The Experimental Investications of the Gibbs's Theory of Surface-Concentration.

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THE EXPERIMENTAL INVESTIGATIONS OF THE GIBBS'S THEORY OF SURFACE-CONCENTRATION.

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I N T R O D U C T I O N.

Surface tension as exhibited in soap films has been known and studied for many years. The mere word "soap-bubbles" sounds childish and simple but in reality is far from it, for the subject of surface-energy or surface-tension has employed the minds of the world's geniuses almost in not entirely down to the present time. Among these may well be mentioned Rayleigh (Proc. Royal Soc. xlvii p281, 1890), Boys(Soap-bubbles and the Forces That Mould Them), Gibbs (Scientific Papers vol.1), and perhaps Freundlich (Kapillar Chemie). Needless to say there are scores of others that find the field of surface -tension a very profitable one.

The great pioneer in theoretical physics and chemistry of modern times, J. Willard Gibbs, in his memoir "Equilibrium of Heterogenous substances" considered the very subject of of surface films of solutions and deduced a theoretical law (Scientific Papers, vol. 1, p 365) connecting the bulk-concentration of a solution with the tension of the surface films. It is the object of this paper to present whatsoever experimental work has been done (including some by the author) that will apply towards a verification of this law.

T H E O R E T I C A L D I S C U S S I O N.

The abstract of Gibbs's work on this point is:-

Consider two homogeneous fluids that are in contact in a non-homogeneous film. Assume that the energy and entropy per unit mass extend homogenous quite up to the surface of discontinuity betwwen the fluids, this surface of discontinuity being approximately of the same nature as a geometrical surface. In the surface film there is an excess of entropy, energy, and each component of the system. The equilibrium as regards temperature and potentials is not affected by a surface of discontinuity. Then the complete variation of the energy of the surface is expressed by

$$de = \theta d\phi + gds + z_1 dn_1 + z_2 dn_2 + \text{- - - - -}$$

where e represents energy, θ temperature, ϕ entropy, g energy per unit surface or film or the surface tension, s area of film, n_1 , n_2 , - - - masses of the components in the surface,and z_1 , z_2 , - - - - the chemical potentials of the various components in the adjacent fluid masses. A better knowledge of this is shown by

$$e = \theta \phi + gs + n_1 z_1 + n_2 z_2 + \text{- - - - -}$$

Differentiating this, allowing everything to vary, and comparing with the former we have

$$dg = -\frac{\phi}{s} d\theta - \frac{n_1}{s} dz_1 - \frac{n_2}{s} dz_2 - \text{------}$$

Gibbs modified this and applied this to an actual case (Gibbs, Scientific Papers, vol. 1, p 235) of liquid mercury and water in a plane surface. Assume that the density of the mercury vapor on one side of the film is equal to that of the liquid mercury on the other. Then $\frac{n_1}{s} = o$, and when the temperature is kept constant we have

$$u = \frac{n2}{s} = - \frac{dg}{dz2} \quad .$$

This represents "the amount of water in the vicinity of the surface above that which there would be if the water vapor just reached the surface without change of density, -----". The only limitations upon this is that the temperature be constant and the surface plane. It might also be wise to add that the first equation and consequently the whole deduction is based upon a reversible cycle. With these conditions in view we have by the law of Dalton $dp_2 = c\, dz_2$, where c is the density of the water vapor. This gives

$$u = - c \frac{dg}{dp_2} \quad .$$

Applying the gas law $p = R\theta c$, we have $dp = R\theta dc$, giving

$$u = - \frac{c}{R\theta} \cdot \frac{dg}{dc}$$

Prof. W. B. Morton (Phil. Mag. April 1908, p 504) deduced a similar expression from independent considerations. It is quoted as follows:

Consider the equilibrium at a surface (say of a solid or liquid) in contact with a solution.

Let g = surface energy per unit of surface.

s = area of surface exposed to the solution.

m = mass of solute adsorbed at the surface of the solid in excess of that normally present.

U = total energy of the heterogeneous film per unit of surface.

The temperature is supposed to be constant. U can be increased:-

(1) by increasing the surface area, in which case the work required = gds

(2) by increasing the concentration of the solute in the interfacial layer. This is proportional to dm namely zdm, where z is the chemical potential of the solute.

Then $dU = gds + zdm$.

Therefore $d(U - zm) = gds - mdz$.

And since d(U - zm) is a complete differential, we have

$$-\left(\frac{dg}{dz}\right)_s = \left(\frac{dm}{ds}\right)_z$$

but $\frac{dm}{ds}$ = mass adsorbed per unit area of surface, i. e. = u;

Therefore $u = -\frac{dg}{dz}$

Now since

$$dz = R\,\theta\,\frac{dc}{c}$$

where c = the concentration of the solute in the bulk of the solution, it follows that

$$u = -\frac{c}{R\theta}\cdot\frac{dg}{dc}.$$

This is the same formula as is given above from Gibbs except that here c represents the bulk concentration of the solute, while above it is the density of the solution. This might be expected since the density of a solution is a function of the concentration. This equation is very important because it connects the quantity adsorbed, i. e. the excess per unit area of component (2) or the solute, with the bulk concentration and surface tension. To verify the law all we have to do is to measure u and determine $\frac{dg}{dc}$

PREVIOUS EXPERIMENTAL WORK.

THE WORK BY S. R. MILNER.

The first piece of work on record that can be applied

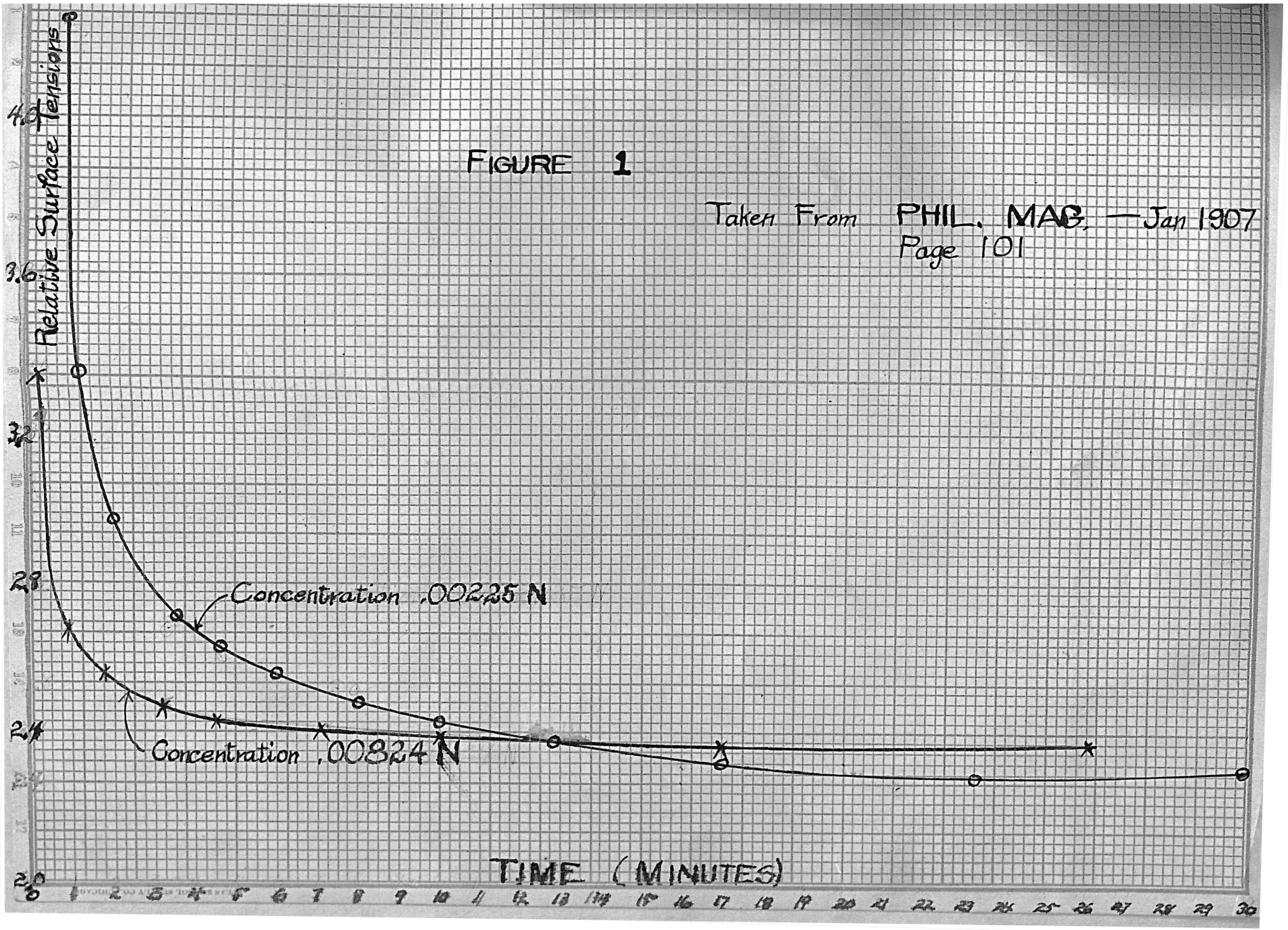

FIGURE 1

Taken From PHIL. MAG. — Jan 1907
Page 101

towards the Gibbs' law is that of S. R. Milner (Phil. Mag. Jan. 1907, p 96). He considered the question as to whether or not the surface film is a pellicle "composed of matter having a smaller capillary tension than that of water". This was suggested by Marangoni in 1871 and reference to it is made by Rayleigh in Proc. Royal Soc. xlvii p 281, 1890. Milner also followed up th suggestion of Rayleigh (above reference) and determined the effect of aging of films upon surface-energy or surface tension. Figure 1 is due to Milner. It is the graph of relative surface tensions with time for two concentrations of sodium oleate in water in contact with air. This shows that for such concentrations or this solute as are practical for this work the surface tensions do not approach their final values until after an interval of two to ten minutes, depending upon the concentrations. This is brought in here for future reference as this factor or time must be reckoned with in any experimental work. Some of his data on variations of tensions with concentrations seem to negate the existence of a surface excess when considered from one point of view, but in another perspective "renders it probable that an excess of considerable magnitude exists even in the dilutest solutions". The curves of time with tensions, in themselves, suggest that the excess is so large that the diffusion takes an appreciable time, even though the thickness of the film is as small as a number of the best determinations (Reinold and Rücker, Phil. Trans. clxxxiv p 505, 1893) seem to indicate.

