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MOLECULAR INTERACTIONS AT OIL/WATER INTERFACES.

PART I. MOLECULAR COMPLEX FORMATION AND THE STABILITY OF OIL IN WATER EMULSIONS.

By J. H. Schulman and E. G. Cockbain.

Received 15*th February*, 1940.

It has been shown recently[1] that when certain substances are injected under monolayers of cholesterol, glaidin, etc., spread on the surface of water, molecular association occurs. Two distinct phenomena could be observed. If interaction occurred only between the polar groups of the monolayer substance and the injected compound, adsorption of the latter on the monolayer took place with concomitant changes in the surface potential, and in some cases, the rigidity of the film. When, in addition to the polar interaction, there was strong association between the non-polar parts of the two reacting species, a penetration of the monolayer occurred with changes in the surface pressure as well as the surface potential. The non-polar association was very sensitive to the stereochemical configurations of the two reacting molecules, since a suitable stereochemical relationship permits the close adlineation of the molecules in the interface. In regard to various polar groups, the hydroxy group of cholesterol and the amino groups of proteins were found to be particularly reactive.

Such results on the formation of inter-molecular complexes are of importance in connection with the formation and stability of oil in water, or water in oil emulsions, since the phenomenon of penetration permits of extremely low interfacial tension, much below that which either component can produce separately. From a study of the properties of these emulsions it was seen that reactions taking place at the oil-water interface were closely analogous to the corresponding reactions at an air-water interface, which have been investigated by the method of surface films.

Experimental.

Systems composed of mineral oil " nujol " and water were studied in the presence of various emulsifying agents. In some cases emulsification occurred spontaneously. If, for example, an aqueous solution of sodium cetyl sulphate is poured into a solution of cholesterol in " nujol," extensive emulsification occurs without any further shaking, although shaking by hand for a few seconds improves the emulsification. In other cases an emulsifying machine was necessary to produce emulsification.

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[1] Schulman and Rideal, *Proc. Roy. Soc. B*, 1937, 122, 29, 46.

The stability of the emulsions was measured by observing the time required for the first visible signs of separation of the two phases. Such a criterion for emulsion stability is dependent on the efficiency of the emulsification process and on the degree of separation which one recognises as clearly visible. However, it is a satisfactory method of comparing the relative stability of different emulsions prepared under the same circumstances.

Influence of Non-Polar Steric Factors on Complex Formation of Emulsion Stability.

Schulman and Stenhagen [2] showed that strong complexes were formed at a water/air interface between sodium cetyl sulphate and cholesterol, cetyl alcohol or elaidyl alcohol ($CH_3(CH_2)_7CH{=}CH(CH_2)_7CH_2OH$ trans isomer). On the other hand, sodium cetyl sulphate formed only a weak complex with oleyl alcohol which is the *cis* isomer corresponding to elaidyl alcohol. In the case of oleyl alcohol, the *cis* configuration of the hydrocarbon chain prevented close adlineation between the sodium cetyl sulphate and the oleyl alcohol molecules at the interface, with the result that the van der Waals forces of adhesion were small and the molecular complex correspondingly weak. To establish whether the same stereochemical factors affected the stability of complexes at an oil/water interface, emulsions of " nujol " in water were prepared, emulsification being brought about by hand-shaking for ten seconds. In the " nujol " was dissolved the oil soluble agent (cholesterol, cetyl alcohol, etc.) and in the water, the sodium cetyl sulphate. Concentrations employed are given in Table I.

TABLE I.

10 c.c. "Nujol."	40 c.c. Water.	Remarks.
140 mg. cholesterol	——	No emulsion.
——	75 mg. Na cetyl sulphate	Very poor emulsion.
140 mg. cholesterol	75 mg. Na cetyl sulphate	Excellent emulsion. (liquid)
140 mg. oleyl alcohol	75 mg. Na cetyl sulphate	Very poor emulsion.
140 mg. elaidyl alcohol	75 mg. Na cetyl sulphate	Very good emulsion (viscous)
140 mg. cetyl alcohol	75 mg. Na cetyl sulphate	Very good emulsion. (grease)

It is to be noted that the state of the interfacial film as observed at the air-water interface, *i.e.* solid, viscous or liquid, is reflected in the nature of the resultant emulsion being respectively a grease, viscous or a liquid emulsion. Thus a cholesterol film penetrated by cetyl sulphate is a liquid film giving a very fluid emulsion when these two stabilising agents are used. But a cetyl alcohol film goes solid on penetration by cetyl sulphate, these two stabilising agents produce a grease for the emulsion.

The viscosity of the penetrated elaidyl alcohol film lies between these two extremes, likewise does the viscosity of the resultant emulsion.

This phenomenon can be easily understood if one imagines that the oil droplets which have a solid interfacial film round them behave as

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[2] Schulman and Stenhagen, *Proc. Roy. Soc. B*, 1938, **126**, 356.

solid spheres, which cannot slip past one another by distortion, as with the liquid spheres, thus giving a great rigidity to the emulsion.

In spite of the qualitative nature of the above experiments, it can be concluded that stabilisation of the oil in water emulsions has been effected by a complex formation at the oil/water interface between the oil-soluble and the water-soluble components added. Furthermore, it is apparent that the stability of a complex at the oil/water interface is very sensitive to non-polar stereochemical relationships, just as it is at a water/air interface. The weak emulsifying power of cetyl sulphate plus elaidyl alcohol (*trans* isomer) illustrates the point particularly clearly. Table I shows the effect of the stereochemical configuration of the oil-soluble component on molecular complex stability and on emulsion stability. The stereochemical configuration of the water-soluble component is likewise important. " Nujol " in water emulsions were prepared using cetyl alcohol or cholesterol as the oil soluble component and sodium stearate, sodium oleate or sodium elaidate as the water soluble component of the emulsifying agent.

Concentrations used are given in Table II, emulsification being brought about as before by hand-shaking.

TABLE II.

10 c.c. "Nujol."	40 c.c. H_2O.	Remarks.
140 mg. cetyl alcohol	250 mg. sodium stearate	Stability of the emulsion good. Viscosity high, giving the emulsion grease-like properties.
140 mg. cetyl alcohol	250 mg. sodium elaidate	Stability good.
140 mg. cetyl alcohol	250 mg. sodium oleate	Stability poor.
140 mg. cholesterol	250 mg. sodium oleate	Stability very poor.
140 mg. cholesterol	250 mg. sodium elaidate	Stability good.

The results in Table II show that sodium elaidate, which is the *trans* isomer corresponding to sodium oleate, forms much stronger complexes with cetyl alcohol or cholesterol than does sodium oleate. This complex formation is difficult to determine quantitatively at an air/water interface owing to the strong and rapid capillary action of the oleate and elaidate.

Effect of Polar Interaction on Complex Formation and Emulsion Stability.

Schulman and Rideal[1] have shown that the penetration of a monolayer at an air/water interface by substances in the underlying solution and the stability of the resulting mixed film are strongly dependent on the degree of interaction between the polar groups of the film substance and the penetrating compound. For example, sodium cetyl sulphate rapidly penetrates a film of cholesterol and a stable equimolecular complex is formed. By substituting cholesterol acetate or cholesterol stearate for the cholesterol only a negligible interaction occurs. It is shown below that the stability of molecular complexes at an oil/water interface is likewise strongly dependent on the degree of polar interaction between the two components of the complex. Thus, Table III shows that a mixture of cetyl sulphate and cholesterol stearate (or cholesterol acetate) does not stabilise "nujol" in water emulsions whereas that of cetyl sulphate and cholesterol gives stable emulsions. Emulsification was produced by hand-shaking.

TABLE III.

10 c.c. "Nujol."	40 c.c. Water.	Remarks.
140 mg. cholesterol stearate	250 mg. cetyl sulphate	No emulsion.
140 mg. cholesterol acetate	250 mg. cetyl sulphate	Very poor emulsion.
140 mg. cholesterol	250 mg. cetyl sulphate	Excellent emulsion.

Schulman and Rideal[4] injected compounds of the type $C_{12}H_{25}X$ (X = various polar groups) under cholesterol films at an air/water interface, and found that the reactivity of the polar groups X towards the alcoholic group of cholesterol could be placed into the following series :—

$$NH_3^+ > SO_4^- > SO_3^- > COO^- > NMe_3^+ > \text{Bile acid anions.}$$

That the same order of reactivity towards cholesterol holds at an oil/water interface can be seen from Table IV, the stability of the emulsions being taken as a measure of the stability of the complexes between cholesterol and the various long chain polar compounds (C_{16} hydrocarbon chains in all cases, except for the bile acids).

TABLE IV.

10 c.c. "Nujol."	40 c.c. Water.	Remarks.
100 mg. cholesterol	70 mg. cetyl sulphate	Stability excellent.
100 mg. cholesterol	70 mg. cetyl sulphonate	Stability excellent.
100 mg. cholesterol	70 mg. sodium palmitate	Stability good.
100 mg. cholesterol	70 mg. cetyl trimethyl ammonium bromide	Stability good.
100 mg. cholesterol	70 mg. sodium taurocholate	No emulsion.
100 mg. cholesterol	70 mg. sodium glycocholate	No emulsion.
100 mg. cholesterol	70 mg. sodium desoxycholate	No emulsion.

The emulsions were prepared by hand-shaking.

Hexadecylamine was not available for inclusion in the above series. A mixture of the C_{17} amine and cholesterol did not stabilise "nujol" in water emulsions at all well at *p*H 7, but gave very good emulsions at *p*H 2·0. The poor emulsion at *p*H 7 was, therefore, probably due to the small solubility of heptadecylamine in water at *p*H 7. A series similar to that shown in Table IV can be obtained, using cetyl alcohol in place of cholesterol. The resulting emulsions, however, are very viscous (" emulsion greases "), and their true stability is rather difficult to determine. The high viscosity of the emulsions is presumably due

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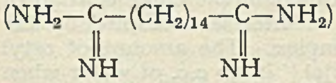
[3] Schulman and Hughes, *Biochem. J.*, 1935, **29**, 1243.
[4] Schulman and Rideal, *Nature*, 1939, **144**, 100.

to the formation of *solid* molecular complexes at the oil/water interface, since it is known that cetyl alcohol and many long chain polar compounds form solid complexes at an air/water interface.

The effect of substituting for the long chain polar compound substances containing a polar group at each end of the chain is of great interest. It has been shown that sodium palmitate, for example, rapidly penetrates films such as cholesterol or octadecylamine with the formation of stable complexes. Cockbain and Schulman[5] found, however, that sodium thapsate ($Na\ OOC(CH_2)_{14}COONa$) penetrated films of octadecylamine at an air/water interface only very poorly, and could readily be squeezed out of the surface to form an adsorbed double layer underneath. In the case of emulsions it is found that sodium palmitate + cholesterol give good emulsions of " nujol " in water, whilst, under the same conditions, sodium thapsate and cholesterol have no emulsifying action. Similarly, Palmityl amidine + cholesterol give fairly good " nujol " in water emulsions under conditions for which cholesterol + palmityl diamidine  $(NH_2-\underset{\underset{NH}{\|}}{C}-(CH_2)_{14}-\underset{\underset{NH}{\|}}{C}-NH_2)$ have no emulsifying action. This contrast between monopolar and dipolar (polypolar) compounds has important biological implications. The latter compounds adsorb on to protein films, but do not penetrate lipoid films. The monopolar compounds penetrate lipoid films readily.

Effect of Concentration of the Emulsifying Agent on Emulsion Stability.

The stability of an emulsion is a function of the size of the dispersed droplets. Other things being equal, emulsions containing large droplets will separate rapidly, and emulsions containing small droplets will separate only slowly. There is plenty of evidence that oil droplets of about 4μ diameter (covered with an adsorbed layer of emulsifying agent) are sufficiently small to separate only slowly. Suppose, then, that a stable emulsion is to be prepared of 10 c.c. of " nujol " in 40 c.c. of water, using cholesterol + cetyl sulphate as the emulsifying agent. The quantity of cholesterol required will be two-thirds the amount necessary to cover 10 c.c. of " nujol " dispersed into droplets of 4μ diameter, with a monolayer of cholesterol, providing that all the cholesterol in the system goes to the oil/water interface. This quantity is 16 mg. The factor $\frac{2}{3}$ is put in because the " nujol " droplets contain an equimolecular complex of cholesterol and cetyl sulphate at the interface and a cetyl sulphate molecule occupies 20 A^2 as compared with 40 A^2 for a cholesterol molecule. That the above deductions are correct is shown in a very striking manner by the experiments described below.

A series of emulsions of " nujol " (10 c.c.) in water (40 c.c.) was prepared, emulsification being produced by hand-shaking for 15 seconds. In every case 75 mg. of cetyl sulphate were dissolved in the water whilst varying quantities of cholesterol were dissolved in the " nujol." The reason for taking 75 mg. of cetyl sulphate will be explained later. It was found that with 25 mg. of cholesterol a very good emulsion was obtained, whilst with 12·5 mg. of cholesterol the emulsion was very poor. 50 mg. or more of cholesterol resulted in emulsions only a little more stable than that

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[5] Cockbain and Schulman, *Trans. Faraday Soc.*, 1939, **35**, 716.

obtained with 25 mg. of cholesterol. This is shown in Fig. 1, where emulsion stability is plotted against the concentration of cholesterol. On the basis of the above calculations 32 mg. of cholesterol could cover 10 c.c. of " nujol " dispersed into particles of about 2μ diameter, with 8 mg. of cholesterol the particles would have to be about 8μ diameter. It can be seen that stable emulsions are obtained as soon as sufficient cholesterol is used to cover " nujol " droplets between 3 and 4μ * diameter with a monomolecular film (a mixed film with cetyl sulphate).

With a mixture of cetyl sulphate and cholesterol as emulsifying agent, more cetyl sulphate than cholesterol should be required in order to obtain stable emulsions. Schulman and Stenhagen[2] showed that an equimolecular complex of cetyl sulphate and cholesterol at an air/water interface collapsed at surface pressures about 8 dynes/cm., but when an excess of sodium cetyl sulphate (2×10^{-6} g./c.c.) was present in the underlying solution, the complex was stable up to pressures of 48 dynes/cm. Thus an excess of cetyl sulphate underneath the equimolecular cholesterol-cetyl sulphate complex greatly increases the stability of the complex. From Schulman and Stenhagen's results we can calculate the concentration of cetyl sulphate required to stabilise 1 $cm.^2$ of interface occupied by the equimolecular cholesterol-cetyl sulphate complex. The amount of cetyl sulphate required to stabilise 10 c.c. of " nujol " in 40 c.c. of water when the " nujol " is dispersed into particles 4μ in diameter is calculated to be 58 mg. To test this calculation a series of emulsions of " nujol " (10 c.c.) in water (40 c.c.) was prepared by hand-shaking. In all cases 100 mg. of cholesterol were dissolved in the " nujol " and varying quantities of cetyl sulphate were dissolved in the water. The results are shown in Fig. 2, where the emulsion stability is plotted against amount of cetyl sulphate. With less than 18·5 mg. of cetyl sulphate, no stable emulsions are obtained. Above 18·5 mg. the emulsion stability increases in direct proportion to the amount of cetyl sulphate until the latter is about 75 mg., after which the emulsions are permanent for a long time, and differences are difficult to discern. The agreement between the calculated value of 58 mg. and the observed value of 75 mg. is quite satisfactory. Actually, by calculation, 75 mg. of cetyl sulphate is just sufficient to stabilise the 10 c.c. of " nujol " when present as droplets 3μ in diameter. The proportionality in Fig. 2 between stability and cetyl sulphate concentration rather suggests that one is stabilising more and more " nujol " droplets of 3μ diameter until the whole of the " nujol " is stabilised as droplets of this diameter.* Experimentally the first signs of any emulsion stability were observed with

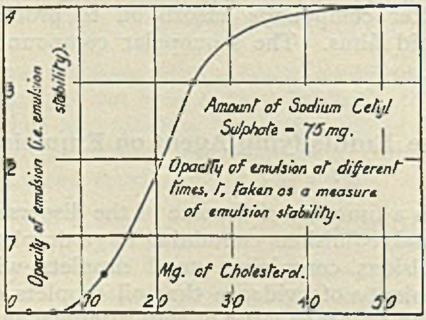

FIG. 1.

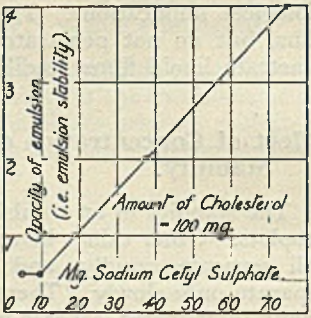

FIG. 2.

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* In the stabilised emulsions the maximum number of droplets were of the order 4-3 μ diameter, this fact has also been generally established for oil droplets in stabilised emulsions. Harkins and Muckhergee and King (1939).

18·5 mg. cetyl sulphate which is sufficient to stabilise the " nujol " into droplets of 12μ diameter. It is of interest that according to Harkins,[6] droplets of this diameter are just small enough to show emulsion properties. The calculated concentration of cetyl sulphate, which, when mixed with cholesterol, was required to stabilise the " nujol " in water emulsions was obtained from Schulman and Stenhagen's data on the stability of a cholesterol-cetyl sulphate complex at an air/water interface. The agreement, therefore, between the calculated and observed concentrations is another confirmation of the close analogy between phenomena occurring at air/water and " nujol "/water interfaces.

The Stability of "Nujol" in Water Emulsions.

It has been shown in the preceding sections that intermolecular reactions taking place at a " nujol "/water interface are very similar to those which occur at an air/water interface. A detailed knowledge of the latter reactions is now available, so that one can deduce the factors which are important for the stabilisation of " nujol " droplets in water. The one difference between " nujol "/water and air/water interfaces is that " nujol " causes an expansion of liquid films present at the interface. If the interfacial films are brought into a closely packed condensed state, however, all the " nujol " is eliminated from the interfacial monolayer. We may consider a mixture of " nujol " and water; if a substance such as cholesterol or cetyl alcohol is dissolved in the " nujol " there will be a certain aggregation of the molecules at the oil/water interface in accordance with Gibbs' Law, but owing to the solubility of cholesterol or cetyl alcohol in the oil phase, the interfacial tension lowering will not be very large. Similarly, if a water soluble substance such as cetyl sulphate is dissolved in the water phase, the crowding of the molecules at the interface will not be large unless high concentrations of cetyl sulphate are used, *e.g.* 2 or 3 per cent. Thus we find that cholesterol and similar oil soluble substances do not emulsify " nujol " at all whilst compounds like cetyl sulphate or soaps in high concentration only emulsify " nujol " with difficulty.

The conditions required for the production of stable emulsions are satisfied if complexes of certain types are formed at the oil/water interface. The function performed by such complexes are described below, taking the cholesterol-cetyl sulphate complex as an example.

(1) The complex must consist of at least 2 components, one of which is appreciably soluble in water, and the other appreciably soluble in oil, and the complex must be a stable one. Under these conditions, molecules of both types are held in the interface. The cholesterol cannot pull the cetyl sulphate molecules into the oil phase and the cetyl sulphate cannot pull the oil soluble cholesterol into the water. Since the complex remains stable when formed, only minute concentrations of each component are required to cover the oil/water interface and stabilise the emulsion.

(2) The interfacial tension must be negligibly small, so that the dispersion of the oil in the water phase involves as small an increase in free energy as possible. It has been shown by Schulman and Rideal[1] that stable complexes at an air/water interface lower the surface tension[2] as much as 60 dynes/cm. (for the above-stated example), which is much greater than the surface tension lowering of 40 dynes/cm., or less, pro-

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[6] Harkins, *J. Physical Chem.*, 1932, **36**, 98.

[7] Lyons and Rideal, *Proc. Roy. Soc. A*, 1929, **124**, 322.

duced even by the concentrated cetyl sulphate solution at an air/water interface[8] (at the equivalent concentration lowering of the surface tension, is only 22 dynes). The interfacial tension of the soap at an oil/water interface can go down to about 3 dynes/cm., so that, by analogy with the air/water interface results, the interfacial tension of stable complexes at an oil/water interface must be very small indeed. Each component of the complex holds the other component at the interface so that a very high concentration is obtained at the interface.

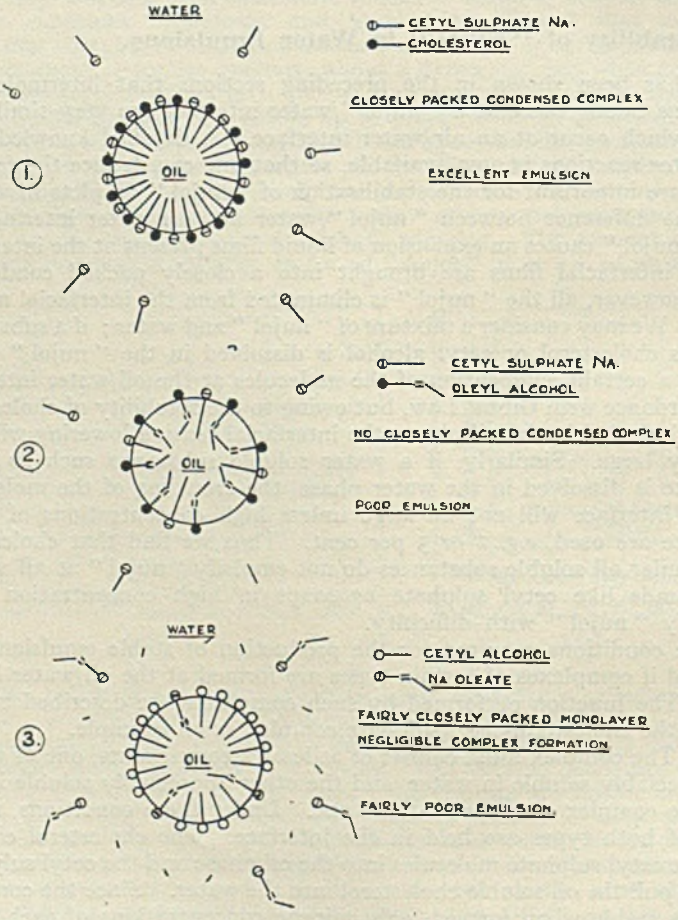

Fig. 3.

(3) In conditions (1) and (2) the stability of the interfacial film and the interfacial tension lowering have both been stressed. These two factors depend markedly on the presence of an excess of the water soluble component under the equimolecular mixed film.

