Second Liversidge Lecture.

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Surface Forces and Chemical Equilibrium.

I INTEND to discuss a problem of surface chemistry. It is well known that surface reactions are of the greatest importance in technical and biological processes. But these reactions are generally very complicated and it is therefore worth while to examine what we know about the simple case of a chemical equilibrium being influenced by surface forces.

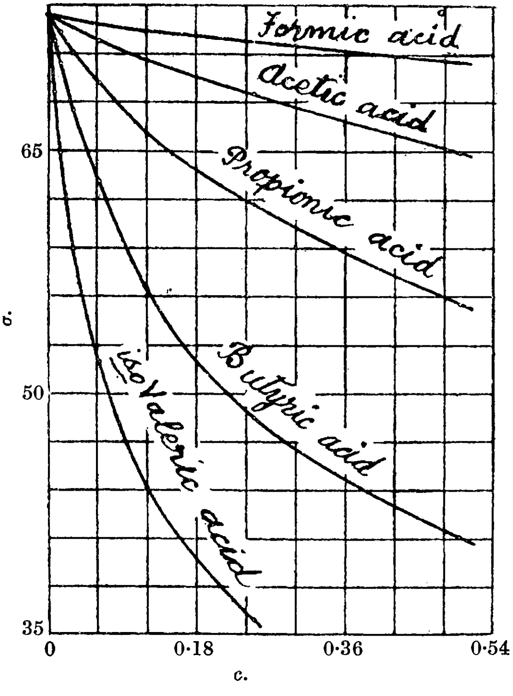
J. J. Thomson ("Applications of Dynamics to Physics and Chemistry," London, 1888, p. 234) was the first to point out that a chemical equilibrium ought to be influenced by capillarity. This celebrated treatise has always appeared to me as the true successor of Gibbs's thermodynamical papers from which the chemist of to-day may still derive many suggestions. In it we find the sentence : "If the surface tension increases as a chemical action goes on, the capillarity will tend to stop the action, while, if the surface tension diminishes as an action goes on, the capillarity will tend to increase the action." Thomson attempted to prove this theoretical conclusion by experiments on the so-called "dead space." As is well known, alkali acts on chloral hydrate in aqueous solutions to yield chloroform, which separates throughout the solution as a white deposit of droplets except for a thin surface film where the solution is in contact with the air. This phenomenon was noticed first by Liebreich (*Z. physikal. Chem.*, 1890, **5**, 529). Now Monkman showed that the surface tension increases while this reaction is proceeding. This might at first sight make an explanation of the "dead space" possible on the assumption that the formation of the chloroform is retarded in the surface, since surface tension increases. Yet, however satisfactory this explanation may appear, it is inadequate. The real explanation is probably much simpler. Budde (*ibid.*, 1891, **7**, 586; *Wied. Ann.*, 1892, **46**, 173) showed that the absence of chloroform droplets in the uppermost layer is probably merely the result of evaporation, the whole phenomenon being most sensitive to small differences in temperature. This earlier attempt to verify Thomson's theory was therefore not altogether successful.

In the 40 years which have elapsed since then, a number of investigators have taken up this question. No case has been found simple and clear enough to afford a complete test of the theory;

the facts, however, agree with it on the whole. Before entering upon these investigations in detail, permit me to discuss some generalisations which I shall use.

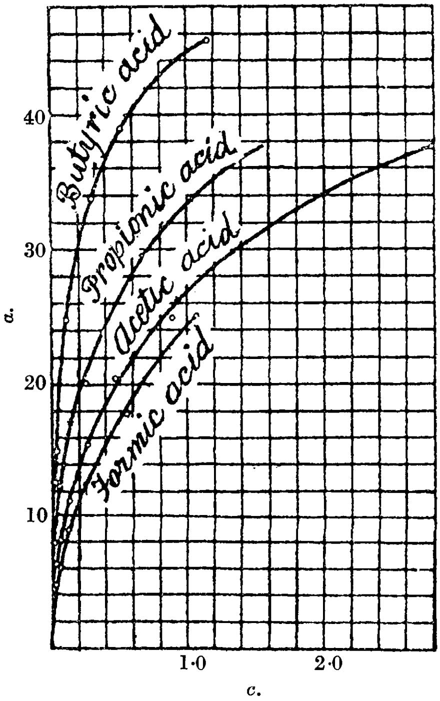
Increase and decrease of surface tension caused by the dissolved substances are related to a change of concentration of these substances in the surface according to Gibbs's equation. If the surface tension increases or decreases with increasing concentration, the surface contains respectively less or more of the dissolved substance than the liquid in bulk. Let us call this change of concentration in the surface "adsorption." We then may assume that a substance is adsorbed negatively if it raises the surface tension, and is adsorbed positively if it lowers the surface tension. And Thomson's relation between capillarity and chemical equilibrium may be expressed in the following way: the displacement of chemical equilibrium in a surface takes place in a direction favouring those substances which lower the surface tension and are therefore adsorbed positively. Such substances are said to exert "capillary action," an expression which is perhaps not defined quite sharply.

