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FILMS. THE SPREADING OF LIQUIDS AND THE
SPREADING COEFFICIENT

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Introduction

The spreading of a liquid as a film upon the surface of a solid or another liquid is a phenomenon which is of importance not only in nature, but also in connection with many technical processes. Thus it is difficult for petroleum to penetrate sand which is already impregnated with water, and for water to penetrate sand wet by oil. It seems improbable that much progress will be made in the study of the wetting of solids by liquids until some knowledge has been obtained of the criteria which determine the spreading of one liquid upon another. Up to the present time no definite evidence has been presented to show what factors determine the spreading, and more particularly the non-spreading, of a liquid. It is the purpose of the present paper to prove that the criterion of spreading or non-spreading may be presented in a very simple way in terms of a very simple and thermodynamically determined coefficient, which will be termed the *spreading coefficient*.

The data determined for this purpose will be found to give additional evidence, other than that already presented in earlier papers from this Laboratory, which indicates that the electromagnetic forces around a molecule are in general different at different parts of the molecule, and are often arranged unsymmetrically. In this sense the molecular forces may

be said to be chemical, though it is undoubtedly more accurate to designate them as electromagnetic.

Theories of Spreading

Three different views of the criterion of spreading have been expressed in the literature. These are listed below.

1. All liquids spread on a pure surface.
2. A liquid *b* will spread on a liquid *a* if $T_a > T_b + T_{ab}$, where T_{ab} represents the interfacial tension between the two liquids, and T_a and T_b , the respective surface tensions. The condition for non-spreading is $T_a < T_b + T_{ab}$.
3. Liquids whose molecules are polar or contain polar groups, spread on water.

In addition to these a fourth view has been developed in this Laboratory.

4. A liquid will spread if its work of surface cohesion W_C is less, and will not spread if its work of surface cohesion is greater, than its work of adhesion W_A with respect to the surface of the liquid or solid upon which the spreading is to occur. The *spreading coefficient*, which under the conditions hereafter specified gives a measure of the tendency to spread, is defined as

$$S = W_A - W_C$$

Rayleigh¹ and some other investigators seem to have taken the point of view that all liquids will spread on pure water. While this may not justify the conclusion that all liquids spread on a pure surface, it is nevertheless only a milder expression of the same attitude. The fundamental underlying principle here seems to be that all substances attract each other, and this should cause spreading. Rayleigh came specifically to this conclusion in the case of water through his experiments on oleic acid, in which case there is formation of a film with the excess acid staying in the form of a lens. He concluded that whenever there is apparently a case of non-spreading, it is caused by a contaminated surface. The surface may be contaminated either by foreign grease or by some of the seemingly non-spreading material itself, which has spread already on the surface. Such, for example, is Rayleigh's explanation of the apparent non-spreading of carbon disulfide which, he considers, actually spreads, but because of the volatility of its vapors, the film evaporates before it has time to reach the end of the pan. It must be remarked that other liquids as volatile as carbon disulfide, such as ether, will, nevertheless, spread over a large area. Rayleigh evidently mistook the distillation of carbon disulfide from the lens onto the dust-covered surface as spreading of the liquid. Even if this should be a true explanation in the case of carbon disulfide, the same line of reasoning cannot be extended to liquids such as the higher paraffins or the halogenated naphthalenes. There is not the least indication of spreading in these liquids, and all have high boiling points.

The third point of view listed above, that liquids whose molecules contain polar groups spread on water, while those which do not contain

¹ Rayleigh, "Scientific Papers," III, 1887-92, 351, 397, 513, 562, 572.

such groups do not spread, is due to Langmuir. While this conclusion may possibly be justified if a liquid is not supposed to have spread unless it forms a monomolecular film, it gives a somewhat inadequate point of view in regard to spreading in general.

The Neumann Triangle of Forces

The second method of specifying the conditions for spreading, as listed above, was derived very early from a consideration of the Neumann triangle of forces. This assumes the surface tension of the under liquid to be pulling in one direction, and the surface tension of the upper liquid, together with that of the interface, to be pulling in the other direction. Motion of the edge of the drop takes place in the direction of the greater pull. Hardy, in his important work on composite surfaces, gives evidence for this idea as based on measurements with carbon tetrachloride, a paraffin oil, cyclohexane, and carbon disulfide.

Opposition to this point of view has been expressed by many workers in this field: Quincke,² Margaroni,³ Worthington,⁴ Rayleigh,¹ and others.

The Spreading Coefficient

It would seem that the criterion for spreading might be expressed in a way much more easily justified theoretically if it could be developed entirely from the thermodynamics of surfaces. When a drop of liquid is placed upon the surface of another liquid *a* spreading may occur. If it does, the surface of the liquid *a* disappears, while its place is taken by substantially an equal area of the surface *b* plus an equal area of the interface *ab*, provided the surface of *b* and the interface *ab* do not lose their identity. If they do, then only one composite surface *c* takes the place of the surface *a*.

The spreading coefficient may be developed by thermodynamic reasoning, provided the former of the two hypotheses of the preceding paragraph is used as a basis. Since only large scale motion is of importance in spreading, only the *free* surface energies are involved. The free energy decrease *S* which occurs in spreading is obviously given by the expression

$$S = \gamma_a - (\gamma_b + \gamma_{ab}) \quad (1)$$

where γ_{ab} represents the free energy of the surface or interface. The work of adhesion W_A , or the work necessary to pull apart the 1 sq. cm. of the interface *ab*, is given by the equation of Duprè as

$$W_A = \gamma_a + \gamma_b - \gamma_{ab} \quad (2)$$

since all that occurs is the disappearance of the surfaces *a* and *b* and the appearance of the interface *ab*. The work of cohesion is that necessary to create inside a liquid an area equal to 2 sq. cm., or more specifically to

² Quincke, *Phil. Mag.*, [4] 41, 245 (1871).

³ Margaroni, *Pogg. Ann.*, 143, 348 (1871).

