selenic acid has been developed, as well as one for the detection of small amounts of sulfuric acid in the presence of selenic acid.

4. It has been demonstrated that the electrolysis of selenic acid or of its salts under conditions favorable to the formation of persulfates from the analogous compounds of sulfur yields neither perselenic acid nor perselenates.

5. The dehydration of crystalline copper selenate was studied and the temperature of its complete dehydration was determined.

6. A method for the determination of selenium in selenates by the use of hydrazine hydrate is described.

7. The preparation and properties of three new ammonates of copper selenate are described.

ITHACA, N. Y.

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

AN ELECTROMAGNETIC HYPOTHESIS OF THE KINETICS OF HETEROGENEOUS EQUILIBRIUM, THE STRUCTURE OF LIQUIDS, AND COHESION.

BY WILLIAM D. HARKINS AND H. H. KING.

Received November 2, 1918[1].

While Gibbs[2] in his remarkable treatise "On the Equilibrium of Heterogeneous Substances" has given a very broad treatment of his subject from the thermodynamic standpoint, nothing is included which would give any idea of the probable distribution of any component (A) between a set of phases (*a*), (*b*), (*c*), ——, from a knowledge of the properties of (A) alone, and those of the phases (*a*), (*b*), (*c*), ——, before any of the component (A) has been mixed with them. It is the purpose of this paper to indicate that the general nature of such a distribution can be predicted in most cases from the standpoint of the hypothesis that it is conditioned not only by the motion of the molecules (vibrations apparent as temperature, and probably rotations as well), but also by the intensity and the nature of the electromagnetic field surrounding them. Since all recent theories of the structure of the atom assume it to consist of a system of negative electrons built up around a positively charged nucleus, the atom, and therefore the molecule, would on this basis be surrounded by an electric field. Inasmuch as there is considerable evidence that the electrons are in motion (the magnetic properties of substances, etc.), this is also

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[1] This paper was received Nov. 2, 1918, and was later revised and received after revision, April 5, 1919. Any later additions have been made in the form of notes.

[2] Gibbs, *Trans. Conn. Acad.*, Oct., 1875; May, 1876, 108–248, and May, 1877–July 1878, 343–524.

to be considered as a magnetic field. Such a composite field is usually said to be electromagnetic.[1]

That the application of this hypothesis is not a simple problem is indicated by the electrical duality of such a field, and by the fact that while a part of the combinations between atoms or molecules in such a system may be similar in nature to primary valence unions—presumably a fitting of one or more of the outer electrons of one atom into the electronic system of another atom—other molecules or atoms may be held together, though very much less firmly, by forces which still remain after all of the electron fittings have been made. In this preliminary paper only the more general features of the hypothesis will be considered, that is, only those which can be treated on the basis of a general knowledge of the intensity of the electromagnetic field around the molecule. The greatest obstacle to the application of this hypothesis is the meagerness of our knowledge of the characteristics of this field, which in this paper will be designated as the *stray field* of the molecule, since this field gets out beyond the electronic constituents of the molecule.

Solubility and Electromagnetic Environment.

The first problem which will be considered is, given two components (A) and (B), each in a phase by itself, with both phases at the common temperature (T), when will these two phases be miscible, and when will they be practically insoluble in each other. Let (A) be in the liquid state. Then the relation is not difficult to find, for we know that (A) mixes with itself, so perfect miscibility should result when the stray fields around the molecules of (B) are sufficiently like those around those of (A). Likeness of fields in this sense means likeness in intensity, and presumably in the rate at which this intensity falls off with the distance from the molecule. A sufficient likeness of stray fields is also the condition which must hold if Raoult's law

$$p_A = P_A \frac{N_A}{N_A + N_B} = p_A x_A, \; p_B = P_B \frac{N_B}{N_A + N_B} = P_B x_B$$

is to be valid. Here p_A and p_B are the vapor pressures of (A) and (B) over the mixture, P_A and P_B are the vapor pressures of the pure liquids, and x_A and x_B are the mol fractions of (A) and (B) in the mixture. If (A) is a liquid and if the stray field around the molecules of (B) is very nearly the same as that around the molecules of (A), then (B) will usually be a liquid also, if under the same pressure. The mass of the molecule, and its shape, are other factors which have some influence in this connection. If the stray fields around the molecules of (A) and (B) are sufficiently different in intensity, then the two substances will be practically insoluble in each other.

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[1] Wm. Mc. C. Lewis, *Phil. Mag.*, 28, 104–16 (1914).

Since the intensity of the stray field falls off more rapidly with the distance around some molecules than around others, it is not possible to give a list arranged in order of increasing intensity of the stray field which is correct in all respects. Thus, while the intensity of the field close to the atoms of the heavy metals is very high, it undoubtedly decreases rapidly with the distance. On the other hand there are facts which seem to indicate that the forces around the oxygen or nitrogen atoms of organic compounds or of water, or such atoms as are commonly called "polar," extend to a greater distance, although their intensity is less at the ordinary atomic distances. However, the following list may be considered to give something of this order of increasing intensity for a limited number of substances. This list has been obtained for the most part from a consideration of the *surface-tension relations* of substances, and is as follows, beginning with those substances around whose molecules the stray field is weakest: helium, neon, hydrogen (molecular, not atomic), argon, krypton, xenon, nitrogen, oxygen, methane, carbon monoxide, and the following organic compounds: saturated aliphatic hydrocarbons, aromatic hydrocarbons, sulfides, mercaptans, halogen derivatives (methyl chloride, carbon tetrachloride, chloroform, and ethylene chloride, with rapidly increasing fields) unsaturated hydrocarbons, ethers, esters, nitro compounds, nitriles, aldehydes, ketones, alcohols, amines, acids, and unsaturated acids. Following these are water, molten salts, heavy metals, boron and carbon. The list of organic substances is arranged for derivatives with short hydrocarbon chains. A lengthening of the chain causes a displacement in the direction of lower intensity for polar derivatives, but probably toward higher intensity in the case of the hydrocarbons themselves. It will be seen that in general the greater the distance between the substances in this list, the less their solubility in each other, the closer together the more soluble. For organic substances, though the present list is much more extensive, it is in agreement with that found by Rothmund from solubility data.[1] It is well known that metals in general give concentrated solutions only with metals, carbon (hydrogen), and other similar substances; molten salts dissolve salts or water; organic liquids are miscible unless at the very extremes of the list of organic substances; water dissolves salts or organic substances which are close to it in the list. An interesting illustration of this relation is given by data on the organic halogen derivatives listed above. The solubility of carbon tetrachloride per 1000 g. of water is 0.0052 mols, while that of chloroform which lies closer to water, is 0.068; and methylene chloride, approaching water still more closely, has a solubility of 0.236. This is also the order of increasing hydrogen content of the molecule, but that this is not the determining factor is indicated by the fact that methyl chloride and methane, similar compounds containing

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[1] Rothmund, *Löslichkeit und Löslichkeitsbeeinflussigung*, Leipzig, 1907, p. 118.

still more hydrogen, are much less soluble in water. In organic compounds the intensity of the stray field is much higher adjacent to what are commonly called double bonds, than it is near single bonds, and this intensity grows much larger still if triple bonds are introduced. Corresponding to this the solubility of ethane with its single bond between two carbon atoms, is 0.0507 volume of gas per volume of liquid; that of ethylene with its double bond is 0.1311, or more than twice as great, while acetylene with its triple bond has a solubility of 1.105, or about 22 times more than that of the single bonded compound.