FIG. 1.



It may be rather bold not to confine these speculations to liquid–gas or liquid–liquid surfaces, where we are really able to measure surface tension, but to extend them to surfaces of solid substances. Here we are not able to measure surface tension, at least not with any degree of precision, but we can easily enough find phenomena which may be considered as phenomena of adsorption. There is a great similarity in the behaviour of these different boundaries. Let me remind you of two facts. First, the so-called rule of Traube holds good in aqueous solutions even if the second phase is a gas, a liquid such as mercury, or a solid such as charcoal. According to this rule, capillary activity increases strongly and regularly as we ascend any homologous series of organic substances. This becomes clear, for instance, in the decrease of surface tension in solutions of fatty acids as shown in Fig. 1, and in accordance with Gibbs's rule the adsorption increases as we rise in such a series. Figs. 2 and 3 show adsorption isotherms of fatty acids on charcoal and on siloxen ($Si_6O_3H_6$), an enormously porous and strongly adsorbing substance prepared from calcium silicide ($CaSi_2$). The second fact is that organic (and many inorganic) acids and bases exhibit much greater capillary activity than their salts: they lower the surface tension more strongly and are accordingly adsorbed in a higher degree by most adsorbents. This may be explained by assuming that the ions are less active in this respect than the undissociated molecules.

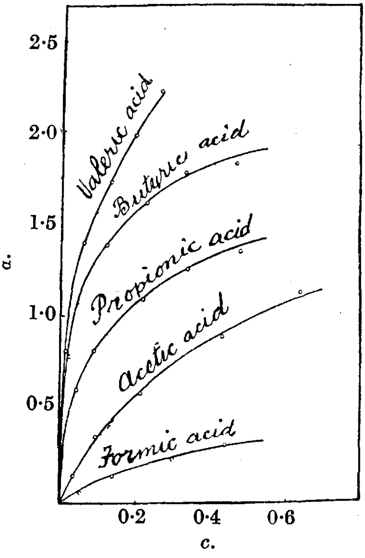
Fig. 2.



I am sure that surface chemistry will suffer many changes in the near future. But even if the ground on which we tread is not very firm, nevertheless I believe that we may generalise Thomson's relation and say that, on any surface, substances which are adsorbed strongly are formed in large amount and the chemical equilibrium is therefore shifted in this direction.

Let me now return to the subject of my lecture. I shall commence by discussing a phenomenon which is rather complicated but has been known for a long time. If charcoal is shaken with salt solutions, especially those of salts with organic ions like dyes or alkaloids, the two ions are not always adsorbed in equivalent amounts; a dye kation, for instance, may be adsorbed more strongly than an inorganic anion, hydrogen ions replacing the lacking kations in the solution. This kind of exchange adsorption was perhaps considered to be of no great interest; it was assumed simply that some foreign substance (*e.g.*, ash) in the charcoal exchanged some of its ions for ions from the solution. This explanation had to be given up, however, when Bartell and Miller (*J. Amer. Chem. Soc.*, 1922, **44**, 1866; 1923, **45**, 1106; Miller, *ibid.*, 1924, **46**, 1150; 1925, **47**, 1270) showed that a very pure charcoal made from sugar and containing less than 0·01% of ash behaved in a similar way: it adsorbed acids from salt solutions, the solution being alkaline after adsorption had taken place. The amount of acid calculated from the alkalinity of the solution agreed excellently with the amount found directly by washing the sugar charcoal with an organic solvent and titrating the acid. There was also a very distinct parallelism between the amount of acid adsorbed from the salt solution and the adsorbability of these acids in pure solution, for instance, for a benzoate, an oxalate, and a chloride. Here we really seem to have a hydrolysis of the salt caused by adsorption, a shifting of an equilibrium in such a direction that the production of the more strongly adsorbed substances—the acids—is favoured.

Fig. 3.