⁴ Worthington, *Phil. Mag.*, [5] 18, 364 (1884).

break apart a bar of liquid 1 sq. cm. in area in such a way as to give two surfaces, each 1 sq. cm. in area, and is given as

$$W_C = 2\gamma_b \quad (3)$$

A combination of 1, 2, and 3, gives

$$S = W_A - W_C$$

which exhibits the extremely simple relation that spreading occurs if the adhesion between the 2 liquids is greater than the cohesion in the liquid which is in the position for spreading, while spreading does not occur if the cohesion is greater than the adhesion. It is obvious that a positive value of the spreading coefficient corresponds to spreading, a negative to non-spreading. It is also evident that because the liquid *b* spreads upon *a*, it is not at all a necessary conclusion that *a* spreads upon *b*. Thus the spreading coefficient is given above for the case where *a* is the liquid whose surface is already formed. The coefficient for *a* to spread upon *b* is $S = \gamma_b - (\gamma_a + \gamma_{ab})$ so a high surface energy for the liquid *a* acts in favor of spreading when *a* is the lower liquid, and against spreading when *b* is the lower liquid. *Corresponding with this it is found that almost all organic liquids spread upon water, while water spreads upon very few organic liquids.*

Definition of the Term "Film"

A definition of the term "film" which is suited to characterize films which exist upon liquids and solids, does not seem to have been given in any previous publication. A *film* exists wherever a layer, which has a different composition from the body of the liquid or solid, is present at the boundary surface, provided the area and form of this layer are independent of the gravitational forces acting. Whenever the area and the form of the layer depend upon both the surface and the gravitational forces, a *lens* exists. If the area and the form of the layer are determined primarily by the containing vessel, the phase may be said to be present in *bulk*.

Films may be said to be *non-composite* and *composite*. In a non-composite film the total surface energy is additive in that it is equal to the value of the interfacial energy when both phases are present in bulk, plus the value of the surface energy which film-forming material possesses when it exists in bulk in equilibrium with the phase upon which the film rests. In a composite film the total surface energy is less than this—so films may be very different in their degree of compositeness.

Since the distinction between a film and a lens, as given in the last paragraph, may not seem to be sufficiently definite, it will be given below in a slightly different form. The layer of liquid at a phase boundary may be considered to constitute a film whenever the gravitational forces which tend to change its form or area are inappreciable in comparison with the surface forces which are active.

Theoretical Justification of the Spreading Coefficient

Of the 89 values of the spreading coefficient thus far determined, as shown in Table I, only two have a numerical value less than 1 erg, which corresponds to a force of 1 dyne per cm. It will be seen that when the thickness of the upper layer is as great as 1μ or 10^{-4} cm., or approximately *one thousand molecules*, the layer may still be characterized as a film, since the gravitational force produced is of the order of only 4×10^{-6} dynes in the case of an organic liquid or water. Even when the thickness is 10μ or 10^{-3} cm., the gravitational effect is only about 0.0005 dynes per cm. Abundant evidence has been obtained both in this Laboratory and by Langmuir, that the range of molecular forces for appreciable effects is very minute, and less than the distance across ordinary molecules. It is thus probable that such forces are inappreciable at distances of 5×10^{-8} cm. Thus a film may have a thickness more than a thousand times the range of molecular forces, and so may have complete independence with respect to the upper surface of the film and its interface with the lower liquid.

From this point of view the spreading coefficient should be entirely significant at thicknesses between the upper limit of an order of 1000 molecules or more, and some lower limit which probably approaches closely to only a few molecules in thickness.

Experimental Justification of the Spreading Coefficient

The use of the spreading coefficient as an index of spreading would be justified if a large number of spreading coefficients could be determined with considerable accuracy, provided the liquids spread when the coefficient is positive, and do not spread when it is negative. Such a justification has already been obtained in the present investigation, for it is shown that this is true of the 89 liquids listed in Table I; only one exception is found, and in that case the magnitude of the spreading coefficient is so low that its sign is doubtful.

The coefficients of spreading listed in Table I apply only to the spreading of the pure liquid upon an entirely clean water surface. If the surface of the water is impure, then the surface tension of the water, which occurs as a positive term in the spreading coefficient equation, is lowered, so the coefficient which should be used in this case has a lower value than the one given. Thus it has in no case been found that a pure liquid with a negative coefficient will spread, but it is often found in rough experiments that a liquid with a positive coefficient will not spread, due to the presence of a slight impurity on the surface of the water. As, organic liquids also, even when purified with great care, often differ slightly in their purity, the spreading coefficient relative to water should be determined by the use of a part of the same sample of liquid as was used in the spreading

experiments. This was not done in the one exceptional case mentioned above, that of carbon tetrachloride, which has a very low positive coefficient relative to water of 1.06 dynes per cm., as determined by Harkins and Cheng. Unfortunately the liquid used in the determination of the coefficient was not available. It was found that, when the purest carbon tetrachloride which could be easily produced was put on a pure water surface, spreading did not occur. The spreading coefficient for this liquid has such a low value that it might be easily in error enough to account for such an exceptional result. Octane, with a still lower coefficient of only 0.22 dynes per cm., spread readily, while as stated above no liquid with a negative coefficient was found to spread.

TABLE I
THE SPREADING COEFFICIENT OF ORGANIC LIQUIDS ON WATER^a AT 20°

Substance	Formula	S or	
		$W_A - W_C$	Observer
Ethyl alcohol	C_2H_5OH	50.4	
Methyl alcohol	CH_3OH	50.1	
Propyl alcohol	C_3H_7OH	49.1	
Dipropylamine	$(C_3H_7)_2NH$	48.60	R
Butyl alcohol	C_4H_9OH	48.30	
<i>Iso</i> -butyl alcohol	$(CH_3)_2CHCH_2OH$	48.20	
Propionic acid	C_2H_5COOH	45.77	
Butyric acid	C_3H_7COOH	45.66	
Ethyl ether	$(C_2H_5)_2O$	45.50	D
Acetic acid	CH_3COOH	45.20	
Acetonitrile	CH_3CN	44.4	
<i>Iso</i> -amyl alcohol	$(CH_3)_2CHCH_2CH_2OH$	44.3	
<i>Iso</i> -valeric acid	$(CH_3)_2(CH_2)_2COOH$	43.89	D
Methyl ketone	$(CH_3)_2CO$	42.37	D
<i>Di-isobutyl</i> amine	$((CH_3)_2CHCH_2)_2NH$	40.47	R
Methylbutyl ketone	$CH_3COCH_2CH_2CH_2CH_3$	37.58	D
<i>Sym</i> -octyl alcohol	$CH_3OHC_8H_{17}$	37.32	Ch
Heptylic acid	$CH_3(CH_2)_5COOH$	37.12	Ch
Methylhexyl carbinol	$CH_3CHOH(CH_2)_5CH_3$	36.67	D
<i>N</i> -octyl alcohol	$C_8H_{17}OH$	35.74	Cii
Formic acid	$HCOOH$	35.5	
Butyronitrile	$CH_3(CH_2)_2CN$	34.36	R
<i>Iso</i> -amyl chloride	$(CH_3)_2CHCH_2CH_2Cl$	33.88	R
Ethylpropyl ketone	$CH_3CH_2CO(CH_2)_2CH_3$	33.75	D
Ethyl carbonate	$(C_2H_5O)_2C=O$	33.63	D
<i>Iso</i> -valeronitrile	$(CH_3)_2CHCH_2CN$	32.63	R
Heptaldehyde	$CH_3(CH_2)_5CHO$	32.22	C
Undecylenic acid (at 25°)	$C_{10}H_{21}COOH$	32.02	R
Methylhexyl ketone	$CH_3CO(CH_2)_5CH_3$	31.92	D

^a The values of W_C from which the spreading coefficient were calculated relate to the pure dry organic liquids, but the latter in spreading become saturated with water, therefore still more exact information in regard to spreading would be given if W_C were determined by the use of liquids saturated with water.