In analyzing a solubility problem it is well to consider the attraction between the molecules of (A), between those of (B), and also that between (A) and (B). Consider octane and water which are mutually insoluble. It has sometimes been considered that this insolubility is due the fact that water molecules attract each other more than they do molecules of octane, and that octane molecules attract each other more than they do molecules of water. Now the work of this laboratory shows that while the molecules of water do attract each other much more than those of octane, on the other hand the molecules of octane attract those of water very slightly more than they do those of octane. The much greater attraction of the water molecules for each other is a sufficient cause to produce immiscibility, since it is only necessary that when a group of water molecules is once formed the mutual attraction shall be great enough to cause the molecules of water to leave the group less often than they enter it so long as there is an appreciable quantity of water in the octane. The octane molecules are thus left in a phase by themselves.

Since an increase in the intensity of the stray field around the molecule is accompanied by an increase in molecular attraction, it causes an increase in the cohesion of the liquid or of the solid, so in its application to pure liquids the above theory gives predictions which are similar to those obtained by that of Hildebrand,[1] that liquids of like cohesions are miscible, while those whose cohesions are very unlike are practically insoluble in each other. However, solubility is a molecular scale phenomenon, so there are certain advantages of a molecular theory. Moreover, the theory presented here has a much wider range of application, since it may be used to indicate the internal structure of a liquid, to predict the distribution of components between different phases, interfaces, and surfaces (these will be designated by the term *regions*), and is of great importance in theories of ideal and non-ideal solutions. In other words, it is a theory of what is called by Washburn[2] the "*thermodynamic environment*." This in the sense of our theory would be designated as the *electromagnetic environment*.

[1] Hildebrand, THIS JOURNAL, 38, 1452–73 (1916).

[2] Washburn, *Physical Chemistry*, Chap. XIII, pp. 134–42, also pp. 143, 224, 273.

Relation of the Intensity of the Intermolecular Electromagnetic Field to Cohesion and Valence.

An inspection of the list given in the last section of the paper, which arranges substances in the order of increasing intensity of the stray field, will show that they are also arranged in order of increasing cohesion. Elementary substances such as helium and neon, which have the least cohesion of all known substances, give no chemical compounds, and therefore have a valence of zero. Those which are linked together in their crystals by ordinary valence linkages, which has been shown by Bragg to be true for carbon in the diamond, give the highest cohesion. This very plain correlation between valence and cohesion has been recognized by a number of investigators. Among them, A. P. Mathews may be mentioned as presenting relations between surface tension, cohesion and valence. However, when the cohesion between molecules, instead of between atoms is considered, the ordinary valence theory has manifest disadvantages, which disappear if the combinations between atoms, and between molecules as well, are supposed to be due to the fitting of the electrons from one atom or molecule into the incomplete outer shell of electrons of another atom or molecule. The most useful valence hypothesis of this nature has been presented by G. N. Lewis.[1] This theory gives a complete explanation of cohesion in liquids and solids. Now a high cohesion means a high melting point and a high boiling point, a low compressibility, vapor pressure surface tension, and coefficient of expansion, while a low cohesion is accompanied by just the opposite effects, so all of these cohesional effects are explained by considering the electronic fittings. Since, according to the hypothesis presented in the present paper, cohesion is supposed to be due to electrical and magnetic, or electromagnetic forces, the stray field holding the molecules together may be said to have a high intensity when the cohesion is high, and to be low when the cohesion is low. The principal advantage which follows the consideration of the cohesional forces as due to electromagnetic forces from the atoms, is that cohesion has been used as a term to indicate a large scale phenomenon, and has no direct reference to the molecular structure of the material, while, since the electromagnetic forces come from the atoms—their positive nuclei and electrons—attention is at once given to the idea that the forces around the different parts of a molecule, or even of an atom, may have widely varying intensities.

The periodic table model formerly presented by Harkins and Hall[2] divides the elements into periods and cycles, which are presumably related to the number of electrons in different electronic shells of the atom. Thus, according to our knowledge of the charge on the α-particle (the nucleus

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[1] THIS JOURNAL, 38, 762–85 (1916).

[2] *Ibid.*, 38, 169–221 (1916).

of a helium atom) the first electronic shell outside the nucleus contains two electrons, while the second contains 8, all of which are present in the *complete* (from the valence standpoint) outer shell of neon. According to the calculations of Debye and of Vegard,[1] using the X-ray spectra as a basis, in the more complex atoms the first shell changes to 3, and the second to 7 electrons, but these calculations are of doubtful accuracy. The classification into cycles and periods for the elements of the periodic system, is given in Table I. This table is practically that given in the paper just cited, except for the correction of an error which we have recognized for two years, that is the consideration of Period 7, as given below, as similar to Period 6. Another change is in the numbering of the periods. In the first paper we attempted to preserve, as much as possible, the original numbering of Mendeléef, though the numbering as given below was recognized as preferable.

TABLE I.

Periods and Cycles in the Periodic System of the Elements.

	Cycle 1.		
Period 1.	First very short period	H–He	$= 2 = 2 \times 1^2$ elements.
	Cycle 2 $= 4^2$ elements.		
Period 2.	First short period	Li–Ne	$= 8 = 2 \times 2^2$ elements.
Period 3.	Second short period	Na–A	$= 8 = 2 \times 2^2$ elements.
	Cycle 3 $= 6^2$ elements.		
Period 4.	First long period	K–Kr	$= 18 = 2 \times 3^2$ elements.
Period 5.	Second long period	Rb–Xe	$= 18 = 2 \times 3^2$ elements.
	Cycle 4.		
Period 6.	First very long period	Cs-Nt	$= 32 = 2 \times 4^2$ elements.
Period 7.		Eka–Cs–U incomplete.	

According to Lewis' theory, the last element in each period as given above is considered as having a *complete* outer shell of electrons and this shows no tendency to form a more complete system. Such atoms may be said to have an almost entirely self-contained electromagnetic field. They form no chemical compounds, and their attraction for each other is extremely small, so that in the liquid or solid state they have an extremely small cohesion.

Elements in the middle of the periods, such as carbon, iron, osmium, etc., may be said to have outer shells of electrons which are *half complete*. Such elements show an extremely high cohesion,[2] in fact all of their so-called physical properties are just the opposite of those listed above for complete systems of electrons. Atoms such as chlorine, oxygen or nitrogen

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[1] *Phil. Mag.*, **35**, 293 (1918).

[2] The cohesion is the highest for these elements since the number of electronic linkages is the greatest. The cohesion depends upon the number of linkages, but also upon their stability, which is particularly high in the diamond where 4 of the linkages are made by each atom.

which have a nearly complete outer shell of electrons, complete the shell by entering into partnership with similar atoms, thus producing a molecule which usually consists of a small number of atoms. This molecule has a much more complete outer shell of electrons than the atoms from which it is built, so the cohesion in substances made up from these molecular aggregates is small. In elementary substances atoms with a small number of electrons in the outer shell, as lithium, aluminium carbon, etc., can only complete their shell by building up a space lattice. In the case of lithium if each atom is considered to be at the center of a cube in a cubic lattice, the single valence electron for each atom is sufficient to give an electron at every corner of every cube except at the surface of the solid, where the incompleteness will result in a stray surface electromagnetic field. In the case of salts, such as lithium chloride, the outer shell of the metallic element has so few electrons that these electrons will pass into the outer shell of a non-metallic element, giving a salt which has complete shell for the "negative" element, and a nearly empty shell for the positive element. If lithium or sodium chloride enters into a cubic lattice, then the chlorine atoms surround the atom of the metal in order to complete the electronic outer shell of the latter. The number of electronic connections is greater than in the case of either atomic lithium or molecular chlorine, and the cohesion, melting point, etc., are correspondingly higher.

