hand, possibly either our toluene contained a slight aliphatic impurity[1] (a rather unlikely contingency, considering our use of several samples from different sources) or theirs contained traces of some other contamination, since it is so very difficult to purify completely a compound of carbon, even by countless distillations, from substances with nearly the same boiling point. Crystallization is safer, and will be applied to this case in the near future.

Many other determinations of a variety of organic substances have been made with the help of these improved methods. The results will be communicated in the near future in a publication of the Carnegie Institution of Washington, to which we are much indebted for generous assistance in this work.

Summary.

In this paper there are described improvements in various details of the procedure of calorimetric combustion, to wit: means of effective closing with less risk of injury to the platinum lining and cover of the bomb; means of burning volatile liquids without loss; a method of automatically controlling the temperature of the environment about the calorimeter so as to make the combustion more convenient and more truly adiabatic; and means of evaluating the incompleteness of combustion if any volatile carbon compounds should remain unburned. New determinations of the heat of combustion of toluene (10,158 18°-calories or 42.47 kilojoules per gram, weighed in vacuum) are recorded.

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

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.

[SURFACE TENSION. V.]

BY WILLIAM D. HARKINS, F. E. BROWN AND E. C. H. DAVIES.[2]

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In this paper data will be presented for the work done when the surfaces of two liquids come together to form an interface. The numerical value of this work in ergs per square centimeter is characteristic of each

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[1] For example, 2,4-dimethylhexane, boiling point 110°, L. Clarke, THIS JOURNAL, 30, 1148 (1908). Octanes have higher specific heats of combustion than toluene. Richards and Jesse, *Ibid.*, 32, 292 (1910).

[2] The experimental work of this paper was begun by E. C. Humphery in 1912, and was continued in 1913 by F. E. Brown. The delay in its publication has been caused by the fact that until recently we had not determined accurately the corrections in-

class of compounds, and the data shows in a very striking manner that the film of any liquid in contact with water is composed of molecules oriented so that the active (or polar) group at the end of any hydrocarbon chain is in contact with the water. The double bond of an unsaturated hydrocarbon, and the double bonds in the benzene ring, act in this respect like polar groups. It will be shown that the attraction between water and another liquid is one of the important factors in the determination of the solubility of the other liquid in water.

If it is imagined that a single liquid is divided into two parts by a horizontal plane, and that when this imaginary plane is lifted the upper layer rises with it, then, where before there was no surface, two surfaces now appear. Let us suppose the liquid to be water at 20°, then, since the surface tension of water at 20° is, according to our measurements, 72.8 dynes per cm., the free energy per square cm. is 72.8 ergs. The total energy of the two surfaces, each of which may now be supposed to have an area of 1 square cm., will be 145.6 ergs. If the two surfaces now approach and meet one another, this free energy disappears, since there is now no surface energy at the imaginary interface. Now let the lower liquid be water and the upper benzene. The free surface energy of the two surfaces would be 72.80 (for water)+28.98 (for benzene) = 101.79 ergs. At the same temperature the free energy of the one sq. cm. of the interface which is formed when they meet is 35.0. The decrease of free energy, 66.7 ergs, is equal to the work done by the two liquids on each other as they approach. The values given are correct, however, only when neither of the single liquids has been exposed to the vapor of the other. Let us call the decrease in free energy which occurs when two liquids A and B approach each other, $-\Delta\sigma_{AB}$. At 25° the values become:

$$\sigma_{H_2O} = 72.05, \qquad \sigma_{C_6H_6} = 28.17, \qquad \sigma_{H_2O.C_6H_6} = 34.68,$$

$$\sigma_{H_2O} + \sigma_{C_6H_6} = 100.22, \qquad -\Delta\sigma_{H_2O - C_6H_6} = 65.54.$$

The amount of work necessary to separate the liquids after their surfaces have come together, is, however, not the same as this, since the surface tension of each liquid is affected by the presence of the other. Thus when mutually saturated at 25° the free surface energies become

$$\sigma'_{H_2O} = 60.19, \qquad \sigma'_{C_6H_6} = 27.90, \qquad \text{sum} = 88.09.$$

The decrease of free energy when the two mutually saturated liquids come together is

$$-\Delta\sigma'_{H_2O.C_6H_6} = 43.41.$$

volved in the drop-weight method which we have used. This method is undoubtedly the most accurate of all of those which have been devised, but it has given the most inaccurate results because the corrections which have been used by workers other than ourselves are incorrect. Mr. Brown will soon publish his accurate determinations of these corrections.

