3. The effect is ascribed to increased adsorption and complex formation as between silver halide and developer. The bearing of this on the theory of development is discussed.

4. In addition there is a fogging action of dilute potassium iodide solutions on silver bromide emulsions, which is ascribed to nucleus infection of the grain.

ROCHESTER, N. Y.

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

THE ORIENTATION OF MOLECULES IN SURFACES, SURFACE ENERGY, ADSORPTION, AND SURFACE CATALYSIS. V. THE ADHESIONAL WORK BETWEEN ORGANIC LIQUIDS AND WATER.[1]

BY WILLIAM D. HARKINS, GEORGE L. CLARK AND LATHROP E. ROBERTS.

Received January 12, 1920.

In 1913 Hardy[2] showed that the magnitude of the work done by the attraction between the surfaces of an organic liquid and water during their approach to form an interface, is characteristic for a number of classes or organic liquids. Later Harkins, Brown, and Davies[3] found that whenever the organic liquid contains polar groups in its molecules, this work is very much larger than when they are absent; so much higher that the data made it evident that at the interface such polar groups as —OH, —COOH, —CHO, —CN, —$CONH_2$, —SH, —NH_2, —$NHCH_3$, —NCS, —COR, —COOM, —COOR, —NO_2, —$C(H)=CH_2$, —C≡CH, or groups which contain oxygen, nitrogen, sulfur, iodine, bromine, chlorine, double or triple bonds, turn toward the water. The work of Langmuir[4] indicates a similar orientation in monomolecular surface films of organic substances. A theory of heterogeneous equilibrium worked out by Harkins and King[5] indicates, however, that the orienting forces in the case of such *monomolecular* organic films are in general more powerful than those at the surface of the pure organic liquid, and also greater than those acting on the organic molecules at the interface with water. From the standpoint of the theory

[1] Practically all of the data in this paper were determined during the years 1914–17 or earlier, as the work was interrupted by the war. Some of the data presented here were obtained in this laboratory as early as 1912.

[2] *Proc. Roy. Soc.* (*London*), 88A, 303–33 (1913).

[3] THIS JOURNAL, 39, 354–64 (1917); also Harkins, Davies and Clark, *ibid.*, 39, 541–96 (1917).

[4] *Met. Chem. Eng.*, 15, 468 (1916); THIS JOURNAL, 39, 1848–1906 (1917); *Proc. Nat. Acad. Sci.*, 3, 251–7 (1917).

[5] THIS JOURNAL, 41, 970–92 (1919).

of Harkins and King it is, therefore, not to be expected that the indications of orientation will be so marked at interfaces as they are in thin films. However, the evidence obtained at interfaces is more extensive and more varied in its nature.

Table I presents data for the work of surface attraction between water and about 70 organic liquids. In this table the first column gives the name of the substance and the formula; the second (γ_l), the free surface energy of the organic liquid; the third ($W_A/2$) gives half of the adhesional work per sq. cm. for comparsion with Col. 2; the fourth (γ_i), the interfacial free energy; the fifth (W_A), the surface adhesion, all in ergs per sq. cm. The sixth column gives the initial of the investigator, and the seventh, eighth and ninth the densities of the pure organic liquids and those of the 2 phases after mixing.

The data in this table are of considerable value in the study of the orientation of molecules in interfaces, and of the characteristics of polar and of non-polar groups in organic compounds. It will be shown later that they are also fundamental in connection with adsorption and surface catalysis. In order that the meaning of the data in terms of cohesion and of adhesion may be appreciated it is essential to present a mechanical illustration. Imagine a bar of solid with a cross section of one sq. cm. If this bar could be pulled *without a lateral compression* until it breaks at a plane perpendicular to its length, the work necessary to pull the bar apart would be equal to 2γ, or twice the free surface energy per sq. cm. of the solid. Thus 2γ may be called the cohesional (or tensile) work for a bar of unit cross section. Col. 2, in Table I, gives the value of the free surface energy (γ), which may best be considered in connection with the other data, as half the cohesional work, or γ is equal to $W_C/2$. For comparison with these values the third column (3) gives the values for $^1/_2$ the adhesional work between the organic substance and water ($W_A/2$). The adhesional work is that which is done by the surfaces of 2 different liquids when one sq. cm. of one approaches the same area of the other. It is the work which would be used up in pulling apart a bar of unit cross section, one end of which consists of one liquid and the other end of the other, if the break could be made at the junction of the two liquids in such a way that they are entirely separated. Thus $W_A/2$ which refers to adhesion, is entirely comparable with $W_C/2$, which is the free surface energy of a liquid, which in turn is numerically equal to the surface tension of the liquid. It will be shown in other papers by Harkins that the adhesional work and energy are related to the heat of adsorption and the heat of wetting, and that the equations are very simple.