Ethyl <i>iso</i> -valerate	$(\text{CH}_3)_2\text{CHCH}_2\text{COOC}_2\text{H}_5$	30.71	R
Monochloro-acetone	$\text{CH}_2\text{ClCOCH}_3$	30.42	C
<i>Tert</i> -butyl chloride	$(\text{CH}_3)_3\text{CCl}$	29.46	D
<i>Asym</i> -dichloro-acetone	$\text{CHCl}_2\text{COCH}_3$	26.46	C
<i>Iso</i> -butyl chloride	$(\text{CH}_3)_2\text{CHCH}_2\text{Cl}$	26.43	D
Nitromethane	CH_3NO_2	26.32	C
Ethyl capronate	$\text{CH}_3(\text{CH}_2)_4\text{COOC}_2\text{H}_5$	25.64	Ch
Mercaptan	$\text{C}_2\text{H}_5\text{SH}$	24.86	D
Oleic acid	$\text{C}_{17}\text{H}_{33}\text{COOH}$	24.62	R
<i>Iso</i> -amyl butyrate	$(\text{CH}_3)_2\text{CHCOO}(\text{CH}_2)_4\text{CH}(\text{CH}_3)_2$	24.61	R
Aniline	$\text{C}_6\text{H}_5\text{NH}_2$	24.45	C
Heptene	$\text{CH}_3(\text{CH}_2)_4\text{C}=\text{CH}$	22.40	Ch
Ethyl nonylate	$\text{CH}_3(\text{CH}_2)_7\text{COOC}_2\text{H}_5$	20.88	D
Trimethyl-ethylene	$\begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{C}=\text{C} \\ \diagup \\ \text{CH}_3 \end{array} \begin{array}{c} \text{H} \\ \diagdown \\ \text{C} \\ \diagup \\ \text{CH}_3 \end{array}$	18.85	D
Methylene chloride	CH_2Cl_2	17.97	C
Ethyl bromide	$\text{C}_2\text{H}_5\text{Br}$	17.44	C
Benzaldehyde	$\text{C}_6\text{H}_5\text{CHO}$	17.25	C
<i>Iso</i> -amyl nitrate	$\text{C}_6\text{H}_{11}\text{NO}_3$	14.82	R
Chloroform	CHCl_3	13.04	C
Anisole	$\text{C}_6\text{H}_5\text{OCH}_3$	11.76	R
Phenetole	$\text{C}_6\text{H}_5\text{OC}_2\text{H}_5$	10.66	R
<i>p</i> -Cymene	$\text{C}_8\text{H}_4\text{CH}_3\text{C}_3\text{H}_7$	10.10	R
<i>Iso</i> -pentane	$(\text{CH}_3)_2\text{CHCH}_2\text{CH}_3$	9.44	D
Benzene	C_6H_6	8.94	Ch
<i>o</i> -Xylene	$\text{C}_6\text{H}_4(\text{CH}_3)_2$	6.85	R
Toluene	$\text{C}_6\text{H}_5\text{CH}_3$	6.84	
"Higher" paraffin		6.72	Ch
<i>p</i> -Xylene	$\text{C}_6\text{H}_4(\text{CH}_3)_2$	6.70	R
Tetrachloro-ethane		6.44	Fa
<i>m</i> -Xylene	$\text{C}_6\text{H}_4(\text{CH}_3)_2$	6.19	
Ethyl benzene, mesitylene	$\text{C}_6\text{H}_3(\text{CH}_3)_3$	5.59	R
Trichloro-ethylene		5.09	Fa
<i>o</i> -Nitrotoluene	$\text{C}_6\text{H}_4\text{CH}_3\text{NO}_2$	4.15	C
<i>m</i> -Nitrotoluene		4.13	C
Nitrobenzene	$\text{C}_6\text{H}_5\text{NO}_2$	3.76	C
Di- <i>iso</i> -amyl (decane)	$(\text{CH}_3)_2\text{CH}(\text{CH}_2)_4\text{CH}(\text{CH}_3)_2$	3.76	R
Hexane	C_6H_{14}	3.41	Ch
Chlorobenzene	$\text{C}_6\text{H}_5\text{Cl}$	2.31	C
β,β' -dichloro-ethyl sulfide	$(\text{ClCH}_2\text{CH}_2)_2\text{S}$	1.62	E
Pentachloro-ethane		0.67	Fa
Octane	C_8H_{18}	0.22	Ch

B. Liquids which Form Lenses on Water

Carbon tetrachloride		1.06(?)	Ch
<i>p</i> -Bromotoluene	$\text{C}_6\text{H}_4\text{BrCH}_3$	- 1.29(30°)	Fa
Ethylene dibromide	$\text{C}_2\text{H}_4\text{Br}_2$	- 3.19	Ch
Monobromobenzene	$\text{C}_6\text{H}_5\text{Br}$	- 3.29	F
<i>o</i> -Monobromotoluene	$\text{C}_6\text{H}_4\text{CH}_3\text{Br}$	- 4.20	F
Perchloro-ethylene	C_2Cl_4	- 6.42	F
Carbon disulfide	CS_2	- 6.94	C
Phenyl mustard oil	$\text{C}_6\text{H}_5\text{NCS}$	- 7.68	F

TABLE IB. (Continued)

Substance	Formula	S or	
		$W_A - W_C$	Observer
Monoiodobenzene	C_6H_5I	- 8.74	F
Bromoform	$CHBr_3$	- 9.58	F
α -Monochloro-naphthalene	$C_{10}H_7Cl$	- 9.74	F
Tribromohydrin	$CH_2BrCHBrCH_2Br$	- 11.06	F
"Stanolax"		- 13.44	F
Liquid petrolatum, Squibb's		- 13.64	F
α -Monobromo-naphthalene	$C_{10}H_7Br$	- 13.86	F
Acetylene tetrabromide	$C_2H_2Br_4$	- 15.64	C
Methylene iodide	CH_2I_2	- 26.46	F
Diphenyl methane	$(C_6H_5)_2CH_2$		
Diphenyl dichloromethane	$(C_6H_5)_2CCl_2$		
Tribromo-ethylene	C_2HBr_3		
<i>p</i> -Bromotoluene at 30°		- 1.29	Fa
C Clark	D Davies	Fa Fanselow	R Roberts
Ch Cheng	E Ewing	F Feldman	

Spreading as Related to the Presence of Polar Groups in the Molecule

The 71 liquids listed in the first section of Table I were found by careful experiment to spread on the surface of pure water. These 71 liquids include hexane, octane, a higher paraffin, benzene, *iso*-pentane, toluene, *p*- and *m*-xylene, decane (di-*iso*-amyl), ethyl benzene, chlorobenzene, *iso*-butyl chloride, *tert*-butyl chloride, *iso*-amyl chloride; a sufficient list to prove that the presence of a polar group is not essential for spreading.

