III. ADSORPTIVE STRATIFICATION IN GELS, III.

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(With Plate II.)

THE first record of the formation of noticeable structures by the diffusion of precipitating reagents appears to have been made by Runge [1855], who experimented with a number of pairs of inorganic reagents in blotting paper. In 1874 Monnier and Vesque observed the production of large crystals by slow diffusion through strips of filter paper and gels respectively. Three years later Ord allowed ammonium oxalate to diffuse through an isinglass gel in an open tube immersed in calcium chloride solution. The precipitate consisted first of growth forms changing into spherites towards the calcium chloride. The diffusion of solutions into gels was studied extensively by Pringsheim [1895] in 1890 and 1892. The results of his experiments were communicated to the Berlin Academy in 1891 and 1892, but not published until 1895. Pringsheim allowed two solutions, capable of interacting with the formation of a precipitate, to diffuse in opposite directions through gelatin gels contained in the horizontal portion of a graduated U-tube of special form. The rates of diffusion for different concentrations and various reagents were observed, and the important law discovered that, after the meeting of the reagents, diffusion took place only from the hypertonic into the hypotonic reagent. From the number of his experiments it would be surprising if Pringsheim had not observed cases of band formation, especially as U-tubes favour this result. However, such concentrated solutions were employed, from $N/2$ to $12N$, as usually to prevent stratification of the precipitate. Nevertheless examination of his illustrations shows the formation of two bands in several cases. As a botanist he refers to the occurrence: "In many cases not one but two separated precipitates are produced, which may perhaps be due to dissociation phenomena."

The first observation of a series of layers must be ascribed to Lupton [1892]. Unfortunately Lupton did not investigate the phenomenon, and the nature of his bands is left to conjecture. But in 1896 Liesegang [1896], continuing Pringsheim's experiments, obtained the remarkable series of silver dichromate rings now well known. The original experiment was made with a drop of silver nitrate on a glass plate coated with 5 per cent. gelatin containing a small quantity of potassium dichromate. Liesegang rightly perceived the

importance of the phenomenon and commenced an experimental study, the first part of which was published [1898] in a pamphlet which has not been available in London until recently. In these researches he used mostly ammonium dichromate in gelatin gels contained in glass tubes inverted in aqueous silver nitrate. He showed that the spaces between the layers are completely free from unchanged ammonium dichromate, since silver nitrate poured over a plate preparation produced no further effect. Plates examined with X-rays showed dark shadows, corresponding to the A-lines as he called them, with the spaces almost clear. "There is extraordinarily much more silver in the A-lines than in the spaces."

Liesegang also obtained "essentially similar structures" with other insoluble precipitates. Ammonium chromate gave rings almost exactly like those of the dichromate. Using lead nitrate, instead of the silver salt, the bands were wholly like the silver dichromate ones, but not so sharp, and the spaces were filled with a cloudiness due to yellow lead chromate. A-lines were also obtained with lead iodide and thiosulphate, the latter giving sharp white lines separated by glass clear spaces, and with silver ferric oxalate and Prussian blue. Liesegang perceived that wider study of the phenomena might enable biologists artificially to imitate the structures of living organisms. He suggested that banded agates might have arisen in this way and warned microscopists that their methods of staining might lead to the production of fresh structures in the objects under examination.

After having inspected Liesegang's "astonishing" preparations, Ostwald interpreted the A-lines as due to supersaturation, remarking that "Precipitates which appear in the colloidal form give no A-lines, neither do those which are ordinarily (i.e. visibly) crystalline; whatever is the reason in such cases has not yet been discovered" [1897]¹. The posthumous theory of the late Lord Rayleigh [1919] is essentially similar.