Recent investigations by Frumkin (Frumkin and Donde, *Ber.*, 1927, **60**, 1816; Bruns and Frumkin, *Z. physikal. Chem.*, 1929, *A*, **141**, 141; Burstein and Frumkin, *ibid.*, pp. 158, 219) have shown, however, that the conditions are more complicated and that the electrical influence of the ions cannot be neglected. He activated an ash-free sugar charcoal in an electric furnace under a high vacuum up to 1000°, taking care that no air came in contact with the charcoal before it had adsorbed the dissolved substances. This charcoal did not appreciably adsorb weakly adsorbable inorganic substances such as hydrochloric acid or sodium hydroxide. If, however, the charcoal came in contact with air or oxygen it was able to adsorb acids such as hydrochloric acid but not alkalis. On the other hand, if the sugar charcoal was heated to 1000° in an atmosphere of hydrogen and carefully kept from the air, its behaviour was reversed : it adsorbed alkalis but not acids. Frumkin believes, therefore, that charcoal behaves like a gas electrode. If it contains oxygen, it gives off hydroxyl ions to the solution and takes up anions from it; the solution turns alkaline and loses an equivalent amount of anions. If the charcoal contains hydrogen, hydrogen ions are given off to the solution, kations are taken up from it, and it turns acid, losing an equivalent amount of kations. The adsorption of a weak and strongly adsorbable acid such as benzoic acid is not influenced by treating the sugar charcoal with hydrogen in the way described. In the case of the salts of weak acids, we may assume, therefore, that we really have a displacement of the equilibrium in the first sense, but especially for strong electrolytes the conditions are markedly modified by the presence of gases. In any case, we have no very well-defined case of the shifting of a chemical equilibrium by surface forces.

Experiments which leave no doubt as to the existence of such a displacement were recently made by Deutsch (*Ber.*, 1927, **60**, 1036; *Z. physikal. Chem.*, 1928, **136**, 353), in the Dahlem laboratory of the Kaiser Wilhelm Institut für physikalische Chemie. He found that indicators in solutions near their turning point changed their colour if the solution was shaken with an indifferent fluid such as benzene, toluene, etc. If, for instance, a solution of bromothymol-blue in a hydrogen-ion concentration of p_H 7·4 is treated in this way, the colour changes from blue to yellow. This change of colour only takes place as long as fine drops of benzene are emulsified in the aqueous solution; it disappears as soon as the two phases have separated again. The more strongly the fluid is shaken, the more pronounced the colour becomes, because the droplets formed are finer and more numerous, their interface being accordingly larger. There can be no doubt that the colour change is caused by the emulsification, that is, by the formation of the large interface. The phenomenon is absolutely reversible, and may be repeated indefinitely. The colour changes as if the p_H had altered from 7·4 to 6·2. The shifting of the equilibrium between the different ions and molecules characteristic for this indicator is of this order of magnitude.

This might be explained by assuming that the hydrogen-ion concentration in the surface of the droplets is different from that in the bulk of the liquid; but this does not hold, for if we take an indicator which is not an acid dye, such as malachite-green, it also changes on being shaken with an indifferent fluid. The change of the p_H which we would like to make responsible for the colour change has, however, a reversed sign in this case. With malachite-green the colour changes from yellow to green; this would correspond to a change of p_H from 0·5 to 1·5. Table I, as given by Deutsch, shows that acid and basic dyes seem to behave throughout in this way.

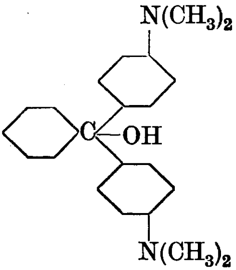
TABLE I.

Indicator.	Solvent.	Colour of solution.	Colour on shaking.	Change of p_H corresponding to colour change.
Guinea-green	About 1·0*N*-HCl	Yellow	Bluish-green	From 0·0 to 0·6
Malachite-green	,, 0·4 ,,	Yellow	Bluish-green	,, 0·5 ,, 1·5
Brillant-green	,, 0·25 ,,	Yellow	Greenish-blue	,, 0·7 ,, 2·0
Methyl-violet	,, 0·1 ,,	Green	Blue	,, 1·0 ,, 2·0
Thymol-blue	,, 0·016 ,,	Yellow	Reddish-violet	,, 2·8 ,, 1·6
Tropæolin 00	,, 0·016 ,,	Orange-yellow	Red	,, 2·8 ,, 1·8
Bromothymol-blue	Mixture of distilled and undistilled water.	Blue	Yellow	,, 7·4 ,, 6·2

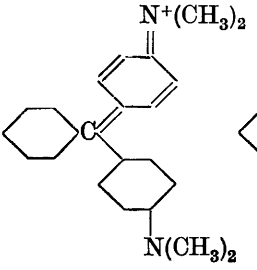
The change of interfacial tension agrees with Thomson's relation, as far as it has been tested hitherto, and in so far as it was sufficiently large to be tested. With malachite-green, for instance, the interfacial tension is lowered to 22% if the concentration of hydrochloric acid is changed from 0·43 to 0·25*N*, and the hydrogen-ion concentration (p_H) alters correspondingly from about 0·5 to 0·7. This change causes a colour change similar to that which happens on shaking.

