

graphite, together with the material which E. D. Campbell considers unsaturated hydrocarbons. Such material when treated with selenium oxychloride gives a black extract, showing that at least part of the material has been acted on. It is possible that a further study of this reaction may throw some light on the constitution of iron and steel.

The same care is used in the laboratory in handling selenium oxychloride as with any other highly corrosive liquid. Its vapors have shown no other physiological action than that of the hydrochloric acid produced by its hydrolysis with the mucous membranes.

MADISON, WIS.

## THE ORIENTATION OF MOLECULES IN SURFACES. VI. COHESION, ADHESION, TENSILE STRENGTH, TENSILE ENERGY, NEGATIVE SURFACE ENERGY, INTERFACIAL TENSION, AND MOLECULAR ATTRACTION.

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### Introduction.

This paper presents data which were obtained in order to exhibit the relation between the chemical properties of organic liquids and the total amount of energy which is used in separating them from water or from themselves. It includes somewhat complete data, the first of the sort to be obtained, on the surface and interfacial energy relations of 12 organic liquids.

### Work of Adhesion.

The equation developed by Dupré in 1869<sup>1</sup> gives the *adhesion work* ( $W_A$ ) involved in the approach of 2 unlike surfaces, which is equal to the decrease of free energy during their approach:

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

where  $\gamma_1$  and  $\gamma_2$  give the free energy (numerically equal to the surface tension) of the 2 unlike surfaces before their approach, and  $\gamma_{1,2}$  is the free energy of the interface (numerically equal to the interfacial tension). A recent paper from this laboratory<sup>2</sup> gives values for the work of adhesion toward water of 70 organic liquids at 20°.

Fig. 1 plots the adhesion work toward water for 11 organic liquids at temperatures between 0° and 50°, and presents for comparison the values at 20° for 28 other liquids. It may be noted that the temperature coefficient has specially low negative values (about -0.178) for the 2 halogen compounds, carbon tetrachloride and ethylene bromide, and

<sup>1</sup> Dupré, "Theorie Mécanique de la Chaleur," Paris, 1869, p. 69; Lord Rayleigh, London, *Phil. Mag.*, [5] 30, 461 (1890); Hardy, London, *Proc. Roy. Soc.*, 86B, 634 (1911).

<sup>2</sup> Harkins, Clark and Roberts, *THIS JOURNAL*, 42, 700-12 (1920).

specially high negative values (about 0.3) for heptaldehyde, the higher paraffin, and heptin.

### Work of Surface Cohesion.

Since  $\gamma$  is zero when the 2 liquids become identical, the Dupré equation reduces to

$$W_{SC} = -\Delta\gamma = 2\gamma$$

where  $W_{SC}$  represents the work of the surface cohesion. The free sur-

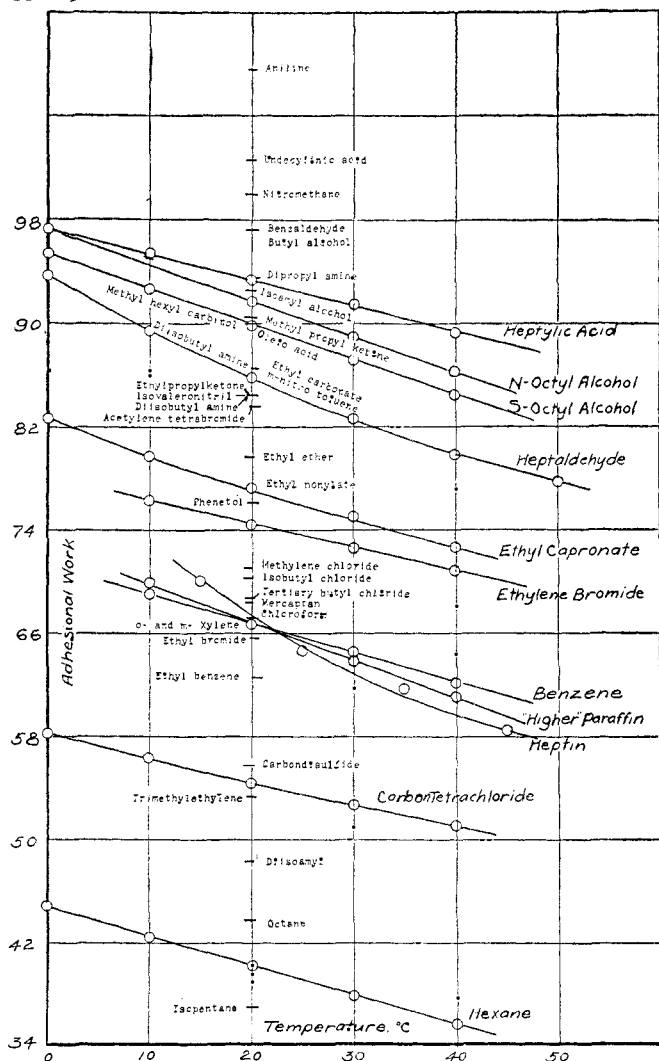


Fig. 1.—Adhesional work, ergs per sq. cm., between organic liquids and water. (The names of the substances represented by the curves are given at the right while the names given in the middle of the diagram represent substances for which the values are given at 20° only.)

face energy ( $\gamma$ ) is usually measured in ergs per sq. cm. It is evident that  $W_{SC}$  is the work necessary to break a bar of liquid or solid with a cross section of one sq. cm., in such a way as to give 2 plane surfaces of one sq. cm. each, that is the break must occur perpendicular to the long axis of the bar. This amount of work is clearly that which would be done in the determination of the tensile strength of a steel or other metal bar, if the test could be carried out under ideal conditions, which are that the bar during the test must remain of uniform cross section, and the break must occur in such a way as to give 2 surfaces which are as closely plane as the surface of a liquid, though in the actual tests this condition is not met, since the bar is much distorted. The work of surface cohesion may therefore be called the tensile work ( $W_T$ ). This is equal to the tensile force integrated through the distance necessary to pull the 2 surfaces completely apart, or

$$W_T = \int_{s_0}^{\infty} F_T ds = 2\gamma.$$

Fig. 2 plots the free surface energy ( $\gamma$ ), or one-half the tensile work, on the Y-axis and the temperature on the X-axis. It may be noted that