Expressed in a general form

$$\sigma_A + \sigma_B = \sigma_{AB} + (-\Delta\sigma_{AB}).$$[1]

This expression is of great value in a study of the processes which occur in the surfaces when two liquids approach each other, or are separated from one another, since data may be secured for the work involved when a large number of liquids are allowed to approach one other liquid, such as water. This gives some measure of the relative attractions exerted by a water surface upon the surfaces of other liquids as they vary in composition.

TABLE I.—VALUES OF THE CHANGE OF FREE SURFACE ENERGY ($-\Delta\sigma$) WHEN 1 CM². OF INTERFACE IS FORMED BETWEEN THE TWO LIQUIDS.

Substance and formula.	t.	σ liquid.	σ water.	Sum $\sigma_1 + \sigma_W$.	σ interface.	$-\Delta\sigma$.	Observer.
I.—Inorganic Compounds.							
Water, H_2O	20.0°	72.8	72.8	145.6	..	145.6	B. D.
Carbon bisulphide, CS_2	16.0°	33.52	73.38	106.90	54.09	52.81	H. B.
II.—Paraffin and Related Cyclo Hydrocarbons.							
Isopentane, $(CH_3)_2CH_2CH_2CH_3$	20.0°	13.72	72.80	86.52	49.64	36.88	D.
Hexane, C_6H_{14}	25.0°	18.71	72.05	90.76	49.54	41.22	H. N.
Cyclohexane, C_6H_{12}	16.8°	25.80	73.26	99.06	60.60	38.46	H. B.
Octane, C_8H_{18}	20.0°	21.77	72.80	94.57	48.61	45.96	D.
Oil C, higher paraffins	17.0°	31.81	73.23	105.04	57.25	47.79	H. B.
	20.0°	30.83	72.80				D.
III.—Olefine Hydrocarbons.							
Octylene, $CH_3(CH_2)_5CH : CH_2$	17.0°	22.33	73.23	95.56	22.66	72.90	H. B.
Trimethyl ethylene, $(CH_3)_2C = CHCH_3$	20.0°	17.26	72.80	90.06	36.69	53.37	D.
IV.—Halogen Derivatives.							
Chloroform, $CHCl_3$	20.0°	27.3	72.80	100.10	27.7	72.45	A.
Carbon tetrachloride, CCl_4	17.0°	27.59	73.23	100.82	52.63	48.19	H. B.
Ethyl iodide, C_2H_5I	16.0°	29.85	73.38	103.23	40.02	63.21	H. B.
V.—Alcohols.							
Methyl alcohol, CH_3OH	20.0°	22.7	72.80	95.5	..	95.5	
Methyl alcohol, CH_3OH	20.0°	22.7	(σ_{CS_2}	$\sigma_1 + \sigma_{CS_2}$			
			34.5	57.2	0.82	56.38	A.)
Ethyl alcohol, C_2H_5OH	20.0°	22.4	72.80	95.2	..	95.2	
Isobutyl alcohol, $(CH_3)_2CHCH_2OH$	18.0°	23.0	73.09	96.09	1.76	94.33	A.
Isoamyl alcohol, $(CH_3)_2CH(CH_2)_2$-OH	20.0°	24.1	72.80	96.90	4.42	92.48	A.
Octyl alcohol, $CH_3(CH_2)_6CH_2OH$	20.0°	27.49	72.80	100.29	8.52	91.77	D.
Cyclohexanol, $(CH_2)_5CHOH$	16.2°	34.23	73.35	107.58	3.92	103.66	H. B.
V*b*.—Sulfur Alcohols.							
Mercaptan, C_2H_5SH	20.0°	21.82	72.80	94.62	26.12	68.50	D.
VI.—Ethers.							
Ethyl ether, $(C_2H_5)_2O$	20.0°	17.10	72.80	89.90	10.70	79.20	D.