Before entering into the intricate question of determining what chemical changes are taking place in the interface, and how they are to be explained, I should like to point out that this phenomenon is found, not only at the interface of two liquids, but also at the surface of fluids in contact with a gas phase. It is not quite so easy to demonstrate it there, because the foam of the liquid has to be sufficiently stable to make the colour change visible. This is the case with thymolsulphonephthalein. If we shake a solution of this indicator having a p_H of about 2·8 with air or in a vacuum, where the gas phase contains only water vapour, the foam turns reddish-violet, whereas the bulk of the liquid remains brownish-yellow.

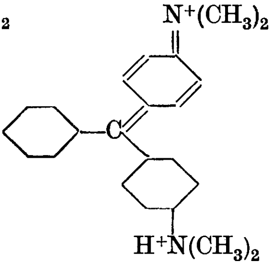
It is no easy question to determine what chemical reactions are occurring in the interface. The reactions of these indicators are far from simple. There are generally quite a number of ions of different valency, a series of isomeric forms, and in many cases also amphoteric ions. Deutsch believes that the case of malachite-green permits us to draw certain conclusions. Under the conditions of the experiments, we have to consider 5 kinds of molecules (Rötger, Diss., Berlin, 1924) : 3 of a carbinol structure—an undissociated form and 2 ions—and 2 of a quinonoid structure—a univalent blue kation and a bivalent yellow kation. It seems very likely that we have to deal only with the transformation of this yellow kation into the blue one. This would account for the colour change and for the fact that the reactions proceed quickly, whereas the conversions of the carbinol into the quinonoid forms go much more slowly. We have accordingly the change of a bivalent ion into a univalent one. This means that at the interface a less dissociated substance is formed. A similar conclusion may be drawn from the acid dye bromothymol-blue : the colour change at the interface agrees with the formation of a less dissociated molecule. Deutsch ventured to generalise these experiences and assumed that in all cases the formation of undissociated or less dissociated molecules is favoured in the



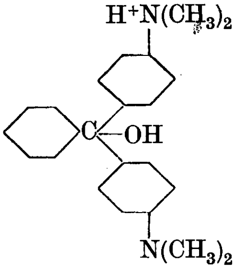
(I; Colourless.)



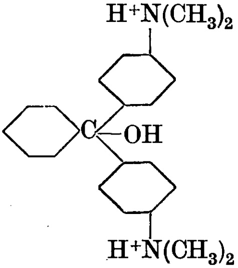
(II; Blue.)



(III; Yellow.)



(IIA; Colourless.)

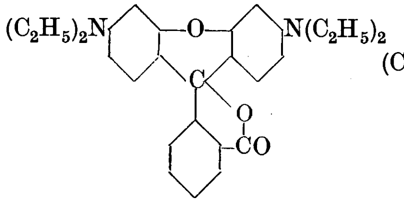


(IIIA; Colourless.)

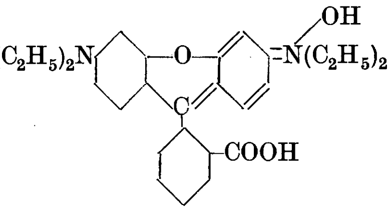
interface touching the gas phase or the phase of an organic liquid. This would agree with the general conception that the undissociated molecules are more strongly adsorbed than the ions by many adsorbents. I must confess, however, that Thiel (*Z. Elektrochem.*, 1929, **35**, 266), for instance, who is a very good specialist in indicators, is not convinced that these colour changes found by Deutsch are always in accordance with the production of less dissociated molecules. He believes that in quite a number of cases, for instance with tropæolin and thymol-blue, the colour change at the interfaces is caused by the formation of other ions which need not be considered as less dissociated. In the case of tropæolin it is an amphoteric ion, and in that of thymol-blue most likely the ion of a carbonium base. We do not know enough about such ions to say whether their capillary activity is especially pronounced.

Rather surprising results were found by investigating the interface from the other side, so to speak. Deutsch dissolved the colourless base of rhodamine-0 in benzene and shook this solution with water. The emulsion formed turns deep red; in this case the phenomenon depends upon the droplets of water dispersed in the benzene. The colour disappears practically when the phases are separated again, the water in bulk being only weakly coloured from the red base of the dyestuff. This phenomenon is again markedly independent of the nature of the interface. If a piece of filter paper is dipped into the colourless solution of the base in benzene it turns red; this is also the case if dry quartz powder is used instead of filter paper.