The supersaturation theory was subjected to mathematical analysis by Morse and Pierce [1903]. Working with potassium chromate in the gel, the reaction takes place in accordance with the relation:

For equilibrium in the presence of the solid phase the concentrations must satisfy the relation:

$$\text{Ag}^{\cdot 2} \times \text{CrO}_4'' = k, \dots\dots\dots(1)$$

where k is the solubility product. Morse and Pierce inquired whether there is a relation in the case of a supersaturated solution similar to (1), with, however, a different constant, that defines the limit of supersaturation, e.g.

$$\text{Ag}^{\cdot 2} \times \text{CrO}_4'' = H. \dots\dots\dots(2)$$

Assuming that the formation of a precipitate has no influence on the progress

¹ It has previously been shown, Bradford [1917], that the adsorption theory explains both these facts.

of the diffusion, by the application of Fick's law, they were able to obtain the formula:

$$H = \frac{4U_0^2 V_0}{\pi^{\frac{1}{2}}} \left[\int_{\frac{x}{2a\sqrt{t}}}^{\infty} e^{-\beta^2} d\beta \right]^2 \cdot \int_{-\frac{x}{2b\sqrt{t}}}^{\infty} e^{-\beta^2} d\beta, \dots\dots\dots(3)$$

where x is the distance of a band from the surface of the gel, t the time from the commencement of the experiment, U_0 and V_0 are the original concentrations of the reaction components, a^2 and b^2 their diffusion constants, and β is merely a constant of integration.

From this Morse and Pierce deduced that $\frac{x}{\sqrt{t}}$ must be constant, which they were able to verify, that the change of concentration of the solution in the gel can be neglected and that:

$$H = 1.4 \times 10^{-6} \left(\frac{\text{mol.}}{\text{litre}} \right)^3$$

and

$$a^2 = 1.54 \left(\frac{\text{cm}^2}{\text{day}} \right).$$

This indicates that, with N AgNO_3 and $N/75$ K_2CrO_4 , precipitation occurs at each new band when the concentration of the silver ion is about $N/200$, that of the chromate being unaltered at $N/75$. Moreover, since the ordinary solubility product of silver chromate is 5.1×10^{-13} , the supersaturated gelatin at the concentration of precipitation held in solution $\frac{\sqrt[3]{1.4 \times 10^{-6}}}{\sqrt[3]{5.1 \times 10^{-13}}}$ or 140 times the amount of silver chromate required to saturate it in the presence of the solid phase. It will also be noted that the figure, 1.54, found for the diffusion constant of silver nitrate in gelatin is much greater than that in pure water, 1.13 to 1.20, determined by Kawalki. These deductions are very remarkable and it will be endeavoured to show that they are contrary to fact. Morse and Pierce also obtained bands in gelatin with lead sulphate; silver oxalate, carbonate, phosphate, thiocyanate and bromide; cobalt hydroxide; barium oxalate; mercurous bromide and carbon dioxide. They also found that bands were produced in capillary tubes in aqueous solution, which broke down after the formation of two or three.

The supersaturation theory has been criticised by a number of writers. Bechhold [1905] considered that, in addition to supersaturation, the production of banded precipitates was influenced by the solubility of the precipitate in one or other of the salts present or formed by the reaction, and by the coagulating or inhibiting effect of ions, as in the case of suspensions and colloid solutions. By mixing 1 cc. of silver nitrate solutions of different strengths with 3 cc. of $M/100$ $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ in 2.5 per cent. gelatin sols, Bechhold found that deep turbidity was produced with a concentration as low as $M/533$ of AgNO_3 .

The metastable product can be calculated from this value:

$$\text{Ag}^2 \times \text{Cr}_2\text{O}_7'' = \left[\frac{1.88 \times 10^{-8}}{4} \right]^2 \cdot \left[\frac{3 \times 10^{-2}}{4} \right] = 1.64 \times 10^{-9}.$$

It will be seen that although silver dichromate is more than twice as soluble

as the chromate, yet the metastable product calculated from Bechhold's figures is very much less than that deduced from the supersaturation theory for the latter substance by Morse and Pierce.

Since nitrates tend to liquefy the gelatin, Bechhold thought they should favour the formation of a precipitate, and this would be the effect of the ammonium nitrate formed in the reaction. Similar experiments were therefore made both with $N/160$ and $N/320$ AgNO_3 mixed with $M/100$ $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ in 5 per cent. gelatin containing increasing amounts of $(\text{NH}_4)\text{NO}_3$. The turbidity increased to a maximum, diminished and again increased. Parallel experiments in water without gelatin showed similar maxima and minima, though somewhat less definite. These latter results are particularly interesting as they suggest that ordinary supersaturated solutions are affected by ions in the same way as sols. The question of the relation of sols to supersaturated solutions is in urgent need of further study, which would probably throw much light on the nature of solution.

