mother liquor ends of the series, respectively, agreed within the experimental error of 6 parts in one hundred thousand.

The β-ray activities agreed within the experimental error of 1%.

These observations indicate that the nitrates of radium D and lead on the one hand and radium B and lead on the other hand could hardly be separated, if at all, by less than 100,000 crystallizations.

Hence one might infer that the molal solubilities of the nitrates are probably essentially identical. The outcome gives strong experimental support for the hypothesis that isotopes are really inseparable by any such process as crystallization.

CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

THE ORIENTATION OF MOLECULES IN THE SURFACES OF LIQUIDS, THE ENERGY RELATIONS AT SURFACES, SOLUBILITY, ADSORPTION, EMULSIFICATION, MOLECULAR ASSOCIATION, AND THE EFFECT OF ACIDS AND BASES ON INTERFACIAL TENSION.[1]

(SURFACE ENERGY VI.)

BY WILLIAM D. HARKINS, EARL C. H. DAVIES AND GEORGE L. CLARK.[2]

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Introduction: Double Electrical Layers.

The investigations presented in this paper were started as a study of the effect of chemical constitution upon the energy relations at the surface of a single liquid, and at the interface between two liquids and were sug-

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[1] This paper is a direct continuation of a paper in the March (1917) JOURNAL on "The Structure of the Surfaces of Liquids, and Solubility as Related to the Work Done by the Attraction of Two Liquid Surfaces as They Approach Each Other."

[2] A part of the work in this paper was done by Harkins in 1909 in the Institut für physikalische Chemie and Electrochemie in Karlsruhe, at the suggestion of Professor Fritz Haber, and we are indebted to him for the suggestion that we continue the work in this country. Parts of the paper were presented at the Boston meeting of thel Socety in 1909, and at the New Orleans meeting. Another part was prepared in abstiract for presentation at the Symposium on Colloids held by the American Chemica Society in September, but was not accepted. An abstract of a paper presented at this Symposium by Irving Langmuir gives somewhat similar views to some of those developed by us, and for this reason it has been thought best to publish at once the data we have collected. Our accumulation of data has been greatly delayed by the fact that the correction curve is still incomplete, though work was begun upon it in this laboratory four years ago, and we have wished to hold our other results until they can be made as accurate as possible. The curve is almost complete, and our further results upon this subject will soon be ready for publication. The work of Langmuir and that which we present in this paper, while developed independently from somewhat different starting points, are alike in that we have both developed *the same fundamental idea: that surface tension phenomena in general are dependent upon the orientation and packing of molecules in surface layers, and that the forces involved in this action are related to those involved in solution and adsorption.* Our interest in this subject originated

gested by the work of Haber and Klemenciewicz,[1] Haber and Harkins and of Cameron and Oettinger upon the potential differences at surfaces and their relation to the surface energy changes.

Cameron and Oettinger,[2] using a theory developed by Helmholtz,[3] found that the potential difference at the interface water-glass has the value of approximately five volts. Helmholtz's theory is represented by the formula

$$E = \frac{P}{4\pi\eta\kappa}(\phi_l - \phi_s),$$

where E is the electromotive force between two cross sections of a conducting liquid flowing through a tube of glass or other insulating material, P is the pressure between these two cross sections, η the viscosity of the liquid, κ the specific conductivity of the solution, ϕ_l represents the potential of the liquid and ϕ_s that of the solid insulator. This formula holds where Poiseuille's law is valid, whenever the potential difference between the two cross sections is not led into an external circuit, and in case the last layer of liquid adhering to the glass does not slip. Lamb[4] proposed a modification of the theory in which he assumed that the change of liquid is confined to the last layer. Earlier experimental work than that of Cameron and Oettinger, carried out by Edlund,[5] Haga,[6] Clark,[7] Dorn,[8] Saxen,[9] and Zollner,[10] gave very nearly the same value, which seems at first sight very large for such a potential difference. On the other hand, the electric endosmose experiments of Weidemann,[11] Quincke,[12] and Freund,[13] give considerably smaller potential differences at similar interfaces, but *all of the workers have agreed* (which is most important in this work) *that there is evidence that in all such cases a potential difference of at least a moderate magnitude exists.*

Haber and Klemenciewicz[14] found that the interfaces water-glass and

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in work on the interfaces between liquids, while that of Langmuir originated in work on liquid films, and each worker realizes that the other reached his conclusions independently. We wish at this time to express our appreciation of the very beautiful work which Langmuir has done and is doing on liquid films.

[1] *Z. physik. Chem.*, **67**, 385 (1909).

[2] *Phil. Mag.*, [6] **18**, 586–603 (1909).

[3] *Wied. Ann.*, **7**, 337 (1879).

[4] *Phil. Mag.*, [5] **25**, 52 (1898).

[5] *Wied. Ann.*, **1**, 161 (1877); **9**, 95 (1880).

[6] *Ibid.*, **2**, 326 (1877).

[7] *Ibid.*, **2**, 336 (1877).

[8] *Ibid.*, **5**, 20 (1878); **9**, 513 (1880); **10**, 71 (1880).

[9] *Ibid.*, **47**, 46 (1892).

[10] *Pogg. Ann.*, **148**, 640 (1873).

[11] *Ibid.*, **87**, 321 (1852).

[12] *Ibid.*, **113**, 44 (1879).

[13] *Wied. Ann.*, **7**, 44 (1879).

[14] *Z. physik. Chem.*, **76**, 385–431 (1909).

water-benzene, act as hydrogen electrodes, so that a change from normal concentration of hydrogen ions to the same concentration of hydroxyl ions, causes a change in electromotive force of such a cell amounting to 0.812 volt = 14 × 0.058. Where both solutions are 0.01 N this value becomes 10 × 0.058 = 0.580 volt, and at 0.001 N it becomes 8 × 0.058 = 0.464 volt, so that near the neutral point between acid and base there is a very rapid change in electromotive force.

However, after all allowances are made for the effects of hydrogen or hydroxyl ions, there still remains to be explained the potential which exists between pure water and glass, benzene, oil, or any liquid with which water is not miscible. Thus Hardy, in a paper written in 1911,[1] speaks of the "remarkable" potential difference which he found between oil and the water on which it was floating.

The Polar Setting of Polar Molecules in Surfaces.

The idea that these potential differences and the other energy relations at surfaces, together with certain phenomena of adsorption, colloid formation, and solubility, might be explained on the basis of the polar setting of molecules in surfaces occurred to one of the writers a number of years ago. On the basis of our recent theories of the structure of the atom, that is that the atom consists of a positively charged nucleus, surrounded by a system of widely separated negative electrons, it would seem that in all molecules there would be stray fields, and that on the whole these stray fields might be expected to be more apparent in the vicinity of the atoms which in the molecule occupy a relatively large volume. This idea as to the polar setting in surfaces seems to have occurred to Hardy, as will be seen from the quotation which follows. However, that Hardy himself seemingly did not realize the import of this statement which he wrote, will be seen by those who read his paper, for his interpretation of his work on films and at interfaces is wholly based upon the older ideas. Thus it would seem that he was so thoroughly imbued with the older ideas that he could not use the new ones which came into his own mind. In considering the corpuscular theory of matter he[2] says:

> "If the stray field of a molecule, that is of a complex of these atomic systems, be unsymmetrical, the surface layer of fluids and solids, which are closely packed states of matter, must differ from the interior mass in the orientation of the axes of the fields with respect to the *normal*[3] to the surface, and so form a skin on the surface of a pure substance having all of the molecules oriented in the same way instead of purely in random ways. The result would be the polarization of the surface, and the surfaces of two different fluids would attract or repel each other according to the sign of this surface."

From our work, and from the data in the literature, we find that considerable support can be obtained for the hypothesis that the different

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[1] *Proc. Roy. Soc.*, (*B*) 84, 220 (1911).

[2] *Ibid.*, (*A*) 86, 634 (1911–12).

[3] The emphasis on this word has been added by the writers of this paper.

parts of a molecule may exhibit what may be called different solubilities. If the molecule is short and compact, such a difference would not be perceptible, but in the case particularly of such molecules as are normal derivatives of long hydrocarbon chains, the evidence seems clear. To take as an example a special case, it seems very apparent that in the case of such a long molecule as that of soldium palmitate, $C_{15}H_{31}COONa$, the long hydrocarbon chain is quite insoluble, while that end of the molecule which contains the —COONa group is very soluble. Whether the sodium palmitate molecule will be soluble or insoluble depends upon which of these effects predominates.

Adsorption and the Polar Setting of Molecules in Surfaces.

In order to study the differential solubility of molecules it is necessary to consider both the laws of adsorption, and the energy relations at surfaces, but at first we will give the evidence from the first standpoint alone. From Gibbs' law of adsorption, $\Gamma = \frac{-N}{RT}\frac{d\gamma}{dN}$, where N represents the molar concentration of the solution, γ is the surface tension in dynes per centimeter, and Γ is the excess concentration of the solute per unit of area in the surface of the solution, the amount of adsorption of a solute may be easily judged from the change of the surface tension with the concentration of the solution. However, this equation is *valid only when the concentration of the adsorbed substance in the film is small.* This condition has often been thought to be that the solution must be dilute, but our results on aqueous sodium oleate solutions indicate that the sodium oleate in the film has an exceedingly high concentration at 0.001 *N*, and at 0.002 *N* or less the sodium oleate molecules have become as tightly packed as when the solution is 0.1 *N*, so, in all probability, even at 0.002 *N*, the film consists largely of a layer of sodium oleate molecules, with possibly singly and multiply charged oleate ions, and OH^- or H^+ ions. THE FILM IS THUS ENTIRELY SATURATED EVEN AT THESE LOW CONCENTRATIONS OF THE SOLUTION.

If aqueous solutions are first considered, it will be found that the solvent will reject the hydrocarbon chain, but retain the HOOC— or NaOOC— group. So far as our measurements have now extended, the adsorption of a substance in a benzene-water interface is greater for any certain salt than it is in the water surface, whenever the organic radical is of such a nature that it would be expected to be soluble in benzene, but whether or not this is a general relationship, has yet to be determined. When other active groups which are joined to hydrocarbon chains are considered, it is found that the same rules hold. Thus acetonitrile, with two carbon atoms, is miscible with water in all proportions, but the solubility decreases rapidly with the length of the hydrocarbon chain, so much so that while propionitrile is quite soluble, the six carbon atom nitriles are only *very slightly* soluble; methyl alcohol dissolves short chain paraffins, but not those with long chains while in C_5H_{12} it is itself almost insoluble.

We thus find that a polar group, such as COOH, SO_3H, OH, CN, NH_2, etc., and their salts will drag into solution in water a short slightly polar chain, such as a hydrocarbon, but as the length of the slightly polar chain increases, the solubility of the compound with one end polar and the other slightly polar rapidly decreases. Also, as the length of the slightly polar, which may be called the insoluble end of the molecule, increases, the adsorption in the surface liquid-vapor from a polar solution increases. For example, while the surface tensions at 0° of acetic and butyric acid are, respectively, 28.8 and 27.8, and are therefore not very different, butyric acid lowers the surface tension of water much more rapidly, and is therefore much more adsorbed than acetic acid. The adsorption of the 9 carbon atom acid[1] nonylic acid is much greater than that of butyric acid, so large indeed that in 0.00079 molar solution the γ of water is lowered from 75.3 to 40. The increase in adsorption in such solutions is easily explained if, as already assumed, the water tends to throw out the insoluble radical, but to hold the one which is soluble. If this is true, there should be an average orientation of such solute molecules in a water surface, with the active or polar end toward the liquid and the slightly polar end toward the vapor. At an *interface* betweem two liquids, the polar end would be expected to turn toward the polar liquid, and the slightly polar end toward the slightly polar liquid. Also, in the case of a single pure liquid, if it is of a polar type, it would be expected that the polar ends of the molecules would have an orientation toward the *inner* side of the surface. From this standpoint the ends of the molecules which stand outward in the surface of a pure substance consisting of molecules containing a moderately long paraffin chain attached to a polar group, should not be very different from those in a liquid paraffin, since in both cases the extreme outer surface would be made up of paraffin groups. The more direct evidence in regard to the surface of pure liquids will be considered later.

From the standpoint of the ideas thus far presented, the positive adsorption in a liquid surface of organic acids or salts of organic acids, depends upon the fact that one end of the molecule is less soluble than the other end; in other words, as indicated by the values given in the previous paper, the attraction of the solvent for one end of the molecule is much greater than that for the other. The positive or negative adsorption in liquid surfaces from the liquid is simply due to the fact that most substances are either more or less soluble in the surface of a liquid than in the body of the liquid. Thus a substance which is dissolved in a liquid will be neither positively or negatively adsorbed only when it is exactly

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[1] Forch, *Wied. Ann.*, **68**, 811 (1899).

the same as the solvent in its properties. Since no substance other than the solvent meets this condition, all solutes must be adsorbed either positively or negatively. However, if the solute is much like the solvent, the adsorption may be so small as not to be recognized experimentally. If, as will be later assumed, the molecules in the surface of a pure liquid are set in a much more definite orientation than those in the interior of a liquid, this fact alone should make the solubility of solutes in the surface different from that in the liquid. In addition to this the surface is a region of discontinuity, which would also affect the relative solubility of the solute.

Since, as the laws of thermodynamics show, any process which will occur of itself in the surface will be accompanied by a decrease of free energy, that is of surface tension, a substance will be more soluble in the surface than it is in the liquid whenever its presence in the surface decreases the free surface energy (Gibbs' Law). A substance which in a surface makes the transition to the adjacent phase less abrupt will reduce the surface tension, and substances which make the transition less abrupt are those which are more like the adjacent phase than is the liquid itself. This is but another example of the application of the most general of all solubility principles, "*similia similibus solvuntur.*" However, in determining whether certain molecules can make the transition from the solvent to the adjacent phase less abrupt, the properties of the whole molecules of the solute cannot be taken into consideration, since it is the end of the molecule which projects into the adjacent phase which must meet this condition. Where water is the solvent, inorganic salts and bases are less soluble in the surface than in the interior of the liquid, and so are negatively adsorbed, since they have higher surface tensions than water, and if they were to heap up in the surface they would increase the free surface energy, which is contrary to the second law of thermodynamics. If the salt of a long hydrocarbon chain is the solute, then the hydrocarbon if it were alone would have a much smaller surface tension than water, so it is forced to the surface, while the —COOM group remains dissolved in the water, or at least united to the water by an attraction of a chemical nature. On the other hand, acetic acid has a higher surface tension than either chloroform or carbon tetrachloride, yet it lowers the surface tension of either of them when present in small percentages.

Since, however, the molecules in the surface may be oriented, and since the electromagnetic fields of different kinds of molecules undoubtedly have a mutual influence which would not be entirely colligative, it might be easily possible for a solute A, which when alone and pure, has a larger surface tension than the solvent B to be positively adsorbed, and lower the surface tension of B. In the case of binary liquid mixtures, where the concentration of the substance present in the smaller amount is still moderately high, Gibbs' adsorption formula cannot be expected to hold. So it is not surprising that certain binary mixtures have a minimum point in their surface-tension curve. Examples of such mixtures, as found by Whatmough,[1] are CS_2 and dichloroethylene, acetic acid and ethyl iodide, acetic acid and tetrachloromethane, acetic acid and benzene, acetic acid and $CHCl_3$, tetrachloromethane and chloroform, benzene and ethyl iodide. The explanation of such surface-tension relations as this is undoubtedly much the same as that which would explain compressibility of the solutions, since Whatmough found with these mixtures that the surface-tension curve is similar to the inverted compressibility curve.

In the consideration of the orientation of molecules in surfaces it has seemed important to know the magnitude of the effects of ions on surface tension, so the next section of the paper will be devoted to that subject.

The Effects of Acids and Bases on the Interfacial Tension between Water and a Second Liquid Phase.

The importance of the effect of acids and bases on interfacial tension has been pointed out by Haber and Klemenciewicz.[2] An active part of a muscle is always electrically negative toward the parts at rest, and the active muscle is acid in reaction while the resting muscle is slightly alkaline. An acid reaction always causes the phase which corresponds to the water at the water-benzene interface, to become negative and in the muscle this aqueous phase is represented by the sarcoplasma in which the fibrilles (sarcostyles) of the muscles are imbedded. As has already been stated, such an interface acts as a hydrogen electrode, and therefore exhibits large changes of potential for small changes of hydrogen and hydroxyl ion concentration near the neutral point between acid and base. It is of importance in this connection that the blood and most of the other fluids of the body are very slightly alkaline ($C_{H^+} =$ between 6×10^{-8} and 2×10^{-8}, $C_{OH^-} = 1.2 \times 10^{-7}$ to 3.6×10^{-7}. The production of carbonic or lactic acids in the muscles during activity changes the reaction to acid, and thus gives a change of electromotive force which locally may be not inconsiderable, even though there is only a very little difference in carbonic acid concentration between venous and arterial blood, for the concentration of the blood is measured only after considerable diffusion has taken place and the blood is kept very nearly neutral by the presence of buffers (carbonates, phosphates, etc.). There is thus a sufficient explanation for the electrophysiological phenomena in the organism.

Bernstein[3] has suggested that the motions of the muscles are due to changes of the surface tension. Now since a change of the electrical

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[1] *Z. physik. Chem.*, 39, 169, 190 (1901).

[2] *Loc. cit.*

[3] Pflüger's *Archiv. gesampte Physiologie.* 85, 271 (1901); 122, 129 (1908); *Naturwissenschaftl. Rundschau,* 1901, 413, and 1904, 197.

potential at a liquid phase boundary must give a change in surface tension, the following provisional hypothesis might be made in regard to the motions of the muscles. In some way a chemical change of slightly stable molecules causes acid production, which changes the phase boundary potential, and this in turn causes a change in surface tension, which would be sufficient to account for the motion of the muscles, provided the magnitude of the surface-tension change is sufficiently great. Bernstein found that the microscopically observable structure of the structural elements of the muscles was not sufficiently fine to account for muscular action, even on the basis of capillary changes of a moderate magnitude. Now since the potential changes are fully as apparent at water-glass, or water-benzene interfaces as in the muscles, if the changes of surface tension in the muscles are electro-capillary in nature, then the effect might possibly be observable in the case of the benzene-water interface. The point at issue is whether the change of surface tension of electrocapillary origin is of moderate magnitude or is so small as to be practically unimportant. It is just on this point that we find practical agreement in the literature. Many references can be cited from papers in which important conclusions in regard to physiological processes, emulsification, surface energy, etc., have been drawn, from the supposed fact that a base lowers the surface tension at the water-benzene interface, and with great rapidity near the neutral point. This was the result found experimentally by von Lerch,[1] working in Nernst's laboratory, in 1902.

There are a number of facts obtained by qualitative observations which seem to support von Lerch's conclusion. Since this is an important point, some of these observations will be described. Wilson[2] states:

> "When chloroform is placed in a test tube or other vessel of glass, standing on a horizontal surface, it exhibits, like other substances which wet a solid, a curved surface with the concavity upwards. If water or an aqueous solution of nitric, sulfuric, or muriatic acid be poured upon the stratum of chloroform. the surface of the latter immediately changes the direction of its curve, and becomes convex upwards, the convexity induced being however, much greater than the previous concavity. If, on the other hand, an aqueous solution of potash soda, or ammonia. be placed above the chloroform. the latter ceases at its upper limit to present a serviceable curvature upwards or downwards, and shows a surface which, to the unassisted eye, appears to be flat."

Bancroft, in a paper on emulsions,[3] explains this flattening caused by bases as follows:

> "Swan's hypothesis that the flattening takes place only when chemical action is possible, is proved wrong by the fact that benzene acts exactly in the same way. While the flattening is clearly due to a change of surface tension it cannot depend on the absolute value of the water phase, because Wilson found the effect of alkali to be the

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[1] Drude's *Ann.*, 9, 434 (1902).

[2] *J. Chem. Soc.*, 1, 174 (1848); see also *J. Phys. Chem.*, 19, 276.

[3] *J. Phys. Chem.*. 19, 280 (1915).

same qualitatively whether sodium chloride was present or not, whereas the addition of salt increases the surface tension of the water phase. What happens is that hydroxyl is adsorbed at the dineric interface, lowering the surface tension and causing the organic liquid to flatten. This is confirmed by the experiments of von Lerch, who determined the surface tension by means of the rise in capillary tubes."

If, as von Lerch has found, the interfacial tension of an aqueous solution of a base against benzene decreases very rapidly near the neutral point, then since a dilute strong acid has almost no effect on this interfacial tension, it should be possible to use this change in surface tension as an indicator between a strong acid and a strong base. On trying this by the capillary height method in 1909 it was found by Harkins that indeed this procedure would serve as an indicator in case the glass of the capillary tube was not of too good quality. Even with Jena hard glass, however, there was a slight indication of the change, but of nowhere nearly so great a magnitude as that obtained by von Lerch, who found that 0.27 *N* sodium hydroxide caused the very great decrease of 36%.

The fact that the capillary tube method in no case gave the same results in duplicate determinations unless the time the solution was kept in the tube was nearly the same, and that even quartz capillaries gave very poor results, suggested that the capillary height method is not suited for the solution of such a problem as this.

Results obtained on a number of strong bases, by the drop weight method as corrected by Harkins and Brown, show that they have little effect upon the interfacial tension benzene-water. At the first addition of base there is seemingly a very slight drop in interfacial tension of only 1% or 2%, and then for higher concentrations than 0.001 *N* the surface tension rises with the concentration of the base. This very small drop is probably caused by the electrocapillary effect, but the magnitude of the change seems too small to account for the movement of the muscles.

That the explanation given for the effect of a base in flattening a benzene-water interface, that it is due to a lowering of the surface tension (and it would have to be a very large lowering to account for the phenomenon) is entirely incorrect, is evident when it is found that when the concentration of the base is sufficient to cause the flattening, the *increase* of interfacial tension is very large. Thus at 20° where the interfacial tension benzene-pure water is 35.03 dynes, the corresponding value for a solution 5.92 *N*, which gave a good flattening effect, is 47.07, or an increase of more than 34%. The effect is probably due to the change in the angle of contact caused by the presence of the base.

While the results obtained by us seem to indicate that the theory that muscular motion is due to the action of the phase boundaries in the muscles as hydrogen electrodes and the resultant electrocapillary effect, is not supported by our measurements, they do not have any bearing on the question as to whether muscular motion is due to some other capillary phenomenon. In fact it has been very difficult for us to think of any force other than that of surface tension, which could be used to account for the motion of the muscles. We would like to suggest that the changes in capillarity are much more likely to be due to other kinds of adsorption than that in which the hydrogen and hydroxyl ions act as they do on a reversible hydrogen electrode, in other words, to adsorptions in which the chemical nature of the surface has more effect than it does at a hydrogen electrode.

One of the most prominent of theories of muscular motion at the present time is that it is due to the imbibition of water under the influence of acids or bases, that is to the swelling of the gel in a direction transverse to the long axis of the muscle and a shortening in the longitudinal direction. The cause of this phenomenon is not known, but supposedly it is due to adsorption of the acid or base at the phase boundaries.