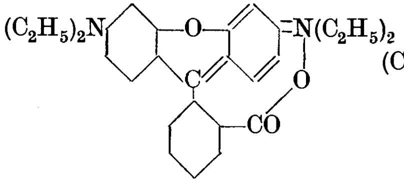
These experiments seem important in many respects. We see that a substance—in this case, the red base of the dye—may be formed at an interface, remaining very stable there, this substance being only formed in a very small amount or practically not at all when the area of the interface is too small. Further, it looks very much as if the change on the benzene side of the interface were a reversal of that on the aqueous side; that is, on the latter side, less dissociated substances seem to be favoured, these substances very often being such as would have dissolved in the organic liquid or in the gas phase (generally in the phase of the smaller dielectric constant) if such a solution were possible. On the benzene side, on the other hand, the same red substance, which is dissolved in the water, seems to be favoured. That this form is more dissociated than the colourless form in the benzene is most probable. We have to take into account the following possibilities. The colourless base is most likely a lactoid form. This is made plausible by the fact that some rhodamine dyes, which are esters, dissolve in benzene with a red or yellow colour and do not have a colourless base. Now the constitution of these esters is such that conversion into the lactoid form is impossible. Therefore, this is most probably a colourless



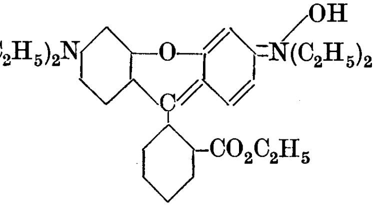
Lactoid base.



p-Quinonoid ammonium base.



Betaine form.



Ester.

form of the base which is able to be formed by those dyes that are not esters. The red form of the base has most likely a quinonoid structure. We have two possibilities: an ammonium base of quinonoid structure, or the betaine form of the base. Some facts seem to indicate that we ought to prefer the latter. The ammonium base would need one more molecule of water than the betaine form. Now the presence of water does not seem absolutely necessary for the formation of the red base at an interface, for, if the benzene solution of the base is carefully dried with sodium, and if quartz powder, previously heated to redness and carefully protected from moisture, is added, the quartz turns red nevertheless. The change we are dealing with is therefore most likely the transition from the colourless lactoid form into the red betaine form. Now, according to the investigations of Bredig, Küster, and others, the betaine form has a great tendency to exist as an amphoteric ion. This is most likely the red substance with which we have to deal. The latter is to be considered as decidedly more dissociated, or at any rate as less saturated, than the lactoid form. The substance formed in the benzene side and soluble in water is therefore one which we may consider to be more dissociated.

Also, in the case of those rhodamine dyes like "rhodamine 6G extra" and "rhodamine 3G extra," which have the constitution of esters and dissolve in organic liquids in a coloured form, a change of colour takes place on shaking with water and on other interfaces. The bases of the two dyes mentioned are yellow in benzene solution, and red in aqueous solution, in which they are much less soluble. When the benzene solution is shaken with water the colour turns red, and the same is the case if quartz is added to the benzene solution. The change is always in favour of the substance in the aqueous solution. This is perhaps in every case the amphoteric ion of the betaine form. In order that this substance be formed we must assume that the esters partly undergo a dissociation at the interface into the betaine form and alcohol.

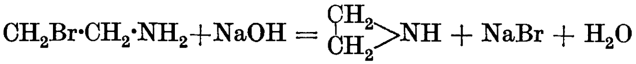
I should like to mention some more experiments which show in quite different cases how different interfaces may behave similarly. Fajans (Fajans and Hassel, *Z. Elektrochem.*, 1923, **29**, 495; Fajans and Wolff, *Z. anorg. Chem.*, 1924, **137**, 221) has investigated the adsorption of dyes on silver halides. Substances like silver eosinate suffer a distinct change of colour provided that the adsorbing surface of silver halides is covered with silver ions. This is the case if it is precipitated from a solution containing a surplus of silver ions. The colour changes from a pinkish-yellow with a green fluorescence to a distinct red on the surface of the halide. Now Deutsch and Fajans showed that the same colour change takes place at other interfaces. If a solution containing 0·01% of sodium eosinate and 0·01 mol. of silver nitrate (a solution which is pinkish-yellow with a green fluorescence) is shaken with benzene or pentane, a red precipitate is formed at the interface. The same happens if it is merely shaken with air. Instead of the silver salt a copper salt may also be used.

