direct electric lighting circuit. On a 240 volts circuit the current used is 3.5 amperes with 120 volts across the arc. It will be noted that a water supply is necessary, a circulation of four pints per minute being required.

LIGHT BATH TREATMENT BY THE CARBON ARC LIGHT.—The experience of Reyn of Copenhagen, confirmed by other observers, is that the best illuminant is carbon arc light. The spectrum of the carbon arc more nearly approaches that of the sun than does that of mercury vapour, and in the experience of the London Hospital, this is further increased by the use of carbons with a tungsten paste core, tungsten giving a spectrum of great richness in ultra-violet rays.

The installation is very simple. A large carbon arc lamp, working at 50 amperes and 70 volts, is suspended from the ceiling at three to three and a half feet above the floor. Around this, at a distance of from three to four feet, the patients, nude, are seated on stools. The whole of the body is exposed, first the front and then the back, the sittings being of half an hour's duration at first, and these are gradually increased up to four hours a day. When the front of the body is under treatment the eyes are carefully protected by a thick mask. The tungsten paste cored carbons used are (+) cored, 25 mm., (–) solid, 18 mm., both 12 inches long.

GENERAL TREATMENT BY MERCURY-VAPOUR LAMP.—The apparatus consists of a quartz lamp or "burner" containing mercury vapour, behind which are placed reflectors of various shapes. The lamp is mounted on a stand which permits its being placed at an appropriate height. It is worked off any direct electric current, and is inexpensive to run. The practical life of a "burner" is, in the larger types, about 1000 hours. A very high actinic illumination is obtained. The patient lies or stands while under treatment, usually at a distance of about three feet, but with the larger model supplied by the Hewitt Electric Company, the maximum distance at which a patient is sensible of the radiation is eighteen feet. At the beginning of the treatment the exposures are given to small areas, and both the area and the duration may be gradually increased until the whole of the back or front of the body is exposed for half an hour. An inflammatory

reaction, redness, slight vesication with subsequent desquamation, are common, and after a series of exposures, the skin in the majority of patients becomes strongly pigmented. Several of these lamps may be placed in a suitable apartment, the patients being allowed to move about. The mercury-vapour lamp has been used with success in the treatment of tuberculosis of the skin, glands, bones, and joints. Care is required in the dosage, and it is advisable to estimate the intensity of the actinic rays by a chromo-actinometer. This is specially necessary when a new "burner" is installed.

It has been shown that rickets can be prevented in animals fed on a ricket-producing diet if the surface of the body is exposed to the radiations from a mercury-vapour lamp, and there is an important field of usefulness for this form of radiotherapy carried out with due precautions in the treatment of early rickets in children.

CONCLUSION.—The sphere of usefulness of the light bath is being explored in several directions. A committee appointed by the Medical Research Council is studying the biological action of light, and several valuable investigations have been made. Among others it has been demonstrated that the bactericidal power of the blood of animals can be greatly increased by the exposure of the animal to actinic light. Clinical observation shows that there is a remarkable effect upon the metabolism of the human subject; dull, lethargic patients rapidly become bright, cheerful, and active. The body weight increases in many instances. Chronic tuberculous affections of the skin, mucous membranes, bones, and joints heal rapidly. Other chronic processes, such as rheumatoid arthritis, have also been benefited. The value of light in the prevention and treatment of rickets has been noted above. A course of treatment usually lasts three to five months. Patients whose skin pigments well usually do best, but there is no evidence to show that it is the pigmentation which is the curative factor. At present it can only be considered an index. Evidence so far points to the actinic rays producing some possibly chemical change in the blood which gives it greater power to destroy bacteria and their products.

Some Aspects of the Physical Chemistry of Interfaces.¹

By Prof. F. G. DONNAN, C.B.E., F.R.S.

IN recent years a great deal of attention has been paid by chemists, physicists, and physiologists to the phenomena which occur at the surfaces or interfaces which separate different sorts of matter in bulk. Things could happen in these regions which did not occur in the more homogeneous and uniform regions well inside the volume of matter in bulk. A surface or surface layer represents a sort of thin cross section which can be probed and examined much more readily than any part of the inside bulk. The living organisms of plants and animals are full of surfaces and membranes. What can happen at surfaces is therefore a matter of great importance for the science of living things.