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[1] Dupre, "Theorie Mécanique d. l. Chaleur," Paris, 1869, p. 69; Lord Raleigh, *Phil. Mag.*, [5] 30, 461 (1890).

TABLE I—(*continued*).

Substance and formula.	t.	σ liquid.	σ water.	Sum $\sigma_1 + \sigma_W$.	σ interface.	—$\Delta\sigma$.	Observer.
VII.—Acids.							
Formic acid, $HCOOH$	20.0°	37.3	72.8	110.1	...	110.1	
Acetic acid, CH_3COOH	20.0°	27.6	72.8	100.4	...	100.4	
Isovaleric acid, $(CH_3)_2CH_2CH_2$-$COOH$	20.0°	25.33	72.8	98.13	2.73	95.4	D.
Caprylic acid, $CH_3(CH_2)_6COOH$	18.1°	28.82	73.07	101.94	8.217	93.72	H. B.
Ricinoleic acid, $C_6H_{13}CHOHCH_2$-$CH = CH(CH_2)_7COOH$	16.0°	35.81	73.38	109.19	14.25	94.94	H. B.
Oleic acid, $CH_3(CH_2)_7.CH = (CH_2)_7$-$COOH$	20.0°	32.27	72.80	105.07	16.05	89.02	H. B.
Oleic acid	20.0°	32.50	72.80	105.30	15.50	89.80	D.
Ethyl capronate	20.0°	25.81	72.80	98.61	25.46	73.15	B. D.
VIII.—Esters and Salts.							
Ethyl nonylate, $C_9H_{19}COOC_2H_5$	20.0°	28.04	72.80	100.84	23.88	76.96	B.
Ethyl carbonate, $(C_2H_5)_2CO_3$	20.0°	26.31	72.80	99.11	12.86	86.25	D.
Castor oil, glyceryl { Stearate, Ricinoleate, Etc.	17.0°	37.14	73.23	110.37	22.63	87.74	H. B.
IX.—Nitriles.							
Acetonitrile, CH_3CN	20.0°	29.04	72.80	101.84	...	101.00	
X.—Aromatic Hydrocarbons.							
Benzene, C_6H_6	10.0°	30.25	74.28	104.53	35.38	69.15	H. H.
Benzene, C_6H_6	20.0°	28.98	72.80	101.78	34.97	66.18	H. H.
Benzene, C_6H_6	20.5°	29.21	72.73	101.94	34.45	67.49	H. B.
Benzene, C_6H_6	25.0°	28.35	72.05	100.40	34.68	65.72	H. H.
Benzene, C_6H_6	30.0°	27.71	71.30	99.01	34.38	64.63	H. H.
Benzene, C_6H_6	40.0°	26.44	69.81	96.25	33.79	62.46	H. H.
Toluene, $C_6H_5CH_3$	25.0°	27.7	72.05	99.75	36.10	63.65	H. H.
m-Xylene, $C_6H_4(CH_3)_2$	25.0°	28.3	72.05	100.35	37.60	62.75	H. H.
Ethyl benzene, $C_6H_5C_2H_5$	17.5°	29.62	73.16	102.78	31.15	71.63	H. B.
Styrene, $C_6H_5CH : CH_2$	19.0°	32.14	72.93	105.07	35.48	69.59	H. B.
p-Cymene, $CH_3C_6H_4CH(CH_3)_2$	13.5°	28.75	73.76	102.51	39.41	63.10	H. B.
XI.—Halogen Derivatives.							
Benzene iodide, C_6H_5I	16.8°	40.35	73.26	113.61	45.67	67.94	H. B.
XII.—Alcohols.							
Benzyl alcohol, $C_6H_5CH_2OH$	22.5°	39.71	72.42	112.13	4.75	107.38	H. B.
XIII.—Amino Derivatives.							
Dimethyl aniline, $C_6H_5N(CH_3)_2$	25.0°	36.02	72.05	108.25	25.78	82.47	H. H.
XIV.—Esters.							
Ethyl phthalate, $C_6H_4(COOC_2H_5)_2$	20.5°	37.34	72.73	110.07	16.27	93.8	H. B.
Ethyl cinnamate, $C_6H_5C_2H_2$-$COOC_2H_5$	19.5°	38.42	72.87	111.29	21.36	89.93	H. B.
Ethyl hydrocinnamate, $C_6H_5(CH_2)_2$-$COOC_2H_5$	21.5°	35.08	72.57	107.65	20.19	87.46	H. B.