One of the principal effects of the presence of a polar group is, as has been shown frequently by Harkins and his co-workers, to increase the work of adhesion (W_A). Since when a very polar group, such as —OH, —COOH, —CONH, —CHO, —CN, —CONH₂, etc., is present, W_A is very high, the term W_C in the equation, $S = W_A - W_C$, is never large enough to give a negative value of the spreading coefficient. Nevertheless, when the work of adhesion toward water is small, the liquid may still spread if W_C is still smaller. Thus hexane, for which the value of W_A is very small (40.23 ergs), spreads, since W_C is extremely small (36.86), and the value of S is 3.37. The work of cohesion in octyl alcohol is nearly 20 ergs greater, so octyl alcohol is able to spread only because W_A is also greater (by the remarkably great value 51.71) than that for hexane. This illustrates the fact that the extremely great effect of the presence of a polar group in producing spreading is due to the fact that in general it increases the work of adhesion toward water very much more than it increases the work of cohesion.

One of the most important factors in determining the magnitude of the spreading coefficient toward water is the dissymmetry of the molecule. In general the value of the coefficient increases as the electromagnetic

field of force around the molecule becomes more unsymmetrical. This is due to the fact that with unsymmetrical molecules the work of adhesion toward water is much greater in comparison with the work of cohesion, than in the case of symmetrical molecules, since when the liquid is torn from water the strongest field must be ruptured, while when it is separated from itself, only the weakest field is broken. Much more detailed discussions of the general factors which influence these values, will be found in previous papers of this series.⁵

Non-spreading Liquids

It has been indicated in the preceding paragraph that one of the important factors in producing a non-spreading liquid is that the intensity

TABLE II

THE INTERFACIAL RELATIONS OF TWELVE NON-SPREADING LIQUIDS (ON WATER)
(Energy value in ergs per sq. cm.)

Substance and formula	Work of cohesion/ γ or $W_C/2$	Work of adhesion/ $W_A/2$	Inter-facial tension γ_i	Work of adhesion $-\Delta\gamma$ or W_A	Density pure liquid	Density organic phase	Density aqueous phase	Spreading coefficient $S = W_A - W_C$
Perchloro-ethylene, C_2Cl_4	31.74	28.53	47.48	57.06	1.6216	1.6219	0.99844	- 6.42
Bromoform, $CHBr_3$	41.53	36.74	40.85	73.48	2.8854	2.8818	1.0004	- 9.58
Tribromohydrin, $CH_2BrCHBr-CH_2Br$	45.36	38.83	38.50	79.66	2.4171	2.4152	0.99892	-11.06
Methylene iodide, CH_2I_2	50.76	37.53	48.50	75.06	3.3190	3.3180	0.99908	-26.46
Monobromobenzene, C_6H_5Br	36.26	34.62	39.83	69.23	1.5016	1.5013	0.99862	- 3.29
<i>o</i> -Monobromotoluene, <i>o</i> - $C_6H_4BrCH_3$	35.85	33.75	41.15	67.50	1.4218	1.4318	0.99823	- 4.20
Mono-iodobenzene, C_6H_5I	39.70	35.33	41.84	70.66	1.8258	1.8255	0.99832	- 8.74
α -Monochloronaphthalene, $C_{10}H_7Cl$	41.80	36.93	40.74	73.86	1.1706	1.1700	0.9982	- 9.74
α -Monobromonaphthalene, $C_{10}H_7Br$	44.59	37.66	42.07	75.32	1.4836	1.4739	0.99828	-13.86
Phenyl mustard oil, $C_6H_5N:CS$	41.44	37.60	39.04	75.20	1.1326	1.1331	0.99795	- 7.68
"Stanolax"	30.69	23.97	55.55	47.94	.8604	.8605	0.99816	-13.44
Liquid petrolatum, Squibb	31.12	24.30	55.32	48.60	.8880	.8878	0.99825	-13.64

⁵ See especially Harkins, Clark and Roberts, THIS JOURNAL, 42, 700-12 (1920); and Harkins and Cheng, *ibid.*, 43, 51 (1921). In the latter paper a few of the values of S are misstated.

of the molecular field of force shall be evenly distributed around the molecule.

Before the beginning of this investigation Hardy had found 4 non-spreading liquids: carbon tetrachloride, paraffin oil C, cyclohexane and carbon disulfide. The present investigation has determined the spreading coefficient for carbon disulfide, and has added 16 non-spreading liquids to the list. The coefficients for these liquids are given in Table IB, and the complete data for the newly determined coefficients in Table II.

It will be seen that, as with the paraffins, spreading may be due to a low value, less than 50, of the free energy of attraction toward water (work of adhesion), but in many more instances is brought about when this value is as high (about 75) as if they were esters, which spread to a monomolecular film. *Thus non-spreading is usually due to a high value of the work of cohesion of the substance.*

Non-spreading seems to accompany the presence of the =S or =CS or phenyl groups, or that of chlorine, bromine or iodine, as substituents in paraffins, in benzene or in naphthalene, even when the unsubstituted compound spreads easily. When only one chlorine atom is present in a paraffin derivative it seems to be polar and produces the opposite effect, considerably increasing the spreading coefficient, while with several chlorine atoms the coefficient is decreased. Bromine, and especially iodine are much more effective than chlorine as substituents for producing non-spreading. The above groups are evidently of the type which have a high attraction for themselves without having an especially high attraction for water.

Preparation and Purification of Materials

The materials used in the course of this investigation were purified mostly by fractionation in a high vacuum, only the middle fractions being used for surface-tension work. Whenever possible, the liquids were purified by recrystallization in freezing mixtures as preliminary to fractional distillation. No attempt was made to purify "Stanolax" or Squibb's "Liquid Petrolatum." The water used in the interfacial-tension work was high-grade conductivity water. Precautions were taken to guard against contamination from foreign sources such as carbon dioxide in the air.