So far as this table alone is concerned, columns giving the values of the cohesional work (2γ) and of the adhesional work (W_A), would undoubtedly be somewhat more easily interpreted by those unfamiliar with the

TABLE I.—THE WORK DONE WHEN ONE SQ. CM. OF THE SURFACE OF AN ORGANIC LIQUID APPROACHES ONE SQ. CM. OF A WATER SURFACE TO FORM AN INTERFACE, TOGETHER WITH THE SURFACE TENSIONS AND INTERFACIAL TENSION.

$t = 20°$. Water = 72.80 ergs. $W_A = -\Delta\gamma$.

1. Substance and formula.	2. γ_l or $W_c/2$.	3. $W_A/2$.	4. γ_i.	5. $-\Delta\gamma$ or W_A.	6. Observer.	7. Density pure liquid.	8. Density organic phase.	9. Density aqueous phase.	10. $W_A-2\gamma$.
I. Inorganic Compounds.									
Water, H_2O	72.80	72.80	...	145.6	D	....	...	...	...
IIa. Paraffins.									
Isopentane, $(CH_3)_2CHCH_2CH_3$	13.72	18.44	49.64	36.88	D	....	...	...	9.44
Hexane. C_6H_{14}	18.43	19.99	51.25	39.98	D	....	...	...	9.44
Octane, C_8H_{18}	21.77	21.88	50.81	43.76	D	....	...	...	0.22
Di-iso-amyl (Decane)	22.24	24.12	46.80	48.24	R	0.72216	0.72253	0.99696	3.76
Higher paraffins (about $C_{16}H_{34}$), containing benzene derivatives	30.83	31.51	40.61	63.02	D	....	...	...	1.36
IIb. Unsaturated Paraffins.									
Trimethyl ethylene, $(CH_3)_2C=CH(CH_3)$	17.26	26.68	36.69	53.37	D	....	...	...	18.85
IIIa. Primary Alcohols.									
Methyl, CH_3OH	22.7	47.7	...	95.5	..	....	...	...	50.1
Ethyl, C_2H_5OH	22.4	47.6	...	95.2	..	....	...	...	50.4
Propyl, C_3H_7OH	23.7	48.2	...	96.5	..	....	...	...	51.1
Butyl, C_4H_9OH	24.5	48.6	...	97.3	..	....	...	...	49.1
Isobutyl, $(CH_3)_2CHCH_2OH$	22.8	46.9	1.8	93.8	..	....	...	...	48.3
Iso-amyl, $(CH_3)_2CHCH_2OH$	24.1	46.2	4.4	92.5	..	....	...	...	48.2
Octyl, $(CH_3)(CH_2)_8OH$	27.53	45.88	8.52	91.77	D	....	...	...	44.3
IIIb. Secondary Alcohols.									
Methylhexyl carbinol, $CH_3CHOH(CH_2)_5CH_3$	26.52	44.85	9.61	89.71	D	....	...	...	36.67