The highest cohesion is found for carbon[1] in the form of diamond, where there are 4 linkages for every atom—each linkage being considered as being made by two electrons—that is, the linkages may be considered as ordinary valence unions. The completeness of the outer shell of electrons may be judged by the magnitude of the cohesion in a liquid or a solid made up of molecules of the one type. Whenever the outer electronic shell of an atom or of a molecule, is incomplete, the electromagnetic field binding either the atoms or the molecules together, has a much higher intensity than when the shells are complete. When the atomic

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[1] Note on an hypothesis of the Polar Nature of Organic Compounds. Even in organic compounds, such as methane and carbon tetrachloride the valence electrons vibrate more with the carbon than with the hydrogen, and with the chlorine more than with the carbon, so that the carbon acts as a more positive element in some compounds than in others. Positive and negative characteristics are transmitted along hydrocarbon chains, as in the case of the dicarboxylic acids. Thus the solubility of the 2-carbon acid is 8.6, that of the 3-carbon acid is 73.3, or nearly 10 times as much, while that of the 4-carbon acid drops to 10.6. Beyond this the solubility still alternates; from 63.9 for 5-carbon atoms to 2 for 6, 5.0 for 7, 0.16 for 8, 0.24 for 9, 0.10 for 10, and to practical insolubility for 11. Thus, even the carbon compounds seem to be distinctly polar because they have a greater affinity for electrons than hydrogen, etc., and a smaller affinity than chlorine, etc. The polarity is, of course, very much smaller than that of salts. I expect to treat this vibration hypothesis in a paper now being prepared.—W. D. Harkins.

shells are complete as defined above, the cohesion increases with the total number of non-nuclear electrons, or with the area of the outside shell. Thus the cohesion in niton with its 86 non-nuclear electrons is more than 60 times what it is in helium with its two outer electrons. The cohesion in liquid or solid nitrogen, oxygen, chlorine, fluorine, bromine, etc., is not an index of the attractions between the atoms, but only between the molecules, while that in metals or in carbon is a direct index of the atomic attractions, though the attractions between pairs of atoms when alone would not be expected to be the same as when the whole lattice is filled out.[1] The internal latent heat of vaporization of a solid or liquid is the energy necessary to separate it into such units, molecules or atoms, as are present in the gaseous state; the free surface energy plus the latent heat of the surface, gives the amount of energy necessary to separate the single phase into parts, leaving plane surfaces. In the case of carbon tetrachloride the latent heat of vaporization per molecule is 41×10^{-14} ergs at 20°, while for the separation into plane surfaces the energy is 18×10^{-14}. For chloro form the energy of total separation of a molecule is higher, but the energy of separation into two plane surfaces is lower, while for ethyl alcohol the former value rises still higher (69×10^{-14}), while the latter falls still lower (13×10^{-14} ergs). This indicates that the energy necessary for the separation depends on what part of each molecule is separated. A large number of similar values will be presented in a paper now being prepared.

Application to Interfaces and to Distribution between Regions.

The relation between the valence hypothesis of Lewis and cohesion has been presented in the last section to indicate what is meant by the term, "the stray electromagnetic field" of an atom, a molecule, or a substance. Since the molecules are supposed to be bound largely by electrons held in common by two or more atoms, or two or more molecules, this field is only a stray field in the sense that it strays from one atom or molecule directly into a second atom or molecule. In this laboratory we have obtained experimentally a large number of data bearing directly on the cohesional and "adhesional" relationships of substances, so the further direct discussion of the application of Lewis' hypothesis will be left to a paper now partly written, which presents these data. Our attention will now be directed to the action of the electromagnetic fields which hold the atom together. It is apparent that if these fields are mostly concerned with electronic fittings, that such a field will fall off very rapidly

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[1] Thus, according to this idea there are *no molecules* in a diamond or in a pure metal such as mercury or platinum, but an atom of argon is also a molecule since its electromagnetic field is largely self contained. The outer shell of electrons in the carbon atoms in the surface of a diamond is always incomplete, so a diamond is never complete enough to be a molecule.

in intensity as the molecules are separated from the positions in which these fittings are made.

While in applying the hypothesis, the intensity of the stray fields around the molecules is of primary importance, at least one additional principle must be used if the direction which any change will take by itself is to be predicted. As might be expected the second law of thermodynamics is of fundamental importance in this connection, and for this purpose it may be stated in the form: Any change which takes place by itself in a system will proceed in the direction which will result in a decrease in the free energy of the system. Thus a surface will decrease in area by itself, but will not increase. Since a rapid variation of the intensity of the stray field with the distance in any direction, is accompanied by a high concentration of free energy, the second law indicates that in any change which takes place by itself, the variation in the stray field becomes less abrupt. If we imagine the surface of a liquid up to a bounding surface plane, to have just the same structure as the interior of the liquid, then the actual surface always has a smaller free energy than would be given by calculation for this imaginary surface, and therefore the drop in intensity of the stray electromagnetic field at the actual surface is always less than it would be at a surface of the structure of the imaginary surface. Since a molecule is often made up of several species of atoms, the stray field around it is often unsymmetrical. Thus many organic molecules, such as the primary normal alcohols, acids, amines, nitro compounds, nitriles, ethylene and acetylene derivatives, etc., consist of a paraffin chain, around which the stray field has a relatively low intensity (a so-called nonpolar group), while at the other end of the molecule there is a group containing oxygen or nitrogen, sometimes with metals in addition, around which the intensity of the stray field is relatively high (a polar group). Such molecules may be designated as *polar-nonpolar*, and designated by the symbol ○——, where ○ represents the polar, and ○—— the nonpolar end of the molecule. If molecules of this type, such as butyric acid (C_3H_7COOH) are put in a two-phase system consisting of a polar liquid such as water, and a nonpolar liquid such as octane, then the free energy of the interface will be less when the transition from one liquid to the other is made by molecules of butyric acid, with their polar ends turned toward the water, and their nonpolar ends turned toward the octane, since in this way the abruptness of the transition is decreased.

The problem here arises as to the distribution of molecules of the polar-nonpolar type between the two liquid phases and the interface between them. It may be considered that each region (phase, surface, or interface) exerts a certain restraining force upon (has affinity for) the solute molecules. Since at equilibrium the thermodynamic potential of the solute is the same in all of the regions, it may be considered that the concentration of the solute (at equilibrium) in each phase, interface or surface, gives an index of the restraining force exerted by that region upon the solute molecules. Let us now assume that we have a number of exactly similar two-phase systems, each of which consists of equal volumes of a polar liquid, such as water, and a nonpolar liquid such as octane, with an interface of a definite area between them, and into each of these systems we put N molecules of the polar-nonpolar type ○——. The hypothesis indicates that with a given polar group the distribution of the N molecules will vary in such a way that with an increase in the length of the nonpolar part of the molecule, the number of molecules, and therefore the restraining force in the octane will increase, while in the water both of these will decrease. The reverse of this occurs when with a given nonpolar chain, there is an increase in the number of polar groups. The greatest restraining force would be exerted on such molecules when they are in the interface, where the nonpolar end of the molecules could turn toward the nonpolar liquid, and the polar end toward the polar liquid. Since the restraining force is greatest at the interface, the concentration in this region should also be the greatest, which agrees with the facts as found by experiment. This case is more complicated than when the volume phases alone are considered, so it will be discussed in a later section of the paper.