Thus the theoretical work of Milner leaves the question

of a surface excess very much in doubt, but in his experimental work he actually proved its existence. His results were more qualitative than quantitative. The probable error surely is very large. The results are about ten times larger than those calculated from the formula $u = -\frac{c}{R\theta} \cdot \frac{dg}{dc}$. His own statements are about as follows:-

"The ultimate values of the surface tensions seem to be independent of the concentrations; this is contrary to the thermodynamic theory of the process." This discrepancy may be accounted for, partially at least, by two factors. Evidently the time factor is one, for the time allowed for diffusion of the oleate into the film was about two seconds, while it should have been about four hundred times this for the more concentrated solutions. This would keep down the rate of formation of the bubbles or foam , and would make a larger error in the stronger solutions than in the weaker ones. Thus the values of the surface excess are too small. The other factor is the excess solution carried out with the foam. Every film when existing in the form of foam has two surfaces exposed to the air, consequently it may be expected that the film has two surface layers, the thickness of each being the radius of [illegible] molecular attraction for the solution under consideration and also some excess solution between these surface layers that does not drain out, at least not until after some considerable time. Therefore from this quarter we may justly say that the volume of the foam as recorded is too small by an error per-

haps as large as fifty per cent. Whether this would cause an increase or a decrease in the variation of surface excess with concentration the writer has not decided definitely, but he believes the error would tend to increase any variation that might exist.

Since the thermodynamic theory is based upon a perfectly reversible process, we must conclude from the above considerations that the formation of the surface excess in sodium oleate solutions is an irreversible process. This conforms with the observed fact that the excess forms however dilute the solution may be. This will result in the condition that the film will become saturated in finite concentrations, when irreversibility will exist because of the precipitation of the oleate into another phase. This is supported by the follwing facts:-

(1) An insoluble scum, increasing with time, is formed on the surface of the oleate solutions.

(2) Large numbers of white flakes on films that have thinned considerable and then allowed to contract. Under these conditions the film would be super-saturated with oleate or the oleate would beprecipitated out in one form or another.

(3) The tension increases when the surface is increased; also, when the surface is diminished, it does not decrease but even tends to increase.

From these considerations it looks very probable that reversibility is lacking. If it is, the formula must be

deduced again with this condition changed accordingly, but before we demand such a thing rashly let us consider the remaining work on this subject.

THE WORK BY W. C. M. LEWIS.

The work of Lewis is novel in that it deals with liquid-liquid interfaces. In the first he uses a hydrocarbon oil in contact with aquous solutions of sodium glycocholate, congo red, and methyl orange. A series of tests were made to show that the oil was chemically inert towards the solute and the solution. The above solutes were chosen because they are soluble in water and lower the interfacial tension between water and oil. The molecular weight (used in connection with the value of R) was determined by the lowering of the freezing point of water and the raising of the boiling point of water and alcohol. That of sodium glycocholate was found to be 140. Phil.Mag..April 1908, p 505.

The object of the experiment was to form a large surface of the oil against the solution when a certain amount of the solute would be adsorber, thereby changing the bulk concentration of the original solution. This would necessitate an accurate knowledge of the concentration before and after the experiment so that the change and the mass adsorbed can be determined with the required degree of accuracy. The method adopted was to determine the surface tensions for the oil with various known concentrations. By interpolation from a curve from this data the concentration of any solution can

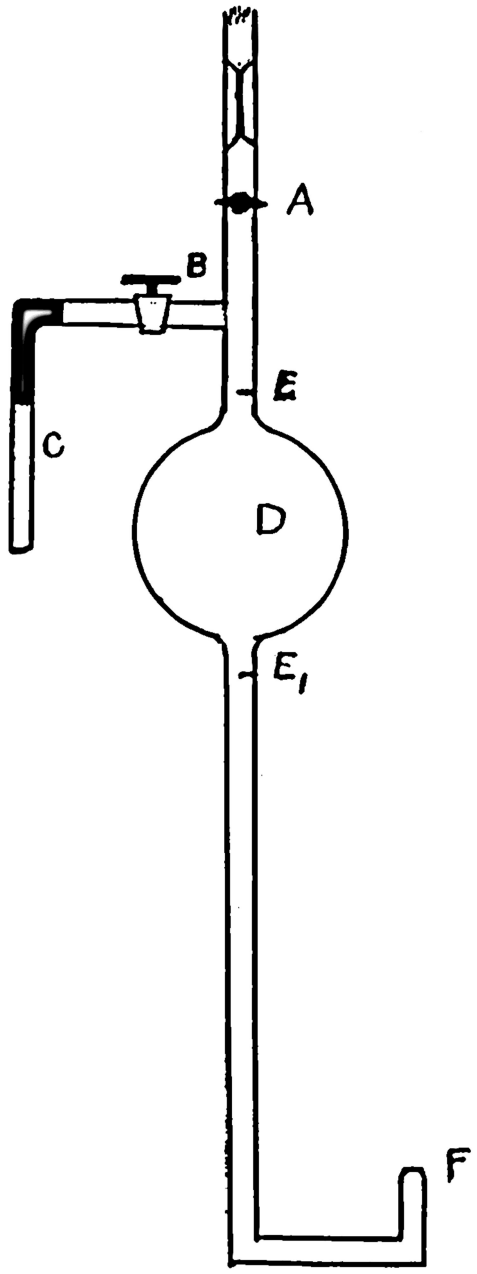

FIG. 2.

then be accurately determined after the surface tension of the solution has been determined. This proved to be a very sensitive method as the change of surface tension is very marked for a small change of concentration, especially in such weak solutions as are necessary for this work.

For determining the surface tensions the drop-pipette method was used. The apparatus is shown in fig. 2. By suction at C the bulb is filled through F to the point E. The aperture F is carefully wiped before using, and the pipette is placed in a fixed position relatively to the solution in all determinations. EF is about 3 cm. in length and the capacity of EE_1 about 45cc. In starting, the cock A is opened full the air being allowed to enter slowly through the capillary above. The bubbles or drops of oil form at intervals of 12 to 15 sec. and gradually rise through the solution which is a denser fluid. This is really a dynamic application of a static theory, but nevertheless the relative tensions as determined by the number of oil drops formed while the oil falls from E to E_1 is quite accurate. The tension is taken to be proportional to the weight of a drop. In this case the total volume and density are constant and the only remaining factor is the number of drops; hence, the number of drops gives relative tensions, the variation being inversely to the number. For our work, however, we must have absolute values. These can be obtained quite easily after we have one absolute value, say of the oil with pure water. Absolute values are possible with the drop-pipette. The theory and applications are found in Lewis, Phil. Mag. April 1908, p 508; Kohlrausch, Ann. d. Physik, vol. xx, p798, and vol. xxii; p 191;