Experimental Methods

Spreading.—All spreading experiments were performed in a pan 76 x 28 x 5.7 cm. made of galvanized iron. The blades used for sweeping the surface were made of the same material; they were simply strips of iron with the edges cut in and bent 90° so as to fit and press against the pan closely. Either strongly ignited talcum powder or lycopodium was dusted upon the surface before sweeping. In dealing with non-spreading liquids, where the talcum or lycopodium is intended simply as an indicator of non-spreading, both are equally good; but with spreading liquids, when it is desirable to measure the area of the film, talcum is probably the better material to use.

All experiments on water surfaces were performed with distilled water, about 7 liters being used to fill the pan. The pan and sweeping blades were always thoroughly scraped, and washed with hot water before use, and the surface of the water was swept two or three times before every experiment; but many more times than this in doubtful cases.

Surface and Interfacial Tension.—The experimental work on surface and interfacial tensions was done by the drop-weight method, as standardized in this Laboratory. In all calculations the table of corrections given by Harkins and Brown was used.⁶ Because of the fact that the liquids used were of a high boiling point, the surface and interfacial tension results are presumably of a high degree of accuracy. For measurements of the tensions of the films a heavy machined brass tray is used.

Behavior of Spreading Liquids

It seems worth while to point out that liquids may be divided into classes with reference to the way in which they spread on water.

1. Liquids which spread to a more or less uniform, permanent sheet, but not a monomolecular layer. Such is the behavior of the paraffin oil mentioned above and also of all the paraffin oils which give the familiar Newtonian colors on oily water.

2. Liquids which spread to form a monomolecular layer, any excess oil remaining in the form of a lens or lenses. Such are the films studied by Rayleigh, Miss Pockels, Marcelin, Devaux, Labrouste, Hardy, Langmuir and Adam.⁷

3. Liquids which are either volatile or more or less soluble in water and thus leave no lenses in spreading, even if used in considerable quantity. They either do, or do not, go through the Newtonian color stage, and finally disappear by evaporation or solution. It should be noted that even in the case of soluble substances such as the lower alcohols, solution probably starts by a spreading on the surface.

Insolubility as an Accompaniment of Non-spreading

It would seem that the difference between the adhesional work and the cohesive work ($W_A - W_C$) should be important as a factor in determining solubility (though not so important as in the case of spreading) since the solubility of a substance also seems to depend on the difference between the attraction of the solute for the solvent and for itself. However, there is this distinction: in spreading on water it is the most active or polar part of the molecule which is chiefly involved, while the whole molecule takes part in solution. From this standpoint it is to be expected that spreading

⁶ Harkins and Brown, *THIS JOURNAL*, 41, 499 (1919).

⁷ Rayleigh, "Scientific Papers," Vol. III, 341-580 (1887-92); IV, 425 (1892-1901); VI, 534 (1911-19). Pockels, *Nature*, 43, 437 (1891). Marcelin, *Ann. Physik*, 1, 19 (1914). Devaux, papers from 1903; see review in "*Smithsonian Ann. Reports*," 1913, p. 261. Hardy, *Proc. Roy. Soc.*, 86A, 634 (1911-12). Labrouste, *Compt. Rend.*, 158, 627-9. Langmuir, *THIS JOURNAL*, 39, 1848-1906 (1917). Adam, *Proc. Roy. Soc.*, 96A, 336-51 (1921).

on water is a more common phenomenon than a considerable solubility in water, since spreading is a solution of only the most active or soluble part of the molecule.

In spreading it is not necessary for the molecules of the solute to penetrate between and push apart those of the solvent, as must be done in solution.

Corresponding with this, it is found that all non-spreading liquids are practically insoluble. Liquids with very high spreading coefficients with reference to water are miscible with it, provided the slightly polar part of the molecule is sufficiently small. Although the value of the coefficient for ether is moderately high (45) it is not miscible with water, since 2 ethyl groups are present in the molecule. Most liquids whose coefficients have positive values less than 10 are insoluble or only slightly soluble in water.

Effect of Impurities on Spreading

That impurities on the surface prevent spreading has been pointed out by many investigators; that active impurities in a non-spreading liquid, may cause it to spread, has been shown by Hardy⁸ and others. A simple and beautiful experiment illustrates the latter effect. A large lens of "Liquid Petrolatum, Squibb"—presumably any other oil with a high negative coefficient would give similar effects—is formed in the middle of the surface of a sheet of water in a large tray. A drop of oleic acid is then placed upon the center of this lens. After a short period, considerable movement is noticed adjacent to this point and then, very suddenly, the lens is broken up into a great number of fragments which seem to be projected with almost explosive violence toward the edges of the tray. If the oleic acid is mixed with the oil before it is put on the surface, the material separates into a large number of minute drops, separated by a thin film, the drops moving constantly on the surface. The thin film evidently contains a considerable proportion of oleic acid.

Thickness of the Films

Liquids of the first class, such as the lower paraffins, which give a permanent sheet on water thicker than a monomolecular layer, often exhibit Newtonian colors, an indication that they are of the order of a thousand molecules thick. All of these liquids have low positive values of the spreading coefficient. If the coefficient is high, monomolecular films seem to be formed. Since high values are found only when polar groups are present in the molecules of the spreading liquid, it would seem that the presence of such groups is essential for the formation of a *monomolecular film*.

The films formed by some of the pure hydrocarbons have some resem-

⁸ Hardy, *Proc. Roy. Soc.*, **88A**, 313 (1913).

blance to those which contain impurities in small amounts, since their thickness is not uniform, and they exhibit long wide ribbons of thicker film, with streaks of thinner spotted film between. In some cases the water from the lower layer may have the effect of an impurity in the upper layer.

It should be kept in mind that the spreading coefficients listed in Table I have been calculated from surface tension results obtained by the use of the dry organic liquids, and the values are somewhat different in the case of soluble or slightly soluble liquids when they are wet. This in general lowers the surface tension of the organic liquid, and so increases the spreading coefficient.

Langmuir⁹ states that substances containing no polar groups, such as benzene and cymene, should not spread, and this statement is repeated by W. C. McC. Lewis.¹⁰ Nevertheless, benzene spreads readily and has a positive coefficient equal to 8.9, while cymene and the xylenes also form no lenses on a clean water surface. The idea that such liquids do not spread is supposed to be due to Hardy, but a study of his papers has failed to reveal any reference to the non-spreading of benzene.¹¹ On the contrary he states that benzene spreads on a pure water surface,¹² although he obtained lenses on a contaminated surface. The benzene used in our experiments was purified with extreme care, and was that used in this Laboratory for the determination of the surface tension of benzene.

