FORCES NEAR THE SURFACES OF MOLECULES

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In the early development of the kinetic theory, during the last century, it was usual to consider the molecules of gases as rigid spheres, which exerted no forces on one another except at the instant of contact. In this way it was possible to account quantitatively with fair accuracy not only for the effects of pressure and temperature on the volume, but also for the viscosity, heat conductivity, and diffusion of gases, and other phenomena involving the free paths of the molecules.

By considering also attractive forces which varied with some power of the distance between the centers of the molecules, van der Waals was able to account for the main features of the transition from the gaseous to the liquid state, and also explained in a satisfactory manner the departures from the ideal gas laws which are shown by all gases at high pressures.

As new properties of matter are brought into consideration, or as a deeper understanding of them is needed, it is necessary to postulate additional properties of the molecules, and to know more accurately the nature of the forces acting between them. For example, to deal with the properties of electrolytes it is necessary to consider electric charges on the molecules or ions. In 1912 Debye showed that the electrical properties of many dielectrics could be accounted for by assuming that the center of gravity of the electrons in a molecule did not coincide with the center of gravity of the positive charges of the nuclei. Thus the molecule possessed what we call a dipole moment, which can be measured as the product of an electric charge by the distance through which it is displaced. It is found, for example, that a molecule of water possesses a dipole moment of 1.8×10^{-18} electrostatic units. A moment of this magnitude could be produced by having an electron at a distance of 0.37×10^{-8} cm. from a proton. Since there are 10 electrons in a water molecule, it is only necessary that the center of gravity of these electrons shall lie at a distance of 0.037×10^{-8} cm. from the center of gravity of the three nuclei in the molecule. Thus displacements of the electrons to distances minute compared with the diameter of the molecule can account for even the largest values of dipole moments that have been observed.

H. B. Hardy (1) in 1912 and the writer (2) (3) in 1916 pointed out that the fields of force around many chemical molecules must be very unsymmetrical, and that this resulted in an orientation of the molecules at the surfaces of liquids and in adsorbed films on solids. It was also found that the shapes which the molecules could assume, and which were determined by their chemical structures, were of great importance in connection with such properties as surface tension.

Within recent years, particularly through the work of Debye and his students, a great deal of knowledge has been accumulated regarding the electrical forces in liquids and solutions which contain ions and dipoles. Particularly in the study of electrolytes has this work cleared up many of the most serious difficulties of earlier theories.

There is now no need of drawing distinctions between chemical and physical forces. The chemist recognizes that many of the forces with which he has been dealing are electrical in nature, for, after all, molecules are built up of electrons and positive nuclei, and their interactions must necessarily be electrical. However, the simple classical theory of electrical forces based on Coulomb's law is wholly insufficient to account for chemical properties. With charged particles obeying Coulomb's law only, the minimum of potential energy is obtained when the positive and negative particles coincide. There must be something corresponding to repulsive forces holding the particles apart.

REPULSIVE FORCES BETWEEN MOLECULES

In many of the later developments of the kinetic theory where the molecules were regarded as rigid spheres, the repulsive forces which must counteract the attractive forces were assumed to act only during collisions—that is, at the instant of contact of the spheres (4). No explanation was attempted of the internal forces within the molecule which could result in this repulsion between molecules.

In order to account for the compressibility of solids, Born and Landé (5) have assumed that the repulsive force between molecules (or ions) varies inversely as a power of the distance between the centers of the molecules. Thus in the case of halide salts of the alkalies, such as NaCl, KI, etc., they showed that the compressibility indicated that the repulsive force varied inversely as the tenth power of the distance, while the attractive force resulting from the charges on the ions varied inversely as the square, in accord with Coulomb's law. Born (6) also attempted to show that the inverse tenth power law for repulsion could be deduced by assuming that the electrons and the ions were arranged with cubic symmetry as at the corners of a cube. This attempt, however, must be regarded as a failure for two reasons. First, the method of mathematical expansion which was used is not legitimate when applied to distances as short as those between ions in salts; and, second, Born assumed that the cubical ions were all orientated so that their edges were parallel. This kind of orientation would be unstable under the forces assumed, for these forces would tend to orientate one cubical ion so that its corner would come opposite the face of another ion, and in this case the repulsive force would be replaced by an attractive force which would act in addition to the force between the ionic charges. Although such orientation of ions as Born assumes might conceivably exist in solid crystals from causes which he does not discuss, it is clear that it cannot be the cause of the repulsive forces, since the elimination of the orientation by melting the salt does not greatly alter the density or the compressibility.

Debye (7) has developed a theory which seems to give a better picture of the repulsive forces. Assuming the electrons to move in orbits in accord with Bohr's theory, he finds that the electric field around a molecule is a pulsating or partly oscillating field increasing in amplitude very rapidly as the surface of the molecule is approached. Thus when an electron approaches a molecule it acquires, in addition to any motion of translation it may have, an oscillatory motion due to the pulsating field. Debye shows that this oscillatory motion tends to be 180° out of phase with the field producing it, and then shows, that because of the non-uniformity of the electric field near an atom the resulting force will be one of repulsion.

On this theory the repulsive forces between molecules are due to the perturbations in the electron orbits in one molecule, caused by the motions of the electrons in their orbits in the neighboring molecules. The repulsive force thus does not originate from a molecule as a whole, but comes from the close approach of electrons in the two molecules. This would seem to indicate that we may profitably regard these forces as *surface forces,* and should express them as functions of the distances between the surfaces of the molecules rather than in terms of the distances between the centers. This conception affords a justification, to a large extent, of the theory which regarded molecules as rigid elastic spheres.

Even if we accept Debye's picture of the origin of repulsive forces, we see that it really only refers the cause back to the quantum theory, by which the stable orbits of the electrons in the molecule are determined. At present, however, problems of this kind are treated by wave mechanics instead of by a consideration of orbits of electrons. For a few simple cases, such as interactions between hydrogen molecules, Hund and London have been able to calculate the forces by means of wave mechanics. But it will probably be a long time before definite knowledge of repulsive forces can be obtained in this way for more complicated molecules.