According to our ideas, which we hope to test fully, the necessary condition for an adsorption of this nature is quite likely that polar groups (such as COOH, OH, NH_2, or any others which are polar) must be present in the molecule of the adsorbing substance. Such groups are present in gelatin and fibrin which are often used in experiments on imbibition, and the effects of acids, bases, and salts on this phenomenon.

Table I and Fig. 1 give the data for the change of the interfacial tension between water and benzene as influenced by sodium hydroxide, barium hydroxide, and hydrochloric acid. The data on hydrochloric acid were obtained in this laboratory by Harkins and Humphery who used the capillary height method. The results on the bases are those given by the drop weight method. This latter method involves the use of a correction curve, as was first pointed out by Rayleigh. This curve was calculated on a theoretical basis by Lohnstein, but his assumptions and calculations were such as to give results about 5% in error in the most used part. A preliminary experimental determination of this curve was made by Harkins and Humphery, and a very careful investigation in regard to its position is now under way in this laboratory. While the curve is now more accurately known than ever before, and the results obtained are very much more accurate than those given by the capillary height method, it has been thought best to give the values of the corrections ($f\ r/a$) which have been used in the calculation of the surface tension, so that they may be possible at any time to recalculate the results on the basis of an even more correct function.

The sodium hydroxide used in this work was prepared from sodium from two well-known manufacturers, designated by (K.) and (B.). In all cases about four-fifths of each stick was washed away by conductivity water and rejected. A few results were obtained in solutions made directly from sodium, but no appreciable difference was found.

The results obtained on acids and bases therefore indicate that marked changes in the interfacial tension between two liquids of the nature of benzene and water, caused by adsorption, cannot be attributed to the adsorption of hydroxyl ions. The cause of such a behavior in the case of such substances as gels must be of some other nature, such, for example, as molecular adsorption, or by the adsorption of H^+ or OH^- ions by highly active or very complex molecules.

TABLE I.—THE EFFECTS OF ACIDS AND BASES ON THE INTERFACIAL TENSION BETWEEN WATER AND BENZENE.

Interface at 25° between a Water Solution of Barium Hydroxide and Benzene, Mutually Saturated by Rotating for 12 hrs. in Thermostat.

Point.	N.	Interfacial density.	W.	a^2.	r/a.	$f\,r/a$.	γ.
41	0.0000	0.12331	0.06646	57.39	0.626	0.630	34.69
42	0.0001	0.12331	0.06630	57.25	0.627	0.630	34.60
43	0.001	0.12343	0.06406	55.35	0.638	0.629	33.49
44	0.01	0.12416	0.06397	55.04	0.640	0.628	33.49
45	0.1	0.13246	0.06539	52.90	0.654	0.626	34.34

Interface at 25° between a Water Solution of Sodium Hydroxide and Benzene, Mutually Saturated by Rotating for 12 hrs. in Thermostat.

46	0.0000	0.1233	0.06629	57.25	0.627	0.630	34.60
47	0.0005	0.1233	0.06548	56.55	0.631	0.630	34.17 K.
48	0.011	0.1239	0.06609	56.80	0.630	0.630	34.49 B.
49	0.019	0.1241	0.06617	56.77	0.630	0.630	34.53 B.
50	0.021	0.1243	0.06609	56.62	0.631	0.630	34.49 B.
51	0.042	0.1253	0.06553	55.78	0.635	0.629	34.25 K.
52	0.142	0.1296	0.06597	54.37	0.644	0.628	34.54 K.
53	0.184	0.1319	0.06594	53.49	0.649	0.627	34.51 B.
54	5.92	0.3354	0.08647.	28.63	0.886	0.604	47.07 B.

WATER-SOLUTION-BENZENE.

Hydrochloric Acid (H, H).

Conc., normal........	0.000	0.0049	0.0098	0.0492	0.0980	0.987
Surface tension........	34.64	34.68	34.67	34.63	34.69	34.81

Energy Relations at Surfaces.

The interfaces commonly called surfaces are of several kinds: liquid-vapor, liquid-liquid, liquid-solid, and solid-solid. The thermodynamics of saturated films has been treated by Dupre,[1] Lord Rayleigh[2] and more thoroughly by Gibbs[3] and by Einstein.[4] The following treatment is somewhat different from that presented by any of these workers, and has some advantages:

The surface film may be either saturated or unsaturated, and a part of the treatment presented will be applicable to either case.

Let S = the entropy of the whole surface, s of unit area.
U = intrinsic energy of the total surface.
u = the intrinsic energy of unit area.

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[1] "Theorie Mecanique de la Chaleur" (Paris. 1869).

[2] *Phil. Mag.*, [5] **30**, 461 (1890)

[3] Scientific Papers. Vol. I. p. 219. *et seq.* (1906).

[4] *Ann. Physik*, **4**, 513 (1901).

γ = the free surface energy per unit area, or the surface tension per unit length.
c = the specific heat of the surface, where specific refers to unit area and not to unit mass.
A = the area of the film.
l = the latent heat of the surface per unit area.
Q = the total heat added to the surface.

These quantities may be thought of as applying to a film of infinitesimal thickness, but since this is not the true thickness for the actual film, they represent the surface densities. Thus U, as Gibbs states, denotes the excess of the energy of the actual mass which occupies the total volume considered, over that energy which it would have if on each side of the surface the density of energy had the same uniform value quite up to that surface which it has at a sensible distance from it.

From the first law

$$dQ = d(Au) - \gamma\, dA = A\frac{\partial u}{\partial T}\, dT + \left[A\frac{\partial u}{\partial A} + (u - \gamma)\right] dA \qquad (1)$$
$$= C\, dT + l\, dA.$$

This equation is perfectly general.

We will define c as follows:

$$c = \frac{1}{A}\left(\frac{dQ}{dT}\right)_{dA\,=\,0} = \frac{du}{dT} \qquad (2)$$

Equation 1 now becomes:

$$dQ = Ac\, dT + l\, dA = AC\, dT + (l + \gamma)\, dA - \gamma\, dA \qquad (3)$$

Let the film be saturated, and the definition of a saturated film will be that u and γ are functions of T only.

$$d(Au) = A\frac{du}{dT}\, dT + u\, dA = Ac\, dT + (1 + \gamma)\, dA \text{ is an exact differential,} \qquad (4)$$

$$\text{and } c,\ l = f(T) \text{ only.} \qquad (5)$$

$$c = \frac{\partial}{\partial T}(l + \gamma) = \frac{du}{dT}. \qquad (6)$$

$$u = l + \gamma. \qquad (7)$$

$$l + \gamma = \int c\, dT \text{ and is a definite function of T.} \qquad (8)$$

From the Second Law

$$dS = \frac{dQ}{T} = \frac{Ac}{T}\, dT + \frac{l}{T}\, dA \text{ is an exact differential.} \qquad (9)$$

$$\frac{c}{T} = \frac{\partial}{\partial T}\left(\frac{l}{T}\right) \quad\text{or}\quad c = \frac{\partial(l/T)}{\partial \ln T}. \qquad (10)$$

Combine (6) and (10), and

$$T\frac{\partial}{\partial T}\left(\frac{l}{T}\right) = \frac{\partial}{\partial T}(l + \gamma), \qquad (11)$$

or

$$\frac{\partial l}{\partial \mathrm{T}} - \frac{l}{\mathrm{T}} = \frac{\partial l}{\partial \mathrm{T}} + \frac{\partial \gamma}{\partial \mathrm{T}}.$$

or

$$l = -\mathrm{T}\frac{\partial \gamma}{\partial \mathrm{T}} = -\frac{\partial \gamma}{\partial \ln \mathrm{T}}. \qquad (12)$$

Equation 7 now becomes

$$u = (\gamma + l) = \gamma - \mathrm{T}\frac{\partial \gamma}{\partial \mathrm{T}}. \qquad (13)$$

$$c = \frac{\partial}{\partial \mathrm{T}}\left(\gamma - \mathrm{T}\frac{\partial \gamma}{\partial \mathrm{T}}\right) = \frac{\partial \gamma}{\partial \mathrm{T}} + \frac{\partial l}{\partial \mathrm{T}} = \frac{\partial l}{\partial \mathrm{T}} - \frac{\partial l}{\partial \mathrm{T}} - \mathrm{T}\left(\frac{\partial^2 \gamma}{\partial \mathrm{T}^2}\right)$$

or

$$c = -\mathrm{T}\left(\frac{\partial^2 \gamma}{\partial \mathrm{T}^2}\right). \qquad (14)$$

Equation 1 is fundamental for saturated and unsaturated surfaces, and Equations 13 and 14 for saturated films.

The experimental results indicate that over moderate ranges of temperature γ is a linear function of the temperature, or $\frac{d\gamma}{d\mathrm{T}} = k$. So long as this is true u, the total surface energy per unit area, is independent of the temperature. This constancy of u makes it a very much more characteristic function than either the free surface energy or the latent heat of the surface (1). Table II shows that, indeed, the total surface energy is not only largely independent of temperature, but is also very characteristic of any special class of compounds. In so far as γ deviates from a linear function u will vary with the temperature, so that even a greater regularity might have been obtained by calculating u from data taken at corresponding states. However, the regularities in the values of u as they have been obtained are extremely striking.

So long as $\frac{d\gamma}{d\mathrm{T}}$ is a straight line, c, which is equal to $-\mathrm{T}\frac{d^2\gamma}{d\mathrm{T}^2}$, is zero; or the superficial specific heat is zero, as was found by Einstein. This indicates that *under this condition* all of the energy of formation of a surface ($= u$ or $\gamma + l$) goes into the surface in a potential form, and this in turn seems to show that the energy is stored up by some configuration of the surface layer. The fact that the total surface energy is almost independent of the temperature indicates that this configuration is almost the same for various temperatures, but it is quite likely that there may be some change in the relative distances of the molecules due to thermal expansion. Although thus far what we have found agrees well with the ideas of Einstein, our other results do not so well agree with a generalization which he introduces, that for every atom in the molecule there is a field of molecular attraction which is independent of the manner in which it is joined to other atoms, and that the summation of all these atomic attractions determines the free surface energy. This special question will be treated in a paper which is now in preparation.

If we now imagine that inside a liquid plane area of 1 sq. cm. exists, and then pull the liquid apart over this area, so that two surfaces each 1 sq. cm. in area are formed, then, as shown in the previous paper, the increase in free energy is 2γ. Now Equation 13 shows that at the same time there is a cooling of the surface equal to $2\,l$, so that the kinetic energy of the molecules aids in pulling the surfaces apart. The total energy $2u$ involved in this process may be imagined to be used up, (1) in giving orientation to the two sets of molecules on both sides of the imaginary plane, while still in the liquid, and (2) in pulling the two oriented surfaces apart. By this it is not meant that the process takes place in this order, but only that the end result is the same as the result of these two steps. While we have at present no way of determining the relative amounts of energy involved in the two steps, it would seem that the amount of energy involved in (1) is relatively small, and that the greater amount is that of step (2). Now, if we knew the laws according to which the electromagnetic forces vary in the fields between and in the molecules which make up the surface layers, it would be possible to get a solution of our problem. However, since this is not known, it seems better to solve the converse problem, that of determining the rate at which these forces fall off, from the data on surface energy.

Equation 12 indicates that if the free surface energy decreases with the temperature, as is usually the case, the formation of the surface will have a cooling effect, while if it increases with the temperature, as it does in the case of the two anisotropous liquids, ethyl *p*-azoxybenzoate, and ethyl *p*-ethoxybenzalamino-α-methyl-cinnamate, there will be a heating effect. In either case the first effect is to increase the free surface energy. It is evident that a contraction of an ordinary surface lowers its tension, and that the free surface energy of a fresh surface, between two phases which may exist together, is greater than that of an old one. If a surface is thought of as being formed with infinite speed, then the changes which follow are such as to lower the free energy.

From thermodynamics we learn that the arrangement of the molecules in the surface of a liquid must be such as to make the free surface energy (γ) a minimum. Now, since

$$\gamma = u - \mathrm{T}s, \tag{15}$$

and when the change is not isothermal T changes, and when the change is not reversible the superficial entropy (s) changes, the condition for an isothermal reversible change in the surface is that there shall be a decrease in the total superficial energy (u) just equal to that of the superficial free energy (γ), so under the given conditions the configuration must be such as to make the total surface energy a minimum.

According to Jaeger, if curves are plotted with γ as the vertical axis, and with T horizontal, the curves are of three types, all of which slope rapidly downward as the temperature increases. The most common type of γ, T curves is type 3, which is convex toward the T axis. If we assume that all of the three curves begin at the same point on the γ axis, and end at a common point on the T axis, the curves take the form given in Fig. 1.

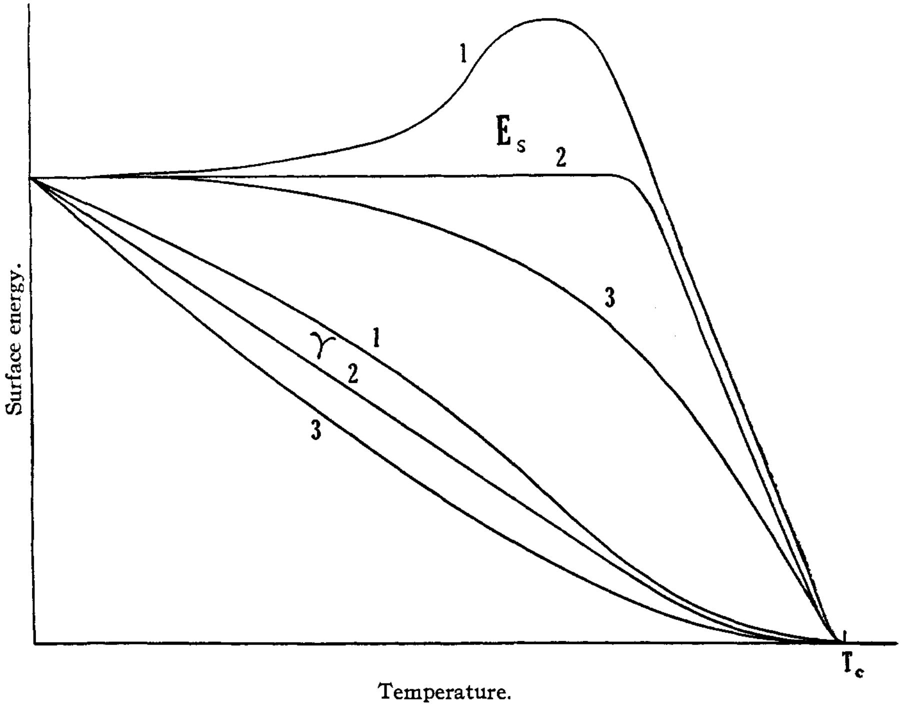


Fig. 1.—The free energy (γ) and the total energy (E_s) of liquids.

The curve representing the total surface energy is given by Curve 3*a*. This curve at first slopes gently, and finally rapidly downward when the γ curve becomes almost parallel to the T axis. When the curve is linear the total energy remains constant until this curve becomes convex to the T axis, when the *u* curve falls very rapidly. It will be seen that the type 1 curve for γ must change into a type 3 curve before it reaches the T axis.

These relations indicate that the specific heat of the surface is not wholly independent of the temperature, and that it approaches zero with extreme rapidity as the critical temperature is approached, so the surface film thickens rapidly and rapidly loses the orientation of its molecules just before the critical temperature is reached.

TABLE II.—THE TOTAL AND FREE SURFACE ENERGIES OF LIQUIDS, THE TEMPERATURE COEFFICIENT OF SURFACE TENSION, AND THE LATENT HEAT OF THE SURFACE.

No.	Name.	γ_0.	$273\frac{d\gamma}{dt}$.	E_s.	$\frac{d\gamma}{dt}$.	$\frac{d\gamma/dt}{\gamma_0}$.	Temp.	t.	γ_t.	M. W.	Obs.
			I. Inorganic Compounds.								
1	Water, H_2O	75.87	42.25	118.1	0.1511	0.00199					B. D.
2	Bromine, Br_2	51.0	144.5	195.5	0.5300	0.01040					Quincke
	Bromine, Br_2	48.24						0°	48.24		
3	Sulfur, S	60.27	3.82	64.09	0.0140	0.000232					
4	Sulfur chloride, S_2Cl_2	45.73	37.90	83.6	0.139	0.00304	15.5–78.3°	15.5	42.3		R. S.(c)
5	Thionyl chloride, $SOCl_2$	34.50	38.83	73.3	0.142	0.00412	19.8–45.9	19.8	30.8		R. S.(c)
6	Sulfuryl chloride, SO_2Cl_2	32.24	38.83	71.1	0.142	0.00440	15.9–46.3	15.9	29.0		R. S.(c)
7	Phosphorus trichloride, PCl_3	31.72	35.84	67.6	0.131	0.00413					R. S.(c)
	Phosphorus trichloride, PCl_3							35.6	27.39		M. B.(c)
8	Phosphorus oxychloride, $POCl_3$	35.20	35.43	70.6	0.130	0.00369					R. S.(c)
9	Carbon bisulfide, CS_2	37.71	43.91	81.6	0.1607	0.00426					R. S.(c)
	Carbon bisulfide, CS_2	33.9	37.9	71.8	0.139	0.00409	(—21)–21.5	21.5	30.9	76.14	J. K.
	Carbon bisulfide, CS_2							20.13	32.65		M. B.
10	Silicon tetrachloride, $SiCl_4$	18.75	28.63	47.4	0.105	0.00560	18.9–45.5	18.9	16.3		R. S.(c)
11	Nickel tetracarbonyl, $Ni(CO)_4$	16.79	30.08	46.8	0.110	0.00655	19.8–45.9	19.8	14.2		R. S.(c)
12	Nitrogen tetroxide, N_2O_4	30.67	45.73	76.4	0.167	0.00544					R. S.(c)
			II. Paraffin Hydrocarbons.								
13	Hexane, C_6H_{14}	21.31	28.15	49.5	0.1032	0.00484					M.(c)
14	(Cyclohexane, C_6H_{14})	(29.8)	(45.8)	(75.6)	(0.168)	(0.00564)	9–40				J.
15	Octane	23.36	25.04	48.4	0.092	0.00394					R. S.(c)
16	Decane (diisoamyl), ($C_{10}H_{22}$)	23.76	22.86	46.6	0.084	0.00353					M. (c)
17	Liquid paraffin	32.38	21.80	54.2	0.0798	0.00246					H. D.
			III. Halogen Derivatives.								
18	Chloroform, $CHCl_3$	28.77	30.94	59.7	0.1134	0.00394					R. A.
	Chloroform, $CHCl_3$	29.70	36.60	66.3	0.134	0.00461	(—22)–25				J.
19	Carbon tetrachloride, CCl_4	29.35	32.84	62.2	0.120	0.00409	11.8–68.0	11.8	26.93		R. G.(c)
	Carbon tetrachloride, CCl_4	29.28	33.81	63.1	0.124	0.00423	21–45.9	21.0	25.85	153.8	W. S.(c)
	Carbon tetrachloride, CCl_4	28.50	34.90	63.4	0.128	0.00449	(—18)–25.0				J.
20	Ethyl iodide, C_2H_5I	33.53	37.51	71.0	0.137	0.00409					R. S.(c)
	Ethyl iodide, C_2H_5I	30.4	29.4	59.8	0.108	0.00354	(—20.5)–20.4	20.4	28.1		J. K.
21	Ethylene chloride, $C_2H_4Cl_2$	35.31	37.95	73.3	0.139	0.00394	34.1–60.0	34.1	30.57		M. B.
	Ethylene chloride, $C_2H_4Cl_2$	34.1	38.9	73.0	0.142	0.00417	(—20)–29.9	29.9	30.1		J. K.
22	Ethylidene chloride, $C_2H_4Cl_2$	28.15	33.31	61.5	0.122	0.00433	34.1–56.9	34.1	23.99		M. B.
	Ethylidene chloride, $C_2H_4Cl_2$	25.7	31.3	57.0	0.115	0.00447	(—21)–30.4	30.4	22.4		J. K.

23	Ethylene bromide, $C_2H_4Br_2$	40.51	35.87	76.4	0.131	0.00323					R. A.
24	Isobutyl bromide, $(CH_3)_2.CH.CH_2Br$	27.1	31.0	57.1	0.123	0.00454	(—20)–25°				J.
25	Acetylene tetrachloride, $C_2H_2Cl_4$	36.7	35.9	72.6	0.132	0.00359	(—21)–29.9	29.9°	32.7	167.86	J. K.
26	Acetylene tetrabromide, $C_2H_2Br_4$	50.7	34.0	84.7	0.1246	0.00246	(—21)–30.4	30.4	46.7	345.46	J. K.
	IV. Nitroso and Nitro Derivatives.										
27	Nitromethane, CH_3NO_2	39.69	40.04	79.7	0.146	0.00368					M.(c)
	Nitromethane, CH_3NO_2	38.1	32.6	70.7	0.119	0.00313	(—21.5)–30.1	30.1	34.3	61.03	J. K.
28	Nitroethane, $C_2H_5NO_2$	34.92	32.86	67.8	0.120	0.00344	16.6–79.6	16.6	32.0		R. S.(c)
29	Dimethyl-nitrosoamine, $(CH_3)_2N.NO$	33.64	33.20	72.8	0.122	0.00363					M.(c)
30	Bromonitromethane, $CH_2(NO_2)Br$	45.7	34.6	80.3	0.127	0.00277	(—18.5)–25.7	—18.5	48.3	139.99	J. K.
	V. Alcohols.										
31	Methyl alcohol, CH_3OH	23.5	19.4	42.9	0.071	0.00306	(—20)–20.8	20.8	22.0	32.03	J. K.
32	Ethyl alcohol, C_2H_5OH	23.3	21.7	45.0	0.080	0.00343	(—24)–25				J.
	Ethyl alcohol, C_2H_5OH	23.99	22.39	46.4	0.082	0.00342					M.(c)
	Ethyl alcohol, C_2H_5OH				0.081						R. G.(c)
33	Propyl alcohol, $CH_3.CH_2.CH_2.OH$	25.32	22.01	47.3	0.081	0.00320					M.(c)
		24.9	21.7	46.6	0.080	0.00321	(—21)–25				J.
34	Iso-propyl alcohol, $CH(CH_3)_2OH$	23.21	20.44	43.6	0.075	0.00323					M.(c)
35	Butyl alcohol, $CH_3(CH_2)_3OH$	26.11	22.16	48.3	0.081	0.00310					M.(c)
36	Iso-butyl alcohol, $CH(CH_3)_2CH_2OH$	24.4	21.7	46.1	0.079	0.00324	(—12)–50				J.
	Iso-butyl alcohol, $CH(CH_3)_2CH_2OH$	24.08	22.00	46.1	0.081	0.00368					R. S.(c)
37	*n*-Butyl alcohol, C_4H_9OH	25.87	22.82	48.7	0.084	0.00325					R. S.(c)
38	Iso-amyl alcohol, $(CH_2)_2CH(CH_2)_2OH$	25.71	22.25	48.0	0.0778	0.00303					R. S.(c)
39	*n*-Octyl alcohol, $CH_3(CH_2)_7OH$	29.10	21.70	50.8	0.0795	0.00273					D. H.
40	Glycol, $C_2H_4(OH)_2$	49.34	24.52	73.9	0.0935	0.00189					R. S.(c)
41	Glycerin, $CH_2OH.CHOH.CH_2OH$	65.28	16.35	81.6	0.0598	0.00096					W.
	Glycerin, $CH_2OH.CHOH.CH_2OH$	70.6	47.3	117.9	0.173	0.00245	26–74.5	26	66.1	92.06	J. K.
42	Allyl alcohol, $CH_2:CH.CH_2.OH$	27.29	24.31	51.6	0.081	0.00297					M.(c)
	VI. Ethers.										
43	Ethyl ether, $C_2H_5.O.C_2H_5$	19.31	29.06	48.4	0.117	0.00606					R. S.(c)
	Ethyl ether, $C_2H_5.O.C_2H_5$	19.2	28.0	47.2	0.102	0.00531	(—20)–30				J.
44	Ethyl propyl ether, $C_2H_5.O.C_3H_7$	21.59	30.15	51.7	0.110	0.00509					
	VII. Esters and Salts.										
45	Methyl formate, $HCOOCH_3$	28.50	42.82	71.3	0.1569	0.00551					R. S.(c)
46	Ethyl formate, $HCOOC_2H_5$	34.25	36.57	70.8	0.097	0.00283					M.(c)
	Ethyl formate, $HCOOC_2H_4$	26.30	37.20	63.5	0.136	0.00517	(—16)–25				J.
47	Ethyl chloroformate, C_2H_4ClCOO	29.6	38.0	67.6	0.139	0.00469	(—21)–25				J.
	Ethyl chloroformate, C_2H_5ClCOO	29.21	34.12	63.3	0.1246	0.00426					R. S.(c)

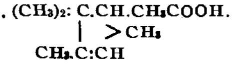
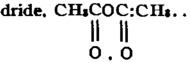
TABLE II (*continued*).