Bechhold realised that, if the ammonium nitrate formed by the reaction plays a part in the ring formation, an increase in the concentration of this salt must cause a change in the ring structure. The bottom of a glass dish was covered half with a layer of 5 per cent. gelatin containing $M/20$ $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ and half with chromated gelatin with addition of $N/4$ $(\text{NH}_4)\text{NO}_3$. A drop of silver nitrate was placed over the division. The rings in the ammonium nitrate half were appreciably wider than in the other half and very slightly closer, so that separation of the bands was not apparent till a greater distance from the centre. This shows that the formation of the bands is undoubtedly affected by the presence of soluble salts in the gel. However the concentration of the $(\text{NH}_4)\text{NO}_3$ was six times greater than would be produced in an ordinary experiment. Similar ideas, though without further direct experimental support, were suggested later. In a lecture at the Royal Institution in 1912, Sir J. J. Thomson supposed that the soluble substances produced by the reaction might act in a similar way to certain bodies known as stabilisers which prevent the precipitation of colloidal solutions, and Freundlich and Schucht [1913] thought that the formation of a precipitate might be due to autocatalytic coagulation by electrolytes.

It seemed desirable to add increments of by-product more comparable with the concentration in which they are usually produced. Tubes containing (1) 20 cc. of $N/20$ Na_2CO_3 agar gel and (2) the same with $N/20$ NaCl were treated with 5 cc. of dilute CaCl_2 solution. Diffusion proceeded at the same rate in each tube with the formation of bands at distances below the surface of the gel in mm. as follows:

(1)	20.5	22.5	25	28	32.5	35.5
(2)	20.5	22.5	24.5	—	33	35.5

In another experiment 15 cc. of $N/5$ K_2CrO_4 solution was poured on (3) 15 cc. $N/200$ $\text{Pb}(\text{NO}_3)_2$ agar gel, and (4) the same gel with addition of KNO_3 to $N/100$.

The tubes developed beautiful series of clear-cut strata of lead chromate very close together, the average distance of the last twenty layers being respectively 0.70 and 0.67 mm. Comparison with Bechhold's result shows that any influence of the by-product of the reaction is to reduce the distance between the strata, i.e. to inhibit separation of the bands, but such effect is practically negligible.

Hatschek [1911, 1, 2; 1912] used a number of fresh compounds and studied for the first time reactions in various gels, including the inorganic gel of silicic acid. He showed that precipitates tend to form larger crystals in gels than in aqueous solution and that the particles of banded precipitates are usually microscopic spherical aggregates, and was able [Hatschek and Simon, 1912] to explain by his results many features of the occurrence of gold in quartz. He [1914] showed that the supersaturation theory is inadequate to explain the complicated phenomena of stratified precipitation. If, as Ostwald thought, the silver dichromate is deposited on the ring from the neighbouring region which is supersaturated in regard to this salt, it should be impossible to produce a second set of rings in a tube already containing one, or to obtain a stratified precipitate in a gel previously sown with crystals of the insoluble precipitate. Nevertheless he obtained perfect stratifications of lead iodide in agar containing suspended lead iodide [1912] and his pupil, de Whalley, succeeded in producing a second system of lead chromate bands in agar, superposed on a finer system of strata of the same substance [Hatschek, 1914]. These experiments appear to show that bands can form although supersaturation is prevented.

Liesegang [1914] showed that strata of silver dichromate do not form in gelatin which has been purified from mineral matter by soaking in slowly changing water. It is necessary to add gelatose and a small definite amount of (citric) acid for each particular concentration of soluble dichromate in the gel. The bands are however thicker and more widely spaced than in the unwashed gelatin. Further addition of acid yields a continuous mass of colloidal silver dichromate. Moreover it has been found that neither silver chromate nor dichromate forms bands in agar gel. Indeed the nature of the gel appears to have a very remarkable influence on the form of the precipitate in all cases. This was first insisted upon by Hatschek as a necessary consideration for a complete theory of the phenomenon. Hatschek's view of the inadequacy of the supersaturation hypothesis was endorsed by Wo. Ostwald [1917].