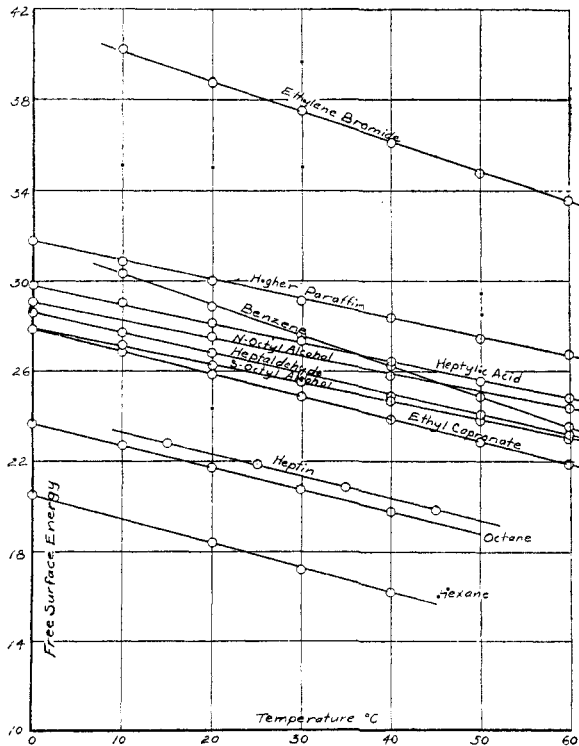


Fig. 2.—The free surface energy (or surface tension) of organic liquids. This equals one-half the tensile work per sq. cm.

through the limited temperature range the tensile work is a linear function of the temperature, and that this is also the case when the molecular free surface energy is plotted, as in Fig. 3. This plot gives  $1/2$  of the tensile work for the area covered by one molecule, when this area is calculated on the not altogether correct hypothesis that this area is equal to the  $2/3$  power of the average volume occupied by one molecule.

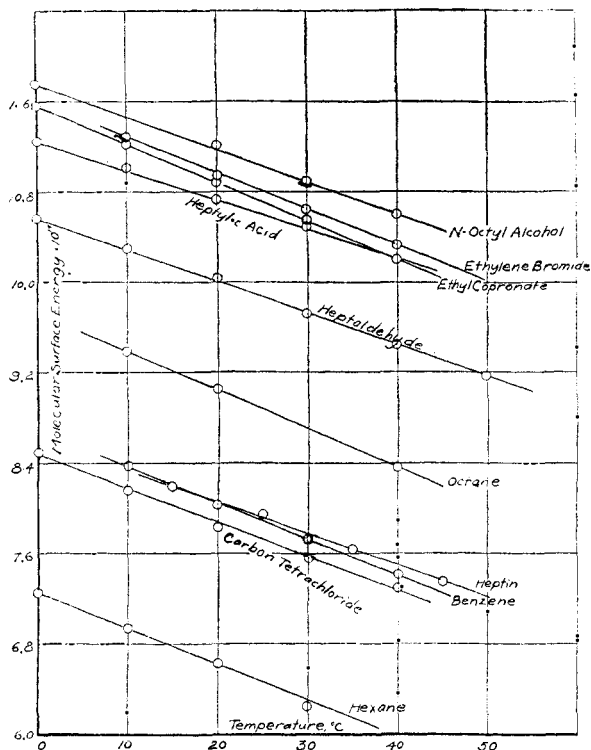


Fig. 3.—The free surface energy of organic liquids in ergs  $\times 10^{14}$  for the area occupied by one molecule (calculated on the incorrect assumption that this area is given by the  $2/3$  power of the volume of the molecule).

#### Interfacial Tension and Free Interfacial Energy.

Fig. 4, which presents plots for the free interfacial energy (or interfacial tension) for 10 liquids, indicates that while the temperature coefficient ( $d\gamma/dt$ ) of free surface energy is always *negative*, that for *interfacial* energy, though usually negative, is sometimes positive as in the cases of secondary octyl alcohol, heptaldehyde, heptin, and the higher paraffin. The coefficient may also be very small, as in the case of ethyl capronate and heptane, or large as in the case of the 2 halogen compounds. What is more remarkable is that it may have a positive value at one temperature and a negative at another, as with heptaldehyde, and presumably also with heptin.

Since for a saturated surface the latent heat  $l$  is related to the temperature coefficient of free surface energy by the following equation,

$$l = -T \frac{d\gamma}{dt}$$

the latent heat of an interface may be either positive or negative; positive when the interfacial tension decreases, and negative when it increases with the temperature. Thus the interfaces between water and

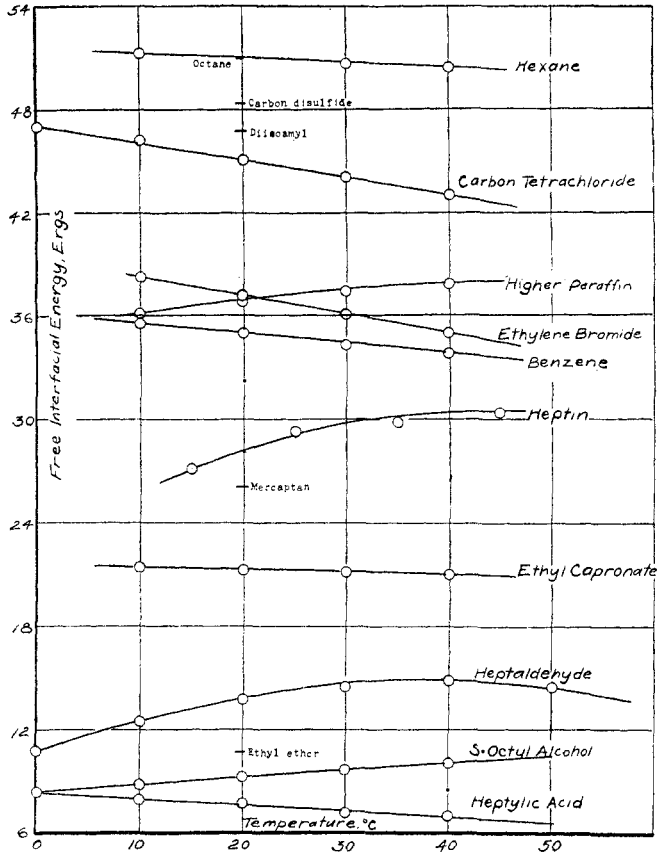


Fig. 4.—The free interfacial energy (or surface tension) between organic liquids and water.

any one of the liquids, secondary octyl alcohol, "higher paraffin," heptin, and heptaldehyde (up to 40°), contrary to the usual rule, rise in temperature when they are expanded.