(4) The interfacial film must be a condensed liquid film, condensed because a high interfacial concentration of the complex is necessary, liquid because the film must be easily reformed on distortion.

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[8] Powney and Addison, *Trans. Faraday Soc.*, 1937, **33**, 1243.

(5) For oil in water emulsions the oil droplets must be electrically harged. In fact, one of the chief actions of the complex is to crowd ions into the interface, since ions on their own repel one another, and thus yielding only vapour films at the interface. It will be shown later that if a complex consisting of 2 neutral molecules is formed at the interface, water in oil emulsions are obtained.

In Fig. 3 is given a diagrammatic representation of the conditions existing at the interface of a stabilised oil droplet (" nujol ") in water. Three different complexes which show marked differences in stabilising power are illustrated.

The three diagrams represent the three possible types of stereochemical packing at the interface. More molecules are crowded at the interface in diagram (1) than in (3) than (2). The emulsion stability actually decreases in this order.

Ease of Formation of Emulsions.

With some emulsifying agents, emulsification of " nujol " in water can be brought about merely by hand-shaking for 2 or 3 seconds. We call this " spontaneous " emulsification. With other agents emulsification can only be produced by using high powdered homogenisers. Whether or not emulsification is spontaneous depends on the interfacial tension σ of the system. If σ is extremely small, *e.g.* a fraction of dyne per cm., very little energy is required to break up the oil into droplets as small as 4μ in diameter. Hand-shaking is, therefore, sufficient. If σ is several dynes/cm. a considerable amount of such energy is necessary to disperse the oil into droplets of 4μ diameter, necessitating the use of an emulsifying machine. Adsorption of the emulsifying agent on to the oil droplets, artificially created by the homogeniser, occurs, the interfacial tension thereby being lowered.

For this adsorption process to be effective large concentrations of soap are necessary. Clearly, the condition of a very low interfacial tension would be of no avail in the easy formation of emulsions if the oil droplets produced immediately coalesced. A second condition can, therefore, be postulated, namely that the interfacial film of emulsifying agent should prevent the coalescence of the droplets. By using an emulsifying agent consisting of 2 components which form a suitable molecular complex at an oil/water interface, the above 2 conditions can be satisfied. As described in the last section, molecular complexes of the type cholesterol-cetyl sulphate present at an oil/water interface lower the interfacial tensions to negligible values and at the same time stabilise the oil droplets. For systems in which molecular complexes are used as emulsifying agents, the conditions required for spontaneous emulsification are the same as the conditions necessary for the production of emulsions of high stability, *i.e.* the interfacial tension should be very low, the interfacial molecular complex should be stable, and in the liquid condensed state, the oil droplet as a whole should be electrically charged. This charge is obtained by crowding ionic emulsifying agents, by means of a complex, into the interface.

It may be noted that if the molecular complex film is a viscous film, the resulting emulsion is very viscous and grease-like, and vigorous hand-shaking is necessary to form the emulsion, even if the interfacial tension is very low.

It seems possible that the ultimate limit to the size of the oil droplets present in an emulsion (assuming excess of emulsifying agent is present) is determined by the Brownian movement of the droplets. Certainly, Brownian movement becomes very marked with droplets less than $0{\cdot}5\mu$ in diameter, and no stable emulsions could be made containing droplets smaller than this. This diameter is at least ten times greater than that of soap micelles, which are associated molecular complexes. On the above view, it will be seen that living cells bounded by a membrane cannot be expected to be smaller than $0{\cdot}5\mu$ in diameter unless the membrane is very rigid. For if they were, Brownian movement would tend to bring about fusion of the cells. The biological significance of this will be mentioned elsewhere.

Special Complexes.

Bile Acids.

It has been found both from film penetration and emulsion stability experiments that the bile acids do not form complexes with long chain alcohols, cholesterol, glycerides or proteins. That they have an affinity for long chain fatty acids is shown by the following experiments. 200 mg. of sodium desoxycholate dissolved in 40 c.c. of water were added to 10 c.c. of oleic acid. A good emulsion was produced on hand-shaking. Good emulsions were also obtained using sodium glycocholate and sodium taurocholate instead of sodium desoxycholate, but no emulsions were obtained with the bile acid salts using " nujol " or long chain glyceride oils. The biological significance of these results will be mentioned elsewhere.

Proteins.

The same general rules for oil in water emulsions with protein as the water soluble component of the emulsifying agents can be applied, as already mentioned, for the lipoids.

0·66 per cent. gelatin solution is a poor emulsifying agent for " nujol " but if cholesterol be added to the oil phase a greatly enhanced emulsion is obtained. Similarly, other substances which are known to form complexes with proteins at the air/water interface greatly enhance the emulsion properties of the protein. Thus oleic acid, or elaidic acids, or oleyl alcohol aid the emulsion. There is some evidence that these substances work better than the saturated compounds.

The general order of reactivity of these compounds, as measured by emulsion stability, is the following (with gelatine),

cholesterol > oleic acid > oleyl alcohol > elaidic acid > stearic acid > cetyl alcohol.

Summary.

1. It is shown that molecular interactions occurring at a " nujol "/ water interface are closely analogous to the corresponding interactions at an air/water interface which have been widely studied with the Langmuir Trough apparatus.

2. The stability of " *nujol* " *in water* emulsions depends on the properties of the interfacial film of emulsifying agent. Optimum stability of the emulsion is obtained under the following conditions: (*a*) the interfacial film must be electrically charged; (*b*) the interfacial film must be stable and in the " condensed " state, *i.e.* as many charged molecules as

possible should be crowded into the interface. In this way, the interfacial tension is reduced to extremely small values.

3. The above two conditions are satisfied when the interfacial film consists of a molecular complex of two suitable substances, one of which is an oil soluble substance and the other an ionisable water soluble substance.

4. The stability of the interfacial complex film is markedly increased by the presence of excess water-soluble molecules above that necessary for a monolayer around the droplets, whereas only a monolayer is necessary for the oil-soluble component (for the cholesterol " nujol " system).

5. The stability of a " *nujol* " *in water* emulsion depends markedly on the nature of the two components chosen to form the interfacial complex film. The stability of such films runs parallel with the stability of the same films at an air/water interface, and depends on the van der Waals forces of attraction between the non-polar parts of the two components and on the interaction between the respective head groups. Hence alterations in the size of the non-polar residues, the stereochemical configuration of these residues, the nature of the polar heads, etc., cause alterations in the molecular packing and stability of the interfacial complex films and alterations, therefore, in the stability of the " *nujol* " *in water* emulsions, the stability of the emulsion can be deduced from a knowledge of the stability of the corresponding molecular complex at an air/water interface.

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MOLECULAR INTERACTIONS AT OIL/WATER INTERFACES.

PART II. PHASE INVERSION AND STABILITY OF WATER IN OIL EMULSIONS.

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In Part I[1] the conditions necessary for the formation of " nujol " in water emulsions were given. Two of the conditions were as follows : (1) the interfacial film must be in the liquid condensed state, and (2) the film must be electrically charged. It will be shown below that in order to produce phase-inversion of such emulsions the electric charge on the oil droplets must first be removed, whereupon the oil in water emulsion breaks. If, in addition, the composition of the aqueous and oil phases is such as to enable a solid condensed film, or, better, an " inter-linked " solid condensed film, to be formed at the interface, then an inversion process occurs with the formation of a water in oil emulsion. This is true for different types of emulsifying agents and over a wide range of conditions.

[1] Schulman and Cockbain, *Trans. Faraday Soc.*, 1939, **35**, 716.

Positively Charged Long-Chain Compounds as Emulsifying Agents.

When heptadecylamine is dissolved in " nujol " (10 c.c.) and shaken with N/100 HCl solution (10 c.c.) an oil in water emulsion is obtained. (The stability of the emulsion is rather poor, as would be expected from the conclusions of Part I.) Table I shows the effect of adding various salts and acids to this oil in water emulsion. The type of emulsion so obtained (oil in water or water in oil) and the nature of the interfacial film at an air/water interface are given. The continuous phase was determined in the usual way by admixture of the emulsion with water or oil and by addition of water-soluble or oil-soluble dyes.

TABLE I.

Emulsifying Agents.	Interfacial Film.	Emulsion Type.
(1) Heptadecylamine HCl (*p*H 2·0) *	Liquid (charged +) †	Oil in water.
(2) (1) + $(NaPO_3)_3$	Solid (neutral)	Water in oil.
(3) (1) + Na_2SO_4	Solid (neutral)	Water in oil.
(4) (1) + tannic acid	Liquid (charged +)	Oil in water.
(5) Heptadecylamine + Na tannate (*p*H 7 to 8)	Solid (neutral)	Water in oil.
(6) Heptadecylamine + 3N. HCl	Solid (multilayer) Film (neutral)	Water in oil.
(7) Heptadecylamine alone (*p*H 7·0)	Amine too soluble in the oil phase to form any emulsion at all.	

* Charge was determined by Cataphoresis experiments.

† Heptadecylamine HCl films, owing to repulsion between like charges in single component films are really vaporous. On neutralisation of these charges by the polyvalent negative anions the film is solidified, showing that the film is no longer charged.

It can be seen in Table I that when the interfacial film at an air/water interface is solid, water in oil emulsions are obtained. The difference in rigidity of a given film at an air/water and an oil/water interface will be merely one of degree. It can be concluded, therefore, that a rigid, or at least a very viscous, film at the oil/water interface favours the formation of a water in oil emulsion. In example (1) the interfacial film will not only be liquid but also positively charged, owing to the ionisation of the amine hydrochloride. The ionised film molecules will undoubtedly repel one another and have a marked freedom of movement. By the addition of polyvalent negative ions, as in (2) and (3), the positive charge on the amine molecules is neutralised, and two or more of the molecules are inter-linked, depending on the valency of the anions added. The movement of the film molecules is, therefore, restricted, giving a rigid or viscous film. Thus a requirement for the formation of water in oil emulsions is that the interfacial film should be uncharged. The addition of tannic acid in examples (4) and (5) is of great interest. At *p*H 2·0 an oil in water emulsion is obtained; at *p*H 7 to 8 a water in oil emulsion. The conversion of one emulsion into the other by a change of *p*H was found to be a reversible phenomenon. Cockbain and Schulman showed that at *p*H 2·0 tannic acid interacts only weakly with long-chain amine films at an air-water interface, the amine film remaining liquid and ionised. This explains why emulsion

(4) in Table I is of the oil in water type. At *p*H 7 to 8, tannic acid reacts strongly with an amine film, converting it from a liquid to a rigid solid state. Hence emulsion (5) is of the water in oil type. Tannic acid at *p*H 7 to 8 acts in the same way as a polyvalent negative ion because a *multiple-point* polar interaction occurs with the amine film. Heptadecylamine in " nujol " forms a water in oil emulsion with 3 N. HCl solution. An amine film on 3 N. HCl at an air/water interface is in the viscous liquid or solid state. Actually we consider the film to be a multi-layer film such as is obtained with soap films spread on very alkaline solutions. In addition to the rigidity of the amine film on 3 N. HCl, it is very probable that the diffuse ionisation of the amine hydrochloride is largely suppressed by the high

$$[R\,NH_3]^+\,Cl^- \rightleftharpoons R\,NH_3^+ + Cl^-$$

concentration of chloride ions, so that the interfacial film is uncharged. (These are the conditions in which salting out occurs probably by removal of the diffuse layer by the high ionic concentration and consequent discharging of the micelle on a " mass law " action.) The result is that emulsion (6) is of the water in oil type.

Long-chain quaternary ammonium compounds are too soluble in water and too highly ionised to form other than highly expanded vaprous films at an oil/water interface. Hence, lissolamine (cetyl trimethyl ammonium bromide) in dilute solution has very little emulsifying action on " nujol "/water systems. But if the lissolamine molecules are held in the interface by cholesterol from the oil phase, good oil in water emulsions are obtained as explained in Part I. Table II shows the effect of adding salts or tannic acid to such emulsions.

TABLE II.

Emulsifying Agents.	Interfacial Film.	Emulsion Type.
(1) Lissolamine (*p*H 7) *	Lissolamine too soluble in water phase to form an emulsion.	
(2) Lissolamine + cholesterol (*p*H 7)	Liquid condensed (charged +)	Oil in water.
(3) (2) + Na_2SO_4	Liquid (charged +)	Oil in water.
(4) (2) + $(NaPO_3)_3$	Solid (neutral)	Water in oil.
(5) (2) + tannic acid (*p*H 3)	Solid (neutral)	Water in oil.

* Charge determined by Cataphoresis experiments.

We conclude that divalent sulphate ions are unable to neutralise the charge on the highly ionised quaternary ammonium salt, or to rigidly interlink the lissolamine molecules. These processes do occur in the presence of trivalent phosphate ions over a wide *p*H range, and in the presence of tannic acid at *p*H 3. The marked differences between heptadecylamine (Table I) and lissolamine (Table II) are probably not due entirely to differences in the degree of ionisation. Thus, the presence of three methyl groups round the nitrogen atom in lissolamine might hinder association between the positively charged lissolamine molecules at the interface and polyvalent anions in the aqueous phase. It has been established experimentally that in mixed films of quaternary ammonium salts and long-chain alcohols, complex formation is strongly inhibited by steric factors connected with the quaternary ammonium group. No steric hindrance effects are observed when a long-chain amine is substituted for the quaternary ammonium compound.

In the case of oil in water emulsions, a stable interfacial film was produced by using an emulsifying agent consisting of two suitable long-chain molecules which formed a complex. With water in oil emulsions, the use of *two* long-chain compounds should not, in general, be necessary, since rigid and uncharged interfacial films can be produced by the association of a single long-chain compound with polyvalent ions of the opposite charge present in the aqueous phase.

Negatively Charged Soaps as Emulsifying Agents.

When negatively charged soaps are employed as emulsifying agents, the conditions necessary for the production of water in oil emulsions are the same as those formulated in the previous section. These conditions are :—

(1) The interfacial films should be uncharged.
(2) The film should be rigid, or at least very viscous.

The above requirements are fulfilled when long-chain carboxylic acid molecules are inter-linked at an oil/water interface by polyvalent metal ions. It is well known that oil in water emulsions stabilised by negatively charged long-chain carboxylates are inverted to water in oil emulsions by the addition of Ca or Ba salts, for example. Similarly, when " nujol " in water emulsions are stabilised by a complex of cholesterol and sodium cetyl sulphate or cholesterol and sodium palmitate, addition of Ba or Ca salts produces a phase inversion. At an air/water interface, liquid complex films of cholesterol + sodium cetyl sulphate (or sodium palmitate) turn solid on injection of Ba or Ca salts into the underlying solution. Sodium palmitate alone will normally give an emulsion of " nujol " in water. On addition of strong caustic soda to this emulsion, inversion occurs at $p\text{H} > 14$. It is probable that the diffuse ionisation of the sodium palmitate is suppressed by the strong caustic soda, so that the interfacial soap film is largely uncharged,

$$[\text{R COO}]^- \text{Na}^+ \rightleftharpoons \text{R COO}^- + \text{Na}^+.$$

In addition, the interfacial film is probably solid, since it has been shown that soap films spread on strongly alkaline solutions at an air/water interface are solid multilayer films.[2] The inversion of Na palmitate emulsions at very high $p\text{H}$ values is exactly analogous to the inversion of heptadecylamine emulsions at very low $p\text{H}$ values. Addition of aluminium or thallous salts to " nujol " in water emulsions stabilised by a cholesterol-Na palmitate mixture produces inversion of the emulsions. It is interesting that thallous salts, which are *monovalent*, give water in oil emulsions. It is known, however, that monovalent thallous (or silver) soaps are unionised. Furthermore, they would almost certainly form solid films.

Since the polyvalent metal soaps are insoluble in water or " nujol " (except, perhaps, aluminium soaps at high temperatures), the corresponding water in oil emulsions cannot be prepared directly, but must be produced by an inversion process.

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[2] Bikerman, *Proc. Roy. Soc.*, *A*, 1939, **170**, 131.

Direct Preparation of Water in Oil Emulsions.

To obtain directly a water in oil emulsion it is necessary to bring the emulsifying agent to the oil/water interface, so as to form a film which is uncharged and rigid. A very good example is the use of digitonin plus cholesterol as the emulsifying agent. Digitonin is a *neutral* molecule readily soluble in water, and has no emulsifying action by itself on "nujol"/water systems. Nor has cholesterol any emulsifying action by itself. But if an aqueous solution of digitonin is added to a solution of cholesterol in "nujol," excellent water in oil emulsions are obtained. The cholesterol and digitonin are both held at the oil/water interface owing to strong complex formation, giving a rigid and uncharged interfacial film. At an air/water interface, cholesterol-digitonin complexes form very rigid films indeed.

If an acid saponin is used in place of the digitonin, "nujol" in water emulsions are obtained. This is because acid saponins are negatively charged molecules and the acid saponin-cholesterol complex formed at the oil/water interface will also be negatively charged. In addition, it is known that acid saponin-cholesterol complexes at an air/water interface form viscous liquid but not rigid films.

If, in the above experiments, cholesterol acetate or cholesterol stearate be substituted for the cholesterol, hardly any emulsification occurs. As already described in Part I, this is due to the fact that no molecular complexes are formed between cholesterol esters and saponin or digitonin.

A general characteristic of water in oil emulsions is that under the microscope the water droplets have irregular shapes. They appear to be contained in "sacks." We attribute this appearance to the rigid nature of the film surrounding the water droplets, the film molecules being fixed as in a 2-dimensional crystal. Osmotic forces might cause alterations in the shape of the "sacks."

On the other hand, all oil in water emulsions which we have examined contain completely spherical droplets, owing to the interfacial film being in the liquid condensed state. With a liquid interfacial film, the oil droplets could easily regain their spherical shape after being deformed in any way.

The Mechanism of the Phase Inversion Phenomenon.

In emulsions of oil in water, the interfacial film is in the liquid condensed state, and is electrically charged. The fact that the water is the continuous phase must mean that the oil droplets are electrically charged; since water, being an ionising medium, enables charged oil droplets to repel one another,* owing to the formation of a diffuse layer or ionic atmosphere around the oil droplets, so that a stable oil in water emulsion can be obtained (providing that the physical characteristics of the interfacial film fulfil the conditions set out in Part I[1]). If, however, the oil were the continuous phase, the fact that the interfacial film consisted of charged molecules could not prevent the dispersed water droplets from coalescing because oil being a non-ionising medium, no electrical diffuse layer or ionic atmosphere can be built up. If, furthermore, the charged interfacial film were an interlinked solid, no coalescence would be likely to occur because of mechanical reasons (see

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* See Theory of *G* Potentials.

requirements for stable water in oil emulsions). However, the above film would not be a rigid interlinked solid, since films consisting of charged molecules are either liquid or gaseous, but not interlinked, owing to repulsion between the molecules in the film. Fig. 1*a* shows diagrammatically, oil droplets dispersed in water and stabilised by a liquid condensed mixed film such as cholesterol + sodium cetyl sulphate. The adsorbed diffuse double layer of sodium cetyl sulphate is also represented, and the oil droplets are given a negative charge because of the negatively charged cetyl sulphate ions.

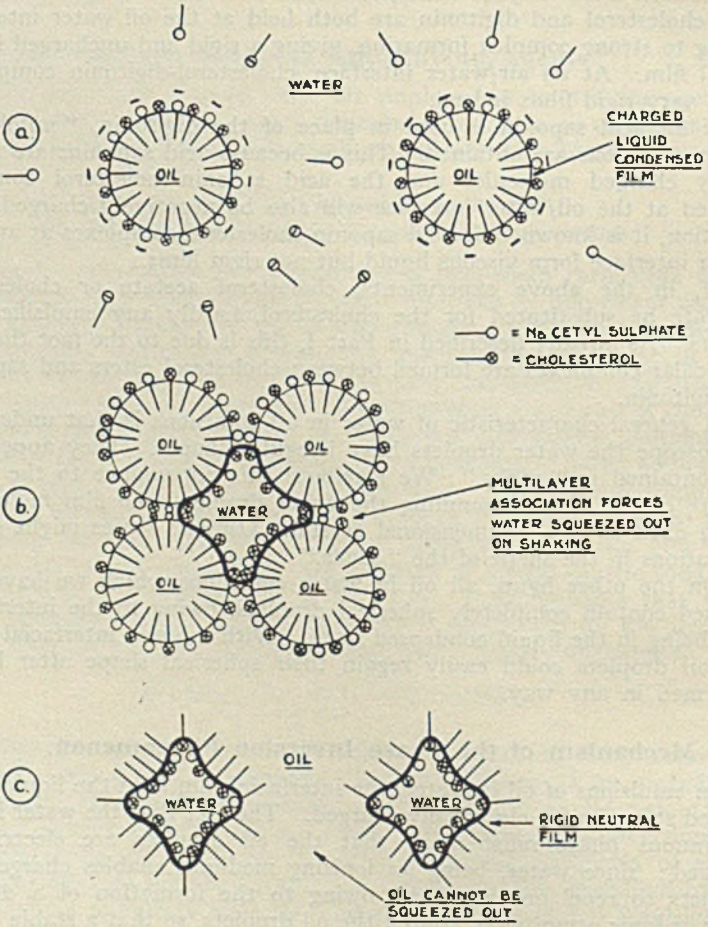

Fig. 1.

In Fig. 1*b* is shown the state of affairs after polyvalent kations (Ca^{++} or Ba^{++}, for example) have been added to the oil in water emulsion. Adsorption of the kations has destroyed the negative charge on the oil droplets, thus allowing them to coalesce, the diffuse double layer of sodium cetyl sulphate having been removed by kations in the process.

During the process of coalescence, water molecules can be squeezed out from between the oil droplets very readily because the interfacial film molecules have a strong tendency to align themselves with their polar heads together, as in their normal crystal packing (see diagram, Fig. 2).

In this connection it is significant that, in the Langmuir-Blodgett technique for obtaining multilayers on metals, the conditions required to produce film deposition are analogous with those necessary for the formation of water in oil emulsions. In film deposition, the molecules of the multilayer are known to be oriented in the normal crystal packing arrangement shown in Fig. 2. Thus, the Ca salt of a long-chain fatty acids or the phosphate salt of a long-chain amine is deposited in double lattice form when built up as a multilayer on metals. The same substances stabilise water in oil emulsions. The reason for the film deposition and for the coalescence of oil droplets covered by an uncharged interfacial film is that water is so readily squeezed out from between the polar heads of the film molecules enabling them to take up their normal crystal packing arrangement.