This may be explained in the following way. We start with a dilute solution of the eosinate of the heavy metal which is strongly dissociated and therefore shows the colour of the anion of the dye. On shaking, a large interface is formed, and the equilibrium is shifted in the direction of the undissociated salt, which, being less soluble, is precipitated. On the surface of the silver halide we also have the formation of the undissociated salt. This is why the colour change is the same at all interfaces. We are not able to decide whether this change of colour is caused by a deformation of the dye molecule, as Fajans believes, or whether an isomeric molecule (in the strict sense of the word) is formed.

Here we are already dealing with cases which are not strictly reversible and therefore do not belong rigidly to the scope of this lecture. Numerous irreversible reactions at interfaces are known in which insoluble substances are formed. I need only mention the acid soap on the surface of soap solutions (Laing, *Proc. Roy. Soc.*, 1925, *A*, **109**, 28) and the denaturisation which proteins undergo if we shake their solution with air or other gases (Ramsden, *Z. physikal. Chem.*, 1904, **47**, 336).

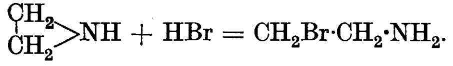
Deutsch's experiments are valuable in that they show definitely that a displacement of chemical equilibrium at interfaces really exists and may be found in quite a number of cases. In some respects they leave much to be desired. It seems hardly possible to develop them in a quantitative form, since we are unable to assign a definite area to the interface. Furthermore, the chemical changes occurring are rather complicated. I therefore should like to discuss yet another case where precisely these points seem to be much simpler. Certainly there is another gap which cannot be filled in yet.

We may consider with certain restrictions that an equilibrium constant is equal to the ratio of the velocity coefficients of the forward and the reverse reaction. If we have a displacement of equilibrium at an interface, we may expect that the velocity of the one reaction will be increased, and that of the other diminished. A case of that kind was investigated by Juliusburger and myself. In homogeneous aqueous solutions we have the following two reactions :



$$CH_2Br\cdot CH_2\cdot NH_2+NaOH = \left.\begin{array}{l}CH_2\\ CH_2\end{array}\right>NH + NaBr + H_2O$$

and

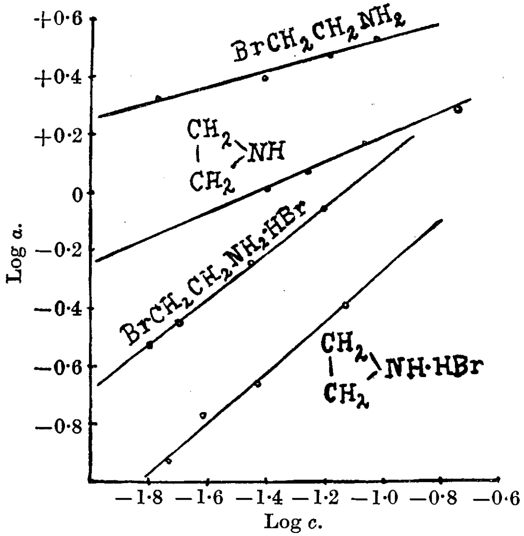


$$\left.\begin{array}{l}CH_2\\ CH_2\end{array}\right>NH + HBr = CH_2Br\cdot CH_2\cdot NH_2.$$

Bromoethylamine is unstable in alkaline solution and is transformed into the isomeric hydrobromide of dimethyleneimine, whereas in hydrobromic acid solution the hydrobromide of the latter is reconverted into bromoethylamine. [The formula of the substance formed in alkaline solution was the cause of some discussion. It was first considered to be the hydrobromide of vinylamine, $CH_2{:}CH\cdot NH_2$, but later investigations of Marckwald (Howard and Marckwald, *Ber.*, 1899, **32**, 2036; Marckwald, *Ber.*, 1900, **33**, 765; Marckwald and Frobenius, *Ber.*, 1901, **34**, 3544) showed that we have in any case to deal with an imine.] The velocity of the two reactions is easy to measure quantitatively : in the alkaline solution the amount of bromine ions increases—it is just doubled if, as is generally done, we start with the hydrobromide of bromoethylamine; and in the hydrobromic acid solution the amount of bromine ions diminishes. Now in acid solutions a secondary reaction goes on, the dimethyleneimine polymerising to a small extent; although this disturbance is not sufficiently marked to prevent us from measuring the velocity coefficients in acid solution, yet, since it is irreversible, it does not allow us to find the point of equilibrium in neutral solutions. Both reactions are well defined and are not affected by impurities. The transformation of the bromoethylamine is a reaction of the first order, and the reverse reaction is of the second order, the velocity being proportional to the imine and bromine-ion concentrations.