The quantum theory teaches that each electron in an atom is characterized by four quantum numbers, which are integers. Not all quantum numbers are possible; there are, for example, certain conditions (selection rules) which they must satisfy. The normal atom or molecule, with which the chemist is concerned, is one in which the electrons are so arranged that the total energy is a minimum, subject to the quantum rules that must be fulfilled.

It seems that the factor of greatest importance to the chemist is that which is known as the Pauli principle, which states that no two electrons in an atom can have the same combination of four quantum numbers. It is this principle which underlies the Periodic Table of the elements, and in a similar manner determines the arrangement of electrons in a molecule. It is through the development of methods of this kind that our greatest hope lies in obtaining a better understanding of the nature of repulsive forces.

For most practical purposes it is best for the chemist to regard molecules of organic substances as having shapes suggested by chemical structural formulas, and as having surfaces which are rather rigid so that strong repulsive forces are called into play for only moderate deformations. For many purposes it is still useful to look upon the surfaces as completely rigid.

ATTRACTIVE FORCES BETWEEN MOLECULES[1]

Whereas the quantum theory seems essential in an understanding of the repulsive forces, the classical laws, such as the Coulomb law, are largely sufficient for dealing with the attractive forces between molecules. For example, the Debye-Hückel theory of electrolytes (8) is based on the Coulomb law, the Poisson equation, and the Boltzmann equation—all laws of classical mechanics.

In discussing forces between molecules, Debye has classified molecules in three groups: "(1) ionic, (2) polar and (3) non-polar." The ionic type is represented by electrolytic ions, such as K^+, NO_3^-, etc., and gaseous ions. In these molecules the number of electrons is unequal to the number of positive charges of the nuclei of atoms, so that the molecule as a whole has an electric charge which is some multiple of e, the charge of an electron. The polar type is represented by molecules which have a dipole moment—that is, uncharged molecules in which the center of gravity of the negative charges does not coincide with that of the positive. Non-polar molecules thus include all molecules which

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[1] The term "molecule" is to be used in its broad sense, which includes atoms and ions.

are uncharged and in which the centers of gravity of the positive and negative particles coincide. From Debye's point of view such molecules may correspond to quadrupoles, octopoles, etc. For example, positive and negative charges arranged alternatively at the corners of a square will give a quadrupole, at the corners of a cube an octopole. In forming clear conceptions of the attractive forces between molecules it is useful to consider the actual magnitude of the forces involved.

Ions

The electric field at a distance r from a univalent ion having a charge e is $e/\epsilon r^2$, where ϵ is the dielectric constant of the medium. The charge of the electron, e, is equivalent to 1.43×10^{-7} volt centimeter and thus the electric field is $1.43 \times 10^{-7}/\epsilon r^2$ volts per centimeter, and the electric potential corresponding to this force is $1.43 \times 10^{-7}/\epsilon r$. If we take for r the value 3×10^{-8} cm., which corresponds roughly to the distance between two ions in contact, we find the electric field to be 1.6×10^8 volts per centimeter and the potential to be 4.8 volts. Taking for ϵ the value 80, corresponding to the dielectric constant of water, we would obtain values only one-eightieth of those given. However, it is doubtful if the conception of dielectric constant is entirely justified at distances as short as this for we can hardly speak of two molecules in contact as being in a medium having known electrical properties. At distances several times greater than the molecular diameter the use of dielectric constant in this way is justified.

The applications of the Debye-Hückel theory to electrolytes prove that the forces at these larger distances are of vital importance in an understanding of the properties of ions. According to the Coulomb law the force between two ions varies inversely as the square of the distance. In electrolytic solutions the increased concentration of positive ions around negative ions, and vice versa, causes the force between two given ions to decrease with increasing distance more rapidly than according to the inverse square law.

Polar molecules

At a distance r from a dipole molecule having an electric moment μ the electric potential is $\mu \cos \theta/r^2$, where θ is the angle between the radius vector r and the axis of the dipole. It can thus be found that at a distance r along the dipole axis the electric field is $-2\mu/r^3$, this force being in a direction of the polar axis. At a distance r in the equatorial plane of the dipole the electric force is also in a direction parallel to the polar axis but has the magnitude $+\mu/r^3$.

Debye (9) has shown that in general because of thermal agitation a dipole (or quadrupole) molecule in a gas or liquid is changing its orientation so fast that we must not regard the force produced by a dipole as a steady force, but a rapidly fluctuating force, and under these conditions many of the effects produced by the force are proportional to $\overline{E}^2$ or the mean square field. The effective force can thus vary inversely as the sixth power of the distance from the dipole.

Non-polar molecules

If the molecule is a quadrupole the instantaneous force in any given direction will vary inversely as the fourth power of the distance, and thus the effective fluctuating force will vary inversely as the eighth power of the distance. With more symmetrical molecules the forces will vary inversely with still higher powers of the distance.

Under the influence of forces of the kinds we have been considering the various types of molecules in liquids respond in different ways. Positive ions tend to concentrate around negative ions in the manner considered by the Debye-Hückel theory (8). Dipole molecules tend to be orientated by the field in the neighborhood of the ion. Thermal agitation tends to prevent this orientation, so that only when the dipole molecule is very close to the ion is the orientation of the molecule complete.

The dipole molecule, orientated in a field, tends to move in the direction towards which the field is of greater intensity. The change in potential energy is mE, where E represents the change in field strength and m is the effective dipole moment (average moment) in the direction of the field.

A field insufficient to orientate the dipoles completely gives an effective dipole moment m, which according to Debye (10) is

$$m = \mu^2 F/3kT$$

where F is the electric force tending to produce the orientation. Since the energy available for producing motion of translation in a dipole is proportional to mF, we see that at large distances dipoles attract one another in proportion to F^2 and therefore in inverse proportion to the sixth power of the distance. If, however, we consider a fixed dipole (for example one attached to a large organic molecule) acting on another dipole at a very short distance so that the latter is orientated by the field of the former, then the force of attraction will vary inversely as the fourth power of the distance.