Experimental study reveals many minor points for which it is difficult, or impossible, to account on Ostwald's hypothesis. Moreover it seems particularly hard to devise a direct proof of the supersaturation theory. The only experimental evidence so far adduced in its favour appears to be the verification by Morse and Pierce of the constancy of the ratio of the distance of a band from the surface of the gel and the square root of the time of formation. This is by no means a direct proof of the theory. Moreover, as already pointed out, the results deduced at the same time for the metastable product and the diffusion

constant of silver nitrate, as well as the non-diffusion of hypotonic reagent are remarkable. Indeed the latter is at once seen to be incorrect by working with a highly-coloured solute in the gel.

It appeared to be a simple matter to make a direct test of the value of the metastable product which could be compared with that required by the supersaturation theory. 5 per cent. gelatin gels of Nelson's "crystal" leaf gelatin were prepared containing decreasing amounts respectively of potassium dichromate and chromate. These were treated with dilute solutions of silver nitrate of suitable concentration. The silver nitrate was always hypertonic, so that, by Pringsheim's law, the precipitate should always be formed in the gel.

The value found by Morse and Pierce for silver chromate was $H = 1.4 \times 10^{-6}$. Since the solubility of silver dichromate is 0.0319 mols per litre, as compared with 0.048 mols per litre for the chromate, the value of the metastable product for silver dichromate, which would correspond to that found by Morse and Pierce for the chromate, would be $\frac{1.4 \times 10^{-6}}{5.1 \times 10^{-13}} \times (1.9 \times 10^{-4})^3 = 1.9 \times 10^{-5}$. Below these values of H no precipitate should be formed. Yet it has been seen that Bechhold obtained a deep turbidity in 2.5 per cent. gelatin sols with concentrations of dichromate corresponding to $H = 1.64 \times 10^{-9}$. Since reactions in gelatin gels must take place in the liquid dispersion medium [Bradford, 1918] which contains only a few tenths of one per cent. of gelatin, the protective effect of the gels could not be greater than in the sol state. The experiments in gels are tabulated below:

$K_2Cr_2O_7$	$AgNO_3$	H	Table I.
$M/200$	$M/50$	2.0×10^{-6}	Red surface precipitate in flakes, faint bands at 1.6, 2.3 mm. Then beautiful black spherites of $Ag_2Cr_2O_7$, up to 0.17 mm. diam., to depth of 1.5 cm.
$M/250$	$M/50$	1.6×10^{-6}	Red surface layer in flakes, faint bands at 1.3, and 3.6 mm. A few spherites below
$M/300$	$M/50$	1.33×10^{-6}	Red dusty ppt. above, faint layers at 0.8 and 3 mm.
$M/350$	$M/50$	1.1×10^{-6}	Faint dusty layer above, very faint layer at 0.4 mm.
$M/300$	$M/100$	1.6×10^{-7}	Fine dusty ppt. on surface. Ochre coloration below.
$M/400$	$M/100$	1.25×10^{-7}	Dusty red ppt. on surface. Ochre coloration below.
$M/500$	$M/100$	1.0×10^{-7}	No distinct ppt. on surface. Ochre coloration.
$M/1000$	$M/100$	5.0×10^{-8}	No distinct ppt. on surface. A few black spherites of ? $Ag_2Cr_2O_7$, 0.03 mm. in diam. to depth of 4 or 5 cm. below surface.

K_2CrO_4	$AgNO_3$	H	Table II.
$M/200$	$M/70$	1.0×10^{-6}	Beautiful series of bands at 0.0, 0.4, 0.8, 1.3, 1.9, 2.3, 3.1*, 4.7*, 6.8*. Clusters of spherites at 7.0 and 9.0 mm., largest 0.02 mm. diam.
$M/400$	$M/70$	5.0×10^{-7}	Thin red layers at 0.0, 0.6, 1.6, 2.5, 4.0, broken at 5.2 mm. Spherites down to 12.4 mm., largest 0.01 mm. diam.
$M/800$	$M/70$	2.5×10^{-7}	Red surface layer with faint band in ochre opalescence extending to 1.5 cm.
$M/400$	$M/140$	1.25×10^{-7}	Fine red ppt. on surface.
$M/800$	$M/140$	6.25×10^{-8}	Fine ppt. on surface.
$M/800$	$M/210$	2.75×10^{-8}	Faint ppt. on surface.