In the general case, where a component (A) is distributed between a number of phases (*a*), (*b*), (*c*), etc., the distribution will take place in such a way that when equilibrium is obtained the highest concentration of (A) will be found in the phase between whose molecules (or atoms if there is no formation of molecular aggregates) the intensity of the forces (and probably rate at which the intensity fall off with the distance) due to the electromagnetic field is most nearly similar to that around the molecules of (A). The least concentration of (A) will be found in the phase whose field is the most different from this, and in the other phases the concentration will increase as the properties of the phase approach those of (A) in the respect under consideration. The concentration in the various interfaces will be discussed in later paragraphs.

In the application of this very simple hypothesis certain complications must be kept in mind. The cohesion in nitrogen, for example, may be said to be due to the intermolecular field which is weak, and not to the interatomic field between the pairs of atoms, which is strong. In a like manner, if two butyric acid molecules unite to form a double molecule, the stray field is weakened, and the solubility in polar liquids such as water is greatly decreased, while that in slightly polar liquids such as octane, is greatly increased. The butyric acid is little associated in a dilute aqueous solution because most of its combinations will be made with the water (hydration) which is present in much a higher concentration than the acid. In extremely concentrated aqueous solutions, mostly butyric acid, the acid may be said to be associated to a considerable extent.

Relation at Surfaces and Interfaces.

While at the surface of a solid or liquid the amount of gas adsorbed at a given gas pressure increases in general both with the cohesion of the solid or liquid, and also with that in the liquefied gas, provided the surface is not saturated, there are exceptions to this rule which may be explained on the basis of electronic fittings according to the valence hypothesis of Lewis. That the above rule is in general true is indicated by many facts: The adsorption on a mercury surface is much greater than that on a water surface in the case of the ordinary gases which do not react with either surface to form molecular aggregates; and the adsorption on a carbon surface increases with the boiling point of the adsorbed gas, etc. Thus the general case may be considered from the standpoint of cohesion (or adhesion) and deductions obtained which are in accord with the facts.

To a certain extent either of the above methods may be used to advantage at the interface between two liquids, but in some respects it seems simpler to use the hypothesis in regard to the intensity of the stray electromagnetic fields, although all 3 theoretical methods of consideration are related to each other. If two phases, (A) with the higher and (B) with the lower intensity of stray field uniting the molecules, could be put in contact in such a way as to have the field of each perfectly uniform up to a plane phase boundary or interface between them, then the whole drop in intensity between the two phases would occur in a surface of infinitesimal thickness; so, at least by certain methods of mathematical analysis, the free surface energy would be infinite. While this is not an actual case it suggests the idea that as the thickness of the transition layer increases the free surface energy diminishes. *With a given thickness of the surface layer the* free surface energy increases as the intensity of the stray field in (B) decreases, so the maximum free surface energy is reached when (B) is a vacuum, and is nearly realized when it is a dilute vapor or gas.

In so far as the cohesion of a liquid is an index of the average intensity of the stray field in a liquid it might be expected that the free surface energy between the given liquid A and a fluid phase B would thus increase as the cohesion in B decreases, *provided the thickness of the surface film remains constant.* The values of the cohesion which should be used in such a comparison are not, however, those for pure liquids, but should be the results obtained for the saturated solution of each liquid in the other—if equilibrium values are desired. It is manifestly true that the equilibrium value of the interfacial free energy between miscible liquids is always zero.

While a treatment of interfacial free energy from the standpoint of the relations of the average stray fields or of the related cohesion, is as satisfactory as is usual when problems, to a considerable extent molecular are treated from the standpoint of large scale phenomena, a more satisfactory theory may be obtained by considering at the same time, the molecular and atomic structure of the interface. An earlier paper from this laboratory[1] shows that when the Liquid A is water, and the Liquid B consists of chain molecules, one end of each of which consists of a hydrocarbon chain, around which the intensity of the stray field is low, and the other end contains oxygen or nitrogen atoms, or double or triple bonds, around which the intensity of the stray field is relatively high, the free interfacial energy is low.

The transition from one electromagnetic stray field to the other would be made more gradual by a setting of the oxygen or the active atoms toward the water, and the hydrocarbon chains toward the benzene. The orientation in this case could not be expected to be perfect (in a undirectional sense) because two effects oppose a setting in the specified manner: (1) *The motion of the molecules in all cases partly prevents the orientation from being absolute*, so the orientation is a function of the temperature; it decreases as the temperature rises, and wholly disappears at the critical temperature; and (2) liquids of the type of B contain active (or polar) atoms, which also have a considerable attraction for the polar atoms of the surface film. The orientation is more complete at surfaces than at interfaces.

Adsorption at Interfaces.

A two-phase system consisting of the phases (*a*) and (*b*) with a constituent (C) distributed between them, will now be considered. If the phase (*a*) consists of the vapor of (B′) mixed with the vapor of (C), where (B′) is taken as the only component in (*b*) aside from (C), then there are only two components. If (*a*) is also a liquid consisting of a component (A) then there are 3 components. The drop in intensity between the two stray fields is greater in the former case, since the intensity of the field in a dilute vapor is extremely low.

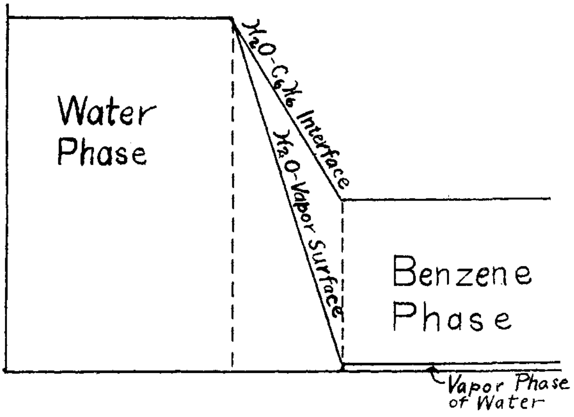

Fig. 1.

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[1] This Journal, 39, 354–64 (1917), especially Table I, pp. 356–7.

These two cases are illustrated by Fig. 1, where the ordinates represent the average intensity of the stray fields in the different cases.

The drop in intensity is more rapid at the interface water-vapor, since the interfacial film is of practically the same thickness in both cases. If the third component (C) consists of molecules of the polar-nonpolar type (○——) and is present in both phases, then by diffusion these molecules will pass into the interface, and when present in the interface in a sufficient number, will thicken the film and so decrease the free interfacial energy.