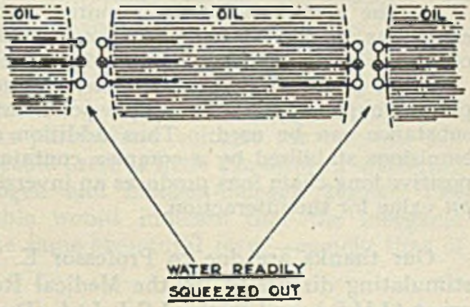

FIG. 2.

Fig. 1*b* shows a number of oil droplets in the coalesced state after removal of the charge on the oil droplets. If, now, the interfacial film is rigid and especially if a cross-linking of the film molecules has occurred to give the crystal packing arrangement described above, the water " sacks " enclosed by the coalesced oil droplets will themselves be stabilised, and will float away. This process is represented in Fig. 1*c*. The emulsion is now of the water in oil type and the interfacial film molecules have their long hydrocarbon chains directed outwards from the water " sacks." No coalescence of these water " sacks " will occur, because the oil cannot be squeezed out from between them. On the contrary, the hydrophobic chains of the film molecules will adhere to the oil molecules of the continuous phase just as ionic head groups in interfacial films adhere to water molecules in emulsions of the oil in water type. Water " sacks " of irregular shape are typical of all water in oil emulsions, the irregular shape being due to the necessary rigidity of the interfacial film.

Summary.

1. Emulsions of *water in " nujol "* are obtained when emulsifying agents are added which form interfacial films possessing certain characteristics. These are (*a*) the interfacial film should possess no electric charge ; and (*b*) it should possess considerable rigidity. Thus, water containing digitonin when added to " nujol " containing cholesterol, forms a *water in oil* emulsion directly. Similar behaviour is shown when water is added to " nujol " containing palmitic acid plus heptadecylamine.

2. *Oil in water* emulsions are inverted to *water in oil* emulsions if they are treated in such a way as to make the interfacial film fulfil the above two conditions. Addition of polyvalent ions to oil in water emulsions stabilised by a complex of the opposite charge produces two effects : (*a*) the interfacial film is discharged enabling the oil droplets to coalesce by a squeezing out

of the water between the interfaces of the oil droplets; (*b*) a marked increase in the rigidity of the interfacial film is brought about through an interlacing of the film molecules by the polyvalent ions. In this way water "sacks" dispersed in oil are obtained. The water sacks do not coalesce on approach because of the strong affinity between the hydrocarbon chains of the interfacial films and the surrounding oil medium which prevents the oil being squeezed out from between approaching water sacks.

3. The above conditions required for the formation of *water in oil* emulsions are similar to those necessary for the production of multilayers on metals using the Langmuir-Blodgett technique.

4. In place of polyvalent ions, charged molecules containing many polar groups capable of multiple point interaction with the film-forming substance can be used. Thus addition of tannic acid to oil in water emulsions stabilised by a complex containing long chain amines or other positive long chain ions produces an inversion of the emulsion at a suitable *p*H value for the interaction.

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STUDIES OF THE STRUCTURES OF SOME INORGANIC PENTAHALIDE MOLECULES IN THE VAPOUR PHASE, BY ELECTRON DIFFRACTION.

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The structural form of some inorganic pentahalides has been the object of recent investigations. Braune and Pinnow [1] have examined PF_5 and IF_5 using the method of electron diffraction by the vapours. They concluded that PF_5 is best represented by a regular trigonal bipyramid structure. It was impossible from the electron diffraction results to assign any definite structure to the IF_5 molecule, but it was shown that the I—F distance is uniform. More recently, Brockway and Beach [2] have reinvestigated PF_5 by the electron diffraction method, and their results, considered together with the observed zero dipole moment in this compound,[3] show conclusively that PF_5 has a regular trigonal bipyramid structure. Ewens and Lister [4] investigated the structure of $MoCl_5$ using electron diffraction by the vapour. Their examination favoured the trigonal bipyramid structure. The Raman spectra of liquid and solid PCl_5 have been studied by Moureu, Magat,

[1] Braune and Pinnow, *Z. physikal. Chem., B*, 1937, **35**, 239.
[2] Brockway and Beach, *J.A.C.S.*, 1938, **60**, 1836.
[3] Linke and Rohrmann, *Z. physikal. Chem., B*, 1937, **35**, 256.
[4] Ewens and Lister, *Trans. Faraday Soc.*, 1938, **34**, 1358.

and Wetroff,[5] who concluded that in the liquid state, PCl_5 has the trigonal bipyramid structure, and that in the solid state, the molecule is a complex ionic structure. Powell, Clarke and Wells [6] from the X-ray crystallographic examination of PCl_5, have shown that the ions in the crystal are $[PCl_4]^+[PCl_6]^-$. Rouault and Schomaker [7(a), (b)] from electron diffraction studies of PCl_5 in the vapour phase, conclude that the molecule is a trigonal bipyramid, but that there are two distances for the P—Cl links, differing by about 0·10 A. The pentahalides $NbBr_5$, $NbCl_5$, $TaBr_5$ and $TaCl_5$ have now been investigated in the vapour state by the method of electron diffraction. The results show that the above compounds are best represented by the regular trigonal bipyramid model. The molecule $NbBr_5$ is particularly suitable for electron diffraction study, since in this molecule there is little disparity in scattering power between the metal-halogen and halogen-halogen terms. The complete evidence now available would indicate that the inorganic pentahalides as a class have the same structural form—namely that of the regular trigonal bipyramid.

Experimental.

The chlorides of Nb and Ta were prepared by the action of pure dry Cl_2 on the powdered metals at a temperature of about 250° C. The compounds were purified by repeated sublimation in a stream of pure dry nitrogen. The bromides of the metals were also prepared by the direct method. The Br_2, carefully purified from Cl_2, and dried, was passed in a dry N_2 stream over the powdered metals at about 300° C. The bromides were purified by sublimation in a dry N_2 stream. It was found necessary to purify the $NbBr_5$ more completely by sublimation *in vacuo*. The manipulation of the compounds was carried out in a dry N_2-filled box, because of the extreme sensitivity of the compounds to the moisture of the air.

The diffraction patterns from the vapours of the compounds were photographed in the apparatus described by de Laszlo.[8] The photographs were taken with the following oven temperatures :

$TaCl_5$ . .	160-180° C.	$NbCl_5$ . .	150-170° C.
$TaBr_5$ . .	180-200° C.	$NbBr_5$ . .	200-230° C.

The camera distance was 28·05 cm., and the electron wave-lengths about 0·06 A.

Electron Diffraction by Niobium Pentabromide.

The photographs for this compound showed five maxima, whose intensities appeared to decrease fairly regularly with increasing diameter. The rings appeared to be symmetrical with the exception of the third maximum which shaded off markedly towards the outside, and gave the appearance of a shelf in between the third and fourth maxima. The shelf was not sufficiently distinct to allow of accurate measurement.

The observed s_0 $\left(= 4\pi \frac{\sin \theta/2}{\lambda}\right)$ values, and the visually estimated intensities of the maxima, are given in Table I. The positions of the maxima and minima were measured visually on a comparator. The C values given in Table I, are the " weighted " intensities of the maxima, calculated by the method of Schomaker and Degard.[9] The C values

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[5] Moureu, Magat and Wetroff, *C.R.*, 1937, **205**, 276.

[6] Powell, Clarke and Wells, *Nature*, 1940, **145**, 149.

[7] (*a*) Rouault, *C.R.*, 1938, **207**, 620 ; (*b*) Schomaker, reported in Pauling, *Nature of the Chemical Bond*, 1939, footnote, p. 103.

[8] de Laszlo, *Proc. Roy. Soc., A*, 1934, **146**, 662.

[9] Degard and Schomaker, *J.A.C.S.*, in press.

TABLE I.

Max.	Min.	I.	C.	$s_{obs.}$	s_A.	s_B.	s_C.	s_D.	l_A.	l_B.	l_C.	l_D.
1		10	10	(3·29)	3·57	2·80	3·14	3·58	(2·496)	—	—	(2·503)
						3·50	—	—	—	—	—	—
				—	—	4·17	—	—	—	—	—	—
	1			(4·80)	5·02	5·12	4·16	4·98	(2·405)	(2·453)	—	(2·386)
2		10	18	5·81	6·28	6·17	5·97	6·07	2·486	2·443	—	2·403
	2			6·99	7·40	7·38	6·85	7·75	2·435	2·428	—	2·550
				—	—	—	7·58	—	—	—	—	—
				—	—	—	8·20	—	—	—	—	—
3		7	12	7·95	8·43	8·46	9·02	8·83	2·439	2·448	—	2·555
				—	9·32	9·37	—	—	—	—	—	—
				—	9·88	10·00	—	—	—	—	—	—
	3			10·02	10·68	10·78	10·90	9·85	2·451	2·474	—	—
				—	—	—	—	10·85	—	—	—	—
				—	—	—	—	11·30	—	—	—	—
4		6	5	10·93	11·75	11·90	11·80	12·14	2·473	2·504	—	2·555
	4			12·25	13·08	13·07	12·93	13·36	2·456	2·454	—	2·508
5		3	1	13·25	14·20	14·10	14·55	14·40	2·465	2·448	—	2·500
Mean . .									2·458	2·457	—	2·512
Average deviation . .									0·014	0·018	—	0·042

Final value . . Nb—Br 2·46 ± 0·03 A.

are obtained by multiplying each of the visually estimated intensities by the factor s_0^2 . exp. $(-as_0^2)$, where a is chosen so that the coefficient of the strongest ring is ten times that of the weakest.

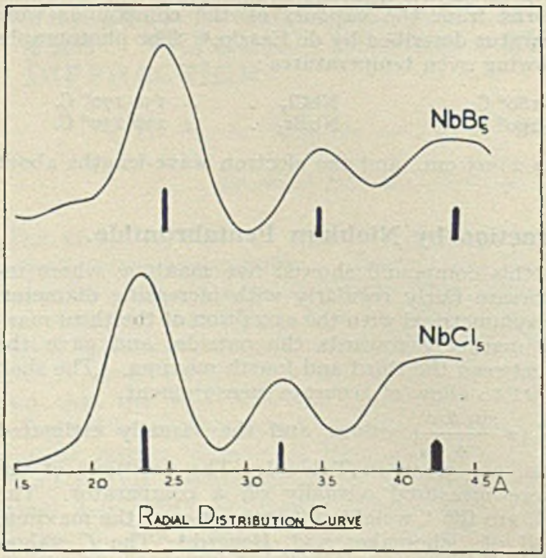

FIG. 1.

The radial distribution curve, calculated from the observed s values, and the C values, is reproduced in Fig. 1. This curve shows peaks at distances corresponding to

Nb—Br = 2·46 A.
and Br—Br = 3·51 A.

From these values it follows that there are a number of Br—Nb—Br angles of 90°.

Assuming a uniform Nb—Br distance of 2·30 A. four models were investigated by the correlation method. The choice of this distance merely affects the scale, and not the form of the theoretical scattering curves, so that the true value of the assumed distance may subsequently be obtained by simple proportion from the observed and calculated s values.

The models investigated are described below :

Model A. The Br atoms occupy the corners of a regular trigonal bipyramid, with the Nb atom at the centre.

Model B. The Br atoms at the corners of a square pyramid with the Nb atom at the centre of the base.

Both models A and B have a number of Br—Nb—Br angles of 90°, according to the requirements of the radial distribution results.

Model C. A regular planar model, with all the Br—Nb—Br angles = 72°.

Model D. The Br atoms at the corners of a square pyramid, with the Nb atom centrally placed *above* the square base, so that the angle Br—Nb—Br is 105°.

The theoretical scattering curves for each of the above models are reproduced in Fig. 2.

The qualitative differences in these four curves are well marked, and the comparison of curves C and D with the general appearance of the plates is itself sufficient to rule out the corresponding models.

Curve C has an unsymmetrical second maximum, and a shelf on the inside of the third maximum. The plates showed the shelf on the outside of the third maximum, and the second maximum was quite symmetrical.

Curve D is unsatisfactory in the regions of the second and third minima, and the fourth maximum. The shading off (shelf) occurs on the inside of the fourth maximum so that the third minimum would lie nearer to the third maximum than to the fourth, whereas the plates show the third minimum to be displaced distinctly towards the fourth maximum.

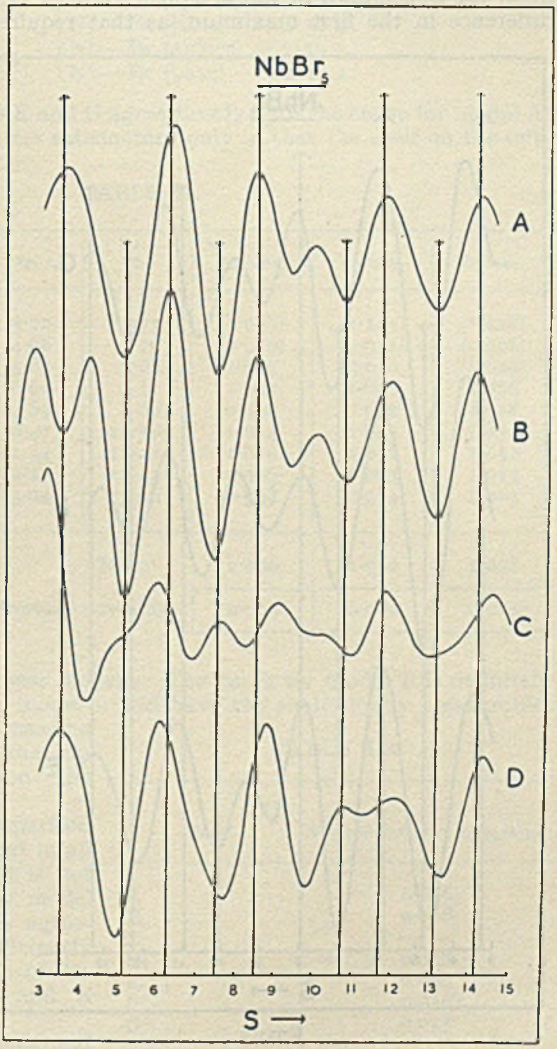

Fig. 2.

The most marked difference in the curves A and B lies in the first maximum. Whereas curve A has a perfectly symmetrical first maximum, curve B has it clearly split into two parts. The plates obtained from

$NbBr_5$ were exceptionally clean and distinct and there was absolutely no indication of any disymmetry or splitting in the first maximum. The qualitative comparison of the theoretical curves with the photographic plates, definitely favours Model A (the trigonal bipyramid) and would certainly rule out Models C and D. Model B is incompatible with the observed first maximum. Although it is unwise (as a general rule) to rely upon the appearance of the first maximum, it is felt that such a marked difference in the first maximum, as that required by models A and B, would be observable on the plates.

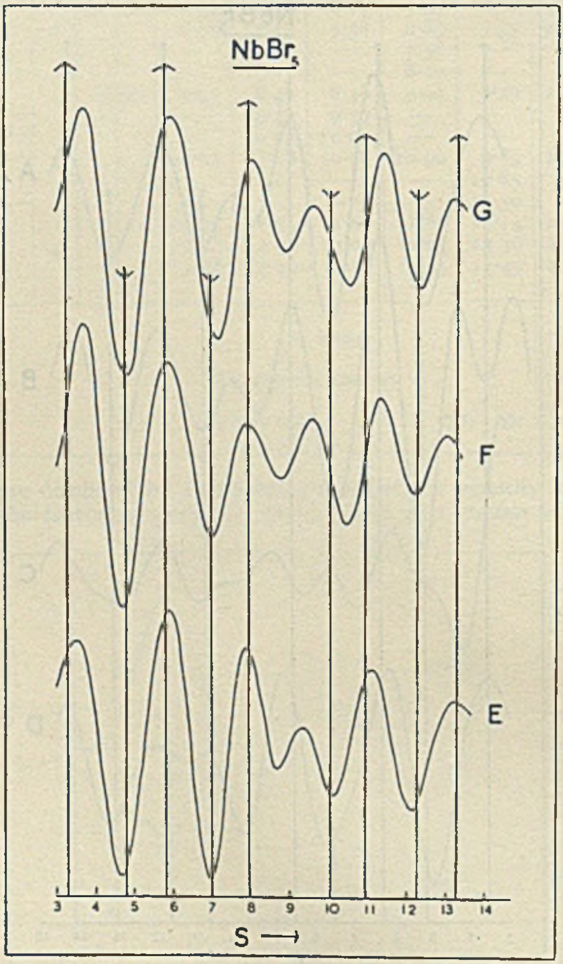

Fig. 3.

Table I gives the s values for the four calculated curves and the distances of the Nb—Br link derived from these values (*i.e.*, 2·30 . $s_{\text{calc.}}/s_{\text{obs.}}$) in the various models. This table shows that the best quantitative agreement is given by curve A, although this is only slightly better than that of curve B.

It would be expected that the models A and B should give theoretical scattering curves similar to one another, since both models have a number of Br—Nb—Br angles of 90°, and consequently have many of the Br—Br distances equal. Model B is likely to be less stable than Model D, because in the latter the weighted mean of the Br—Br distances is 3·77 A., as compared with 3·86 A. in the former, and the potential energy of repulsion between the Br atoms is larger. Consequently, although the model B is in good agreement with the electron diffraction results (except in the unreliable region of the first maximum), it is in itself a less likely structure than model D—which has been shown to be far less in agreement with the experimental results than model A. It may therefore be concluded that of the models considered, the most satisfactory is the regular trigonal bipyramid, with a Nb—Br distance = 2·46 ± 0·03 A.

In view of the reported variation of the lengths of the P—Cl bonds in PCl_5,[7(a), (b)] it was deemed necessary to consider some trigonal bipyramid models with unequal distances. Three such models were therefore examined by the correlation method, the theoretical scattering curves for which are shown in Fig. 3. The models were all of the trigonal bipyramid type, with dimensions as follows:

$$\textbf{Model E.}\begin{cases}\text{Nb—Br (apices)} = 2{\cdot}50\ \text{A.}\\ \text{Nb—Br (base)} = 2{\cdot}40\ \text{A.}\end{cases}$$

$$\textbf{Model F.}\begin{cases}\text{Nb—Br (apices)} = 2{\cdot}60\ \text{A.}\\ \text{Nb—Br (base)} = 2{\cdot}30\ \text{A.}\end{cases}$$

$$\textbf{Model G.}\begin{cases}\text{Nb—Br (apices)} = 2{\cdot}50\ \text{A.}\\ \text{Nb—Br (base)} = 2{\cdot}30\ \text{A.}\end{cases}$$

The curves for models E and G agree closely with the curve for model A, in general form, and are less satisfactory only in that the shelf on the outside is more marked in these models. The curve for model F is definitely unsatisfactory, since this model would have the shelf clearly measurable, and the intensities of the maxima do not follow closely the intensities estimated from the plates.

TABLE II.

$s_{\text{obs.}}$	s_E.	s_F.	s_G.	$s_E/s_{\text{obs.}}$	$s_F/s_{\text{obs.}}$	$s_G/s_{\text{obs.}}$
(3·29)	3·53	3·70	3·71	(1·073)	(1·125)	(1·128)
(4·80)	4·70	4·66	4·79	(0·979)	(0·971)	(0·998)
5·81	5·90	5·87	5·98	1·015	1·010	1·029
6·99	7·00	6·99	7·17	1·001	1·000	1·026
7·95	7·92	7·89	8·09	0·996	0·992	1·018
10·02	10·16	10·47	10·58	1·014	1·045	1·056
10·93	11·14	11·34	11·48	1·019	1·038	1·050
12·25	12·20	12·27	12·43	0·996	1·002	1·015
13·25	13·23	13·04	13·29	0·998	0·984	1·003
			Mean	1·006	1·010	1·028
			Average deviation	0·009	0·018	0·015

TABLE IIA.

Model.	Average Deviation $s_{\text{calc.}}/s_{\text{obs.}}$
A . . .	0·006
B . . .	0·008
C . . .	—
D . . .	0·018
E . . .	0·009
F . . .	0·018
G . . .	0·015

The quantitative comparison of these curves shows that in all three cases the agreement is not as good as that given by model A; but the quantitative agreement of curve E is sufficiently close to make a definite choice between the models E and A impossible.

The measured *s* values and the values of the $s_{\text{calc.}}/s_{\text{obs.}}$ ratios for the models E, F, and G are given in Table II. The average deviations from the mean values of these ratios for all the models considered are given subsequently.

Model A is therefore in the best quantitative agreement, but the agreement is only slightly better than in model E. It is therefore not possible to state that in $NbBr_5$ all the Nb—Br links are of the same length, although it can be stated that the link lengths do not deviate from the mean value (2·46 A.) by more than ± 0·05 A.

Electron Diffraction by Niobium Pentachloride.

The photographs for this compound showed five rings, the intensities of each decreasing regularly with increasing diameter. The maxima appeared symmetrical with the exception of the third which fell away slowly on the outside. The observed *s* values and intensities are given in Table III.

The radial distribution curve, reproduced in Fig. 1, showed strong peaks at distances corresponding to the internuclear distances :

Nb—Cl = 2·29 A. Cl—Cl = 3·23 A. .

From these values it follows that there are a number of Cl—Nb—Cl angles of 90°.

Assuming a Nb—Cl distance of 2·00 A., three models were investigated by the correlation method. These models were similar to those described for $NbBr_5$.

Model A.—Regular trigonal bipyramid.

Model B.—Square pyramid, Cl—Nb—Cl angles = 90°.

Model C.—Planar model.