No.	Name.	γ_0.	$273 \frac{d\gamma}{dt}$.	E_S.	$\frac{d\gamma}{dt}$.	$\frac{d\gamma/dt}{\gamma_0}$.	Temp.	t.	γ_t.	M. W.	Obs.
48	Amyl formate, $HCOOC_5H_{11}$	25.3	25.42	50.7	0.093	0.00368					M.(c)
49	Ethyl urethane, $NH_2COOC_2H_5$	36.68	25.78	62.5	0.0944	0.00257				89	G. B.
	Ethyl urethane, $NH_2COOC_2H_5$	37.4	26.7	64.1	0.098	0.00621	60–105°	60°	31.5		T. M.
50	Ethyl acetate, $CH_3COOC_2H_5$	26.84	34.59	61.4	0.1267	0.00472					R. S.(c)
	Ethyl acetate, $CH_3COOC_2H_5$	26.55	33.70	60.3	0.1234	0.00465					R. G.(c)
	Ethyl acetate, $CH_3COOC_2H_5$	25.5	37.2	62.7	0.136	0.00533	(—21)–25				J.
51	Amyl acetate, $CH_3COOC_5H_{11}$	27.04	26.82	53.9	0.098	0.00362					R. G.(c)
	Amyl acetate, $CH_3COOC_5H_5$	26.6	26.8	53.4	0.098	0.00368	(—20)–25				J.
52	Methyl cyanacetate, $CNCH_2COOCH_3$	41.5	34.9	76.4	0.128	0.00308	(—18)–25				J.
53	Ethyl cyanacetate, $CNCH_2COOC_2H_5$	37.8	30.5	68.3	0.112	0.00296	(—17)–25			113.07	J.
	Ethyl cyanacetate, $CNCH_2COOC_2H_5$	37.86	28.74	66.6	0.105	0.00293	17.5–83.9	17.5	34.91		W. S.(c)
54	Propyl cyanacetate, $CNCH_2COOC_3H_7$	35.9	20.5	56.4	0.075	0.00209	(—21)–25				J.
55	Isobutyl cyanacetate, $CNCH_2COOCH_2CH(CH_3)_2$	32.5	22.4	54.9	0.082	0.00252	(—21)–74				J.
56	Amyl cyanacetate, $CNCH_2COOC_5H_{11}$	31.2	19.6	50.8	0.072	0.00231	(—17)–69				J.
57	Isoamyl trichloroacetate, $CCl_3COOC_5H_{11}$	31.17	26.15	57.3	0.096	0.00308	0–60				M.(c)
58	Ethyl propionate, $CH_3CH_2COOC_2H_5$	25.73	30.28	56.0	0.1108	0.00431					R. A.
59	Methyl isobutyrate, $(CH_3)_2CHCOOCH_3$	25.7	34.4	60.1	0.126	0.00490	(—21)–23				J.
60	Ethyl isobutyrate, $(CH_3)_2CHCOOC_2H_5$	24.6	27.8	52.4	0.102	0.00415	(—21)–25.2				J.
61	Methyl butyrate, $CH_3CH_2CH_2COOCH_3$	28.46	31.00	59.46							R. A.
62	Isobutyl isobutyrate, $(CH_3)_2CHCOO(CH)(CH_3)_2$	24.6	24.0	48.6	0.088	0.00358	(—21)–25				J.
63	Isoamyl butyrate, $C_3H_7COOC_5H_{11}$	26.18	25.93	52.11	0.095	0.00363	0–60			158.2	M.(c)
64	Isobutyl valerate, $C_4H_9COOC_4H_9$	25.21	25.93	51.14	0.095	0.00377	0–60			162	M.(c)
65	Amyl stearate, $C_{17}H_{35}COOC_5H_{11}$	31.36	21.65	53.0	0.079	0.00252	30–60			354	M.(c)
66	Methyl malonate, $CH_2(COOCH_3)_2$	39.39	34.39	73.8	0.126	0.00320					M.(c)
67	Ethyl malonate, $CH_2(COOC_2H_5)_2$	34.02	28.94	63.0	0.1057	0.00311					M.(c)
	Ethyl malonate, $CH_2(COOC_2H_5)_2$	33.6	27.2	60.8	0.100	0.00298	(—20)–26				J.
68	l-Amyl malonate, $CH_2(COOC_5H_{11})_2$	30.37	22.82	53.2	0.0836	0.00275	23–79.3	23.0	27.57	244.19	W. S.(c)
69	Ethyl bromomalonate, $CHBr(COOC_2H_5)_2$	36.4	34.5	70.9	0.126	0.00346	(—20)–26				J.
70	Butyryl malonic diethyl ester, $C_4H_9COOCHCH_2$-$(COOC_2H_5)_2$	33.63	27.27	60.9	0.0999	0.00297	0–60			260	M.(c)
71	Amyl succinate, $(CH_2)(COOC_5H_{11})CH_2.COOH$	22.58	21.56	44.1	0.078	0.00345					M.(c)
72	Diamyl succinate, $(CH_2)_2(COOC_5H_{11})_2$	29.56	20.81	50.4	0.076	0.00257	30–60			258	M.(c)
73	Diethyl oxalate, $(COOC_2H_5)_2$	34.9	28.6	63.5	0.105	0.00301	(—20)–26				J.
	Diethyl oxalate, $(COOC_2H_5)_2$	33.14	29.4	62.5	0.1076	0.00325					
74	Ethyl lactate, $CH_3CH(OH)COOC_2H_5$	31.69	27.55	59.2	0.1009	0.00318				118	M.(c)
	Ethyl lactate, $CH_3CH(OH)COOC_2H_5$	31.63	27.33	59.0	0.100	0.00316	17.3–81.2	17.3		28.9	W. S.(c)
75	Diethyl malate, $CH(OH)COOC_2H_5CH_2COOC_2H_5$	36.22	25.87	62.2	0.0948	0.00262	30–60			125	M.(c)

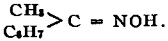
76	Diamyl malate, $CH(OH)COOC_5H_{11}CH_2COOC_5H_{11}$	29.83	17.99	47.8	0.066	0.00221	30–60^b			M.(c)
77	Ocnanthyl malic diethyl ester, $C_6H_{13}COO.CH.COO$-$C_2H_5CH_2COOC_2H_5$	32.28	23.06	55.3	0.084	0.00260	0–60		302	M.(c)
78	Caprilyi malic diethyl ester, $C_7H_5COO.CHCOOC_2H_5$-$CH_2COOC_2H_5$	32.35	24.18	56.5	0.0886	0.00274	0–60		316	M.(c)
79	Pelargonyl malic diethyl ester, $CH_3(CH_2)_7COO.CH$-$COOC_2H_5CH_2COOC_2H_5$	31.99	20.25	52.24	0.074	0.00231	0–60		330	M.(c)
80	Caprinyl malic diethyl ester, $CH_3(CH_2)_8COO.CH$-$COOC_2H_5CH_2COOC_2H_5$	32.37	23.62	56.0	0.0865	0.00267	0–60		344	M.(c)
81	Ethyl caproylmalate, $C_2H_5COOCHOCOC_5H_{11}C_2H_5$-$CO_2CH_2$	32.56	23.54	56.1	0.086	0.00264	8–55.2	8°	30.7	288	R. G. (c)
82	Maleic diethyl ester, $(CH.COOC_2H_5)_2$	34.57	16.90	51.5	0.062	0.00179	19.8–79.3	19.8	32.31	172.01	W. S.(c)
83	Fumaric diethyl ester, $C_2H_2(COOC_2H_5)_2$	34.48	29.59	64.1	0.108	0.00314	17.6–74.1	17.6	31.56	172.01	W. S.(c)
84	Fumaric di-1-amyl ester, $C_2H_2(COOC_5H_{11})_2$	30.99	22.54	53.5	0.083	0.00268	17.4–73.2	17.4	28.64	256.19	W. S.(c)
85	Mesaconic di-1-amyl ester, $C_3H_4(COOC_5H_{11})_2$	31.39	22.54	53.9	0.083	0.00264	27.4–74.5	27.4	28.23	270.2	W. S.(c)
86	Citraconic di-1-amyl ester, $C_3H_4(COOC_5H_{11})_2$	31.24	27.33	58.6	0.100	0.00320	24.8–82.6	24.8	27.86	270.2	W. S.(c)
87	Chloromaleic dimethyl ester, $C_2HCl(COOCH_3)_2$	39.99	33.24	73.2	0.122	0.00305	20.3–75.5	20.3	36.36	178.5	W. S.(c)
88	Chlorofumaric dimethyl ester, $C_2HCl(COOCH_3)_2$	41.22	33.24	74.5	0.122	0.00296	20.6–76.3	20.6	37.51	178.5	W. S.(c)
		41.30	32.05	73.3	0.117	0.00283	30–60				M.(c)
89	Chlorofumaric diethyl ester, $C_2HCl(COOC_2H_5)_2$	36.52	30.99	67.5	0.1125	0.00308	15.6–57.6	15.6	33.67	206.6	W. S.(c)
		36.14	27.27	63.4	0.099	0.00274	30–60				M.(c)
90	Chloromaleic diethyl ester, $C_2HCl(COOC_2H_5)_2$	36.00	27.90	63.9	0.102	0.00283	15.5–70.7	15.5	33.35	206.6	W. S.(c)
91	Chlorofumaric diamyl ester, $C_2HCl(COOC_5H_{11})_2$	32.49	23.11	55.6	0.085	0.00261	27.6–75	27.6	29.22	290.6	W. S.(c)
		31.44	21.08	52.5	0.077	0.00245	30–60				M.(c)
92	Dimethyl tartrate, $CH_3OOC(CHOH)_2COOCH_3$	47.5	26.3	73.8	0.096	0.00202	45–90				J.
93	Diethyl tartrate, $C_2H_5OOC(CHOH)_2COOC_2H_5$	40.3	29.3	69.6	0.107	0.00266	25–75				J.
94	Acetoacetic methyl ester, $CH_3COCH_2COOCH_3$	33.65	29.53	63.2	0.108	0.00321					
95	Acetoacetic ethyl ester, $CH_3COCH_2COOC_2H_5$	34.4	28.5	62.9	0.104	0.00302	(—20)–25				J.
96	Monomethyl acetoacetic methyl ester, CH_3COCH-CH_3COOCH_3	35.7	31.3	67.0	0.114	0.00319	0–25				J.
97	Dimethyl acetoacetic ethyl ester, $CH_3COC(CH_3)_2$-$COOC_2H_5$	31.75	29.19	60.9	0.1068	0.00336					
98	Diethyl acetoacetic ethyl ester, $CH_3CO.C(C_2H_5)_2$-$COOC_2H_5$	30.03	25.50	55.5	0.0904	0.00301					
99	Methyl propyl acetoacetic ethyl ester, $CH_3COC(CH_3.$-$C_3H_7)COOC_2H_5$	32.4	34.0	66.0	0.124	0.00383	0–25				J.
100	Ethyl isocyanate, C_2H_5NCO	33.72	28.92	62.6	0.106	0.00314					
101	Allyl isocyanate, $CH_3CH : CH.NCO$	35.66	32.10	67.8	0.1175	0.00330					
102	Ethyl thiocyanate, C_2H_4SCN	38.52	33.78	72.3	0.1236	0.00321	17.6–78.4	17.6	35.3		R. S.(c)
103	Ethyl isothiocyanate (mustard oil), C_2H_4NCS	38.42	35.74	74.2	0.1308	0.00340	18.4–46.0	18.4	35.0		R. S.(c)

TABLE II (*continued*).

No.	Name.	γ_0.	$273\frac{d\gamma}{dt}$.	E_s.	$\frac{d\gamma}{dt}$.	$\frac{d\gamma/dt}{\gamma_0}$.	Temp.	*t*.	γ_t.	M. W.	Obs.
104	Allyl isothiocyanate, $CH_2{:}CH.CH_2NCS$	34.59	31.41	66.0	0.115	0.00332	18.4–46.0°	18.4°	31.5		R. S.(c)
105	Butyl isothiocyanate, C_4H_9NCS	33.60	28.83	62.4	0.106	0.00315	11.2–55.2	11.2	31.3	115	R. G.(c)
106	*sym.*-Diethyl sulfide, $(C_2H_5O)_2SO$	31.41	27.55	59.0	0.1009	0.00321	30–60			138	M.(c)
		31.41	29.02	60.4	0.106	0.00337	21–62.6	21.0	28.28		W. S.(c)
107	Dimethyl succinate, $CH_3OCO(CH_2)_2COOCH_3$	37.0	31.2	68.2	0.114	0.00309	25.2–75.9	25.2	34.1	146.08	J. K.
108	Diethyl bromoisosuccinate, $CH_3CBr(CO.OC_2H_5)_2$	32.7	27.3	60.0	0.0999	0.00305	(—21)–25.1	25.1	30.4	254.03	J. K.
109	Glyceryl triformate, $C_3H_5(O.COH)_3$	49.6	30.4	80.0	0.111	0.00224	0–50.3	50.3	44.0	176.06	J. K.
110	Glyceryl triacetate, $C_3H_5(O.COCH_3)_3$	36.9	15.0	51.9	0.055	0.00149	(—19)–21	21	35.6	218.1	J. K.
111	Glyceryl tributyrate, $C_3H_5(O.COC_3H_7)_3$	31.8	15.8	47.6	0.058	0.00182	(—20.5)–20.9	20.5	33.0	302.2	J. K.
112	Glyceryl tricapronate, $C_3H_5(O.COC_5H_{11})_3$	31.5	23.3	54.8	0.0854	0.00271	(—20)–21	—20	33.4	386.3	J. K.
113	Glyceryl tricaprylate, $C_3H_5(O.CO.C_7H_{15})_3$	30.1	13.6	43.7	0.0497	0.00165	0–50.3	50.3	27.6	470.4	J. K.
114	Glyceryl tricaprinate, $C_3H_5(OCOC_9H_{19})_3$	29.3	12.9	42.2	0.0472	0.00161	35.4–90.5	35.4	27.6	554.49	J. K.
115	Glyceryl triaurinate, $C_3H_5(O.COC_{11}H_{23})_3$	32.9	15.6	48.5	0.057	0.00174	64.7–126	64.7	29.2	638.59	J. K.
116	Glyceryltripalmitate, $C_3H_5(O.CO.C_{15}H_{31})_3$	34.6	17.8	52.4	0.065	0.00189	64.3–125.5	64.3	30.4	801.74	J. K.
117	Glyceryltristearate, $C_3H_5(O.CO.C_{17}H_{35})_3$	35.2	20.9	56.1	0.0766	0.00217	121–185	121	26.0	890.88	J. K.
118	Glyceryltrioleate, $C_3H_5(O.COC_{17}H_{33})_3$	37.2	38.1	75.3	0.139	0.00375	(—17)–21	21	34.8	884.82	J. K.
119	Butter	33.1	18.0	51.1	0.066	0.00197	40.2–94.8	40.2	30.5		J. K.
120	Margarine	34.8	26.0	60.8	0.0952	0.00274	40.2–94.8	40.2	31.0		J. K.
121	***assym.***-Diethyl sulfite, $(C_2H_5O)_2SO$	37.08	27.89	65.0	0.102	0.00275	17.6–71.5	17.6	35.15	138	W. S.(c)
122	Isobutyl acetate, $CH_3COOCH_2CH(CH_3)_2$	25.71	27.03	52.7	0.099	0.00385	23.8–59.2	23.8	23.35		M. B.
	VIII. Alcoholic Derivatives.										
123	Mercaptan, C_2H_5SH	24.62	38.21	62.8	0.140	0.00568	2–16.7	2	23.6		R. S.(c)
124	Monochlorohydrin, $C_3H_5(OH)_2Cl$	50.79	26.76	77.5	0.098	0.00193	17–80.2	17	47.61	110.5	W. S.(c)
125	Monoacetin, $CH_2(OH)CH_2(C_2H_3O_2)$	45.05	24.36	69.4	0.0929	0.00206	17–70	17	42.12	134.1	W. S.(c)
126	Epichlorohydrin, $CH_2Cl.CHOCH_2$	38.0	37.3	75.3	0.136	0.00359	(—21)–30.3	30.3	34.0	42.5	J. K.
	IX. Acids and Anhydrides.										
127	Formic acid, $HCOOH$	39.52	28.84	68.4	0.1056	0.00267					M.(c)
	Formic acid, $HCOOH$	39.0	24.6	63.6	0.090	0.00230	9.2–64.8	9.2	38.1	46.02	J. K.
128	Acetic acid, CH_3COOH	29.61	26.26	55.9	0.0961	0.00325					M.(c)
	Acetic acid, CH_3COOH	29.7	28.5	58.2	0.104	0.00350	26–70				J.
129	Propionic acid, CH_3CH_2COOH	27.80	29.12	56.9	0.1067	0.00384					
	Propionic acid, CH_3CH_2COOH	29.06	27.84	56.9	0.102	0.00351					R. S.(c)
130	Butyric acid, $CH_3.CH_2.CH_2COOH$	27.76	26.79	54.5	0.098	0.00354					
	Butyric acid, $CH_3.CH_2.CH_2COOH$	28.94	25.50	54.4	0.0934	0.00323					R. S.(c)
131	Isobutyric acid, $CH(CH_3)_2COOH$	27.18	24.61	51.8	0.090	0.00331					R. S.(c)
	Isobutyric acid, $CH(CH_3)_2COOH$	26.99	26.30	53.3	0.096	0.00364					M.(c)

132	Isovaleric acid, $(CH_3)_2CH.CH_2COOH$	26.25	23.03	49.28	0.0844	0.00322				
133	Isocaproic acid, $(CH_3)_2.CH(CH_2)_2COOH$	28.12	22.04	50.2						R. S.(c)
134	Camphinic acid,  $\begin{array}{l}(CH_3)_2\text{: }C.CH.CH_2COOH \\ \quad\quad\quad\;\; \vert \quad > CH_2 \\ \quad\;\; CH_3.C\text{:}CH\end{array}$	37.0	30.7	67.7	0.112	0.00303	0–95°			J.
135	Acetic anhydride,  $\begin{array}{c}CH_3COC\text{:}CH_3 \\ \Vert \quad \Vert \\ O\,.\,O\end{array}$	35.18	34.81	70.0	0.1275	0.00363					R. S.(c)
136	Monochloroacetic acid, $CH_2ClCOOH$	41.7	28.7	70.4	0.105	0.00253	80.2–118.5	80.2°	33.3	94.49	J. K.
137	Dichloroacetic acid, $CHCl_2COOH$	38.1	27.3	65.4	0.100	0.00262	0–41	41	34.0	128.95	J. K.
138	Trichloroacetic acid, CCl_3COOH	33.3	21.3	54.6	0.078	0.00235	80.2–136.5	80.2	27.8	163.4	J. K.
139	Levulinic acid, $CH_3COCH_2CH_2COOH$	41.6	20.5	62.1	0.075	0.00180	25.5–81.5	25.5	39.7	116.06	J. K.

X. Aldehydes, Ketones, Ketoximes, and Lactones.

140	Paraldehyde, $(CH_3CHO)_3$	28.52	31.21	59.7	0.114	0.00400				M.(c)
141	Chloral, CCl_3CHO	27.60	32.86	60.5	0.1205	0.00436	19.4–45.8	19.4	24.5		R. S.(c)
142	Acetone, CH_3COCH_3	26.09	35.63	61.7	0.130	0.00498					M.(c)
	Acetone, CH_3COCH_3	26.18	31.78	58.0	0.116	0.00443					R. S.
	Acetone, CH_3COCH_3	25.5	34.1	59.6	0.125	0.00440	(—20)–35				J.
143	Methyl propyl ketone, $CH_3COC_3H_7$	26.0	27.9	53.9	0.102	0.00392	(—20)–25				J.
	Methyl propyl ketone, $CH_3COC_3H_7$	27.73	29.72	57.4	0.108	0.00389	13–79.9	19	25.38		R. G.(c)
	Methyl propyl ketone, $CH_3COC_3H_7$	28.02	30.59	58.6	0.112	0.00399	16.7–78.4	16.7	25.4		R. S.(c)
144	Dipropyl ketone, $C_3H_7COC_3H_7$	27.61	28.68	56.3	0.105	0.00380	10–60			114	M.(c)
145	Methyl propyl ketoxime,  $\begin{array}{c}CH_3 \\ C_3H_7\end{array}\!\!>C = NOH$	31.21	26.49	57.7	0.097	0.00311	11.8–66.8	11.8	29.0	101	R. G.(c)
146	Methyl ethyl lactone,  $CH_3C_2H_5\underbrace{CHCH_2CH_2CO}_{O}$	26.74	32.93	59.7	0.120	0.00449					M.(c)
147	Diethyl lactone, $C_8H_{14}O_2$	26.75	28.16	54.9	0.103	0.00385					M.(c)
148	Methyl hexyl lactone, $C_{11}H_{20}O_2$	28.51	25.75	54.3	0.095	0.00333					M.(c)
149	Acetyl acetone, $CH_3COCH_2COCH_3$	32.94	28.41	61.3	0.104	0.00308					M.(c)
	Acetyl acetone, $CH_3COCH_2COCH_3$	31.6	29.6	61.2	0.108	0.00343	(—21)–25.2	25.2	29.2		J. K.

