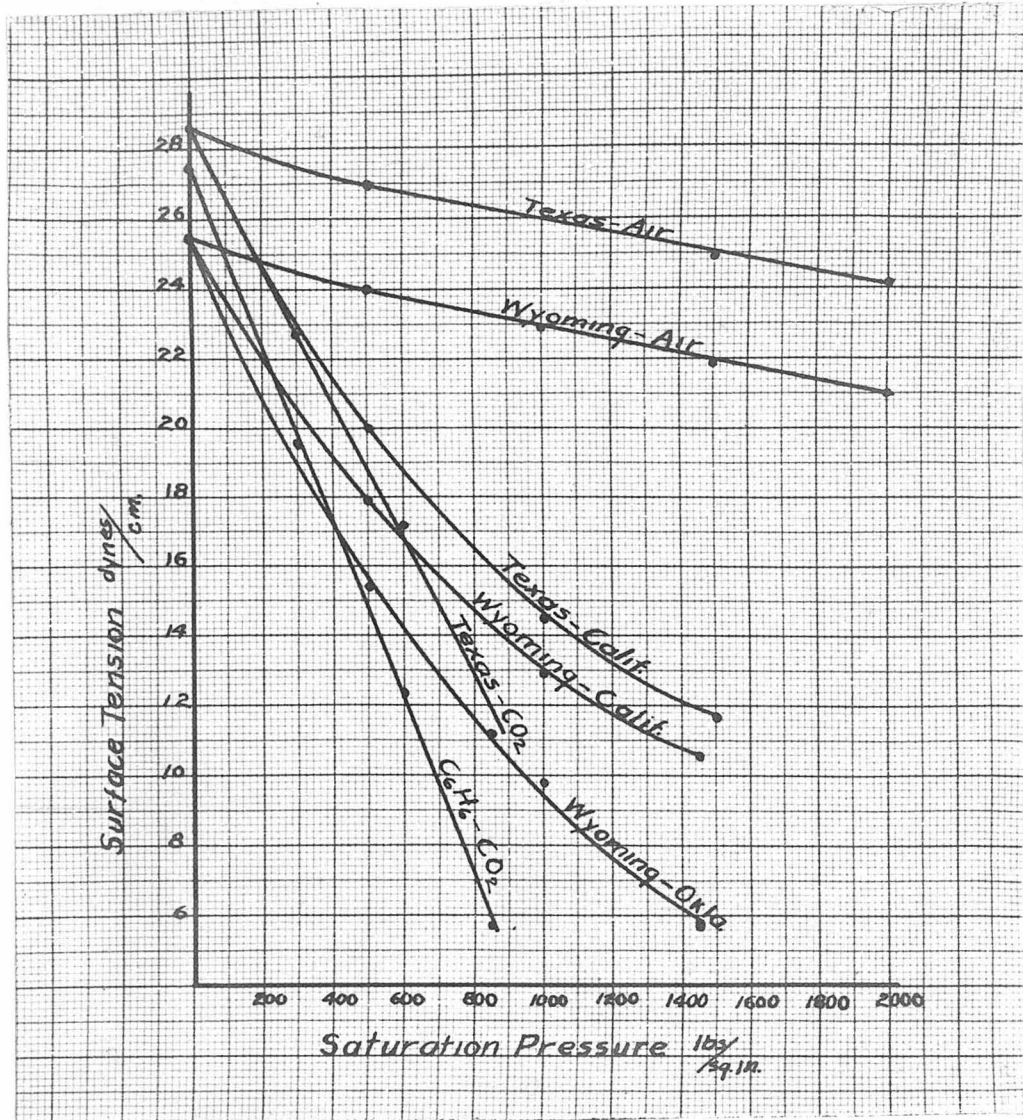gases used is known at present.   This is the sample from