An essential characteristic of the ordering or arraying

of molecules and atoms which seems to occur at surfaces may consist in *special orientation*. In the chemical and physical actions occurring in a volume of liquid the bulk of which is large compared with its surface, the molecules or atoms probably move towards each other with every sort of orientation. Should, however, some special orientation be characteristic of interfaces, then it is clear that such interfaces will exhibit new phenomena due to this special sort of arraying. Moreover, if we are dealing with molecules which are ionised into electrically polar constituents, or which, if not actually dissociated, can be treated as electrically bi-polar, it follows that, if orientation occurs at interfaces and surfaces, then electrical double layers and electrical potential differences may be set up at such boundaries.

¹ From the presidential address delivered to Section B (Chemistry) of the British Association at Liverpool on September 14.

The field of force surrounding an attracting molecule may in reality be very "irregular," and may be specially localised around certain active or "polar" groups. Its region of sensible magnitude may be very variable and relatively small compared with molecular dimensions. The chemical constitution of the molecule is now regarded as determining the varying nature of the field of force surrounding it, so that parts of the molecule possessing high "residual chemical affinity" give rise to specially powerful regions of force. In this way the older "physical" theories of cohesion according to central forces with uniform orientation have been to some extent replaced, or at all events supplemented, by "chemical" theories according to which the attractive force-fields are highly localised round active chemical groups and atoms, are relatively minute in range, and can be saturated or "neutralised" by the atoms or groups of neighbouring or juxtaposed molecules.

W. B. Hardy has been the chief pioneer in the development of these newer theories, having been led thereto by his researches on surface tension, surface films, composite liquid surfaces, and static friction and lubrication. If γ_A be the surface tension of a liquid A, γ_B that of another practically immiscible liquid B, and γ_{AB} the interfacial tension at the interface A/B, then the quantity $W = \gamma_A + \gamma_B - \gamma_{AB}$ represents the decrease of free surface energy, and therefore the maximum work gained, when a surface of A is allowed to approach normally and touch a surface of B at constant temperature. Comparing different liquids A with water as a constant liquid B, Hardy has shown that the quantity W is extremely dependent on the chemical constitution of A, and is especially high when A contains the atomic groups characteristic of alcohols, acids, and esters. Thus, for such saturated substances as octane, cyclohexane, CS_2 and CCl_4 , the values of W at ordinary room temperature lie between 21 and 24. Compare with these values the following:

(a) Introduction of a hydroxyl group:	
Octyl alcohol	46
Cyclohexanol	51.4
(b) Introduction of a carboxyl group:	
n-Caprylic acid	46.4
Oleic acid	44.7

The natural inference from results such as these is that the cohesive forces are essentially chemical in origin and that they depend in large measure on the presence of "active" atoms or groups of atoms, namely, those possessing strong fields of "residual chemical affinity"; in other words, powerful and highly localised stray fields of electrical or electromagnetic force (or of both types). The existence of such atoms or atomic groups is strong presumptive evidence of the unsymmetrical fields of force postulated by Hardy and therefore of the molecular orientation at surfaces.

This question of the orientation of molecules at the surfaces of liquids has been greatly extended in recent years by a detailed study of the extremely thin and invisible films formed by the primary spreading of oily substances on the surface of water. In a continuation and development of the work of Miss Pockels, the late Lord Rayleigh showed many years ago that when olive oil forms one of these invisible films on

water there is no fall in surface tension until the surface concentration reaches a certain very small value. He made the highly interesting and important suggestion that this concentration marks the point where there is formed a continuous layer just one molecule thick. In the case of olive oil, he found this critical thickness to be 10^{-7} cm., and concluded that this number represented the order of magnitude of the diameter of a molecule of the oil. This method was greatly developed by Devaux.

Although these researches had firmly established the theory of the formation of a unimolecular surface layer and therefore of the existence of a new "two-dimensional" phase of matter, we owe it to I. Langmuir to have made a very important advance by connecting this conception with the ideas of chemically active groups and molecular orientation. Influenced, no doubt, by the ideas of Hardy, Langmuir reasoned that the formation of these primary unimolecular films must be due to the presence of active groups in the molecules, which are attracted inwards towards the water and thus cause the long open chain molecules of the fatty acids to be oriented on the water surface with their long hydrocarbon axes vertical and side by side.