An electric field of intensity F, acting on a non-polar molecule, causes a deformation, or polarization, of the molecule so that it acquires a dipole moment m given by

$$m = \alpha F$$

where α is the polarizability. A liquid made up of non-polar molecules of this kind will have a dielectric constant ϵ which is greater than unity, and the *molar polarization* of the liquid is calculated from ϵ by means of the equation

$$P = \left(\frac{\epsilon - 1}{\epsilon + 2}\right) \frac{M}{\rho}$$

where M is the molecular weight and ρ is the density of the liquid. The relation between P and α is given by the equation

$$P = \frac{4\,\pi}{3} N\,\alpha = 2.54 \times 10^{24}\,\alpha$$

where N is the Avogadro number, 6.06×10^{23}. The quantity P has the dimensions of a volume and is thus measured in cubic centimeters. For ordinary organic liquids the value of P is roughly about 0.3 of the volume of a gram-molecule. A few values of P and α are given in table 1. From the value $\alpha = 10^{-23}$, which is of the order of magnitude found in most organic liquids, we can calculate that the electric field needed to give to a non-polar molecule a dipole moment of 10^{-18} is $F = 3.0 \times 10^7$ volts per centimeter. This is the field that would exist at a a distance $r = 7 \times 10^{-8}/\sqrt{\epsilon}$ cm. from an electron. A field of this magnitude would be found at the distance $r = 2.7 \times 10^{-8}/(\epsilon)^{1/3}$ in the direction along the axis of the dipole.

From the foregoing discussion, we see that the effects of the electric fields of molecules are of three kinds which we may classify as (1) segregation, (2) orientation, and (3) deformation. As an example of segregation, we have the segregation of positive ions around negative ions in electrolytes. Dipole molecules become orientated in the field produced by any other molecule and thus are attracted toward the molecule producing the field. Non-polar molecules, under the influence of fields of other molecules, become deformed or polarized so that they acquire a dipole moment in the direction of the field and are thus attracted by the molecule producing the field.

TABLE 1

Values of P and α

	P	α
	cc.	
H_2	5.8	2.28×10^{-24}
N_2	13.6	5.4
CH_4	21.0	8.3
C_6H_6	25.8	10.2

In estimating quantitatively the magnitude of the segregation and orientation that result from molecular fields, we may apply the Boltzmann equation;

$$\frac{n_1}{n_2} = A\,\epsilon^{\lambda/kT}$$

where n_1 and n_2 represent the relative numbers of molecules in two given positions, or orientations, and λ is the work done in transferring a molecule from one of these states to another.

The constant A involves the ratio of the *a priori* probabilities of the molecules in the two regions or states under consideration. These probabilities are frequently dependent upon geometrical factors, but often involve a knowledge of the quantum phenomena accompanying the change in state. The quantity ϵ in this equation is the base of the natural system of logarithms, 2.718; k is the Boltzmann constant, 1.37×10^{-16} erg per degree; T is the absolute temperature.

We see from the Boltzmann equation, that when the constant A is not too far removed from unity, the effects of segregation and orientation usually begin to be important only when the energy λ becomes of the same order of magnitude as kT. At room temperature the value of kT is 4.1×10^{-14} erg, which is the energy that an electron would acquire in falling through a potential of 0.025 volt.

In Debye's theory for the contribution of dipole molecules to the dielectric constant of liquids, it is shown that the effective dipole moment m of the dipole molecules (of moment μ) is $\frac{1}{2}\mu$ when the field is of such intensity that the work done by the field in orientating the molecule is equal to $2kT$.

The segregation of ions of one sign around an ion of the opposite sign will be marked at distances r less than that at which the potential is 0.025 volt; that is, when r is less than $57 \times 10^{-8}/\epsilon$ cm. If ϵ has a low value, of a few units only, then even in very dilute solutions, where the distances between the ions are more than ten times greater than the molecular diameters, the ions will tend to be swept out of the solution and brought into contact with each other. This is in accord with the fact that such salt-like substances as NaCl, whose crystals are held together by forces of the Coulomb type, are practically insoluble in organic liquids of low dielectric constant. On the other hand, in water and other liquids of high dielectric constant, in solutions of even moderate concentration, the ions are far enough apart so that their potentials with respect to one another are less than kT, which agrees with the fact that these salts are soluble in these liquids, and that their solutions behave as electrolytes.

We have seen that to orientate the larger portion of dipole molecules in liquids requires a field F which makes μF greater than 2 kT. This means that a field of about 2.4×10^7 volts per centimeter is needed for the orientation. The work done when the orientated molecule is brought into the field is of the same order of magnitude, so that a field sufficient to cause nearly complete orientation of dipole molecules will also cause marked segregation. A field of 2.4×10^7 will exist at a distance $r = 8 \times 10^{-8}/(\epsilon)^{\frac{1}{2}}$ cm. from a univalent ion, or at a distance $r = 3 \times 10^{-8}/(\epsilon)^{\frac{1}{3}}$ cm. along the axis of a dipole molecule having a moment $\mu = 10^{-18}$. In other directions than along the dipole axis the force will be less and therefore the distance at which effective orientation or segregation occurs will be less than that just given.

From these calculations we conclude that the interaction between dipole molecules of moment 10^{-18} can cause mutual orientation only when they are practically in contact. If they were separated by one additional molecule, so that the distance between centers is 6×10^{-8} cm., even if they were still orientated, the force would be only one-sixteenth as great, since it varies inversely as the fourth power of the distance. However, at this greater distance, the orientation would be far from complete, so that the force would actually vary inversely as the sixth power of r, and would thus be only one sixty-fourth as great as if the molecules were in contact.

The electric force necessary to deform a molecule sufficiently to give it a dipole moment $\mu = 10^{-18}$ (viz., 3×10^7 volts per centimeter) is practically the same as that needed to produce orientation of a dipole molecule having this same moment. Thus when two dipole moment molecules are in contact, the dipole moment which each possesses is practically doubled because of their mutual deformation.