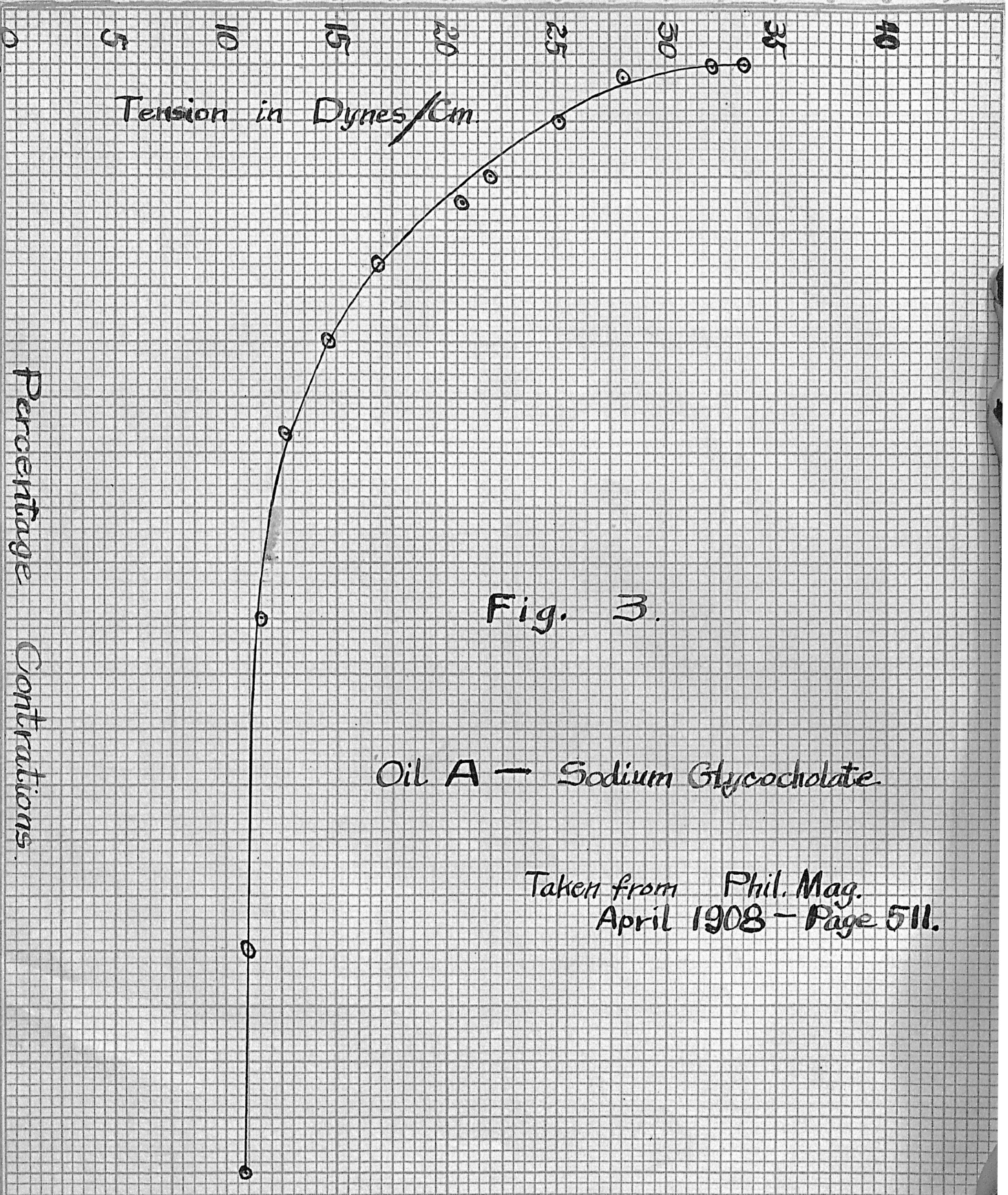

Fig. 3.

Oil A — Sodium Glycocholate.

Taken from Phil. Mag.
April 1908 — Page 511.

and Lohnstein, Ann. d. Physik, vol. xx, p 237, 606, and vol. xxi p 1030 (1906). Lewis used two oils which he called A and B. The absolute surface tensions of these oils against water are respectively 33.6 and 48 dynes /cm. The absolute tensions for the various concentrations were then determined by taking proportions of the one absolute value, these proportions being in each case the ratio of the drop number for pure water with that for the concentration under consideration. Fig. 3 gives the results of oil A for sodium glycocholate solutions; the curve for oil B is quite similar to that given in the accompaning figure.

MEASUREMENT OF THE ADSORPTION COEFFICIENT.

Lewis first determined the adsorption coefficient experimentally at a very curved surface by placing a small known quantity of oil in a shaker with about a half liter of solution and turning it with a motor for a number of hours. This formed an emulsion. With a microscope with a scale in the eyepiece the average diameter of the emulsion droplets was determined. From this was calculated the number of drops and the total surface. A drop number for tension was taken through the emulsion, assuming that the fine oil droplets had no effect on the pipette. "Justification of this is afforded by the concordance between the results obtained for the adsorption by this method and by an entirely different method to be described later." The volume of the oil was detremined by weighings, the density being known. The results of determinations with each oil are:

	Oil A	Oil B
Vol. of solution	500 cc	250 cc
Drop number before experiment	483	531
" " after "	459	507
Tensions before experiment	12.80 dynes/cm.	- -
" after "	13.44 " "	- -
Concentration before experiment	.318 %	.317 %
" after "	.295 %	.290 %
Fall in concentration	.023 %	.027 %
Mass adsorbed	(500cc) .115 gm.	(250cc) .067 gm.
Vol. of oil emulsified	.447 cc	.160 cc
Av. radius of droplet	.0000425 cm.	- - -
Total number drops formed	1.3×10^{12}	- - -
Total adsorbing surface	31 553 cm^2	11 058 cm^2.
u (odserved)	3.6×10^{-6} gm/cm^2	5.9×10^{-6}

Another determination with oil B with a solution the original concentration of which was about .2 % gave $u = -4.7 \times 10^{-6}$ gm./$cm.^2$, as the observed value, and with a calculated value of 5.5×10^{-8} gm./cm^2. This gives the observed value about 85 times the calculated value.

A study of the probable error does not take care of this great discrepancy, but places most of the doubt on errors in the determination of the average radius of the droplets in the emulsion. Taking account of this it is found that the method is too insensitive to show trustworthy values for u corresponding to solutions of concentrations of .2 % and .317 %, as the values obtained differ by less than the experimental error.

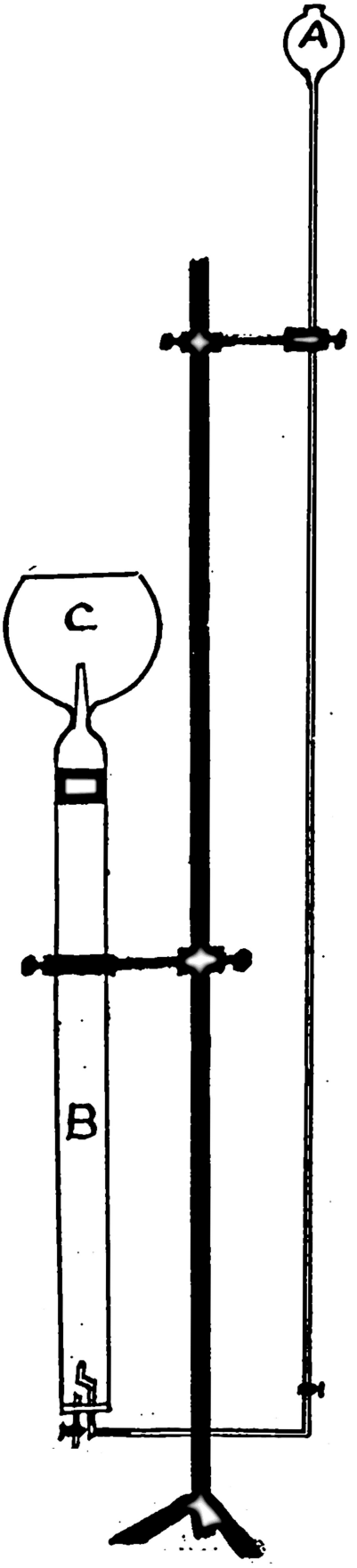

FIG. 4

To overcome this large experimental error, and to work with a surface as nearly plane as possible, and because of the large discrepancy between the observed and calculated results, a new method was necessary. The new form of apparatus is shown in Fig. 4. It is about 150 cm. high, the bulb A holding 168 cc, B and C about a liter, the diameter being about 1 cm. B and C are filled with the solution upon which the determination is to be made, and A is filled with the oil to be used. A pinch-cock between A and B lets the oil flow into B at the desired rate. The oil is broken up into drops which rise, carrying with them an excess of the solute,which has adsorbed on their surface,. through the constriction into C. Here they coalesce, returning the excess of the surface film to the solution above the constriction, thereby increasing the concentration. The constriction is to prevent diffusion. When A is empty the rubber connection near the top of B is pinched and the solution in B is drained off below. The concentration of this is then determined by a drop number with the pipette, in connection with the curve of fig. 3. Two examples are given for oil B with a solution of .25 % concentration of sodium glycocholate.

	I st	2 nd
Total vol. oil used	168 cc	504 cc
Total time of dropping	7940 sec	20520 sec
Total number of drops	9925	- - -
Total adsorbing area	3192 cm^2	7414 cm^2
Concentration before experiment	.25 %	.25 %
" after "	.243 %	.243 %

Change in concentration	.007 %	- -
Total mass adsorbed (from 250 cc).	.0175 gm.	.022 gm
u (observed)	5.4×10^{-6} gm/cm^2	3.1×10^{-6} gm/cm^2
u (calculated)		3.6×10^{-8} gm/cm^2.

These results are of about the same order of magnitude as those derived from the emulsion method. The degree of planeness is close to that desired; the size of the drops is about the same as of those used in the pipette in carrying out the measurements of $\frac{dr}{dc}$, hence any error from this point will enter in both the orserved and the calculated results to about the same extent. The results from the two methods seem to indicate that the curvature of the surface has very little or no effect, unless the error from this source is masked by some greater error. Lewis compares the conditions of his experiment with those of Gibbs's deduction as follows:-

(1) a. "The adsorbing surface is plane."

b."It may be readily assumed that adsorption measurements made at the surfaces of oil drops of sensible magnitude approximate exceedingly closely to those at a plane surface."

(2) a. "The solvent is to show no concentration at the interface."

b. "This was simply assumed to be the caes, no means of testing its validity having as yet suggested itself."

(3) a. "For the particular equation used in this paper, there is supposed to be only one component

capable of being adsorbed."

b."This follows from the general experimental conditions, the solute, the sodium glycocholate , being the only substance whose adsorption is measured."