IIIc. Sulfur Alcohols and Sulfur Derivatives.									
Mercaptan, C_2H_5SH	21.82	34.25	26.12	68.50	D	....	...	...	24.86
Carbon disulfide, CS_2	31.38	27.91	48.36	55.82	C	1.261	1.2596	0.9972	—6.94
IV. Ethers.									
β,β-Dichloro-ethyl sulfide	42.82	43.63	28.36	87.26	E	1.2732	...	...	1.62
Ethyl ether, $(C_2H_5)_2O$	17.10	36.45	10.70	79.70	D	....	...	...	45.50
Va. Ketones.									
Methyl ketone, $CH_3COCH_2CH_2CH_2CH_3$	24.15	45.33	6.28	90.67	D	....	...	...	42.37
Methylbutyl ketone, $CH_3COCH_2CH_2CH_2CH_3$	25.49	44.28	9.73	88.56	D	....	...	...	37.58
Methylhexyl ketone, $CH_3CO(CH_2)_5CH_3$	26.79	42.75	14.09	85.50	D	....	...	...	31.92
Ethylpropyl ketone, $CH_3CH_2CO(CH_2)_2CH_3$	25.39	42.76	13.58	84.53	D	....	...	...	33.75
Vb. Chloro-ketones.									
Monochloro-acetone, $CH_2ClCOCH_3$	35.27	50.98	7.11	100.96	C	1.170	1.1581	1.0029	30.42
Asym. dichloro-acetone, $CHCl_2COCH_3$	31.91	45.14	14.43	90.28	C	1.236	...	1.0170	58.37
VIa. Acids.									
Formic, HCOOH	37.3	55.0	...	110.1	..	....	...	...	35.5
Acetic, CH_3COOH	27.6	50.2	...	100.4	..	....	...	...	45.2
Propionic, C_2H_5COOH	27.02	49.9	...	99.81	..	....	...	...	45.77
Butyric, C_3H_7COOH	27.07	49.9	...	99.8	..	....	...	...	45.66
Isovaleric, $(CH_3)_2(CH_2)_2COOH$	25.33	47.6	2.73	94.55	D	0.91740	0.92148	0.99728	43.89
Heptylic, $(CH_3)(CH_2)_5COOH$	28.31	47.3	6.56	94.75	D	....	...	...	38.13
VIb. Unsaturated Acids.									
Undecylinic (Note 1)	30.64	51.35	10.14	102.70	R	0.90604	0.90762	0.99610	42.42
Oleic	32.50	44.81	15.68	89.62	R	....	...	...	24.62
VIIa. Esters (Containing the $-\overset{\ulcorner O -}{C} = O$ Group).									
Iso-amyl butyrate, $(CH_3)_2CHCOO(CH_2)_2CH(CH_3)_2$	25.19	37.50	23.00	74.99	R	0.86272	0.86280	0.99672	24.61
Ethyl isovalerate, $(CH_3)_2CHCH_2COOC_2H_5$	23.68	39.03	18.39	78.07	R	0.86484	0.86576	0.99705	30.71
Ethyl capronate, $CH_3(CH_2)_4COOC_2H_5$	25.81	36.57	25.46	73.15	..	....	...	...	21.53
Ethyl nonylate, $CH_3(CH_2)_7COOC_2H_5$	28.04	38.00	23.88	76.96	B	....	...	...	18.88

TABLE I (*continued*).