**The Energy of Surface Cohesion.**

The total energy of a surface is given by the equation

$$E_S = \gamma + l$$

so the total energy of surface cohesion may be represented as

$$E_C = -\Delta E_S = 2(\gamma + l) = 2E_S.$$

It is evident that the total energy of surface cohesion is equal to the total tensile energy ( $E_T$ ), or

$$E_T = -\Delta E_S = 2E_S.$$

Thus the total energy used in pulling apart a bar of unit cross section in such a way as to form 2 unit plane surfaces, is equal to twice the total surface energy. It is also equal to the force of surface cohesion ( $F_{SC}$ ) integrated through the distance necessary to pull the 2 surfaces completely apart, or

$$E_T = \int_{S_0}^{\infty} F_{SC} ds.$$

Fig. 5 gives the total surface energy, or *one-half the total energy of surface cohesion* for 10 of the liquids already considered.

It may be noted that the values are low in the case of hexane, heptane and octane. The presence of the triple bond at the end of the hydrocarbon chain evidently has no appreciable effect in increasing the total tensile energy, and even the addition of an oxygen atom at or near the end of the

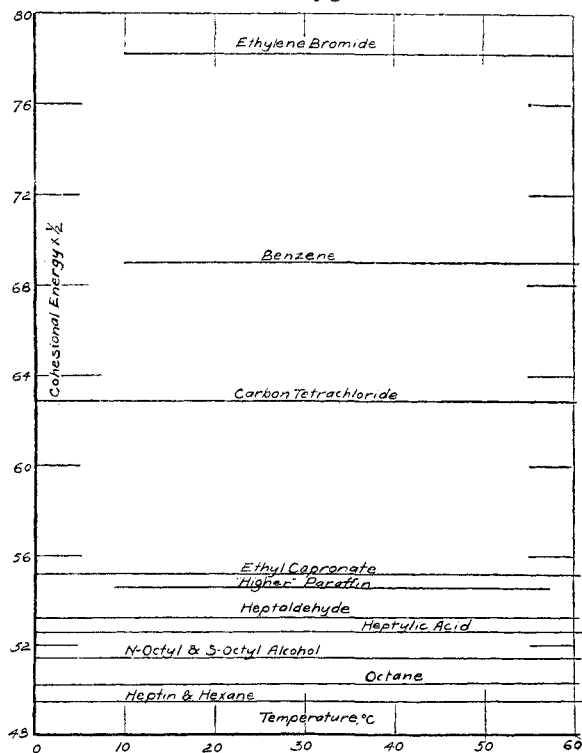


Fig. 5.—The energy of surface cohesion in organic liquids in ergs per sq. cm.

chain increases the value by only about 2%, while the carboxyl and aldehyde groups have considerably more, but still not a very large effect (about 6 and 7%). The unsaturated groups in benzene, contrary to the lack of effect as the result of the triple bond in heptin, produce an extremely marked increase (approximately 40%). This is easily explained by the orientation hypothesis. When a bar of heptin is pulled apart the break occurs where the intermolecular electromagnetic field is weakest, that is between the hydrocarbon chains, and in order that this may be the case the hydrocarbon groups turn into the nascent surface in the process of its formation. In the benzene molecule, on the other hand, the symmetry is so great that the break must occur between certain of the unsaturated groups, that is, where the molecular electromagnetic field and the resulting attraction are high. That the tensile energy of ethylene dibromide on account of its symmetry, is much higher than that of ethylidene bromide, is explainable in a similar way.

#### Energy of Adhesion.<sup>1</sup>

The equation presented in an earlier paper gives the total adhesional energy ( $E_A$ ), and is as follows:

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

The energy of adhesion is equal to the total surface attraction ( $\pi''$ ), due to molecular attraction, integrated through the distance necessary to pull the 2 surfaces completely apart, or

$$E_A = \int_{s_0}^{\infty} \pi'' ds = E_1 + E_2 - E_{1,2}.$$

The only experimental results which have been obtained in this connection are those given in this paper, and these are plotted in Fig. 6.

It will be seen that the total adhesional energy, like the similar cohesive energy, seems from these results to be in general independent of the temperature, at least over a moderate range of temperature. For the liquids where this is true, very low values are given by hexane, and octane, as in the case of the cohesive energy, but it is remarkable that the symmetrical halogen derivatives, carbon tetrachloride and ethylene dibromide, which gave *specially high values* for their *tensile energy*, give *specially low values* for the adhesional energy toward water, while the octyl alcohols, which give *specially low values* for their *tensile energy*, give *high values* of the *adhesional energy*. Thus the addition of *one oxygen*

<sup>1</sup>The equations given in this paper are based entirely upon thermodynamics, with the exception that they involve the assumption that the surface may be treated as a reversible engine, even although material flows into the surface when it forms, and out when it disappears which is the assumption involved in practically all of the applications of thermodynamics to surfaces which method has the one justification that it has worked in the past. It is obvious that deductions which are based so directly upon thermodynamics, cannot be specially novel.

atom to the 26 atoms present in a molecule of octane, increases the tensile energy by only 2%, but it increases the *adhesional energy* by about 65%,<sup>1</sup> an extremely large increase. This, again, is easy to explain on the basis of the orientation hypothesis, since on account of the strong electromagnetic field between the hydroxyl groups of water and of an alcohol, the oxygen atoms of the alcohol turn toward the water. Thus the *adhesional energy* toward water is determined by the *strongest fields* in the molecules, while the *tensile energy* is determined by the *weakest*.