The drop in the intensity of the stray field shown in Fig. 1 may be considered as a restraining and an orienting force, similar to that existing in the field in air between the north and south poles of a magnet; and the molecules which are oriented as similar to small magnetized needles between them. The restraining force on the needles increases as the rate of fall of the magnetic intensity increases (increase of magnetic flux, or in the number of lines of force), so the restraining force holding the molecules might be expected to increase with the total drop of intensity of the stray field between the two phases, since the molecules of (C) in the interface bridge the total distance between the two phases.

If the molecules of (C) are thus held in the interface by a restraining force the molar activity or the molar fugacity (molar escaping tendency) of (C) will be much less in the interface than in either of the two-volume phases, so that the concentration of (C) in the interface must be much greater than that in either of the volume phases to give a condition of equilibrium.

Since the fall of intensity at the interface water-vapor is much greater than that between water and benzene, the restraining force is much greater in the former case, so the average activity of the *molecules* of (C) will be much less at the water-vapor interface; and therefore to give equilibrium, the diffusion pressure of (C), in the two phases, *water-vapor* will be much less to give a certain concentration of (C) in the interfacial film, than when the two phases are *water-benzene*. This is true so long as the thickness of (C) does not increase beyond that of a monomolecular layer. The present investigation shows that the facts are in accord with the above theory in cases so far investigated.

It will be shown in a later section that if μ is the adsorption in gram molecules per sq. cm., and c is the concentration of the solute in one phase, and c' the concentration in the other, the value of the adsorption is given by the equation

$$\mu = -\frac{1}{RT} c \left(\frac{\partial \gamma}{\partial c}\right)_T = -\frac{1}{RT} c' \left(\frac{\partial \gamma}{\partial c'}\right)_T.$$

Here c and c' represent the actual number of gram molecules present, or more properly their activity, and not the formula concentration. If C

represents the formula concentration, then $c = iC$. From the formula it is apparent that all that needs to be considered is the concentration (or the osmotic pressure in more general formulas given later) in *one* of the phases, together with the rate of change of the surface tension with the concentration. It is simpler to choose the phase in which i is nearly one. The above equation may be written

$$\mu = -\frac{1}{RT}\left(\frac{\partial\gamma}{\partial\, ln\, C}\right)_T$$

so in Fig. 2, which gives the surface tension on the Y-axis, and the logarithm of the concentration on the X-axis, the adsorption is equal, at any point on the curves, to $2.303/RT$ multiplied by the slope of the curve $\partial\gamma/\partial\, log\, c$ at that point.

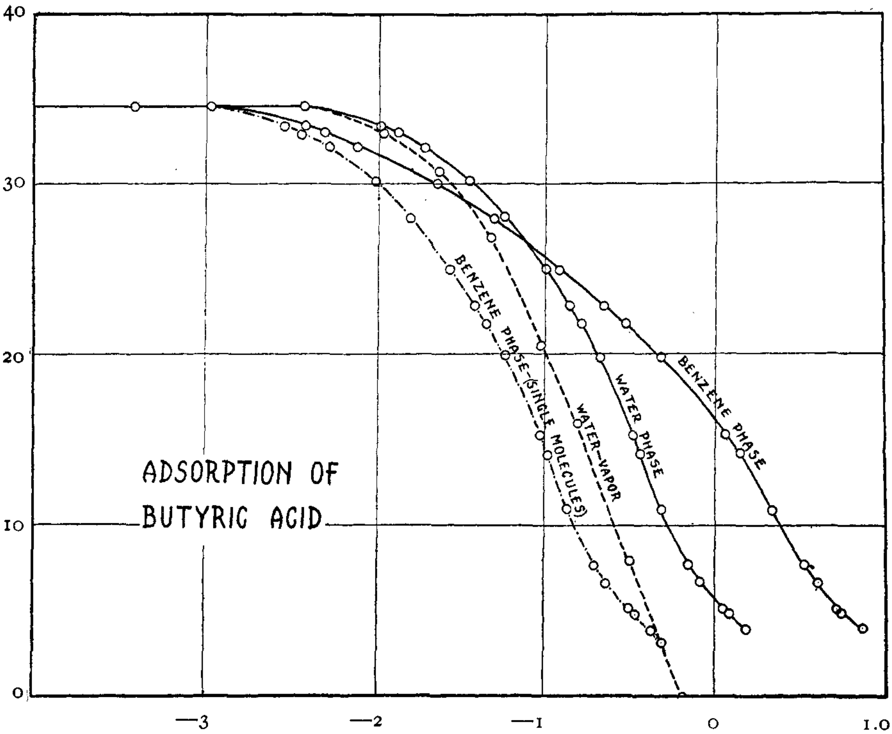

Fig. 2.—Surface tension, adsorption and association of butyric acid. The curve Benzene Phase-(single molecules) gives the logarithm of the concentration the butyric acid would have in benzene if it were not associated, or the concentration of the single molecules. The horizontal distance between this curve and that for the benzene phase gives the change of the logarithm of the formula concentration due to association. If the antilogs are taken for each curve their difference is the *formula* concentration of the associated butyric acid.

TABLE II.

C_A mols per 1000 g. solution.	Water layer. Density.	C_B mols per 1000 g. solution.	Benzene layer Density.	C_W/C_B.	C_W^2/C_B.	Surface tension at interface γ.
1.494	....	7.572	....	0.1973	0.294	3.91
1.180	1.0041	5.788	0.9130	0.2039	0.240	4.84
1.123	1.0039	5.430	0.9127	0.2068	0.232	4.96
0.7199	1.0014	3.356	0.9066	0.2145	0.154	7.399
0.4804	1.0001	2.220	0.8902	0.2164	0.099	11.00
0.3689	0.9997	1.429	0.8914	0.2611	0.096	14.22
0.3501	0.99961	1.098	0.8884	0.3188	0.111	15.41
0.2088	0.9996	0.4705	0.88104	0.4438	0.116	19.40
0.1651	0.9994	0.3060	0.8793	0.5395	0.088	21.80
0.1351	0.9988	0.2127	0.8797	0.6351	0.085	22.95
0.09795	0.9986	0.1138	0.8837	0.8610	0.084	25.00
0.04824	0.9985	0.05821	0.8804	1.2066	0.070	28.00
0.0353	0.9982	0.02305	0.8787	1.5314	0.054	30.10
0.01996	0.9982	0.008072	0.8787	2.4730	0.049	32.20
0.01372	0.9982	0.005100	0.8782	2.6902	0.036	33.00
0.00382	0.9982	0.00130	0.8779	...	...	33.49
0.001087	0.9982	0.00040	0.8779	...	...	34.60

TABLE III.