Working by means of the method of Devaux, Langmuir put these ideas to the test of experiment, and determined the internal molecular dimensions of a unimolecular layer. Calculation of the average distance between two adjacent carbon atoms in the three acids gave the value 1.4×10^{-8} cm. This distance must be of the order of magnitude of the distance between the centres of the carbon atoms in the crystal structure of a diamond, which is now known to be 1.52×10^{-8} cm.

These regularly oriented and unimolecular surface films on water have been recently investigated in a very detailed and careful manner by N. K. Adam, who has improved the method employed by Devaux and Langmuir. From a closer analysis of the relationship between the force of surface compression and the surface concentration (expressed as area occupied per molecule), he has shown that a distinction must be made between the close packing of the polar or active end groups (head groups) of the molecules and the subsequent close packing of the hydrocarbon chains.

Some interesting results have also been obtained in Sir William Bragg's laboratory by Dr. A. Müller. In these experiments layers of crystallised fatty acids on glass plates have been examined by an X-ray photographic method. From these results it appears that the unit cell is a long prism, the cross section of which remains constant for the substances investigated, whilst the length of the prism increases linearly with the number of carbon atoms in the molecule. The increase in length of the unit prism per carbon atom in the molecule is found to be 2.0×10^{-8} cm. Since it appears likely that there are two molecules arranged along the long axis of each unit cell (prism), it would follow that the increase in the length of the molecule per carbon atom added is 1.0×10^{-8} cm. Comparing this result with the value for the distance between the carbon centres in the diamond lattice, it would appear that the carbon atoms in the long hydrocarbon chains of the higher saturated fatty acids are arranged in a zig-zag, or more probably in a spiral or helix.

If this be the case, the closer packing or compression of the juxtaposed molecules in the unimolecular films, as revealed in the investigations of Devaux, Langmuir, and Adam, may be to some extent explained by the straightening out of these zig-zags, or perhaps by the "elastic compression" of the helices.

As pointed out by Langmuir, the question of the formation of unimolecular surface films can be attacked in a different manner. It is known that gases or vapours can be condensed or adsorbed by solid and liquid surfaces. The question then arises, does the formation of primary unimolecular films ever occur in such cases? It will be recollected that Hardy made the suggestion that the formation of the primary unimolecular film in the spreading of oily substances on water might be due to adsorption from the vapour. In order to examine this question, Mr. T. Iredale has recently measured in my laboratory the fall in the surface tension of mercury caused by exposing a fresh mercury surface to vapours of increasing partial pressure. The excess surface concentration q of the adsorbed vapour can then be calculated by means of Gibbs's formula

$$q = - \frac{\rho d\gamma}{dp},$$

where γ = surface tension, and ρ and p denote the density and partial pressure of the vapour respectively. Working with the vapour of methyl acetate, Iredale found in this way that at a temperature of 26° C. and a partial pressure of 62 mm. of mercury, $q = 4.5 \times 10^{-8}$ gm. per square centimetre of surface. From this result we can readily calculate that there are 0.37×10^{15} molecules of methyl acetate adsorbed per sq. cm., and that the area per molecule is 27×10^{-16} sq. cm. As under the conditions corresponding to this calculation the molecular surface layer was probably not quite saturated (in the unimolecular sense), we may expect the value found to be of the same order of magnitude but somewhat greater than the values found by Adam for the cross section of the head group of the higher saturated fatty acids (25×10^{-16}) and of the esters (22×10^{-16} for ethyl palmitate and ethyl behenate). We may, therefore, say that Iredale's results appear to indicate the formation of a primary unimolecular layer built up by adsorption from the vapour phase.

Langmuir has measured the adsorption of a number of gases at low temperatures and pressures on measured surfaces of mica and glass, and has arrived at the conclusion that the maximum quantities adsorbed are always somewhat less than the amounts to be expected in a unimolecular surface layer. E. K. Carver, who has measured the adsorption of toluene vapour on known glass surfaces, has arrived at a similar conclusion. The view that the *maximum* adsorption from the gas phase cannot exceed a unimolecular layer has, however, been much criticised.