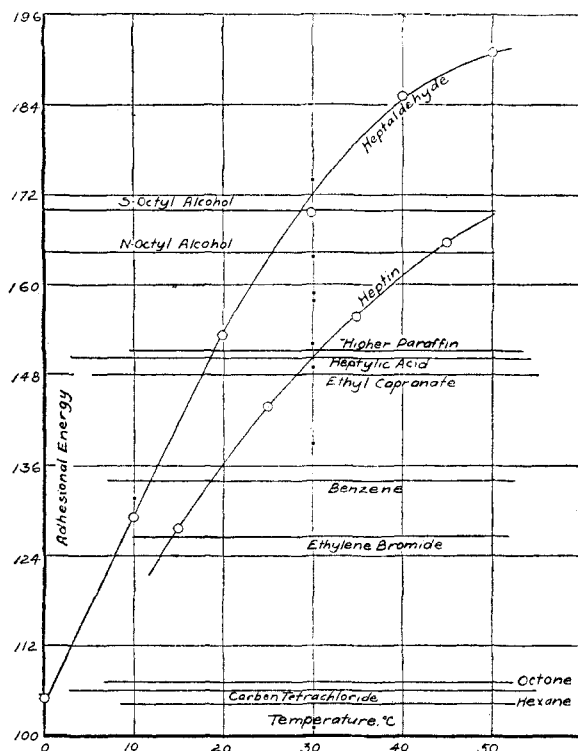


Fig. 6.—The adhesional energy between organic liquids and water in ergs per sq. cm.

It is found, contrary to some opinions which have been expressed, that the tensile energy, or the total surface energy, of the higher paraffin is considerably higher (10%) than that of hexane, while the adhesional energy is very much higher (45%).

The adhesional energy of both heptin and heptaldehyde, increases very rapidly with the temperature. This fact will be discussed in connection with later results.

<sup>1</sup> Earlier papers of this series have shown that similar relations hold for the tensile and adhesional work, which is only a part of the energy effect considered above.



### Negative Surface Energy.

Not only Donnan, but also Tolman and Wolfgang Ostwald, have assumed the existence of a *negative surface tension* or free energy surface. The investigations carried out in this laboratory have convinced the writers that it is improbable that the existence of a negative free surface energy for a free, uncharged plane surface will be discovered. Our data indicate, however, that a number of uncharged, plane interfaces have a *negative total energy*, provided the same simple thermodynamic equation as is used for surface is applicable to the surfaces known as interfaces.

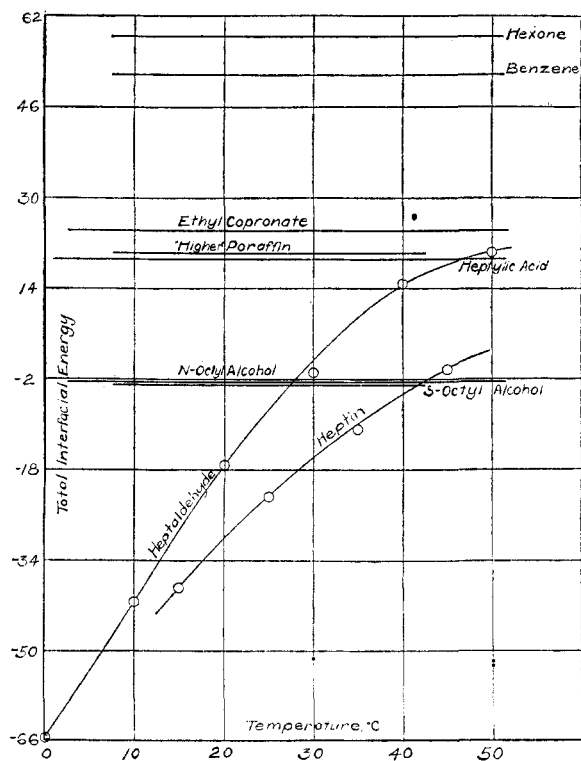


Fig. 7.—The total interfacial energy between organic liquids and water in ergs per sq. cm. The curves for heptin and heptaldehyde are determined from a differential and are therefore not at all accurate.

Thus, contrary to the rule found in the past, the surface or interface between normal or secondary octyl alcohol and water gives off energy when it is extended, but, nevertheless, the surface cannot be formed without the expenditure of work. The apparent contradiction is probably due to the fact that while the molecular motion of an ordinary sur-

face *aids* in its formation, in the case of the interface under discussion it *hinders* the extension of the surface. In certain temperature ranges heptin and heptaldehyde give large negative values for the interfacial energy, though the largest negative values are probably considerably too large, for the errors are considerable, since the numbers include values obtained by means of a temperature coefficient, which involves a tangent to the surface tension curve.

### Energy of Cohesion.

The cohesive energy of a solid or a liquid may be defined as the energy which would be liberated in the formation of the solid or liquid from its individual molecules, the molecules in its initial state being placed so far apart that they do not attract each other appreciably. This is equal to the latent heat of vaporization plus the heat absorbed in the expansion of the vapor until it becomes very dilute, minus the external work of vaporization, or it is equal to the internal latent heat of vaporization when the liquid is vaporized at a low pressure.

### Internal Pressure or Cohesion.

The internal pressure of a liquid or a solid has been defined as the rate of transfer of momentum across a unit plane area inside the liquid or solid; and the average force of attraction across this unit area, which is numerically equal to the internal pressure, is the cohesive force, or the cohesion.

While the work and total energy of adhesion and of surface cohesion, and the energy of cohesion, may all be obtained from experimental results by the use of simple and exact thermodynamic equations, this is not true of the internal pressure or cohesion. As a matter of fact, there is at present no known means of calculating the cohesion, but there are many methods, which do not agree among themselves, of calculating from inexact equations, values which for various liquids are supposed, when arranged in order of magnitude, to lie in the same order in general as the cohesions themselves. In fact, the cohesion is often defined as equal to  $a/v^2$ , the pressure correction term in van der Waals' equation. However, since this equation is far from exact in its application to liquids, it is obvious that the cohesion calculated cannot represent at all accurately the internal pressure.