1. Substance and formula	2. γ_l or $W_c/2$.	3. $W_A/2$.	4. γ_i.	5. $-\Delta\gamma$ or W_A.	6. Observer.	7. Density pure liquid.	8. Density organic phase.	9. Density aqueous phase.	10. $W_A-2\gamma$.
VII*b*. Esters Containing the —O — C(=O)— Group.									
Ethyl carbonate, $(C_2H_5O)_2 = C = O$	26.31	43.12	12.86	86.25	D	....	...	...	59.94
VIII. Halogen Derivatives.									
Methylene chloride, CH_2Cl_2	26.52	35.50	28.31	71.01	C	1.3478	1.3286	1.0018	17.97
Chloroform, $CHCl_3$	27.13	33.65	32.63	67.30	C	1.485	1.4831	1.0002	13.04
Carbon tetrachloride, CCl_4	26.66	28.07	43.26	56.15	C	1.590	1.5846	1.9972	2.83
Ethyl bromide, C_2H_5Br	24.16	32.88	31.20	65.76	C	1.441	1.4463	1.0001	17.44
Ethylene dibromide, CH_2BrCH_2Br	38.71	37.48	36.54	74.97	C	2.178	2.1773	0.9991	—2.4
Acetylene tetrabromide, $CHBr_2CHBr_2$	49.67	41.82	38.82	83.65	C	2.9620	2.9588	0.9986	—5.69
Isobutyl chloride, $(CH_3)_2CHCH_2Cl$	21.94	35.15	24.43	70.31	D	....	...	...	26.46
Ter. butyl chloride, $(CH_3)_3CCl$	19.59	34.32	23.75	68.64	D	...	...	...	29.34
Iso-amyl chloride, $(CH_3)_2CHCH_2CH_2Cl$	23.48	40.42	15.44	80.84	R	0.86962	0.87146	0.9955	33.88
IX. Nitro Compounds and Nitrates.									
Nitromethane, CH_3NO_2	36.82	49.98	9.66	99.96	C	1.1385	1.1288	1.0184	26.32
Iso-amyl nitrate (Note 1)	27.18	...	30.80	69.18	R	0.99710	0.99745	1.0059	42.2
X. Nitrils.									
Acetonitril, CH_3CN	28.4	50.5	...	101.0	..	....	...	...	...
Butyronitril, $CH_3(CH_2)_2CN$	28.06	45.24	10.38	90.48	R	0.79040	0.79426	0.99201	34.36
Isovaleronitril, $(CH_3)_2CHCH_2CN$	26.03	42.34	14.14	84.69	R	0.79106	0.79294	0.99622	32.63
XI. Amines.									
Dipropyl amine, $(C_3H_7)_2NH$	22.54	46.84	1.66	93.68	R	0.73853	0.81620	0.98844	48.60
Di-isobutyl amine, $((CH_3)_2CHCH_2)_2NH$	22.05	42.28	10.28	84.57	R	0.74428	0.74763	0.99680	40.47

XII. Aromatic Hydrocarbons.									
Benzene, C_6H_6	28.86	33.31	35.03	66.63	..	....	...	...	8.91
Toluene, $C_6H_5(CH_3)$	29.89	33.31	36.06	66.63	..	....	...	...	6.84
o-Xylene, $C_6H_4(CH_3)_2$	29.89	33.31	36.06	66.63	R	0.87810	0.87806	0.99707	6.85
m-Xylene, $C_6H_4(CH_3)_2$	28.72	31.81	37.89	63.63	..	....	...	...	6.19
p-Xylene, $C_6H_4(CH_3)_2$	28.33	31.68	37.77	63.36	R	0.86444	0.86494	0.99680	6.70
Ethyl benzene, mesitylene, $C_6H_3(CH_3)_3$	28.51	31.30	38.70	62.61	R	0.86124	0.86140	0.99717	5.59
p-Cymene	28.09	30.24	34.61	66.28	R	0.85618	0.85630	0.99702	10.10
XIII. Halogen Derivatives.									
Chlorobenzene, C_6H_5Cl	33.08	34.23	37.41	68.47	C	1.057	1.1047	0.9972	2.31
XIV. Amino Derivatives.									
Aniline, $C_6H_5NH_2$	42.58	54.80	5.77	109.61	C	1.022	1.0216	0.9990	24.45
Dimethyl-aniline, $C_6H_5N(CH_3)_2$	...	...	...	....	..	....	...	...	...
XV. Nitro Derivatives.									
Nitrobenzene, $C_6H_5NO_2$	43.38	45.26	25.66	90.52	C	....	1.2012	0.9976	3.76
o-Nitrotoluene, $C_6H_4CH_3NO_2$	41.46	43.53	27.19	87.07	C	1.168	1.1599	0.9972	4.15
m-Nitrotoluene	40.99	43.05	27.68	86.11	C	1.168	1.1547	0.9971	4.13
XVI. Aldehyde Derivatives.									
Benzaldehyde, C_6H_5CHO	40.04	48.66	15.51	97.33	C	1.0504	1.0445	0.9981	17.25
XVII.									
Anisol, $C_6H_5OCH_3$	35.22	41.10	25.82	82.20	R	0.99327	0.99270	0.99715	11.76
Phenetol, $C_6H_5OC_6H_5$	32.74	38.07	29.40	76.14	R	0.96474	0.96474	0.99820	10.66

C = Clark. R = Roberts. D = E. C. H. Davies. E = D. T. Ewing.