Taking the electric field near a dipole to be proportional to r^{-3}, and remembering that the distance between the center of one molecule and the surface of its neighbor is only one-third the distance to the surface of the far neighbor, we realize that the electric field intensity at one side of the dipole molecule is twenty-seven times as great as at the opposite side.

The latent heat of evaporation of a liquid expressed per molecule gives the energy which must be expended to separate the molecules of liquid from one another. Pentane, a non-polar liquid, which boils in the neighborhood of room temperature (36°C.), has a heat of evaporation of about 40×10^{-14} erg per molecule, which is roughly equal to 10 kT. According to the rough empirical rule of Trouton, the absolute boiling points of liquids are proportional to their latent heats of evaporation, so that in general, to the same degree of approximation, the heats of evaporation per molecule for all liquids will be about 10 kT, where T is the temperature at the boiling point. This can be looked upon as a consequence of the Boltzmann law. The coefficient A in this case, however, is quite different from unity.

The energy involved in the close approach of ions to within molecular dimensions is far greater than 10 kT—at least when the medium is one of low dielectric constant. Thus we are not surprised at the fact that substances built up of ions are solid bodies which melt and boil only at very high temperatures, and are soluble only in liquids of high dielectric constant.

We have found that the energies involved in the approach of dipole and non-polar molecules (having values for μ of about 10^{-18}, and for α of 10^{-23}) to within a distance of 3×10^{-8} cm. is approximately equal to kT ($T = 300$°K). Since a given molecule will usually be in contact with about a dozen others, it is to be expected that the energy necessary to separate a molecule from all its neighbors would be of the order of magnitude of 10 kT. In fact, we can reasonably expect values larger than this because of the fact that the greatest effects will be produced in the deformation of the molecule on its side facing the adjacent molecule ($r = \frac{1}{2}$ molecular diameter), the electric field there being about eight times greater than at the center of the molecule.

We thus have an explanation of the fact that liquids whose molecules have the properties we have postulated will, in general, have boiling points considerably above room temperature. When the molecules are in contact the energies of the non-polar molecules are not very greatly different from those of the dipole molecules—at least are of the same order of magnitude. In this we have an explanation of the fact that the boiling points of liquids containing dipole molecules are only moderately higher than those of non-polar substances. It is possible, for example, to have liquids whose molecules are dipoles, such as anhydrous hydrogen chloride, which boil at temperatures far below room temperature.

Our analysis of the known electrical forces causing the interactions of molecules thus leads us inevitably to the conclusion that the forces involved in holding together the molecules of organic liquids are acting almost wholly between molecules *in contact*, and that in general no serious error would be made in neglecting all forces which act at greater distances. This conclusion is, I believe, thoroughly justified in the case of all liquids built up of non-polar molecules. It applies with reasonable accuracy to most liquids having molecules containing dipoles. But in general, where liquids contain free ions the range of the forces is much greater, and we must then take into account the Coulomb forces which act at greater distances.

For many years, in connection with studies of adsorption, surface tension, and the kinetics of heterogeneous reactions, the writer has found it extremely useful to explain these phenomena in terms of actions between molecules *in contact.* From an empirical point of view the results have justified this method of attack. In many ways this conception is in accord with chemical tradition, for the chemist has always considered that chemical action between molecules takes place between molecules in contact.

The physicist, probably ever since the time of Newton, has been rather inclined to consider forces which vary as some power of the distance, or to deal with fields of force which extend throughout space. The remarkable success of the physicist in the development of the atomic theory, and more recently, in some of the applications to chemical phenomena, such as those involved in the properties of electrolytes, seems to have made many chemists and physicists believe that these methods would also provide the solutions to more complicated chemical problems.

It must be emphasized, however, that the physicist, in attempting to calculate the manner in which dipole molecules or nonpolar molecules will interact in liquids, meets problems which are mathematically so complicated that it is necessary to make simplifying assumptions. For example, the potential energy of dipole or non-polar molecules with respect to one another is expressed as an infinite series in which the successive terms involve as factors $1/r$, $1/r^2$, $1/r^3$, etc. The coefficient of the first term for the case of dipole molecules is 0, the coefficient of the second term is then calculated with great care and often with great difficulty; and although the coefficients of the third and subsequent terms are known not to be zero, these terms are neglected because of the fact that they involve higher powers of r. We have seen, however, that the forces which are primarilv important in liquids are those between molecules in contact, and that a small increase in the distance causes the forces to become very small. For example, with a force varying with $1/r^9$, such as Debye finds with non-polar molecules, the energy involved in the approach of two molecules would fall to one-half value if the distance between the molecules were increased 15 per cent. This change in energy has its effect in the exponent of the Boltzmann equation, so that most of the actions of importance must occur with only still smaller variations in the distance r. It is obvious, therefore, that even for the roughest kind of approximation one is not justified in neglecting the term involving $1/r^3$ in comparison with that which involves $1/r^2$.

As another example of the kinds of approximation that are necessary in treating mathematically the forces between dipole molecules, we have Debye's treatment of the relations between dielectric constant and chemical association (11). He considers the effect of dipoles on one another as the concentration of the dipolar molecule increases in a non-polar solvent. Assuming the molecules to be spheres, complicated equations are derived allowing for the interactions. The result is that the dipole moment per molecule increases with concentration because the molecules tend to line up along a common axis. This is due to the fact that the force along the polar axis is twice as great as in the equatorial plane for a given value of r. An analysis of experimental data, however, shows that in solutions of many dipole substances in non-polar solvents, the polarization per molecule decreases as the concentration increases. Such a result could be explained if the molecule instead of being a sphere were ellipsoidal with the equatorial diameter less than 80 per cent of the polar diameter. The introduction of such a concept would introduce far too great mathematical complications to make an analysis worth while.