The substitution of phenyl groups in methane or ethane gives rise to non-spreading compounds. Thus diphenylmethane, with a surface tension of 37.56 at 26° as determined by D. T. Ewing in this Laboratory,¹³ *does not spread at all.*

The effect of the phenyl group in producing non-spreading, seems to diminish with the length of the hydrocarbon chain. A drop of 1,1-diphenylethane spreads to a circle about 5 cm. in diameter and then divides into a large number of very small lenses which show no tendency to coalesce. When applied to the surface of the water in the form of a very small drop on the end of a glass fiber, it forms a pinhead-like lens. A drop of diphenylpropane spreads to a multicolored sheet; in a short time spots appear in the sheet and then it breaks up into a great number of small lenses. Ditolyl-methane and other substances for which the spreading coefficient has a small positive value, act in this way.

The liquid derivatives of naphthalene, and presumably those of anthracene, seem to be non-spreading, at least this is what is found in the case of the chloro- and bromo-naphthalenes. It seems probable that the 2

⁹ Langmuir, *THIS JOURNAL*, **39**, 1864 (1917).

¹⁰ W. C. McC. Lewis, "A System of Physical Chemistry," I, 2nd ed., 476 (1919).

¹¹ Hardy, *Proc. Roy. Soc.*, **86A**, 610 (1912).

¹² Ref. 11, p. 620.

¹³ Harkins and Ewing, *THIS JOURNAL*, **41**, 1980 (1919).

liquid methyl- and the 2 liquid ethyl-naphthalenes and tetrahydro-naphthalene, do not spread, but unfortunately they could not be obtained in the American market.

The Halogen Compounds

The halides studied in this investigation present interesting relations. It can be seen readily that it is easier to obtain non-spreading liquids by introducing halogens into the aromatic compounds than into those of the aliphatic series. Whereas it takes at least 2 bromine atoms as substituents for 2 hydrogen atoms in methane to form a non-spreading liquid, the introduction of only one such atom into benzene to form monobromobenzene produces the same effect. Further, while the introduction of only one halogen atom into the molecule of a paraffin hydrocarbon is insufficient to form a non-spreading liquid, the accumulation of halogen in the molecule will bring about the desired result; ethyl bromide spreads on water, ethylene bromide forms lenses. A regularity in the effect of different halides can be noticed. While it takes the 4 chlorine atoms of carbon tetrachloride to form a non-spreading liquid, it takes only 2 bromine or 2 iodine atoms in the case of methylene bromide or methylene iodide. A general relation can perhaps be postulated to hold for the halides: the accumulation of halogen in the molecule, if the resulting compound is liquid, should give a non-spreading substance. It is difficult to predict the degree of substitution of hydrogen by halogens required to form a non-spreading liquid. In the case of ethylene bromide or tribromohydrin, the attachment of 1 bromine to every carbon atom results in non-spreading. It can also be laid down as a general rule that the extent of halogen substitution required to give a non-spreading liquid decreases in the order: chlorine, bromine, iodine. The illustrations given above were taken from the aliphatic series; in the aromatic series monochlorobenzene spreads, bromobenzene and iodobenzene do not spread. It was impossible to secure dichlorobenzene (*o* and *m*) or trichlorobenzene (1, 3, 4). It is probable that these liquids, as well as *o*- and *m*-dibromobenzene will not spread on water.

In the case of perchloro-ethylene, C_2Cl_4 , and tribromo-ethylene, C_2HBr_3 , the accumulation of halogen offsets the polarity of the double bond. The non-spreading of perchloro-ethylene could, of course, be attributed to the symmetry of the molecule, but no such explanation can be offered for tribromo-ethylene. The reagents on hand were insufficient to permit any conclusions to be drawn as to whether the accumulation of halogen in the molecule can offset the polarity caused by any other influence outside of the double bond. In this connection it is worth while to compare tribromohydrin and dibromohydrin. Tribromohydrin is a non-spreading liquid, but the replacement of a bromine atom by the polar hydroxyl

group results in a spreading liquid, the hydroxyl group probably being oriented towards the water and thus causing the liquid to spread. It was also found that propylene bromide spreads. Tetrachloro-ethane has a spreading coefficient equal to 6.44, while the substitution of 1 more chlorine atom reduces the value to 0.67.

Sulfur Derivatives

A study of sulfur derivatives is instructive. That the =S group is only very slightly polar has been pointed out by Harkins and his collaborators.¹⁴ It was found in agreement with this that carbon disulfide, CS₂, phenyl mustard oil, C₆H₅N:CS, and *p*-tolyl mustard oil, CH₃C₆H₄N:CS, do not spread on water. The experiments on the first two liquids were performed at 20°, but tolyl mustard oil was tested at 30°, as it is a solid at room temperature. In the case of phenyl and tolyl mustard oils, despite the presence of a nitrogen atom and a double bond, both sources of polarity in the molecule, their combined effect is entirely offset by the nonpolar character of the =CS group. It is important to note the effect of structure on the spreading properties of these liquids. Whereas phenyl mustard oil is a non-spreading liquid, the isomeric phenyl-thiocyanate, C₆H₅.SCN, spreads on pure water. In this case the polar character of the —CN group is revealed. In comparing the lenses of phenyl mustard oil and tolyl mustard oil, it can be seen that the latter gives lenses of a greater curvature.

In the aliphatic series, the only mustard oil obtainable was allyl mustard oil, CH₂:CHCH₂N:CS. It was found to be a spreading liquid; evidently the polar character of the allyl group, due to its double bond, offsets the effect of the mustard oil group.

A few mercaptans were also tried, and were found to spread on water. This behavior was expected on the basis of the polarity of the —SH group, as was pointed out in the previous papers from this Laboratory. In agreement with the spreading of these liquids, the spreading coefficient at 20° of ethyl mercaptan, for example, is 24.86.

Experiments on Camphorated Water

The underlying idea of these experiments was to see to what extent spreading liquids could be made to stay in the form of lenses on water containing a substance in solution which lowers its surface tension. A lowering of the surface tension of water may affect the work of adhesion, $W_A = \gamma_{H_2O} + \gamma_{Liq} - \gamma_i$, in two ways: (1) by decreasing γ_{H_2O} ; (2) by changing γ_i . The direction and magnitude of this last effect is difficult to predict. It was not determined experimentally, because in determining the interfacial tension of an organic liquid against a saturated solution of camphor, the camphor is so largely extracted by the organic phase. Judg-

¹⁴ Harkins, Clark and Roberts, THIS JOURNAL, 42, 707 (1920).

ing from the spreading experiments, it seems that the effect of camphor on the work of adhesion consists chiefly in lowering the surface tension of water.

