complete castration and suffered from want of vigour and general apathy. Lichtenstern then engrafted an undescended testicle from another individual, and as a consequence the symptoms of castration disappeared and the man became normal. Two and a half years later he was still normal, having been married fifteen months. Further cases of testicular transplantation in men are recorded by Lichtenstern as well as by Kreuter and Mühsam, the operation being performed for eunuchoidism and homosexuality, as well as for debility and impotence, and successful results are claimed. In none of these cases does there appear to be definite evidence as to the fate of the graft, but it would appear almost certain that it must have persisted for some time.

Voronoff, whose work on the so-called "monkey gland" has attracted so much attention, began his experiments on the testicular graft at the Collège de France in 1917. His earlier work was upon sheep and goats, in which he grafted young testes into old animals and into animals castrated before puberty. The best results were obtained by grafting the testes into the scrotal sacs, or in the case of aged animals, upon the testes already present. Retterer and Voronoff, in a paper published last summer, tell us that some of these animals are still under observation at the Laboratory of Experimental Surgery of the Collège and that they continue to display sexual vigour and ability to copulate. The success attending these experiments led Voronoff to attempt testicular transplantation upon aged men. In connexion with this work, two points are strongly emphasised; first, the advantage of making the graft in a suitable position and preferably the natural position of the organ; and secondly, the importance of biological affinity between the individual from which the testis is taken and the recipient of the graft; consequently, in carrying out testicular transplantation from animals to men, Voronoff selected the chimpanzee as the most suitable animal from which to obtain the graft, since of all the anthropoid apes this species is believed to be the nearest akin to man. The result of the operation in many instances is claimed to be entirely successful. The walls of the arteries are said to have become softened and the capacity for work increased, and, in short, a complete restoration of mental and muscular vigour is stated to have been attained. In the majority of men so operated upon sexual potency also is said to have been revived.

In some of Voronoff's experiments there is definite evidence concerning the persistence of the graft, and Retterer and Voronoff have described microscopic sections of graft tissue after several months of transplantation. Thus the figure of a section of a goat's testis a year after grafting shows cells which might

reasonably be supposed to have had an internally secreting function, though the tissue as a whole had undergone considerable degeneration and neither spermatozoa nor interstitial cells can be detected. The authors state that the condition of the transplanted chimpanzee's testis is similar, but they do not appear to have recorded the duration of the graft. On the other hand, Thorek, an American surgeon, who has recently confirmed Voronoff in regard to the persistence and efficacy of the chimpanzee graft when made upon man, has described and supplied photographs of sections of such grafts when removed four months after transplantation, and these show an abundance of secretory cells and every evidence of active life, though the seminiferous tubules had undergone incomplete regression. The good results are attributed to a new technique whereby the vascularisation of the graft was greatly improved.

There is one point of importance on which Retterer and Voronoff differ from most physiologists, and this relates to the elements which are responsible for producing the internal testicular secretion. The bulk of the experimental evidence is strongly in favour of the view that the testicular hormone is elaborated by the interseminiferous or interstitial cells, and Steinach, who has called this tissue the "puberty gland," attributes the supposed rejuvenating effects of vasectomy to the hypertrophy of this gland, pointing out that the spermatogenetic tissue after this operation undergoes degeneration as noted by former observers. According to the French investigators, however, the testicular graft does not contain interstitial cells, the rejuvenating function being due to the epithelial cells which continue to discharge the problematical secretion into the circulation notwithstanding the fact that they become converted by poverty of nutrition into "young connective tissue." On the other hand, in Thorek's preparations, the interstitial cells have proliferated and appear to have been functionally active.

In conclusion, it must be emphasised that the work is as yet in the experimental stage. In many of the cases recorded the effects of "suggestion" are not satisfactorily excluded, and the evidence as to the persistence of a functional graft is still meagre. That the histological results are conflicting and that those of Voronoff are contrary to the usual view as to the source of origin of the hormone, are valid reasons for reserving judgment. Nevertheless, it must be pointed out that the accumulation of evidence in support of the contention that a testicular graft obtained from another individual, and even from another species, may exert a definite physiological influence upon the recipient, is considerably greater than many men of science have so far been disposed to admit.

