the lentil is much greater, especially when the acid of the seed is neutralized to litmus.

A rigid comparison of the reactions given by the aqueous extracts of the lentil, both acid and neutral, showed no difference whatever, and in these reactions the extracts agreed strictly with those similarly obtained from the pea, except that with calcium chloride and sulphate heavy precipitates were obtained, readily soluble in a slight excess of calcium or sodium chloride. Extracts of the pea gave only slight precipitates with calcium chloride and none with calcium sulphate.

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# ON THE SPEED OF COAGULATION OF COLLOID SOLUTIONS.

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ONE of the prettiest of projection experiments is the exhibition of the formation of crystals of salts, as ammonium chloride and oxalate, etc. The crystals seem fairly to shoot out over the screen. This speed of crystallization, so strikingly shown by the lantern, appears to be a characteristic property of solutions varying with the nature of the salt and solvent, the temperature, the degree of supersaturation, etc. So far as I know, no careful quantitative work has ever been done on the subject; some rough determinations that I have made with solutions of potassium nitrate indicate that the speed of crystallization is one or two millimeters per second.

Although there is a dearth of data on the subject, it will probably be conceded that the speed with which crystalloidal substances separate out of solution, is comparatively rapid; that is to say, the crystallizing solid traverses appreciable distances in a second or so.

Crystallization does not supervene unless the solution be supersaturated with respect to the solid, and there be at least a trace of a crystal already present to induce the crystallization; a supersaturated solution is then in an unstable condition.

Solutions of many colloids can be made to coagulate or gelatinize by the addition of a mere trace of certain substances. The striking analogy between this phenomenon and that of crystallization has often been mentioned and insisted upon. Solutions of colloids behave as if they were supersaturated and required but a chance to pass over into the solid condition. We cannot expect the speed of coagulation to be very great, for we know how slow is the diffusion of colloids in solution. Still, if there is a true analogy between the processes of crystallization and coagulation, the addition of a small amount of a substance having the power to start coagulation in one part of a colloid solution should result in the spread of the coagulation at a certain rate throughout the whole solution, just as happens in the case of crystalloids in supersaturated solution.

The following experiments have been performed with the object in view of ascertaining whether the analogy presumed to exist in the behavior of solutions of colloids and of supersaturated solutions of crystalloids can stand the test of a severer scrutiny than has yet been accorded it.

## PRELIMINARY EXPERIMENTS.

Two glass tubes of about five mm. bore were bent twice at right angles so as to form wide U-tubes; they had almost identical shapes. These tubes were held in a support side by side, and filled with a solution of colloidal iron prepared as follows:

To a very strong solution of pure ferric chloride in water, an almost saturated solution of ammonium carbonate was added in small portions with thorough agitation until the point of permanent precipitation was nearly reached. The resulting dark red solution was subjected to dialysis in parchment paper tubes until the outside water after twenty-four hours' contact with the tubes showed but faint traces of chlorine.

An analysis of the solution showed that it contained 20.563 grams iron and 7.128 grams chlorine to the liter; as is seen, a not inconsiderable amount of chlorine had refused to pass through the parchment paper.

A thin glass rod was dipped into dilute sulphuric acid, the drop clinging to it when removed was shaken off, and then the end on which but a faint trace of the acid remained was touched to the surface of the solution of iron; coagulation at once supervened at the surface. The tubes were then carefully stopped up with plugs of wax.

The accompanying table summarizes the observations of the position of the coagulum after certain time-intervals and the speed of propagation of the coagulation ; this speed is the ratio of the distance in centimeters passed over by the coagulum to the time in seconds between two observations. No provision was made for keeping the temperature constant, which may have varied by as much as 15°–20°. The behavior of the solution in both tubes was very nearly the same, so that their mean is given.

SPEED OF PROPAGATION OF COAGULATION OF COLLOID IRON SOLUTIONS.

| Time in seconds. | Distance in centimeters. | Speed. |
|---|---|---|
| $36 \times 10^2$ | 0.30 | $833 \times 10^{-7}$ |
| 210 | 0.70 | 402 |
| 470 | 0.55 | 212 |
| 734 | 0.25 | 94 |
| 877 | 0.10 | 71 |
| 1308 | 0.35 | 80 |
| *2641 | *0.55 | 41 |
| 3505 | 0.15 | 17 |
| 4368 | 0.10 | 2 |
| 6096 | 0.11 | 5 |
| 14736 | 0.12 | 1 |
| 43656 | 0.20 | 0.8 |

The table shows that the speeds decrease continually until they practically vanish. The greater speeds at the beginning of the experiment are probably due to the diffusion of the sulphuric acid. It seems not at all unlikely that sulphuric acid enters into chemical combination with dissolved colloidal iron, forming an insoluble compound ; a comparatively small amount of the acid suffices to neutralize and precipitate a large quantity of iron oxide in the colloid state. Whitney's[1] experiments on certain compounds of chromium sulphate seem to be in accord with this view. If it be true, the precipitation of colloids from solution is not a physical phenomenon of supersaturation, but rather one of chemical combination.