A saturated solution of camphor in water was made up, and its surface tension determined by the drop-weight method. The result varied somewhat between the limits 51.1 and 52.0; the lowering of the surface tension of the water is thus 21 ergs per cm.

Spreading experiments were made on this camphorated water following the same technique with respect to dusting and sweeping the surface, as was used with pure water. It was found that the following liquids did not spread on camphorated water: benzene, toluene, the 3 xylenes, mesitylene, nitrotoluene, chlorobenzene, anisole and benzaldehyde, whereas all of them spread on pure water.

The last 2 liquids are particularly interesting, since both contain polar groups having a high attraction for water. The spreading coefficient of benzaldehyde is given in the table as 17.25; this makes it probable that the main effect of camphor on the work of adhesion is in lowering the surface tension of water. It was also found that dimethyl-aniline, a substance with a polar group, did not spread on camphorated water. Nitromethane spreads on camphorated water as one would expect from the magnitude of its spreading coefficient on pure water, 26.32. The behavior of organic liquids on the surfaces of aqueous solutions is a subject of considerable interest and deserves further study.

Experiments on Mercury Surfaces

A recent paper from this Laboratory¹⁵ gave a table of results of interfacial measurements on systems made up of mercury in contact with organic liquids. The column marked S or $W_A - W_C$ shows that the *spreading coefficient is positive in all cases*. It was, therefore, inferred that all these liquids should spread on a perfectly clean mercury surface.

Spreading experiments were made to test this hypothesis. The following liquids were tried and found to spread on mercury: (1) acetone, (2) hexane, (3) ethyl ether, (4) octane, (5) propyl alcohol, (6) nitro-ethane, (7) ethyl alcohol, (8) carbon tetrachloride, (9) toluene, (10) benzene, (11) *o*-xylene, (12) *m*-xylene, (13) *p*-xylene, (14) chloroform, (15) octyl alcohol, (16) nitrobenzene, (17) aniline, (18) water, (19) oleic acid, (20) ethylene bromide, (21) methyl iodide, (22) acetylene tetrabromide.

There are several interesting phenomena to note in connection with these experiments; liquids which do not spread on water, such as carbon tetrachloride, ethylene dibromide or acetylene tetrabromide, nevertheless spread on mercury.

In the case of water, Rayleigh's technique was followed:¹⁶ mercury was

¹⁵ Harkins and Ewing, *THIS JOURNAL*, **42**, 2539 (1920).

¹⁶ Lord Rayleigh, *Sci. Papers*, **III**, 562.

distilled in a vacuum in an all-glass apparatus. A Drechsel wash-bottle attached as a receiver was later cut off from the distilling train, and the mercury used for the experiments siphoned from under the surface. This resulted, as described by Rayleigh, in an exceptionally clean mercury surface. Whether water will spread on such a surface or not depends further on the quality of the water used in the experiments. The quality of the water is probably responsible for the variable success which Rayleigh had with this experiment. Water spread on mercury may be found after a time gathered into a lens, which effect is probably caused by a contamination picked up by the mercury surface.

This experiment was formerly considered of great significance, since it was thought that this was representative of all cases of non-spreading liquids; their non-spreading on water, for example being supposed to be caused by the impure surface of the water. A consideration of the table quoted above shows, however, that if the spreading coefficient is a true criterion of spreading or non-spreading, water should spread on a mercury surface. Now water, of all liquids studied by Harkins, Ewing and Grafton, has the lowest spreading coefficient, so it is readily understood why great precautions must be taken in using both a clean mercury surface and pure water. Since a mercury surface is easily contaminated, the value of the spreading coefficient of water on an impure mercury surface can readily become negative and as a result water easily forms lenses on a mercury surface. The conclusion is, therefore, that the behavior of mercury towards water represents nothing exceptional.

The same method of siphoning the mercury from under the surface was used not only for the experiments with water but also with the organic liquids. A few cubic centimeters of mercury which had been in the delivery tube and had perhaps adsorbed gases, was discarded in every experiment. The spreading of these liquids on mercury always takes place much more slowly than the spreading of the same liquid on water, even although the spreading coefficient is usually much higher in the former case. This illustrates the fact so well known with respect to other phenomena, that the free energy of a change and its speed are by no means proportional to each other.

The Non-spreading of Water on Organic Liquids

While most organic liquids spread on water and have a positive spreading coefficient, the value of the latter is always negative, at least in every case thus far investigated. Thus it is to be expected that *water will in no case spread upon the surface of any organic liquid when the two are mutually insoluble*. It has already been seen that the spreading coefficients given in the table are calculated from data obtained from the pure liquids, and are not strictly applicable unless this condition is met by the lower phase and the film.

Corresponding with this, water was found to spread upon only 1 of the 18 organic liquids investigated, and this one, acetone, is miscible with water.

The form of the lenses produced by organic liquids on water has not been treated in this paper, since Coghill and Anderson have made a study of this subject. The general form of the drops of water which float on the surface of an organic liquid is very different, and does not seem to have been described.

A non-spreading organic liquid will form a lens on water, though sometimes only a very small one if the spreading coefficient has a low numerical value. This lens will always float if it is not too large, since it is upheld by the vertical component of the surface tension of the water at the line of contact. The floating of the lens depends upon the important fact that in no case does the water spread over the surface of the lens. If it did so, then the vertical component of the surface tension of the water would pull the lens downward instead of upward, and it would sink if its density were greater than that of water.

If we now consider what occurs when a *drop of water* is placed upon the surface of an organic liquid with which it is not miscible, it will be seen that since most organic liquids spread on the surface of water, the usual behavior is that described in the following sentences. The organic liquid spreads as a film over the drop of water, and the latter then sinks if it is heavier than the former, but, if it is lighter, *floats as a practically spherical lens. The surface of the organic liquid rises as it approaches such a floating lens, while the surface of water always falls as it approaches a floating lens consisting of an organic liquid.*

The phenomena which accompany the floating of a lens of water upon the surface of a non-spreading organic liquid should be similar to those which occur when a lens consisting of an organic substance floats upon water, but with this important difference: the surface tension of an organic liquid is so small in general that only a very small lens of water can be supported, provided the density of the latter is considerably greater than that of the organic liquid.

The non-spreading of water upon insoluble organic liquids is in good accord with the spreading coefficient relation.

The Spreading Coefficient and the Neumann Triangle

A consideration of the development of the spreading coefficient will show that the same numerical index of spreading could have been deduced from the Neumann triangle of forces, but the development adopted has the great theoretical advantage that it gives the spreading coefficient in terms of free energy instead of force.