Now these reaction velocities were measured in a heterogeneous system, the solutions being shaken with animal charcoal. It was necessary to know the adsorption of the following four substances : bromoethylamine, dimethyleneimine, and the hydrobromide of each. Fig. 4 shows, first, that the well-known adsorption isotherm agrees well with the measurements, for straight lines are obtained in a logarithmic plot. We see further that the bromoethylamine is adsorbed much more strongly than dimethyleneimine, and its hydrobromide more strongly than that of dimethyleneimine. [Here we have a good example of salts being adsorbed much less than their bases.] According to the rule governing the displacement of chemical equilibrium at interfaces, we may expect that bromoethylamine, which has a stronger capillary activity, is more stable on the surface of the charcoal than in homogeneous solutions. The transformation of bromoethylamine into dimethyleneimine in alkaline solution ought therefore to be retarded, and the formation of bromoethylamine in acid solution to be accelerated. This is, indeed, the case, and in a very marked degree, as Figs. 5 and 6 show. We have first (Fig. 5) the velocity of the reaction in alkaline solution, the abscissæ indicating the time (in minutes), and the ordinates the percentage of bromoethylamine transformed; the reaction on the

Fig. 4.



charcoal goes distinctly more slowly than in homogeneous solutions. In acid solutions (Fig. 6) the reaction on the charcoal is strongly accelerated. This latter reaction is disturbed, but only to a very small extent, by the adsorption of hydrobromic acid and some unknown change it undergoes at the surface of the charcoal.

FIG. 5.

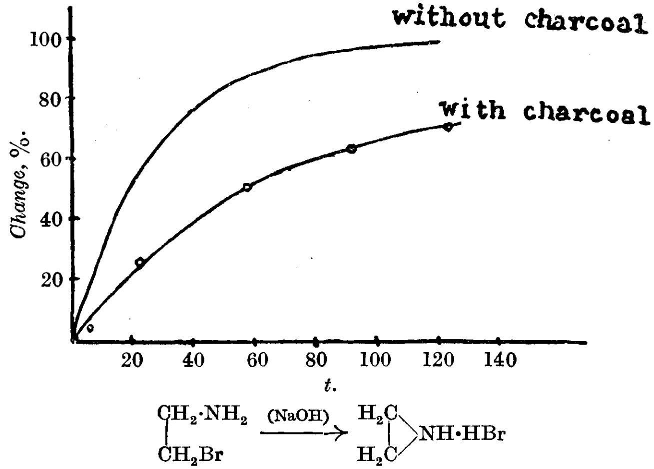
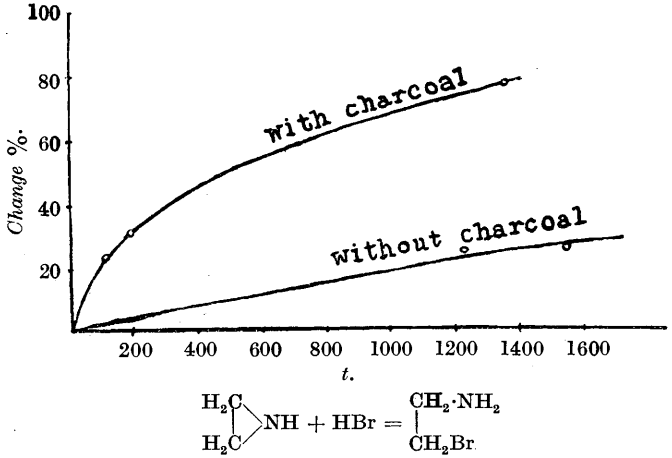


FIG. 6.



It is important to mention that under the conditions of these experiments the adsorption of the reacting substances was very strong, especially in the case of the alkaline solution. The amount of charcoal used was so large (several grams), and the concentration of the reacting substances so low (generally $N/20$ to $N/50$), that the bromoethylamine was adsorbed to about 100%. We are really dealing with a reaction where the reacting substance is entirely in the adsorption layer. The conditions are therefore quite different from those prevailing in most catalytic gas reactions, in which only a small and generally unknown amount is adsorbed and reacts on the surface. In the reverse reaction the degree of adsorption is much lower; the hydrobromide of the dimethyleneimine is adsorbed at the commencement to about 15%.