### Molecular Attraction.

All of the phenomena thus far discussed in this paper may be considered as due to the attraction between the molecules in a liquid or a solid. It is customary to consider the molecules as spheres or as points, with the attractive forces dependent upon the distance between the molecules alone, when they are all alike. It has been shown by Harkins, Brown, Davies, Roberts,

Clark, King, Grafton and Ewing,<sup>1</sup> by a measurement of the amounts of energy involved, and by Langmuir<sup>2</sup> by a less direct method, that the forces around different parts of a molecule may be very different in magnitude. Thus in the case of organic compounds the forces are very much higher between any groups in different molecules containing oxygen, nitrogen, triple, or double bonds, than they are between the hydrocarbon chains. The investigations of this laboratory show that if organic substances are arranged according to the magnitude of their adhesional surface work toward mercury, they are not so arranged with respect to water. In this respect the adhesional forces seem to have something of the specific nature which indicates chemical action, and it is well known that the recent work on crystal structure demonstrates that such crystals as those of diamond and of graphite are held together by primary valence bonds. Langmuir considers all cohesive and adhesional forces as chemical, while van Laar has recently published the results of an extensive series of calculations which show that the square root of van der Waals' constant of attraction  $a$  is additive, and therefore comes to the conclusion that all such forces are physical. The calculations of Einstein,<sup>3</sup> Kleemann,<sup>4</sup> and unpublished calculations by Harkins and Clark,<sup>5</sup> have also given coefficients of *atomic* attraction which are moderately exact constants. Since all of these facts, when considered together, make it probable that cohesive forces are often less specific than those involved in ordinary chemical reactions, while in many cases they are the same valence forces, it seems preferable to use neither of the 2 words, physical or chemical, and to consider that cohesion is due to electrical and magnetic, or electromagnetic forces, which are probably largely electrical. In a paper<sup>6</sup> on "An Electromagnetic Hypothesis of the Kinetics of Heterogeneous Equilibrium, the Structure of Liquids, and Cohesion" a connection has been shown between cohesion and the completeness of the outer or valence shell, of electrons in the atom or the molecule. The cohesion decreases as the completeness of the outer shell of electrons in the molecule increases. Numerous recent papers of Born and Landé<sup>7</sup> show that the

<sup>1</sup> (a) Harkins, Grafton and Ewing, *Proc. Nat. Acad. Sci.*, **5**, 571 (1919).

(b) Harkins, Brown and Davies, *THIS JOURNAL*, **39**, 354-64 (1917).

(c) Harkins, Davies and Clark, *ibid.*, 541-96.

(d) Harkins and King, *ibid.*, **41**, 970-92 (1919); *Proc. Nat. Acad. Sci.*, **5**, 152-9 (1919).

<sup>2</sup> Langmuir, *THIS JOURNAL*, **39**, 1848-1906 (1917); *Proc. Nat. Acad. Sci.*, **3**, 251-7 (1917); *Met. Chem. Eng. Abs.*, **15**, 468 (1916); Fraenkel, *Phil. Mag.*, **33**, 297-322 (1917).

<sup>3</sup> Einstein, Leipzig, *Ann. Physik.*, **4**, 513 (1901).

<sup>4</sup> Kleemann, *Phil. Mag.*, **18**, 39, 491, 901 (1909).

<sup>5</sup> Harkins and Clark, unpublished calculations.

<sup>6</sup> Harkins and King, *THIS JOURNAL*, **41**, 970-92 (1919).

<sup>7</sup> See "Die Aufbau der Materie," by Max Born. Julius Springer, Berlin.

cohesion in a crystal may be calculated from a consideration of the electrical forces involved.

### On the Relation between Cohesion and Cohesional and Adhesional Work and Energy.

A number of attempts have been made to calculate the *cohesion*, which is the cohesional force per unit area or the cohesional pressure, from the *cohesional surface work*, and these attempts have been more or less justified by the fact that the values thus obtained, while not good in numerical agreement with those given by  $a/v^2$ , lie on the whole in the same relative order. Such calculations have been made by Mathews,<sup>1</sup> and by Hildebrand,<sup>2</sup> but neither of them happens to have shown to what extent the cohesion and the cohesional surface work are related. The term  $a/v^2$  may be said to represent, more or less imperfectly it is true, the total effect of the molecular attraction in decreasing the external pressure, which decrease is the cohesion. The cohesional surface work, on the other hand, does not represent the total effect of the molecular attraction, even as it acts in a surface, since the molecules move into the surface not only by means of the energy which is contributed in the form of work, but also by means of the utilization of the kinetic energy of molecular motion, or the latent heat of the surface. Thus the formation of the surface of a pure liquid, with the exception of a few liquids in which liquid crystal formation is involved, is always accompanied by cooling. It is, therefore, the *total cohesional surface energy* and *not the related work*, which represents the total effect of the molecular attraction, or the cohesional effect.

It may seem remarkable, from the point of view of the last paragraph, that the calculation of even the relative cohesion of liquids from a very simple equation,  $\gamma/v^{1/3}$ , where  $v$  is the molecular volume, should give results which lie in somewhat the correct order. This is undoubtedly because, as shown by Harkins and Roberts,<sup>3</sup> the contribution of the kinetic energy of a molecule to the total energy of the surface, is on the whole, independent of the nature of the molecule—at least for such substances as have been used in the calculation of cohesion—and is dependent on the temperature alone. Therefore, so long as the molecular volume is nearly the same, and the orientation of the molecules in the surface is not an important factor, at any definite temperature the latent heat of the surface is nearly independent of the nature of the substance, so that when substances are arranged in the order of their cohesional surface work or their free surface energy, they are also arranged in the general order of their total surface energy.

A second method of calculating the cohesion from the cohesional work

<sup>1</sup> Mathews, *J. Phys. Chem.*, **17**, 603-28.

<sup>2</sup> Hildebrand, *THIS JOURNAL*, **41**, 1067-80 (1919).

<sup>3</sup> Harkins, *Proc. Nat. Acad. Sci.*, **5**, 539-46 (1919).

or free surface energy, is based on the well-known assumption of Stefan,<sup>1</sup> that the average work involved in bringing a molecule to the surface of a liquid, has  $\frac{1}{2}$  of the energy value involved on the average in its complete vaporization. It is obvious from Stefan's paper, that his principle does not involve the *work* but the *total surface energy*, which is supposed to be  $\frac{1}{2}$  of the latent heat of vaporization. That this rule is far from true is indicated by the results of extensive calculations by Harkins and Roberts,<sup>2</sup> which show that the fractional contribution of the surface energy toward the complete vaporization increases with the temperature, with a normal range of from  $\frac{1}{3}$  at lower temperatures to 0.8 or more as the critical temperature is approached, though the higher values are uncertain. Thus a molecule which at a high corresponding temperature passes from the body of the liquid into the surface, goes, in a *fractional sense with reference to energy*, much more nearly into the vapor state than when the corresponding temperature is low.