H. H. = determinations made by Humphery in this laboratory.

D. = determinations made by Davies in this laboratory.

B. = determinations by Harkins and Brown.

H. B. = data calculated from experimental values given by Hardy by the use of corrections determined by Harkins and Brown.

A. = Antonow.

Table I contains the data for the interfacial tensions which have thus far been determined, together with the values of the surface tensions of the pure single liquids which make up the interface. The interfacial tensions are determined by the use of mutually saturated liquids, since otherwise the values obtained would have no definite meaning. In this table the results marked H. B. are calculated from data given by Hardy[1] by the use of corrections determined by us. Hardy's own results are different from these, but were calculated from what, according to our work, are improper corrections. The application of the new corrections lowers his value on paraffin oil by 11%, and raises that on benzene iodide by 10%. The results denoted by A. are those of Antonow, which are not accurate within less than 8%, but since in the cases in which his data have been used the liquids are so soluble in each other that the interfacial tension is small, this percentage error has no appreciable influence on the value of $-\Delta\sigma$ as calculated. In making up this table, in order to make it as general as possible, some acids and alcohols which are very soluble in water have been included. Now it is not possible to determine the interfacial tensions of extremely miscible liquids, since they form no interface, but it may be seen that the results of Antonow show that as the solubility increases the interfacial tension decreases, so that when the interfacial tension of water with octyl alcohol is 8.28, with isoamyl alcohol it is only 4.42, and with isobutyl, the value has decreased to 1.76 for the four carbon atom alcohol. Therefore it is not probable that any very considerable error is made in the calculations, by assuming that the interfacial tensions of liquids mutually soluble in all proportions, are so small[2] as not to materially affect the calculation of the decrease of free energy.

It is found that if the interfacial tension between two liquids is small, the liquids are miscible. That in some cases, however, the surface tension is not the property which actually determines the solubility of a substance as a molecular disperse system (so called true solubility) is shown by the fact that it is possible to make water colloidally soluble in benzene or benzene in water (emulsification) by adding a substance which causes the interfacial tension to drop to a low value, but in this way benzene cannot be made to dissolve in water as a molecular disperse phase, that is a true solution of any considerable concentration with benzene as a

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

[2] This assumption gives values for the very soluble substances which are not less to be trusted than Antonow's experimental results, but both involve the difficulty that the process of interdiffusion of two soluble liquids at their interface, cannot be prevented.

solute cannot be formed. The fact that low interfacial tension may be taken to indicate true solubility in the case of two PURE liquids, and colloid solubility in the other case cited, may be taken to indicate that true and colloidal solubility are related. Let us take the case of an emulsion of benzene in water as stabilized by sodium oleate, as an example of colloid formation, and suppose that the drops of benzene are of such a size that the emulsion is stable and that the interfacial tension (benzene drop-sodium oleate water) is either zero or very low. If the interfacial surface could now be scraped off so rapidly that no time would be given for adsorption, then the surface tension would rise to a comparatively large value.

Thus the necessary condition of the formation of a molecularly disperse solution is that as the particles grow smaller, the surface tension must not increase, and this condition is not met by stable emulsions or colloids.

Polar liquids are in general mutually soluble. Also slightly polar liquids such as hexane or octane are soluble in other slightly polar liquids, but are not soluble in very polar liquids. However, even in the case of polar substances there is not always complete miscibility, though in general markedly polar substances are mutually soluble when both are liquids at the temperature of the experiment. It seems probable that the nature of the polarity may also be of influence. Thus while the very polar salts of potassium and sodium are in general soluble in water, they are not very soluble in methyl cyanide which, however, is not so polar as water. On the other hand the halogen salts of silver are very little soluble in water, but are very soluble in ammonia and somewhat soluble in methyl cyanide. However, the solubility of these salts in ammonia depends upon the formation of ammonia complexes, and it is to be noted that ammonia forms complex ions with elements which have *low atomic volumes*, and *are also metals*. Complexes in methyl cyanide are being studied by Mr. Nash in this laboratory, and he has found that while ammonia is a much better and methyl cyanide a slightly better solvent for the silver halides than water, the silver ammonia and other metal ammonia complexes are much more insoluble in methyl cyanide than in water, so that the cobalt-ammines, for example, are easily prepared in this solvent as very slightly soluble precipitates. Silver sulphide is much more soluble in methyl cyanide than in water, and in general salts with atoms of high atomic weights are relatively more soluble in ammonia and in methyl cyanide than in water.