XI. Amino Derivatives.

150	Monomethylamine, CH_3NH_2	...	...	...	0.129	.....	(—12)–(—70)				J.
	Monomethylamine, CH_3NH_2	20.1	35.4	55.5	0.130	0.00647	(—49)–(—12)				J.
151	Dimethylamine, $(CH_3)_2NH$	18.1	24.4	42.5	0.089	0.00492	(—23)–5				J.
152	Trimethylamine, $(CH_3)_3N$	16.9	26.0	42.9	0.095	0.00562	(—40)–(—4)				J.
153	Ethylamine, $C_2H_5NH_2$	21.4	26.7	48.1	0.098	0.00458	(—33)–9.9				J.
154	Diethylamine, $(C_2H_5)_2NH_2$	20.8	27.1	47.9	0.099	0.00476	(—21)–35				J.
155	Triethylamine, $(C_2H_5)_3N$	20.0	25.4	45.4	0.093	0.00465	(—21)–25				J.

Table II (continued).

No.	Name.	γ_o.	$273\frac{d\gamma}{dt}$.	E_s.	$\frac{d\gamma}{dt}$.	$\frac{d\gamma/dt}{\gamma_o}$.	Temp.	t.	γ_t.	M. W.	Obs.
156	*n*-Propylamine, $C_3H_7NH_2$	22.3	28.1	*50.4*	0.103	0.00462	(—21)–25°				J.
	n-Propylamine, $C_3H_7NH_2$	24.30	31.90	56.2	0.1168	0.00479					T. M.
157	Dipropylamine, $(C_3H_7)_2NH$	23.5	29.3	52.8	0.107	0.00455	(—19)–30				J.
	Dipropylamine, $(C_3H_7)_2NH$	24.40	28.32	52.7	0.104	0.00425					T. M.
158	Tripropylamine, $(C_3H_7)_3N$	23.6	24.2	47.8	0.088	0.00373					J.
	Tripropylamine, $(C_3H_7)_3N$	24.45	20.30	44.7	0.074	0.00304					T. M.
159	Isopropylamine, $(CH_3)_2CHNH_2$	19.4	30.5	49.9	0.112	0.00577	(—20)–25				J.
160	Allylamine, $C_3H_5NH_2$	26.0	31.8	57.8	0.116	0.00446	(—15)–40				J.
161	*n*-Butylamine, $CH_3(CH_2)_2NH_2$	23.8	28.9	*52.7*	0.106	0.00445	(—21)–25				J.
162	Isobutylamine, $(CH_3)_2CHCH_2NH_2$	22.4	22.5	44.9	0.083	0.00371	(—20)–55				J.
163	Di-isobutylamine, $(C_4H_9)_2NH$	23.2	26.2	49.4	0.096	0.00414	(—20)–56				J.
164	Tri-isobutylamine, $(C_4H_9)_3N$	23.4	15.3	38.7	0.056	0.00239	(—22)–56				J.
165	Tertiarybutylamine, $(CH_3)_3CNH_2$	19.4	27.8	47.2	0.102	0.00526	(—30)–20				J.
166	Isoamylamine, $(CH_3)_2CHCH_2CH_2NH_2$	23.7	27.0	50.7	0.099	0.00418	(—20)–40				J.
	Isoamylamine, $(CH_3)_2CHCH_2CH_2NH_2$	25.62	27.70	53.3	0.102	0.00396					T. M.
167	Di-isoamylamine, $(C_5H_{11})_2NH$	24.6	25.4	50.0	0.093	0.00378	(—20)–50				J.
168	*n*-Amylamine, $CH_3(CH_2)_3CH_2NH_2$	24.1	23.5	*47.6*	0.086	0.00357	(—21)–25				J.
169	Triamylamine, $(C_5H_{11})_3N$	25.95	23.13	49.1	0.085	0.00327					T. M.
170	Tertiaryamylamine, $(CH_3)_2C_2H_5CNH_2$	22.4	25.2	47.6	0.092	0.00411	(—20)–40				J.
171	*n*-Hexylamine, $CH_3(CH_2)_4CH_2NH_2$	26.9	20.5	*47.4*	0.075	0.00279	(—18)–50				J.
172	Isohexylamine, $(CH_3)_2CH(CH_2)_3NH_2$	24.8	21.1	45.9	0.077	0.00310	(—20)–40				J.
173	*n*-Heptylamine, $CH_3(CH_2)_5CH_2NH_2$	26.1	21.1	*47.2*	0.077	0.00295	(—18)–25				J.
174	Dimethylnitrosoamine, $(CH_3)_2N.NO$	41.6	35.5	77.1	0.130	0.00312	20–75	20°	39.0	74	T. M.
175	Diethylnitrosoamine, $(C_2H_5)_2N.NO$	34.9	28.4	63.3	0.104	0.00298	20–75	20	32.8	102	T. M.
	XII. Acid Chlorides and Amides.										
176	Acetyl chloride, CH_3COCl	28.0	39.8	67.8	0.146	0.00521	14.8–46.2	14.8	25.8		R. S.(c)
177	Formamide, $HCONH_2$	59.6	25.5	85.1	0.094	0.00158	0–48				J.
	Formamide, $HCONH_2$	59.41	25.68	85.1	0.094	0.00158					T. M.
	Formamide, $HCONH_2$	60.06	22.29	82.2	0.082	0.00137					M.(c)
178	Acetamide, CH_3CONH_2	47.62	27.83	75.5	0.102	0.00214					T. M.
179	Propionamide, $CH_3CH_2CONH_2$	39.02	24.73	63.7	0.091	0.00232					T. M.
180	Lactamide, $CH_3CH(OH)CONH_2$	50.54	21.91	72.4	0.080	0.00178					T. M.
	XIII. Nitriles.										
181	Acetonitrile, CH_3CN	30.82	35.90	66.7	0.132	0.00427					
	Acetonitrile, CH_3CN	32.15	36.81	68.9	0.135	0.00419					R. G.(c)
182	Propionitrile, CH_3CH_2CN	28.34	31.39	59.73	0.115	0.00405					R. G.(c)

183	Butyronitrile, $CH_3.CH_2.CH_2.CN$	29.20	28.23	57.4	0.1034	0.00354					M.(c)
	Butyronitrile, $CH_3.CH_2.CH_2.CN$	29.20	30.0	59.2	0.110	0.00376	20–60	20	27	69	T. M.
184	*Valeric nitrile*, $CH_3(CH_2)_3CN$	26.91	27.59	54.5	0.101	0.00375					
185	Lactonitrile, $CH_3CH(OH)CN$	38.3	26.5	64.8	0.097	0.00253	20–60	20	36.4	71	T. M.
186	Isobutylacetonitrile, $(CH_3)_2CH.CH_2CH(COCH_3)CN$	28.3	25.1	53.4	0.092	0.00325	20–60	20	26.5	97	T. M.
187	Methylene cyanide, $CH_2(CN)_2$	53.3	29.3	82.6	0.107	0.00201	36.1–80.9	36.1	47.9	66	W. S.(c)
188	Capronitrile, $C_5H_{11}CN$	27.1	21.6	48.7	0.080	0.00292	(—22)–29.9	—22.0	28.7	97.1	J. K.

XIV. Aromatic Hydrocarbons.

189	Benzene, C_6H_6	31.7	39.1	70.8	0.140	0.00442	5–55				J.
	Benzene, C_6H_6	31.6	39.0	70.6	0.143	0.00452	5–55				J.
	Benzene, C_6H_6	31.64	36.9	68.5	0.135	0.00427	20.5–55	20.5	28	78.05	W. S.(c)
	Benzene, C_6H_6	31.55	35.64	67.2	0.130	0.00413					R. S.(c)
190	Toluene, C_7H_8	30.76	31.32	62.1	0.115	0.00373					R. G.(c)
	Toluene, C_7H_8	30.69	31.27	62.0	0.115	0.00373	21.2–78	21.2	27.4	92.1	W. S.(c)
	Toluene, C_7H_8	31.6	34.3	65.9	0.125	0.00369	(—21)–2.6				J.
191	*m*-Xylene, $C_6H_4(CH_3)_2$	29.7	28.87	59.5	0.106	0.00356					D. F.
	m-Xylene, $C_6H_4(CH_3)_2$	31.28	22.3	63.6	0.118	0.00378					M. B.
	m-Xylene, $C_6H_4(CH_3)_2$	31.44	36.35	67.8	0.133	0.00423	18.4–59	18.4	28.1	106.1	W. S.(c)
192	*o*-Xylene, $C_6H_4(CH_3)_2$	31.06	29.3	60.4	0.107	0.00346					M. B.
193	*p*-Xylene, $C_6H_4(CH_3)_2$	29.31	29.1	58.4	0.107	0.00363					M. B.
	p-Xylene, $C_6H_4(CH_3)_2$	32.1	31.5	63.6	0.115	0.00358	25–86				J.
194	Ethyl benzene, $C_6H_5.C_2H_5$	31.15	29.76	60.9	0.109	0.00350	21–60	21	28.86		M. B.
195	Cymene, $C_6H_4<^{CH_3}_{C_3H_7}$	30.18	26.57	56.7	0.098	0.00323					R. G.(c)
	Cymene, $C_6H_4<^{CH_3}_{C_3H_7}$	29.74	25.12	54.9	0.092	0.00309	18.7–59.5	18.7	28.02		M. B.
196	Mesitylene, $C_6H_3(CH_3)_3$	30.49	26.65	57.1	0.098	0.00319	11.4–65	11.4	28.3	120	R. G.(c)
	Mesitylene, $C_6H_3(CH_3)_3$	30.3	28.9	59.2	0.106	0.00350	(—20.8)–25				J.
	Mesitylene, $C_6H_3(CH_3)_3$	30.04	24.57	54.6	0.090	0.00300	23.5–57.3	23.5	27.9		M. B.
197	Pseudocumene, $C_6H_3(CH_3)_3$, 1.2.4	32.4	24.4	56.8	0.089	0.00275	(—21)–25				J.
198	Triphenyl methane, $(C_6H_5)_3CH$	46.6	25.6	72.2	0.094	0.00202	138–194				J.
199	Diphenyl methane, $(C_6H_5)_2CH_2$							59	34.82		M. B.
200	Diphenyl, $(C_6H_4)_2$	40.41	24.88	65.3	0.0911	0.00225					D. F.
201	Sylvestrene, $C_{10}H_{16}$	28.3	24.8	53.1	0.091	0.00321	(—20)–25.8	—20	30.1	136.1	J. K.
202	Terebene, $C_{10}H_{16}$	28.7	25.1	53.8	0.092	0.00321	(—22)–29.9	—22	30.7	136.1	J. K.

XV. Halogen Derivatives.

203	Chlorobenzene, C_6H_5Cl	35.61	30.61	66.2	0.113	0.00316	18.7–62.1	18.7	32.47	112.5	W. S.(c)
	Chlorobenzene, C_6H_4Cl	34.83	32.19	67.02	0.118	0.00338					R. A.
	Chlorobenzene, C_6H_5Cl	34.80	33.3	68.1	0.122	0.00350					R. G.(c)
	Chlorobenzene, C_6H_5Cl	35.9	34.0	69.9	0.124	0.00345	(—16)–25				J.

TABLE II (*continued*).

No.	Name.	γ_0.	$273\frac{d\gamma}{dt}$.	E_s.	$\frac{d\gamma}{dt}$.	$\frac{d\gamma/dt}{\gamma_0}$.	Temp	*t*.	γ_t.	M. W.	M. P.	Obs.
204	Bromobenzene, C_6H_5Br	39.9	36.6	76.5	0.134	0.00336	(—18)–25°					J.
	Bromobenzene, C_6H_5Br	35.45	32.93	68.4	0.121	0.00341	38.3–59.7	38.3°	34.65			M. B.
205	Iodobenzene, C_6H_5I	43.24	26.79	70.0	0.114	0.00264	23.5–59.6	23.5	40.12	204		M. B.
	Iodobenzene, C_6H_5I	39.10	23.5	62.6	0.086	0.00220	(—21)–40.4	—21	41.0		—26	J. K.
206	Fluorobenzene, C_6H_5F	29.22	17.20	46.42	0.063	0.00216	9.3–34.5	9.3	28.63			M. B.
207	*m*-Dichlorobenzene, $C_6H_4Cl_2$	38.5	34.8	73.3	0.127	0.00330	(—22)–25					J.
208	*p*-Dichlorobenzene, 1,4-$C_6H_4Cl_2$	34.8	24.6	59.4	0.090	0.00259	60.3–130	60.3	29.4	147	52	J. K.
209	*p*-Fluorobromobenzene, C_6H_4FBr	37.2	32.3	69.5	0.118	0.00324	(—21)–25					J.
210	*m*-Fluorobromobenzene, C_6H_4FBr	31.5	35.1	66.6	0.128	0.00406	(—20)–25					J.
211	*p*-Dibromobenzene, $C_6H_4Br_2$	40.8	25.4	66.2	0.093	0.00228	94.8–144.5	94.8	32	236	89	J. K.
213	*p*-Chlorotoluene, $CH_3C_6H_4Cl$	35.8	31.5	67.3	0.115	0.00321	25–70					J.
214	*o*-Bromotoluene, $CH_{3(1)}C_6H_4Br_{(2)}$	36.5	26.7	63.2	0.098	0.00268	(—20)–40	—20	38.4	171	—27	J. K.
	XVI. Nitroso and Nitro Derivatives.											
215	Nitrobenzene, $C_6H_5NO_2$	45.83	31.13	77.0	0.114	0.00249						M.(c)
	Nitrobenzene, $C_6H_5NO_2$	44.9	27.4	72.3	0.100	0.00223	5–70					J.
216	*o*-Nitrotoluene, $CH_3.C_6H_4.NO_2$	43.3	29.3	72.6	0.107	0.00247	0–70					J.
217	*p*-Nitrotoluene, $CH_{3(1)}C_6H_4.NO_{2(4)}$	40.9	24.3	65.2	0.089	0.00218	60.2–115	60.2	35.5	137	57.5	J. K.
218	*o*-Dinitrobenzene, $C_6H_4(NO_2)_2$	50.5	26.2	76.7	0.096	0.00191	126–176	126	38.4	168	117	J. K.
219	*m*-Dinitrobenzene, $C_6H_4(NO_2)_2$	52.1	28.1	80.2	0.103	0.00198	95–155	94.8	42.3	168	91	J. K.
220	*p*-Dinitrobenzene, $C_6H_4(NO_2)_2$	48.5	21.9	70.4	0.080	0.00165	176–226	176	34.4	168	172	J. K.
221	*m*-Fluoronitrobenzene, $C_6H_4FNO_2$	40.1	32.8	72.9	0.120	0.00299	0–64.5	64.5	33.6	141	—1	J. K.
222	*p*-Fluoronitrobenzene, $C_6H_4FNO_2$	41.2	30.8	72.0	0.112	0.00272	24.5–74.2	74	32.8	141	26.5	J. K.
223	*o*-Chloronitrobenzene, $C_6H_4ClNO_2$	45.1	30.7	75.8	0.112	0.00248	31.2–89	89	35.1	158	33	J. K.
224	*m*-Chloronitrobenzene, $C_6H_4Cl.NO_2$	45.1	34.2	79.3	0.125	0.00277	46–90	46	34.4	158	44.5	J. K.
225	*p*-Chloronitrobenzene, $C_6H_4Cl.NO_2$	42.7	25.6	68.3	0.094	0.00220	90–155	155	28.2	158	83.5	J. K.
226	*o*-Bromonitrobenzene, $C_6H_4BrNO_2$	47.4	31.8	79.2	0.116	0.00245	46–95	95.2	36.3	202	43	J. K.
227	*m*-Bromonitrobenzene, $C_6H_4NO_2$	46.2	28.1	74.3	0.103	0.00223	61–110	110	34.9	202	56.5	J. K.
228	*p*-Bromonitrobenzene, $C_6H_4NO_2$	43.8	26.2	70.0	0.096	0.00219	127–178	178	29.3	202	127	J. K.
229	*o*-Iodonitrobenzene, $C_6H_4I_{(1)}NO_{2(2)}$	48.9	26.2	75.1	0.096	0.00196	61–114	61	43.1	249	50	J. K.
230	*m*-Iodonitrobenzene, $C_6H_4I_{(1)}NO_{2(3)}$	50.1	30.0	80.1	0.110	0.00220	25.7–83	25.7	47.3	249	36	J. K.
231	Chlorodinitrobenzene, $C_6H_3Cl_{(1)}(NO_2)_{2(2,4)}$	51.24	25.9	77.1	0.095	0.00185	60.4–114	60.4	45.5	203	51	J. K.
232	1,2-Dichloro-4-nitrobenzene, $C_6H_3Cl_{2(1,2)}NO_{2(4)}$	44.5	25.7	70.2	0.094	0.00211	46–95	46	40.2	192	43	J. K.
233	1,3-Dichloro-4-nitrobenzene, $C_6H_3Cl_{2(1,3)}NO_{2(4)}$	44.9	27.8	72.7	0.102	0.00227	35–95	35	41.3	192	34	J. K.
234	1,4-Dichloro-2-nitrobenzene, $C_6H_3Cl_{2(1,4)}NO_{2(2)}$	43.5	23.5	67.0	0.086	0.00198	60.5–115	60.5	38.3	192	55	J. K.
	XVII. Amino Derivatives.											
235	Aniline, $C_6H_5NH_2$	45.4	28.9	74.3	0.106	0.00233	0–70					J.

	Aniline, $C_6H_4NH_2$	45.94	27.3	73.2	0.100	0.00218						
	Aniline, $C_6H_4NH_2$	45.42	32.6	78.0	0.119	0.00262						R. G. (c)
236	Dimethyl aniline, $C_6H_4N(CH_3)_2$	37.86	30.7	68.6	0.112	0.00297						D. F.
	Dimethyl aniline, $C_6H_5N(CH_3)_2$	38.95	31.12	70.1	0.114	0.00293	21.5–59.5	21.5	36.5			M. B.
	Dimethyl aniline, $C_6H_5N(CH_3)_2$	39.4	29.8	69.2	0.109	0.00277	26–86	26				J.
237	Methyl aniline, $CH_3C_6H_4NH$	42.37	31.94	74.3	0.117	0.00276	24.6–59.7	24.6	39.49			M. B.
	Methyl aniline, $CH_3C_6H_5NH$	40.1	30.8	70.9	0.113	0.00282	(—18)–49.3	—18	42.2	107	—57	J. K.
238	Ethyl aniline, $C_2H_5C_6H_5NH$	38.78	28.94	67.7	0.106	0.00273	35.8–58.7	35.8	34.99			M. B.
	Ethyl aniline, $C_2H_5C_6H_5NH$	38.32	39.13	77.4	0.1433	0.00374						D. F.
239	Diethyl aniline, $C_6H_5N(C_2H_4)_2$	38.32	39.13	77.45	0.143	0.00374						D. F.
240	*m*-Nitroaniline, $C_6H_4NH_2NO_2$	54.0	24.9	78.9	0.091	0.00168	124–170	124.2	42.7	138	112	J. K.
	m-Nitroaniline, $C_6H_4NH_2NO_2$	54.1	25.1	79.2	0.092	0.00168	124–170	124.2	42.7	138	112	J. K.
241	*p*-Nitroaniline, $C_6H_4NH_2NO_2$	60.9	25.6	86.5	0.094	0.00154	151–171	151	46.7	138	147	J. K.
	p-Nitroaniline, $C_6H_4NH_2NO_2$	60.6	25.1	85.7	0.092	0.00152	151–184.5	151	46.7	138	147	J. K.
242	*o*-Chloroaniline, $C_6H_4Cl_{(1)}NH_{2(2)}$	43.6	29.2	72.8	0.107	0.00245	(—19)–29.7	—19	45.7	128	0	J. K.
243	*p*-Chloroaniline, $C_6H_4(NH_2)_{(1)}Cl_{(4)}$	45.0	26.5	71.5	0.097	0.00216	74.6–121	74.6	37.8	128	70	J. K.
244	*p*-Nitro-monomethylaniline, $C_6H_4(NHCH_3)_{(1)}NO_{2(4)}$	63.8	30.8	94.6	0.113	0.00177	155.2–210	155	46.3	152	152	J. K.
245	Nitrosomethylaniline, $C_6H_5N(NO)CH_3$	45.7	25.1	70.8	0.092	0.00201	0–58.6	0	45.7	136	13	J. K.
246	Diisobutylaniline, $C_6H_5.N(CH_2.CH(CH_3)_2)_2$	32.8	28.9	61.7	0.106	0.00323	0–55.7	0	32.8	205	—79	J. K.
247	*o*-Toluidine, $CH_3.C_6H_4.NH_2$	43.1	30.3	73.4	0.111	0.00257	(—20)–25					J.
248	3-Nitro-*o*-toluidine, $CH_{3(1)}C_6H_3(NH_2)_{(2)}(NO_2)_{(3)}$	48.6	24.6	73.2	0.090	0.00185	105–170	105	39.2	152	96	J. K.
249	5-Nitro-*o*-toluidine, $CH_{3(1)}C_6H_3(NH_2)_{(2)}(NO_2)_{(5)}$	65.4	43.1	108.5	0.158	0.00242	142–184.5	142	43.0	152	128	J. K.
250	3-Nitro-*p*-toluidine, $CH_{3(1)}C_6H_3(NH_2)_{(4)}(NO_2)_{(3)}$	48.9	28.1	77.0	0.103	0.00211	121–185	121	36.4	152	117	J. K.
251	Benzylamine, $C_6H_5.CH_2.NH_2$	41.4	31.4	72.8	0.115	0.00278	20–75	20	39.1	107		T. M.
252	Dibenzylamine, $(C_6H_5CH_2)_2NH$	41.1	30.0	71.1	0.110	0.00268	(—18.5)–41.5	—18.5	43.3	197	—70	J. K.
	Dibenzylamine, $(C_6H_5CH_2)_2NH$	42.82	29.23	72.15	0.107	0.00250						T. M.
253	Tribenzylamine, $(C_6H_5CH_2)_3N$	48.12	35.14	83.3	0.1287	0.00267						T. M.
254	Diphenylamine, $(C_6H_5)_2NH$	45.33	27.72	73.05	0.102	0.00224						T. M.
	Diphenylamine, $(C_6H_5)_2NH$	44.5	26.5	71.0	0.097	0.00218	60.5–114	60.5	38.6	170	54	J. K.
255	Phenylmethylnitrosamine, $(C_6H_5CH_3)N.NO$	47.4	33.3	80.7	0.122	0.00257	20–75	20	45	136		T. M.
256	Formanilide, $CHO.NH.C_6H_5$	42.2	23.7	65.9	0.087	0.00206	60–105	60	39.0	121		T. M.
257	Acetanilide, $C_2H_3O.NH.C_6H_5$	46.0	24.6	70.6	0.090	0.00196	120–160	120	35.2	135		T. M.
258	Methyl acetanilide, $C_6H_5.N(CH_3)C_2H_3O_2$	42.3	26.5	68.8	0.097	0.00229	105–145	105	32.1	149		T. M.
259	Ethyl acetanilide, $C_6H_5.N(C_2H_5)C_2H_3O_2$	40.6	28.7	69.3	0.105	0.00259	60–105	60	34.3	163		T. M.