#### The Solubility of Heptin and Heptaldehyde.

The peculiar interfacial energy relations of heptin and heptaldehyde suggested that the solubility of these substances in water would probably decrease with a rise of temperature, and experiments made on these substances showed that this is true.

The solubility of heptaldehyde was determined volumetrically by the use of a liter flask with a neck which consisted of a 2 cc. pipet graduated to 0.01 cc. arranged with a device to lower the top level of the solution for shaking and to raise it again for purposes of measurement. Some inaccuracy is caused by the sticking of a film of heptaldehyde, an oily liquid, to the side of the flask, but this was allowed for as closely as was possible. The solubility of heptin was found by a determination of the surface tension-concentration curve in water, using for one determination the saturated solution and for another a solution of known concentration. While this method, as worked out by Harkins and Clark, is extremely accurate in many cases, the surface tension curve of heptin is not well suited for accurate work. The solubility results are presented in the table below.

TABLE I.  
Solubility of Compounds Containing Seven Carbon Atoms Per Molecule  
Mols per 1000 g. Water.

° C.	Heptaldehyde.	Heptin.	Heptylic acid. <sup>a</sup>
0	0.0273	...	..
17	..	0.022	..
20	0.0206	...	0.0224
40	0.0158	0.004	..

<sup>a</sup> The result for heptylic acid was obtained by Dr. George L. Clark. It is considerably more accurate than the other data.

<sup>1</sup> Stefan, Leipzig, *Ann. Physik.*, 29, 655 (1886).

<sup>2</sup> Unpublished.

A clear saturated solution of water in heptaldehyde when heated to 40° became milky, due to the separation of droplets of water. The same phenomenon to an even more marked degree was observed in a similar experiment with water in heptin. This indicates that the solubility of water in each of these liquids decreases as the temperature rises. The data indicate that the number of carbon atoms in the above compounds is a more important factor in influencing the solubility than the change from an aldehyde group to a triple bond and to a carboxyl group.

### Experimental Methods and Accuracy of the Work.

All of the experimental work on surface tension was carried out by the extremely accurate drop weight method as worked out by Harkins and Humphrey for interfacial tension between 2 liquids, and by the method of Morgan as modified by Harkins and Brown in the case of the liquid-vapor interface.

While the method for the determination of interfacial tension by the drop-weight method as worked out in this laboratory is very nearly, or possibly quite, as accurate as that for the determination of the surface tension of a single liquid, which has been brought to a high degree of precision at temperatures when the vapor pressure is not too high, it should be kept in mind that the interfacial tension is in general much more sensitive to the presence of small amounts of impurities. When it is found, for example, that the values given in the present paper do not agree exactly with those given for the independent measurements cited in some of our earlier papers, the deviation is, in general, to be ascribed to a difference in the sample of the organic substance used.

TABLE II.  
The Surface Tension of Organic Liquids at Different Temperatures (Dynes per Cm.).

	0°.	10°.	20°.	30°.	40°.	50°.	60°.
Hexane.....	20.52	...	18.43	17.22	16.27	...	...
Octane.....	23.70	22.73	21.77	20.76	19.82	...	...
Higher paraffin.....	31.80	30.87	30.04	29.20	28.45	27.50	26.77
Benzene.....	...	30.26	28.90	27.61	26.25	24.91	23.54
Heptin <sup>a</sup> .....	...	(22.80)	(21.92)	(20.88)	(19.88)	...	...
<i>n</i> -Octyl alcohol <sup>b</sup> .....	(29.09)	27.53	...	...	(25.85)	...	(24.38)
<i>s</i> -Octyl alcohol.....	27.93	27.17	26.28	25.51	24.74	23.84	23.01
Heptaldehyde.....	28.64	27.72	26.84	25.84	24.96	24.08	23.19
Heptylic acid.....	29.84	29.05	28.14	27.39	26.49	25.59	24.82
Ethyl capronate.....	27.89	26.88	25.87	24.90	23.81	22.91	21.89
Carbon tetrachloride....	29.38	28.05	26.70	25.54	24.41	23.22	22.38
Ethylene bromide.....	...	40.28	38.79	37.54	36.15	34.80	33.59

<sup>a</sup> The surface tension values for heptin were determined at temperatures 5° above the temperature given. Thus the value given under 10° was determined at 15°, and that given under 20° was determined at 25°, etc.

<sup>b</sup> The value of the surface tension of *n*-octyl alcohol under 0° was determined at 0.16°, that given under 40° was determined at 39.87°, and that given under 60°, at 59.67°.

The organic liquids were specially purified for this work, the heptaldehyde being the most difficult liquid to obtain pure. The heptin was prepared by Professor Nicolet.

TABLE III.

The Interfacial Surface Tension between Water and Various Organic Liquids at different Temperatures (Dynes Per Cm.).

	0°.	10°.	20°.	30°.	40°.	50°.	60°.
Hexane.....	...	51.25	...	50.66	50.48	...	...
Octane.....	...	51.01	50.81	...	49.58	...	...
"Higher" paraffin.....	...	36.16	36.87	37.42	37.82	...	...
Benzene.....	...	35.56	34.96	34.34	33.84	...	...
Heptin <sup>a</sup> .....	...	...	28.11	...	...	...	...
<i>n</i> -Octyl alcohol.....	7.75	...	...	8.97	9.32	...	...
<i>s</i> -Octyl alcohol.....	8.44	8.80	9.24	9.65	10.04	...	...
Heptaldehyde.....	10.78	12.51	13.74	14.41	14.82	14.50	12.13
Heptylic acid.....	8.34	7.93	7.54	7.13	7.00	...	...
Ethyl capronate.....	21.03	21.42	21.29	21.15	21.02	...	...
Carbon tetrachloride.....	46.97	45.97	45.05	44.04	43.04	...	...
Ethylene dibromide.....	...	38.28	37.20	36.08	35.03	...	...

<sup>a</sup> The interfacial tension of heptin was found to be 27.15 at 15°, 29.29 at 25°, 29.66 at 35°, and 30.38 at 45°. The value at 20° is given in the table.

### Defining Equations.

The equations used in the calculation of results are given below.