NOTE 1.—All data were taken at 20°, except those for undecylinic acid which were obtained at 25°. The interfacial tension of isoamyl nitrate was not determined against pure water, but against a 0.177 *N* KCl solution, since the liquid and pure water have almost identical densities.

NOTE 2.—The density data in the above table are of value, since from them an estimate may be obtained of either the solubility of the organic liquid in water, or of water in the organic liquid.

subject, than the half values given in the table. The purpose in the use of $W_C/2$ and $W_A/2$ is to make these terms directly comparable with the surface tension values given in tables of constants. The most extensive table of this kind was presented in an earlier paper from this laboratory.

The data in this table are in general easy to interpret in terms of the theory that the molecules in a surface or an interface between two liquids are oriented. If the orientation of the organic molecules is considered, it seems self-evident that the effects of such an orientation, and also its extent, depend upon the degree of dissymmetry in the organic molecule. An entirely symmetrical molecule (or atom in the case of monatomic liquids) would not orient at all, but such a molecule or atom probably does not exist. Molecules as symmetrical as those of the short chain saturated paraffins, carbon tetrachloride, etc., would not be expected to show such evidences of orientation as those molecules which may be considered as heavily loaded, from the standpoint of the stray electromagnetic field, at one end of the molecule, and very light, in the same sense, at the other. The table gives evidence that saturated paraffin groups have a small attraction for water, and that groups containing oxygen or nitrogen, hydrosulfide, or any of the other groups specified in the first part of this paper, that is what are termed "polar groups," have a relatively high attraction for water. The orientation has been already considered in connection with similar data obtained in this laboratory, together with the data of Hardy,[1] and this earlier paper should be consulted for the introduction to the discussion of the much more extensive data presented here.

Whenever $W_A/2$ (Col. 3) is greater than $W_C/2$ (Col. 2), then the work of attraction between the organic liquid and the water is greater than that between the parts of the organic liquid itself; that is, the adhesional work is greater than the cohesional work. This is the relation in most cases, but for the following 3 liquids the work due to the cohesional attraction is the greater: carbon disulfide, ethylene dibromide, and acetylene tetrabromide. It is striking that, judging by the formulas, all of these molecules are extremely symmetrical. The difference between these column multiplied by 2, which is equal to $(W_A - W_C)$, or the excess of the adhesional over the cohesional work, is given in Col. 10. Low values of this quantity are obtained in 3 ways: first, as in the case of the "nonpolar" paraffins both the adhesional and the cohesional work are low, usually of the order of 40 ergs. per sq. cm.; second, the organic molecule is slightly polar, but the polarity is distributed over a considerable part of the organic molecules, as in the case of benzene and its paraffin derivatives, when both values are somewhat larger (about 60); and third, when a considerable part of the molecule of the organic substance becomes

[1] Harkins, Brown and Davies, THIS JOURNAL, 39, 354–64 (1917).

more polar, as in the case of nitrobenzene, and the nitrotoluenes (about 86). The adhesional work becomes much higher than the cohesional whenever the polar group is in just one part of the molecule, while the rest is non-polar, and particularly when the polar group is at one end of the molecule. Thus the excess of the adhesional over the cohesional work ($W_A - W_C$) is to a considerable extent an index of the total symmetry of the molecule, and indicates how symmetrically the molecules lie in the surface and interfaces.

Consider carbon disulfide and ethyl mercaptan. The cohesional work in the former is much higher, 62.8 instead of 43.6, yet the attraction between water and carbon disulfide (adhesional work = 55.8) is much less than that between water and mercaptan (68.5).