* Layers composed of spherites.

It will be seen that with $H = 1.0 \times 10^{-6}$, which is already less than Morse and Pierce's figure, silver chromate still forms a beautiful series of bands. The concentration at the bottom of the tube must be very much less than this value. In all the experiments there was some subsidiary white precipitate, as always occurs with silver nitrate in gelatin. Actually, with very low values of H , the amount of white precipitate was much greater than that of the chromate, so that the effective value of H for the silver chromate must have been considerably less than that corresponding to the concentrations used. As the ionic product becomes smaller, the density of the precipitate in the surface layer of the gel becomes less until, even under the microscope, it is difficult to determine whether the precipitate is formed in the gel or in the solution. Pringsheim's law indicates that the precipitate is always in the gel. But, without making any assumption in regard to this, it is certain that silver dichromate and chromate respectively form precipitates with values of H lower than 1.1×10^{-6} and 2.5×10^{-7} , corresponding to the appearance of a layer below the surface. These are respectively 16 and 6 times less than indicated by the supersaturation theory¹. These experiments are sufficient to invalidate the assumption made by Morse and Pierce, that the formation of a precipitate does not affect the head under which diffusion takes place. That is to say the precipitate does affect the course of the diffusion.

Consideration of the facts (a) that the hypotonic reagent is removed from the spaces between the layers and (b) that only precipitates which are either colloidal or extremely finely divided separate into strata, leads naturally to the conclusion that it is the adsorbing action of the large surface of the precipitate which removes the solute from the layer of gel in its vicinity, so that the hypertonic reagent, diffusing through, has to traverse an exhausted zone of gel before meeting with sufficient solute to produce a new band.

Microscopic examination of the precipitates which occur in banded form usually shows that they consist of spherites. In the case of silver chromate and dichromate in gelatin, and manganese sulphide in agar, the individual particles are generally too small for their nature to be determined. In the majority of cases the beautiful spherical particles are easily visible, sometimes, as in the case of copper carbonate in agar and calcite in silicic acid, the spherites are large enough to show distinct banding and give a dark cross and colour rings in polarised light. The origin and structure of spherites has been discussed as far as seemed possible at present in a previous paper [Bradford, 1918]. Further work is in progress. For the purpose in view it is sufficient to recall that these apparently globular crystals actually consist of a great many radial needles, so that small spherites have an enormous specific surface and may be regarded as being in the colloidal state. A few precipitates, such as calcite in silicic acid gel, appear first, in the more concentrated regions, as tiny perfect rhombohedra, which become more aggregated, as the velocity of crystallisa-

¹ These figures receive confirmation from some experiments to be published shortly.

tion diminishes with dilution of the reagents, and finally occur as perfect spherites of macroscopic size.

In all the cases examined, therefore, banded precipitates have very large specific surface and may be expected to behave in the same way as finely divided solids in adsorbing dissolved substances from their vicinity. This effect occurs in the filtering of solutions through fine powders, where the dissolved particles are retained by the solid. It is well illustrated by Dreaper and Davis' night-blue experiment.

The marked adsorption of solutes containing like ions by sparingly soluble solids is generally recognised, and may well be akin to the remarkable attraction of nutrient material from solution by growing crystals, both being probably of electrical origin. Indeed the adsorption of solute in the formation of banded precipitates may be looked upon as comparable with the mechanism of crystal growth. Consequently it can hardly be doubted that precipitates, formed in media which can hold them in place, will tend to remove the soluble reaction components from their vicinity, and this effect will be the more marked the greater the specific surface of the precipitate. Moreover, since the reagent diffusing into the gel is always in excess, any of the solute in the gel, which is adsorbed, will be precipitated with the formation of fresh surface. The adsorbing surface is, therefore, always "clean" with regard to the solute in the gel.