Mols per 1000 g. water.	Water layer. Density.	Mols per 1000 g. benzene.	Benzene layer. Density.	C_W/C_B.	C_W^2/C_B. Interface.	Surface tension. γ.
1.710	1.0053	30.450	0.9148	0.056	0.096	3.91
1.310	1.0041	14.339	0.9130	0.091	0.119	4.84
1.239	1.0039	12.487	0.9127	0.099	0.122	4.96
0.7674	1.0014	5.490	0.9066	0.139	0.107	7.399
0.5017	1.0001	3.195	0.8902	0.157	0.078	11.00
0.3743	0.9997	1.866	0.8914	0.200	0.075	14.22
0.3614	0.99961	1.387	0.8884	0.260	0.094	15.41
0.2116	0.9996	0.5603	0.88104	0.377	0.079	19.40
0.1676	0.9994	0.3590	0.8793	0.466	0.078	21.80
0.1369	0.9988	0.24704	0.8797	0.554	0.075	22.95
0.09909	0.9986	0.1302	0.8837	0.760	0.075	25.00
0.0485	0.9985	0.0665	0.8804	0.729	0.035	28.00
0.0355	0.9982	0.02629	0.8787	1.35	0.047	30.10
0.02011	0.9982	0.009194	0.8787	2.18	0.043	32.20
0.01376	0.9982	0.005797	0.8782	....	...	33.00
0.0039	0.9982	0.001481	0.8779	....	...	33.40
0.0011	0.9982	0.000457	0.8779	....	...	34.60

The solute represented by Fig. 2 (data in Tables I and II), is butyric acid, and the two systems are water–vapor, and water–benzene. The curve marked I. B. P. is that which would be obtained by plotting the interfacial tension against the logarithm of the concentration of the butyric acid in the benzene phase, if the butyric acid in the benzene were not associated. The first measurements on this system were made for use in developing the theory of orientation of molecules in surfaces and interfaces, in the year 1913, by E. C. Humphrey, and were made by the capillary height method. These measurements were not considered precise enough, so the results given here are those obtained later by H. H. King, who used the drop-weight method in the form developed by Harkins and Humphrey, the most complete account of which will be found in a paper by Harkins and Brown.[1] The results on interfacial tension for the lower concentrations were obtained by the capillary height method.

Using the above equation the adsorption of butyric acid at both interfaces was calculated. When the concentration in the aqueous solution was 0.04 mol per 1000 g. of water, 1.00 × 10^{14} molecules were found to be present in one sq. cm. of the film between *water and benzene*, while if the benzene is not present the concentration of the aqueous phase needs to be only *one-third* as great to be in equilibrium with just the same number of molecules in the surface film. This shows that the molar activity or fugacity of the molecules in the interface between water and benzene is three times as high as on the surface of water, when both films have the same concentration of about 1.0 × 10^{14} molecules per sq. cm.

In order to give 1.5 × 10^{14} molecules per sq. cm. in the interface between water and benzene the concentration in the aqueous phase must be 0.1 mol per 1000 g. of solution, while to give the same number of molecules on the surface of water the concentration needs to be only 0.02 mol, or the difference in activity is nearly the same as that described in the preceding paragraph.

As the number of molecules per sq. cm. in the surface film increases the amount of solvent in the film becomes so small that the activity of the solute molecules in the film changes very rapidly when calculated on the basis of the concentration of solute in the film, so the number of solute molecules in the film remains practically constant over quite wide ranges of concentration of the adjacent liquid phases. A film of this kind has been designated by Langmuir as of one molecule in thickness. At the interface under discussion this constant film is obtained while the concentration in the aqueous phase varies from 0.20 to 0.50 mol[2] of butyric acid to 1000 g. of solution, while with the water phase alone the same concentration in the surface, 2.77 × 10^{14} molecules per sq. cm. is obtained at concentrations between 0.05 and 0.625 mol, showing for the *lowest* concentration at which this film is obtained, somewhat the same average ratio in the activity in the film, that is, the butyric acid in the interface has again an activity 3 or 4 times greater than that at the surface of water. These results indicate that, corresponding to the theory, *the restraining force on the butyric acid molecules is much greater at the surface of the water than it is at the interface—water-benzene.* This may be stated in the forms

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[1] THIS JOURNAL, 41, 499, (1919.)

[2] Here the *lower* concentration only is significant for the present discussion, since at the higher concentration the film begins to thicken. This will be discussed later.

For equal concentrations in the aqueous phase the adsorption of substance: of the type of the higher organic acids, alcohols, amines, etc., always greater at the surface of water than it is at the interface between water and an organic solvent of the type of benzene or a paraffin.

The data for acetic and other acids in water will be given in the next paper of this series.

Calculation of the Adsorption at Interfaces.

In calculating the adsorption at interfaces the difficulty was met that none of the adsorption formulas which we were able to find take into consideration the presence of the solute in more than one phase. Since, even when water is the only solvent, the solute may be, and usually is in the vapor phase, the equations should take account of this fact. The adsorption formula development here presented was worked out for use in this paper by Professor A. C. Lunn of the Department of Mathematics, University of Chicago. It is based on the laws of thermodynamics and the equation for maximum work considered in connection with osmotic pressure.

$$\text{Notation.—}\left.\begin{array}{l}\lambda = \text{latent heat}\\ \mu = \text{adsorption}\\ a = \text{area}\\ \gamma = \text{surface tension}\end{array}\right\}\text{ of film.}\quad\left.\begin{array}{l}p,p' = \text{osmotic pressures}\\ l,l' = \text{latent heats}\\ v,v' = \text{volumes}\\ r,r' = \text{dilutions, or recip-}\\ \quad\text{rocals of concentrations}\\ \quad(c,c')\end{array}\right\}\text{ of volume phases.}$$

s = entropy
c = thermal capacity of system
M = total mass of solute
q = heat added to system
w = work done by system
ψ = Helmholtz free energy

The first law of thermodynamics may be stated in the form

$$dq = c\ dt + l\ dr + l'\ dr + \lambda da. \qquad (1)$$

The equation for reversible work is

$$dw = p\ dv + p'\ dv' - \gamma da. \qquad (2)$$

The negative of the differential of the function of Gibbs, or of the Helmholtz free energy, is defined as

$$\begin{aligned} -d\psi &= d\ (st) - (dq - dw) \\ &= s\ dt + t\ ds - (dq - \gamma dw) \\ &= \mathrm{s}\ dt + dw \qquad (3) \\ &= s\ dt + p\ dv + p'\ dv' - \gamma da. \qquad (3b)\end{aligned}$$

The total mass of solute (M) is given by the following equation:

$$M = vc + v'c' + \mu a$$

$$\text{or}\quad v/r + v'/r' = M - \mu a \qquad (4)$$

Since r and r' are related at a given temperature, and also p and p', the independent variables may be taken as t, r, v, and a. Then p, p', l, l', λ, μ, and γ, will be functions of r and t.

The mass of substance in the phase represented by primed letters is given as follows:

$$m' = v'c' = v'/r' = M - \mu a - v/r \qquad \text{so}$$

$$v' = r'(M - \mu a - v/r) \tag{5}$$

so

$$\begin{aligned} dv' &= \left(\frac{\partial r'}{\partial r}\,dr + \frac{\partial r'}{\partial t}\,dt\right)\left(M - \mu a - \frac{v}{r}\right) \\ &\quad - r'\left(a\frac{\partial \mu}{\partial r} - \frac{v}{r^2}\right)dr - r'\,a\frac{\partial \mu}{\partial t}\,dt \\ &\quad - \frac{r'}{r}\,dv - r'\,\mu\,da \end{aligned} \tag{6}$$

$$\begin{aligned} &= \left[\frac{\partial r'}{\partial t}\left(M - \mu a - \frac{v}{r}\right) - r'a\frac{\partial \mu}{\partial t}\right]dt + \\ &\qquad \left[\frac{\partial r'}{\partial r}\left(M - \mu a - \frac{v}{r}\right) - r'\left(a\frac{\partial \mu}{\partial r} - \frac{v}{r^2}\right)\right]dr \\ &\qquad - \frac{r'}{r}\,dv - r'\,\mu da. \end{aligned} \tag{7}$$