(1) Free surface energy, or half the value of the cohesive work:

$$\gamma_l = \frac{W_s}{2} = \frac{mg}{2\pi r\psi(r/v^{1/3})}$$

(2) Free interfacial energy against water:

$$\gamma_i = \frac{gv(d_1 - d_2)}{2\pi r\psi(r/v^{1/3})}$$

where  $v$  is the volume of the drop,  $d_1$  is the density of water saturated with the organic liquid in question, and  $d_2$  the density of the organic liquid saturated with water;  $(d_1 - d_2)$  becomes  $(d_2 - d_1)$  when the organic phase is heavier than the water phase. Other letters have the same meaning in Equation 1.

(3) Work of adhesion:

$$W_A = \gamma_{H_2O} + \gamma_l - \gamma_i$$

(4)

$$S = W_A - W_c = (\gamma_{H_2O} + \gamma_l - \gamma_i) - 2\gamma_l = \gamma_{H_2O} - (\gamma_i + \gamma_l).$$

(5) Molecular surface energy:

$$\gamma_m = \left(\frac{M}{Nd}\right)^{2/3} \gamma_l$$

where  $M$  is the molecular weight,  $N$  the Avogadro constant  $6.06 \times 10^{23}$ ,  $d$  the density of the pure liquid at the temperature in question.

(6) Cohesional energy:

$$E_c = 2E_s = 2(\gamma_l + l_l) = 2\left[\gamma_l - T\left(\frac{d\gamma}{dt}\right)_l\right]$$

where  $T$  is the absolute temperature,  $(d\gamma/dt)_l$  is the entropy of surface formation determined experimentally, and  $-T(d\gamma/dt)_l$  is evidently the latent of surface formation.

(7) Total interfacial energy:

$$E_i = \gamma_i + l_i$$

(8) Adhesional energy:

$$E_A = E_{s(\text{H}_2\text{O})} + E_{s(\text{org. liq.})} - E_{s(\text{interface})} = \gamma_w + \gamma_l - (\gamma_i + l_i) + l_w + l_l$$

(9) Entropy of surface formation of the organic liquid:

$$\left(\frac{d\gamma}{dt}\right)_l$$

(10) Temperature coefficient:

$$\left(\frac{d\gamma}{dt}\right)_l \div \gamma_0$$

where  $\gamma_0$  is  $\gamma_l$  at  $0^\circ$ . In cases where this value is not determined it is extrapolated.

(11) Entropy of the interface:

$$\left(\frac{d\gamma}{dt}\right)_i$$

(12) Temperature coefficient of the interface:

$$\left(\frac{d\gamma}{dt}\right)_i \div \gamma_0$$

where  $\gamma_0$  is  $\gamma_i$  at  $0^\circ$ .

(13) Surface entropy per area occupied by one molecule:

$$\left(\frac{d\gamma}{dt}\right)_m$$

(14) Temperature coefficient of adhesional work:

$$\frac{dW}{dt}$$

In the following table Col. 6 gives the free surface energy in ergs times  $10^{14}$  for the area in the surface occupied by one molecule, calculated on the not altogether correct assumption that this area is equal to the  $2/3$  power of the average volume occupied in the liquid by one molecule. Col. 12 gives the entropy of the surface in ergs times  $10^{16}$  for the same area. This may be termed the "association constant," and has a normal value of about  $2.96 \times 10^{-16}$  ergs per molecular area. Note that the values given in Col. 13 are not far from  $1/273$ , the coefficient of expansion of a gas.



TABLE IV.  
The Surface and Interfacial Energy Relations of Organic Liquids at 20°.  
A Summary of Constants.

1	2	3	4	5	6	7	8
Liquid.	$\gamma_l$ .	$\gamma_i$ .	$W_A$ .	$\frac{S = W_A - W_C}{W_C}$ .	$\gamma_m^{10^{14}}$ .	$E_s$ .	$E_i$
Water.....	72.80	...	...	..	6.99	117.1	...
Hexane.....	18.43	50.92	40.23	3.41	6.63	49.5	58.30
Octane.....	21.77	50.81	43.76	0.22	9.06	50.2	59.90
"Higher" paraffin.....	30.04	36.87	66.80	6.72	...	54.6	20.60
Benzene.....	28.90	34.96	66.74	8.94	8.04	69.0	51.70
Heptin.....	22.32	28.15	67.00	22.40	8.05	49.5	-19.60
n-Octyl alcohol.....	27.53	8.53	91.80	35.74	11.22	50.5	-2.96
s-Octyl alcohol.....	26.28	9.24	89.88	37.32	10.78	50.4	-2.60
Heptaldehyde.....	26.88	13.74	85.90	32.22	10.04	53.4	-17.10
Heptylic acid.....	28.14	7.54	93.40	37.12	10.73	52.6	19.20
Ethyl capronate.....	25.87	21.29	77.38	25.64	10.89	55.2	24.20
Carbon tetrachloride.....	26.70	45.05	54.45	1.06	7.84	62.9	73.90
Ethylene bromide.....	38.79	37.20	74.39	-3.19	10.94	78.2	68.80

Liquid.	9	10	11	12	13	14	15
	$E_A$ .	$\left(\frac{d\gamma}{dt}\right)_l$	$\left(\frac{d\gamma}{dt}\right)_i$	$\left(\frac{d\gamma}{dt}\right)_m^{10^{16}}$	$\frac{\left(\frac{d\gamma}{dt}\right)_l}{\gamma_o}$	$\frac{\left(\frac{d\gamma}{dt}\right)_i}{\gamma_o}$	$\left(\frac{dW_A}{dt}\right)$
Water.....	...	-0.1511	..	-1.30	-0.00199	...	...
Hexane.....	104.3	-0.1060	-0.0250	-3.23	-0.00507	-0.00049	-0.234
Octane.....	107.4	-0.0970	-0.0310	-3.40	-0.00410	...	-0.200
"Higher" paraffin.....	151.1	-0.0838	+0.0552	..	-0.00260	+0.00150	-0.293
Benzene.....	134.3	-0.1364	-0.0570	-3.20	-0.00430	-0.00160	-0.231
Heptin.....	147.1	-0.0963	+0.1630	-2.90	-0.00396	...	-0.250
n-Octyl alcohol.....	164.6	-0.0791	+0.0392	-2.88	-0.00270	+0.00510	-0.275
s-Octyl alcohol.....	170.1	-0.0821	+0.0402	-2.65	-0.00290	+0.00480	-0.271
Heptaldehyde.....	153.4	-0.0908	+0.1050	-2.77	-0.00320	...	-0.308
Heptylic acid.....	150.5	-0.0836	-0.0335	-2.60	-0.00290	-0.00400	-0.201
Ethyl capronate.....	148.1	-0.1000	-0.0100	-3.43	-0.00360	-0.00050	-0.250
Carbon tetrachloride.....	106.1	-0.1166	-0.0983	-3.00	-0.00400	-0.00210	-0.177
Ethylene bromide.....	126.4	-0.1338	-0.1083	-3.20	-0.00320	-0.00280	-0.179