Perhaps the greatest objection to a mathematical treatment of the properties of liquids in terms of power laws of force is that it becomes practically impossible to take into account the effects resulting from the complicated shapes of molecules which must characterize organic substances, according to the structural formulas of the chemist. If now we assume that the forces between molecules come into play only at their areas of contact, we have simplified the problem mathematically to such an extent that we can take into account our knowledge regarding the shapes of the molecules which can be furnished us by the chemist. Of course, in so doing we are making approximations, but the errors so introduced will, I believe, usually be far less than those which are often made by the physicist in dealing with these problems. I should like to outline now the ways in which a conception of surface forces can be developed to give concrete pictures and quantitative results for many problems which are too difficult to handle by the method involving the power laws of force.

In considering that the interactions between molecules occur at their surfaces of contact, it is not necessary to assume that the nature of the forces at any given part of the surface is characteristic wholly of the atom underlying the surface. The chemist knows, for example, that the properties of an organic molecule are not simply the sum of the effects due to the separate atoms in the molecule. If one of the hydrogen atoms in the methyl group of acetic acid be replaced by a chlorine atom, the effect of the greater charge on the kernel of the chlorine atom as compared with that of the hydrogen atom which it replaces, is to displace the electrons in the carboxyl group in the direction towards the chlorine atom. This displacement of the pair of electrons which hold the nucleus of the hydrogen atom of the carboxyl group causes the hydrogen nucleus to be held less firmly, and thus makes it easier for the hydrogen nucleus to pass over to a water molecule (in aqueous solutions of acetic acid) to form an OH_3^+ ion, which is the so-called hydrogen ion characteristic of acids. We thus have a clear indication of an alteration in surface forces which may extend over the whole surface of the molecule as a result of the replacement of a hydrogen atom by a chlorine atom.

We may form a clearer conception as to the magnitude of these changes in the surface forces due to effects transmitted from atom to atom in the molecule, by considering the chlorine-substituted fatty acids. In table 2 the values of the dissociation constant K for some of these acids are given as taken from Landolt-Börnstein tables. In the third column, under the heading ln r, is given the natural logarithm of the ratio of K for the acid in question to the value of K for normal acetic acid. According to the Boltzmann equation, this quantity should be equal to λ/kT, where λ represents the difference between the work necessary to remove a hydrogen ion from the given acid molecule and from an acetic acid molecule. Since kT is equivalent to 0.025 volt, we can obtain the value of λ in volts by multiplying the values of ln r by 0.025; the last column of the table gives these values.

TABLE 2

Dissociation constants of chlorine-substituted fatty acids

	K	ln r	VOLTS
Acetic acid	1.85×10^{-5}	[0]	0
Chloroacetic	155.0	+4.44	0.1053
Dichloroacetic	5000.0	7.6	0.190
Trichloroacetic	20000.0	9.3	0.233
Propionic acid	1.4×10^{-5}	[−0.26]	−0.006
α-Chloropropionic	147.0	4.36	0.1045
β-Chloropropionic	8.6	1.53	0.0382
Butyric acid	1.5×10^{-5}	[0.21]	−0.0053
α-Chlorobutyric	139.0	4.30	0.1038
β-Chlorobutyric	8.9	1.57	0.0392
γ-Chlorobutyric	3.0	0.48	0.012

Comparing the monochloro acids with each other, we see that all three of the acids in which the chlorine is in the α-position give

$\lambda = 0.105$ volt. The two acids with chlorine in the β-position give $\lambda = 0.039$ volt. The single γ-chloro acid for which data are available gives $\lambda = 0.012$ volt.

From theoretical considerations we should expect that any state of strain which is transmitted from atom to atom along a hydrocarbon chain should decrease exponentially as the distance increases. The above data thus leads to the conclusion that the electric polarization produced by the presence of a chlorine atom in a hydrocarbon chain decreases in the ratio 2.7: 1 in being transmitted from one carbon atom to the next. If instead of chlorine we should substitute other radicals, we mght obtain electric forces of different magnitudes, but in any case we should expect this ratio 2.7: 1 to apply to the decrease in the force from atom to atom. A considerable effect is thus transmitted from one atom to the next, but very little is transmitted as far as the second or third atom.

This result justifies us in attributing definite properties to different parts of the surface of the molecules of aliphatic compounds. For example, the field of force around a carboxyl group in a fatty acid should be independent of the length of the hydrocarbon chain, provided that this is more than about two carbon atoms long. That is, the forces near the surface of the carboxyl group should be practically constant for all the acids higher than propionic acid and would be roughly the same in the case of acetic acid, but might be considerably different in the case of formic acid. Similarly, we should not be able with any reasonable accuracy to regard the field of force around the carboxyl group as due merely to the super-position of the effects of the hydroxyl group and the carbonyl group, for these two groups are too close together in the molecule to be without important effect on one another.

PRINCIPLE OF INDEPENDENT SURFACE ACTION

From the foregoing analysis of the forces acting between molecules of various types, we conclude that there is a large class of substances for which we are justified in regarding the forces between two molecules in contact as being dependent mainly on the nature of the surfaces of the molecules which are in contact.

This principle of independent surface action (12) will always be only an approximation to the truth, but there are many cases where it applies with sufficient accuracy and so greatly simplifies the problems of the interactions between molecules that useful results are obtained in problems so complex that no solution is otherwise possible. Let us consider some of these problems.