Some Aspects of the Physical Chemistry of Interfaces.¹

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

LET us now inquire how far the phenomena which are characteristic of a gas-liquid interface occur also at the interface between two immiscible or partially miscible liquids. Many years ago it was shown by Gad and by Quincke that a fatty oil (such as olive oil)

is very readily dispersed in the form of an emulsion by a dilute solution of caustic soda. Some experiments which I once made showed that a neutral hydrocarbon oil could be similarly emulsified in a dilute aqueous solution of alkali if one of the higher fatty acids was dissolved in it, whilst the lower fatty acids do not

¹ Continued from p. 870.

produce a similar action. It was shown that the action runs parallel to the lowering of interfacial tension and must be ascribed to the formation of a soap, which lowers the interfacial tension and concentrates at the interface. These phenomena have been further investigated by S. A. Shorter and S. Ellingsworth, by H. Hartridge and R. A. Peters, and by others.

If a substance which is dissolved in one liquid A, and is practically insoluble in another liquid B, is found to have, in very dilute solutions, a strong effect in lowering the tension at the interface A-B, the following interesting questions arise:

(1) What is the amount of the surface concentration or adsorption per sq. cm. of interface?

(2) Can it be calculated by means of the simplified Gibbs equation?

(3) How does the surface adsorption vary with the concentration?

(4) Does the "saturation" value correspond to the formation of a unimolecular layer?

Some of these questions were experimentally investigated in my laboratory by W. C. McC. Lewis. For the liquid A water was chosen, and for B a neutral hydrocarbon oil. Working with sodium glycocholate as the surface-active substance, it was found that the experimentally measured surface adsorption q was much greater than that calculated by means of the equation

$$q = - \frac{cd\gamma}{RTdc}$$

Comparing the values with those previously obtained for the air-liquid surface, it is clear we are not dealing with simple unimolecular layers, but with adsorption layers or films many molecules thick. On the other hand, if we calculate from Lewis's results the surface area per molecule as deduced from the surface tension measurements by the simplified Gibbs formula, we arrive at values which are consistent with the gradual building up of a unimolecular layer (of possibly heavily hydrated molecules or micelles). It is possible, therefore, that the Gibbs equation gives the surface concentration of the primary unimolecular "two dimensional" surface phase, and that any building up of further concentrations beyond this layer does not affect the surface tension. In a later investigation Lewis determined the surface adsorption of aniline at the interface mercury-aqueous alcoholic solution, and found in this case a very fair agreement between the observed and calculated results. This case is more favourable, since we can be in little doubt concerning the molecular weight of the solute units. We may conclude, therefore, that Lewis's measurements in this case point to the building up of a primary unimolecular layer, unaccompanied by any further concentration or "condensation" of molecules or colloidal micelles.

Experiments similar to those of Lewis have been very recently made by E. L. Griffin, who has measured directly the adsorption of soaps from aqueous solutions at a mineral oil-water interface. The results obtained are as follows:

Substance.	Average Surface per Molecule adsorbed.
Sodium Oleate	48×10^{-16} sq. cm.
Potassium Stearate	27×10^{-16} sq. cm.
Potassium Palmitate	30×10^{-16} sq. cm.

NO. 2825, VOL. 112]

These figures are very interesting, for they would appear to indicate the formation of unimolecular surface layers.

We have seen that in the case of the air-water surface there exists an electrical separation or potential difference in the surface layer, and that certain substances can produce pronounced variations, or even reversals in sign, of this electrical double layer. It becomes a matter, therefore, of great interest to inquire whether similar phenomena occur at the interface between two immiscible liquids, and, if so, to ascertain whether such electrical charges or double layers bear any relation to the "stability" of pure emulsions, or fine dispersions of one liquid in another. It is well known that those disperse or finely heterogeneous states of matter known as colloidal solutions depend in part for their stability on the existence of such electrical potential differences. We might expect, therefore, that an investigation of these emulsion systems would throw some light on the general theory of what are called "suspensoid" or "lyophobic" colloidal states.