Fig. 4.   Curves showing surface tension of
oil as function of saturation pres-
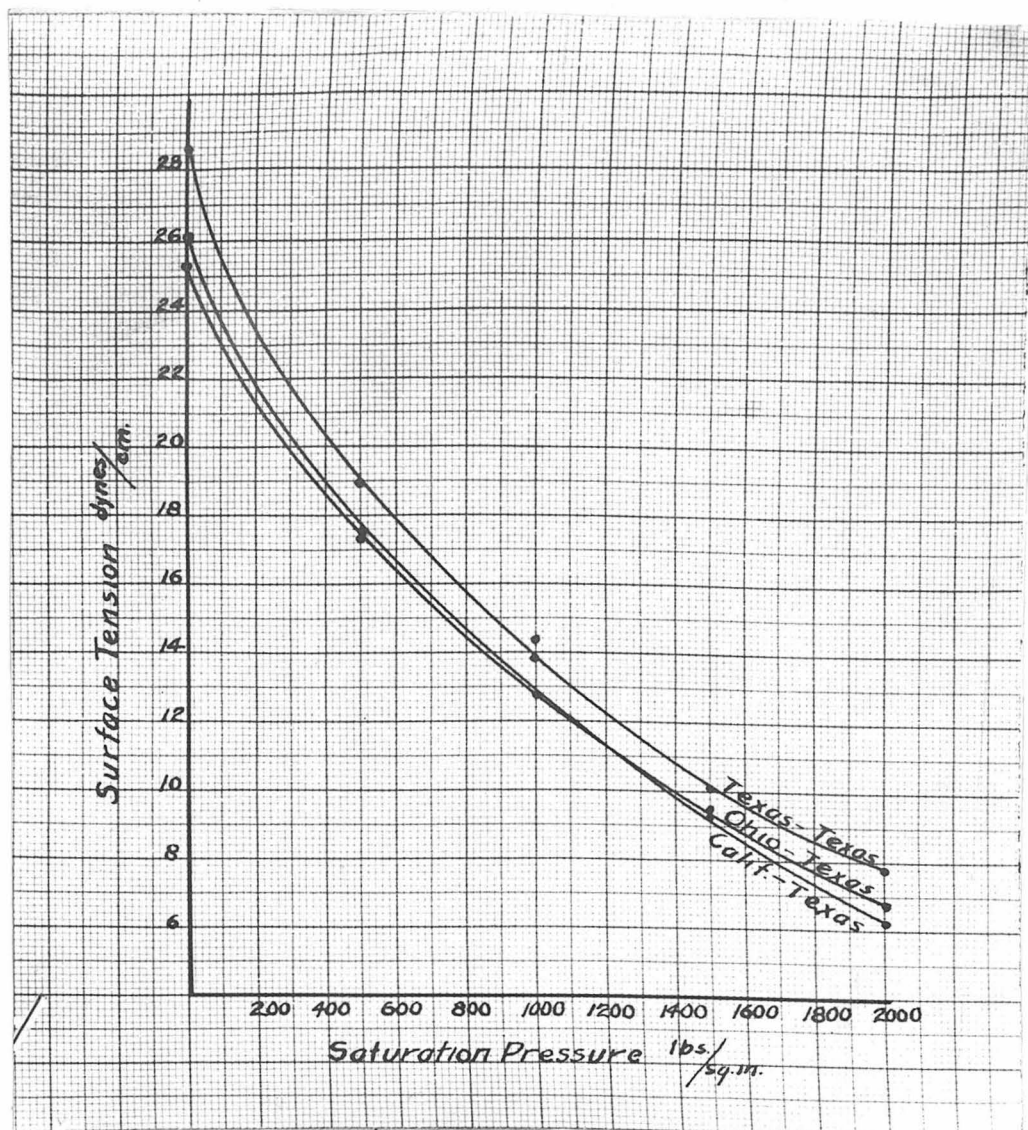sure for various oil-gas combinations.

Fig. 5. Curves showing surface tension
of oil as function of saturation
pressure for various oil-gas
combinations.

Seal Beach, California and the analysis is as follows:

Methane	87.83%
Ethane	4.52%
Propane	3.61%

Isobutane	0.62%
n – Butane	1.26%
Isopentane and higher	2.16%

Summary

Part I. <u>CATAPHORESIS IN ROTATING ELECTRIC FIELDS</u>

A new method of making cataphoresis measurements on colloid particles has been developed and tested. The method makes use of a rotating electric field which causes the particles to move in circles. In this way it is easily possible to test the effect of variable speed of the particle on the distribution of the diffuse electric double layer surrounding it. The results obtained indicate that this effect is negligible. Furthermore, it has been discovered that the mobility of the small particles (below 10^{-4} cm in diameter) fluctuates widely and this is made very evident to the eye by the fluctuations in the circular paths of the particles. The fluctuations are quite violent with particles as small as 10^{-6} cm in diameter. Considerable study of these variations has been made as well as an attempt to explain them qualitatively.

Part II. THE VARIATION IN THE SURFACE TENSION OF
GAS-SATURATED PETROLEUM WITH PRESSURE
OF SATURATION.

The surface tension of a number of samples of crude petroleum has been measured by the capillary rise

method, as a function of the amount of gas dissolved in the oil under pressure. Oils and natural gases are used which have been obtained from various fields throughout the country. The oils are saturated with the gases at various pressures up to 2000 pounds per square inch and curves given to show how the surface tension varies with the saturation pressure. The results show that in all cases curves of the same general type are obtained and at 2000 pounds pressure the surface tension for the natural oils and gases has fallen off to 15 to 40 per cent of its original value.

Acknowledgments