The former is a symmetrical molecule, and the latter is unsymmetrical. The hydrosulfide group is evidently more polar than the divalent sulfur atom, but when the mercaptan lies in contact with the water most of the hydrosulfide groups are turned toward the water, and when they are pulled from it the polarity of the group is evident in the high value of the adhesional work. The =S group, not being so polar, gives a considerably smaller value, which is 12.7 ergs less. However the attraction between the sulfur of carbon disulfide and water, and also that between the sulfur in the different molecules of the carbon disulfide itself, is much greater than the attraction between hydrocarbon groups such as C_2H_5—. Now when a bar of carbon disulfide is pulled apart to make 2 surfaces, sulfur must be pulled away from sulfur, so the cohesional work and also the total cohesional energy are relatively high, the former having a value of 62.76 ergs per sq. cm. However when mercaptan is pulled apart, sulfur (—SH) does not need to be pulled from sulfur, but the sulfur turns under the surface, and only the hydrocarbon groups have to be pulled apart, so the work of separation is low (only 43.6). However, the work of separation is not so low as if the sulfur were absent, since what is given above is a static theory, and the kinetics of liquids indicates that some of the hydrosulfide groups will be kept in the surface of the mercaptan, by the kinetic motion of the molecules. A paper by Harkins to be published in a few weeks in the *Proceedings of the National Academy of Sciences* shows that the heat motion of the molecules is an important factor in such cases as this, and also at interfaces. In all previously investigated cases, except when liquid crystals are being transformed in the surface, the heat motion *aids* in the formation of a surface. The paper will show that in some cases with molecules which are polar at one end and not at the other, the heat motion hinders the formation of the surface, *since it hinders the orientation of the molecules.*

A comparison of the halogen derivatives is also instructive. The co-

hesional work for carbon tetrachloride, chloroform,[1] and methylene chloride is almost the same (53.32, 54.26, 53.04), but the adhesional work toward water rapidly increases in the order given (56.16, 67.30, 71.0). Here the increasing polarity is not in evidence in the cohesional but is present in the adhesional work, since when the pure liquids are pulled apart the increase of cohesional work due to an increase of polarity is counterbalanced by the concomitant increase of dissymmetry, which allows the less polar parts of the molecules to be oriented into the surface. At the interface, however, it is the most polar part which is turned into the interface, so the effects add together instead of subtracting. Also the adhesional work for isobutyl and tert. butyl chloride are practically as high as in the case of methylene chloride, since the chlorine is turned toward the water, but the cohesional surface work drops to very low values, 43.88 and 39.18 ergs per sq. cm.

Both carbon tetrachloride and ethylene dibromide give the same value for the cohesional work as for the adhesional work, but, as the number of bromine atoms in the compound increases (acetylene tetrabromide) the cohesional work becomes the higher. These compounds have very symmetrical molecules.

A comparison of isopentene with trimethyl ethylene, and of octane with octylene shows that the introduction of a double bond increases the cohesional work very slightly and the adhesional work very greatly, especially in the latter case, where the double bond is at the end of the molecule. These facts are again exactly in accord with the orientation theory. For octane the cohesional work is 43.54, while for octylene it is almost the same, or 44.66, so the introduction of the double bond has little effect. The values of the adhesional work for octane is practically the same as that for the cohesional work, but the addition of the double bond in octylene raises the value by about 60%.

Substances of the type of the primary alcohols, mercaptans, acids, amines, nitriles, nitro compounds, or derivatives with double or triple bonds at one end, may be classified as compounds with polar-non-polar molecules of the general formula O——, where the O represents a polar and ———— a non-polar group. While the polar group may have either a higher or a lower weight than the non-polar, the action of the molecule in a liquid is analogous to that which would be obtained in a system of models made up with a heavy and a light end, if the models could be taken out of an external gravitational field, and turn freely under the action due to the mutual gravitational field, the chief difference being that the gravitational field is much less intense than the elec-

[1] The molar internal latent heat of vaporization for carbon tetrachloride is almost identical with that of chloroform, 7520 for the former and 7455 for the latter at 0°. The error in the determinations is greater than this difference.

tromagnetic field at small distances, but dies off much more slowly. At the surface of a closely crowded aggregation of such models in motion the heavy ends would, on the average, be very much more likely to turn inward toward the body of the aggregation, but at the interface between such an aggregation and a second set of models consisting of weighted parts alone, these models would turn toward the weighted system. We may thus speak of the electromagnetically light and heavy ends of the molecules of this type in place of the non-polar and polar ends. The interpretation of the data presented in this paper may easily be made by the reader on the basis of such a set of models. For molecules of the type under discussion it will be seen that the cohesional work is always low, and the adhesional work is toward water always high. The work of this laboratory indicates that the same relations hold toward mercury[1] except that in this case bromine and especially iodine act as if they are much more heavily loaded in this sense than oxygen or nitrogen, which is just the opposite of their relative order toward water. Thus oxygen or nitrogen, and especially bromine and iodine, turn toward the mercury.