XVIII. Phenols.

260	Phenol, C_6H_5OH	42.27	28.62	70.9	0.105	0.00248						B. G.
	Phenol, C_6H_5OH	40.8	25.4	66.2	0.093	0.00228	41.2–94	41.2	37.0	94	41	J. K.
261	1,2,4-Dinitrophenol, $C_6H_3(OH)_{(1)}(NO_2)_2$	52.5	24.8	77.3	0.091	0.00173	125.4–186	125	41.1	184	114	J. K.
262	2,4,6-Trichlorophenol $C_6H_2(OH)Cl_3$	42.6	24.6	67.2	0.090	0.00211	70–140	70.2	36.3	197	69.5	J. K.

TABLE II (*continued*).

No.	Name.	γ_0.	$273\frac{d\gamma}{dt}$.	E_S.	$\frac{d\gamma}{dt}$.	$\frac{d\gamma/dt}{\gamma_0}$.	Temp.	t.	γ_t.	M. W.	M. P.	Obs.
263	*o*-Nitrophenol, $C_6H_4(NO_2)OH$	42.5	23.9	66.4	0.088	0.00207	52–108	52	38.0	139	45	J. K.
264	*m*-Nitrophenol, $C_6H_4(NO_2)OH$	46.1	15.0	61.1	0.055	0.00119	110–170°	110°	40.0	139	96	J. K.
265	*p*-Nitrophenol, $C_6H_4(NO_2)OH$	54.3	25.7	80.0	0.094	0.00173	117–176	117	43.3	139	113	J. K.
266	Thiophenol, C_6H_5SH	41.67	33.42	75.1	0.122	0.00293						M.(c)
	Thiophenol, C_6H_5SH	42.55	34.09	76.6	0.125	0.00294	16.9–76	16.9	39.19	110		W. S.(c)
267	*o*-Cresol, $CH_3C_6H_4OH$	40.61	29.0	69.61	0.106	0.00261						B. G.
	o-Cresol, $CH_3C_6H_4OH$	38.1	22.4	60.5	0.082	0.00215	40.3–95	40.3	34.8	108	30	J. K.
268	*m*-Cresol, $CH_3C_6H_4OH$	38.63	25.8	64.4	0.094	0.00244						B. G.
269	*p*-Cresol, $CH_3C_6H_4OH$	40.0	30.0	70.0	0.110	0.00275						Feustel
	p-Cresol, $CH_3C_6H_4OH$	36.6	22.9	59.5	0.084	0.00230	25.6–83	25.6	34.5	108	37	J. K.

XIX. Phenol Derivatives.

No.	Name.	γ_0.	$273\frac{d\gamma}{dt}$.	E_S.	$\frac{d\gamma}{dt}$.	$\frac{d\gamma/dt}{\gamma_0}$.	Temp.	t.	γ_t.	M. W.	M. P.	Obs.
270	Anisol, $C_6H_5OCH_3$	37.3	28.1	65.4	0.103	0.00276	(—21)–45					J.
	Anisol, $C_6H_5OCH_3$	37.98	34.09	72.1	0.125	0.00329	18.4–64	18.4	34.57	108		W. S.(c)
	Anisol, $C_6H_5OCH_3$	37.64	33.08	70.7	0.121	0.00322	11.1–63	11.1	35.0			R. G.(c)
271	Phenetol, $C_6H_5OC_2H_5$	35.50	32.40	67.9	0.119	0.00334	10.5–63.5	10.5	33.2			R. G.(c)
	Phenetol, $C_6H_5OC_2H_5$	34.6	30.2	64.8	0.110	0.00318	(—21)–45					J.
272	*p*-Nitrophenetol, $C_6H_4(NO_2)_{(1)}OC_2H_5{}_{(4)}$	41.3	23.5	64.8	0.086	0.00208	70.2–140	70.2	35.3	167	60	J. K.
273	*p*-Nitroanisol, $CH_3O_{(1)}.C_6H_4(NO_2)_{(4)}$	46.2	24.0	70.2	0.088	0.00191	60.5–115	60.5	40.9	153	55	J. K.
274	*o*-Nitroanisol, $CH_3O_{(1)}C_6H_4(NO_2)_{(2)}$	50.8	25.5	76.3	0.094	0.00185	0–45					J.
275	Anethole, $CH_3O.C_6H_4CH : CHCH_3$	38.8	28.7	67.5	0.105	0.00271	25–95					J.
	Anethole, $CH_3O.C_6H_4CH : CHCH_3$	37.98	28.57	66.6	0.105	0.00270						M.(c)
276	Guaiacol, $C_6H_4(OH)OCH_3$	46.4	32.3	78.7	0.118	0.00254	26–86					
	Guaiacol, $C_6H_4(OH)OCH_3$	40.68	31.21	71.9	0.114	0.00280	19.6–78	19.6	37.3			R. S.(c)
277	Thymol, $(CH_3)_2CHC_6H_3OH(CH_3)$	34.2	21.6	55.8	0.079	0.00231	0–70					J.
278	Resorcin monomethyl ether, $C_6H_4OH_{(1)}(OCH_3)_{(3)}$	51.6	48.8	100.4	0.178	0.00345	0–46					J.
279	Resorcin dimethyl ether, $C_6H_4(OCH_3)_{(1)}(OCH_3)_{(3)}$	41.3	32.7	74.0	0.121	0.00293	(—20)–26					J.
280	Hydroquinone dimethyl ether, $C_6H_4(OCH_3)_{2(1,4)}$	41.6	28.7	70.3	0.105	0.00252	66–106					J.
281	2-Nitroresorcinol, $C_6H_3(OH)_2NO_2$	49.6	30.6	80.2	0.112	0.00226	90.7–140	90.7	39.5	139	85	J. K.
282	Veratrol, $C_6H_4(OCH_3)_{2(1,2)}$	42.5	39.8	82.3	0.146	0.00344	0–47.3	0	42.5	138	22	J. K.
283	4,5-Dinitro-veratrol, $CH_3OC_6H_2(NO_2)_2OCH_3$	54.5	28.1	82.6	0.103	0.00189	130.8–182	130.8	41.0	228	130.5	J. K.

XX. Acids.

No.	Name.	γ_0.	$273\frac{d\gamma}{dt}$.	E_S.	$\frac{d\gamma}{dt}$.	$\frac{d\gamma/dt}{\gamma_0}$.	Temp.	t.	γ_t.	M. W.	M. P.	Obs.
284	α-Dihydro campholenic acid, $C_5H_6(CH_3)_3CH_2COOH$	34.3	29.2	63.5	0.107	0.00312	0–54.1	34.3		170	glassy —79	J. K.

XXI. Esters and Salts.

285	Methyl benzoate, $C_6H_5COOCH_3$	39.82	30.59	70.4	0.112	0.00281	10.5–57.6°	10.5°	37.3	136		R. G.(c)
	Methyl benzoate, $C_6H_5COOCH_3$	41.0	34.5	75.5	0.126	0.00307	0–74					J.
286	Ethyl benzoate, $C_6H_5COOC_2H_5$	37.0	26.4	63.4	0.097	0.00262	(—20)–25					J.
287	Benzyl benzoate, $C_6H_5COOCH_2C_6H_5$	45.2	28.6	73.8	0.105	0.00232	(—22)–25					J.
288	Methyl *o*-salicylate, $C_6H_4(OH)COOCH_3$	41.8	31.1	72.9	0.114	0.00273	(—20)–25					J.
289	Ethyl *o*-salicylate, $C_6H_4(OH)COOC_2H_5$	39.1	29.1	68.2	0.106	0.00271	0–45					J.
290	Phenyl *o*-salicylate, $C_6H_4(OH)COOC_6H_5$	45.7	27.3	73.0	0.100	0.00219	0–45					J.
291	Diethyl phthalate, $C_6H_4(COOC_2H_5)_2$	39.21	29.81	69.0	0.109	0.00278	10–60			222		M.(c)
	Diethyl phthalate, $C_6H_4(COOC_2H_5)_2$	39.81	27.61	67.4	0.101	0.00254	20–77.8	20	36.62			W. S.(c)
292	Diamyl phthalate, $C_6H_4(COOC_5H_{11})_2$	32.18	19.12	51.3	0.070	0.00217	30–60			306		M.(c)
	Diamyl phthalate, $C_6H_4(COOC_5H_{11})_2$	32.77	22.54	56.3	0.082	0.00250	20–75	20	31.12			W. S.(c)
293	Methyl cinnamate, $C_6H_5CH : CHCOOCH_3$	43.4	28.7	72.1	0.105	0.00242	45–90					J.
	Methyl cinnamate, $C_6H_5CH : CHCOOCH_3$	37.78	28.67	66.5	0.105	0.00278						M.(c)
	Methyl cinnamate, $C_6H_5CH : CHCOOCH_3$	40.27	27.89	68.16	0.102	0.00253	17.6–79.3	17.6	37.28	162		W. S.(c)
294	Ethyl cinnamate, $C_6H_5CH : CHCOOC_2H_5$	39.67	29.29	69.0	0.107	0.00270						M.(c)
	Ethyl cinnamate, $C_6H_5CH : CHCOOC_2H_5$	39.1	27.6	66.7	0.101	0.00258	25.7–80	25.7	36.5	176	6.5	J. K.
295	Hydrocinnamic propyl ester, $C_6H_5CH_2CH_2COOC_3H_7$	35.23	26.48	61.7	0.097	0.00275	19–80.5	19	33.39	192		W. S.(c)
296	Hydrocinnamic isopropyl ester, $C_6H_5CH_2CH_2COOC_3H_7$	33.94	25.66	59.6	0.094	0.00277	18.5–71.7	18.5	32.2	192		W. S.(c)
297	Hydrocinnamic amyl ester, $C_6H_5CH_2CH_2COOC_5H_{11}$	33.55	24.02	57.6	0.088	0.00262	16–83.8	16	32.14	220		W. S.(c)
298	Ethyl α-dihydrocampholenate, $C_5H_6(CH_3)_3CH_2COOC_2H_5$	29.3	22.1	51.4	0.081	0.00277	(—21)–40.4	—21	31.0	198	Turbid —79	J. K.
299	Phenyl isocyanate, C_6H_5NCO	42.49	28.83	71.32	0.106	0.00248						
300	Phenyl isothiocyanate, C_6H_5NCS	44.69	33.39	78.1	0.122	0.00273	13.2–54.8	13.2	41.5	135		R. G.(c)
301	Phenyl urethane, $NH_2COOC_6H_5$	41.7	25.9	67.6	0.095	0.00228	60–105	60	36.0	165		T. M.
302	Ethyl phenylpropionate, $C_6H_5CH_2CH_2COOC_2H_5$	41.28	28.74	70.0	0.105	0.00254	15.6–66.5	15.6	38.41	174		W. S.(c)
303	Isobutyl phenylpropionate, $C_6H_5CH_2CH_2COOC_4H_9$	36.82	24.79	61.6	0.091	0.00247	16.7–62	16.7	34.21	202		W. S.(c)
304	Ethyl-benzoyl-lactate, $C_6H_5COCH_2CHOHCOOC_2H_5$	37.67	27.03	64.7	0.099	0.00263	30–50			222		M.(c)
305	Benzyl-ethyl malonic diethyl ester, $C_2H_5OCOC(C_2H_5)(C_7H_7)COOC_2H_5$	39.0	36.6	75.6	0.134	0.00344	0–45					J.

XXII. Aldehydes.

306	Benzaldehyde, C_6H_5CHO	44.8	29.7	74.5	0.109	0.00243	0–71					J.
	Benzaldehyde, C_6H_5CHO	41.94	30.6	72.6	0.112	0.00267						M.(c)
307	Anisaldehyde, $CH_3O_{(1)}C_6H_4CHO_{(4)}$	44.9	31.7	76.6	0.116	0.00258	0–46.5	0.0	44.9	136	2.5	J. K.

XXIII. Ketones.

308	Benzophenone, $C_6H_5COC_6H_5$	44.9	26.7	71.6	0.098	0.00218	50.3–104	50.3	40.0	182	48.5	J. K.
	Benzophenone, $C_6H_5COC_6H_5$	47.60	31.84	79.5	0.117	0.00245	19–72.4	19	44.18	182		W. S.(c)
309	Acetophenone, $C_6H_5COCH_3$	43.4	36.0	79.4	0.132	0.00304	25–71					J.
310	3,4,3′,4′-Tetrachlorobenzophenone, $C_6H_3Cl_2COC_6H_3Cl_2$	49.3	25.1	74.4	0.092	0.00187	154–201.8	154	35.1	320	142	J. K.

TABLE II (*continued*).

No.	Name.	γ_0.	$273\frac{d\gamma}{dt}$.	E_s.	$\frac{d\gamma}{dt}$.	$\frac{d\gamma/dt}{\gamma_0}$.	Temp.	t.	γ_t.	M. W.	M. P.	Obs.
311	2,4,2',4'-Tetrachlorobenzophenone dichloride, $C_6H_3Cl_2CCl_2C_6H_3Cl_2$	39.5	14.5	54.0	0.053	0.00134	156–218°	156°	31.2	375	140	J. K.
312	Linalol, $C_{10}H_{18}O$	29.45	24.06	53.5	0.088	0.00299	8–55	8	27.7			R. G.(c)
	XXIV. Nitrogen Base Derivatives.											
313	Phenyl hydrazine, $H_2NNC_6H_5$	44.02	20.71	64.73	0.076	0.00172						
	Phenyl hydrazine, $H_2NNC_6H_5$	48.0	34.7	82.7	0.127	0.00265	20–60	20	45.5	108		T. M.
314	Azoxybenzene, $C_6H_5N_2OC_6H_5$	43.6	21.3	64.9	0.078	0.00179	55.8–115	55.8	39.3	198	36	J. K.
	XXV. Acid Amides.											
320	Benzamide, $C_6H_5CONH_2$	47.20	19.18	66.3	0.070	0.00149						T. M.
321	Phenylacetamide, $C_6H_5CH_2CONH_2$	46.4	21.8	68.2	0.080	0.00172	160–180	160	33.6	135		T. M.
322	Salicylamide, $OHC_6H_4CONH_2$	51.1	21.0	72.1	0.077	0.00151	140–170	140	40.3	137		T. M.
	XXVI. Nitriles.											
323	Benzonitrile, C_6H_5CN	40.9	31.9	72.8	0.117	0.00286	20–60	20	38.6	103		T. M.
	Benzonitrile, C_6H_5CN	40.65	34.25	74.9	0.128	0.00315						M.(c)
324	Phenylacetonitrile, $C_6H_5CH_2CN$	43.7	31.9	75.6	0.117	0.00269	20–60	20	41.4	117		T. M.
325	Phenylglycolicnitrile, $C_6H_5(CH(OH))_2CN$	45.8	26.5	72.3	0.097	0.00212	20–60	20	43.9	133		T. M.
326	*o*-Toluonitrile, $C_6H_5CH_2CN$	40.1	31.4	71.5	0.115	0.00286	20–60	20	37.8	117		T. M.
	o-Toluonitrile, $C_6H_5CH_2CN$	39.68	29.76	69.5	0.109	0.00277						M.(c)
327	*m*-Toluonitrile, $C_6H_5CH_2CN$	38.8	27.3	66.1	0.100	0.00258	20–60	20	36.8	117		T. M.
	m-Toluonitrile, $C_6H_5CH_2CN$	39.39	26.57	65.9	0.097	0.00246						M.(c)
328	*p*-Toluonitrile, $C_6H_5CH_2CN$	39.0	34.1	73.1	0.125	0.00321	30–70	30	36.5	117		T. M.
	p-Toluonitrile, $C_6H_5CH_2CN$	39.64	29.56	69.2	0.108	0.00273						M.(c)
	XXVII. Metalloid Aromatic Derivatives.											
329	Triphenylstibine, $C_{18}H_{15}Sb$	44.96	25.93	70.9	0.095	0.00211	35.1–77.3	35	41.63	351		W. S.
330	Triphenylphosphine, $C_{18}H_{15}P$	45.17	26.75	71.9	0.098	0.00217	45.7–107	45.7	40.69	262		W. S.
	XXVIII. Heterocyclic Compounds.											
331	Furfurol, α-C_4H_3OC—H └O	43.5	26.2	69.7	0.096	0.00221	(—22)–29.9	—22	45.7	96	—31	J. K.
	Furfurol, α-C_4H_3OC—H └O	44.34	33.3	77.7	0.122	0.00275						M.(c)
332	Thiophene, C_4H_4S	33.5	36.3	69.8	0.133	0.00397	(—19)–29.9	—19	36.0	84	—29.8	J. K.
	Thiophene, C_4H_4S	36.2	41.4	77.6	0.152	0.00419						Schiff
333	Piperidine, $C_5H_{10}>NH$	30.6	32.2	62.8	0.118	0.00386	(—19)–29.4	—19	32.8	85	—9	J. K.

334	Pyridine, C_5H_5N	38.1	37.2	75.3	0.136	0.00357	(—20)–25			J.
	Pyridine, C_5H_5N	39.03	36.47	75.5	0.134	0.00343				D. F.
	Pyridine, C_5H_5N	39.86	39.57	79.4	0.145	0.00364				R. S.(c)
335	Picoline, $C_5H_4(CH_3)N$	36.6	32.3	68.9	0.118	0.00322	(—20)–26			J.
336	Quinoline, C_9H_7N	47.0	33.3	80.3	0.122	0.00260	15.4–78.4	15.4	45.1	R. S.(c)
	Quinoline, C_9H_7N	46.4	30.0	76.4	0.110	0.00237	57.6–108.2	57.6	40.1	B. G.
	Quinoline, C_9H_7N	47.0	37.4	84.4	0.137	0.00291	(—21)–25			J.

J. = Jaeger.
J. K. = Jaeger and Kahn.
M.(c) = Morgan's values corrected.
M. B. = Morgan's data calculated by the correction curve determined by Brown; Morgan considers these his least accurate results.
R. S. = Ramsay and Shields.
R. A. = Ramsay and Aston.
W. = Walden.
G. B. = Guye and Baud.
W. S. = Walden and Schwinne.
T. M. = Turner and Merry.
D. F. = Dutoit and Frederich.
H. D. = Harkins and Davies.

Table II gives results which are of extreme importance in the study of the energy relations of surfaces and therefore the table is invaluable in connection with the theory that the molecules in surfaces are oriented. For several years Harkins and Brown have been engaged in a critical study of the accuracy of the surface-tension data in the literature. In this they have been greatly aided by the work of Richards,[1] since both his work and that done in this laboratory indicate that with the exception of the results of Jaeger and his associates most of the data in the literature are 3% too low. The corrections which should be applied to the existing data will be discussed later in a paper from this laboratory, but we will make use of the corrections since they not only make the data much more accurate from an absolute standpoint, but they also make it much better comparatively in nearly all cases, and for the bearing of the results upon the problem of molecular orientation it is most important that the values should be correct from the comparative standpoint.

Table II gives the values at 0° for the free surface energy in ergs per sq. cm. (γ), the superficial latent heat, which is the latent heat of one sq. cm. of the surface (l), the total energy of the surface per sq. cm. (u, or as given in the table E_s), the temperature coefficient of free surface energy $\left(\frac{d\gamma}{dT}\right)$, and this temperature coefficient divided by the free surface energy at zero degrees $\left(\frac{d\gamma/dT}{\gamma_0} = \alpha\right)$. The temperature coefficient of the surface tension was determined by taking the secant of the curve between two temperatures and determining its slope. The temperatures between which this secant was taken are given in the column marked "Temps." Where no values are given in this column the temperatures were about 10° for the lower and 70° for the upper limit. The temperature range used was usually about 70°, since if the temperature range is too small the experimental errors in the determinations have entirely too much influence, and if too large, the curvature becomes much greater. Since the value of E_s, while largely independent of temperature, is influenced by this curvature, the temperature interval was chosen where the data permitted, with zero degrees centigrade in the middle, so as to give an E_{s0}.

The corrections which have been applied are as follows, where all of the changes represent an increase: The results of Ramsay and Shields (R. S.) have been increased by 3%, those of Renard and Guye (R. G.) by 3.7%, those by Walden and Schwinne by 3.16%, and those of Morgan by 3%. In general, if anything, the corrections applied are too low rather than too high, since it was thought advisable not to overcorrect the data. Thus our work indicates that the most general correction which could be applied to the results of Morgan is 3.67%. However, since

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[1] This Journal, 37, 1656–76 (1916).

the factor is not entirely constant (Tate's law does not hold), if a correction of this magnitude is made, some of the values would be made too high. Thus Morgan's results on water are relatively much higher, and therefore much more nearly correct than those on any other substance, investigated. This is because the value of a^2 for water is such that Morgan's horizontal straight line used for correction, and the Lohnstein correction curve determined by Harkins and Brown meet almost at the value which r/a has for water.

It will be seen that $\frac{d\gamma/dT}{\gamma_0}$ very often has very nearly the value 0.00366, which is the coefficient of expansion of a perfect gas.

Since the total surface energy is practically independent of the temperature (at least for moderate ranges)[1] we have an explanation of the rule given by Freundlich[2] that the temperature coefficient of surface tension of a liquid is in general larger the smaller the surface tension. While this rule has only slight validity, Table III shows that it holds exactly when the substances which are compared have the same surface energies where the substances compared have surface energies of about 72.5. However, if both γ and E_s are plotted against T, it will be seen that this regularity *must hold* from the mathematical relations of the quantities involved. However, in spite of this fact, Table III has some value in that it shows very plainly the range of variation of $\frac{d\gamma}{dT}$ and $\frac{d\gamma/dT}{\gamma}$ with constant E_s as γ varies. It will be seen that octane, with a value of 47 for E_s, does not at all fit; that is, Freundlich's rule is extremely far from true.

A much more interesting table than this would be one on which we are working experimentally, but which is not yet completed. The results in the literature, with which our data agree thus far, indicate that if paraffins of not too long a carbon chain are taken, the normal compounds show a constant value of E_s. The temperature coefficient of these hydrocarbons must therefore *decrease* with the length of the chain, since the surface tension rises. Therefore the latent heat of the surface decreases. Even with a very high boiling paraffin oil which we have investigated, the surface tension is higher, and the latent heat of the surface lower than for any of the short chain compounds. This paraffin was obtained by taking the unsaturated substances from Kahlbaum's liquid paraffin and distilling the mixture of saturated substances which remained. The highest boiling fraction which did not solidify at room temperatures was used. We hope to determine E_s for hydrocarbons ranging in length

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[1] Thus from 0° to 50° the variation for CH_3OH is from 42.9 to 42.2, and for ethyl alcohol it is from 45.0 to 44.2. At —50° however the total surface energies are higher. The temperature variation of E_s will be treated in a later paper.