Investigations with these objects in view were carried out some years ago in my laboratory by R. Ellis and F. Powis. The method employed was to measure directly by means of a microscope the motion of minute globules (suspended in water) under the influence of a known electric field. From the measured velocity and potential gradient, the interfacial P.D. and the electrical charge can be calculated from the theories of Helmholtz, Lamb, and Stokes. The microscopic method has the advantage that the P.D. between the aqueous solution and the glass wall (cover glass or object glass) can be determined simultaneously. It is a remarkable fact that the P.D. between various types of hydrocarbon oils (purified from acid so far as possible) and water was found to be 0.045-0.053 volt, the oil being negative—that is to say, the oil droplet moving towards the anode. If we compare this with the value recently calculated by McTaggart for the P.D. between an air-bubble and water (deduced from a precisely similar type of measurement), namely 0.055 volt, we can draw the conclusion that the potential difference is due to an electric double layer residing in the *surface layer of the water*. The oil droplet moves, therefore, with an attached negative layer or surface sheet, probably determined by hydroxyl ions, this being balanced by a positive layer the charge of which is determined by hydrogen ions.

Perhaps the most remarkable result which has emerged from these electrical investigations of oil suspensions is the relation between the stability of the emulsion and the potential difference of the interfacial double layer. The minute oil globules are in constant Brownian motion and must frequently collide. Why do the forces of cohesion not produce agglomeration or coalescence (coagulation or clearing of the emulsion)? At distances great in comparison with their own dimensions the electric double layers will act practically as closed systems. But when two oil drops approach sufficiently near each other the conditions will be different, since we must expect a repulsive force when two similarly charged outer layers just begin to interpenetrate each other. Hence the answer to the question asked above is that the third factor is the potential difference or electric density of the interfacial double

layer. Other things being equal, the probability P of an encounter leading to coherence will be a diminishing function of the electric intensity π of the similarly constituted double layers, *i.e.* $dP/d\pi$ will be negative. Hence, of the total number of encounters in a given small period of time, the number which lead to coherence should be a maximum at the point of zero potential difference (iso-electric point of Hardy).

Now the experiments of Powis brought out the very important fact that when the interfacial P.D. (whether positive or negative) is above a certain value, which was about 0.03 volt for his conditions, the rate of coagulation or coherence of the oil drops is relatively small, but rapidly increases when the P.D. falls inside the zone $-0.03 + 0.03$ volt. Under definite conditions there exist, therefore, what we may, speaking broadly, call a *critical potential* and a *critical potential zone*. When the P.D. is outside this zone the emulsion is comparatively very "stable." Very small concentrations of electrolytes, which, as we have seen, increase the P.D., increase this stability. As soon as the concentration of any electrolyte is sufficient to bring the P.D. into the critical zone, the stability of the emulsion undergoes a sudden and very marked decrease, and relatively rapid coagulation occurs. Take, for example, the case of thorium chloride. On increasing the concentration we find that the interfacial P.D. traverses successively the following regions:

- (1) Above the critical value (and negative).
- (2) Inside the critical zone (negative and positive).
- (3) Above the critical value (and positive).
- (4) Below the critical value (and positive).

In exact correspondence with this series we find that the emulsion goes through the following states:

- (1) Stable (oil particles "negative").
- (2) Unstable and flocculating (oil particles negative or positive).
- (3) Stable (oil particles positive).
- (4) Unstable and flocculating (oil particles positive).

Here we see a very striking analogue and explanation of the phenomena observed by Joly in studying the effect of aluminium salts on the sedimentation of clays, and of the numerous examples of the so-called "irregular series" observed in the flocculation of suspensoid hydrosols by salts with polyvalent cations.

As Linder and Picton showed, when two suspensoid hydrosols, one negative and the other positive, are mixed, then, depending on the ratio, a stable hydrosol (either positive or negative) can be obtained. In continuation of this work, W. Biltz demonstrated the existence in such cases of a "zone of coagulation," *i.e.* a zone of concentration ratios leading to coagulation. A study of the mutual behaviour of a negative oil emulsion and the positively charged ferric oxide hydrosol provides a complete explanation of this curious phenomenon. When increasing amounts of the iron oxide hydrosol are added to the oil emulsion, it is found that the interfacial P.D. falls to zero, and then reverses its sign, becoming increasingly positive—an action which is due to the adsorption of the positively charged micelles at the oil-water interface. When the P.D. is above a certain value (positive or negative) the system is stable. But within the critical zone a rapid and relatively complete mutual coagulation takes place.