(4) a. "This composent and the solvent in which it is dissolved are supposed to form a single phase.

b."This assumption is implied from the actual example of surface concentration given by Gibbs as exemplifying his theory, viz.:- A mixture of mercury- and water-vapors meeting at a liquid mercury surface, the water being the component which suffers surface-concentration. Mixtures of vapors are essentially mono-phase systems; and the question is, are we dealing with a mono-phase system in the case of aqueous solution of sodium glycocholate? The evidence given by its osmotic behavior in raising the boiling points of water and alcohol and lowering the freezing point of water, is strongly in favor of its being a true electrolyte, and hence of its solution being a monephase system.

Lewis also did some work with dyestuffs. Briefly, his results are:-

Substance	Congo red	Methyl orange
Method	emulsion	emulsion
u (observed)	3.7×10^{-6} gm/cm^2	5.5×10^{-6} gm/cm^2
u (calculated)	2.3×10^{-7} " "	1.2×10^{-7} " "

He expresses the situation well by:- " We have here a further repetition of the observed anomaly." He has no suggestions to offer but works some out in his second and third articles to be taken up next.

As it is the writer's intentions to mention merely the important principles and some of the results he will omit many of the minor details that have been included so far in this paper.

In his second article (Phil. Mag. April 1909) Lewis considered a large number of electrolytes and some non-electrolytes. Most electrolytes raise the air-water tensions but of about twenty examined here all lowered the oil-water tensions. This lowering of the tension means an excess concentration in the surface film. The method of adsorption used was the"large-drop" method. He determined the concentrations chemically for the cations and the anions. The results are:-

Substance	Adsp. cation gm per $cm.^2$		Adsp. anion gm per $cm.^2$	
	Observed	Calculated	Observed	Calculated
Silver Nitrate	2.5×10^{-8}	4.5×10^{-9}	- - -	2.3×10^{-9}
K Cl	5 " "	1.7 " "	10^{-9}	1.6 " "
$Ba Cl_2$	- - -	3 " "	10^{-8}	1.6 " "
$Cu Cl_2$	3.5 " "	2 " "	2×10^{-8}	2 " "

There is a slight selective adsorption, the cation more than the anion.

Among the non-electrolytes considered was saponin. This has always shown an anomalous behavior in contact with air.

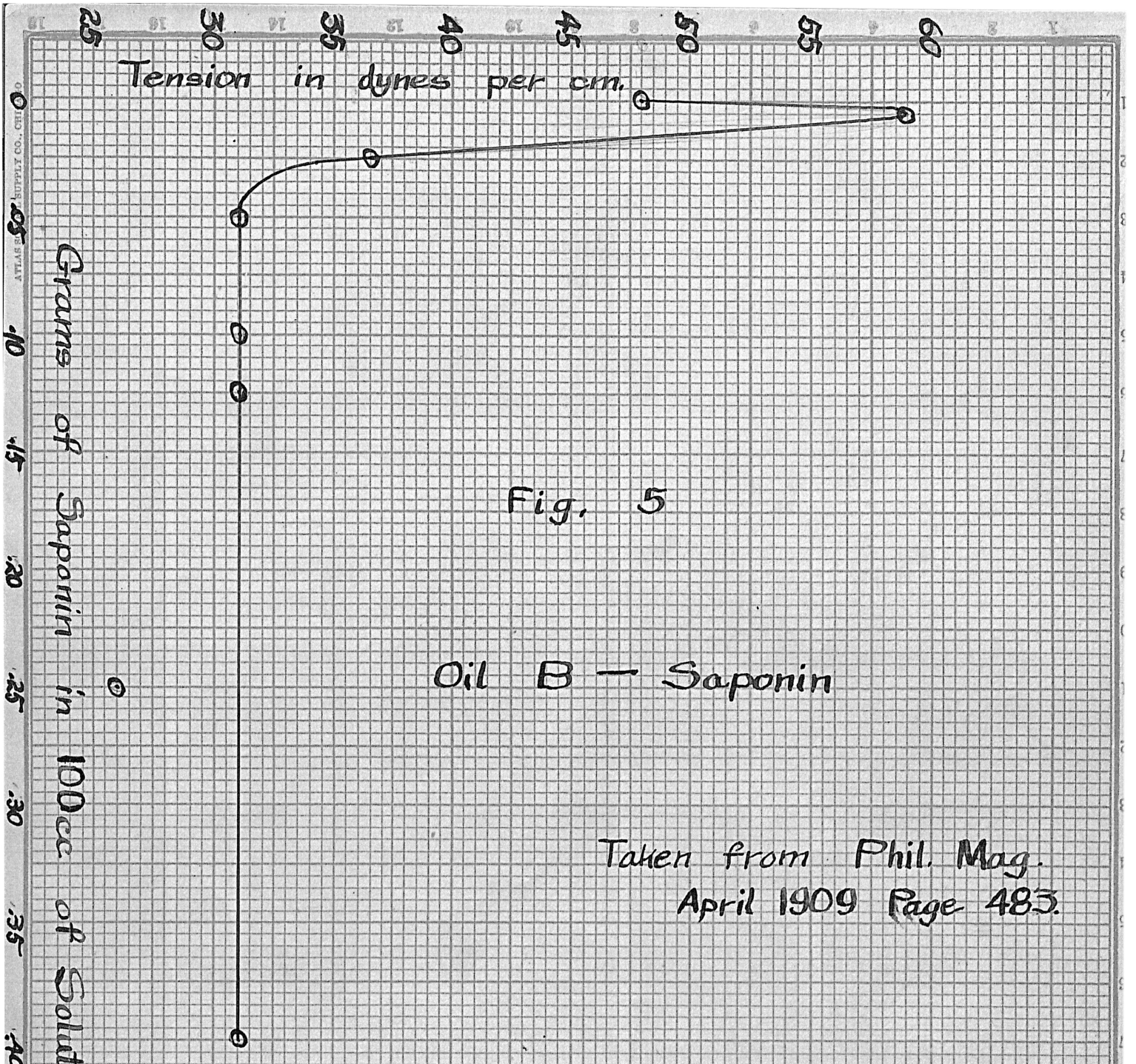

Fig. 5

Oil B — Saponin

Taken from Phil. Mag.
April 1909 Page 483.

It rooms easily showing a marked decrease of surface tension. (S. A. Shorter, Phil. Mag. vol xi, p 317, 1906). The oil-water interfacial tensions are plotted with concentrations in fig. 5. Note the rise at first before the fall of surface tension. Reference was made to a pellicle in connection with surface tension. Air bubbles from sopanin solution appear to gelatinize "so that when once formed they show a crinkled appearance on contraction." Lewis states (l.c. p482), "It seems probable that the gelatinization effects which have been observed at the air surface are also effective at the oil interface. Experiments were carried out to test whether the substance was soluble in oil. It was found to be insoluble." This question of gelatinization will be considered again after more data is presented.

Caffeine, a substance that appeared good from preliminary examinations, was also examined, the emulsion method being used. The results, which are very doubtful, are:-

No.	Drop number before ex.	after ex.	area
1	160	160, 160¼	87130 cm^2
2	160, 160¼	160⅛, 160¼.	127310 "

The corresponding surfaces would have caused a change of 4-5 drops, a number easily determined, if done in connection with sodium glycocholate, congo red, or methyl orange. This shows that caffeine is adsorbed very much less that these other substances. The results of the second determination when worked out give $u = 3.7 \times 10^{-8}$ gm/ cm^2 while the calculated value is 2.4×10^{-8} gm/cm^2. In trying to get a more trustworthy result

by increasing the adsorbing surface it was found that the limit of the method had been reached as 500 cc of solution would not emulsify more than about 2 cc of oil. The above results for caffeine are far from trustworthy, yet they are very close to the calculated value. Hence we can draw the following conclusions

(1) Caffeine in aqueous solution in all probability obeys Gibbs's law quantitatively.

(2) Ordinary inorganic salts—— Potassium chloride, Silver nitrate, Barium chloride, and Copper chloride—— are adsorbed in quantities which are of the same order as the Gibbs's calculated effect, though the experimental values are in all cases greater than the calculated. Caustic soda shows a more marked discrepancy between calculated and observed values.

(3) Complex organic salts——Sodium glycocholate , Sodium oleate, Congo red, and Methyl orange—— show a very large discrepancy between observed and calculated values.

The next question is, "what causes the discrepancies?" Milner (Phil.Mag. Jan. 1907, p98) used the van't Hoff factor "i" to take account of the dissociation. Lewis in effect did this by using the value of R as the general gas constant divided by the molecular weight of the substance in aqueous solution. Another possible cause is the false assumption that the water suffers no surface density change. Evidence of this is found in the phenomenon of the evolution of heat when water is poured upon finely divided powders of silica, quartz, glass,

etc, where chemical action is excluded.

Another anomalous factor to be considered is the surface concentration. The average surface concentration of sodium glycocholate is 37 % while the solubility in bulk solution is 3.9 %. Likewise the corresponding concentrations of methyl orange are 39 % and .078 %. The substances therefore which have shown very great discrepancies as regards Gibbs's theory are those whose surface concentrations greatly exceed their solubility in the solvent. Other substances examined —— Caffeine and the inorganic salts, in no case exceed the ordinary solubility; also, the adsorption of these substances is in very much closer agreement with the Gibbs's theory.