The data of Col. 10 show the excess of the adhesional work toward water over the cohesional work of the organic substance. This is nearly zero for most of the saturated paraffins but increases to about 19 ergs for trimethyl ethylene with its partly surrounded double bond, or by 28 ergs for octylene. In the case of the alcohols, and dipropylamine the excess rises to 50 ergs, while it is 60 ergs for ethyl carbonate and a symmetrical dichloro-acetone, 45 ergs for normal acids and ether, and from 32 to 40 ergs for ketones. Thus all of these liquids have a much smaller surface attraction for themselves than for water. Hydrocarbons of the benzene series and nitro and chlorobenzene on the other hand give low values of $W_A - W_C$, and in this respect are similar to the paraffins. The values for anisol and phenetol rise to 11, for benzaldehyde to 17, and for aniline to 24.

The solubility of the organic substance in water increases in general as $W_A - W_C$ increases, though this, it is apparent, is only one of the factors. According to the orientation theory this term relates mostly to the attractive forces around the more polar end of the molecule, so it is to be expected that the extent and polarity of the rest of the molecule are also important factors, as is evident from the data. The application of this theory to solubility has already been discussed in the previous papers of this series, though the values of $W_A - W_C$ are given here for the first time.

The calculations in this paper are based on the simple thermodynamic equation of Dupré, which may be expressed

$$W_A = -\Delta\gamma = \gamma_1 + \gamma_2 - \gamma_{1,2}$$

[1] Work of Dr. E. H. Grafton and W. W. Ewing.

where $-\Delta\gamma$ is the decrease of free energy when 2 unlike or 2 like surfaces meet. The equation of Harkins gives the total energy change when the surfaces meet as follows:

$$E_A = -\Delta E_S = \gamma_1 + l_1 + \gamma_2 + l_2 - (\gamma_{1,2} + \gamma_{1,2})$$

where E_A is the total energy of adhesion, E_S, the total surface energy, and l is the latent heat of the surface. This equation is more closely related to the molecular attractions than that of Dupré, but its application will be discussed in another paper, which will give the experimental values.

These equations may easily be transformed so as to give the heat of adsorption, and the energy quantities are those which are of importance in surface or heterogeneous catalysis, or what is often termed contact catalysis. The next papers of this series will treat the following subjects: the change of molecular kinetic to molecular potential energy, the steps in the process of vaporization, the attraction of mercury for organic liquids and water, the compression of liquids by adsorption, the absorption of liquids and gases in charcoal, heats of adsorption, and the adsorption of organic acids and alcohols containing from one to ten carbon atoms on a water surface, the adsorption of salts, adsorption at the interface between hexane and water, the hydrolysis of a soap in the surface film, and negative surface energy. These papers are now largely completed.

Summary.

1. This paper gives new determinations of the interfacial tension between organic liquids and water, together with the surface tension of the pure liquid for 34 carefully purified organic liquids, together with similar data for 24 liquids as previously determined in this laboratory. The only determinations available when the work of this laboratory was begun in 1912, consisted of those on 4 liquids by Antonow, and on 20 liquids by Hardy. That the measurements made in this laboratory are much more accurate is due to the painstaking work of Dr. F. E. Brown and Dr. E. C. H. Davies on the corrections involved in the use of the drop weight method. The earlier work has already been summarized in a former paper. A knowledge of such interfacial relations is of fundamental importance in the study of (1) colloids, as in physiological work, (2) adsorption, (3) the spreading of liquids on surfaces, (4) adhesion, including flotation, (5) surface structure, (6) surface catalysis, and (7) lubrication.

2. The data give much evidence in favor of the theory that the molecules in interfaces are oriented. This is in accord with the theory developed both by Langmuir and by Harkins and his co-workers. That there is such an orientation was first suggested by Hardy, but he did not present evidence in favor of the idea. However, he has not been given sufficient credit for his beautiful work on surfaces and interfaces.