These studies of oil emulsions (and of the glass-water interface), by means of the micro-cataphoresis method, have thrown a great deal of light on many previously ill-understood points in the theory of colloids. The following table contains the concentrations (in millimols per litre) of certain electrolytes required to reduce the potential of a certain hydrocarbon oil emulsion from its "natural" value (against pure water) of 0.046 volt to the critical value, 0.03 volt:

—	Concentrations.	Ratios of Concentrations.
KCl . . .	51	2500
BaCl ₂ . . .	1.9	95
AlCl ₃ . . .	0.020	1
ThCl ₄ . . .	0.0070	0.35

These results show the enormous influence of the valency of the cation in a series of salts with the same univalent anion, and explain in a striking manner the analogous effects in the coagulation of lyophobic hydrosols. The exact value of the critical potential and the range of the critical zone will depend, of course, on the experimental definition of "rapid coagulation," and on the concentration, nature, and degree of dispersion of the hydrosol. It is not to be supposed, therefore, that these critical values are constants except under very definite conditions. The fundamental fact is that under given conditions the rate of coagulation of the particles of an oil suspension or of a lyophobic hydrosol undergoes a relatively sudden and very great increase when the interfacial P.D. falls below a certain finite value (positive or negative).

In discussing the "stabilities" of hydrocarbon oil emulsions, it must not be forgotten that I was dealing with very dilute *suspensions* of oil in water, produced by mechanical agitation without the addition of any "emulsifier." I pointed out that in the emulsification of oils in water by means of soap, the soap lowers the interfacial tension and concentrates at the interface. When we wish to produce oil emulsions in the ordinary sense of the term, we must use some such emulsifying agent, and for this purpose many substances are employed, such as soap, gum acacia, gelatin, casein, starch, etc., etc. All these substances concentrate or condense on the surfaces of the oil globules. If we may regard these surface films as very mobile from the molecular-kinetic point of view, it is clear that they will confer an increased degree of stability on the emulsion.

It is probable, however, that the stability of the emulsion is in many cases due to the fact that the surface films possess a very viscous, quasi-rigid, or gel-like character, so that a more mechanical explanation is necessary. As S. U. Pickering showed, oils may be emulsified in water by the gels of certain basic salts; and A. U. M. Schlaepfer has shown that emulsions of water in kerosene oil may be obtained by means of finely divided "carbon." Nevertheless, even in cases where an emulsifier is used, we may hope to succeed in obtaining a more precise physical analysis of the system. It is interesting in this connexion to note that Mr. W. Pohl has recently found in my laboratory that when a neutral hydrocarbon oil is emulsified in

water by means of sodium oleate, the electrical potential difference at the oil-water interface is almost doubled, and that the effects of alkalis and salts on this potential difference are very similar to those found in the case where no emulsifier is employed.

I cannot conclude this account of certain aspects of surface actions and properties without making a passing, though all too brief, reference to the beautiful investigations of Sir George Beilby on the amorphous layer. He has shown that when the surface of crystalline matter is subjected to shearing stress there is produced a surface layer of a vitreous or amorphous character—a “flowed” surface—in which the particular ordered arrangement of the molecules or atoms which is characteristic of the crystalline matter largely disappears. Working at University College, London, Dr. Travers and Mr. R. C. Ray have recently obtained a very interesting confirmation of the Beilby effect. The heats of solution (in kilogram calories per gram mol) of vitreous silica and silver sand (silica as crystalline quartz) in aqueous hydrofluoric acid were found to be

37.24 and 30.29 respectively. After grinding for fifteen hours the corresponding values were 36.95 and 32.46 respectively. If we assume that the internal energy of the amorphous phase produced by grinding is the same as that of the vitreous silica (silica glass), we can calculate from these results that about 31 per cent. of the crystalline silica has been converted by grinding into “amorphous” silica. The densities of silica glass and silver sand were found to be 2.208 and 2.638 respectively. After fifteen hours’ grinding the density of the latter was lowered to 2.528. On the same assumption as before, it follows that about 26 per cent. of the quartz has been converted into the vitreous condition. The difference between the figures 31 and 26 is doubtless due to the approximate character of the assumption underlying the calculations and to experimental errors. There seems little doubt, however, about the soundness of the main conclusion—namely, that the mechanical action of shearing stress on crystalline matter is to produce a random molecular or atomic distribution in the surface layers.