The theory of adsorption in monomolecular films on solids and liquids (13) is an example of the application of this principle. According to this theory, the force which holds an adsorbed molecule or atom on a surface depends on the character of the surface of contact between the molecule and the solid. If a second layer of molecules should form, the forces holding the molecule to the second layer are thus entirely different from those holding the molecules of the first layer. The rates of evaporation of the molecules from the first layer or from the second layer will differ greatly, especially since they depend upon the magnitude of the forces according to an exponential relation of the Boltzmann type. Two general cases must be considered. If the forces holding the molecules in the first layer are greater than those holding those of the second, there will be a wide range of pressures of the adsorbed gas for which the film will never exceed one molecule in thickness. We thus arrive at the conception that a certain fraction, θ, of the surface is covered by adsorbed molecules, and that the properties of this adsorbed film depend primarily on θ. If the forces between these molecules and the underlying surface are very large compared to those that act between adjacent molecules, then, for example, we may conclude that the rate of evaporation of the adsorbed molecules will be proportional to θ. This simple conception leads to an adsorption isotherm which has been found to hold experimentally in a large number of cases. However, if the forces that act between adjacent adsorbed molecules are not negligible, there will be large deviations from this simple law, but the theory may be easily extended to take into account such forces. The forces may be those of attraction, or, if the molecules become dipoles as a result of the adsorption, or if they become crowded, their interaction may cause repulsive forces.

The second important case (14) to be considered is that in which the forces that hold the second layer of molecules are greater than those which hold the first; or, more generally, the case in which the forces acting between adjacent adsorbed molecules are greater than those with which each of these is held on the underlying surface. There is then great difficulty in getting any appreciable number of molecules in the first adsorbed layer, and single molecules or atoms or groups of molecules in the first layer act as nuclei from which large aggregates or crystals may develop. The condensation of cadmium or mercury vapor on cooled glass surfaces is an example of this type. It is possible to formulate the problem quantitatively and to express the number of nuclei that will form per second as a function of temperature and pressure. The calculated values are in good agreement with those obtained by experiment. If definite numbers of isolated copper atoms are evaporated on to a clean surface, each one serves as a nucleus for the formation of cadmium crystals, when the temperature of the surface and the pressure of the cadmium vapor are carefully regulated, and thus by dark field illumination of the surface the copper atoms can be directly counted. Some experiments made several years ago by Mr. Harold Mott-Smith have shown that this method can be developed to count atoms just as the C. T. R. Wilson method can be used to count ions.

In case the adsorbed atoms on a metallic surface are electrically charged or acquire large dipole moments, electrical forces are brought into play which may make the principle of independent action inapplicable. For example, the rate of evaporation of electrons from a tungsten surface at high temperature is enormously increased by the presence of adsorbed thorium (15) or caesium (16) atoms on the surface. But the increase in the number of electrons which evaporate is not even approximately proportional to the amount of thorium or caesium which is present on the surface. The same is true for the evaporation of positive caesium ions from a tungsten surface. In both of these cases, the heat of evaporation of electrons or ions varies approximately linearly with θ, the fraction of the surface covered by the adsorbed atoms, and thus, according to the Boltzmann equation, the logarithm of the rate of evaporation of electrons or ions varies linearly with θ. In the case of the evaporation of neutral atoms—for example, atoms of oxygen from adsorbed films on heated tungsten filaments—the rate of evaporation is much more nearly proportional to θ.

In studies of the surface tensions of organic liquids (2) (17) and of the properties of adsorbed films of organic substances on water (3) (4) and of oil films on water, the principle of independent action has proved itself particularly useful. It gives immediately a simple reason for believing that these films should rarely be more than one molecule in thickness; or rather, that if they are more than one molecule in thickness, their properties will be markedly different from those of films in which the surface is not completely covered with a single layer. The theory also gives immediately reasons for believing that adsorbed films of many organic substances on water will consist of orientated molecules. Thus the area on a water surface occupied by molecules of the various fatty acids is dependent on an interaction between the carboxyl group and the water, and is independent of the length of the hydrocarbon chain. This simple result, proved by experiment, demonstrates that the molecules are orientated so that the carboxyl group is in contact with the water, leaving the hydrocarbon tails to form a layer above the carboxyl group which will have the properties characteristic of a liquid hydrocarbon.

The theory is equally applicable in pure organic liquids. The total surface energies (surface tension extrapolated to the absolute zero) of hexane and of hexyl alcohol are practically identical. This is readily explained by the orientation of the molecules which prevents the hydroxyl groups from coming in contact with the surface, so that in both cases the actual surface is that of a pure hydrocarbon.

Studies of the surface tension of aqueous solutions of various aliphatic compounds in water prove that in concentrated solutions the surface becomes covered with a closely packed monomolecular film consisting of orientated molecules like those in oil films. With sufficiently dilute solutions, however, the amount of substance adsorbed in the surface is not enough to cover the whole surface with closely packed molecules. Under these conditions, the hydrocarbon chain lies flat in the water surface and the energy needed to transfer any molecule from the surface to the interior increases by a definite amount for each additional CH_2 group in the hydrocarbon chain. This is an excellent example of the application of the principle of independent surface action, each CH_2 group producing its effect independently of the others.

Similar views prove useful in studies of many other properties of matter. Consider, for example, jellies made by amounts of gelatin or soaps in concentrations less than 1 per cent by weight. The elasticity proves the existence of a continuous frame-work of molecules in contact, extending throughout the liquid. The time of relaxation of such jellies serves as a measure of the rate at which the molecules which form the chains separate or evaporate from one another. Guided by these views, I made some experiments, over ten years ago, to determine the diameters of the cross sections of the fibers or rods that must be the elements of the rigid frame-work. For this purpose I made up some dilute gelatin jellies on filter paper and measured the rate at which water could be forced through the jellies by applying a definite pressure. By a modification of Stokes' law which gives the rate of fall of small spheres in liquids, it was possible to calculate the force necessary to move small cylinders of various diameters through a liquid. This law was then checked experimentally by measuring the rate at which water passed through a column of glass-wool having fibers of known size. Applying this law to the case of the motion of water through a gelatin jelly, it was thus possible to calculate the size of the fibers. Only rough experiments were made, but the results showed clearly that the diameter of the fibers was approximately 10^{-7} cm.

I believe that there is real justification for dealing with molecules of this character, at least as a first approximation, as though they followed the same laws as bodies of large size, such as the fibers of glass-wool. Einstein showed, years ago, that Stokes' law could be used, approximately, for the study of the rate of migration of ions through water solutions. I believe that a thorough quantitative study of the forces necessary to drive water through various jellies should give much valuable information as to the structure of these jellies.