[2] *Kapillarchemie*, p. 33.

from one to sixteen carbon atoms. Since E_s is constant, the temperature coefficients of the longer chain compounds must be greater since their critical temperatures are lower. The various possible shapes of the γ and E_s curves have already been given in Fig. 1.

TABLE III.—THE VARIATION OF $-\frac{d\gamma}{dT}$ WITH γ_0.

Name.	E_s.	γ_0.	$-\left(\frac{d\gamma}{dT}\right)_0$.	$-\left(\frac{d\gamma/dT}{\gamma_0}\right)$.
Methyl formate	71.3	28.50	0.1569	0.00551
Thionyl chloride	(73.3)	(34.50)	(0.142)	(0.00412)
Acetylene tetrachloride	72.6	36.4	0.132	0.00359
Anisol	72.1	37.98	0.125	0.00329
Ethyl thiocyanate	72.3	38.5	0.124	0.00321
m-Dichlorobenzene	(73.3)	(38.5)	(0.127)	(0.00330)
p-Toluolnitrile	(73.1)	(39.0)	(0.125)	(0.00321)
Methyl malonate	(73.8)	(39.39)	(0.126)	(0.00320)
Chloromaleic dimethyl ester	(73.2)	(39.99)	(0.122)	(0.00305)
m-Fluoronitrobenzene	72.9	40.1	0.120	0.00299
Benzonitrile	72.8	40.9	0.117	0.00286
Benzyl amine	72.8	41.4	0.115	0.00278
Methyl-*o* salicylate	72.9	41.8	0.114	0.00273
Dibenzylamine	72.15	42.32	0.107	0.00250
o-Nitrotoluene	72.6	43.3	0.107	0.00247
Methyl cinnamate	72.1	43.4	0.105	0.00242
o-Chloronitroaniline	72.8	43.6	0.107	0.00245
1,3-Dichloro-4-nitrobenzene	72.7	44.9	0.102	0.00227
Nitrobenzene	72.3	44.9	0.100	0.00223
Benzyl benzoate	(73.8)	(45.2)	(0.105)	(0.00232)
Triphenyl methane	72.2	46.6	0.094	0.00202
Dimethyl tartrate	(73.8)	(47.5)	(0.096)	(0.00202)
Glycol	(73.9)	(49.34)	(0.094)	(0.00273)
Lactamide	72.4	50.54	0.080	0.00178
Salicylamide	72.1	51.1	0.077	0.00151
Octane	48.4	23.36	0.092	0.00394

From the standpoint of the theory that the molecules in surfaces are oriented, the assumption that a sphere of liquid which contains a gram molecule of the substance, has a *molal surface*, as made by Eötvös, and by Ramsay and Shields, is without value, at least in many cases, since such "molal surfaces," for example in the case of the normal alcohols or acids with varying lengths of chains, would contain a much less constant number of molecules than a unit area. It is thus to be expected that the degree of association calculated by the method of Eötvös, Ramsay, and Shields, is not at all correct. Their method of calculating the critical temperature has no advantage over the use of other functions of the simple temperature coefficient. The discussion given in the preceding paragraph shows that with the chain compounds, as the length of the molecule increases, the temperature coefficient decreases, and this explains why a multiplication by a term containing the molecular weight in the numerator gives a temperature coefficient which is more uniform for such a set of compounds as a class.

We have in preparation a paper on the bearing of this theory on the problem of molecular association. It is interesting to note that Jaeger,[1] from a different standpoint, that of the values which he obtains for the molar temperature coefficients, comes to a conclusion somewhat similar to ours. Thus he says:

> "After what has been said however, it can hardly be quite sure that such a calculation of the degree of association can be thought of as a step in the good direction." "If the supposition now were right that a decrease of the values[2] for $\frac{d\mu}{dT}$ indicated an augmenting degree of association, it would be difficult to imagine why the larger number of liquids show μ, T curves of the Type 3: for from the gradual decrease of $\frac{d\mu}{dT}$ with increasing temperature in these cases. we must conclude that the association of the liquid would increase with increasing temperature. But because by far the most dissociations are accompanied by a heat absorption, the mentioned conclusion could hardly be put in accordance with the laws of the mobile equilibrium." "These facts seem after my opinion to make it very dubious, if the decrease or increase of $\frac{d\mu}{dT}$ with varying temperature can be esteemed any longer to be connected directly with the degree of association of liquids."

That this method for determining molecular association cannot have much value is indicated by the results which it gives. Thus toluene between —71 and —21 is found by Jaeger to give a value of $\frac{d\mu}{dT}$ equal to 3.40, so according to the Eötvös, Ramsay and Shields method of calculation it should be highly dissociated, while between 86 and 109 degrees the constant falls to 1.76, so at this higher temperature toluene should be associated. This is a peculiar behavior for a "normal" liquid. The values for benzene are very similar. These data, if correct, can seem to have only one interpretation, and since this is an important question, we expect to repeat Jaeger's determinations by a different method than the one used by him.

A comparison will now be made between the data presented in Table I of the preceding paper and Table II of this paper. For organic liquids, the values of the surface tensions varies from 18.76 for ether, and 20.7 for hexane, to 59 for formamide and 65 for glycerol; the heats of surface formation lie between 16.3 for glycerin, 19.2 for benzamide, and 19.8 for isopropyl alcohol, as the lower values, up to 35.9 for acetonitrile, 41.5 for methyl formate, 42.6 for carbon disulfide, and 41.42 for thiophen. The total surface energy is more characteristic, since it is not only independent of temperature, but also shows a more evident relation to the

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[1] *Proc. Acad. Amsterdam,* 17, 418–9 (1914).

[2] μ is the molecular free surface energy.

chemical constitution. It is smallest for non-polar compounds in general, and highest for polar compounds and varies from about 46 for alcohols and paraffins to 81.6 for glycerin, 66.37 for formic acid, 66.7 for acetonitrile, about 80 for formamide, 77 for nitromethane, 79 for pyridine, etc. The very polar liquids, such as water (118 ergs), and bromine (195.5 ergs), have very high total surface energies. The work done in the formation of one cm^2. of an interface with water varies from about 40 for the paraffins to very high values (100 or more) for acids and alcohols which are soluble. While not independent of the temperature, the values seem to be closely related to the chemical constitution of the non-aqueous phase.

Tables IV and V give a comparison between the values of the total energy of the formation of the single surface of the liquid, and the work done when one square centimeter of the liquid is brought in contact with one square centimeter of a water surface. From the theory presented in the first part of this paper it might be expected, since water is the most polar of the liquids, that when any of the other liquids contain polar groups, there would be a turning of these polar groups toward the water, the formation of a "double electrical layer" and that considerable work would be done.

TABLE IV.—COMPARISON OF THE DECREASE OF FREE ENERGY WHERE ONE CENTIMETER OF AN INTERFACE IS FORMED BY THE MEETING OF WATER AND A SECOND LIQUID PHASE ($-\Delta\gamma$), AND THE TOTAL ENERGY OF THE SURFACE OF A LIQUID (E_s FOR ONE CM^2.)

I. Paraffins.

$-\Delta\gamma$ is low = 41 for hexane and octane; value increases to about 48 for very long paraffins.

E_s is low = about 47:

Practically constant for the lower paraffins, but rises in the case of a high boiling long chain paraffin. (This is however a mixture.)

Substitution of phenyl groups for H increases the values very much; *e. g.*, triphenyl methane is 72.2.

II. Alcohols.

$-\Delta\gamma$ is high:

For CH_3OH the value is 95.5, or *more than twice as high* as for the paraffins.

Decreases slightly with length of chain to 92.7 for octyl alcohol.

Lower alcohols soluble in water. Higher alcohols not soluble. Lower alcohols, as CH_3OH, not soluble in higher paraffins, as C_7H_{16}.

Extremely high for polyhydric alcohols in direct ratio to the number of OH groups. Soluble in water.

E_s is low:

Practically the same for the paraffins. Value (about 46) very nearly constant as the length of the chain increases.

Alcohols of the iso-hydrocarbons have values uniformly 2 to 3 less than the normal type.

Polyhydric alcohols have values very much higher; *e. g.*, glycol, $C_2H_4(OH)_2$, has a value of about 74, and glycerine is still higher.

Surface tension increases slightly with length of chain and markedly with the number of OH groups; l for glycerol is lower than for monohydric alcohols.

Double bonds in the hydrocarbon chain have little effect upon the surface tension or E_S.

Sulfur alcohols (mercaptans) have approximately the same surface tension as the ordinary type, but very much higher E_S $\left(\frac{63}{45}\right)$.

III. Cyclohexanol.

—$\Delta\gamma$ is very high:

103.7.

E$_s$ is higher than for the hexyl alcohol by about $\frac{1}{5}$ judging by *calculated* value (= 61).

IV. Ethers.

—$\Delta\gamma$ is high:

Ethyl ether = 80.21 or twice as high as for paraffins.

E$_s$ is low:

Ethyl = 47, or same as hydrocarbons or lower monohydric alcohols.

Ethyl-propyl = 50.

It is quite remarkable that the coefficient $\frac{d\gamma/dt}{\gamma_0}$ or α has the highest values for any whole class of compounds, from 0.005 to 0.006.

V. Nitriles.

—$\Delta\gamma$ is high:

Lower nitriles soluble in water, higher nitriles not soluble.

Values for —$\Delta\gamma$ about the same as for acids.

E$_s$ is moderately high.

Relatively the same values as for acids.

Decreases rapidly with increasing length of chain. For very long chains probably decreases almost to the value for paraffins.

For 2 CN groups, both E_S and γ are very high, being, respectively, 83 and 53 for methylene cyanide.

α for simple hydrocarbon nitriles uniformly high, 0.0043 to 0.0033.

VI. Acids.

—$\Delta\gamma$ is very high:

Especially for short chain acids:

Formic 110.

Acetic 100

Caprylic 94.

Decreases rapidly with length of chain.

Same values as for nitriles.

Soluble in water.

Influence of double-bonded carbon not yet determined experimentally.

E$_s$ is moderately high:

Same values as for nitriles.

Decreases rapidly with length of chain.

Smaller for iso-compounds.

Both the surface tension and the latent heat decrease with the length of the chain, but the surface tension decreases much the more rapidly.

Successive chlorination of an acid, causes a very rapid decrease in both γ and E_S, but in this case the total energy decreases much the more rapidly.

α for acids is uniformly high and averages very close to the coefficient of a perfect gas, 0.00366. The value for chloro-acids is very much less.

E_s for anhydrides is always higher than for the corresponding acid.

VII. Acid Amides.

$-\Delta\gamma$ is high:

E_s is high:

Higher than for either nitriles or acids.

Increases rapidly with length of chain.

Increased considerably by alcohol groups.

VIII. Esters.

E_s is moderately high:

About the same as for acids.

A very uniform decrease with increasing length of chain in acid group; and also in alcohol group; *i. e.*, methyl formate is higher than either methyl acetate or ethyl formate.

Slightly higher for esters of iso-acids than for those of *n*-acids.

Introduction of NH_2 group causes slight increase in surface tension and a *greater decrease* in E_s.

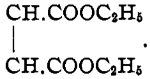
CN group causes increase in surface tension of about 10 and also an increase in E_s.

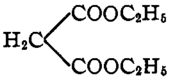
Values for esters of dibasic acids higher than for corresponding monobasic acids in surface tension but remarkably similar in latent heat of the surface; E_s for ethyl malonate practically the same as for ethyl acetate.

Cl and Br increases markedly.

Esters of stereoisomeric acids higher for *cis*-form than for *trans*-form.

Glyceryl esters *descend* in the value of E_s as well as γ to the C_9H_{18} group and then rapidly *ascend* with the introduction of higher groups.

Uniform distribution in molecules of (*COOR*) *groups, that is*, attachment to different C atoms when in pairs, gives higher values than non-uniform distribution or when attached to the same C atom. This may be shown in several cases, *e. g.*, ethyl fumerate,  $\begin{array}{l}CH.COOC_2H_5\\ |\\ CH.COOC_2H_5\end{array}$. has higher values than ethyl malonate,



IX. Ethyl Iodide.

$-\Delta\gamma$ is about $\frac{1}{2}$ higher than for paraffins, showing the polarity of the iodine atom.

E_s is $\frac{71}{49}$ greater than for hexane.

X. Chlorine and Sulfur Compounds.

$-\Delta\gamma$ chloroform (72.4) about $\frac{1}{2}$ larger than for CCl_4 (48.19).

Carbon bisulfide (52.8) nearly as low as CCl_4.

E_s very nearly the same for both $CHCl_3$ and CCl_4.

Successive introduction of any halogens in C_2H_5 group raises both E_s and γ.

Uniform distribution of chlorine atoms when in pairs gives higher values for E_s and γ than non-uniform; *e. g.*, ethylene chlorine (CH_2ClCH_2Cl) has higher values than ethylidene chloride ($CH_3.CHCl_2$). This is in accordance with the theory that the active groups are drawn from the surface. In ethylidene chloride therefore the CH_3 group would undoubtedly by *in* the surface while in ethylene chloride, a higher surface tension must result from the fact that the 2 chlorine atoms are attached to different carbon atoms instead of only one, *and therefore one chlorine atom must be near the surface in this case. This same relationship is found to hold with 2 CN or 2 COOR groups.*

XI. Unsaturated Paraffins.

—$\Delta\gamma$ is higher than for the paraffins. Thus the single unsaturated bond at the end of an eight carbon atom chain as in octylene increases the value from 41 to 73—an enormous increase. Thus the value for octylene is higher than for octane, but much lower than for the corresponding acid or alcohol.

XII. Strongly Polar Substances.

—$\Delta\gamma$ is extremely high:

E_s is very high: $H_2O = 118.1$.

$Br_2 = 195.5$.

XIII. Benzene, Cyclohexane and Hexane.

—$\Delta\gamma$ for benzene is high: $\frac{70}{48} \times$ hexane; $\frac{70}{38} \times$ cyclohexane.

E_s is high: Values are in the following order: cyclohexane, 75; benzene, 68; hexane, 49.

The surface tension increases: hexane, 21.3; cyclohexane, 29.8; benzene, 31.6.

l is 28 for hexane, 36 for benzene and is extremely high (45.8) for cyclohexane.

The high values for cyclohexane are so striking that the experimental work should be repeated.

XIV. Benzene Plus Hydrocarbon Group.

—$\Delta\gamma$ is a little less for toluene than benzene; and for *m*-xylene it is more than for the other too.

E_s decreases in the order: benzene, toluene, *m*-xylene, *p*-cymene or with the number and length of the side chains.

Decreases in the order of *m*-, *o*- and *p*- for isomerides, though the surface tension remains practically the same for all three.

XV. Benzene Plus Active Groups.

—$\Delta\gamma$ is very high:

E_s increases in the order: benzene, 65; benzaldehyde. 70.5; phenol, 71; benzonitrile, 72.7; aniline, 73.2; nitrobenzene, 74.8.

TABLE IV B—E_S.

XVI. Ketones and Lactones.

Moderately high values for E_S of the same order as for acids.

Decreases with increasing length of hydrocarbon chain, except when an acyl group replaces an H atom, which causes a slight increase.

All ketones and lactones have values for α near 0.004.

Ketoxime group ($C = NOH$) gives higher surface tension than the ketone group.

XVII. Amino Derivatives.

Values uniformly *low* and very much the same as for alcohols.

γ and E_S increase quite slowly with increasing length of the hydrocarbon chain.

Distinct peculiarity found in the fact that with methyl and ethyl groups, there is a *decrease* in E_S in preceding from mono- to di- and then to tri-alkyl amines, while beginning with propyl amines there is an *increase.*

Amines of iso-hydrocarbons are invariably lower in surface tension than those of the isomeric normal hydrocarbons, and higher than those of the isomeric tertiary hydrocarbons, *e. g.*,

n-Butylamine, $CH_3.CH_2.CH_2NH_2$	23.8
Isobutylamine, $(CH_3)_2CHCH_2.NH_2$	22.4
Tertiarybutylamine, $(CH_3)_3C.NH_2$	19.4

This is entirely in accord with the theory already advanced for chlorides, cyanides and —COOR groups, that uniform distribution (in this case of both C and H) give higher values for γ and E_s than non-uniform.

NO (nitroso) groups almost double the values for γ and E^s, and therefore act as extremely polar groups.

α for all amines is quite high. being in most cases between 0.004 and 0.005.

XVIII. Aromatic Halogen Derivatives.

Moderately high and very little different from the paraffin derivatives. E_s for C_6H_5I and C_2H_5I are practically the same. E_s for chlorobenzene and fluorobenzene are less than for benzene itself. γ and E_s increase in order F, Cl, Br, I, or in the order of the atomic volumes.

Values for di-substitution products decrease in the general way: meta, ortho, para. Since 2 active atoms in the para positions on the benzene ring are attached to opposite ends of the molecule, they may act in the nature of counter-balanced weight, so that the lower atom would have much the less effect than if it were at an angle less than 180° from the other as is the case with the meta and ortho arrangement. It seems to be, therefore, a general rule that where with *benzene* derivatives 2 or more molecular configurations for a given substance are possible. the more *linear* the molecular arrangement, the less will be the free surface energy. This is just the *opposite* of the rule for the hydrocarbons. It is remarkable also that substances which may form liquid crystals follow the rules of the benzene derivatives. With 2 dissimilar atoms however in the para position such as *p*-fluorobromobenzene, the great difference in activity of the 2 atoms at opposite ends of the molecule give a *higher* value for γ and E_s than if they were arranged in meta or otho positions.

XIX. Aromatic Nitro Derivatives.

High values for E_s and γ, similar to nitromethane and nitroethane, showing the extremely high polarity of the NO_2 group.

Decreases with number and length of side chains.

Nitrotoluol has values decreasing as usual in order, meta, othro and para; with CH_3 and NO_2 the two *shifting groups.*

All 6 cases of di-nitro and nitrohalogen substitution products of benzol show the same order for E_s and γ: meta, ortho, para.

NO_2 groups have a greater effect in increasing E_s and γ than halogen atoms; *e. g.*, benzene, 31.6; $E_s = 70$.

Chlorobenzene $\gamma = 35$; $E_s = 68$.

Nitrobenzene $\gamma = 45$; $E_s = 74$.

m-Dinitrobenzene $\gamma = 50$; $E_s = 77$.

It is to be observed that in the three possible structures for dichloronitro benzene, the lowest values for γ and E_s are obtained for the isomer which has the chlorine atoms in the 1.4 positions or at opposite ends of the molecule. The one NO_2 group has the effect of increasing the values.

XX. Aromatic Amino Derivatives.

High values for E_s and γ, very much higher than is the case with the paraffin amino derivatives. NH_2 almost as polar as NO_2.

Correspond almost exactly with the related NO_2 derivatives.

Decrease with number and length of the alkyl radicals replacing H in the NH_2 group; *e. g.*, aniline is higher than nonomethyl aniline which is higher than monoethyl aniline or dimethyl aniline.

The group C_6H_5 in the substituted anilines has exactly the same effect apparently as H, for γ and E_s in diphenylamine. for example, have the same values as for aniline. Similarly tribenzylamine has a much higher value for E_s than does aniline.

The total effect of the NH_2 seems much less than NO_2 or halogens. Hence with NO_2 or Cl, the *p*-anilines have slightly higher values than the *m*-isomerides.

XIX. Phenols.

High values for E_s and γ. very much higher than the alcohols, though slightly less than for the aromatic amines. for OH acts here as if less polar than NH_2.

Behavior in general is the same as that of the corresponding amines; NO_2 and halogens have same effect. and *p*-phenols have highest values.

XX. Phenolic Derivatives.

The ethers have moderately high values for E_s and γ but appreciably less than for the phenols.

Values decrease with increase in length of the chain opposite to C_6H_5.

NO_2 groups in para position with OCH_3 or 2 OCH_3 groups in such relation as in hydroquinone dimethyl ether, give far lower values for E_s than isomers of the meta or ortho type.

XXI. Aromatic Esters.

E_s for benzoates does not differ greatly from esters of formic or acetic acid, but values of γ for the former are 25% higher and l correspondingly lower.

Values decrease with increase in length of alkyl chain. but $C_6H_5CH_2$ has effects very similar to CH_3.

OH groups produce practically no effects.

Phenyl urethane has values only slightly greater than ethyl urethane.

Double bonds in the ester give higher values than single bonds. Hence cinnamic acid and esters have higher γ and E_s than hydrocinnamic esters.

As is invariably the rule, isothiocyanates have higher values for γ, l and E_s than isocyanates. The sulfur atom has always a greater effect than the O.

XXII. Aromatic Ketones.

Moderately high, greater than alkyl ketones by a fraction which with some degree of constancy prevails between corresponding alkyl and aromatic compounds.

An interesting relationship is found with tetrachlorobenzophenone whose value for γ is about 4 larger than that of benzophenone. Replacing the ketone oxygen by 2 chlorine atoms to form tetrachlorobenzophenone, values for γ. l. and E_s are all *greatly* reduced. The unsaturated nature of the oxygen atom in ketones and ethers especially, as apparent particularly in its power to form oxonium derivatives, must account in part for this behavior.

XXIII. Aromatic Amides.

Slightly *lower* but otherwise similar to alkyl amides in value. The OH has a greater effect in increasing values than for any other class of compounds.

XXIV. Nitriles.

High values similar to alkyl nitriles.

C_6H_5CN higher than benzene $= \frac{74}{70.5}$.

C_6H_5CN higher than C_6H_5Cl $= \frac{74}{68}$.

C_6H_5CN higher than $C_6H_5NO_2 = \frac{74}{73}$.

C_6H_5CN higher than $C_6H_5OH = \frac{74}{66}$.

C_6H_5CN higher than $C_6H_5OCH_3 = \frac{74}{65}$ and is the same as $C_6H_5NH_2$ and C_6H_5CHO.

XXV. Metalloid Aromatic Derivatives.

Triphenyl stibine and triphenyl phosphine show very high values. corresponding very closely to triphenyl methane which has 1 C atom in the same position as the Sb or P atoms.

XXVI. Heterocyclic Compounds.

All high in γ and E_S, and almost the same values as those for aromatic hydrocarbons, pyridine has values only very slightly greater than has benzene. It is quite evident that there is a greater loss of identity for particular atoms in ring structures than in chains.

Discussion of the Substitution Products of the Paraffins.