The Spreading of Films on Solids

Since the free surface energy of solids is in general much higher than of liquids, and since in general the interfacial tension is less than that of the surface tension by a greater amount, the value of S in the expression $S = \gamma_s - (\gamma_i + \gamma_{s,i})$ may be expected to be positive with practically all organic liquids. However, it is extremely difficult to prepare a clean solid surface, so non-spreading may often result as the effect of the lowering of the free surface energy by the contaminating substance.

Summary

1. It is found that the spreading of films is in general related to what is defined thermodynamically as the "spreading coefficient." Liquids for which the value of this coefficient S is positive will spread, while those for which it is negative will not spread. Actually, the value of the system relates to the system, spreading liquid—substance upon which the spreading occurs, and may be quite different when A spreads upon B , from what it is when B spreads upon A . For example, most organic liquids have positive coefficients with reference to spreading upon water, and thus will spread into a film; but water has a negative coefficient with reference to most organic liquids, and will not spread over them. The value of the coefficient is defined by the equation

$$S = W_A - W_C \quad (1)$$

in which W_A is the work of adhesion for the interface of the two liquids, and W_C is the work of cohesion of the liquid which is applied to the surface of the other liquid or the solid, upon which the spreading might occur. Thus a liquid will *not* spread if its work of cohesion, which indicates its attraction for itself, is greater than the work of adhesion, which indicates its attraction for the body upon which the spreading will *not* occur. The values of W_A and W_C are given by the equations:

$$W_A = \gamma_a + \gamma_b - \gamma_{ab} \quad (2)$$

$$W_C = 2 \gamma_b \quad (3)$$

so the value of the spreading coefficient may be defined in wholly experimental terms as

$$S = \gamma_a - (\gamma_b + \gamma_{ab}) \quad (1')$$

Here a represents the liquid whose spreading upon b is under consideration.

2. The experiments were made with organic liquids on the surface of water, with water on the surface of organic liquids, and with water and organic substances on the surface of mercury. They demonstrate the value of the proposed spreading coefficient as a criterion of spreading.

3. Monomolecular films are produced on water only when the spreading coefficient has a relatively high value. Since these high values seem to occur only when the spreading substance contains a polar group in its molecules, it may be concluded that the presence of such groups is essen-

tial for spreading on water to a monomolecular film, but not at all essential for the production of a film which is thicker than this.

4. Definitions are given of the terms film, composite-film, and non-composite-film.

5. Contrary to the opinion of some writers, benzene is found to spread upon a clean water surface.

6. The non-spreading of organic liquids upon water is brought about by the presence in the organic molecule of chlorine, bromine, iodine, =S, =CS, or by phenyl groups.

7. Liquids which do not spread upon water are insoluble in it, but insoluble liquids may spread upon water.

8. Adding camphor to water seems to reduce the value of the spreading coefficient; so many liquids which have low positive coefficients on pure water will not spread on camphorated water; but those whose coefficients are sufficiently high are found to spread.

9. The values of the spreading coefficients of water and organic liquids upon mercury have been found to be positive in every case thus far investigated in this Laboratory. Water and 22 of the other liquids were tested with reference to their spreading upon a pure mercury. All of these liquids were found to spread, as corresponds with the positive values of the coefficients. The coefficients for the spreading of mercury upon water and organic liquids are, on the other hand, all negative. This corresponds with the fact that mercury will not spread upon any of their surfaces.

10. Since the free surface energy of almost all inorganic solids is high, their work of cohesion is high, and the work of adhesion is also high with reference to practically all liquid substances. Since the work of cohesion in water and organic liquids is in general low, the values of the coefficient of spreading of these liquids upon such solids should be positive, and in general their values should be high. Thus the spreading of these liquids should occur upon such solids when their surfaces are pure. The frequently occurring phenomenon of non-spreading is thus indicated to be due to the presence of an already existent film upon the solid substance. The removal of such films may be brought about by vaporization, or by the more common process of substituting one film for another. This is the ordinary function of soap, soap solutions, and other cleansing agents. It is difficult for petroleum to penetrate sands which have been wet by water, and for water to penetrate sands which have been wet by petroleum, though either substitution may be brought about in time. Many oil wells cease to produce petroleum because the sand becomes wet with water. Lubrication, and many other similar phenomena depend upon the wetting of solids by films.

11. The principles worked out in this paper by the use of liquids

should be applicable to the spreading of films upon solids, and this is indeed the main purpose behind the present investigation. Solids have not been used in the experiments on account of the difficulty of determining their surface cohesion, that is their surface tension.

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

SOME APPLICATIONS OF OXYGEN ELECTRODE, AIR ELECTRODE, AND OXIDATION POTENTIAL MEASUREMENTS TO ACIDIMETRY AND ALKALIMETRY

BY N. HOWELL FURMAN

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Introduction

In this investigation an attempt has been made to extend the general principles of electrometric analysis, which have been pointed out by Böttger,¹ Hildebrand,² and others,³ to the problem of the determination of alkali or acid in the presence of strong oxidizing agents. Immediate practical importance centers, of course, in those cases in which the oxidizing agent is highly colored.⁴ In such cases, apparently the only general method available is that of conductance titration. Küster and Grüters⁵ found that the conductance method gave excellent results in the determination of free alkali or acid in the presence of permanganate ion, or of acid in the presence of dichromate ion; the method failed, however, in the determination of free alkali in the presence of chromates.

The author has found that the electrometric method affords a quite general solution to this problem. As the neutral point is passed, sharp inflections are obtained in the titration curves, which are constructed by plotting as abscissas the number of cubic centimeters of reagent used, and as ordinates the electromotive force readings of some one of the following cells.

(A) Platinized platinum	Oxygen air	Acid or alkaline solution of oxidizing agent	Normal calomel electrode
(B) Platinized platinum			
(C) Platinized platinum			
(D) Smooth platinum			

¹ Böttger, *Z. physik. Chem.*, **24**, 253 (1897).

² Hildebrand, *THIS JOURNAL*, **35**, 847 (1913).

³ For an extended bibliography, see W. M. Clark, "The Determination of Hydrogen Ions," Williams and Wilkins Co., 1920, pp. 214, 219, 239, *et seq.*

⁴ Mr. C. D. Marlatt of the Martin Dennis Co., Newark, N. J., pointed out to the author the importance of the measurement and control of the alkalinity of chromate solutions, together with some of the difficulties which he had encountered. (Private communication.)

⁵ Küster and Grüters, *Z. anorg. Chem.*, **35**, 454 (1903).