3. The paper gives values for the work necessary to pull apart a column of an organic liquid, which is equal to twice the free surface energy, and is termed the cohesional work for a bar of unit cross section. Values are also given for the adhesional work against water. This is the work done when one sq. cm. of an organic liquid approaches a similar area of water. This is one of the important factors in determining solubility in water, and the values are also an index of the polar nature of the most polar part of the organic molecule.

4. The evidence presented may best be considered by an example, which is only one of the many cases included in the data. From the formula it may be considered evident that carbon disulfide has an extremely symmetrical, and mercaptan (CH_3CH_2SH) a very unsymmetrical molecule. Now it takes much more work to pull apart a bar of carbon disulfide than of mercaptan, that is the cohesional work is much higher in the former case (62.8 instead of 43.6), yet the work of attraction or the adhesional work between water and carbon disulfide is much less (55.8) than it is between water and mercaptan (68.5). These remarkable facts are very simply explained in the paper from the standpoint of the orientation theory. The data show that the presence of a polar group in any part of an organic molecule, no matter how large the non-polar part of the molecule may be, increases very greatly the attraction of the organic liquid for the water, which is strongly in support of the orientation theory. Thus the attraction between octane and water is relatively small, the adhesional work being only 43.76 ergs. The octane molecule contains 8 carbon and 18 hydrogen atoms, or 26 atoms in all, yet the introduction of only one oxygen atom at the end of the chain more than doubles the adhesional work, and increases it to 91.77 ergs. The similar introduction of one oxygen atom into isopentane increases the adhesional work toward water from 36.9 to 92.5, or a remarkable increase of 150%. The substitution of an amine group for a hydrogen atom at the end of the chain causes an increase of the same magnitude, as does the substitution of —COOH, —CN, =CO, or any similar groups. The great magnitude of the effect, when it is considered that the addition of one atom to 26 causes an increase of 132%, is remarkably strong evidence that the oxygen is turned toward the water.

5. It is found that the only 3 cases out of 58 is the cohesional work of an organic liquid greater than its adhesional work toward water. The liquids are carbon disulfide, ethylene dibromide, and acetylene tetrabromide. The excess of the adhesional over the cohesional work increases as the symmetry of the molecule decreases. This is also very strong evidence in favor of the orientation theory.

6. The data indicate that the benzene series hydrocarbons aar considerably more polar than the paraffin hydrocarbons. Aniline is found to

be extremely polar in comparison with most of the organic liquids. The polar characteristics of the benzene derivatives are distributed much more over the whole molecule than is the case with the paraffin derivatives.

7. Attention should be called here to an error which is sometimes made in connection with the orientation theory, which is that the total surface energy, and the free surface energy, or the surface tension, are all due to the orientation of the molecules. This is just the opposite of the truth, since the surface energy is due to the stray surface field, and this field is decreased, and not increased, by the orientation. The general law for surfaces as presented by Harkins, Davies and Clark is: 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 field of the atom. Since it is the *free* energy which is decreased by the orientation, thermodynamics tells us that the orientation will take place of itself.

The work of this paper, as well as that of the 4 earlier papers of this series, was made possible by a grant made in 1911 from the C. M. Warren Fund of the American Academy of Arts and Sciences.

CHICAGO, ILLINOIS.

[PLANT PHYSIOLOGICAL AND FERMENTATION INVESTIGATIONS, BUREAU OF PLANT INDUSTRY, U. S. DEPARTMENT OF AGRICULTURE.]

THE RELATION BETWEEN THE TOTAL ACIDITY, THE CONCENTRATION OF THE HYDROGEN ION, AND THE TASTE OF ACID SOLUTIONS.

BY R. B. HARVEY.

Received January 16, 1920.

In some determinations of the hydrogen ion concentrations of various fruits, including apples and tomatoes, the author found that sour varieties gave nearly the same value as did less sour varieties. The small variation in the hydrogen ion concentration of 30 varieties of tomatoes from P_H 4.148 to 4.565 seems insufficient to account for the difference in taste. This suggested the question: "What do we taste in acid solutions, hydrogen ion concentration or total acidity?"

Opinions of various persons differs, but most seem to believe that the concentration of hydrogen ions is the important factor. Some work by