As the adsorption progresses, solute will diffuse from the more concentrated region of the gel into the depleted zone, and a concentration gradient will be set up, the diffusion becoming more rapid as the concentration in the neighbourhood of the precipitate diminishes. The process will continue until the concentration of the adsorbed solute, at the surface of the precipitate, is reduced to the value corresponding to the solubility product of the solid under the particular circumstances. When this happens, the concentration of the solute in the adjoining region of gel must be very much less than this value, but will gradually increase in the direction away from the precipitate. In this manner a considerable zone of gel will be practically exhausted of solute. Any hypertonic reagent diffusing into this region will not cause the formation of a precipitate, since the ionic product will be less than the critical value. The growth of the band under consideration will then have ceased. A new layer will eventually be commenced at a distance from it, where the hypertonic reagent finds sufficient concentration of solute in the gel. In this paper the actual process of precipitation, whether through the formation of sols or supersaturated solutions, is not considered. Much further work appears to be necessary before the mechanism of precipitation in gels can be completely elucidated. It will be seen, however, that although some kind of supersaturation may, and probably usually does, occur to a greater or less degree before precipitation, this is not necessary for the formation of separate bands, and could hardly account for the occurrence of bands of very insoluble substances, such as silver chloride, which the writer has obtained several millimetres apart in agar, this gel having much less protective effect than gelatin.

It will thus be seen that the adsorption theory is almost diametrically opposed to the supersaturation theory. For whereas the latter hypothesis attributes the formation of bands to the influence of supersaturation preceding precipitation and requires that no appreciable diffusion shall occur of the solute dissolved in the gel, the former theory needs no assumption as to the mechanism of precipitation and claims exhaustion of the solute from the region of the gel in the vicinity of the precipitate.

Direct proofs of adsorption are readily forthcoming. By working with deeply coloured solutes it is possible to watch the progress of the adsorption in the neighbourhood of the precipitate. With silver chromate in gelatin the white subsidiary precipitate due to impurities makes it difficult to observe the exhaustion of the gel. But with lead chromate in agar the effect is easily seen. When viewed for the first time the phenomenon is almost astonishing. This is shown in Fig. 1, Pl. II, which is reproduced from a previous paper.

It has been objected that the adsorption theory takes no account of the influence of the gel. However, it has been shown [Bradford, 1917] that the different effects obtained with the same insoluble substance in different gels can be explained as due to the influence of the gel, or reaction medium, on the factors K and P in von Weimarn's formula, which determine the specific surface of the precipitate and therefore its adsorbing power. By the application of von Weimarn's theory it is possible to obtain silver chromate and dichromate strata in agar gel which, in absence of subsidiary precipitate, are, if possible, more beautiful than in gelatin. It is hoped to publish these experiments shortly. The same recipes give good rings in filter paper.

Both these and plate preparations in agar show the adsorption effect even more strikingly than with lead chromate. A ring of perfectly colourless gel gradually develops round each band of precipitate, the precipitate ceases to grow, and nothing can be seen except the slowly widening colourless zone. Suddenly a fresh ring commences with a deep reddish-yellow coloration at the edge of the colourless zone where it joins the yellow colour of the soluble chromate.

These experiments with coloured solutes show conclusively that the gel is actually exhausted of solute in the vicinity of the precipitate. Whether the effect be due to adsorption, or to any other cause to be determined, it is sufficient to account for the separation of the bands.

There is however little room for doubt that the colourless zone is really due to adsorption. It can easily be shown that finely divided powders actually have the power of producing a similar result. Naturally it would be inferred that the effect would be less noticeable in this case, since, without excess of hypertonic reagent, the adsorbing surface would quickly become contaminated. This is why a fresh series of bands can form upon an old one. Columns of fuller's earth were embedded in 1 per cent. agar gels above the same gels deeply coloured with various dyestuffs. Some of these showed results more intense than others. With night-blue the effect was most extraordinary.