It was thought that possibly the exceedingly small speed observed after the lapse of several days (marked with stars in the table) was not due to the spread of the coagulation but to mechanical jarring and gravity, for the coagulum was in the vertical portion of the tubes and the laboratory was subject to considerable jarring from the busy traffic of the street. The

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[1] *Ztschr. phys. Chem.*, 20. 40, *1896*.

appearance of the coagulum seemed to confirm this, for at the end of the time marked with a star in the table, it had lost the resemblance it at first had to a stack of inverted hollow cones fitting loosely into one another and had assumed the form of piles of disks like rouleaux of coins. In subsequent experiments only horizontally placed tubes were employed in a room quite free from mechanical vibrations.

### DESCRIPTION OF APPARATUS.

A glass tube of about a millimeter bore and twenty cm. in length was fused in the side of a six-inch test-tube so as to be perpendicular to its axis; its extremity was drawn out in a long capillary and turned up through a right angle. A millimeter scale was attached to the horizontal arm.

The solution under investigation was poured into the tube thus prepared and then warmed up to about 40° so as to prevent the subsequent appearance of air-bubbles that might lodge in the narrow tube and separate the column of solution. The apparatus was then fixed in a stand and the end of the capillary tube sealed, and the substance intended to introduce coagulation introduced. A soft cork was inserted in the test-tube and pushed down somewhat; upon this a little mercury was poured and over the mercury a layer of melted wax. In this way evaporation of the solution was prevented. If a speed of coagulation ensued the coagulum would proceed in the horizontal tube where its progress could be measured.

### EXPERIMENTS WITH COLLOID IRON SOLUTION.

The solution was prepared as described on page 376. Its analysis showed it to contain per liter 13.763 grams iron and 2.139 grams chlorine.

A tube was filled with this solution (A) and a second one with the solution diluted with twice its volume of water (B). Coagulation was started in both cases by the addition of a trace of sulphuric acid.

*Solution A.*—The coagulum at first nearly filled the test-tube but did not enter into the side tube; it gradually settled down so that now after twenty months it occupies the lower portion of the tube only below the mouth of the side tube. The solution still has the characteristic red color of dissolved iron but not quite so dark as that of the stock solution. The sulphuric acid added seems to have been insufficient to enter into combination with all the iron.

*Solution B.*—The sulphuric acid added was sufficient to precipitate all the iron in the test-tube. The coagulum at first filled all the main tube and penetrated three millimeters into the side tube. As the coagulum settled, it left the supernatant liquid clear and colorless, while the filament of coagulated iron oxide advanced a little into the horizontal tube. In about six months the coagulum had settled below the side opening leaving a detached filament in the side tube. In the fourteen months, since, the filament has not advanced half a millimeter. Furthermore, while in the vertical tube the liquid is colorless, on the farther side of the plug of coagulated iron oxide, the solution still has a reddish color; the plug appears to act as a semipermeable membrane preventing the farther diffusion of the acid, if, indeed, all the acid has not already entered into combination.

## EXPERIMENTS WITH COLLOID SILICIC ACID SOLUTIONS.

The solution of colloidal silicic acid was prepared by adding dilute hydrochloric acid to a solution of sodium silicate and dialyzing the resulting mixture until nearly free from chlorine. It was observed that if the dialysis was allowed to proceed until all chlorine detectable by silver nitrate solution had left the parchment paper tubes, the solutions generally coagulated as soon as poured into the test-tube or very soon afterwards. A small amount of chlorine, however, kept the solutions from coagulating for a long time. I have now a couple of solutions prepared as above over two years ago which apart from a very slight precipitate in the bottom of the bottles show no signs of coagulation; they are opalescent and contain a little chlorine.

An analysis of the solutions employed in ascertaining the presumed speed of coagulation resulted in 7.3276 grams silica and 0.0374 gram chlorine to the liter.

Two tubes similar to the one described on page 378 were filled with this solution and the following substances added to start coagulation: 1. Some of the solution was boiled and the crusts appearing around the edges of the dish as the water boiled away were washed and added to the solution in the tube. 2. A portion of the silicic acid was coagulated with a little lime-water, the coagulum washed and added.

These tubes have been under observation for over twenty months and have not shown any tendency towards a spread of coagulation. Apart from an extremely slight precipitation they have the same appearance to-day as when first prepared.

### EXPERIMENTS WITH SOLUTIONS OF EGG ALBUMEN.

The white of a fresh egg was cut through many times with a pair of scissors and mixed with three times its volume of water and filtered. A few drops of toluene were added to the filtrate and the whole thoroughly shaken together.

A tube was filled with this solution and some carefully washed coagulated albumen obtained by adding nitric acid to a portion of the same solution added.

The tube has been standing now for about twenty months, and no trace of a spread of coagulation is discernible. The coagulated albumen added has settled down to the bottom of the test-tube, and the solution has turned slightly yellow. There is no indication of putrefaction, however; the toluene seems to prevent that very well.

### CONCLUSIONS.

The above experiments, made with solutions of colloids of quite different nature, seem to prove that coagulation started in one part of a solution does not necessarily spread through the whole body of the solution. The analogy assumed hitherto between colloid solutions and supersaturated crystalloid solutions does not seem to be more than seeming, and has no foundation in fact. It is extremely improbable that colloid solutions are comparable with supersaturated solutions.

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