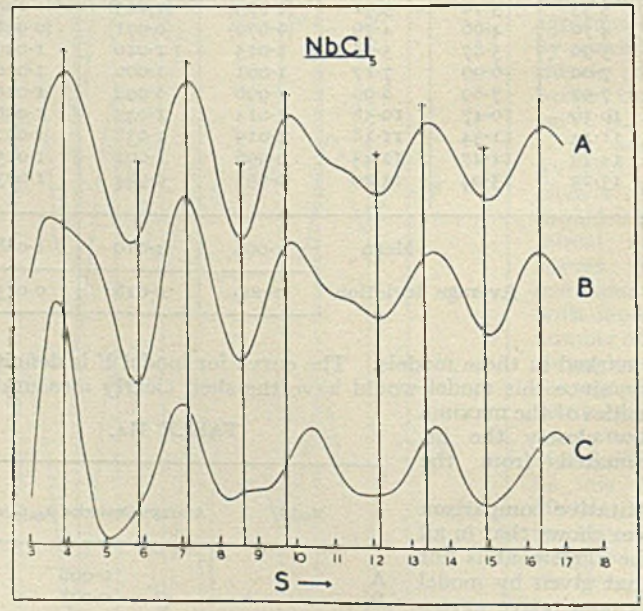

FIG. 4

The theoretical intensity curves derived from these three models are shown in Fig. 4.

Curve C is unsatisfactory : it shows no sign of the observed shading off of the third maximum on the outside, instead this appears on the inside. Curves A and B are very similar except in the region of the first maximum. The appearance of this on the plates was perfectly symmetrical, and there was no sign of the disymmetry that curve B shows. Quantitatively, the best agreement is given by model A, although the agreement is only slightly better than that of model B. The quantitative agreement of model C is poor, and the planar model can be definitely ruled out.

On the whole, the experimental evidence is more in favour of model A than of model B, and furthermore, the considerations of the stability of model B, described under $NbBr_5$, apply equally in the chloride. The

s values for the three calculated curves, and the Nb—Cl distances derived from these values (*i.e.* 2·00 . $s_{\text{calc.}}/s_{\text{obs.}}$), are given in Table III.

The value found for the Nb—Cl distance is 2·29 ± 0·03 A.

TABLE III.

Max.	Min.	I.	C.	$s_{\text{obs.}}$	s_A.	s_B.	s_C.	l_A.	l_B.	l_C.
Niobium Pentachloride.										
1		10	10	(3·39)	3·93	3·50	3·70	(2·319)	(2·065)	(2·183)
	1			(5·11)	5·62	5·79	5·00	(2·200)	(2·266)	(1·957)
2		10	19	6·25	7·14	7·07	6·94	2·285	2·262	2·237
	2			7·52	8·53	8·53	8·20	2·269	2·269	2·181
3		7	12	8·48	9·83	9·86	10·32	2·318	2·325	2·434
	3			10·62	12·11	12·13	11·94	2·281	2·284	2·249
4		4	4	11·67	13·42	13·54	13·56	2·300	2·320	2·324
	4			13·02	14·98	15·00	14·87	2·301	2·304	2·284
5		3	1	14·26	16·40	16·24	16·67	2·300	2·278	2·338
					Mean . . .			2·293	2·293	2·292
					Average deviation .			0·013	0·021	0·062
				Final value : Nb—Cl = 2·29 ± 0·03 A.						
Tantalum Pentabromide.										
1		10	10	(3·12)	3·37	3·08	3·23	(2·484)	(2·270)	(2·381)
	1			(4·80)	4·66	5·03	4·32	(2·233)	(2·410)	(2·070)
2		10	22	5·85	6·23	6·14	6·08	2·449	2·414	2·390
	2			7·03	7·54	7·40	7·12	2·467	2·421	2·329
3		8	20	7·97	8·56	8·50	9·13	2·470	2·453	2·635
	3			9·88	10·47	10·60	10·17	2·437	2·468	2·367
4		6	10	11·04	11·50	11·80	11·92	2·396	2·458	2·483
	4			12·32	13·16	13·02	13·00	2·457	2·431	2·427
5		3	3	13·37	14·38	14·13	14·50	2·474	2·431	2·494
	5			14·68	15·60	15·35	15·74	2·444	2·405	2·466
6		3	1	15·84	17·00	17·44	16·88	2·468	2·532	2·451
					Mean . . .			2·451	2·446	2·449
					Average deviation .			0·020	0·028	0·065
				Final value : Ta—Br = 2·45 ± 0·03 A.						
Tantalum Pentachloride.										
1		10	10	(3·18)	3·86	3·78	3·73	(2·428)	(2·377)	(2·346)
	1			(5·09)	5·40	5·65	5·30	(2·122)	(2·220)	(2·083)
2		10	24	6·16	7·10	7·05	6·97	2·305	2·289	2·263
	2			7·51	8·65	8·56	8·48	2·304	2·280	2·258
3		6	16	8·58	10·00	9·95	10·30	2·331	2·319	2·401
	3			10·44	11·95	11·95	11·77	2·289	2·289	2·255
4		3	6	11·57	13·24	13·46	13·50	2·289	2·327	2·334
	4			13·02	14·95	14·96	14·89	2·296	2·298	2·287
5		1	1	14·28	16·52	16·32	16·62	2·314	2·286	2·328
					Mean . . .			2·304	2·298	2·304
					Average deviation .			0·011	0·014	0·043
				Final value : Ta—Cl = 2·30 ± 0·02 A.						

Electron Diffraction by Tantalum Pentabromide.

The photographs for this compound showed six rings, the intensities of each decreasing with increasing diameter. The maxima appeared to be symmetrical with the exception of the third which fell off slowly towards the outside. The *s* values and measured intensities are given in Table III. The radial distribution curve (reproduced in Fig. 5) showed strong maxima at distances corresponding to

$$\text{Ta—Br} = 2{\cdot}47 \text{ A.}$$
$$\text{Br—Br} = 3{\cdot}45 \text{ A.}$$

From these values it follows that there are a number of Br—Ta—Br angles of 90°.

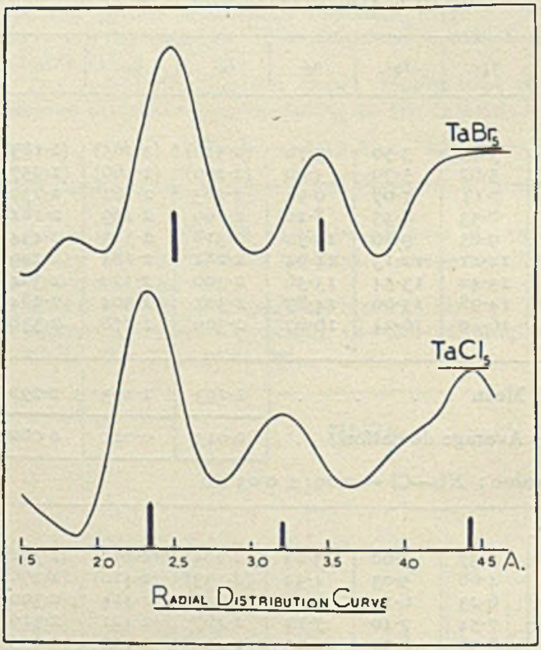

Fig. 5.

Assuming a Ta—Br distance of 2·30 A., three models were studied by the correlation method. The models were similar to those chosen in the investigation of NbBr$_5$.

Model A — regular trigonal bipyramid.

Model B—square pyramid, Br—Ta—Br angles = 90°.

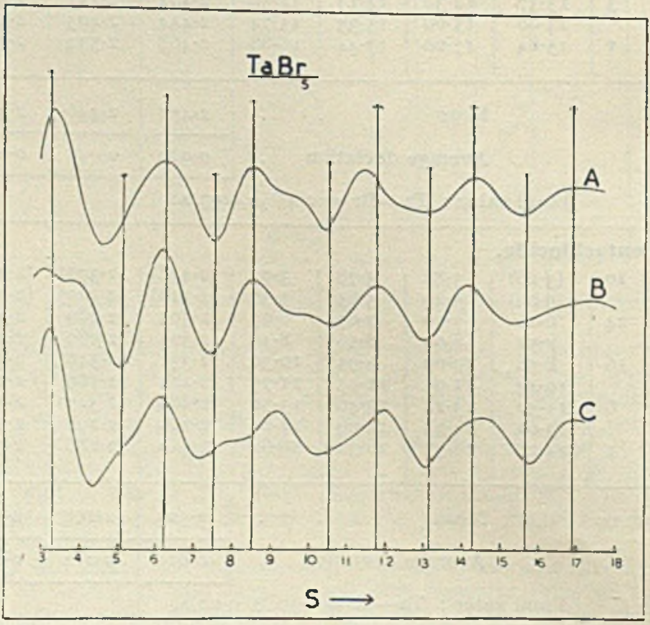

Fig. 6.

Model C—planar model.

The theoretical scattering curves for these three models are shown in Fig. 6.

The appearance of curve C at once suggests that the planar model is impossible. This curve is unsatisfactory in the regions of the third maximum and the second and third minima. The shading off of the third maximum appears on the inside in curve C, whereas the plates show the shelf on the outside. The only appreciable difference in curves A and B occurs in the first maximum. The plates showed the first maximum to be quite symmetrical, and there was no sign of the shelf which model B would require. Quantitatively, curve A is slightly better than curve B, and very much better than curve C. The experimental evidence, therefore, favours model A rather than model B, and rules out model C completely.

The *s* values for the three calculated curves, and the Ta—Br distances derived from these values (*i.e.*, 2·30 . $s_{\text{calc.}}/s_{\text{obs.}}$) are given in Table III.

The value for the Ta—Br distance was found to be 2·45 ± 0·03 A.

Electron Diffraction by Tantalum Pentachloride.

The photographs for this compound showed five rings, the intensities of which decreased fairly regularly with increasing diameter. The maxima appeared symmetrical with the exception of the third, which fell away more slowly on the outside, the succeeding minimum falling nearer the fourth maximum.

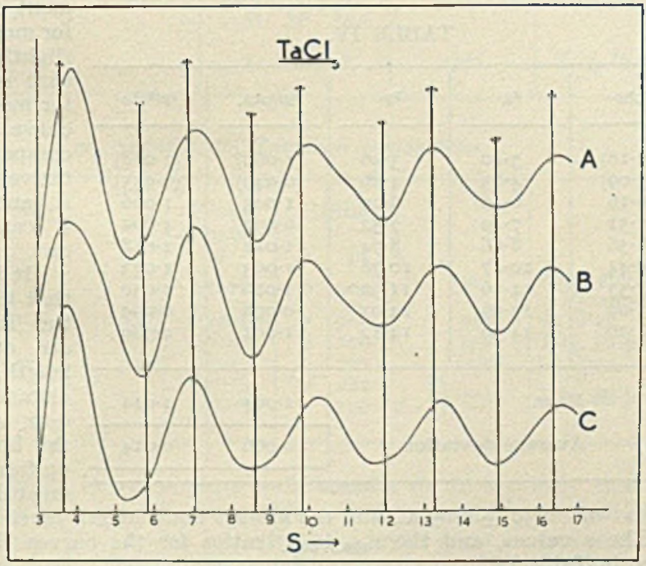

FIG. 7.

The observed *s* values and estimated intensities are given in Table III.

The radial distribution curve is reproduced in Fig. 5, and showed peaks at distances corresponding to

$$\text{Ta—Cl} = 2{\cdot}32 \text{ A. and Cl—Cl} = 3{\cdot}20 \text{ A.}$$

Assuming a Ta—Cl distance of 2·00 A., three models were investigated by the correlation method, similar to those chosen in the previous pentahalide investigations :

Model A—regular trigonal bipyramid.

Model B—square pyramid, with Cl—Ta—Cl angles = 90°.

Model C—planar model.

The theoretical scattering curves derived from the above three models are shown in Fig. 7.

Curve C is unsatisfactory in the region of the third minimum—there is no indication of the observed shading off of the third maximum, with consequent displacement of the third minimum towards the fourth maximum.

The general form of the two curves A and B is almost identical, and it is impossible in this compound to choose between the models A and B from either qualitative or quantitative comparison of the curves.

The s values for the three calculated curves, and the derived Ta—Cl distances (*i.e.* 2·00 . $s_{\text{calc.}}/s_{\text{obs.}}$) are given in Table V.

The best value for the Ta—Cl distance is 2·30 ± 0·02 A.

Two further trigonal bipyramid models, in which the distances Ta—Cl were not assumed to be uniform, were investigated by the correlation method. The models had the dimensions :

Model E. Ta—Cl (apices) = 2·35 A.
Ta—Cl (base) = 2·25 A.
Model F. Ta—Cl (apices) = 2·40 A.
Ta—Cl (base) = 2·20 A.

The scattering curves for these models are in all essentials similar to the curve for model A, and are not reproduced. The quantitative agreement of the curve for model E is only slightly inferior to that of the curve for model A. The curve F is poor compared quantitatively with curve A, and the model F can be ruled out.

TABLE IV.

$s_{\text{obs.}}$	s_{E}.	s_{F}.	$s_{\text{E}}/s_{\text{obs.}}$	$s_{\text{F}}/s_{\text{obs.}}$
(3·18)	3·40	3·46	(1·069)	(1·088)
(5·09)	4·83	4·86	(0·949)	(0·955)
6·16	6·19	6·20	1·005	1·006
7·51	7·49	7·52	0·997	1·001
8·58	8·68	8·74	1·012	1·018
10·44	10·47	10·78	1·003	1·033
11·57	11·76	11·92	1·016	1·030
13·02	13·00	13·01	0·998	0·999
14·26	14·30	14·12	1·001	0·989
Mean . . .			1·005	1·011
Average deviation .			0·006	0·014

It is concluded that if in $TaCl_5$ all the Ta—Cl bonds are of the same length, that this distance is 2·30 ± 0·02 A.; but, if the bonds are not uniform, each bond must lie within the limits of 2·30 ± 0·05 A., and the *average* bond length must be 2·30.

The s values, and the $s_{\text{obs.}}/s_{\text{calc.}}$ ratios for the curves E and F are given in Table IV.

Discussion.

The electron diffraction investigation of the four pentahalides described in this paper shows that in all cases the most satisfactory representation of the structure is the trigonal bipyramid. The only alternative form compatible with the experimental results is the square pyramid described as model B. Because of the greater repulsion between bromine atoms, this model is less stable than model D, which is, however, not acceptable on experimental grounds. A conclusive choice between the models A and B could be made from measurements of the dipole moments of these compounds. In the case of PF_5, the dipole moment of the vapour has been measured and found to be zero—so that in this compound the trigonal bipyramid is the only acceptable structure.

It would appear that the trigonal bipyramid form is general for the class of compounds of the type MX_5. This structure has been shown to obtain also in such mixed pentahalides[10] as PF_3Cl_2, and substituted pentahalides[11] as Me_3SbX_2. The general stereochemical form of the pentahalides suggests a common bond orbital type existing in these compounds. The problem of directed valency in 5-co-ordinated compounds has been recently treated by Kimball,[12] from the group theory point of view. This author concludes that the trigonal bipyramid form occurs when bond orbitals of the types sp^3d and spd^3 are employed, and that the square pyramid structural form should be found with bond orbitals of the types sp^2d^2, sd^4, p^3d^2 and pd^4. The valence configuration d^5 has the bonds directed along the slant edges of a pentagonal pyramid.* The possible valency configurations for the relevant Group 5 elements, and their characteristics, are summarised in the following table :—

Phosphorus Pentahalides.

Neon core	3*s* 3*p* 3*d*		
(10)	2 222 2	sp^3d	Trig. Bi-pyr.

(*a*) *Niobium,* (*b*) *Tantalum pentahalides.*

	Penultimate	Ultimate				
(*a*) Krypton core . .	*d*	*s*	*p*	*d*		
(36)	22222	0	000		d^5	Pentagonal Pyramid.
	02222	2	000		sd^4	Sq. Pyr.
	00222	2	200		spd^3	Trig. Bi-pyr.
(*b*) Hafnium core . .	00022	2	220		sp^2d^2	Sq. Pyr.
(68)	00002	2	222		$\left.\right\}$ sp^3d	Trig. Bi-pyr.
	00000	2	222	2		

Orbital theory in its present state enables us to say only that the first sp^3d arrangement for the niobium and tantalum pentahalides is more likely than the second, because the *d* levels must be less stable in the ultimate group than in the penultimate group. No definite choice between the remaining five states can be made. The experimentally observed trigonal bipyramid structures in these compounds indicates, however, that the spd^3 or sp^3d valency configurations are preferred.

As was explained in the experimental section, the question as to

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[10] Brockway and Beach, *J.A.C.S.*, 1938, **60**, 1836.

[11] A. F. Wells, *Z. Krist.*, 1938, **99**, 367.

[12] G. E. Kimball, *J. Chem. Physics*, 1940, **8**, 194.

* The pentagonal pyramid structure has not been considered in the experimental section for any of the pentahalides. There is no doubt, however, that this structural form will not be in agreement with the diffraction results. The halogen-metal-halogen angles in such a structure must be less than 72°, and the radial distribution results indicate that at least some of these angles are approximately 90°.

whether the metal-halogen links in the niobium and tantalum pentahalides are of uniform length, or vary in a similar manner to the reported variation in the link distances in phosphorus pentachloride, cannot be conclusively answered. The diffraction results show that the length of a metal-halogen link in the niobium and tantalum pentahalides does not vary from the experimentally determined link length in the regular trigonal bipyramid model by more than ± 0·05 A., and that the average length of the M—X link is that determined in the regular trigonal bipyramid model.

The bond lengths in the niobium and tantalum pentahalides are about 0·10 A. shorter than the normal covalent bond lengths for these compounds. There is some uncertainty in the normal covalent radii of Nb and Ta, and the values taken here are the metallic radii. (Goldschmidt values for co-ordination number six.)

Compound.	Observed M-X Distance.	Metal Atom Radius (in A).	Calc. M-X Distance (in A).	Per Cent. Shortening.
$NbBr_5$ . .	2·46 ± 0·03	1·40	2·54	3·2 %
$NbCl_5$ . .	2·29 ± 0·03	1·40	2·39	4·2 %
$TaBr_5$ . .	2·45 ± 0·03	1·40	2·54	3·5 %
$TaCl_5$ . .	2·30 ± 0·02	1·40	2·39	3·8 %

The contraction of the links in these compounds is of the same order of magnitude as the contractions observed in $MoCl_5$ and IF_5, and not quite as great as that in PF_5.

Summary.

The structures of niobium and tantalum pentabromides and pentachlorides in the vapour phase have been investigated by electron diffraction. The compounds have the trigonal bipyramid structure, and the observed bond lengths are :

Nb—Br = 2·46 ± 0·03, Nb—Cl = 2·29 ± 0·03 : Ta—Br = 2·45 ± 0·03 : and Ta—Cl = 2·30 ± 0·02 A.

The significance of the experimental results has been discussed.

The authors are indebted to Professor N. V. Sidgwick, F.R.S., for his interest and advice, to the Department of Scientific and Industrial Research for a maintenance allowance to one of them (H.A.S.), to the Royal Society for the loan of an electric calculating machine, and to Imperial Chemical Industries Ltd. for a grant towards the cost of the research.

The Dyson Perrins Laboratory,
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STUDIES OF THE STRUCTURES OF BISMUTH CHLORIDE AND BROMIDE MOLECULES IN THE VAPOUR PHASE, BY ELECTRON DIFFRACTION.

By H. A. Skinner and L. E. Sutton.

Received 27th March, 1940.

The structure of several of the trihalides of the Group 5B elements have been determined, and give a series of experimental results, whose eventual interpretation should be of considerable importance in the elucidation of the cause or causes of the shortening of metal-halogen links. The diffraction experiments with the bismuth halide vapours were undertaken to complete further the investigated structures of the Group 5B trihalides.

Experimental.

Bismuth bromide was prepared by passing a stream of pure dry N_2 carrying pure dry Br_2 vapour, over a sample of pure metallic Bi, at about 250°. The compound was purified by repeated sublimation in a dry N_2 stream.

Bismuth chloride was prepared by the direct action of pure dry Cl_2 on heated metallic Bi, and purified by repeated sublimation in a stream of dry nitrogen.

The diffraction by the compounds was studied in the apparatus described by de Laszlo.[1]

The samples of the compounds were contained inside a pyrex tube within a copper oven. The best oven temperatures for photographing the patterns from the vapours were found to be $BiBr_3$ at 220°-230° C., and $BiCl_3$ at 220°-230° C.

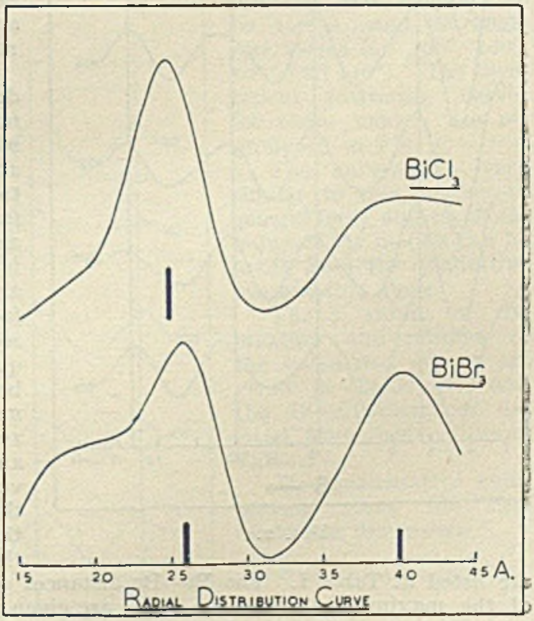

Fig. 1.

Diffraction by Bismuth Bromide.

Nine plates were measured, each showing five maxima, which appeared to be symmetrical. The first two rings were very intense, the other three appeared to decrease in intensity-

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[1] de Laszlo, *Proc. Roy. Soc., A,* 1934, 146, 662.

regularly with increasing diameter. The observed *s* values and the estimated intensities of the maxima are given in Table I. The radial distribution curve, calculated from these values, is reproduced in Fig. 1. This showed peaks at distances corresponding to Bi—Br = 2·58 A., and Br—Br = 4·02 A. These values indicate that bismuth bromide has a pyramidal structure, with the Br—Bi—Br angle = 101°.

TABLE I.

Max.	Min.	*I.*	$s_{obs.}$	$s_{90°}$	$s_{98°}$	$s_{102°}$	$s_{106°}$	$s_{112°}$
1		10	(3·44)					
	1		4·35					
2		9	5·25	5·45	5·30	5·27	5·22	5·30
	2		6·67					
3		5	7·87	7·70	8·00	7·96	7·87	7·78
	3		9·11					
4		3	9·99	10·40	10·18	10·16	10·35	10·35
	4		10·40					
5		1	12·26	12·58	12·86	12·75	12·60	12·60

Assuming this to be the correct model, and allotting a value of 2·60 A. to the Bi—Br distance, five theoretical scattering curves were calculated, for models in which the Br—Bi—Br angle varied (90°, 98°, 102°, 106° and 112°).