Very useful pictures of the mechanism involved in the viscosity of liquids and of diffusion in liquids and solids may be had by considering that molecules in contact exist in two states: one in which the surfaces are rigidly connected, the other in which they are entirely free to move. The behavior of the molecules is thus analogous to that of a gas condensing on a solid; the molecules of the gas strike the surface, remain adsorbed for a certain time, and then evaporate off again. Applying this conception to molecules in liquids, we see that the motion of the molecules past each other, involving viscosity and diffusion, depends upon the relative times during which the molecules are in this rigid, or in this mobile contact. These times can be calculated from an equation of the Boltzmann type in terms of the energy difference between the two states. This theory accounts for the frequent occurrence of temperature coefficients of viscosity and diffusion, which agree with the Boltzmann equation. It seems also to account for the fact that the viscosity of different members of a series of hydrocarbons increases in geometrical proportion to the length of the chain. It would seem that the principle of independent surface action should afford a means for the development of a simple theory of viscosity which would take fully into account the shapes and sizes of the molecules and of the different chemical groups contained in the molecules.

The principle has also found many applications in connection with the mechanism of heterogeneous chemical reactions. The interaction of oxygen and hydrogen and of carbon monoxide and oxygen at low pressures in contact with a heated platinum filament (18) has shown that equations which are based directly on this principle are in excellent agreement with the experimental results over very wide ranges of pressure and temperature. For example, the experiments showed that at low temperatures the reaction velocity was accurately proportional to the partial pressure of oxygen and inversely proportional to the pressure of carbon monoxide. This behavior could be completely accounted for by assuming that the rate of reaction was determined by the rate at which oxygen molecules could reach holes in the films of adsorbed carbon monoxide which were left by evaporation of carbon monoxide molecules, or which were formed by the removal of the carbon monoxide by the oxygen which reached these holes. The poisoning effect of the carbon monoxide was due to the fact that the opportunity for the oxygen to reach the holes was decreased if the carbon monoxide molecules were able to fill up the holes before the oxygen arrived. It seems difficult to reach quantitative agreement with these experiments except by the application of the principle of independent surface action.

The interaction of hydrogen and oxygen in contact with tungsten filaments at temperatures ranging from 1500° to 2500°K is another illustration of a similar kind. Oxygen acts to form WO_3 at a rate proportional to the oxygen pressure (19). Oxygen atoms *in the adsorbed oxygen film* do not react with one another and with the tungsten to form WO_3 even at the highest temperatures. At 1500°K the life of oxygen atoms on the surface is of the order of years; at 1860°K it is about 25 minutes; and at 2070°K it is 15 seconds. When the atoms leave the films at the higher temperatures they do so as free atoms, not as molecules. Thus, even in the presence of minute pressures of oxygen, the tungsten surface is practically completely covered with a single layer of oxygen atoms. Oxygen molecules which strike this surface condense on it, but evaporate from this second layer at a relatively high rate; but while thus adsorbed, they move freely over the surface and are able to fill up any holes that form in the first layer. Also the molecules, while adsorbed in the second layer, have a certain probability of interacting with those of the first layer and with the underlying tungsten to form WO_3, and the holes thus formed by the removal of oxygen from the first layer are soon filled up bythe migration of the molecules of the second layer.

Hydrogen molecules are not able at any temperature to react directly with the oxygen in either of the first or second layers (10), but if they reach the tungsten at one of the holes in the first layer, they react immediately with the adjacent oxygen. Thus when the oxygen pressure falls to a certain low critical value, the hydrogen completely removes all the oxygen from the surface, and it does this suddenly. The hydrogen which then strikes the film is dissociated into atoms to an extent that depends upon the temperature, and the atomic hydrogen formed goes to the bulb and reacts with the WO_3 which has previously been deposited there.

This theory which can readily be stated quantitatively appears to be in complete agreement with all the experimental facts, so that again we find support for the principle of independent surface action.

The molecules in adsorbed films on solutions of organic substances in water are frequently in a state of a two-dimensional gas. Oil films on water may exist as solid or liquid films. In the case of so-called expanded films (12), the heads of the molecules act as a two-dimensional gas, while the tails form a two-dimensional liquid. The molecules of oils adsorbed on solids, such as those that are responsible for some of the lubricating properties of oils, and those involved in the phenomena of flotation of ores, usually show little or no tendency to move over the surface. In other words, the molecules appear to be attached rigidly to the surface.

Many of the equations that were developed in the quantitative studies of the velocities of heterogeneous reactions assumed that bare spots on the surfaces were distributed over the surface according to statistical laws. Such statistical distribution would not occur unless the molecules possessed a certain degree of mobility over the surface, for the molecules that are removed by the reaction are those that are adjacent to holes already existing. Volmer and others have shown experimentally that adsorbed atoms frequently possess great mobility even on solid surfaces and thus act like two-dimensional gases of high viscosity.

I believe that the principle of independent surface action will be useful in studying many properties of organic substances which have hitherto been too complicated to be treated quantitatively. Within recent years I have made some attempts of this kind.

When a liquid is separated into two parts, along a surface having an area of 1 sq. cm., two new surfaces with a total area of

2 sq. cm. are formed. The surface tension or free surface energy measures the work done per unit area in forming the new surfaces. The total surface energy γ, which is equal to the free surface energy extrapolated back to the absolute zero, represents the total energy change per unit area. For all the pure hydrocarbons, such as pentane and nonane, γ is equal to about 48 ergs cm.$^{-2}$. The fact that this value is practically independent of the length of the hydrocarbon chain proves that the surface forces are very nearly uniform over the whole of the hydrocarbon molecule.

When a hydrocarbon, such as hexane, evaporates, molecules pass from the interior of the liquid into the vapor. If we consider a drop of hexane liquid to be removed from a large volume of the liquid into the free space above it, the work that would be needed to form this drop would be equal to $S\gamma$ where S is the surface area of the drop. Since we are regarding molecules as having surfaces possessing certain properties, we may say that the work necessary to remove a single molecule of hexane from the liquid, which is the latent heat of evaporation per molecule, will also be equal to $S\gamma$, where S is now the surface area of the molecule and γ is the surface energy of the molecule per unit area.