The only remaining factor for explaining the discrepancy is "some irreversible phenomenon of the nature of gelatinization upon the oil surface." In agreement with this is the excess of the surface concentrations above the accepted values of solubility. Saponin is said to be perfectly miscible with water. Even though this cannot be true, the permanence of the tensions at comparatively dilute solutions cannot be explained by the solubility having been reached. Potts, like Milner, has shown a discrepancy for sodium oleate very similar to that of sodium glycocholate. Freundlich and Losev (Zeit. Phys. Chem. vol. lix, p 284, 1907) found an irreversible process in connection with certain dyestuffs and charcoal. An amorphous precipitate, insoluble in water, was formed on the surface of the charcoal. Milner found an insoluble scum on sodium oleate solutions. From all this we very probably justified in saying

that these discrepancies are due to gelatinization.

As stated above there seems to be a slight selective adsorption of the cation. In this connection there is some doubt because of the large experimental errors in the chemical determinations of the concentrations. Local electrolysis has been assigned as the probable cause. In this case the heterogeneous layer separating the solution and the oil acts as the "electrolytic medium." This must result from a potential-difference between the oil and the water. Lewis reports that he investigated this question with apparatus similar to that described by Burton in Phil. Mag. 11 p 434, 1906. For the oil he had been using in the adsorption experimentsin connection with water he found a potential difference of .15 volt, the oil being negative. This would naturally lead one to expect that the cation would be adsorbed selectively.

In his third article (Zeit. f. phys. Chemie, B, lxxiii, S 129, May 1910) Lewis reported some work done with a few marked changes although the basic principles are the same as those he had been using. He used a solution of 20% ethyl-alcohol and 80% water as a new solvent, and mercury as a new adsorbent. The changes necessary in the apparatus are practically accounted for by something very little short of invertion.

Analin was invostigated, the mean of several drop numbers being used in each case. Three determinations give

(1) $u = 2.1 \times 10^{-8}$ gm/cm^2.

(2.) $u = 3.2 \times 10^{-8}$ gm/cm^2

(3) $u = 2.7 \times 10^{-8}$ gm/cm^2,

as opposed to the calculated value of

$u = 1.0 \times 10^{-8}$ gm/cm^2.

Evidently this is practically in agreement with the Gibbs's law.

In his former work with caffeine Lewis mentioned that perhaps mercury could be used to a better advantage than oil. He surely had in mind the high surface tension between mercury and water. He obtained with mercury a theoretical value of $u = 2.2 \times 10^{-8}$ but was unable to get an experimental value.

Sodium glycocholate was studied again, but in connection with mercury. he obtained an experimental value of $u = 3.7 \times 10^{-7}$ as opposed to the theoretical value of 1.5×10^{-8}? In this case the observed value is about 25 times the calculated value. This is not as large as it was with oil but the difference is very great even yet.

In trying to find the adsorption of a mercury salt—— $HgSO_4$ —— with mercury he found trouble because of electro-capillary adsorption. The theory of this is:- Given a surface S, a tension g, the electrical charge q, the potential difference v, and U the total energy of the surface layer. U can be changed by (1) a change of the surface; (2) a change of the electrical charge. Then

$$dU = gds + vdq.$$

or $$d(U-vq) = gds-qdv$$

Since $d(U-vq)$ is a complete differential then

$$\left(\frac{dg}{dv}\right)_s = -\left(\frac{dq}{ds}\right)_v$$

If now the charges on the "plates" of the condersor of ions are

changed, the change is expressed by

$$dv = \frac{dm_1}{a} \qquad \text{or} \qquad dv = \frac{dm_2}{b}$$

where a and b are the electrical equivalents of the cations and the anions, and dm_1 and dm_2 are the corresponding values or quantities from which the charge dq is taken. If we substitute these in the above expression we have:

$$\frac{dm_1}{ds} = -\, a \frac{dg}{dv} \qquad \frac{dm_2}{ds} = -\, b \frac{dg}{dv} \,,$$

but " $= u_{(cation)}$ and " $= u_{(anion)}$.

Therefore $u_c \mp u_a = -(a \mp b)\frac{dg}{dv}$.

This electrocapillarity will be in addition to the adsorption of the salt, so we have as the complete formula, if $u_{(salt)} = u_s$

$$u_s \mp u_c \mp u_a = -\left/ \frac{c}{RT} \cdot \frac{dg}{dc} \mp (a \mp b)\frac{dg}{dv} \right/$$

The theoretical value of u_s alone for $HgSO_4$ is 2.7×10^{-7} . From Freundlich, Kapillarchemie, Seite 185, the value of $\frac{dg}{dv}$ is found to be 3.86×10^{4} when expressed in electrostatic units. This gives $u_c \mp u_a = 3 \times 10^{-8}$. This value is practically the same as that calculated by a different method by Warburg (Wied. Ann. 41, 11, 1890) . So far as is known no complete value for $u_s \mp u_c \mp u_a$ is given for $HgSO_4$.

THE WORK BY F. G. DONNAN AND J. T. BARKER.

The work of Donnan and Barker (Proc. Royal Soc. Series A, vol. 85, p 557) was done with air in connection with aqueous solutions of nonylic acid and saponin. They used practically the same methods as Lewis used, including the drop-pipette for the determination of concentrations, and the bubble method for the formation of the adsorbing area. Their chief difficulty was convection of the solution through all parts of the apparatus,

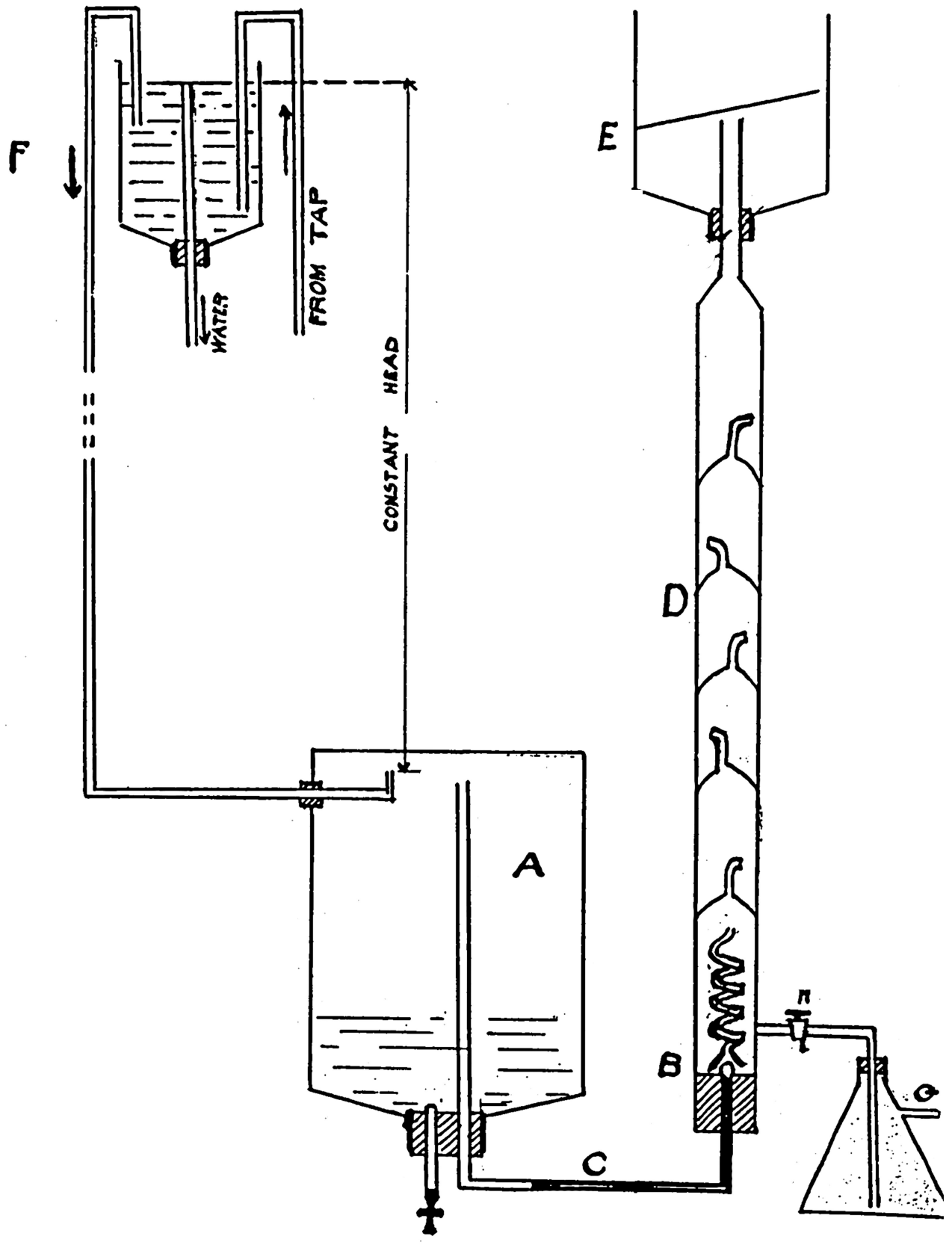

FIG 6

thereby preventing the desired localization of the decrease of the concentration. They broke up the streaming motion of the liquid into a series of localized eddies. The form of apparatus finally employed is shown in fig. 6. The apparatus was filled by the application of pressure at G which forced the solution from the flask through H into the fractionated column. Air at constant pressure was delivered from A through the capillary C and broken up into bubbles at B. These passed through the coil in about 15 sec. and then travelled more or less rapidly through the sections of the column to the surface where the bubbles broke returning the excess to the bulk of the solution.