Perhaps the most striking result which we have found is that when an alcohol surface approaches a water surface, the work done per cm^2. is extremely high (more than twice as high than when a paraffin surface approaches a water surface) and varies little with the length of the hydrocarbon chain. On the other hand, the total energy used in the building of a surface of alcohol molecules on pure alcohol, is practically the same as for the surface of a paraffin. This is easily explained on the basis that the upper surface of the outer layer of alcohol molecules on alcohol is actually the same as if the liquid is a paraffin. That is only the least polar end of the alcohol molecule, where the stray field is least, is oriented outward in the surface, so that after all a paraffin surface is built up. If, however, this surface is brought up to a water surface, the work done by a paraffin surface would be only about 41 ergs per sq. cm., while the actual work done by the alcohol is 92 ergs. Thus an alcohol surface at the vapor phase acts as a very slightly polar paraffin surface, while toward water the action is that of a group with a strong electromagnetic field. This indicates that when brought in contact with water, the molecules in the alcohol surface turn around so that the hydroxyl groups unite with the water.

Another fact brought out in Table IV should be emphasized: that the distribution of active groups among the carbon atoms causes the total surface energy (and both the surface tension and the latent heat of the surface) to be much higher than when the same number of active groups are attached to one of the carbon atoms of the chain, for in the latter case an inactive paraffin group will rise to the surface when the active group orient into the interior, but in the former case there is no inactive group which can be brought to the very outer surface.

Table V shows that as the length of the hydrocarbon chain increases the total surface energy of all of the monosubstitution products approaches that of the hydrocarbons, but at different rates, most rapidly for the alcohols, and then for the amino compounds and acids in order, and least rapidly for the NO_2, $COOCH_3$ and $CONH_2$ derivatives. The most apparent relation here is first to the number and activity of the latent valences, and second, to the volume of the group, and an increase in either of these increases the distance to which the influence of the active group extends, and causes also an increase in the total surface energy for the short-chain compounds. This discussion might be continued at great length and the evidence for the orientation of the molecules, in the surfaces of the different substances, presented in detail, but the application of the general principles already given to Table II to V will make it easy to decide what the effects are in the individual cases.

TABLE V.—VALUES OF THE TOTAL SURFACE ENERGY (E_s) OF THE *Normal* PARAFFINS AND THEIR NORMAL DERIVATIVES.[1]

Total number of carbon atoms.	Paraffin.	OH.	NH_2.	CN.	I.	SH.	COOH.	NO_2.	$COOCH_3$.	COCl.	$CONH_2$.
1	..	43	55.5	..	..	..	68 M. 64 J.	79.7 M. 70.7 J.	71	..	85
2	..	45	48.1	68	59.8	62.8	57	67.8	70 M. 63 J.	68	75
3	..	46.6	50.4	59.7	..	..	57	..	..	..	64
4	..	48.3	52.7	59.2	..	..	54	..	59	..	..
5	..	..	47.6	51.5	..	..	..	..	51	..	..
6	49.5	..	47.4	54.5	..	..	..	..	..	..	..
7	..	..	47.2	48.7	..	..	..	..	..	..	..
8	48.4	50.8	..	..	..	..	..	..	..	..	..
Symmetrical Di-Substitution Products.											
	Cl	OH	..	..	..	..	..	..	..	..	..
2	73	74	..	..	..	..	..	..	..	..	..
Unsymmetrical Di-Substitution Products.											
2	61	..	..	..	..	..	..	..	..	..	..

Discussion of the Substitution Products of Benzene. Monosubstitution Products.

In Table VI a comparison is given between the values of γ and E_s for benzene and its different mono- and di-substitution products. The monosubstitution products are arranged in the order of decreasing values of E_s, beginning with acetophenone ($E_s = 79.5$), and, ending with fluorobenzene with the extremely low value of 46.4, which, however, may not be correct. The first 15 groups given in the table have higher total surface energies than benzene. *It is quite remarkable that all of the groups which are the more active in this sense contain nitrogen, sulfur, or oxygen atoms*, and all of these atoms have *latent valences*. This fact, together with the double bonds present as in the NO_2 or CHO groups, or the triple

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[1] We are now working experimentally on the completion of this table.

bond of the CN group, may explain in a large measure this increase in surface energy.

When the ketones are compared it is found that acetophenone, with the CH_3 and C_6H_5 groups has a much higher total surface energy (79.5) than benzophenone (71.6), which is balanced by a C_6H_5 group on each side. When substituted in benzene both of the groups NHC_2H_5 (77.4) and NHC_6H_5 (73) give a larger E_s than —$NHCH_3$ (70.9), while it will be seen that toluene (65.9) (—CH_3 substitution), has a higher value than either ethyl benzene (60.9) or diphenyl (65). Also one ethyl group when substituted for a hydrogen atom of the amino group in aniline (74.3) increases the total surface energy to 77.4, while the substitution of a second ethyl group has no effect. The —$NHCH_3$ (70.9) group is about as active in this sense as —$N(CH_3)_2$ (69).

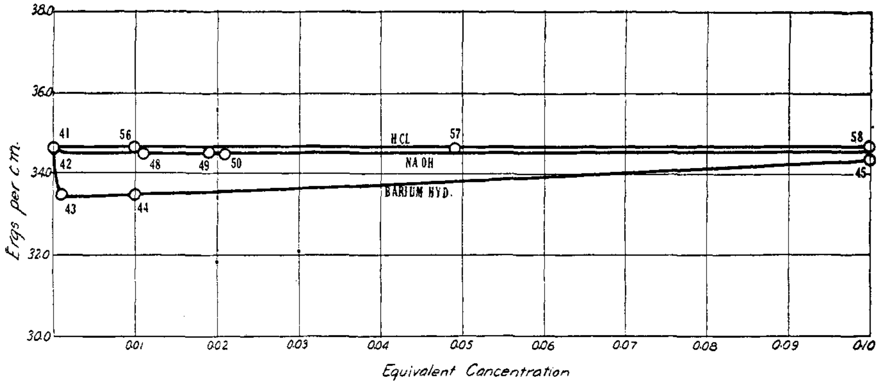

Fig. 2.—The effect of bases upon the interfacial free surface energy between water and benzene.

Di-substitution Products.

It is of EXTREME INTEREST THAT IN EVERY CASE FOR WHICH WE HAVE ANY DATA THE PARA BENZENE DI-SUBSTITUTION PRODUCT HAS THE LOWEST TOTAL SURFACE ENERGY OF THE THREE ISOMERS, WHENEVER THE TWO GROUPS ARE EXACTLY ALIKE, and the meta compounds always have the highest E_s, except in the one case of two —OCH_3 groups, when the ortho derivative gives a higher value. *This is exactly the opposite of the rule found for the substitution products of the paraffins, for here in the benzene series symmetry leads to small values of total surface energy.*

The Orientation of Benzene Substitution Products in Surfaces.

A study of Table VI will bring out many remarkable relationships, but we will discuss only those which have a very marked bearing on the orientation of benzene molecules and its substitution products on vapor-benzene surfaces.

TABLE VI.—THE TOTAL SURFACE ENERGY AND FREE-SURFACE ENERGY OF BENZENE AND ITS MONO- AND DI- (AND TRI-) SUBSTITUTION PRODUCTS.

Benzene. $\gamma = 31.6$. $E_s = 70.6$.

Mono-substitution Products.

	γ.	E_s.
$COCH_3^{J.1}$	47.7	79.5
$NCS^{R.G.}$	44.7	78.1
$NH(C_2H_5)^{M.B.}$	38.3	77.4
$N(C_2H_5)_2^{D.F.}$	38.3	77.4
$NO_2^{M.}$	45.8	77.0
$COOCH_3^{J.}$	41.0	75.5
$SH^{M.}$	41.6	75.1
$CN^{M.}$	40.6	74.9
$CHO^{J.}$	44.8	74.5
$NH_2^{J.}$	45.4	74.3
$COOCH_2C_6H_5^{J.}$	45.2	73.8
$NHC_6H_5^{T.M.}$	45.3	73.0
$COC_6H_5^{J.K.}$	44.9	71.6
NCO.	42.5	71.3
$NHCH_3^{J.K.}$	40.1	70.9
$I^{M.B.}$	43.2	70.0
$N(CH_3)_2^{J.}$	39.4	69.2
Br.	35.4	68.4
$OC_2H_5^{J.}$	35.5	67.9
$NH_2COO^{T.M.}$	41.7	67.6
$Cl^{R.A.}$	34.8	67.0
$CONH_2$.	47.2	66.3
$OH^{J.K.}$	40.8	66.2
CH_3.	31.6	65.9
OCH_3.	37.3	65.4
$C_6H_5^{D.F.}$	40.4	65.3
$N_2O.C_6H_5^{J.K.}$	43.6	64.9
$H_2N.NH^{T.M.}$	44.0	64.7
$COOC_2H_5$.	37.0	63.4
C_2H_5.	31.1	60.9
F.	29.2	46.4

Di-substitution Products.

	Meta highest—para lowest.												Para lower.				Ortho highest. Para lowest.			
	2 NO_2.		2 Cl.		Cl-NO_2.		Br-NO_2.		CH_3-OH.		2 CH_3.		OCH_3-NO_2.		2 CH_3.		I-NO_2.		2 OCH_3.	
Ortho......	50.5	76.7	37.2	69.5	45.1	75.8	46.2	74.3	38.1	60.5	31.1	60.4	50.8	76.3	30.5	56.2	48.9	75.1	42.5	82.3
Meta.......	52.1	80.2	38.5	73.3	45.1	79.3	47.4	79.2	38.6	64.4	31.3	63.6					50.1	80.1	41.3	74.0
Para.......	48.5	70.4	34.8	59.4	42.7	68.3	43.8	70.0	36.6	59.5	29.3	58.4	46.2	70.2	32.4	54.6	41.1	70.3	41.1	70.3

	Para highest.														Para highest. Ortho lowest.				Single cases.									
	F-NO_2.		F·Br.		Cl·NH_2.		OH·NO_2.		NO_2·NH_2.		$NHCH_3$-NO_2.		OH·OCH_3.		CH_3·NO_2.		CN·CH_3.		CH_3·Cl.		CH_3-Br.		CH_3O-CHO.		2 $COOC_2H_5$.		2 $COOC_5H_{11}$.	
Ortho......					43.6	72.8	42.5	66.4	54.1	79.2			46.4	78.7	43.3	72.6	39.68	69.5	35.8	67.3	36.5	63.2			39.2	69.0	32.2	51.3
Meta.......	40.1	72.0	31.5	66.6			46.1	61.1	54.0	78.9	45.7	70.8					39.38	65.4										
Para.......	41.2	72.0	37.2	69.5	45.0	71.5	54.3	80.0	60.4	86.5	63.8	94.6	51.6	100.4	40.9	65.2	39.64	69.2					44.9	76.6				

Single cases (continued).	OH·$COOCH_3$.		OH·$COOC_2H_5$.		OH·$COOC_6H_5$.		CH_3·NH_2.		OH·$CONH_2$.	
Ortho......	41.8	72.9	39.1	68.2	54.7	73.0	43.1	73.4	51.1	72.1
Meta.......										
Para.......										

Benzene. $\gamma = 31.6$. $E_s = 70.6$.

Tri-substitution Products.

2 Cl.NO_2.

	γ.	E_s.
$Cl_{(1,2)}.NO_{2(4)}$............	44.5	70.2
$Cl_{(1,3)}.NO_{2(4)}$............	44.9	72.7
$Cl_{(1,4)}.NO_{2(2)}$............	43.5	67.0

2 NO_2.Cl.

	γ.	E_s.
$NO_{2(2,4)}Cl_{(1)}$.........	51.2	77.1

3 CH_3.

	γ.	E_s.
1,2,4.................	32.4	56.8
1,3,5.................	30.0	54.6

2 NO_2.OH.

	γ.	E_s.
$OH_{(1)}NO_{2(2,4)}$........	52.5	77.3

CH_3.NH_2.NO_2.

	γ.	E_s.
$CH_{3(1)}.NH_{2(4)}NO_{2(3)}$.....	48.9	77.0
$CH_{3(1)}.NH_{2(2)}NO_{2(5)}$.....	48.6	73.2
$CH_{3(1)}.NH_{2(2)}NO_{2(6)}$.....	65.4	108.5

NO_2.2OH.

	γ.	E_s.
$NO_{2(2)}.OH_{(1,3)}$........	44.6	80.2
$NO_{2(2)}.OH_{(1,4)}$.......	41.6	70.3

3 Cl.OH.

	γ.	E_s.
$OH_{(1)}.Cl_{(2,4,6)}$........	42.6	67.2

The small letters give the initials of the obervers.

While we will make use of the plane formula for benzene in explaining the relationships, this is only because this formula is the more easy to present, and from the study thus far made of the space formulas suggested by different writers, it would seem that the use of the best of them would not materially change our interpretation.

This interpretation is based on a number of facts which seem quite conclusive when all of them are considered together. As presented in the preceding paper of this series,[1] and summarized in Table IV of this paper, the decrease of free energy when a benzene surface meets a water surface at 20° is 66.8 ergs per sq. cm., and this is about 67/48 higher than for hexane, and 67/38 higher than for cyclohexane. Now, as has already been explained, one double bond at the end of an eight carbon atom paraffin increases the similar value for the decrease of free energy from 46 for octane to 72.9 for octylene, thus proving the high attraction of the double bond for water. From this standpoint the higher attraction of benzene for water is due to the presence of what are commonly called the three double bonds. Now all of the carbon atoms of benzene are affected by these double bonds so that all of the carbon atoms are strongly attracted by the water surface. From this standpoint we adopted, sometime ago, the provisional working hypothesis that the benzene ring would lie, what may be described as flat on the surface. Now the free energy decrease at the same temperature when a benzene surface meets a benzene surface, is also moderately high, 57.8 ergs, so we also adopted as a working hypothesis, the idea that on a benzene surface the molecules lie flat also.[2]

This, however, while reasonable, was not at all convincing until we found in addition the following striking facts: First, it has already been found that among the *paraffin derivatives* there is evidence that the chains are oriented perpendicular to the surface. Now when active groups are attached to the opposite ends of the molecules, as has been found, the surface energy rises markedly above that found for a non-symmetrical distribution of active groups. Among the benzene derivatives the *rule is exactly the opposite, that the para or symmetrical compounds give the smallest values.* This would seem to be because only when the two groups are para can both active groups turn down into the liquid and leave the benzene ring flat on the surface.

When the two groups are either ortho or meta, the active groups turn downward, since both groups act in the same direction; this tilts the benzene ring and thus stretches out the residual bonds (of the double bonds which attract the molecule to the molecules just inside the surface). When these bonds stretch out, a considerable stray field is developed, and the

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[1] THIS JOURNAL. 39, 354 (1917).

[2] Thus we have reached a similar general conclusion in regard to the setting of the benzene ring to that recently presented at a meeting of the society by Langmuir (*Metallurgical and Chemical Engineering*, Oct., 1915).

surface energy is increased. These are the general rules which hold when the two groups are of the same activity.

Let us now consider what should happen if the two active groups differ considerably in activity. In this case the more active group would turn downward, and the less active group would be raised toward the vapor phase. If this group is at all active, the surface energy should be increased, and since it is only when the two groups are para that an active group can thus be raised to any extent out of the surface, it need not be considered surprising that *under these conditions the surface energies of the para compounds, which otherwise have the lowest values, now become the highest.* Let us first consider cases where one of the groups is the very active —NO_2 group, which would turn downward into the liquid. When the second group is the relatively inactive (in the sense of this work) group F, the value for the para compound is 72, and therefore only a little higher than for benzene (70.6). Now if the group which is thus raised high in the surface is increased in activity the values for the para compounds increase in order as follows: OH (80) while for meta the value is now only 61 and for ortho, 66. With NH_2 as the raised group the para value is 86.5, or *extremely* high, while the ortho and meta remain lower. When the para groups are NO_2 and $NHCH_3$ the value rises to 94.6, while for OH and OCH_3 it reaches the *extremely surprising value of 100.4.* If, however, the raised para group is very inactive, as CH_3, the surface energy is lowered instead of raised.

An extremely striking set of results is that for benzene and its nitro derivatives: Benzene = 70.6 and *p*-dinitrobenzene = 70.04. Here the two perfectly balanced groups, even though very active, exert no influence on the total surface energy. However, *one* unbalanced nitro group raises E_s to 77, two ortho groups to 76.7, and two meta groups to 80.2.

Even more remarkable is the bearing of the data on the tri-substitution products. We will consider first the three nitro toluidines, with the nitro group the most active, the amino group also active, and the methyl group the least active. If all of these groups are on one side of the ring and adjacent the value (73) is only slightly higher than for benzene, if the nitro group is meta to the methyl, and the amino group is para, then E_s rises to 78, but if as in $1CH_3\text{-}2NH_2\text{-}5NO_2C_6H_3$ the nitro and amino groups are directly opposite, E_s rises to the astonishingly high value of 108, which is the highest known value for any benzene derivative.

In opposition to these increases of total surface energy it is found that the substitution of paraffin groups in benzene decreases the surface energy, since the less active groups rise to the surface and give the surface more of the character of a paraffin. It is perhaps of interest to note that benzophenone (E_s = 71.6) has only a very slightly higher value than benzene.

While what we have written may seem to indicate that what we assume is a static theory of the surface, this is by no means the case, for we recognize that the atoms and molecules must be vibrating, in a somewhat similar way to the atoms and molecules in a solid. A molecule which "evaporates" and passes into the vapor comes from the surface (and not from below the surface) when its energy of vibration in a direction perpendicular to the surface becomes so great that it is able to overcome the attractions of the surrounding molecules.

The Surface Tensions of Aqueous Solutions of Sodium Oleate and Magnesium Oleate and of their Interfaces with Benzene.

It has been shown that the absorption of a paraffin acid or its salt increases with the length of the hydrocarbon chain. In order to illustrate this effect we have chosen for investigation a substance sodium oleate, in which the paraffin chain is so long that it is very highly adsorbed. While many investigations of this kind have been made, in none of them, so far as we have been able to discover, have accurate methods been employed, and this substance was chosen because it is adsorbed so greatly that it is extremely efficient in the formation of emulsions. The hydrocarbon chain is so long that even although it is an unsaturated substance, oleic acid is insoluble in water, so that, since sodium oleate is partly,

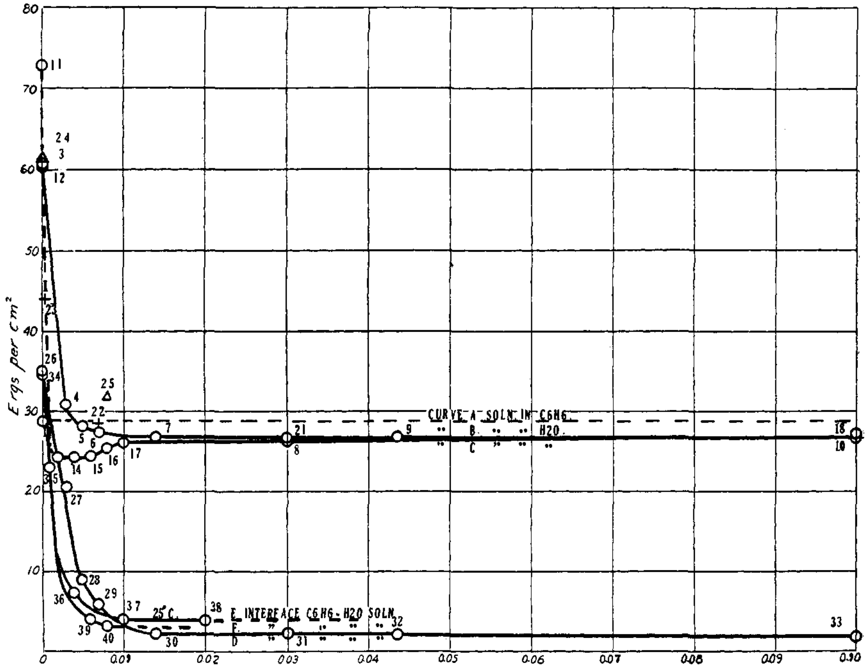

Fig. 3.—The effect of sodium oleate upon the free surface energy of water, and also at the interface between water and benzene. The heavy horizontal lines indicate *saturated films*.

though not highly, hydrolyzed by water, there is the additional complication in this case that the acid may separate out as a colloid. It would be expected that the sodium oleate or the oleic acid, insofar as they are adsorbed in the molecular form, would be set with the —COOH or —COONa group toward the water. Now the paraffin chain is so insoluble that even when a colloid is not visible, it is found by investigations on the conductivity of such solutions that the ions have formed very heavy multiply charged aggregates or miscelles. These aggregates carry a negative charge, and would seem to consist of a considerable number of the negative ions of the salt. The formation of these aggregates is quite likely connected with the insolubility of the hydrocarbon chains, and they form with the saturated compounds such as sodium palmitate, just as they do with the oleate.

The data for these solutions are given in Table VII and Fig. 3.

TABLE VII.—THE SURFACE TENSIONS OF SODIUM OLEATE SOLUTIONS, AND THEIR INTERFACIAL TENSIONS TOWARD BENZENE.

Point.	N.	W. g.	a^2.	$\frac{r}{a}$.	$f\frac{r}{a}$.	γ in dynes.
Curve A. Benzene Saturated with Solid Sodium Oleate at 20°.						
1	0.0000	0.02654	6.70	0.911	0.603	28.86
2[1]	0.00008	0.02660	6.71	0.919	0.604	28.88
Curve B. Aqueous Solution of Sodium Oleate after Rotating with Benzene and Allowing to Stand Overnight, 20°.						
3	0.0000	...	...	...	...	60.19 (25°)
4	0.003	0.03487	6.31	1.172	0.599	30.86
5	0.005	0.02976	5.77	1.142	0.599	28.24
6	0.007	0.03098	5.61	1.242	0.601	27.47
7	0.014	0.02820	5.47	1.173	0.599	26.77
8	0.03	0.03012	5.41	1.265	0.603	26.48
9	0.0436	0.02839	5.50	1.170	0.599	26.94
10	0.1	0.02811	5.45	1.175	0.599	26.68
Curve C. Aqueous Solution of Sodium Oleate.						
11	0.0000	0.07001	...	...	...	72.81
12	0.0001	0.05744	12.36	0.677	0.623	60.46
13	0.002	0.02222	4.94	1.068	0.600	24.29
14	0.004	0.02218	4.96	1.068	0.600	24.28
15	0.006	0.02240	5.00	1.063	0.600	24.48
16	0.008	0.02315	5.17	1.046	0.600	25.30
17	0.01	0.02389	5.33	1.030	0.601	26.07
18	0.1	0.02866	5.54	1.166	0.599	27.20
Aqueous Solution of Sodium Oleate after Emulsification of the Benzene Layer.						
19[1]	0.007	0.02450	5.48	1.016	0.599	26.82 (centrifuged)
20[1]	0.007	0.02905	5.23	1.288	0.603	25.54 (not centrifuged)
21	0.03	0.03043	5.47	1.259	0.603	26.75

[1] Points not plotted.

TABLE VII (*continued*).

Curve D. Interface after Rotating Sodium Oleate Water Solution with Benzene and Allowing to Stand Overnight at 20°.