These curves are reproduced in Fig. 2. They do not differ from one another markedly in general appearance, and it is not possible to choose any one model from qualitative comparison alone, although the curves for the angles 106° and 112° are comparatively unsatisfactory in the region of the second maximum. The quantitative agreement is best for the curves of the models with angles 98° and 102°, and the general appearance of these curves is in very good agreement with the plates. The *s* values of the maxima and minima of the five calculated curves are listed in Table I. The Bi—Br distances derived from the *s* values of the maxima (*i.e.*, 2·60 . $s_{calc.}/s_{obs.}$) are given in Table II. From these tables it is seen that the best quantitative agreement is given by the models with Br—Bi—Br angles of 98° and 102°, with the Bi—Br distance of 2·63 A. The model finally chosen is therefore taken as

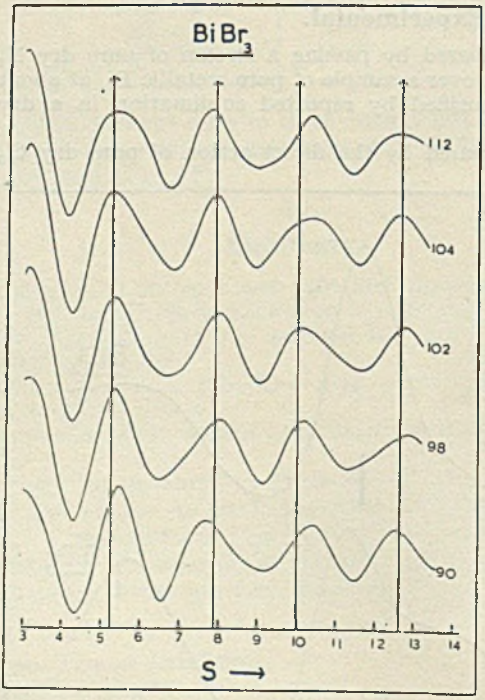

FIG. 2.

$$\text{Bi—Br} = 2{\cdot}63 \pm 0{\cdot}02 \text{ A.}$$

$$\text{Br—}\widehat{\text{Bi}}\text{—Br} = 100 \pm 4°.$$

Diffraction by Bismuth Chloride.

Six plates showing five rings were measured. The rings appeared to be symmetrical and decreased in intensity with increasing diameter, the first two rings being considerably more intense than the others.

TABLE II.

Max.	l_{90}.	l_{98}.	l_{102}.	l_{106}.	l_{112}.
2	2·70	2·62	2·61	2·58	2·62
3	2·54	2·64	2·63	2·60	2·57
4	2·71	2·65	2·64	2·69	2·69
5	2·59	2·65	2·63	2·60	2·60
Mean .	2·63	2·64	2·63	2·62	2·62
Av. dev.	0·07	0·01	0·01	0·04	0·04

Best value : Bi—Br = 2·63 ± 0·02 A.

Br—$\widehat{\text{Bi}}$—Br angle = 100 ± 4°.

The measured *s* values and estimated intensities are given in Table III, and the radial distribution curve is reproduced in Fig. 1. This curve showed peaks at distances corresponding to Bi—Cl = 2·45 A. and Cl—Cl = 4·05 A. The radial distribution results indicate that the $BiCl_3$ molecule is a triangular pyramid with Cl—$\widehat{\text{Bi}}$—Cl = 111°.

Assuming this model to be correct, five models were examined by the correlation method. In each model, the Bi—Cl distance was assumed to be 2·45 A., and the angle was varied (90°, 96°, 100°, 106° and 110°). The theoretical scattering curves for these models are reproduced in Fig. 3.

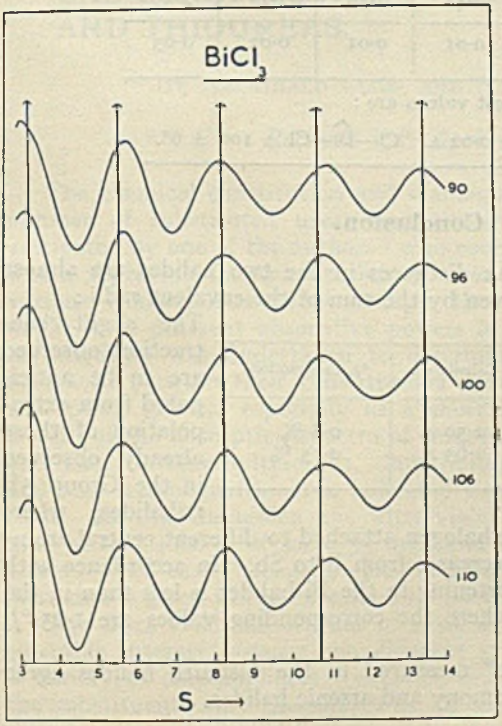

Fig. 3.

The curves are very similar to one another in general form, and no choice between the models can be made from the qualitative examination alone.

The *s* values of the maxima and minima of the calculated curves are given in Table III, and the Bi—Cl distances derived from these values in Table IV.

The quantitative comparison gives the best model the dimensions :

Bi—Cl = 2·48 ± 0·02 A.

and

Cl—$\widehat{\text{Bi}}$—Cl = 100° ±6°.

TABLE III.

Max.	Min.	I.	$s_{obs.}$	$s_{90°}$	$s_{96°}$	$s_{100°}$	$s_{106°}$	$s_{110°}$
1		10	(3·32)	3·12	3·22	3·23	3·20	3·20
	1		(4·64)					
2		9	5·62	5·78	5·72	5·68	5·66	5·78
	2		6·99					
3		5	8·26	8·24	8·35	8·40	8·33	8·30
	3		9·69					
4		3	10·72	11·00	10·88	10·80	10·90	10·95
	4		12·16					
5		1	13·43	13·40	13·45	13·50	13·40	13·40

TABLE IV.

Max.	$i_{90°}$	$i_{96°}$	$i_{100°}$	$i_{106°}$	$i_{110°}$
1	(2·30)	(2·38)	(2·38)	(2·36)	(2·36)
2	2·52	2·49	2·48	2·47	2·52
3	2·44	2·48	2·49	2·50	2·46
4	2·51	2·49	2·49	2·49	2·50
5	2·44	2·45	2·46	2·44	2·44
Mean .	2·48	2·48	2·48	2·48	2·48
Av. dev.	0·04	0·01	0·01	0·02	0·03

Therefore, the best values are :

Bi—Cl = 2·48 ± 0·02 A.   Cl—$\widehat{\mathrm{Bi}}$—Cl ± 100 ± 6°.

Conclusion.

The bismuth-halogen link distances in the two halides are almost the normal link distances given by the sum of the covalent radii :

Compound.	Observed Bi-X.	Calculated.	°/₀ Contraction.
$BiCl_3$	2·48 ± 0·02 A.	2·50 A.	0·8 %
$BiBr_3$	2·63 ± 0·02 A.	2·65 A.	0·75 %

The slight contractions observed are to be anticipated from extrapolation of those already observed in the Group 5B trihalides, where it is found that for the same halogen attached to different central atoms the percentage shortening decreases from P to Sb. In accordance with this rule, the percentage shortening in the Bi halides is less than in the corresponding Sb halides, where the corresponding values are 1·25 °/₀ and 1·2 °/₀.

The bond angles of 100° measured in the bismuth halides agree closely with those in the antimony and arsenic halides.

Summary.

The structures of bismuth tribromide and trichloride have been investigated by the electron diffraction method. Both compounds have a pyramidal structure, with the dimensions :

(1) $BiBr_3$: $\text{Bi—Br} = 2{\cdot}63 \pm 0{\cdot}02$ A.

$\text{Br—}\widehat{\text{Bi}}\text{—Br} = 100° \pm 4°$.

(2) $BiCl_3$: $\text{Bi—C} = 2{\cdot}48 \pm 0{\cdot}02$ A.

$\text{Cl—}\widehat{\text{Bi}}\text{—Cl} = 100° \pm 6°$.

The authors are indebted to the Royal Society for the loan of a calculating machine, to Imperial Chemical Industries Ltd. for a grant towards the cost of the research, and to the Department of Scientific and Industrial Research for a maintenance allowance to one of them (H.A.S.).

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THE ULTRA-VIOLET ABSORPTION AND CHEMICAL CONSTITUTION OF SUBSTITUTED UREAS AND THIOUREAS.

By Archibald Clow and N. L. Helmrich.

Received 17*th April*, 1940.

The chemical constitution and diamagnetic susceptibility of a large number of substituted ureas and thioureas have already been investigated by one of the authors [1] who concluded that no static formula would represent the constitution of urea or its derivatives. As the various constitutions deduced from the diamagnetic susceptibilities might have different absorptive powers in the ultra-violet, the present investigation was undertaken to determine whether a parallel could be traced between their constitutions deduced magnetically and their absorption spectra, especially as a short investigation by Rivier and Borel [2] of the absorption spectra of thiourea, trimethylthiourea (normal and *iso*), tetramethylthiourea, dimethyldiphenylthiourea (normal and *iso*) and tetraphenylthiourea indicated that such a parallel did indeed exist. In this discussion the ultra-violet absorption curves between 2200 A. and 4000 A. of some 35 urea and thiourea derivatives are correlated with their chemical constitutions. A list of the compounds discussed is given in the experimental part.

The ultra-violet absorption of urea derivatives should be of considerable interest because the different possible constitutions contain a variety of chromophores : $=C=O$, $-NH_2$, $=C=S$, $-S-H$, while the substituents may themselves be chromophoric, *e.g.*, phenyl groups,

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[1] Clow, *Trans. Faraday Soc.*, 1937, **33**, 381 ; 1938, **34**, 457.

[2] Rivier and Borel, *Helv. Chim. Acta*, 1928, **11**, 1219.

or transparent within the range discussed, *e.g.*, methyl or ethyl groups.[3] Practically nothing has been done spectroscopically on urea beyond the researches of Rivier and Borel already mentioned and the various determinations of the absorption of urea and thiourea.[4] Data for the ultraviolet absorption of thio-compounds are equally scanty.[5, 6] Several workers in closely related fields, however, have obtained results of considerable importance. As early as 1913 V. Henri [7] concluded that substances with labile molecules such as urea would absorb strongly in the ultra-violet, but this has been criticised first by Radalescu [8] and subsequently by Ramart-Lucas.[9] Closely related to the absorption of substituted urea derivatives is the work on the absorption of substituted amides and thio-amides by Hantzsch,[10] Amagat,[11] the Freymanns [12] and Ramart-Lucas.[13] The considerable evidence that amides and thio-amides exist in solution in two forms, normal and imido-hydrin, led Hantzsch to investigate the absorption of substituted acid amides and thio-amides on which he showed that (*a*) CCl_3CONH_2 and $CCl_3C(OCH_3){=}NH$, (*b*) $C_6H_5CONH_2$ and $C_6H_5C(OC_2H_5){=}NH$ have similar continuous absorption curves. From this he concluded that these amides exist, at least partially, in the imido-hydrin form, the absorption of the dimethyl derivative $C_6H_5CONMe_2$ being quite distinct. These compounds present a close parallel to iso-ureas. It should be noted that a marked solvent effect was displayed by these amides.[14] With regard to the thio-amides CH_3CSNH_2 and $C_2H_5CSNH_2$, these display strong selective absorption while $CH_3C(SC_2H_5){=}NH$ shows weak continuous absorption, from which Hantzsch concluded that the former are true amides. As above, this is relevant to the absorption of iso-thioureas. On account of the conclusions obtained, the study of the absorption curves of mono- and di-substituted diamides [15] is of considerable importance, the presence of the $—CH_2—$ group having at least partially the effect of detaching the two chromophores from one another.[16] While $ArNHCOCH_2CONH_2$ and $ArNHCOCH_2CONHAr$ have the same type of absorption curve, the completely substituted compound $Ar_2NCOCH_2CONAr_2$ is distinctive, being more transparent and only absorbing further into the ultra-violet. Ramart-Lucas concludes, therefore, that the $ArN{=}C(OH)CH_2—$ group should have its absorption bands nearer the visible and of greater intensity than those of $ArNH—C({=}O)CH_2—$, and most of the amides investigated had constitutions corresponding with the first formula. These changes are the same as may take place in substituted ureas.

When the results of the above investigations are applied to the interpretation of the absorption spectra of urea and its derivatives it is found

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[3] Ramart-Lucas, *Bull. Soc. Chim.*, 1932, v. I, 289.

[4] (*a*) Henri and Bielecki, (*b*) Castille and Ruppol, *Tables Annuelles*, 1930, vii, 789.

[5] Lorenz and Samuel, *Z. physik. Chem.*, *B*, 1931, **14**, 219.

[6] Ley and Arends, *ibid.*, 1932, **15**, 311.

[7] Henri, *C.R.*, 1913, **156**, 1979.

[8] Radalescu, *Bull. Soc. Sci. de Cluj* (*Roumania*), 1928, 4, 297.

[9] Ramart-Lucas, *C.R.*, 1928, **186**, 1301.

[10] Hantzsch, *Ber.*, *B*, 1931, **64**, 661.

[11] Amagat, *C.R.*, 1934, **198**, 2172.

[12] Freymann and Freymann, *ibid.*, 1936, **202**, 1850.

[13] Ramart-Lucas, *Bull. Soc. Chim.*, 1937, v, 4, 478.

[14] Scheibe, *Ber.*, *B*, 1924, **57**, 1330.

[15] Ramart-Lucas, *Bull. Soc. Chim.*, 1934, v, 1, 525.

[16] *Ibid.*, 1932, iv, **51**, 289.

that the problem is one of considerable complexity on account of the several factors which influence the absorption. The introduction of substituents which are not themselves chromophores should not, at least in the higher members of a homologous series, influence the absorption,[17] but these same substituents may alter the constitution of the urea molecule to one or other of the possible alternative constitutions with a resulting change in absorption due to the formation of new chromophores within the molecule. The substituent may, however, be chromophoric as in the case of a phenyl group, which possesses a very characteristic selective absorption, and this substituent in addition may, as above, alter the chemical constitution. Further, the presence of two or more chromophores close to one another may exert a mutual influence on the absorption, *e.g.*, the disappearance of the fine bands characteristic of the aromatic ring in all the phenyl substituted ureas discussed, which must be attributed to the chromophore already present in the molecule.

Experimental.

(a) Materials.—The compounds measured were obtained from a variety of sources or were made in the laboratory. Each specimen was subjected to a thorough purification, usually by recrystallisation from pure ethyl alcohol, constancy of melting-point after further purification being taken as the criterion of purity. Those compounds which are liquids were liquid air distilled immediately before use. Wherever possible distilled water was used as the solvent in the determination of the absorption curves, but where the solubility of the substance in water was too small, as in the case of the phenyl derivatives, pure ethyl alcohol was used instead.[18] The solvent used is indicated in the figures. Where the urea or thiourea was a liquid it was measured both as a pure liquid and in solution, though, a micrometer cell not being available, it was not possible to make the comparison over the whole range.

(b) Methods.—The spectra were photographed with a Hilger Quartz Spectrograph and Spekker Photometer using tungsten steel electrodes as the source of illumination. The accuracy of the optical system and the transmission of the photometer were checked by examining the absorption spectrum of A.R. K_2CrO_4 which had been recrystallised ten times from distilled water, the absorption curve obtained being in complete agreement with that given by v. Halban and Eisenbrand.[19] The pure liquids were contained in Hilger quartz faced absorption tubes giving layer thicknesses between 1 and 10 mm., while the solutions were contained in 10 cm. tubes. The extinction coefficient was calculated according to the equation $\log_{10} I_0/I = \epsilon . c . d.$ I_0 and I being the respective intensities of the incident and transmitted light, c the concentration in g. mol. per litre, d the depth of the absorption path in cm. The logarithm of ϵ is plotted against the wave-length λ in A. throughout. The following substances were measured: Urea: N-methyl-urea; N-ethyl-urea; N-phenyl-urea; O-methyl-*iso*-urea; O-ethyl-*iso*-urea hydrochloride; N . N-dimethyl-urea; N . N-diphenyl-urea; N . N′-dimethyl-urea; N . N′-diethyl-urea; N . N′-dimethylol-urea; N . N′-diphenyl-urea; N . N—N′ . N′-tetramethyl-urea; N . N—N′ . N′-tetraethyl-urea; N . N′-dimethyl-N . N′-diphenyl-urea; N . N′-diethyl-N . N′-diphenyl-urea. Thiourea: N-methyl-thiourea; N-ethyl-thiourea; N-phenyl-thiourea; N-allyl-thiourea; O-methyl-*iso*-thiourea-hydrochloride; N . N-dimethyl-thiourea; N . N-diphenyl-thiourea; N . N′-dimethyl-thiourea; N . N′-diethyl-thiourea;

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[17] Ley, *Ber.*, *B*, 1921, 54, 363.

[18] Clow andPearson, *Nature*, 1939, 144, 209.

[19] v. Halban and Eisenbrand, *Proc. Roy. Soc.*, *A*, 1927, 116, 160.

N-phenyl-N′-ethylol-thiourea ; N . N-dimethyl-N′-phenyl-thiourea ; N . N-diphenyl-N′-acetyl-thiourea ; N . N-dipropyl-N′-*o*-tolyl-thiourea ; N . N—N′ . N′-tetramethyl-thiourea ; N . N—N′ . N′-tetra-ethyl-thiourea ; N . N—N′ . N′-tetraphenyl-thiourea ; N . N′-dimethyl-N . N′-diphenyl-thiourea.

Part I.—Urea Derivatives.

Discussion.

(a) The Absorption of True Carbamides.—When ureas, in which all four hydrogen atoms had been replaced by alkyl or aryl groups, were investigated magnetically, an absolute confirmation of their accepted constitution as true carbamides was obtained, consequently it will be advantageous to consider the absorption of these ureas first. From the point of view of diamagnetism it was not necessary, but for the present discussion the tetra-substituted ureas must be divided into two groups, depending on the substituent itself being chromophoric or otherwise. The absorption curves of the tetrasubstituted ureas formed without chromophoric groups are given in Fig. 1, those containing chromophoric groups being discussed with the phenyl ureas. The absorption curves of N . N—N′ . N′-tetramethyl-urea and N . N —N′ . N′-tetraethyl-urea reveal that over the range investigated there is practically no difference between the absorption of the pure substance and its solution in alcohol. Both tetra-ureas display marked end absorption, the shape of the curves being in marked contrast to the selective absorption characteristic of a compound like acetone containing a single chromophore with a pronounced selective absorption maximum at 2730 A. The effect of the additional chromophoric groups is evidently to displace this band towards the ultra-violet, as well as to increase the absorption. The introduction of even one —NH$_2$ group into acetone, giving CH$_3$CONH$_2$, causes a marked change in the trans-

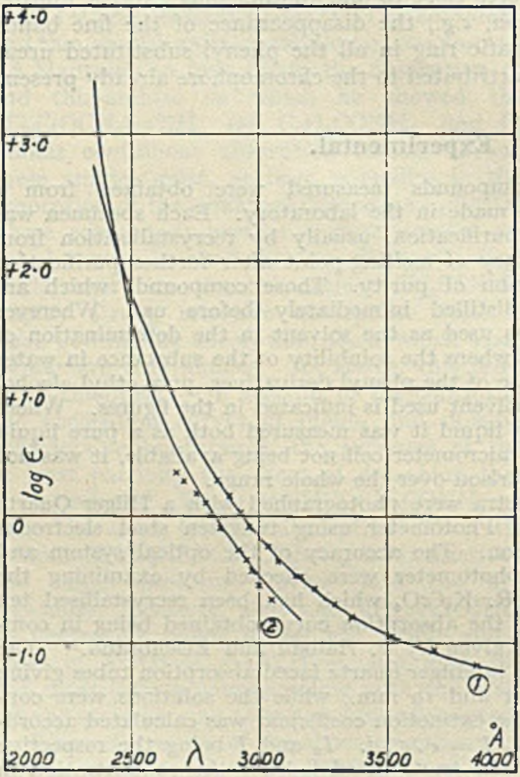

FIG. 1.—(1) N . N—N′ . N′-tetramethyl-urea.
(2) N . N—N′ . N′-tetraethyl-urea.
× × × pure liquid.
——— soln. in alcohol.

mission of the molecule,[10] which is also true of urea itself as will be seen in the following section.

(b) The Absorption of Incompletely Substituted Ureas.—On substitution a series of changes in the constitution of urea takes place, the extent of the change depending on the nature and position of the substituent. The diamagnetic susceptibility of urea itself suggested that it was a zwitterion which on mono-substitution passed to an equilibrium between the zwitterion and the amino-imino constitution. This was true of N-methyl-urea, N-ethyl-urea and N-propyl-urea, the equilibrium lying in general close to the amino-imino form. The absorption spectra of urea and mono-substituted ureas will be found in Fig. 2, where it will be seen that there is, neglecting the difference in intensity, a marked similarity between their absorption and that of urea. All display end absorption like the tetra-substituted ureas, but the increased absorption which resulted from complete substitution is very striking, the increase being more than can readily be accounted for simply by the successive introductions of alkyl groups. Indeed the increase in absorption is indubitably suggestive of a change in constitution, and if the structures conforming with the diamagnetic susceptibilities are taken as a guide, an absorption of the type just given would represent the absorption of the urea molecule when its constitution is that either of a zwitterion or of the amino-imino form.

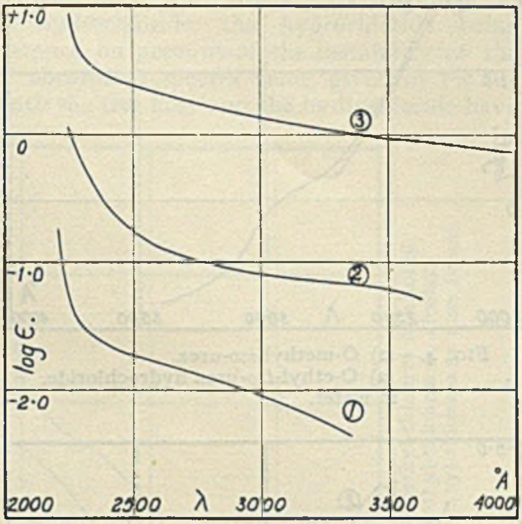

FIG. 2.—(1) Urea.
(2) N-methyl-urea.
(3) N-ethyl-urea.
in water.