The volume of air delivered was determined by the difference of weights of water before and after the experiment. This was done as follows:- Before starting the experiment all water was drained from A and the pressure regulated as desired. Then the experiment was run. The water in A at the end of the experiment was drained off and weighed. Then the water aws allowed to come to equilibrium under the same pressure as in the experiment. This was drained off and weighed. The difference gave the volume of air consumed at the hydrostatic pressure in A in addition to the atmospheric pressure. It was necessary to correct for half of the hydrostatic pressure in the column D because of the expansion of the bubbles on rising. This expansion if neglected would have caused an error of 4 %.

Possible errors that were obviated were adsorption by the stopper at the lower end of D and vaporization. The stopper used was a paraffined cork. This was found to remove nonylic acid from a fresh solution, but reached an equilibrium for any one

concentration after about 24 hours contact. The corks were always saturated before being used. The question of vaporization was investigated by bubbling air through a blank experiment for about 24 hours. The results are:

Concentration	Drop number before	Drop number after
.00243 %	349	348
.005	410.4	410.1
.00806	482	481

At first the apparatus was water-jacketed to prevent changes of temperature. This was thought necessary to prevent expansion of the glass tube thereby returning some of the concentrated solution into the weakened solution, and also because the surface tension is a function of the temperature. Parallel experiments showed that this precaution was unnecessary with the present degree of sensitiveness of the apparatus. The drop-pipette, however, was water-jacketed and carefully shielded from all vibrations and air currents because an error of a fraction of a drop in the drop number was quite large as the total effect observed was a difference of about 4 drops in a total of about 350 to 450 drops.

A factor of such great importance that if neglected would render all results worthless is the spped of dropping from the pipette. For the nonylic acid they were capable to keep the rate of dropping at 8.3 drops per minute, or so close to this that the results could be duplicated to a fraction of a drop. For the saponin,which had the high molecular weight of 1260, it was found that the drop number varied greatly with the speed of dropping; consequently, it was necessary to obtain

the drop number of each solution as a function of the speed of dropping, and then interpolate for a definite slow speed. This variation was supposed to be due to the slow diffusion from the weak solution into the surface layer of high concentration. For the saponin two curves for the variation of surface tension with concentration were made. One was made with the tensions given by the drop numbers obtained when the total time of emptying the pipette was constant, being 50 minutes. These results are plotted in curve I (of a certain figure not reproduced in this paper). The other curve, No. II, (also not reproduced here) was obtained from the drop numbers given by a constant speed of dropping.

The speed of the formation of the air bubbles in the adsorption tube D had no noticeable effect.

On the whole the process of computing the results is the same as that given for the work of Lewis; therefore, only the various means of the results will be given here together with the calculated values. Because of some doubt as to what value to use for the van't Hoff factor "i" the results are given for both values of 1 and 2; also, since their curve of variation of tension with concentration does not agree perfectly with that of Forch (Wied. Ann. vol. 68, p 801, 1899), the values are computed from each curve. It must be born in mind that the temperature at which Forch worked is not the same as that at which Donnan and Barker worked; therefore, the results of the latter are probable more reliable for this purpose than those of Forch. The comparison is:

Concentration	u x 10^7 observed	u x 10^7 calculated From curve of Forch (18^0)		From curve of D. & B. (16.5^0)	
		1 = 1	1 = 2	1 = 1	1 = 2
0.00243	0.95	0.58	0.29	0.55	0.26
0.00500	1.52	1.23	0.61	1.14	0.57
0.00759	1.09	1.58	0.79	1.26	0.63
0.00806	0.915	1.63	0.81	- -	- -

The observed values when plotted with concentration show a maximum near the concentration of 0.00500. The calculated values increase with the concentration and do not show a maximum. The observed and calculated values agree as to order of magnitude. The agreement for 1 = 2 is the better at high concentrations. "Considering the difficulty of measuring such small changes or concentration in the extremely dilute solutions employed, the agreement must be regarded as affording a verification of Gibbs' fundamental equation."

In the case of saponin three determinations were made for the one concentration of 0.0072 %. They are given together with the calculated values derived from the two curves', "1" being used as 1,

u x 10^7 observed gm/cm^2	u x 10^7 calculated $\frac{dg}{dc}$ from curve I	$\frac{dg}{dc}$ from curve II
5.2	1.36	1.60
2.6	"	"
-3.1	"	"
Mean 3.6	"	"

The comment of Donnan and Barker is The observed value

is about double the calculated value, but, considering the difficulties and uncertainties of the determinations, the agreement is not unsatisfactory. It would appear, therefore, that no irreversible "gelatinisation" occurs in the surface-layer of an aqueous saponine solution, at all events in the case of moderately-fresh solutions. Possibly the "gelatinous skins" which may form on standing are due to secondary causes, or at all events to slow irreversible effects."

THE WORK BY THE AUTHOR.

The author has done some towards a verification of the Gibbs's law. H considered the proposition from the standpoint of cell action; i.e., can the action of the living cell in any way be connected with the phenomenon of surface concentration? He was unable to find definitely the chemical compounds that go to make up the cell and the body fluids, so he attacked the problem of aqueous solutions in contact with their vapors, or a definite mixture of the vapors with some air.

The osmotic effects were first made the basis of consideration. If a gram equivalent of a substance be dissolved in 22.4 liters of water the vapor pressure of the solution differs from that of the pure water by 1 atmosphere. Is this pressure change due to the bulk concentration of the solution or to the concentration of the surface layer between the solution and its vapor? If due to the surface concentration, this principle can be used to measure the surface concentration. It was investigated by means of the apparatus shown in fig. 7. A is a U-tube a little larger than the dimensions shown . It was closed by rubber stoppers pierced by small glass tubes. D is a

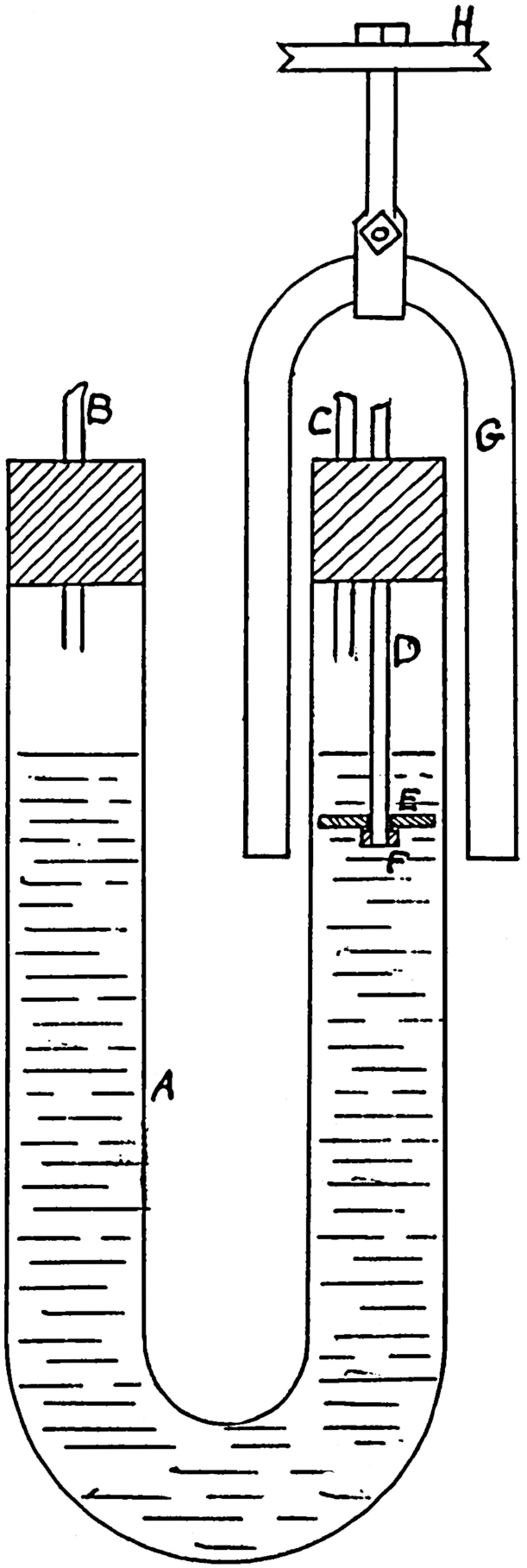

FIG. 7

small iron rod upon which is placed E a small soft iron bar, that is free to turn, and F a small metal disc shrunk on the end of D. G is a horse-shoe magnet turned by an electric motor by means of the pulley H. The bearing between H and G is omitted. The bar E assumes a position longitudinally between the poles of the magnet, and follows the magnet around when it is turned. The space in both arms of the tube was to be filled with only the vapor of the solution. This condition was realized by boiling the solution to such an extent that the air had all been carried out with the vapor. While still hot a flame was applied to the small glass tubes B and C; these were drawn out and sealed. The quantity of solution used was such as would leave the surface about 5 mm. above the bar E, the turning of which was to prevent the formation of the surface excess in this arm of the U-tube. In the other arm, which was quiet, the surface excess could reach a maximum. In this case the concentration in the film being greater in the arm B than C, there would be different vapor pressures in the two arms. If the surface concentration were less than the bulk concentration, as is the case with most inorganic salts, the difference of vapor pressures would be in the reverse direction from that set up in the case of a surface-excess. In this manner methyl orange was tested. The magnet was turned at a speed of about 50 revolutions per minute. As determined visually by the motion of the surface, the bar E stirred the solution quite well. After being stirred for about an hour there was no visible effect of one surface being depressed and the other raised as a result of the difference of the vapor

pressures in the two arms of the tubes. For fear that some air had not been eliminated from one or both arms, it was opened, cleaned, and tried again with another specimen of the same solution. No effect was observed. It may be that the right concentration or the right kind of a solute was used but the method was abandoned and at present we are forced to conclude:- The vapor pressure of a solution depends upon the bulk concentration and not upon the concentration of the surface layer between the solution and its vapor.