Point.	N.	W. g.	a^2.	$\frac{r}{a}$.	$f\frac{r}{a}$.	γ in dynes.
26	0.0000	0.06646 (25°)	...	...	...	35.03
27	0.003	0.01052	35.32	0.182	0.734	20.63
28	0.005	0.009818	15.46	0.698	0.620	9.00
29	0.007	0.002811	10.05	0.342	0.692	5.85
30	0.014	0.0009869	3.82	0.555	0.641	2.22
31	0.03	0.0009085	3.52	0.578	0.638	2.05
32	0.0436	0.0009284	3.60	0.572	0.639	2.09
33	0.1	0.001903	3.07	1.57	0.609	1.78

Curve E. Sodium Oleate Water Solution against Benzene at 25°.

34	0.0000	0.06646	57.40	0.626	0.630	34.68
35	0.001	0.02694	38.14	0.444	0.664	23.00
36	0.004	0.007910	12.17	0.787	0.611	7.36
37	0.01	0.004236	6.64	1.065	0.599	4.02
38	0.02	0.004656	7.29	1.016	0.599	4.42

Curve F. Interface Sodium Oleate Water Solution (Shaken Vigorously with a Little Benzene and Allowed to Stand Overnight) against Benzene Saturated with Water Water at 20°.

26	0.0000	....	...	...	...	35.03
39	0.006	0.004196	6.89	1.046	0.600	3.98
40	0.008	0.001486	5.55	0.660	0.661	3.24

Sodium Oleate in Water when Hydrolysis is Prevented by the Addition of NaOH to the Solution (No. 24 was in 0.0002 *N* NaOH, No. 25 was in 0.008 *N* NaOH).

11	0.0000	0.06994	...	...	...	72.88
24	0.0001	0.05835	12.53	0.672	0.624	61.32
25	0.008	0.02928	6.50	0.933	0.604	31.79

Benzene Saturated with Solid Magnesium Oleate at 20°.

1	0.0000	0.02654	6.70	0.911	0.603	28.86
22	0.007	0.02638	6.65	0.922	0.604	28.64

Magnesium Oleate in Water Solution at 20°.

11	0.0000	0.06994	...	...	...	72.88
23	0.0005	0.04117	90.2	0.792	0.612	44.12

Interface, Water Saturated with Magnesium Oleate and Benzene Saturated with Magnesium Oleate at 20°.

55a	0.0000					35.03
55	[0.007 benzene] [0.0005 Mg(Ol)]$_2$	0.004568	7.51	1.001	0.600	4.33

Surface Tension of the Oleic Acid used in Preparing the Above Sodium and Magnesium Oleate.

56	pure	0.02998	7.44	0.872	0.605	32.50

Discussion of Fig. 3. The Surface Tensions of Oleate Soap Solutions.

The data obtained from the experiments on oleates and on the strong bases are shown graphically by the curves in Fig. 3 and in tabular form in Tables VII and I. In these tables N represents the normality of the solutions as made up; W is the drop weight in grams (corrected to vacuum), a^2 is the capillary constant in mg. per mm.^{2}, $f\frac{r}{a}$ is the correction factor which has been applied.

Experimental.

In discussing the experimental data the plan will be adopted of considering each curve in Fig. 3 separately, as well as the results given in the Table IV.

Curve A indicates that a saturated solution of sodium oleate in benzene (point 2) has practically the same surface tension as pure benzene (1). The curve is so short that it would not be seen on the scale of the figure, so it has been extended to the right as a dotted line to indicate the height at which it lies in the extremely dilute solutions. Evaporation of the saturated solution showed that it contained about 1 part of sodium oleate to 40000 parts of benzene.

Curve D represents the interfacial tension between two layers obtained by rotating aqueous sodium oleate solutions with benzene and allowing to stand in the 20° thermostat until the next day. If this rotating is not done very carefully the benzene will become slightly cloudy due to the formation of small amounts of the emulsion. No subsequent standing will serve to separate this emulsion, so the rotating at most, only serves to some extent to prevent hydrolysis and to attain a partial saturation of the aqueous solution with the benzene and of the benzene with the water. Hence in these runs we had aqueous solutions of sodium oleate containing small amounts of benzene, run against benzene containing slight amounts of an emulsoid.

It is noticed that at about 0.01 N the curve falls lower than the other two interfacial curves (E and F) for which we did not allow the benzene, used in the interfacial determinations, to acquire any emulsoid particles. It is at a concentration of about 0.01 N that the sodium oleate is the best emulsifying agent. Hence we would expect that the emulsoid particles acquired by the benzene layer with even a careful rolling would be sufficient to make the surface tension lower than when no emulsoid particles were present in the benzene (Curves E, F).

Curve B shows the values for the surface tensions of the aqueous sodium oleate phase after rotating with the benzene as for Curve D. Determinations were also made of the surface tension of the benzene layer in each case. This varied slightly with the amount of rotation, but was almost as high as that of the pure benzene. The average was about 28.5 dynes for the benzene layers. It will be noted that the surface tension does not drop so rapidly nor quite so far as for the aqueous solutions of sodium oleate which contain no benzene. The benzene seems to materially lessen the hydrolysis of the sodium oleate. That this hydrolysis is an important factor in the lowering of the surface tension is shown by the data for points 24 and 25, for which the solutions were made by dissolving the sodium oleate in dilute solutions of sodium hydroxide. It is seen that a 0.008 N solution of sodium oleate in 0.008 N sodium hydroxide (point 25) gave a surface tension of 31.79 dynes, while the same strength of sodium oleate made up in water without the sodium hydroxide (point 16 on Curve C) gave a value of only 25.30 dynes.

Curve E indicates the interfacial tension between benzene and aqueous solutions of sodium oleate when no emulsification or rotation had taken place.

Curve F represents the data for the interfacial tension between the layers after the aqueous solutions of sodium oleate were shaken vigorously with about one part of the benzene to 20 parts of the solution.

Small amounts of the benzene were used to obviate any appreciable change in the concentration of the sodium oleate phase which might take place due to the concentration of the sodium oleate in the emulsion. The mixture was allowed to stand at 20° overnight. The lower layer, that of the sodium oleate phase, separated out clear by morning and was drawn out from below the emulsion. The benzene was saturated with water at 20° by repeatedly shaking and immersing in the thermostat at this temperature.

This is the best of the methods studied for determining the interfacial tensions, since the benzene dissolves practically no sodium oleate. It is not feasible to try to obtain the benzene layer from the emulsion after the benzene has been shaken vigorously with the aqueous solutions of the sodium oleate. It is in fact possible to get the benzene by allowing the emulsion to stand until it cracks and the benzene separates out; or this cracking may be hastened by chilling the emulsion in ice. But there are no advantages in doing this and less likelihood of getting the true relations which exist at the boundary between the benzene inside the emulsoid particles and the water phase outside them.

A comparison of Curves E and F show that in general the effect of temperature on the interfacial tension is to raise it. The drop with increasing concentration of the soap is extremely rapid at both 20° and 25°. The interfacial tension at 25° is higher than that at 20° for at least concentrations of the sodium oleate of more than about 0.002 *N*. The direction of this change corresponds with the Gibb's adsorption formula.

Curve C graphically gives the data for the aqueous solutions of sodium oleate in air. It shows that the surface tension drops off very rapidly until at a concentration of about 0.002 *N* we have the lowest surface tension. This is the case for which it appears there is the maximum adsorption of the oleate. At this concentration too, there is a considerable tendency to hydrolyze. The oleic acid produced by this hydrolysis is less soluble than the sodium oleate; hence we would expect this adsorption of the oleic acid at the surface and the subsequently greater lowering of the surface tension. After about this concentration is reached the surface tension increases slowly with decrease of hydrolysis. The increase is slight until a concentration of about 0.01 *N* is reached. Then there is a very slight increase of surface tension with further increase of concentration. As the solution becomes more concentrated the turbidity caused by the presence of the colloid disappears, which indicates that the hydrolysis decreases with increase in the concentration of the solution.

Magnesium oleate of a given concentration lowers the surface tension approximately the same as the lowering obtained from aqueous sodium oleate solutions. We found from the study of the barium hydroxide that it had very little effect on the surface tension. By analogy we should expect that the magnesium hydroxide produced by the hydrolysis of the magnesium oleate should have little effect. Hence the lowering of the surface tension in the cases of both sodium and magnesium oleate is to be attributed to the effect of the oleate radical and to that of the oleic acid produced by hydrolysis. The magnesium oleate is about 14 times as soluble in the benzene as in the water and yet it lowers the surface tension only about 0.2 dyne in the benzene saturated with magnesium oleate. There is thus little tendency for the magnesium oleate to concentrate at the surface of the benzene. Newman[1] has previously observed that the aqueous solution of the magnesium oleate forms the inner phase of this emulsion produced in benzene. In the case of the aqueous solution of sodium oleate in benzene the aqueous solution forms the outer phase.

In the determination of the interfacial tension between water saturated with magnesium oleate and benzene saturated with magnesium oleate (point 55) the rapid accumulation of the solid magnesium oleate at the surface of the drop is interesting.

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[1] *J. Phys. Chem.*, 18, 34 (1914).

Preparation of Materials.

Sodium oleate which was perfectly white and had no appreciable odor, was made from best oleic acid, which had been kept sealed in a glass container, and a slight excess of sodium hydroxide in absolute aclohol. It was found that it is not advisable to use a water solution of the sodium hydroxide. The product was put in a small bottle with a good fitting ground glass stopper and kept in the dark. In the above preparation the sodium hydroxide used was from the same bottle as that whose surface tension is given in Table I (designated by K.). The surface tension of this oleic acid is given in Table IV as 32.50. The latter was clear and practically free from rancid odor.

Magnesium oleate: This was made from some of the above sodium oleate and magnesium chloride. It was washed until free from excess of the chloride.

Benzene: This had been specially purified by F. E. Brown from best thiophene free benzene by three times crystallizing and three times distilling. It distilled over at a constant temperature. Before using the benzene it was again distilled and only the middle fraction taken. In the runs with the bases the further precaution was taken of bringing the benzene to the boiling point by immersing the bottle containing it in boiling water immediately before use. This was done to get rid of the last traces of carbon dioxide. Also, in the work with the bases, special precautions were taken to fill all the vessels used with carbon dioxide-free air. These special precautions were taken because of the fact that the production of the sodium carbonate would tend to raise the surface tension of the sodium hydroxide; and the formation of solid barium carbonate in the barium hydroxide would make the determinations practically valueless. For in either case we are measuring very small changes of surface tension.

The solubility of sodium oleate in benzene is only about 1 part in 40000 whereas that in water as a true solution is unknown, but in a colloidal form it is practically unlimited. For example, 7.6 g. of sodium oleate were rotated with 21.5 g. of conductivity water in the 20° thermostat in a sealed tube. After about a week the mixture was a very viscous colloidal solution. With smaller quantities the solution is less viscous.

Water: All aqueous solutions were made in water collected in the absence of air. This water had a surface tension of 72.8 at 20°.

The drop weight method as used in the determinations of the interfacial tension was practically the same as described by Harkins and Humphrey.[1] It was found advisable after constant temperature was attained in running these measurements to allow the first drop to fall before the reading of the pipet was made. This insured a fresh surface when the run began.

Three different interface pipets were used during the determinations. The diameters of their tips were measured on our calibrated micrometer which reads to 0.001 mm. The radii were 0.1084 cm., 0.2744 cm., and 0.4745 cm., respectively. The pipets were calibrated by the use of water at 20°.

The different sizes of tips were essential so that the value of $\frac{r}{a}$ should come on a part of the correction curve which we have determined accurately. This is an important precaution, as may be seen by reference to point 27 in Fig. 3, where the tip was much too small for that particular determination and the result obtained obviously faulty. Values on these solutions have been obtained by some workers by the use of a single stalagmometer, and it is evident such results would not even be comparatively correct when the surface tension varies through such wide ranges as in the interfacial

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[1] THIS JOURNAL, **38**, 236 (1916).

surface tensions of the oleates; whereas by the proper choice of radii for the tips the absolute surface tensions are obtained. It will be noted that only a few determinations were made where $\frac{r}{a}$ was smaller than 0.575 or over 1.3. For this range of values the new curve is now quite satisfactory.

Molecular Orientation in Surfaces as Related to the Formation of Emulsions.

When Newman, working with Bancroft in 1914, found that while sodium oleate in solution will give emulsions of benzene in water, and the oleate salts of a metal with a valence higher than one, will give emulsions of water in benzene, we were working experimentally in this laboratory on the adsorption of these long hydrocarbon chains. Now while Bancroft seemed to think that this work indicated that the liquid with the higher surface tension forms the inner phase, it seemed to us that the only apparent relation was that to the *number of oleate radicals* in the molecule of the protective colloid (sodium oleate, or magnesium oleate). Therefore it quite possibly may be the orientation,[1] and the form of the molecules together with adsorbed ions in the interface between the dispersoid particles (or small drops), and the dispersion medium which determine the surface energy relations, and therefore the size of the drop at which it becomes stable. In other words, this idea is that the drop would be stable whenever the molecules, together with adsorbed ions, etc., in the interface fit the curvature of the drop. The molecules in the curved surface would not need to be all of the same kind. If the molecules do not fit in the curved surface, the drop will not be perfectly stable, and will either decrease or increase in size if given time.

From the standpoint of this idea of molecular orientation and molecular fitting the free surface energy of small drops should vary with the radius of curvature (in addition to the pressure effect which is usually taken into consideration), and we have been working on the surface energy relations of large drops (curvature so large as to be practically planes from the standpoint of the results) only as an introduction to work on the surface-tension relations at highly curved surfaces.

Fig. 3, and Table VII, present some very interesting relations. Thus 0.0001 molar sodium oleate reduces the surface tension of water from 72.8 to 60.46 ergs per cm^2., and even when 0.0002 molar sodium hydroxide is added, to prevent hydrolysis, the surface tension goes as low as 61.32, so the oleate film builds up with extreme rapidity. A 0.014 molar solution decreases the interfacial tension from 35 to 2.22, or to about 6% of

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[1] According to the theory presented in this paper, molecular orientation in the interface is the factor which does determine the stability of emulsoid particles and also the sign and magnitude of the electromagnetic field at the surface of the drop. It should be noticed that all of the best commercial emulsifying agents have *very long molecules*.

its former value. Both the curve at the air-liquid and at the benzene-aqueous solution interface, indicates that the adsorption is enormously rapid at first, and that for the vapor-solution interface at as low a concentration as 0.002 for the adsorbed film has become so closely packed that further increase in the concentration of the solution no longer lowers the surface tension. Thus these films become *saturated* at extremely low concentrations of the saturating substance.

These experiments show that sodium oleate will cause the benzene to form the emulsoid drops even when the outer phase has the higher surface tension when measured alone with a plane surface, so we cannot see that the statement that the inner phase has the higher tension has any meaning. It is also of interest that even for a plane surface the *interfacial* tension drops very low for the solutions which form stable emulsions, and that the value falls as low as 2 ergs. per cm^2. or even less in one case, so the curvature of the surface would not have to produce a very large effect to reduce the surface tension to zero. That the condition for the stability of emulsions and colloids is a zero free-surface energy at the interface outer phase-drop, has been suggested by Tolman. While we are working on this subject from the standpoint of the measurement of surface tension, it is quite probable that work on films on liquids may give results more rapidly than the methods we are using, and much is to be hoped in this direction from the very beautiful experiments now being made by Langmuir on such films.

What is presented in this paper on the problem of the formation of colloids and emulsions is only preliminary in nature, but much may be expected from the application of the principles in regard to the setting of molecules in surfaces to this problem. It is just when the size of the particles becomes extremely small that the setting and the shape of the molecules becomes of extreme importance in determining both the surface energy and the other electromagnetic energy relations. It is realized by us that in this connection ion formation is also of great importance, and this factor will be discussed in a later paper. We have found some very beautiful surface energy relations for substances which form liquid crystals, and these will be published very soon in a short note.

The work presented in this and the other six papers of this series on surface energy relations, has been carried on by the aid of a grant from the C. M. Warren Fund of the American Academy of Arts and Sciences, which was given to us for this work in 1911. We wish to thank Professor A. C. Lunn for the many suggestions which he has given us, and Mr. Finkelstein for preparing the drawings. A correct interpretation of the results on the benzene derivatives would have been very difficult without the remarkable collection of data recently obtained experimentally by Jaeger, and we wish to thank Dr. Morey and Dr. Sosman for obtaining his later papers for us.

Summary.

1. The molecules in the surfaces of liquids seem to be oriented, and in such a way that the least active or least polar groups are oriented toward the vapor phase. The general law for surfaces seems to be as follows: *If we suppose the structure of the surface of a liquid to be at first the same as that of the interior of the liquid, then the actual surface is always formed by the orientation of the least active portion of the molecule toward the vapor phase,* AND AT ANY SURFACE OR INTERFACE THE CHANGE WHICH OCCURS IS SUCH AS TO MAKE THE TRANSITION TO THE ADJACENT PHASE LESS ABRUPT. This last statement expresses a general law, of which the adsorption law is only a special case. If the molecules are monatomic, and symmetrical, then the orientation will consist in a displacement of the electromagnetic fields of the atom. This molecular orientation sets up what is commonly called a "double electrical layer" at the surfaces of liquids and also of solids.

This law if applied to special cases indicates for a few pure liquids the following orientation: In water the hydrogen atoms turn toward the vapor phase and the oxygen atoms toward the liquid. With organic paraffin derivatives the CH_3 groups turn outward, and the more active groups, such as NO_2, CN, COOH, COOM, COOR, NH_2, $NHCH_3$, NCS, COR, CHO, I, OH, or groups which contain N, S, O, I, or double bonds, turn toward the interior of the liquid.

If any of these organic compounds are dissolved in water, their orientation in the water surface is the same as that just given, with the active groups inward. Table IV should be considered as part of this summary.

At interfaces between two pure liquids the molecules turn so that their *like* parts come together in conformity with the general law. With solutions, the solute molecules orient so that the ends of the molecules toward the liquid A are as much like A as possible, and the ends toward B are as much like B as possible. So at interfaces between organic liquids and water, for example, the organic radical sets toward the organic liquid, and the polar group toward the water.

2. If at an interface the transition from a liquid A to the liquid B is made by a saturated film of solute molecules which we may call A-B, that is, they have one end like A and the other like B, then the free surface energy is greatly reduced. For example, with water and benzene with sodium oleate as the solute, the free energy falls as low as 2 ergs per cm^2.

3. If the solvent is polar, such as water, then solutes will in general be positively adsorbed in the surface if they are less polar than water, and the least polar end of the molecule will be turned outward. Solutes more polar than water are negatively adsorbed.

4. Contrary to previous work, our results show that bases do not lower

markedly the interfacial tension between benzene and water. This is an important fact on account of its applications in physiology, some of which are discussed in the paper.

5. The important energy functions at surfaces are the total surface energy (μ or E_s), the free surface energy (γ), the latent heat of the surface (b), and the specific heat of the surface (c), where all are given for unit area. The total surface energy is independent of the temperature so long as $\frac{d\gamma}{dT}$ is a constant, and is more characteristic of chemical constitution than the other functions.

6. The Eötvös-Ramsay-Shields method for the calculation of molecular association is shown to be of little value.

7. An extensive table (Table II) gives the values of E_s, γ, $\frac{d\gamma}{dT}$ and $\frac{d\gamma/dT}{\gamma_0}$ for 336 liquids. Table IV should be consulted as showing the relation of the data to the orientation of the molecules in the surfaces of liquids.

8. The paragraph entitled "Discussion of the Substitution Products of the Paraffins," "Discussion of the Substitution Products of Benzene," and "The Orientation of Benzene Substitution Products" should be consulted in the body of the paper.

9. *Films of solutes positively adsorbed at either liquid-vapor surfaces or liquid-liquid interfaces, frequently become* SATURATED. The rapidity with which this saturation occurs, depends upon the nature of the solute, and increases with the length of the insoluble end of the molecule. Thus sodium oleate in water is very highly adsorbed, and the surface tension of the solution decreases with extreme rapidity. After the concentration of the solution reaches the value 0.002 normal (which is very small), the surface tension no longer decreases, but remains constant up to 0.1 normal or more, which proves that the film has become a saturated one.

10. The stability of emulsoid particles seems to be brought about by orientation of molecules at the interface with the medium of dispersion. The best emulsifying agents, for example, have very long molecules, with a polar or active group at one end of the molecule. For the emulsoid particle to be stable, the molecules which make the transition from the interior of the drop to the dispersion medium, or the molecules of the "film" should fit the curvature of the drop.

From this standpoint the surface tension of very small drops is a function of the curvature of the surface.

Tables VII and VIII, and Fig. 3, give the data for the free surface energy of solutions of sodium and magnesium oleates. The summary of the preceding paper[1] should be consulted for other important principles in regard to molecular orientation in surfaces as related to solubility.

CHICAGO, ILL.

THE ACTION OF MAGNESIUM ON AQUEOUS SOLUTIONS.

BY FREDERICK H. GETMAN.

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Action of Chemically Pure Magnesium.

In a previous communication[2] on the action of metallic magnesium on solutions of potassium chloride, experimental evidence was adduced in favor of the view that the dissolved salt functions merely as a catalyst in the reaction represented by the equation

$$Mg + 2H_2O \longrightarrow Mg(OH)_2 + H_2.$$

The magnesium used in these experiments was found to be 99.66% pure. Notwithstanding this high degree of purity, it is conceivable that the presence of even so small an amount of residual impurity might be sufficient to account for the reactivity of the metal when immersed in a saline solution. In other words, just as there is scarcely any reaction between chemically pure zinc and dilute hydrochloric or sulphuric acids, so also there may be a marked diminution in the rate of reaction between magnesium and a solution of potassium chloride if special precautions are taken to secure a chemically pure sample of the metal.[3] In order to determine the possible influence of small amounts of impurities on the reactivity of magnesium when placed in saline solutions, some experiments were carried out with magnesium which had been purified by distillation.

A sample of magnesium wire, known to contain less than 0.5% of impurity, was cut into short lengths and distilled *in vacuo*. The resulting crystalline deposit of presumably pure magnesium was allowed to cool and then transferred immediately to a 0.1 *M*[4] solution of potassium chloride. Hydrogen began to be evolved at once, but owing to uncertainty as to the extent of surface of metal in contact with the solution it was impossible to make any quantitative comparison with the volume of gas obtained under similar conditions with magnesium wires of known superficial area.

The reaction between distilled magnesium and a 0.1 *M* solution of potassium chloride was also studied, as in our previous paper, by means of the hydrogen electrode.

A cell was prepared as indicated by the following scheme:

$$Hg^+\text{–}Hg_2Cl_2,\ \overrightarrow{0.1\ M\ KCl\ \|\ 0.1\ M\ KCl}\text{–}Pt\text{–}H_2^-$$

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[1] THIS JOURNAL, 39, 354 (1917).

[2] Getman, THIS JOURNAL, 38, 2594 (1916).

[3] The suggestion to test this point experimentally was very kindly made to the author by the Editor of THIS JOURNAL.

[4] The term *M* is used in this article to express molar concentration.