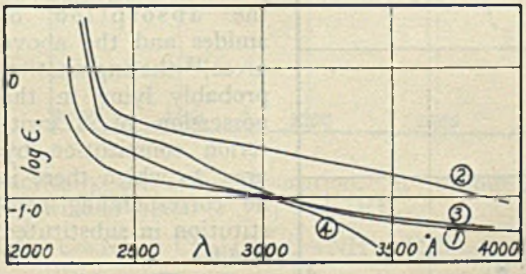

FIG. 3.—(1) N . N-dimethyl-urea.
(2) N . N′-dimethyl-urea.
(3) N . N′-diethyl-urea.
(4) N . N′-dimethylol-urea.
in water.

One of the most important results obtained from the diamagnetic susceptibilities of disubstituted ureas was the difference between the constitutions of N . N and N . N′ disubstituted isomers, the weighting effect of both groups attached to one nitrogen being to stabilise the carbamide constitution. Of the di-substituted ureas only the N . N-dimethyl-urea had a susceptibility approximating to that required for a carbamide constitution, N . N′-dimethyl-urea and N . N′-dimethylol-urea being in all probability substituted zwitterions. In Fig. 3 are given the absorption spectra of N . N- and N . N′-diethyl-urea, N . N′-dimethyl-urea and N . N′-dimethylol-urea. The resemblance between the various curves is still quite definite, but N . N-dimethyl-urea shows a decided deviation from the general form of these curves between the wave-lengths 2400 A. and 2800 A. not unsuggestive of the selective absorption of a carbonyl group and in agreement with its diamagnetic susceptibility.

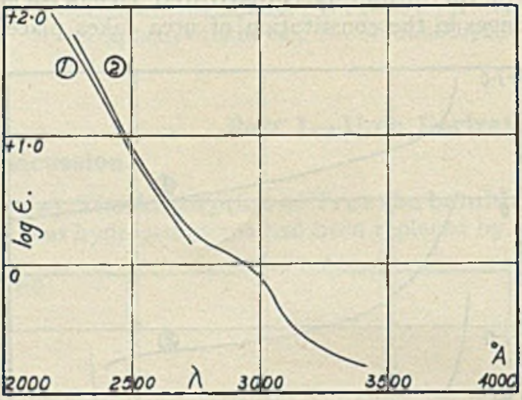

Fig. 4.—(1) O-methyl-*iso*-urea.
(2) O-ethyl-*iso*-urea hydrochloride.
in water.

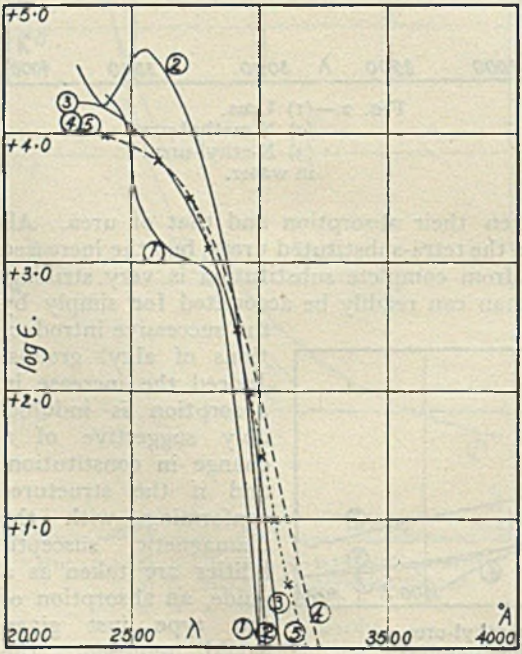

Fig. 5.—(1) N-phenyl-urea.
(2) N . N′-diphenyl-urea.
(3) N . N-diphenyl-urea.
(4) N . N′-dimethyl-N . N′-diphenyl-urea.
(5) N . N′-diethyl-N . N′-diphenyl-urea.
in alcohol.

There does not appear to be any obvious correlation between the changes which take place on substitution in the absorption of amides and the above ureas,[15] the explanation probably lying in the possession of a zwitterion constitution by urea, to which there is no corresponding constitution in substituted amides.

(c) The Absorption of Iso-Ureas.*— According to Hantzsch,[10] on account of the similarity in their absorption spectra the constitutions

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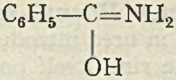
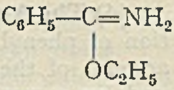
* Measured in this laboratory by Gavin D. Pearson.

of benzamide and its ethyl derivative will be represented by (I) and (II) respectively. Two analogous urea derivatives have been measured, O-methyl-*iso*-urea and O-ethyl-*iso*-urea hydrochloride, the hydrochloride being measured in the second instance on account of the instability of the free O-ethyl-*iso*-urea, their absorption spectra being given in Fig. 4, where it will be seen that both the free base and the hydrochloride have practically the same absorption. It is now possible to compare (*a*) (III) with (IV) and (*b*) (V) with (VI).


$\mathrm{C_6H_5{-}\underset{\underset{\displaystyle OH}{|}}{C}{=}NH_2}$

(I)


$\mathrm{C_6H_5{-}\underset{\underset{\displaystyle OC_2H_5}{|}}{C}{=}NH_2}$

(II)

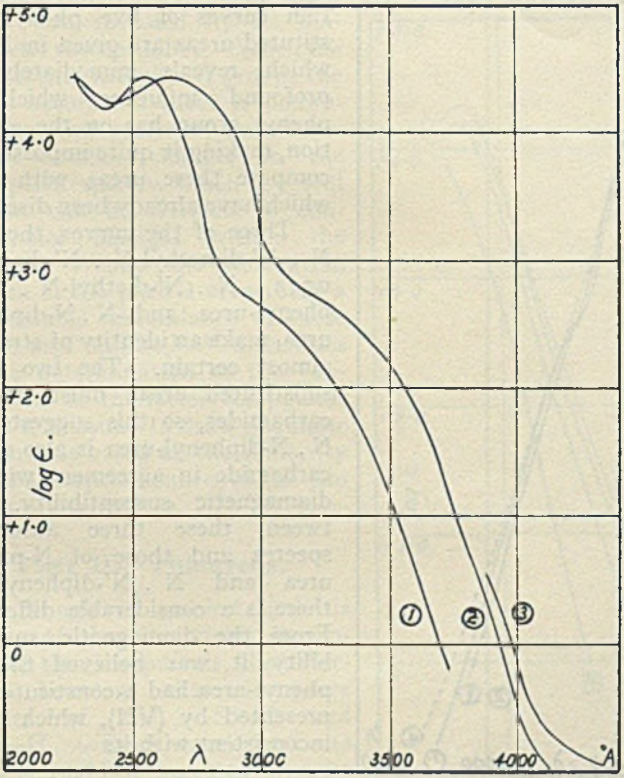
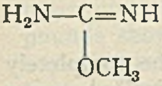
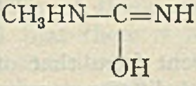


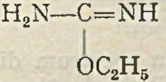
FIG. 6.—(1) N.N—N'.N'-tetramethyl-thiourea in alcohol.
(2) N.N—N'.N'-tetraethyl-thiourea in alcohol.
(3) N.N—N'.N'-tetraethyl-thiourea as pure liquid.


$\mathrm{H_2N{-}\underset{\underset{\displaystyle OCH_3}{|}}{C}{=}NH}$

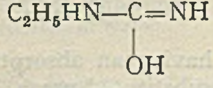
(III)


$\mathrm{CH_3HN{-}\underset{\underset{\displaystyle OH}{|}}{C}{=}NH}$

(IV)


$\mathrm{H_2N{-}\underset{\underset{\displaystyle OC_2H_5}{|}}{C}{=}NH}$

(V)


$\mathrm{C_2H_5HN{-}\underset{\underset{\displaystyle OH}{|}}{C}{=}NH}$

(VI)

As the N-substituted ureas were represented as having a constitution lying between that of a zwitterion and an amino-imino structure it was thought probable that there would be a similarity in the absorption of the normal and *iso*-ureas, but it is evident from the curves just given that the effect of substitution outweighs any other effects that might be present.

(d) The Absorption of Phenyl-substituted Ureas.—The substitution of phenyl groups in urea introduces certain new complications on account of the benzene ring itself possessing an absorption characterised by a number of fine bands. These bands disappear in certain compounds, *e.g.*, diphenyl, and in none of the phenyl substituted ureas investigated has any evidence of them been found. The absorption of the phenyl group would be expected to make a considerable difference between the absorption spectra of alkyl and aryl ureas even if the constitution of the molecules remained identical, a surmise which is borne out by experiment. The absorption curves of five phenyl substituted ureas are given in Fig. 5, which reveals immediately the profound influence which the phenyl group has on the absorption, making it quite impossible to compare these ureas with those which have already been discussed.

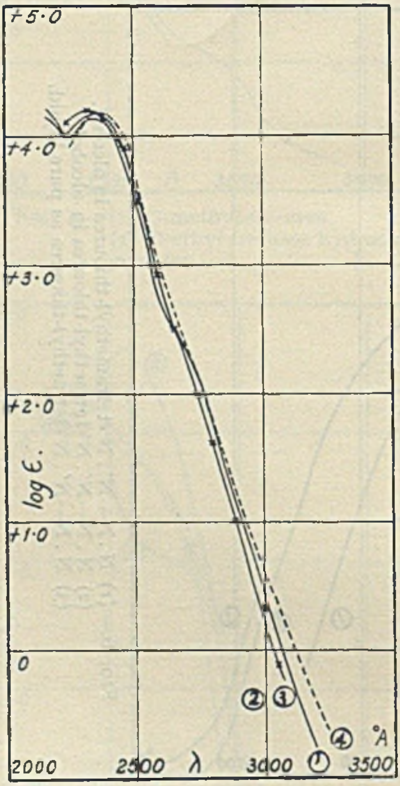
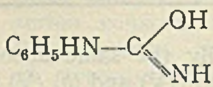


Fig. 7.—(1) Thiourea.
(2) N-methyl-thiourea. x— x
(3) N-ethyl-thiourea.
(4) N-allyl-thiourea.
in water.

Three of the curves, those for N . N′-dimethyl-N . N′-diphenyl-urea, N . N′-diethyl-N . N′-diphenyl-urea and N . N-diphenyl-urea, make an identity of structure almost certain. The two tetra-substituted ureas must be true carbamides, so this suggests that N . N-diphenyl-urea is also a true carbamide in agreement with its diamagnetic susceptibility. Between these three absorption spectra and those of N-phenyl-urea and N . N′-diphenyl-urea there is a considerable difference. From the diamagnetic susceptibility it was believed that N-phenyl-urea had a constitution represented by (VII), which is not inconsistent with its having an absorption spectrum different from that of the completely substituted ureas. Similarly, there is a difference magnetically between the N . N and N . N′-diphenyl-ureas, which was interpreted as arising from the N . N′-diphenyl-urea having an amino-imino structure. Although N-phenyl-urea and N . N′-diphenyl-urea have not identical absorption spectra, this is not inconsistent with the above suggestions regarding their constitutions as the presence of the second phenyl group might be the cause. Further evidence is the difference between the absorptions of N . N′-diphenyl-urea and N . N′-dimethyl-N . N′-di-



$$C_6H_5HN{-}C\begin{matrix}\diagup OH\\ \diagdown\!\!\diagdown NH\end{matrix}$$

(VII)

phenyl-urea, which differ by more than can readily be accounted for by the substitution of two methyl groups for two hydrogen atoms.

Reviewing the ultra-violet absorption of the urea molecule; urea itself is highly transparent, and this transparency is only slightly lessened by mono-substitution, provided always that the substituent is not chromophoric. There is a considerable increase in absorption on complete substitution, but in no case investigated is selective absorption exhibited. N . N-dimethyl-urea alone has an absorption curve which might be differentiated from those of the other ureas, probably attributable to the same difference in constitution which was revealed by its diamagnetic susceptibility. When the substituents are phenyl groups the whole absorption curve is dominated by their presence, but nevertheless smaller changes in the absorption spectra which are still present can be referred to constitutional changes within the molecule. While the absorption spectra of the phenyl ureas bear a considerable resemblance to those of the aryl amides,[13, 15] difficulties in the determination of the constitutions of the latter compounds make it unsound to draw dogmatic conclusions based on the similarity of the absorption curves of the two series of derivatives.

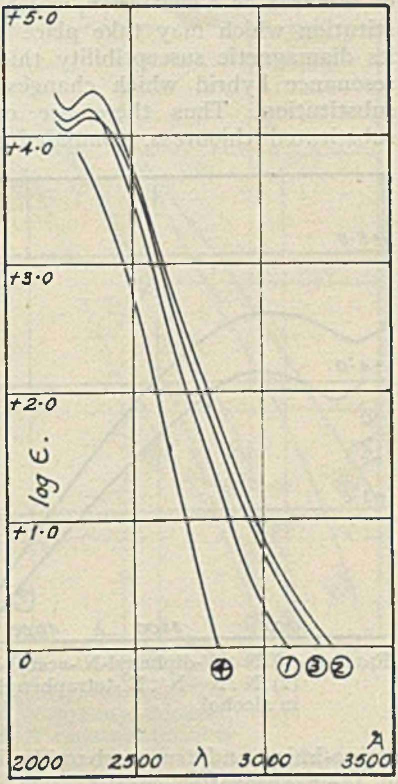


Fig. 8.—(1) N . N′-dimethyl-thiourea.
(2) N . N′-diethyl-thiourea.
(3) N . N-dimethyl-thiourea.
(4) O-methyl-*iso*-thiourea. hydrochloride in water.

Part II.—Thioureas.

Although in general little is known of the ultra-violet absorption of thio compounds, the difference between the absorptive powers of the —S—H and —O—H, =C=S and =C=O groups would be expected to make a considerable difference between the absorptive powers of ureas and thioureas. Furthermore, the magnetic investigation of these compounds showed that there is less variation in the constitution of the thiourea molecule on substitution than in urea, the former molecule not giving a zwitterion as did urea, thus one would expect less variation in the absorption spectra of thioureas than in ureas.

(a) The Absorption of True Thio-Carbamides.—As before it will be advantageous to consider the absorption of the tetra-substituted thioureas first, and in Fig. 6 will be found the absorption curves of N . N—N′ . N′-tetramethyl-thiourea and N . N—N′ . N′-tetraethyl-thiourea, the latter as a pure liquid, over a short range of wave-lengths as well as in solution, which as in the other urea derivatives examined has sensibly the same absorption whether as pure liquid or in solution. These absorption spectra are distinct from those of tetra-substituted urea derivatives. Both compounds have practically the same absorption spectrum which gives indications of consisting of three bands, the third of which does not attain its maximum within the range investigated. It is doubtful if one can assign any of these bands to specific parts of the molecules, as very diverse thio-compounds have absorption spectra of a similar type.[5]

(b) The Absorption of Incompletely Substituted Thioureas.—As already mentioned, there is no magnetic evidence for the existence of thiourea as a zwitterion, which reduces the possible changes in constitution which may take place on substitution. From the value of its diamagnetic susceptibility thiourea appears to be an amino-imino resonance hybrid which changes towards a true thio-carbamide on substitution. Thus there are only two possible constitutions for substituted thioureas, compared with three in the case of urea, in consequence of which less varied absorption spectra are to be expected. Figs. 7 and 8 give the absorption curves of thiourea, N-methyl-, N-ethyl-, N-allyl-, N . N- and N . N′-dimethyl-, and N . N′-diethyl-thiourea, all of which have practically the same absorption curves, with an absorption maximum between 2300 and 2400 A. and an extinction coefficient whose logarithm is about 4.

The diamagnetic susceptibilities of the substituted compounds suggested a constitution made up of both the amino-imino and true carbamide forms, and the pronounced similarity in their absorption spectra is in agreement with their all having the same constitution, which would be nearer that of the unsubstituted thiourea than in the case of urea and its derivatives.

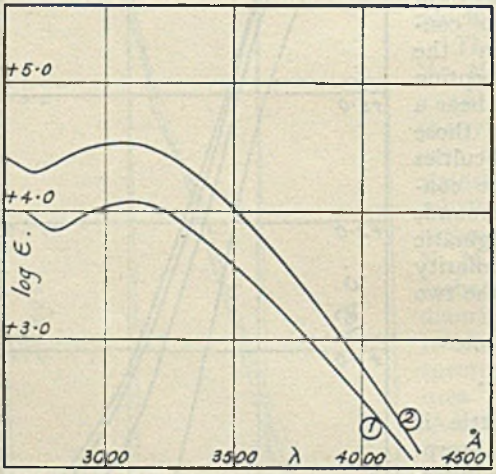


FIG. 9.—(1) N . N′-diphenyl-N′-acetyl-thiourea.
(2) N . N—N′ . N′-tetraphenyl-thiourea.
in alcohol.

While di-substituted thioureas have different diamagnetic susceptibilities for the N . N- and N . N′-isomers indicating a difference in constitution, the difference being in favour of a greater preponderance of thio-carbamide in the N . N-derivatives, the absorption spectra of N . N-dimethyl- and N . N′-dimethyl-thiourea have only fractionally different absorption coefficients, the shape of the absorption curves being practically identical.

(c) The Absorption of Phenyl-Thioureas.—The introduction of phenyl groups into the urea molecule caused a very marked change in the nature of the absorption curve; the same introduction into thiourea, however, does not make such a marked change owing to the fact that the absorption curve of thiourea itself is not unlike the selective absorption curve of the phenyl group. One *o*-tolyl- and eight phenyl-substituted thioureas have been investigated, and as will be seen from Figs. 9 and 10 their absorption spectra fall into two groups, differing considerably in the width and position of the maximum of their absorption band. The first group contains N . N-diphenyl-N′-acetyl-thiourea and N . N—N′ . N′-tetraphenyl-thiourea, the second N-phenyl-, N . N-diphenyl-, N . N′-diphenyl, and N . N′-dimethyl-N . N′-diphenyl-, N . N-dimethyl-N′-phenyl, N-phenyl-N′-ethylol, N . N-dipropyl-N′-*o*-tolyl-thiourea.

The relative positions of the absorption bands in N . N—N′ . N′-tetramethyl-thiourea, N . N′-dimethyl-N . N′-diphenyl-thiourea, and N . N—N′ . N′-tetraphenyl-thiourea are qualitatively the same as those given by Rivier and Borel, who also obtained the very wide absorption band for N . N—N′ . N′-tetraphenyl-thiourea.

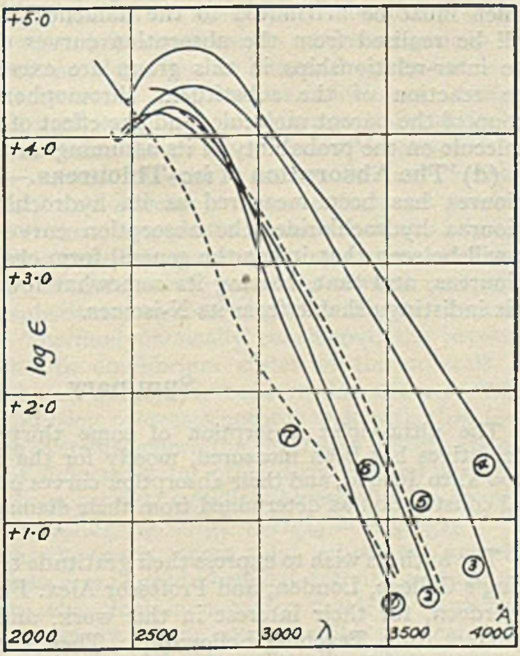


FIG. 10.—(1) N-phenyl-thiourea.
(2) N . N-diphenyl-thiourea.
(3) N . N′-diphenyl-thiourea·
(4) N . N′-dimethyl-N . N′-diphenyl-thiourea.
(5) N . N-dimethyl-N′-phenyl-thiourea.
(6) N-phenyl-N′-ethylol-thiourea.
(7) N . N-dipropyl-N′-*o*-tolyl-thiourea.
in alcohol.

The N.N—N′.N′-tetraphenyl-thiourea in the first group must undoubtedly be a true carbamide, but its absorption band cannot be attributed solely to a thio-carbamide constitution, this form of absorption band being caused rather by the presence of two phenyl groups attached to the same nitrogen atom combined with the impossibility of amino-imino group formation. As N . N-diphenyl-N′-acetyl-thiourea displays the same type of absorption it probably also has a thio-carbamide constitution. Here we also have two phenyl groups attached to the same nitrogen atom, and one of the remaining hydrogen atoms replaced by an acetyl group, so it would appear that the conditions for this type of absorption are firstly the weighting of one end of the thiourea molecule with two groups such as phenyl groups, a methyl or single phenyl group not being sufficient, combined with some deterrent to the formation of an amino-imino structure. This suggestion is strengthened by the further examination of the absorption curves of the thioureas given in Fig. 10, which have their absorption maxima some 400 A. further into the ultra-violet. Here N . N′-dimethyl-N . N′-diphenyl-thiourea has the broadest absorption band which is, however, still distinct from the two thioureas given in Fig. 9. As already suggested this type of absorption does not arise from the presence in the molecule of a =C=S group alone, but rather from the presence of two phenyl groups. From its diamagnetic susceptibility N-phenyl-thiourea was approaching a constitution represented by a pure thiocarbamide, while wholly thio-carbamide constitutions were suggested for N . N- and N . N′-diphenyl-thiourea. None of the phenyl-substituted thioureas have the same type of absorption curve as that characteristic of N . N-N′ . N′-tetramethyl- and N . N-N′ . N′-tetraethyl-thiourea, a difference which must be attributed to the influence of the phenyl group. As will be realised from the absorption curves of these urea derivatives the inter-relationships in this group are exceedingly complex, due to the reaction of the substituent chromophore on the chromophoric group of the parent molecule, and the effect of weighting one end of the molecule on the probability of its assuming an amino-imino constitution.

(d) The Absorption of *iso*-Thioureas.—The absorption of one *iso*-thiourea has been measured as its hydrochloride, *viz.*, *o*-methyl-*iso*-thiourea hydrochloride, the absorption curve being given in Fig. 4. It will be seen that it has the general form characteristic of the simpler thioureas, and that, barring its somewhat lower absorption coefficient, it is indistinguishable from its N-isomer.

Summary.