A second method that offered a little hope in solving this problem was to connect, if possible, the color of a solution with the reflected light. The author hoped to find some spectral line absorbed by reflection. For this purpose copper sulphate and methyl orange were compared. This choice was made because of the strong colors of their respective solutions, that of copper sulphate being a blue while that of methyl orange is a red tinged with yellow. The analysis of the light was made by a high power spectroscope, consisting of two trains of five prisms each. The light was the direct image of the sun. This was reflected on the solutions by a double mirror siderostat. The solutions were interchanged time and again but no lines in the visible spectrum were absorbed by either so far as the author was able to observe. There also seemed to be no flutings or no bands that were partially absorbed . As the colors of the solutions are within the visible spectrum it is perfectly useless to carry this examination the limits of the visible spectrum. Hence, eliminating

polarization, the light coming from a solution is in no way affected by the color of the solution.

The third undertaking of the author was to attack the same problem that Donnan and Barker had undertaken; i. e. adsorption at an air-water interface. He had started this before seeing the article published by these two Englishmen, and therefore had to go through the pioneer work for himself. He tried the upright tube about a meter long with a "trap" near the top very much like that first used by Lewis. After wasting considerable time, having got no results, neither positive or negative, he came to the conclusion that the effect was not observed with that form of apparatus because of one or all of three reasons.

(1) The high velocity acquired by the bubbles dragged the film or excess away as fast as it was formed.

(2) The aperture leading from the collecting chamber to the adsorption chamber was too large, allowing the enriched solution to diffuse out so rapidly that no appreciable excess could be accumulated.

(3) Streaming effects of the solution as a result of the high velocity of the bubbles caused convection throughout the whole apparatus.

He was taking steps to overcome these when he saw the article by Donnan and Barker. This admirable article confirmed one or all of the above conclusions and also furnished a remedy. The idea of streaming was especially confirmed. As stated before in this paper they overcame this by breaking it up into a series

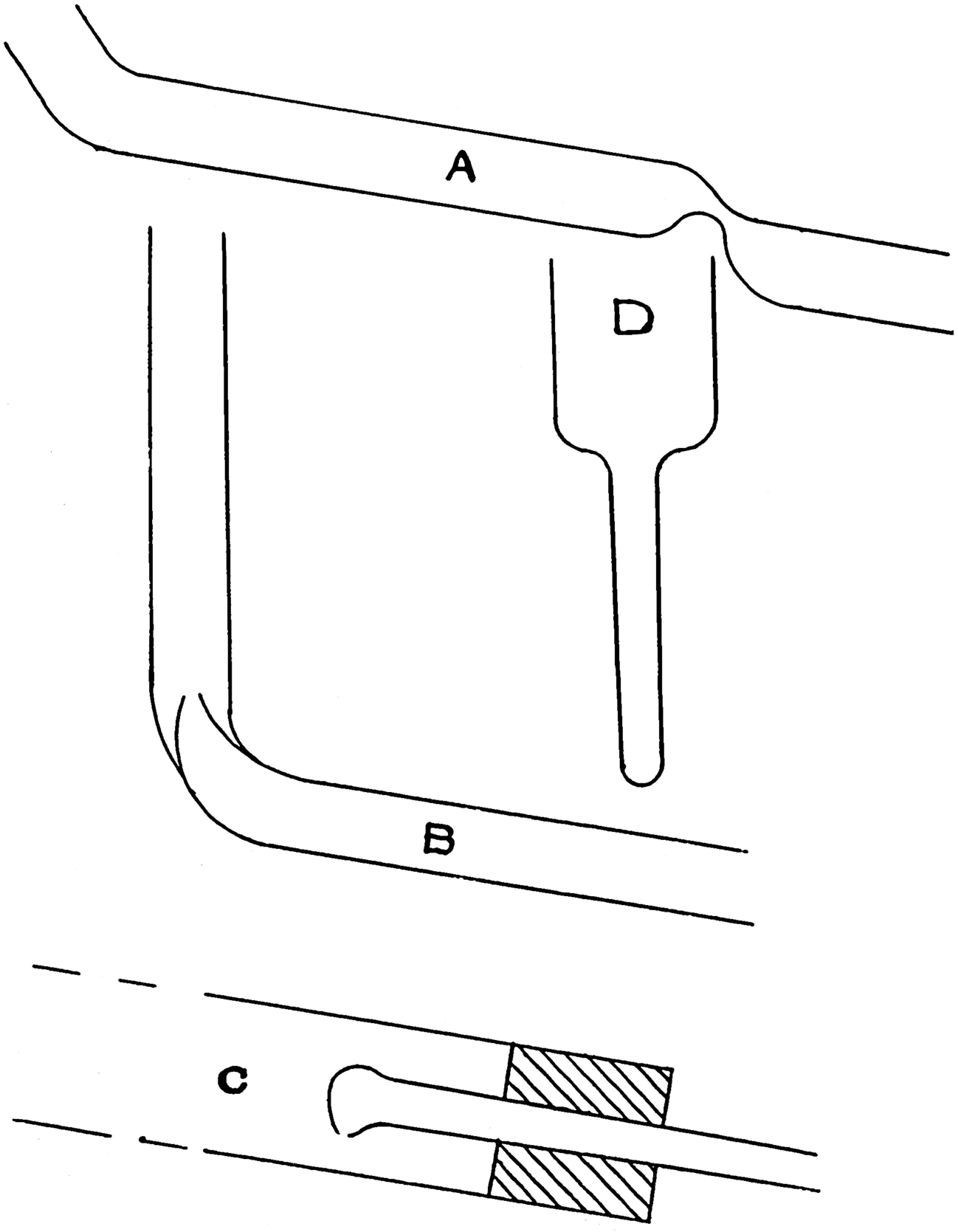

FIG. 8

of local eddies. The author fell upon a method of reducing this velocity to a minimum by inclining the straight tube so close to the horizontal that the bubbles would merely creep along. In fact, it is possible to get the proper combination of all the apparatus that four or five minutes are consumed for the bubbles to travel the length of the 120 cm. tube; when every thing is properly adjusted the bubbles come with such perfect regularity that they do not join before they reach the top. The first form of inclined tubes is shown in fig. 8,B. The upright part was about 10 cm. long, and the inclined part about 120 cm.; the diameter was 1 cm. In the use of this it was noticed that the bubbles acquired considerable velocity in the upright part. To overcome this and to obviate the welding of the glass joint, another form was designed. This is shown in fig. 8,A. It surely had all the advantages of the other form unless the drawn point in B helped to keep down convection. In spite of the good appearance of A it failed to produce results while B did. The solution above the trap was used a given surface would change the concentration of a small quantity of solution very much more than that of a large quantity. The collecting chamber was calibrated by weighing the tube filled with water up to scratches on the tube. The volume was estimated between scratches.

The jet is another piece that was improved upon. Donnan and Barker sealed a piece of large tubing on the end of a capillary. This large tubing was drawn into a sphere and a

hole made directly opposite the capillary. They expressed the necessity to keep the solution from getting into this jet as it would set up a high capillary pressure. The author made a jet as shown in fig.3,C; this is magnified two diameters. This was made from large tubing only, and had the virtue of being able to rid itself of any of the solution that may get into it. By having the walls of the orifice thin, the bubbles broke off evenly and were under perfect control. To prevent the air too rapid motion of the air into the jet, it was passed through a fine capillary —— thermometer —— tube.

Still another point for consideration is in regard to the kind of solutes used. The author made a bold step in undertaking to use volatile substances. These were carefully avoided by all predecessors. The appliance by which this was made possible was a saturator for the air before it entered the jet. It was saturated at the same concentration as was under consideration in the rest of the apparatus. This was done by filling a bottle almost full of the desired solution; it was then closed by a paraffined cork pierced by two pieces of glass tubing. One piece was very much longer than the other. The air was passed through the longer tube to the bottom of the solution and allowed to bubble up to the surface, from which place it passed on to the jet.

Paraffined corks were used without question throughout the apparatus. They were not questioned because Donnan and Barker

found them sufficient after they had soaked in the desired concentrated solution for about a day. The efficiency of the saturator was questioned but not tested for lack of time. Several results seem to show a slight negative effect of about the same quantity. This might have been caused by other things, however. If this negative result is real, it surely is due to the poor efficiency of the saturator or vaporization at the top of the collecting chamber. This vaporization was prevented as much as possible by stopping the top of the tube with a paraffined cork leaving it loose enough for the air to escape after the bubbles broke.