Table I gives the work W done by the attractions of the surfaces of two liquids on each other when they come together. Now

$$W = \int_{s_1}^{s_2} F\,ds \qquad \text{where } F = f(s).$$

$$\text{Let } s = s_1 + u,$$
$$\varphi_m = f(s_{1m} + u),$$
$$W_m = \int_0^\infty F_m du = \int_0^\infty \varphi_m (s_{1m} + u)\, du.$$

Here the force of attraction F is a function of the distance s; and s_1 is the distance between the surfaces when they approach most closely, and may be taken as zero. Whether the attraction can be taken as proportional to the work done depends upon the form of its functional relation to s, or to u, which is s minus s_1. If a law of the following form holds, then the attraction would be proportional to the work, provided the work done in surface mixing is zero. Let

$$\varphi_m = A_m x(u),$$
$$F_m = B_m e^{-\lambda i} = (B_m e^{-\lambda s_{1m}})\, e^{-\lambda u},$$
$$F_m = A_m e^{-\lambda u},$$

where the subscript m refers to the special material, and λ is a universal constant. Even where the form of the function is such that there is not a strict proportionality between the force and the work, the work gives a measure of the relative value of the force.[1]

It may be seen that when 1 sq. cm. of each of the surfaces octane and water come together, the work is 45.96 ergs. For two octane surfaces the value is 43.6, and for water 145.6 ergs. For hexane the corresponding numbers are 41.22, 41.6, and 145.6. From this standpoint it seems that the insolubility of these hydrocarbons is due not to any considerable difference in the attractions hydrocarbon-water and hydrocarbon-hydrocarbon, but to the fact that water attracts water much more than it does the hydrocarbon; so the hydrocarbon has no chance to get into the water in appreciable quantities.

If methyl alcohol is considered, it is found that for alcohol-water the work is 95, for alcohol-alcohol 48.1, and for water-water, the same high value as before. Here, even though water attracts water much more than it does methyl alcohol, water attracts the alcohol much more than the alcohol attracts itself, so the result is that the alcohol goes into solution. With ether the values are: ether-water, 80 ergs; ether-ether, 37.8 ergs; water-water, 155.5 ergs. Here the attraction of ether for water is somewhat less than that of alcohol, and each liquid is only moderately soluble in the other at 20°.

If the behavior of octyl alcohol is now compared with that of other alcohols, it is found that the attraction of octyl alcohol for water is nearly as high as that of methyl alcohol, and though the attraction of alcohol

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[1] The term "attraction" will be used somewhat loosely in this paper, and will mean the value the attraction would have if it followed a law such as that given, and if the free energy of surface mixing is zero.

for alcohol is somewhat increased with the length of the carbon chain, there is no indication from the data of the fact that octyl alcohol is very much the more insoluble. It is therefore apparent that while the values of the decrease in free energy (work done) when two liquids approach each other, which we have assumed to give some measure of the attractions between the surfaces, indicate to a certain extent the solubility relations of two liquids, they are not sufficient to determine these solubilities.

There are other factors involved. One of the most important of these will now be discussed, and the consideration of other factors will be left to later papers. Thus the volume and shape of the molecules, and the extent of their kinetic agitation are undoubtedly of importance. If organic compounds are considered, it is found that while methane, ethane, and the other hydrocarbons are only very slightly soluble in water (according to the data available propane is the most soluble—also propylene is more soluble than ethylene), the substitution for hydrogen of any groups of the nature of —OH, —COOH, —CHO, —CN, or —$CONH_2$, in a hydrocarbon which contains only a very few carbon atoms, increases the solubility very greatly, so that at 20° such substances as methyl, ethyl, and propyl alcohols, formic and acetic acids, methyl cyanide, and acetaldehyde, are miscible with water in all proportions, and 97.5 g. of acetamide are soluble in 100 g. of water at 20°. It will be noticed that the groups which when thus substituted change the hydrocarbons to compounds soluble in water, are just the groups which, according to Table I, increase greatly the attraction between the hydrocarbon and water. The decrease of free energy when an ester comes in contact with water is less than the corresponding value for an acid. Corresponding to this ethyl acetate is less soluble than butyric acid, which contains the same number of carbon atoms.