Obituary.

MR. J. M. WILKIE.

MR. JOHN MATTHEW WILKIE died on November 29 after an operation. He was born at Montrose in 1876, and was educated as a pharmaceutical chemist; after passing his minor in Edinburgh he went to Derby and later to London. In 1900 he was appointed as an assistant analyst, and eventually deputy chief analyst, in the laboratory of Boots Pure Drug Co., where he remained until his death.

Perhaps the best known of Mr. Wilkie’s researches were the estimation of small quantities of lead, published with Mr. Harvey, the silver methods for the determination of phosphoric acid, and the alkaline iodine oxidation of phenols, the last two researches being published in the journal of the Society of Chemical Industry. He also devised a most ingenious method for the estimation of sulphur and oxidised sulphur compounds, which depended on the formation of acid by the bromine oxidation, but this research has only been published in abstract, as he was never quite satisfied that he brought it to a satisfactory completion. These sulphur oxidation methods have, however, been in use at Messrs. Boots’ laboratory for some years with most satisfactory results. The last four years of his life was devoted to an almost monumental research on the determination of minimal quantities of arsenic. Step by step he patiently investigated the points of the method, and at the time of his death his work was concluded, and he was engaged in putting his notes into order for publication. This research was given to the world in abstract at the joint meeting of the Society of Public Analysts with the Nottingham Section of the Society of Chemical Industry at Nottingham on January 17 last.

As secretary to the Nottingham Section of the latter society from 1914 to the present year, he was largely responsible for the success of that Section and the great increase in the membership. He had just become chairman of the Section, and, although he had only presided at one meeting, he signalled that by inaugurating a discussion in which a large number of

young members were persuaded to take part. It was always Wilkie’s policy to encourage and bring forward young talent, so much so that at Mrs. Wilkie’s special request he was borne to his last resting-place by the young men that he used to encourage and talk about so often.

THE issue of *Science* of November 23 contains an appreciative account, by “H. H. W.,” of the life and work of Prof. Robert Wiedersheim, the distinguished professor of anatomy in the University of Freiburg, who died on July 12. Wiedersheim was born on April 21, 1848, at Nürtingen-am-Neckar, and went in succession to the Universities of Tübingen and Würzburg. At Würzburg he obtained his M.D. and became assistant professor under Kölliker (1872–76). In 1876 he went to Freiburg as assistant to Prof. Alexander Ecker, whom he succeeded as professor of anatomy in 1887. This post he held until he retired from active work in 1918. Wiedersheim’s work lay in the fields of human and comparative anatomy. In 1882 he published his “Lehrbuch der vergleichenden Anatomie der Wirbeltiere,” following up this work with the “Grundriss der vergleichenden Anatomie,” covering the same ground in a more concise manner. The last edition of the latter, the seventh, appeared in 1909. A modified translation of the “Grundriss,” by Prof. W. N. Parker, was published in 1886 by Messrs. Macmillan and Co., Ltd. He also published a number of monographs, among which “Das Kopfskelet der Urodelen,” that on the ear of the Ascalaboten, the anatomy of *Salamandrina perspicillata* and *Geotriton fuscus* are best known. With his death an outstanding figure in the history of the comparative anatomy of vertebrates has passed away.

WE regret to announce the following deaths:

Mr. George Wharton James, of Pasadena, California, known for his work on American Indian ethnology, on November 8, aged sixty-five.

Prof. H. Freeman Stecker, professor of mathematics in the Pennsylvania State College, a worker in non-Euclidean geometry, on October 30, aged fifty-six.