Let us now consider another type of formation of surface layers at the surfaces of liquids—namely, the case where a substance dissolved in a liquid concentrates preferentially at the liquid-air or liquid-vapour interface. Gibbs, and later J. J. Thomson, have shown that if a dissolved substance (in relatively dilute solution) lowers the surface tension, it will concentrate

at the surface. That such a phenomenon actually occurs has been qualitatively demonstrated in the experiments of D. H. Hall, J. von Zawidski, and F. B. Kenrick and C. Benson, by the analysis of foams and froths. In 1908 S. R. Milner used the same method in the case of aqueous solutions of sodium oleate, and arrived at a mean value of 1.2×10^{-10} gram mols. excess concentration per sq. cm. of surface. In the case of dilute solution, we can calculate q , the amount concentrated or "adsorbed" in the surface per sq. cm. (excess surface concentration), and Milner calculated from Whatmough's data for aqueous solutions of acetic acid that the "saturation" value of q is 3.3×10^{-10} mols. per sq. cm., from which it follows that the area per molecule in the surface is 50×10^{-16} sq. cm. In a similar manner, Langmuir has calculated from B. de Szyszkowski's data for aqueous solutions of propionic, butyric, valeric, and caproic acids that the surface area per molecule adsorbed in the saturated layer is equal to 31×10^{-16} sq. cm., while Harkins has arrived from his own measurements for butyric acid at the value 36×10^{-16} sq. cm.

In 1911 Dr. J. T. Barker and I made a direct determination of q for a solution of nonylic acid in water. For a practically saturated surface layer it was found that q was about 1.0×10^{-7} gm. per sq. cm., or 3.1×10^{14} molecules per sq. cm. From this result it follows that the surface area per molecule is 26×10^{-16} sq. cm.

These values are not very different from the values found by Langmuir and by Adam for the oriented unimolecular layers of practically insoluble fatty acids resting on the surface of water. That in the present case some of the values are larger might easily be explained on the ground that these adsorption layers are partially, or completely, in the state of "surface vapours." For Adam and Marcelin have recently made the important discovery that the unimolecular surface films investigated by them may pass rapidly on increase of temperature from the state of "solid" or "liquid" surface films to the state of "vaporised" surface films, in which the juxtaposed molecules become detached from each other and move about with a Brownian or quasi-molecular motion.

It is, indeed, highly probable that the molecules which are concentrated in the surface from the state of solution in the liquid phase are not in quite the same situation as the molecules of practically insoluble substances which are placed *on* the surface. In the former case the molecules are still "dissolved," so that they will be more subject to thermal agitation and less able to form a juxtaposed unimolecular layer. They may also be "hydrated." Nevertheless, the agreement as regards order of magnitude in the values of the surface area per molecule in the two types of case is certainly very suggestive and significant.

Let me now direct attention to another very interesting phenomenon relating to the surfaces of liquids and solutions—namely, the existence of an electrical potential gradient or potential difference (P.D.) in the surface layer. The liquid-gas interface offers the simplest case of such interfaces, so the investigation of the potential differences which may exist at this interface is a matter of fundamental interest. In 1896 F. B. Kenrick developed,

on the basis of earlier experiments of Bichat and Blondlot, an electrometric condenser method for the comparative determination of the gas-liquid P.D.'s. The results which he obtained show that substances (such as the aliphatic alcohols and acids) which concentrate at the surface produce a very great change in the surface P.D., whilst highly dissociated univalent inorganic salts, such as potassium chloride, do not. The results obtained by Kenrick have been much extended by an investigation carried out with the same type of apparatus by Prof. T. Thorwaldson in my laboratory. The general result of these experiments can be described in the following terms:

Consider the system:

Aqueous solution of KCl (conc. = c) A	Air	Aqueous solution of KCl (conc. = c) B
--	-----	--

The positive potential of A will be equal to that of B. If we now add to the solution B a small quantity of a substance S (generally a non-electrolyte or weak electrolyte) which has a strong tendency to concentrate at the air-B interface, it is found that the positive potential of A rises markedly above that of B, the value of the quantity, positive potential of A minus that of B, varying with the concentration of S in the way that is characteristic of adsorption phenomena. What is the interpretation of this phenomenon?