### The Spreading Coefficient.

An earlier paper from this laboratory<sup>1</sup> gave the values of  $W_A - W_C = S$ , which may be termed the *coefficient of spreading*, for 70 liquids on water. The present paper presents data from which this coefficient may be calculated at temperatures from 0° to 60° for 12 organic substances. The value of this coefficient decreases rapidly as the temperature rises, in most cases, but increases for benzene, chloroform, and ethylene dibromide. Thus the value for chloroform increases from -0.53 at 0° to 2.33 at 40°, while that for secondary octyl alcohol decreases from 39.49 to 35.05 in the same temperature range. The relation between the spreading of a liquid and the value of this coefficient is now being investigated in this laboratory by Mr. A. Feldman, so the discussion will be left for his paper.

### Summary.

1. This paper presents the first accurate data, and almost the first of any kind, from which the total interfacial energy may be calculated, and

<sup>1</sup> THIS JOURNAL, 42, 700-12 (1920).

discusses the work of adhesion and of surface cohesion, the interfacial tension and free surface energy, the tensile work, the energy of adhesion, of cohesion, and of surface cohesion, the tensile energy, the internal pressure or cohesion, and the related molecular attraction. These relations are illustrated by extensive experimental values obtained for 12 organic liquids as related to water.

2. These data indicate 2 new and important relations. First, that certain surfaces or interfaces between 2 liquids exhibit a *negative surface energy*, or, in other words, energy is given off when the surface is formed. This is just the opposite of what has been found before, for all surfaces previously known, with the exception of the case when crystalline liquids are undergoing transformation—a somewhat extraordinary case—have required the expenditure of energy for their formation. Second, while ordinary surfaces cool off when they are expanded, these surfaces and some others which have been found in this investigation, *rise in temperature when they are formed*. The liquids at whose phase boundary with water a *negative surface energy* is exhibited are heptin (with a triple bond at the end of the chain), normal and secondary octyl alcohol, and heptaldehyde. All of the above liquids and a higher paraffin have a negative latent heat of the phase boundary which indicates that the interface rises in temperature when it is expanded.

3. The addition of *one* oxygen atom to the *26* other atoms present in octane to give octyl alcohol increases the tensile energy by only 2%, while it increases the adhesional energy by 65%, and similar relations are found for the organic acids, aldehydes, and heptin. In contrast with this, it is found that the double bonds increase the tensile energy greatly, about 40%, in the change from hexane to benzene, while the adhesional energy toward water is increased by only about 30%. It is found, too, that the very symmetrical halogen derivatives, carbon tetrachloride and ethylene dibromide, which give *especially high values* for their own *tensile energy*, give *especially low values* for their adhesional energy toward water. The tensile energy of ethylene dibromide, on account of its symmetry, is higher than that of ethylidene bromide. These facts are easily explained on the basis of the hypothesis that the unsymmetrical molecules are oriented in the surface, and therefore give very strong evidence in favor of the orientation hypothesis. When a bar of heptin (or of an organic acid, alcohol, aldehyde, amine, etc.) is pulled apart, the break occurs where the electromagnetic field (largely electrical) and the resulting attraction is weakest, that is between the hydrocarbon chains, and in order that this may be the case the hydrocarbon chains turn into the nascent surface in the process of its formation. In the benzene the symmetry of the molecules is so great that the break must occur between certain of the unsaturated groups, that is where the intermolecular electromagnetic field is high. The fact that the adhesional energy of octane is so

greatly increased by the addition of one oxygen atom to form octyl alcohol, indicates by similar reasoning that the oxygen atoms turn toward the water at their interface. Thus the *adhesional energy* toward water is determined by the *strongest electromagnetic fields* in the molecule, while the *tensile energy* is determined by the *weakest fields*, provided the molecules are unsymmetrical.

4. The solubilities of heptylic acid, heptin, and heptaldehyde have been determined, and are found to be nearly the same, which indicates that the length of the hydrocarbon chain is of more importance in determining the solubility than the nature of the active group at the end of the molecule, provided that the activity of the latter is not too widely varied.

5. For the first time the surface energy relations of a paraffin with a triple bond at the end of the molecule have been worked out. The triple bond is found to increase the adhesional work from about 42 to 67, and the total adhesional energy from 105 to 147, the lower values given being those of the corresponding saturated compounds. The introduction of one oxygen atom increases the adhesional work to 90 and the energy to 164. This indicates that the triple bond has a greater relative effect on the adhesional energy than on the adhesional work at 20° as compared with an hydroxyl oxygen atom.

6. The relations worked out in this paper should be of fundamental importance in connection with the study of lubrication, flotation, and all other adhesional phenomena. Similar data for the adhesional relations between mercury and organic liquids have been worked out in this laboratory.

The writers wish to thank Professor Nicolet, of this laboratory, for the preparation of the heptin used and for advice in regard to the methods for purifying heptaldehyde, and the other organic liquids.

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CHICAGO, ILL.

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[CONTRIBUTION FROM THE FIXED NITROGEN RESEARCH LABORATORY, WAR DEPARTMENT AND THE BUREAU OF SOILS, DEPARTMENT OF AGRICULTURE.]

## THE THERMAL DECOMPOSITION OF GASEOUS NITROGEN PENTOXIDE. A MONOMOLECULAR REACTION.

BY FARRINGTON DANIELS AND ELMER H. JOHNSTON.

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In connection with the work of the Fixed Nitrogen Research Laboratory, it became desirable to measure the rate of decomposition of gaseous nitrogen pentoxide. The reaction was found to be monomolecular, a matter of considerable interest, since only one other gaseous monomolecular reaction, the decomposition of phosphine, has been reported in the literature.<sup>1</sup> Since such reactions are of great importance for the theory

<sup>1</sup> Trautz and Bhandarkar, *Z. anorg. allg. chem.*, 106, 95 (1919).