The ultra-violet absorption of some thirty-five urea and thiourea derivatives has been measured, mostly for the first time, over the range 2200 A. to 4000 A., and their absorption curves correlated with their chemical constitution as determined from their diamagnetic susceptibilities.

The authors wish to express their gratitude to Professor A. J. Allmand, King's College, London, and Professor Alex. Findlay, Marischal College, Aberdeen, for their interest in this work, and to thank the Carnegie Trustees for a Teaching Fellowship. They also wish to acknowledge a gift of several substituted thioureas from Professor E. A. Werner, Trinity College, Dublin.

King's College,
London University.

Marischal College,
Aberdeen University.

EXPERIMENTS ON INCREASING THE CHEMICAL ACTIVITY OF CADMIUM IODIDE BY IRRADIATION.

By J. Arvid Hedvall, P. Wallgren and S. Månsson.*

Received 11*th January*, 1940.

Much attention is nowadays given to the influence of structure or, generally, of lattice building factors on the physico-chemical properties of solids. Some of the most important results of investigations concerning these topochemical problems can be summed up as follows:

There are three kinds of lattice irregularities, which are all of importance for the chemical activity of a solid substance. Schottky and C. Wagner[1] have worked out the theory of the *reversible* lattice defects based on previous work carried out above all by Fajans,[2] Frenkel,[3] v. Hevesy,[4] Jost,[5] Smekal,[6] and Zwicky.[7] These defects are produced by the thermal vibrations of the lattice particles, and are due to interstitially placed particles of great mobility or to migrating lattice holes, from which such particles have been removed, or to the normal ions of the compounds having been substituted by ions of greater charge, or to stoichiometric anomalities. Thermodynamically considered, the reversible defects always correspond to equilibrium states of the crystals. In recent years Wagner and his co-workers have shown that the experimentally determined rate of diffusion processes accords well with that found by this theory. In a few systems, where the reversible defects are very pronounced, and are not influenced by other (irreversible) structural irregularities, it has also been possible to follow kinetically the course of chemical reactions between solids, *e.g.* $2AgI + HgI_2 = Ag_2HgI_4$.

In very many systems, however, where solid substances are characterised by a more or less pronounced chemical activity without possessing ionic conductivity the reaction capacity must be ascribed to other structural defects, generally known as *irreversible* or *topochemical* irregularities. These have been utilised, especially when preparing catalysts and adsorbents. Results obtained during the last twenty or thirty years have shown that it is just this kind of structural influence which is of profound importance in determining the real reaction capacity and surface activity of solids generally.[8] We now know that such

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* Owing to the interruption of Scandinavian mails the authors have been unable as yet to correct proofs of this paper. The Editor is much indebted to Prof. J. D. Bernal for looking through the proof.

[1] C. Wagner and W. Schottky, *Z. physikal. Chem. B*, 1930, **11**, 163; W. Schottky, *Z. Elektrochem.*, 1939, **45**, 33; C. Wagner, *Ber., Deutsch. Keram. Ges.*, 1938, **19**, 207.

[2] K. Fajans, *Z. Krist.*, 1925, **61**, 39; 1928, **66**, 321.

[3] J. Frenkel, *Z. Physik*, 1926, **35**, 652.

[4] G. v. Hevesy, Geiger and Scheel, *Handbuch Physik*, **13**, 286.

[5] W. Jost, *J. Chemical Physics*, 1933, **1**, 466; *Z. physik. Chem. B*, 1936, **32**, 1; *Diffusion und chemische Reaktion in festen Stoffen* (Dresden, 1937).

[6] A. Smekal, Geiger and Scheel, *Handbuch Physik*, **24**: 2, 795-922.

[7] F. Zwicky, *Proc. Nat. Acad. Sci. U.S.A.*, 1929, **15**, 524; *Physic. Rev.*, 1931, **38**, 1772.

[8] J. A. Hedvall, *Reaktionsfähigkeit fester Stoffe* (Leipzig, 1938); *Chemic. Rev.*, 1934, **15**, 139.

irregularities, which do not correspond to equilibrium states, and consequently represent an excess of lattice energy,[9] may be due to an incomplete development of the lattice of the reaction product, formed from substances (or crystallographic modifications of other composition or symmetry) which have been incompletely eliminated (inheritance factors [10]), or due to "frozen" reversible structures, corresponding to higher temperatures. Such states of faulty structure can be produced by quenching substances down to temperatures at which the lattice is too rigid to allow the particles to diffuse into their normal positions. This kind of activity consequently disappears when the rigidity of the lattice in question begins to relax. If the time of heating is adapted to the rate of the structural change, it is often possible to show that the reaction intensity of a substance, the activity of which depends on such lattice anomalities, has a relative maximum at transition temperatures of different kinds.[11]

Since the systematic study of the reaction properties of solids began, about twenty-five years ago, many reactions have been described, which occur in systems of non-conductors, or at such low temperatures that it is impossible to explain the chemical interchange by migrating ions. For example: $BaO + CaSO_4 = BaSO_4 + CaO$ (about 370° C.); $CaO + CuSO_4 = CaSO_4 + CuO$ (about 515° C.);[12] $BaO + CoO . Al_2O_3 = BaO. Al_2O_3 + CoO$ (about 350° C.;[13] $CaO, SrO + Ag_2SO_4 = Ca, SrSO_4 + 2Ag + O$ (about 415° C.; transition point of Ag_2SO_4: 411° C.);[14] and other similar reactions taking place at a transition point of one of the components,[15] *e.g.* the formation of solid solutions or silicates in powder mixtures containing quartz at its transition points (575° C., $\alpha \rightleftharpoons \beta$; about 870° α-quartz-cristobalite).[16] Such systems undoubtedly show that a transport of reacting matter in solid state can also be carried out by other particles than ions.[17]

This can be understood, if we remember that not only the mobility, but also the character of the particles at inner or outer surfaces, or in incomplete reaction films, differ very much from the conditions of the normal interior lattice. No doubt several phenomena of this kind are closely related, on the one hand, to the change of position of those atom complexes of anhydride type the formation of which must precede the thermal breakdown of the lattices of salts of oxygen acids, and, on the other, to the chemical activity of such dipoles of molecular type as are observed in adsorption films on metals.[18]

In fact, however, it is impossible to find a general explanation of the mechanism of reactions of solids. Indeed, the conditions may vary widely, not only from one system to another, but also for the formation of the same reaction product in different temperature intervals. In addition, consideration must also be given to the topochemical influence of different modes of preparing the reacting substances and of the reaction conditions in general.

A third group of lattice changes can influence the physico-chemical activity. We are not limited merely to a thermal influence on the lattice. As was shown some years ago, there is also a connection between the

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[9] R. Fricke, *Z. Elektrochem.*, 1934, 40, 630; 1939, 45, 254.

[10] G. Hüttig, *Sitz.Ber. Akad. Wiss. Wien*, 1936, 7, 648.

[11] J. A. Hedvall, *Reaktionsfähigkeit fester Stoffe* (Leipzig, 1938), p. 141.

[12] *Ibid.*, p. 68.

[13] *Ibid.*, p. 197.

[14] *Ibid.*, p. 73.

[15] *Ibid.*, pp. 127-42.

[16] *Ibid.*, p. 212.

[17] *Ibid.*, p. 132.

[18] *Ibid.*, pp. 69-72; J. H. de Boer and E. J. E. Verwey, *Rec. trav. chim. Pays Bas*, 1936, 443, 675.

magnetic or electric properties of a substance and its chemical activity. In very many combinations of catalysts and substrate reactions we have found an abrupt change in the catalytic effect of ferromagnetic substances when passing through their Curie-intervals.[19] Investigations still going on show that the activation energy of the paramagnetic state above the Curie-point is greater than for the ferromagnetic lattice.[20] Now the catalytic effect is, without exception, greater above the Curie-point, and this can only be understood if we assume that the corresponding disorder of the elemental magnets makes it possible for the greater part of the surface to act as catalysing centres.

The electrical analogy to this *magneto-catalytic effect* has also been found. Many organic substances undergo at fixed temperatures a displacement of the electric fields of their molecules, without change of crystallographic structure, quite in conformity with the change in magnetic properties mentioned. It might be expected that changes of this type would also influence the chemical activity of the substance in question. Experiments carried out with pastilles of *Rochelle salt* have shown that the rate of solution is abruptly changed [21] at 22° C. Above this temperature the polar forces of the OH-radicals seem to cause a strengthening of the lattice, and consequently a smaller chemical activity of the surface,[22] or at least of special crystal faces.

Recent investigations have shown that the irradiation of solids can produce effects other than those generally described as photochemical activation, *i.e.* in the form of real chemical changes in the substance or in an adsorption film by means of excited electrons.

Hedvall and co-workers have found that it is also possible to influence the chemical activity of the surface itself by means of absorbable radiation. Effects of this kind must be due to the fact that the excitation of lattice particles, by removal of electrons to higher levels, changes the binding forces of the lattice and, thus, also the activity of the surface. Accordingly, adsorption equilibria between solids and dissolved substances can be changed by irradiation.[23] The action of light may bring about either an increase or a decrease in the quantity adsorbed per surface unit in comparison with the adsorption in darkness.[24]

Irradiation Experiments with Cadmium Iodide.*

The above-mentioned experiences suggested that substances with fibrous or layer lattices would have different photosensitivity on different surfaces. It might be presumed that the surfaces parallel to the layers, being closely packed with particles bound together by strong forces, would be more stable towards this kind of action than the prism planes sparsely set with more loosely bound atoms or ions.

As typical compounds of this kind we chose CdI_2, which we have used either (*a*) as pastilles of laminæ (surface about 2-3 mm.^{2}), parallel to each other, so that the bounding surface of the cylinder is formed of the thin prism planes, or (*b*) as larger single crystals (basis planes about 6-7

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[19] J. A. Hedvall, *Reaktionsfähigkeit fester Stoffe* (Leipzig, 1938), pp. 162-170.

[20] G. Cohn (as yet unpublished).

[21] J. A. Hedvall, *Reaktionsfähigkeit fester Stoffe* (Leipzig, 1938), pp. 171-4.

[22] J. A. Hedvall, *Atti X. Congr. internat. Chimica Roma*, 1938, II, pp. 255, 268 (discuss. Wulff).

[23] J. A. Hedvall, *Reaktionsfähigkeit fester Stoffe* (Leipzig, 1938), pp. 175-85.

[24] J. A. Hedvall, G. Cohn, A. Assarsson and S. Berger, *Nature*, 1939, **143**, 330.

* Together with P. Wallgren.

mm.^{2}, height of prism faces about 1·2 mm.). The preparations were carefully purified and dried and then kept in vacuum desiccators.

The lattice of CdI_2 is built up as shown in (*A*), in chains or layers. It crystallises in the type[25] *C* : *6*, with a distance of 3 A. between the Cd- and I-ions and 4·21 A. between the layers ($I^- - I^-$).[26]

I^-
Cd^{++}
I^-
(*A*)

During irradiation by a quartz-Hg-lamp the crystals or pastilles were kept in a quartz tube, where if required they could be rotated. The temperature was kept constant at 20° C. during irradiation, and the distance between the quartz tube and the lamp was 15 cm. So that the experiments could be carried out in different atmospheres, a gas current of constant speed (30 c.c./min.) could be passed through the tube. Purifying and drying bottles and U-tubes with P_2O_5 or bottles with H_2O, kept at the proper temperature by means of a thermostat, were used to keep the gas in question dry, or, if desired, at a definite moisture content.

It was found, in perfect accordance with our presumption, that pastilles or single crystals, without exception, became dark coloured only at the prism faces, when irradiated in atmospheres or air, N_2 or H_2 of normal humidity. This effect was observable after only one or two minutes. The basis planes of the cylindrical pastilles, being composed of a number of crystals, became blackened only at the limits between the different laminæ, producing a pattern as by etching (Fig. 1, Plate X.).

No effect could be observed when irradiating by wave-lengths which are not absorbed by CdI_2, even though the irradiation was continued for two hours. Consequently the removal of all visible light by a black filter was of no influence and no action was observed on irradiation by X-rays (Cu anti-cathode). Previous work on the photo-chemical stability of many compounds, *e.g.* Cu-[27] and Ag-halides[28] and sulphides[29] has shown that the presence of water vapour is a necessary condition for the chemical decomposition by light and that even traces of H_2O greatly increase the rate of reaction. We, also, have found in a series of experiments carried out in carefully dried gases that, without exception, there was no visible action on the preparations; all surfaces were unchanged, even after very long exposures.

In other experiments under the same conditions, mixtures of dry N_2 and C_2H_5OH vapour were passed over crystals of CdI_2; visible action of light takes place only if the vapour is not carefully dried. As expected, the reaction always starts at edges, damaged points and scratches.

Accordingly, the photochemical action of ultraviolet light on the prism faces of CdI_2 seems to require the presence of at least small quantities of water. As usual, the photochemical process, which is observed as a dark colouring of the surfaces, is not easy to describe exactly. However, it seems reasonable to presume that the mechanism may be similar to that which Weiss[30] considers probable, when ZnS is irradiated under circumstances similar to those in our experiments:

$$\underbrace{(Cd^{++} + 2I^-)HOH}_{\text{(Adsorption film of } H_2O \text{ on } CdI_2)} + h\nu = I^- + I + H + OH^-;$$

$$\text{and } Cd^{++} + H = Cd^+ + H^+.$$

It is, of course, possible that, under suitable conditions, the decomposition of CdI_2 may proceed further, resulting in the formation of molecular I_2, H_2 and metallic Cd. Although the experimental conditions should

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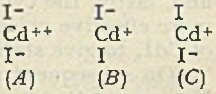
[25] *Z. Krist.*, Erg.-Bd. II (1928-32), p. 247.
[26] *Ibid.*, I (1913-28), p. 189.
[27] J. Plotnikow, *Allgem. Photochem.* (Berlin, 1936), p. 430.
[28] J. Plotnikow, *ibid.*, pp. 446, 451-5.
[29] C. F. Goodeve and J. A. Kitchener, *Trans. Faraday Soc.*, 1938, 34, 902.
[30] J. Weiss, *ibid.*, 1938, 34, 909.

favour a complete decomposition of CdI_2, we were never able to find even traces of the free elements in question. These experiments were carried out as follows: Fine powders of CdI_2 were kept in rotation and irradiated for 5 hours in currents of moist N_2, H_2, or C_2H_4 at temperatures between 20° and 50° C., the gases being afterwards absorbed in small quantities of suitable solvents. After long irradiations the inside wall of that part of the quartz tube in which the powder was kept in rotation became a little dark. No traces of free I_2 or Cd were, however, found, and on treating this dark film with an acid no evolution of H_2 was observed. Water or solutions containing water made the coloration vanish, as was the case if the irradiated crystals were so treated, or if they were kept in a moist atmosphere after the irradiation. When shaking the irradiated powder with an organic solvent, also, no free iodine was found.

These experiences suggest that the photochemical process in CdI_2 can stop at that stage, at which there is an oscillation in the CdI_2 chains between the states (*A*), (*B*) and (*C*), involving a weakening of the binding forces or a loosening of the lattice. No difference was observed between pastilles or crystals prepared as described above and those which had been heated for 3 days at 150° C. This had to be examined because of the possibility of the existence of two modifications of CdI_2.[31] Investigations carried out by G. and B. Aminoff, as yet unpublished, seem to show that only one modification exists, and that the observed structure variations can be explained by displacements of parts of the lattice layers.[32]


$$\begin{array}{ccc} I^- & I^- & I \\ Cd^{++} & Cd^{+} & Cd^{+} \\ I^- & I & I^- \\ (A) & (B) & (C) \end{array}$$

In order that such photochemical action can take place, it is evidently necessary, on the one hand, that valency electrons which are easily removable from their normal levels should be present, and, on the other, that an adsorption film of water, in which the deformation of the water molecules facilitates their dissociation in ions, should be formed.

Regarding the first condition, Werner [33] has established that CdI_2 is a photoelectric conductor, and consequently possesses electrons easily liberated through absorption of radiating energy. As to the formation of a polarised adsorption film of H_2O favourable conditions for such a film evidently exist at the prism faces owing to their unsaturated adsorption forces.

Other observations seem to agree very well with our presumption that crystal faces intersecting lattice layers should possess special adsorption activity. Thus, Hofmann [34] has found a greater adsorption activity of the prism than of the basal faces of graphite, and Wolf and Riehl,[35] when keeping graphite crystals in air containing radioactive emanation, observed that the radiation was mostly emitted from these surfaces or from edges or crystal faults.

Poisoning of the Surfaces against Water Adsorption.

It being proved that the photochemical effect is due to an interaction between loosely bound electrons and a highly activated adsorption film of H_2O and that the combination of these conditions, *i.e.* their accommodation to each other so that an action of light is produced, only takes

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[31] *Z. Krist.*, Erg.-Bd. III (1933-35), pp. 22, 282.

[32] Communication by Professor G. Aminoff (unpublished as yet).

[33] J. Werner, *Z. Physik.*, 1929, **57**, 219; *cf.* also E. Oeser, *ibid.*, 1935, **95**, 699, 715.

[34] U. Hofmann, *Z. angew. Chem.*, 1931, **41**, 845.

[35] P. U. Wolf and N. Riehl, *ibid.*, 1932, **45**, 400.

place at the prism faces, it was of interest to examine whether the effect would fail to appear if the crystals were first treated with substances which are more intensely adsorbed than water.

The choice of poisoning substances was made from the same viewpoint as in flotation technique, *i.e.* the compounds in question should possess high adsorption intensity to CdI_2 and no affinity to water. The experiments were so carried out that vapours of oleic acid, stearic acid, thioglycollic acid, allyl mustard oil, benzene, toluene, phenol, aniline, *o*-toluidine, 1 : 3 : 4-xylidine and pyridine were passed over the crystals for 10 minutes at the lowest temperatures possible by means of an air current. During this treatment the crystals were, of course, not irradiated.

These substances can be divided into four groups, *viz.*, the pure fatty acids (known as water repellers but probably without strong adsorption forces to CdI_2); the two aliphatic compounds, containing S-atoms, which might be assumed to increase the adsorption affinity to CdI_2; benzene, toluene and phenol, which could not be expected to exert great influence, and, lastly, the cyclic compounds, containing NH_2- or N-radicals, where a more effective poisoning effect might be expected, owing to the disposition of CdI_2 to give stable complexes with substances of this kind.

On subsequent irradiation under the same conditions as before (moist N_2), except that two crystals or pastilles—the one being unpoisoned—were always irradiated together in order to facilitate comparison of the observations, the following results were obtained. As expected, *phenol* had no influence, the adsorption film evidently being easily replaced by water. *Benzene* and *toluene*, also, had no influence. The treatment with *fatty acids*, however, showed a distinct effect; the dark colouring of the untreated crystals was, as usual, readily observable within a minute, whereas the poisoned ones remained white much longer. Even after irradiation for 15 minutes or more there was a great difference in colour between the two crystals. The gradual blackening also of the poisoned crystals is probably due to destruction of the poison film by the ultraviolet light. *Thioglycollic acid* exerts about the same effect as the unsubstituted fatty acids. *Allyl mustard oil* is more effective, preventing visible attack of the light for about 10-15 minutes, depending on the duration of the poisoning treatment. Still greater effect is, as expected, obtained with crystals, treated with *aniline* and 1 : 3 : 4-*xylidine*, and especially with *o-toluidine*, which still prevents the action of light after two hours, thus having practically completely poisoned the surface.

As mentioned above, it is not sufficient for an effective poison that one part of the molecule is intensely adsorbed. The part facing outward from the crystal surface must not have great affinity to water. Therefore experiments with crystals treated with dry NH_3 showed no poisoning effect at all. The surfaces were, however, not so uniformly attacked as before, because of the formation of a complex between CdI_2 and NH_3 starting at scratches, edges, or damaged points of the surface.

Pyridine proved, however, to be the most effective poison of all substances tested. Treated with vapour of pyridine and dried in vacuum desiccators the crystals remained white when subsequently irradiated in moist N_2 for hours.

The difference in poisoning effectiveness between aniline, xylidine, *o*-toluidine and pyridine corresponds very well with the differences in the chemical behaviour of CdI_2 towards these substances, with all of which it forms addition products, the intensity of the reactions increasing from aniline to pyridine.

The reaction with pyridine deserves somewhat more detailed description. When used in great excess, the crystals absorb it intensely, developing a considerable reaction heat and swelling like graphite when oxidised to graphite acid. The reaction product remains solid if the proportion $C_6H_5N : CdI_2$ does not exceed about 35 : 1. When kept in a vacuum desiccator the crystals lose the larger part of the pyridine until an equilibrium is attained corresponding to the formula: $CdI_2 . 2C_5H_5N$. This compound is insoluble in water.

It is of interest to mention that $CdBr_2$ and $CdCl_2$ behave in a similar way to CdI_2 towards aniline, xylidine, *o*-toluidine and pyridine. CdF_2, however, behaves differently.

Irradiation Experiments with $CdBr_2$, $CdCl_2$ and CdF_2.

Having shown that the photochemical reaction in CdI_2 is made possible through combination of structural and adsorption factors, it was of interest to examine also the other Cd halides from this point of view. Experiments with them were carried out in exactly the same way.

$CdBr_2$ and $CdCl_2$ were crystallised from solutions in water and dried in exactly the same way as when preparing CdI_2. The CdF_2 used was "*Kahlbaum pro analysi.*"

$CdBr_2$ crystallises [36] in the type *C : 19*.

Br^-
The Cd^{++} chains (*B*) form layers similar to those in CdI_2 crystals.
Br^-
(*D*)

The only difference between the CdI_2- (*C : 6*) and $CdBr_2$-structures consists in the correlation of the anions, which in *C : 6* form a hexagonal, and in *C : 19* a cubic packing,[37] and in the smaller distances between the layers, both of which are caused by differences in volume and polarisation effects of the anions. Exactly as was the case with CdI_2, another "modification" exists, evidently formed when pressing or grinding crystals, and brought about by a periodical displacement of parts of the lattice.[38] This structure represents a kind of intermediate structure between CdI_2 (*C : 6*) and $CdBr_2$. It can be transformed into the normal one (*C : 19*) by heating to about 200° C.

$CdCl_2$ also belongs to type *C : 19*, and the lattice data conform with those of $CdBr_2$, except for the different distance between adjacent layers.