Quincke has shown that a bubble of air in water placed in an electrical potential gradient travels towards the anode—i.e. the bubble behaves as if it were negatively charged. From this it would follow that the P.D. at the air-water interface is such that the *negative* half lies towards the air side. As an electrolyte such as potassium chloride is negatively adsorbed at an air-liquid surface, it is probable that a P.D. of the character indicated by Quincke's experiment exists at the A-air interface. If we accept this conclusion, it follows that the effect of S is markedly to *reduce* this P.D. (or to reverse it). Now the P.D. at the air-water interface is probably due to the existence of a double layer containing hydroxyl ions on the outside and hydrogen ions on the inside, or to oriented water molecules regarded as electrical bi-poles. If S is a non-

electrolyte (or a substance which possesses little self-ionisation), we can understand why its concentration at the surface could result in the reduction of this P.D.

Within the last few years H. A. McTaggart has made a number of experiments on the electric cataphoresis of gas bubbles in aqueous solutions and other liquids. He finds that aliphatic acids and alcohols in aqueous solution reduce the surface P.D., and that this effect runs parallel with their influence on the surface tension of water. He also finds that acids reduce the P.D. These results may be regarded as a corroboration of those obtained by Kenrick. McTaggart has found that the nitrates of tri- and tetravalent cations have a powerful effect in not only reducing but even reversing the P.D. (i.e. the bubble becomes positively charged). His experiments also show that polyvalent negative ions, such as the ferrocyanide ion, act in the opposite direction to the polyvalent cations—i.e. they increase the negative charge on the bubble or diminish a previously existing positive one.

The subjects which I have been discussing have an interesting bearing on the formation and stability of foams and froths. If air be violently churned up with water, only comparatively large bubbles are produced, and these quickly rise to the surface and burst. If now a very small quantity of a substance which concentrates at the air-water interface be added, an almost milk-white "air emulsion" of small bubbles is produced, which rise to the surface and produce a relatively durable froth. It is clear that the diminution in interfacial tension facilitates the subdivision or dispersal of the air. The existence of the surface layer will also confer a certain amount of stability on the resultant froth, since it will give rise to forces which resist the thinning of a bubble wall. Any sudden increase in the surface will produce a momentary diminution in the concentration or "thickness" of the surface layer, and hence a rise in surface tension, which will persist until the normal thickness or concentration is readjusted by diffusion of molecules from the inside volume—a process which in very dilute solution will occupy a perceptible time.

(To be continued.)

Obituary.

DR. ALEXANDER GLEICHEN.

THE sudden and unexpected death of Dr. Alexander Gleichen on October 21 is reported from Berlin. Born at Niederschönweide on September 23, 1862, Dr. Gleichen commenced his higher education at the Neu-Ruppiner Academy, and later studied mathematics and natural philosophy at the University of Berlin. After passing his final examination at the University of Kiel, he became an assistant and then a head teacher at the Kaiser-Wilhelm Academy. At the same time he acted as "Privatdozent" at the Technical High School of Charlottenburg, where he lectured upon geometrical optics, a subject with which his name will always be associated. He also lectured upon mathematics at the Helene Lange College for Women.

Dr. Gleichen's academic career terminated in 1904, when he was called to the German Patent Office, with

which he was connected until the end of 1918. While thus occupied, he was able to produce the *Archiv für Optik*, and later to act as editor of the scientific and technical sections of the optical and mechanical central journal. From 1919 until his death Dr. Gleichen was engaged in the scientific work of the C. P. Goerz optical establishment, where the opportunity was afforded him of applying his special knowledge of ophthalmic theory to the satisfaction of the ever-increasing demands of the spectacle industry.

Beyond Germany, Dr. Gleichen is best known as a writer of optical text-books of particular value to the student whose object it may be later to apply his knowledge to the practice of the art. This combination of theory and practice is most marked in his "Schule der Optik," published in 1914, and in his "Theorie der modernen optischen Instrumente" of 1911. The latter