The concentrations were determined by surface tensions and curves. The tensions were obtained by the capillary method, this being necessary in order to use the small volume of the solution available. At first a small test tube was used as the containing vessle, but because the capillary tube was so large as compared with the test tube, it was very difficult to get the surface level. To overcome this by increasing the surface and yet allow a depth that would permit a correct adjustment of the capillary the form shown in fig.8,D was adopted. This was very satisfactory. The only thing recorded was the height as the diameter of the capillary was aliminated by bringing the meniscus within the tube to approximately the same place. Between every reading the capillary was adjusted, always making the last motion such that the meniscus fell. It was cleaned after two readings by washing in a saturated solution of sodium hydroxid, water, sulphuric acid and potassium bichromate, and water again, and

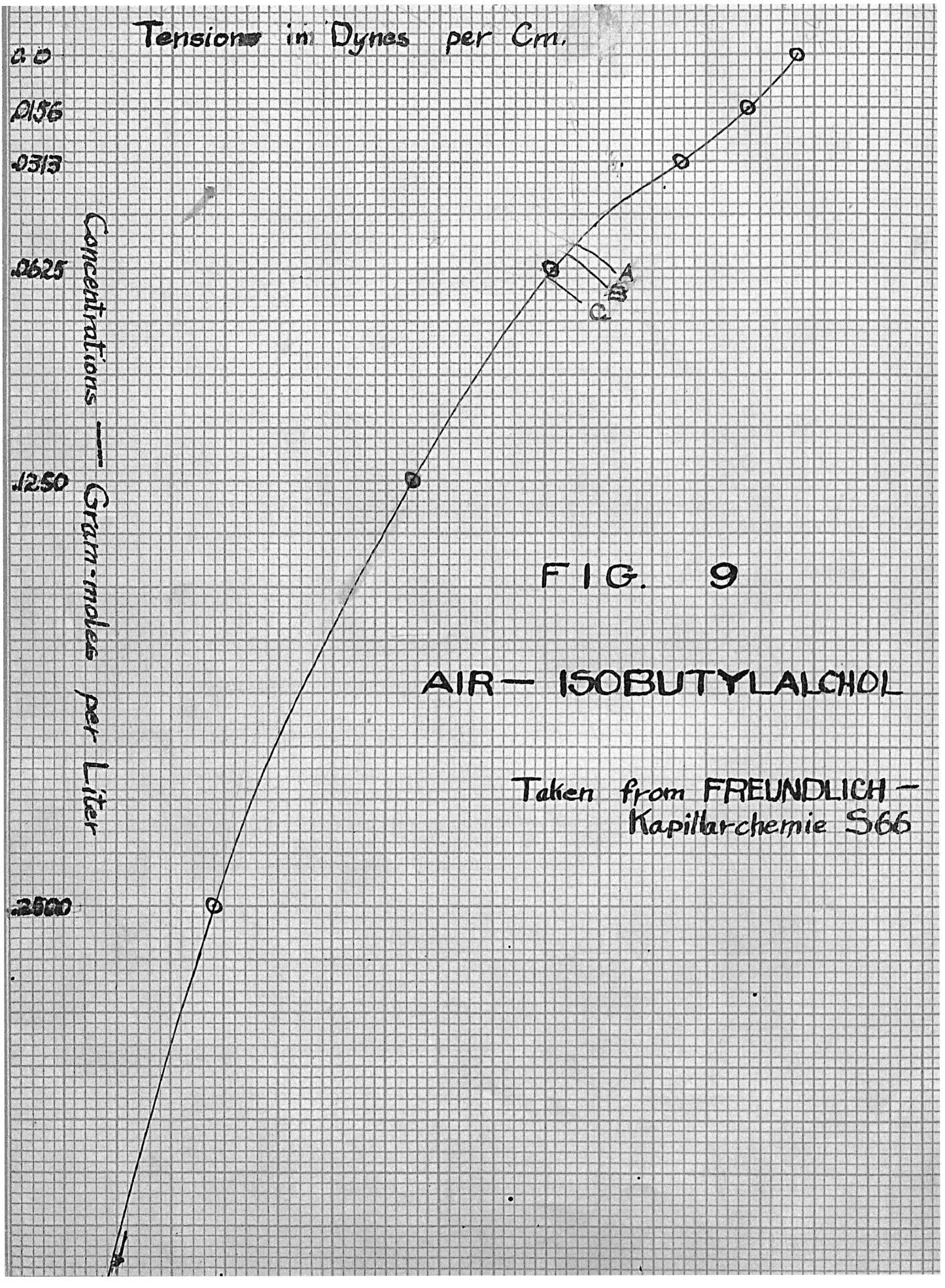

FIG. 9

AIR — ISOBUTYLALCHOL

Taken from FREUNDLICH — Kapillarchemie S66

finally was dried with clean dry air.

The water used was from the Water Analysis sub-department in the Chemistry Department. This was prepared with more care than was any other water available. The determinations of the surface tension of this water are:

63.18 mm	63.61 mm
63.10	63.27
62.72	63.54
63.18	63.28

mean 63.23 mm

One good experiment was obtained with isobutylalcohol ($C_4H_{10}O$). The tension-concentration curve is shown in fig. 9. The data is taken from Freundlich, Kapillarchemie, page 66. Computed from the weighings the concentration of the solution used was 0.0561 moles per liter. This is shown at point A in fig.9. From the curve the tension of this point is 63.8 dynes per cm. As the experiment was ended at 9 o.clock P.M., it was necessary to preserve the solutions until the next day. It was sealed in a test tube with a paraffined cork. In order that the original solution be given the same secondary treatment as the prepared solution, some of the original solution was also sealed in a test tube to stand over night. After standing 16 hours it was tested for tensions. Six results were obtained that the author knows to be questionable. Then followed four results that cannot be questioned. These are:

54.02mm	54.26 mm
54.26	54.46

mean 54.25 mm.

These are uncorrected for density. Assuming the tensions to be strictly proportional to the heights, the absolute tension of this solution should be

$$\frac{54.25}{63.23} \times 74.2 = 63.5 \text{ dynes per cm.}$$

This is point B in fig. 9. This might not be expected to agree with A because the heights are not corrected for density and because A is in question because the weighings upon which A is based were carried only to milligrams while the figures beyond this enter considerably into the computations. This furnishes an indefinite check upon the reliability of the capillary method, as used, to determine surface tensions. The error of 0.3 dyne per cm. is questioned.

The value of u computed for the point B is as follows:

$\theta = 290.$

$R = 1.14 \times 10^6$

molar weght = 74

$\frac{dg}{dc} = 144.4$

$$u = \frac{.0581 \times 74 \times 144.4}{1.14 \times 10^6 \times 290} = 1.88 \times 10^{-6} \text{ gm/cm}^2.$$

The experiment was run for 3h 35m. The rate of bubbling was a little unsteady but was taken at 180 sec for 50 bubbles or 3.6 sec per bubble. This gives the total number of bubbles as 3583. The volume of air displaced was determined in the same manner as Donnan and Barker obtained it. No corrections were made for expansion, etc., as there were only 6 cm. of water to be considered. The error in neglecting this very probable is less than that resulting from neglecting other sources of error. The volume

of air was 34.08 cc. This gives a radius of 0.115 cm., an area of 0.166 cm^2 for each bubble, or a total area of 593.6 cm^2.

The determinations of surface tension of the enriched solution gave

53.16 mm	53.18
53.56	53.42

mean 53.23 mm.

This mean corresponds to an absolute value of 62.6 dynes per cm., and is the point C of fig. 9. From B to C the change of concentration is 0.00689 moles per liter, 0.511 gm per liter, or 0.00336 gr. in the 6.58 cc of solution had in the collecting chamber. This gives as the observed value

$$u = \frac{0.00336}{593.6} = 5.66 \times 10^{-6} \text{ gm/cm}^2.$$

The observed value is three times the calculated value. It is another repetition of the anomalous condition of the observed values being always larger than the calculated. Several other experiments were run with this same solute and with butyric acid, but no effect was observed. In reviewing the data taken, it is noticed that in the above experiment the time needed for a bubble to travel the length of the tube was 89 sec., while those of the experiments that failed were 54 to 68 sec. On one, butyric acid, it was 78 sec, but it is believed that this failed because the air surface passed through was not great enough to make an appreciable effect. The values of the surface tension with concentration for butyric acid are found in Freundlick, Kapillarchemie, page 59.

CONCLUSIONS.

(1) Various men have found that the values or the surface-concentrations of carfeine, anilin, nonylic acid, saponin, and isobutylalcohol are of the same order of magnitude as the theoretical values derived from the Gibbs's equation.

(2) Lewis deduced an extension for the Gibbs law for electro-capillary adsorption. The same method was used in this deduction as Morton used in deducing the Gibbs law from independent considerations.

(3) Irreversible effects in connection with adsorption have been noticed by a number of men. For one substance —— saponin —— this irreversible process has apparently been proved to be due to secondary causes (Lewis vs. Donnan and Barker).

(4) The call that the Gibbs law be deduced again upon the basis of an irreversible process must be withheld for a time. The law quite probable is in error for no positive result has been found less than the computed value.

(5) The closest agreement reached is on a value about two times too big. It may be possible that this is to be accounted for by the large experimental errors.