It might have been objected to these experiments that we were not sure whether the reactions going on in the heterogeneous system are identical with those in the homogeneous system, but we were able to show that this is indeed the case. In alkaline solution the concentration of the bromine ion is doubled under both conditions, and in presence of charcoal the dimethyleneimine formed could be distilled off at temperatures below 60° (its boiling point is 55°), and it formed its characteristic red crystalline salt with potassium bismuth iodide. It is not so easy to show that the reverse reaction is the same as in homogeneous solution, for we have no similar characteristic reagent for bromoethylamine. This, however, could also be shown in the following way: after the reaction had proceeded in acid solution in presence of charcoal, the solution was made alkaline, and the velocity measured with which dimethyleneimine was re-formed from the bromoethylamine originally produced in the acid solution. The reaction velocity coefficient thus measured was identical with that which had been found when bromoethylamine hydrobromide was used at the outset.

The mechanism of the two reactions in presence of charcoal is distinctly different, especially in one point, from that in homogeneous solutions. The reaction of the dimethyleneimine in acid solution is of the second order as in homogeneous solutions, the coefficient being much larger, however. On the other hand, the reaction of the bromoethylamine in alkaline solution does not follow the first order as it does in homogeneous solution. Since the reacting substance is, so to speak, totally in the adsorption layer, it is necessary to use as variable a surface concentration, *viz.*, the amount of amine divided by the amount of charcoal, and with this variable the velocity of the reaction is proportional to the $\frac{3}{2}$ power of the surface concentration. We have not yet found an explanation for this empirical formula, but its discovery would probably provide the clue to a kinetic interpretation of this change of reaction velocity in presence of charcoal.

The behaviour in neutral solution presents some features of interest. As I said before, the equilibrium to be expected cannot be measured exactly because of a secondary reaction which also disturbs the reaction in presence of charcoal; but it is quite clear that the formation of bromoethylamine is favoured strongly. For, starting with a neutral solution of bromoethylamine, about 90% is transformed in the course of a long time in homogeneous solution, whereas in presence of charcoal the reaction stops almost entirely when about 63% is transformed. If, on the other hand, we start with a neutral solution of the hydrobromide of dimethyleneimine, only about 10% is transformed in homogeneous solution, but more than 36% in presence of charcoal.

These experiments agree well with what we might expect from the theory: the equilibrium is displaced in the sense required by Thomson's relation, the formation of capillary active substances being favoured. The experiments show further that a substance, in this case the bromoethylamine, may be more stable at an interface than in homogeneous solution under similar conditions.

May I return once more to the question as to how far surface reactions are of biological importance? I need not emphasise the importance of microstructure and interfaces for protoplasma and life in general, since Professor Donnan did so most convincingly in his Liversidge lecture last year (J., 1929, 1387). Although life never means an equilibrium, but at most a stationary state like a flame or a water jet, a displacement of a chemical equilibrium may make itself felt in the change of reaction velocities, as in our case of the transformation of bromoethylamine into dimethyleneimine. We may therefore assume that the formation of capillary active and strongly adsorbable substances is favoured generally if the aqueous phase which certainly constitutes some part of a protoplasmic entity comes into contact with a solid or a liquid organic substance of small dielectric constant. Many substances of biological importance, indeed, exhibit capillary activity, *e.g.*, the alkaloids and fats.

The fact that at interfaces substances may be formed, and even possess considerable stability, whereas at the same concentrations without the interfaces their existence is transitory, may account for the extraordinary structure of many substances playing important biological rôles. I have always been astonished at the great difference between the organic chemistry of our laboratories and that under biological conditions. Not only is the difference in the methods used remarkable—in laboratories we use a large range of temperatures and a great variety of solvents, whereas Nature utilises a small range of temperatures and a great variety of interfaces—but the substances formed also seem to me to be very different. I doubt whether an organic chemist, knowing nothing about natural products but, on the other hand, well trained in all methods of work and master of all our knowledge of the possibilities of chemical valency and even more, I doubt whether he could have conceived the existence of substances like most alkaloids or cholesterol, lecithin, adrenaline, thyroxine, and many others. This may be caused partly by the fact that we know a good deal of what happens in the bulk of solutions, but very little about what takes place at interfaces. And I mean not only comparatively inert interfaces, such as air or charcoal, but also those which are very reactive. We must realise that we have to deal, not only with the relatively simple displacements discussed in this lecture, but also with a great number of further reactions which may take place if the unstable substances stabilised at an interface react with other substances at the interface or with the molecules of the adsorbent itself. I should not be surprised if the great difficulty which we meet in trying to explain the nature of enzymes is partly due to similar causes. They may be very unstable and active organic substances, perhaps even organic radicals which are stabilised because they are adsorbed at a suitable interface, but they are able to react very energetically in intermediate reactions with other substances also adsorbed on these interfaces.