The molecular surface S for the molecule of vapor may be calculated from the molecular volumes (molecular weight divided by density), assuming the surfaces to be the same as in the case of closely packed spheres. This assumption would probably be quite accurate for large molecules, but would be only a rough approximation in the short chain hydrocarbons. From the known values of the latent heats of evaporation, the values of γ can then be calculated. Practically all of the normal hydrocarbons, with the exception of methane, give the value $\gamma = 34 \pm 1$ ergs cm.$^{-2}$. This value is of the same order of magnitude as the value 48 found from measurements of surface tension. The fact that γ is found to be constant proves that the work done in removing molecules from the liquid to the vapor phase is strictly proportional to the molecular surface. In other words, the latent heat of evaporation is proportional to the two-thirds power of the molecular volume.

This theory can readily be extended to cover the case of the heats of evaporation of the various aliphatic alcohols. If S is the total surface of the molecule of vapor, then aS is the surface of the head of the molecule (hydroxyl group) while cS is the area of the tail (hydrocarbon chain). We may let γ_a and γ_c represent the surface energies per unit area of the heads and tails respectively when the molecule is in the vapor phase. Thus $Sa\gamma_a$ is the total energy of the head and $Sc\gamma_c$ the total energy of the tail.

If the molecules of alcohol in the liquid phase were arranged at random, that is, if they did not orientate each other appreciably, and did not tend to form clusters (segregation), then it may readily be shown that the total interfacial surface energy in the liquid between the hydroxyl groups and the hydrocarbon chains will be $Sac\gamma_{ac}$, where γ_{ac} is the interfacial surface energy per unit area. We should therefore be able to calculate the latent heat of evaporation, λ, from the difference between the energies in the vapor and liquid phases.

$$\lambda = S(a\gamma_a - ac\gamma_{ac} + c\gamma_c)$$

If we take $\gamma_a = 193$, $\gamma_c = 34$, and $\gamma_{ac} = 34$, we get excellent agreement between the observed latent heats of evaporation and the structures of most monobasic alcohols. We have already seen that γ_c is equal to 34 as the value found for the evaporation of pure hydrocarbons. The value $\gamma_{ac} = 34$ was found as a result of experiments on the vapor pressures of mixtures of alcohol and water. The interfacial energy between water and a hydrocarbon is about 59, so that the value 34 is of the right order of magnitude. The surface energy of water is 117, but this naturally represents the surface energy of the least active part of the water molecule, whereas the energy γ_a equal to 193 corresponds to the most active part of the hydroxyl group so that this value also appears reasonable.

In the case of the alcohols having very long hydrocarbon chains another effect can be clearly seen from the experimental results. In the molecule of vapor the hydroxyl group is able to bury itself at least partially among the coils of the hydrocarbon tail, so that the surface energy of the vapor molecule decreases considerably, beginning with chains of five or six carbon atoms in length.

With shorter chains than this, the hydroxyl group is probably fully exposed. Particularly interesting results which are in good agreement with the principle of independent surface action are found in the case of dibasic and tribasic alcohols. The heat of evaporation depends to a great extent on whether the separate hydroxyl groups are able to come into contact with each other in the molecule of vapor and thereby decrease the surface energy.

The theory can readily be extended to calculate the partial vapor pressures of binary solutions. The complete theory, taking into account orientation and segregation of molecules within the liquid, would be very complicated, but in many cases where the forces between molecules are not too strong, these effects can be neglected in a first approximation. Assuming then a random orientation and distribution of the molecules, the total surface energy per molecule in a solution of any given concentration in terms of interfacial surface energies, such as γ_{ac}, and surface fractions, such as a and c, the work done in transferring a molecule from a liquid to a vapor phase can then be calculated, and thus by applying the Boltzmann equation, it is possible to calculate the deviations from Raoult's law. Thus, the partial pressure of any liquid in a binary mixture is given by

$$p_A = AP_A \exp(\varphi S_A \beta^2/kT)$$

where p_A is the partial pressure of the substance A, the total pressure of the pure component A is P_A; the mole fraction of the component A is represented in this equation by A. The quantity S_A is the surface area per molecule of area; φ is a constant characteristic of the binary mixture but independent of the concentration of the components, which can be calculated in terms of such quantities as a, c, γ_{ac}, etc. The quantity β may be called the surface fraction of the component B in the binary mixture of A and B. It corresponds to the ordinary conception of mole fractions but is expressed in terms of the relative surfaces of the molecules instead of the numbers of the molecules. Thus

$$\beta = BS_B/(AS_A + BS_B)$$

This equation with only one adjustable constant, φ, apparently agrees in general better with experimental data than a somewhat similar equation with two adjustable constants derived by van Laar on the basis of thermodynamical considerations.

C. P. Smyth has recently used this equation in connection with his own measures of the vapor pressures of binary mixtures. The agreement, in most cases, is fairly good, but, as is to be expected in the case of more polar molecules, mixtures of alcohols with water show considerable deviations. It is probable that these can in large part be taken into account by developing the theory further to allow for orientation and segregation of the molecules within the liquid.

Views of the type which I have been discussing may thus be applied quantitatively, often with considerable accuracy, in studying the interactions between molecules of organic substances. The energy relations based on the conception of surface forces between molecules, together with the Boltzmann equation, frequently permit decisions to be made as to the mechanism of various surface phenomena. For example, in expanded films of oils on water it has often been assumed that the molecules could remain erect on the surface without touching one another. Simple energy considerations of the kind which we have been using indicate immediately that this is impossible. The tails of the molecules must remain in contact with each other in the case of long chains, but with shorter chains, the molecules may separate but must then lie flat upon the surface of the water. The principle of independent surface action affords one of the greatest safeguards against the setting up of impossible hypotheses.

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