Within about twenty minutes a perfectly colourless narrow zone could be seen below the adsorbing column. This quickly grew, and in 24 hours had reached a depth of four or five millimetres. All this time the sharpness of the colour transition was remarkable. Practically the whole of the region of gel affected was nearly colourless, the change to deep blue taking place almost suddenly. Gradually the colour gradient became less steep as the exhausted zone increased, but the effect persisted for months. Fig. 2 shows the effect after a few days. With catalpo no. 1 and magenta in 1 per cent. agar the result is equally striking and lends itself better to photography, Fig. 3 (after 17 days). From these experiments there can be no doubt that adsorption is capable of causing the extraction of soluble substances from a considerable zone of gel. Similar experiments were also performed with lead chromate as adsorbent and potassium chromate and dichromate as solutes. The concentration of potassium chromate in Fig. 1 was $N/20$, but since $N/200$ best gives bands of lead chromate, this concentration with $N/300$ and $N/100$ was used. The adsorption effect became visible almost instantaneously. It is best seen by standing with the back to the light and holding a piece of white paper sloping backwards at about 45° behind the tube. An exceedingly narrow zone of a much lighter colour immediately becomes visible beneath the column of lead chromate. The effect however increases much more slowly than with the colloidal substances previously examined. Presumably this is due to contamination of the adsorbing surface. Unfortunately also the colour of the dilute gel is not easy to photograph. Fig. 4 shows the effect with $N/300$ K_2CrO_4 after 30 days. The columns of adsorbent were made into a thin cream with water and poured on to the agar gel, care being taken to prevent the lead chromate penetrating between the gel and the tube. By using lead nitrate solution, of the same strength as the potassium chromate in the gel, instead of pure water to moisten the lead chromate, the contamination of the adsorbing surface was reduced and the adsorption progressed almost as rapidly as with dyes. It seemed natural to suppose that this greatly increased effect might be at least partly electric in origin, the chromate anion being attracted by the divalent cation. To test this, equivalent concentrations of sodium hydroxide were used instead of lead nitrate. The adsorption was nearly as great as with the lead nitrate. In confirmation, aluminium sulphate was employed as a trivalent cation. If the adsorption is electrical, the effect should be very much greater in this case. This was fully borne out in the result. A narrow perfectly colourless zone immediately became visible below the lead chromate and the adsorption progressed at least as rapidly as with the dye experiments. Fig. 5 illustrates the condition after two days, with $N/100$ dichromate and aluminium sulphate.

The suggestion is indicated that the mordanting effect of aluminium salts is electrical in origin. The results are also interesting in connection with Harrison's [1911] electrical theory of dyeing. It may also be pointed out that Lewis' experiments [1908] which showed that the surface tension of

water-oil films decreased with increase of temperature, do not necessarily apply to adsorption by solids. If the surface tension of the solid-liquid is due to unbalanced molecular attractions at the common boundary, and if the thermal expansion of the liquid is greater than that of the solid, the unbalanced forces will increase with rise of temperature thus augmenting the surface energy and consequently the adsorption. In confirmation it will be noted that in the case of two liquids such as ether and water, one of which has a much greater thermal expansion than the other, the interfacial surface tension has been found to increase with rising temperature [Antonov, 1907]. The influence of temperature on adsorption by solids has not been studied. But Freundlich [1907] found that charcoal adsorbs more acetic acid from water at higher temperatures, and Pelet and Grand [1907] found the same for methylene blue and crystal ponceau adsorbed by silica, kieselguhr and charcoal. It may be noted, however, that, with solids such as fibres having very great specific surface, their thermal expansion would be greater than in a less disperse state owing to the comparatively large volume of the solid in the surface layer where the intrinsic pressure is released.

In all these adsorption experiments the exceedingly narrow zone immediately beneath the adsorbent is always distinctly less coloured than the remainder of the exhausted region. This is more noticeable in the actual specimens, but can be made out in the photographs.

Numerous facts observed during experimental study appear to lead directly to the assumption of adsorption. The following are particularly striking:

(1) The formation of bands usually ceases long before the bottom of the tube is reached. The hypotonic reagent is invariably so strong that this effect can only be due to the solute in the gel having been exhausted from the lower regions of the tube. This fact also controverts the deduction from the super-saturation theory that the diffusion of the solute in the gel is negligible.