Finally, CdF_2 belongs to another class of symmetry, the fluorite type [39] *C : 1*, and it can, therefore, be presumed that the behaviour of CdF_2 will differ fundamentally from the other compounds.

On irradiating these compounds in moist N_2, it was only that $CdBr_2$ modification which is related to CdI_2 (and produced through stressing the crystals) which was coloured dark after an exposure of some minutes. Irradiation in an atmosphere of dry N_2 had no effect. After heating the $CdBr_2$ for an hour at 200° C., and so bringing it back to its normal type (similar to $CdCl_2$, *C : 19*) no action of light could be observed under the experimental conditions. Similarly, no effect was obtained with $CdCl_2$, nor, of course, with CdF_2.

Obviously it is impossible to claim that no photochemical action takes place, merely because no colour change is observed. It may be that a disturbance also occurs in the layer lattices of the normal modifications of $CdBr_2$ and of $CdCl_2$, without giving rise to a dark colouring.

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[36] *Z. Krist.*, Erg.-Bd. II (1928-32), pp. 246-7.

[37] *Ibid.*, I (1913-28), pp. 742-3.

[38] *Ibid.*, II (1928-32), p. 280.

[39] *Ibid.*, I (1913-28), p. 188.

The facts, however, that (i) a visible effect is obtained with CdI_2, and, though not so strongly, with that modification of $CdBr_2$ which is regarded as a combination of *C : 6* and *C : 19*, (ii) there is markedly less adsorption intensity at the prism faces of the stable $CdBr_2$ and $CdCl_2$ modifications than at those of CdI_2, which also makes weaker polarisation of the adsorbed water molecules probable, and (iii) that the photoelectric conductivities of $CdBr_2$ and $CdCl_2$ [40] are smaller, seem to indicate that the combination of conditions for photochemical action is especially favourable in CdI_2. A difference between CdI_2 and the other Cd halides can also be predicted, because of the greater polarisation effect caused by Cd^{++} on the I^-, which is more sensitive than Br^- and Cl^- (Fajans). This dissimilarity corresponds to the differences in structure mentioned above.

Experiments on the Solubility of Irradiated CdI_2-Crystals.*

It is to be expected that crystals, the surfaces of which are activated through irradiation, will become more intensely attacked by a reactive substance than when they have not been irradiated by absorbable wave-lengths.

We therefore investigated the rate of solution of CdI_2 pastilles, pressed in the way described above. As it was impossible to prepare two pastilles (the one to be irradiated, the other to be protected against the radiation) so perfectly equal as to permit a comparison of their rates of solution, the experiments were carried out with the same pastille.

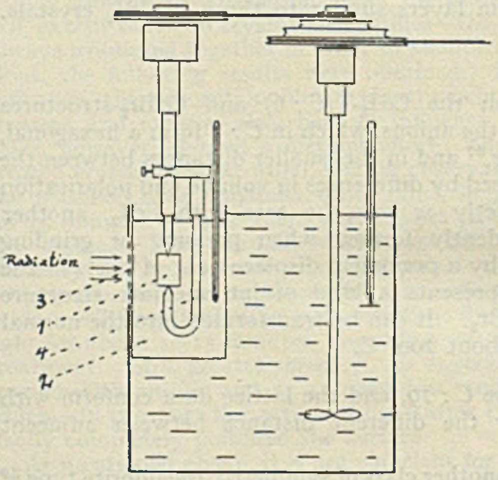

FIG. 2.

It was, of course, necessary to use a solvent which dissolves only a very small quantity of CdI_2, and which does not absorb the wave-lengths which exert the photochemical action on the crystal surface. These conditions are satisfied by a mixture of 92 parts by volume of " normal benzine " (freed from unsaturated hydrocarbons by treatment with H_2SO_4), and 8 parts of alcohol (99·5 % C_2H_5OH + 0·5H_2O). The solution experiments were carried out in a thermostat, the pastille (1) being rotated in a quartz tube (2) containing the solvent (75 c.c.) and placed close to a quartz window (3) on one side of the thermostat (Fig. 2). The pastille is supported by small springy glass bars (4), the upper and lower surfaces being covered by a wax which is not attacked by the solvent. The shortest wave-length emitted from the quartz-Hg lamp was 2350 A. The solvent transmits light of wave-lengths longer than 2130 A. and CdI_2 absorbs wave-lengths shorter [41] than 3700 A. The distance between the lamp (which had a quartz condenser lens) and the pastil was 3-4 cm., and the temperature was kept

[40] G. A. Dina, *Compt. rend.*, 1913, 157, 590, 736.

* Together with S. Månsson.

[41] K. Butkow, *Acta physicochim. U.R.S.S.*, 1935, 3, 205.

constant at 25° C. during an experiment of 30 minutes. Every pastille was placed in a special desiccator communicating with a vacuum pump after the experiment. After 6 hours the solvent had evaporated and the pastils attained constant weight.

The table shows the results obtained under different conditions with pastils 1 to 5. It is seen that an increased rate of solution is produced by irradiation with wave-lengths which can be absorbed by CdI_2. An average effect of about 13 % is attained under the experimental conditions used.

The experiment thus proves that the presumption that surfaces which are photochemically sensitive can also, when irradiated, be activated with regard to their chemical behaviour in general.

(A) Irradiation by Hg-Lamp without Black Filter.

Pastil No.	Weight (in g.).	Quantity Dissolved (in g.).		Difference (in g.).	Effect of the Irradiation (%).
		In Darkness.	When Irradiated.		
1	6·690	0·00210	0·00235	0·00025	+ 11·9
2	8·034	0·00230	0·00254	0·00024	+ 10·5
3	7·194	0·00280	0·00328	0·00048	+ 17·0
1	6·687	0·00187	0·00217	0·00030	+ 16·0
2	8·029	0·00278	0·00310	0·00032	+ 11·5
4	7·854	0·00250	0·00290	0·00040	+ 16·0
				Average	+ 13·8

(B) Irradiation by Hg-Lamp and a Black Filter, Transmitting no Visible Light.

1	6·671	0·00250	0·00276	0·00026	+ 10·4
2	8·010	0·00300	0·00341	0·00041	+ 13·7
3	7·171	0·00258	0·00292	0·00034	+ 13·2
4	7·831	0·00237	0·00268	0·00031	+ 13·1
5	6·590	0·00355	0·00400	0·00045	+ 12·7
				Average	+ 12·6

(C) Irradiation by White Light, containing no Ultraviolet Wave-lengths.

1	6·672	0·00250	0·00240	− 0·00010
2	8·011	0·00258	0·00269	+ 0·00011
3	7·183	0·00260	0·00260	± 0·00000
4	7·840	0·00216	0·00207	− 0·00009
5	6·603	0·00259	0·00263	+ 0·00004
			Average	− 0·00001

Summary.

A short survey is given of the different kinds of faulty structure in crystal lattices, of the conditions for the production of irreversible irregularities or for the existence of the reversible ones in general, and of the importance of imperfectly formed crystals for different branches of chemistry. It is shown that increased chemical activity is caused not only by disturbance of crystallographic symmetry, but also by changes of the magnetic or the electric state of the lattice.

In accordance herewith photochemical effects have been found involving increased surface activity with respect also to the chemical interchange with surrounding materials. Arising from these experiments, the existence of crystals was assumed the photosensitivity of which may vary

with the kind of crystal faces. It was suggested that this might be the case with crystals built up as layer lattices. Experiments carried out with Cadmium halides have, indeed, shown that the prism faces of CdI_2 are especially sensitive, whereas the basal faces are left unattacked by absorbable wave-lengths. The photochemical process requires small quantities of water adsorbed at the surface and, consequently, it can be more or less completely prevented by compounds which are more intensely adsorbed than water. A smaller effect of the same kind has been found when using that modification of $CdBr_2$ which is of the same type ($C : 6$) as CdI_2. No visible action of radiation could be observed with $CdCl_2$ and CdF_2, the lattices of which are more different from the type of CdI_2.

It has also been shown that the surface activity, caused by the photochemical process, involves increased rate of reaction of such parts of crystals; thus the prism faces of CdI_2 when irradiated by absorbable wave-lengths, are more rapidly attacked by a solvent than in darkness, or if radiated by light not being absorbable.

The carrying out of this investigation has been made possible by subventions from the Nobel Committee for Chemistry of the Swedish Royal Academy of Science and the Research Fund of Chalmers Technical College.

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Chalmers Technical College,
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REVIEWS OF BOOKS.

The Mathematical Theory of Non-uniform Gases. By S. Chapman and T. G. Cowling. (Cambridge University Press, 1939, pp. 404. Price 30s.)

To those physicists who are primarily interested in phenomena, the dynamical theory of gases is an unsatisfactory subject. The fundamental principles are few, and can be readily applied to produce a crude theory, but, if we wish to obtain exact formulæ for the coefficients of viscosity, diffusion and thermal conductivity, long and complicated mathematical investigations are necessary. Further, these calculations add nothing to our understanding of the physical processes involved, though they are vitally necessary if we are to be able to deduce anything of value from the experimental material. It follows from the nature of the subject that books dealing with it should either be of an elementary nature or should be fully fledged mathematical treatises. Prof. Chapman and Dr. Cowling have chosen the latter alternative, and have presented the fullest account of the subject which has yet appeared in book form.

The book is a formidable one, even to a mathematical specialist, and the reading is not simplified by the authors' introduction of a new vector and tensor notation, too many of which already exist. Experimental physicists and physical chemists will probably find that the most useful part of the book consists of Chapters 12, 13 and 14, extending over 40 pages, where the various formulæ which have been deduced for different molecular models are compared in detail with the experimental results.

It is clear from even a casual glance at the book that a theory of such great mathematical complexity could not have evolved into such a state of perfection in a short time. The history of the subject is a long one, dating back effectively to Maxwell's paper of 1866, and an admirably written account is given in the historical summary at the end of the book. Although the dynamical equations had been set up at an early date by Maxwell and by Boltzmann, no general solution of them was given until 1916-17, when Chapman and Enskog published solutions independently. This work, and later improvements, forms the main topic of the book, and is now for the first time made widely available. In addition to discussions of the usual topics of viscosity, diffusion and thermal conductivity, treated by Enskog's method, there are also chapters on dense gases, ionised gases and the modifications introduced by the quantum theory. The small section dealing with the effect of the quantum theory on the molecular collisions is necessary to complete the account of the present state of the theory, but the incursion into the electron theory of metals could well have been dispensed with, since there the interest is mainly confined to the dynamics of the motion of the electrons in the crystal lattice, which is not dealt with in the book.

It is probable that the book will become the standard work of reference on the subject.

The Molecular Structure of the Fibres of the Collagen Group. First Procter Memorial Lecture. By W. T. Astbury. (London: International Society of Leather Trades' Chemists, 1940. Pp. 24. Price 2s. 6d.)

Dr. Astbury recently delivered the first Procter Memorial Lecture before the London Conference of the International Society of Leather Trades' Chemists. This has now been published in booklet form and thus made easily available to all workers interested in the problem of the structure of protein molecules or indeed of macro-molecules in general.

The lecture includes a first account of X-ray studies on collagen and elastin fibres carried out by Dr. Astbury and his colleague, Dr. Florence Bell.

The fibres of the collagen group are shown to have a special pattern of their own based on the arrangement of the amino acid residues in the long chain molecule, namely,

- - - - P—G—R—P—G—R - - -

where P represents a proline or hydroxproline residue, G, glycine and R, one or other of the remaining residues. Owing to the presence of the 5-atom ring in proline the stereochemical configuration of the chain differs from the more familiar pattern of the myosin-keratin group of fibres.

Collagen fibres show the property of " supercontraction " just like keratin fibres and there is a definite suggestion in the lecture that the fibrous form of protein molecules only exists as long as the long chain molecules are held extended by intra-molecular forces, and that the single molecule released from these external forces collapses into a looped or 3-dimensional form.

The lecture is written in Dr. Astbury's characteristically lucid style and the International Society of Leather Trades' Chemists have done a good service to chemistry in publishing it as a booklet.

D. J. L.

Elementos de Atomistica. By Professor G. E. Villar. (Montevideo, Impresora Uruguaya, South America. 1939.

Professor Villar has put Spanish-speaking students in his debt by writing this very useful treatise on atomic physics. The treatment is strictly elementary throughout and the book may be read with profit by a university student in the pass grade. The topics usual to a first year course in this subject are covered, and the book can be recommended to English students of physics who desire to extend their knowledge of the Spanish language.

A. F.

Sound. By Dr. E. G. Richardson. Pp. iv + 339. (London: Edward Arnold & Co., 1940. Price, 16s. net.)

Dr. Richardson's treatise, which now appears in its third edition, is too well known to need any detailed description here. The scope of the book remains unaltered, the main changes consisting in a thorough revision of the chapters on impedance, supersonics and sound reproduction. Dr. Richardson keeps fully up to date in his knowledge of the literature of his subject, and his book is to be unreservedly commended as a suitable introduction to advanced study and research in a subject which is advancing with remarkable rapidity.

A. F.

Colloid Chemistry (A Textbook). By Harry Boyer Weiser. (New York: John Wiley & Sons, Inc. 1939.) Pp. viii + 428. Price 24s. net.

Professor Weiser has given us in this volume a sound, well-balanced, and very readable introduction to Colloid Science, in moderate compass. It is more descriptive than profoundly theoretical, but the principal theoretical foundations are clearly given, though some of the mathematical proofs fall short of thorough accuracy.

After a brief introductory chapter there are about 100 pages on Surface Chemistry, in which adsorption is treated at length, and wetting and the structure of surface films rather briefly, but with the principal facts and theories indicated well. Some 35 pages deal with the preparation and purification of sols, and an equal space is devoted to some of their physical properties. The electrical properties and the coagulation of sols fill 80 pages; gels, emulsions, foams, smokes and other topics fill another 80 pages. The last part of the book contains a brief account of some important contact catalyses, and of dyeing and clays. References to the literature are well selected and reasonably numerous.

The reviewer would have liked a better treatment of colloidal electrolytes ; the few pages on this topic, which has come into great prominence lately on account both of its theoretical interest and of its technical importance, are inadequate. Hydrophilic colloids, though better treated, might receive more attention. No attempt is made, probably wisely, to discuss modern synthetic polymers, or the biological applications. A pleasing feature of the book is, however, the frequent indication of various technical applications.

Few errors have been noticed ; on p. 110 the curve for the gaseous film has been displaced upwards so that the limiting value for FA/kT does not reach unity, as it should do, when F is zero ; and if the reference to " blue sky " in the index is looked up, the reader will find only the unsullied whiteness of the excellent paper on which the book is printed. Misprints seem very few.

Students and non-specialists in colloids will thank the author for providing one of the best descriptive introductions to the subject that has yet appeared.

N. K. A.

The Raman Effect and its Chemical Applications. By James H. Hibben and Edward Teller. American Chemical Society Monograph Series. The Reinhold Publishing Corporation, New York, 1939. Chapman & Hall, Ltd., London. 66s. net.

Headings to the main divisions of this book will indicate its purpose and scope. These are : Part I—General Discussion on the Raman Effect ; its Practice and Theory ; Part II, the Raman Spectra of Organic Compounds ; and Part III, the Raman Spectra of Inorganic Compounds.

In the first Part, the Effect is described in simple language, with its relationship to absorption and fluorescence ; the experimental methods for determining the shift of the lines, their intensities and polarisation are then given ; a chapter on the vibration and rotation of polyatomic molecules follows with one on the relationship between infra-red absorption spectra and the Raman Effect ; with finally a discussion on the vibrations occurring in different types of molecules and on such features as anharmonicity.

All this theoretical treatment is admirable and presents a clear picture of the information derivable from this study, enabling the observer to calculate the force systems from observed frequencies.

The application of the Raman Effect to constitutional problems is the theme of Parts II and III. Thus in Part II the Raman Spectra of the aliphatic hydrocarbons and their derivatives and of the aromatic hydrocarbons and their derivatives are discussed, together with accounts of the shift characteristic of the ethylenic and the carbonyl linkages. Indications relative to structure are followed up in a multitude of cases.

Part III dealing with inorganic compounds is perhaps necessarily less systematic, but it covers a wide range. Thus the Raman spectra of gases, phosphorus, sulphur, carbon, water, halogen compounds, acids, sulphur and silicon compounds, oxides, azides and ammonium compounds all come under discussion with a wealth of data embodied in the text.

A bibliography extending to about 2000 references, an index of organic and inorganic compounds, linked up with these references, and a numerical index connecting the subjects mentioned in the bibliography and their discussion in the text, show the thoroughness with which this book has been compiled.

It may be truly said that this work is indispensable to workers in this field and in that of the complementary one of infra-red spectra.

R. R.

Annual Reports on the Progress of Chemistry for 1939. (The Chemical Society. Pp. 458. Price 13s. Post free.)

Perusal of these volumes impresses one more and more each year with the all-embracing influence of physical chemistry on every aspect of chemical advance. Though H. W. Melville with R. P. Bell, M. G. Evans, W. C. Price and J. H. Schulman have written six excellent monographs under the heading " General and Physical Chemistry," occupying in all 83 pages, members of the Faraday Society will read with equal interest many articles under other general heads, notably those of Peierls on the Theory of Nuclear Forces, of Terrey on Heterogeneous Equilibria, of H. J. Emeléus on Reactions in Non-Aqueous Solutions, of Ubbelohde on Crystal Physics, of Hampson and J. M. Robertson on Inorganic and Organic Structures respectively, and, within the 149 pages devoted to Organic Chemistry, those of H. B. Watson on Reaction Mechanisms and of Maitland on Stereochemistry.

The Annual Reports are useful, not solely for the monographs on subjects with which we feel ourselves somewhat familiar, though it is by such we are apt to judge the value of the whole. Their main interest lies in the opportunity they give us to obtain an adequate perspective view of the less familiar, written by experts.

In these days of stress, when there is little time or opportunity to study the vast field of physical and chemical literature, this volume should be more than usually in demand.

ERRATUM.

P. 510. Line 8 from bottom. *For* " thianthren " *read* " phenthiazine."

PRINTED IN GREAT BRITAIN AT THE ABERDEEN UNIVERSITY PRESS, ABERDEEN

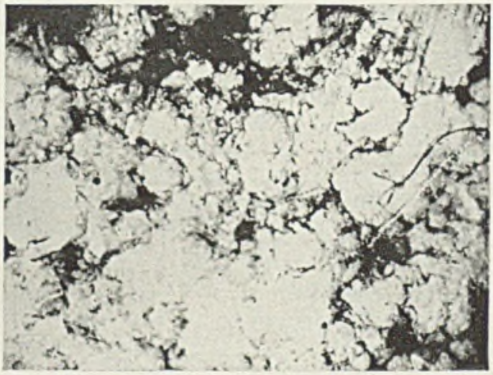

FIG. 1.

[See page 700.

CHEMISTS AND THE CENTRAL REGISTER

As is well known, steps were taken more than a year ago to form a Central Register of persons with technical, scientific and professional qualifications, who could be regarded as available for service in Government Departments in war time, except in so far as they were already engaged on work of greater National importance. In the formation of the Register the Ministry of Labour and National Service was fortunate in securing the cordial co-operation of all the main societies and institutions concerned, and in its operation since the beginning of the war the voluntary assistance of a large number of specialists has been at the disposal of the Ministry.

The Sections of the Register covering Pure Chemistry (Classification No. 706) and Industrial Chemistry (Classification No. 707) contain between them some 6,000 names. The majority of these persons are at present in useful, frequently nationally important, employment, and should not be moved unless it is really necessary in the interests of the country. Every effort is accordingly made to meet the requirements of Government Departments for chemical personnel from the ranks of those who are unemployed, or at least readily available. It is, however, now proving impossible to meet the growing demands for chemists from these groups alone, and it is therefore essential that the names of all chemists of either sex, *especially young men and women*, who are both qualified and willing should be on the Register. Obviously only names which are on the Register can be put forward for the vacancies which are notified. Roughly speaking, tbe minimum qualification for enrolment as a chemist on the Register is a degree in Chemistry or an equivalent qualification, or on the other hand, several years' experience in chemical practice or industry.

Enrolment on the Central Register implies that the persons concerned will be prepared to accept suitable full-time employment offered to them, unless they are already engaged on work of National importance, but the volunteers themselves are the judges of the suitability of the post offered, and only the names of volunteers who have expressed their willingness to be considered for any particular post offered are submitted to the prospective employers. Further particulars of the Central Register, and in particular of the Chemistry Sections, will be supplied on application to the Secretary, Ministry of Labour and National Service, Central Register Branch, Queen Anne's Chambers, Westminster, S.W. 1, and volunteers are asked to write to that address.

CENTRE NATIONAL DE LA RECHERCHE SCIENTIFIQUE

The Centre National has made provision for the publication of a Bulletin d'analyses bibliographiques (Abstracts) which are to appear as soon as possible after publication of the articles which they purport to analyse.

In addition, the Centre is providing for the photographic reproduction on microfilms of the various articles which are abstracted.

For further particulars application should be made to: P. Auger, Centre National de la Recherche Scientifique, Service de Documentation, 18, rue Pierre Curie, Paris, Ve.

Transactions of the Faraday Society

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(*b*) Tables should be reduced to a minimum and, where possible, results should be shown by means of curves rather than tables. Only in exceptional cases may tables be published as well as graphical representations of their contents.

(*c*) Each paper should include a brief summary indicating in general terms its purpose and conclusions.

iii. (*a*) Papers must be typewritten, with double spacing, on one side only of the paper, with a good margin on the left side.

(*b*) **References** should be typed in numerical order (and in the following sequence: journal; date; volume number; page) at the end of the paper; the necessary reference numbers only should appear in the text.

(*c*) Symbols, formulæ and equations should be written or typewritten with great care. The symbols recommended in the Report of the Joint committee of the Chemical Society, the Faraday Society and the Physical Society should be employed.

iv. (*a*) **Line drawings** may in the first instance be submitted in sketch form. For publication, however, they must be made with Indian ink on Bristol-board or preferably tracing *cloth*. Freehand must not be employed and all lines must be firmly and evenly drawn. Drawings should, generally, be capable of reduction to about one-half scale, depending on their nature and complexity; all drawings relating to one paper should be so made that they will all be reduced to the same extent. In the case of curves the ordinates and abscissæ must be drawn in ink and reliance must not be placed on the printed lines of scale paper.

(*b*) Where possible, lettering should be outside the diagram. Lettering should be put in lightly with lead pencil.

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