While a double bond at the end of a hydrocarbon chain increases the attraction for water considerably, from 46 for octane to 73 for octylene, this increase is nowhere nearly so large as that given by —COOH, —CHO, or —OH. From this standpoint, while a short chain hydrocarbon such as ethane should be made more soluble by the introduction of a double bond and the change to ethylene, the increase in solubility should be nowhere nearly so large as if one of the other groups mentioned were substituted. Although as yet we have made no measurements on compounds containing triple bonds, it is to be expected that the triple would attract water more strongly than the double bond. For short chain hydrocarbons there should, then, be an increase in solubility with the number of valences in the bond, in the order ethane, ethylene, and acetylene. Corresponding to this it is found that the solubilities are, respectively, 0.0507, 0.1311, and 1.105 volumes of gas per volume of liquid.

The above facts may be generalized in the statement that the introduction of polar groups causes hydrocarbons to become soluble in water when the hydrocarbon chain is short. If the alcohols are considered as a typical case, then it is seen that after the chain has reached a length of 4 carbon atoms the decrease of free energy, when the surface comes in contact with a water surface, remains almost *constant* as the chain increases in length. However, it is about at this number of carbon atoms that the solubility of the alcohol begins to *decrease rapidly* with the length of the hydrocarbon chain. These facts indicate that the specially large decrease of free energy, when a carbon chain containing a polar group comes in contact with water, must be due to the polar group, and that the decrease in solubility with the length of the chain is not the result of a decrease of attraction between the water and the polar group, but that it is due to the difficulty with which the longer chain is pulled into the water.

The fact that the introduction of a polar group at the end of even a very long hydrocarbon chain increases so greatly the attraction for water, and that the attraction is very nearly independent of the length of the chain, indicates that at all such interfaces the active group must be turned toward, and practically in contact with, the water. In fact, the numerical data seem to indicate that the union between the polar group and the water is of the general nature of a more or less loose chemical combination. The application of this idea as an explanation of adsorption at liquid surfaces, will be given in the next paper of this series.

Since for any single class of substances the value of which is practically constant for unit area, it is plain that it cannot be constant for what is commonly called the molecular surface ($= V^{2/3}$). Thus for isobutyl alcohol and octyl alcohol the respective values for molecular surfaces are 1999 ergs and 2916 ergs. This fact was first noticed by Hardy, and from the standpoint of our hypothesis is easily explained, since if the molecules are oriented with their active groups toward the water, the number of molecules per unit area of different alcohols, at least if the chains are normal, should be the same, while the number per "molecular surface" should increase with the length of the molecules, since the molecular volume increases. The term "molecular surface" has no value in connection with the phenomenon which is under consideration, and presumably is of no use in any case except where the molecules are spherical.

Several additional points of interest may here be noted. Benzene evidently attracts water ($-\Delta\sigma = 67$ ergs at 20°) much more than cyclohexane (38.5 ergs). If we assume the Kekule formula, this increase in the work done by benzene over that done by cyclohexane would be due to the three double bonds, so that all of the carbon atoms should be attracted by the water. From this standpoint the orientation of benzene molecules on a water surface should be very different from that of a derivative of a normal chain compound. If by a measurement of a benzene film the area covered per molecule could be determined, the values given here could be used to compare the relative amounts of work done by the double bond of a hydrocarbon, with that of the double bonds of benzene. On account of the volatility of benzene such experiments should be made with the film resting on a polar liquid at a low temperature.