(2) With certain more colloidal precipitates, e.g. manganese sulphide in agar, a tendency is observed to form large spherical aggregates which have much the same structure and density as the bands, except that they frequently show concentric banding. When one of these spherical aggregates begins to form in the zone where a band will shortly appear, the band does not extend to join the sphere, but a spherical cavity, some 2 or 3 mm. wide, is left surrounding the concretion from which the surface of the cavity is everywhere equidistant. This effect must be due to the solute having been exhausted from the neighbourhood of the aggregate. Indeed its spherical form almost certainly implies that nutrient material has accrued equally from all directions.

(3) A similar phenomenon occurs frequently with certain reagents in agar gel. The hypertonic solution accidentally flows down between the gel and the glass, forming a new base from which it diffuses into the gel producing a precipitate with a surface convex inwards, the direction of growth being thus at right angles to that of the precipitate forming down the tube from the upper surface of the gel. It is then observed that this latter precipitate does

not form in the neighbourhood of that growing from the side. It leaves, instead, a clear zone between them which increases in width downwards as the accidental precipitate has had longer time to exhaust the gel in its vicinity.

An interesting feature is sometimes observed in these experiments which appears to afford direct evidence of the energy of the diffusing particles of the solute in the gel. When the agar gel is prepared by straining through muslin, instead of filtering, it has a slightly cloudy, or more opalescent appearance, which is probably due to the presence of larger gel aggregates. During the growth of the first continuous column of e.g. lead chromate in the tube, the region of gel immediately beneath the precipitate loses not only its colour, but also its opalescence, as if the cloudiness had begun to subside, and the clear space gradually extends towards the bottom of the tube. It seems that in such cases the more agglomerated particles of the gel are broken up by the impacts of the rapidly moving solute particles in their diffusion towards the precipitate. In some cases solid particles appear actually to be driven through the gel towards the precipitate. These may be either larger portions of more or less gelatinous matter which have escaped straining, or, apparently they may even consist of particles of the precipitate. It frequently happens with a heavy precipitate that it appears gradually to settle down through the gel. Possibly this may be due to some bacterial or other alteration in the structure or substance of the gel by exposure to the atmosphere. But cases in U-tubes hardly admit of this interpretation. The following is a typical experiment. $N/30$ NaCl and $N/10$ AgNO₃ solutions were poured into the respective limbs of a U-tube the lower portion of which was filled with pure 1 per cent. agar gel. With the meeting of the reagents in the gel merely a slight diffuse precipitate was produced at first. After two days this filled the area of the tube for a distance of about 1 cm. and had become somewhat less tenuous. The edge of the precipitate towards the sodium chloride had now developed a distinct, though not very dense, disc of silver chloride. The position of this disc was marked on the tube. The disc then expanded into a column of precipitate which formed continuously from this point, gradually becoming more dense. In the meantime, however, the light diffuse precipitate gradually diminished and in four days had practically disappeared. In thirteen days even the commencement of the denser part of the column had become distinctly less marked and had shifted gradually through about 1.5 mm. At this point the concentration of the silver nitrate would probably have been about $N/50$. The disappearance of the precipitate must either have been due to peptisation by this dilute solution, or to the tiny particles having been driven through the gel by the bombardment of the silver nitrate molecules. In this experiment the denser edge of the growing column attained a maximum and appeared as a distinct disc of dense precipitate at about 12 mm. from the commencement of the column. The less dense column continued to grow with the production of a series of such denser bands. The first five were equally spaced, about 1.5 mm. apart, the sixth, at about twice that distance from the

previous band, was the last observed thirteen days from the beginning of the experiment. This production of equally spaced discs is worthy of note, since it has been argued that agates with equidistant bands could not have been due to diffusion into gels. Another similar experiment with 5 cc., respectively, of $N/10$ K_2CrO_4 and $N/5$ $Pb(NO_3)_2$ gave eight successive discs with clear spaces between, all approximately 1.15 mm. apart, followed by a further series 0.9 mm. apart.

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