Substituting (7) in (3*b*):

$$\begin{aligned} \therefore -d\psi &= \left\{s + p'\left[\frac{\partial r'}{\partial t}\left(M - \mu a - \frac{v}{r}\right) - r'a\frac{\partial \mu}{\partial t}\right]\right\}dt \\ &\quad + p'\left\{\frac{\partial r'}{\partial r}\left(M - \mu a - \frac{v}{r}\right) - r'\left(a\frac{\partial \mu}{\partial r} - \frac{v}{r^2}\right)\right\}dr \\ &\quad + \left(p - \frac{p'r'}{r}\right)dv - (\gamma + p'r'\mu)\,da. \end{aligned} \tag{8}$$

In order that this may be an exact differential, the following conditions must be met (9, 10, 11, 12):

$$\begin{aligned} &\frac{\partial}{\partial r}\left\{s + p'\left[\frac{\partial r'}{\partial t}\left(M - \mu a - \frac{v}{r}\right) - r'a\frac{\partial \mu}{\partial t}\right]\right\} \\ &\qquad = \frac{\partial}{\partial t}\left\{p'\left[\frac{\partial r'}{\partial r}\left(M - \mu a - \frac{v}{r}\right) - r'\left(a\frac{\partial \mu}{\partial r} - \frac{v}{r^2}\right)\right]\right\} \end{aligned} \tag{9}$$

$$\frac{\partial}{\partial v}\left\{s + p'\left[\frac{\partial r'}{\partial t}\left(M - \mu a - \frac{v}{r}\right) - r'a\frac{\partial \mu}{\partial t}\right]\right\} = \frac{\partial}{\partial t}\left(p - \frac{p'r'}{r}\right) \tag{10}$$

$$\frac{\partial}{\partial a}\left\{s + p'\left[\frac{\partial r'}{\partial t}\left(M - \mu a - \frac{v}{r}\right) - r'a\frac{\partial \mu}{\partial t}\right]\right\} = -\frac{\partial}{\partial t}(\gamma + p'r'\mu) \tag{11}$$

$$\frac{\partial}{\partial v}\left\{p'\left[\frac{\partial r'}{\partial r}\left(M - \mu\,a - \frac{v}{r}\right) - r'\left(a\frac{\partial \mu}{\partial r} - \frac{v}{r^2}\right)\right]\right\} = \frac{\partial}{\partial r}\left(p - \frac{p'r'}{r}\right) \tag{12}$$

$$\frac{\partial}{\partial a}\left\{p'\left[\frac{\partial r'}{\partial r}\left(M - \mu a - \frac{v}{r}\right) - r'\left(a\frac{\partial \mu}{\partial r} - \frac{v}{r^2}\right)\right]\right\} = -\frac{\partial}{\partial r}\left(\gamma + p'r'\mu\right) \quad (13)$$

$$\frac{\partial}{\partial a}\left(p - \frac{p'r'}{r}\right) = -\frac{\partial}{\partial v}(\gamma + p'r'\mu). \quad (14)$$

(14) is identically satisfied as $0 = 0$.

(10) and (11) give

$$-\frac{p'\partial r'/\partial r}{r} + \frac{p'r'}{r^2} = \frac{\partial p}{\partial r} - \frac{p'\,\partial r'/\partial r}{r} - \frac{\partial p'/\partial r\, r'}{r} + \frac{p'r'}{r^2} \quad (15)$$

$$-p'\mu'\frac{\partial r'}{\partial r} - p'r'\frac{\partial \mu}{\partial r} = -\frac{\partial \gamma}{\partial r} - p'r'\frac{\partial \mu}{\partial r} - \frac{\partial p'}{\partial r}r'\mu - p'\mu\frac{\partial r'}{\partial r} \quad (16)$$

or

$$\frac{\partial p}{\partial r} - \frac{r'\,\partial p'/\partial r}{r} = 0 \quad (15)$$

$$\frac{\partial \gamma}{\partial r} - r'\mu\frac{\partial p'}{\partial r} - 0 \quad (16)$$

$$\therefore\ r'\,\partial p'/\partial r = r\,\partial p/\partial r \quad (17)$$

and

$$\mu = -\frac{\partial \gamma/\partial r}{r'\,\partial p'/\partial r} = -\frac{\partial \gamma/\partial r}{r\,\partial p/\partial r}. \quad (18)$$

or the adsorption in mols is equal to the concentration of the solution times the rate of increase of the surface tension with the dilution divided by the rate of *decrease* of the osmotic pressure with the dilution.

(17) gives $\quad r'/r = (\partial p/\partial p')_{dt = 0}. \quad (19)$

Equation 19 may be written in the form:

$$c/c' = (\partial p/\partial p')_{dt = 0}$$

or the rate of change of the osmotic pressure in one phase with respect to that in the other, at constant temperature, is equal to the ratio of the respective concentrations.

In the special case where the van't Hoff formula holds:

$$pr = RT \qquad p'r' = RT$$

$$\therefore\ r'/r = p/p'; \quad \therefore\ dp/dp' = p/p' \quad (20)$$

isothermally, and p'/p is a function of t; $\therefore$ r'/r is a function of t. which, changing r to $1/c$ gives

$$\mu = -\frac{1}{RT}\frac{c\,d\gamma}{dc} = -\frac{1}{RT}\frac{c'd\gamma}{dc'} - = \frac{1}{RT}\frac{d\gamma}{d\,ln\,c'} = -\frac{1}{RT}\frac{d\gamma}{d\,ln\,c}. \quad (21)$$

The Molar Activity and the Association of Butyric Acid in the Volume Phases.

Since there is only one film between the two phases, the adsorption as calculated from one phase should be the same as that calculated from the other. Now Equation 19, in so far as it holds, signifies that the adsorption is a constant times the slope $(\partial y/\partial x)_{dt=0}$ at any point of the curves which give surface tension plotted on the Y-axis, and the logarithm of the molar concentration on the X-axis (Fig. 2). Whenever y on the curve for the aqueous phase is equal to y on that for the benzene curve, the two phases are in equilibrium and thus Equation 19 indicates that for such points the slopes of the two curves must be equal, or,

$$(\partial y/\partial x)_{dt=0} = (\partial y'/\partial x')_{dt=0}.$$

Now, the figure shows that this is very far from being true, which indicates that the osmotic pressure in one of the two phases, or possibly in both, deviates widely from the gas law. Previous work, however, indicates that weak electrolytes in aqueous solution, when allowance is made for the degree of ionization, give osmotic pressures which are nearly normal at concentrations of 0.5 M or less, such as are involved in this discussion. The large deviation must, therefore, occur in the benzene phase, but in this phase, below one molar, such extremely abnormal osmotic pressures as are required by the slope of the curve, are improbable. This leads to the idea that the concentrations which are plotted on the X-axis for the benzene phase are not molar, but only formula weight concentrations. Only in case the concentrations are actually molar should the curves have equal slopes for all points at which y is the same on both. That the formal concentration in the benzene phase is thus much larger than the molar concentration, especially in the more concentrated solutions, seems the most probable hypothesis, and this means that the association of single into double or triple or even more highly associated butyric molecules increases rapidly with the concentration. If it were not for this association, the curve for the benzene phase would be of the same form as that for the water phase, and would lie entirely to the left of the latter. The two curves would not then cross each other. This crossing of the curves indicates that the formal solubility of the butyric acid in the benzene at all points to the left of the point of crossing, is less than that in the water, while at all points to the right, it is greater. The term solubility has been used here in a new and wholly comparative sense, and indicates that the solute in both phases is in equilibrium with the solute in the interfacial film.