The relatively high value of $-\Delta\sigma$ for ethyl ether (80 ergs) would seem to be due to an attraction of its O atom for that of the water. The replacement of one $C_2H_5^-$ group by H^- gives an alcohol and increases this value to 95.2 ergs, while the substitution of the last organic radical by H gives water, and $-\Delta\sigma$ rises to 145.2 ergs. The replacement of the oxygen atom of ethyl alcohol by sulfur gives ethyl mercaptan, and lowers $-\Delta\sigma$ from 95.2 to 68.5 ergs, and corresponding to this large decrease only about 1.5 g. of mercaptan dissolves in 100 g. of water at ordinary temperatures while ethyl alcohol is missible in all proportions.

Chloroform ($-\Delta\sigma = 72.4$ ergs), if Antonow's data may be trusted, attracts water much more than carbon tetrachloride ($-\Delta\sigma = 48.2$ ergs), so chloroform acts as a much more polar compound. While this difference is not apparent in any of the calculations made on internal pressure by different writers, J. J. Thomson in 1914 classed CCl_4 as non-polar, and chloroform as slightly polar, from the standpoint of specific inductive capacities of the gases.

For ethyl-nonylate the value of $-\Delta\sigma$ is 77 ergs, or about 27 ergs less than for the corresponding acid, and about 31 ergs more than for the hydrocarbon. Since it is undoubtedly the oxygen of the ester which is attracted most to the water, and since the data are for unit area, a part of the decrease in attraction from ester to acid may be due to the fact that the $C_2H_5^-$ group of the ester occupies more space than the hydrogen atom of the acid. In the case of the acid there is the question of dissociation to consider.

Summary.

1. Evidence is presented which seems to indicate that at the interface between another liquid and water, the molecules in the surface of the liquid set themselves in such a way as to turn their most active or polar groups toward the surface of the water. At such surfaces liquids therefore show a structure.

2. The free energy decrease, when the surface of a second liquid approaches that of water (a polar liquid), depends primarily upon the most active or polar group present in the molecule, and in a secondary way upon the shape and size of the molecule.

3. The solubility in water is related to this free energy decrease, which

more or less perfectly measures the attraction of the active group for the water molecule. Thus the presence of a very polar group such as COOH, CO, CN, OH, or $CONH_2$, is sufficient to make the molecule of an organic substance soluble in water if the polar group does not have to pull into the solution a slightly polar group which is too long or too large. While slightly polar groups such as CH_3 are attracted by water, the attraction is much smaller than that of the polar groups. The active groups given above (and ether also) contain either oxygen or nitrogen atoms. The sulfur atom is much less active than either of these, but is much more active than the methyl group. Double or triple bonds between carbon atoms act as active groups, and benzene shows a much larger value for this free energy decrease than the corresponding six carbon atom hydrocarbons which do not contain double bonds.

4. True (or molecularly disperse) *solubility is a molecular scale phenomenon,*[1] and is dependent upon the attractions of the different parts of the various molecules for each other, and upon the shapes and sizes of the molecules which must be fitted together to make a solution. The space occupied by a molecule depends upon the extent of its kinetic agitation so the solubility of substances is highly dependent upon the temperature.

In a later paper we will present a more extended series of data, and will discuss the solubility of slightly polar substances in each other.

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[CONTRIBUTION FROM THE GEOPHYSICAL LABORATORY OF THE CARNEGIE INSTITUTION OF WASHINGTON.]

THE IODOMETRIC DETERMINATION OF SULFUR DIOXIDE AND THE SULFITES.

BY JOHN B. FERGUSON.

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Although the determination of sulfur dioxide is one of the most important in the whole realm of gas analysis, it is only recently that any serious attempts[2] have been made to determine the conditions under which accurate analyses are obtainable, and these attempts have been confined to the determination of small amounts of sulfur dioxide in air in relatively large samples (2500 cc.). Furthermore, the methods advocated by the various investigators are not of general application. The writer, during an extended investigation of volcanic gases, has been confronted with the somewhat different problem of analyzing very accurately small gas samples (30 cc.) containing amounts of sulfur dioxide ranging from 0.3 to

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[1] For an excellent discussion of the related large scale properties of liquids see a paper by Hildebrand, THIS JOURNAL, **38**, 1452–73 (1916).

[2] Report Selby Smelter Commission, *Bull. Bur. Mines,* **98**, 200 (1915); *Chem. Abs.,* **10**, 4, 436 (1917); Seidell and Meserve, *J. Ind. Eng. Chem.,* **6**, 298 (1914).