The curves may be interpreted to indicate that single molecules of butyric acid are more soluble in water than in benzene, when the solubility is calculated on the basis of either 1000 g. of solvent or of solution,[1] but that the associated molecules are more soluble in benzene. That the association of such molecules decrease their solubility in water, and increase their solubility in benzene, is entirely in accord with the theory

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[1] However, on the basis of the mol fraction, the single molecules as well as the double, may be more soluble in benzene than in water.

presented in this paper. Thus the union of single into double molecules, as is seen by the following equation,

○—— + ——○ → ——○○——,

decreases the free field due to the polar groups, and thus decreases the average intensity of the forces of the electromagnetic stray field.[1] This makes the molecules more like the benzene and less like the water. The association of two or more butyric acid molecules, by the union of their oxygen atoms, also lessens the extent of their union with the oxygen of the water, not only by the lessening of the stray field, but also by what may be called steric hindrance, that is, by occupying the adjacent space.

Association as Related to Partition Coefficients.

While the relation of association to the slopes of the surface-tension curves, as pointed out in the last section, is new, the determination of the association of acetic acid in benzene by partition experiments, was the subject of a research by Nernst. The data of Table III give similar partition values for butyric acid. The fifth and sixth columns of the table list the values of $C/_{w}C_{B}$ and C_{w}^{2}/C_{B}, where C_{w} and C_{B} are the formal concentrations of butyric acid in the aqueous and the benzene phases, respectively. It is apparent that neither C_{w}/C_{B} nor C_{w}^{2}/C_{B} is constant, since the first decreases and the second increases with increase of concentration. The values at the lower concentration are somewhat affected by the ionization, while those at the higher concentrations may be affected by deviations from Raoult's law, but at the intermediate values the table shows a much greater constancy for C_{w}^{2}/C_{B}. In this work the analyses of the aqueous phase were made with great care, and any irregularities which occur in the constants are due to the errors in the determination of the concentrations in the benzene phase. We expect to determine the association later by a more direct method, so the quantitative calculations will be left for another paper.

The Adsorption of the Interface Water-Benzene as Compared with that on the Surface of the Water.

Table IV gives values for the adsorption of butyric acid at the interface water-vapor, and similar values for the interface between water and benzene.

Number of Molecules in the Constant or Monomolecular Film.

One of the most interesting and important points brought out by this work as shown by these tables, is that the monomolecular film of butyric acid between water and benzene contains 2.79×10^{14} molecules per sq. cm., while that between water and air (plus vapor) contains 2.77×10^{14},

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[1] Thus the double molecules have two paraffin chains instead of one, and only one polar group, and that in the middle of the molecule.

TABLE IV.

Adsorption at the Interface Water-Benzene.

Formula weights per 1000 g. water.	Mols per sq. cm. × 10^{10}.	Molecules per sq. cm. × 10^{14}.	a. Area per molecule in sq. cm. × 10^{16}.	a. Horizontal diameter of space in cm. × 10^{8}.
0.035	1.631	0.99	101.0	10.0
0.1	2.45	1.48	67.6	8.3
0.2	4.60	2.79	35.9	6.0
0.5				
Adsorption at the Interface Water-Air.				
0.0066	1.078	0.654	153	12.3
0.013	1.70	1.03	96	9.8
0.024	2.87	1.99	59	7.6
0.050	4.50	2.82	36.6	6.05
0.101	4.452	2.753	36.3	6.03
0.159	4.558	[1] 2.763	36.2	6.02
0.322	4.562	2.765	36.2	6.02
0.663	4.566	2.767	36.1	6.01

or, within the limits of error, both films contain the same number of molecules. Thus the presence of benzene as an upper phase does not change the number of butyric acid in this constant or monomolecular layer.

Summary.

In this paper the hypothesis is developed that the distribution of a solute between various regions (phases and interfaces) is conditioned by the intermolecular electromagnetic fields. Cohesion is considered to be due to these fields, and is explained on the basis of the valence theory of G. N. Lewis as being due to intermolecular fitting of electrons in the outer shells of the atoms. The constant surface film of butyric acid on the surface of water is found to contain 2.78 × 10^{14} molecules, while if benzene covers the water phase, the layer contains 2.79 × 10^{14} molecules per sq. cm. Thus the presence of the benzene does not affect the number of molecules in the film. A theory of solubility and of thermodynamic environment is developed, and a hypothesis is presented to explain the variation of the activity, fugacity, or thermodynamic potential of a component, with variations in its environment. Various topics, such as Raoult's law, solubility, melting points, compressibility, coefficient of expansion, latent heat of vaporization, adsorption, and surface structure, are discussed. The theory presented is too complicated for presentation in a summary, and should be looked for in the body of the paper.

The present investigation was carried out by the aid of the C. M. Warren Fund of the American Academy of Arts and Sciences.

A discussion of electrical theories of surface phenomena will be found in

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[1] The numbers inclosed by a bracket represent the constant or monomolecular film.

papers by Hardy,[1] Langmuir,[2] Harkins, Brown and Davies,[3] Harkins, Davies and Clark,[4] and by Fraenkel.[5]

CHICAGO, ILL.

NOTE.

Acknowledgment.—In an article[6] entitled "A Study of Conditions Affecting the Precise Determination of Zinc as the Sulfide," by Harold A. Fales and Gertrude M. Ware, omission was made of an acknowledgment due to Prof. H. T. Beans, of Columbia University. The investigation described in this article was proposed by Dr. Beans and carried out under the direction of Dr. Fales during the absence of Dr. Beans in Government service. It is regretted that the omission of this acknowledgment occurred in the original publication. HAROLD A. FALES.

NEW YORK, N. Y.

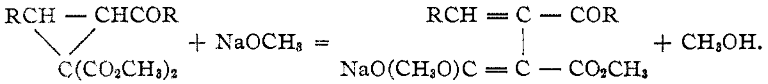
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY.]

STUDIES IN THE CYCLOPROPANE SERIES. IV.

BY E. P. KOHLER AND T. L. DAVIS.

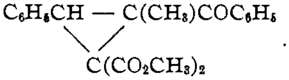
Received February 25, 1919.

One of the most characteristic properties of the cyclopropane derivatives under investigation in this laboratory is the ease with which the ring is opened by alcoholates. The product is a metallic derivative of an isomeric ethylenic ester.



The principal object of the present investigation was to secure additional information on this obscure process.

In earlier papers we assumed that the metallic derivative is formed as a result of two reactions—addition of alcoholate followed by loss of alcohol. We therefore selected for the present work dimethyl 2-phenyl-3,3-methylbenzoyl-cyclopropane dicarboxylate.



Owing to the presence of the methyl group in the 3 position in this sub-

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[1] Hardy, *Proc. Roy. Soc.*, **86B**, 634 (1911–12).

[2] Langmuir, THIS JOURNAL, **39**, 1848–1906 (1917); *Proc. Am. Acad.*, **3**, 251–7 (1917); abstract in *Met. Chem. Eng.*, **15**, 468 (1916).

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

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