The Effect of Crystallinity on Rhythmic Precipitation.

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The two-dimensional precipitation of insoluble metal salts has been followed in cellulose filter-paper, and some techniques for improving crystallinity of gelatinous precipitates have been examined; improvement in this property leads to rhythmicity in the precipitation.

Rhythmic precipitation, first observed by Liesegang (*Z. physikal. Chem.*, 1897, **23**, 365), occurs with a wide range of insoluble materials. When a drop of concentrated silver nitrate solution is placed on a layer of gelatin gel impregnated with potassium chromate, silver chromate is precipitated, not as a continuous precipitate, but in a series of concentric rings separated by clear gel. The position of the rings follows a geometric progression law, $x_n = ak^n$, where x_n is the distance of the nth ring from the origin of diffusion; a and k are constants, k being known as the spacing coefficient (Jablczynski, *Bull. Soc. chim.*, 1923, **33**, 592).

Several hypotheses have been put forward to explain this phenomenon. Ostwald (*Z. physikal. Chem.*, 1897, **27**, 265) postulated that the material formed by metathesis is originally present as a highly supersaturated metastable solution and is precipitated only after a high degree of " supersaturation " or " supersolubility product " has been reached. According to Dhar and Chatterjee's coagulation hypothesis (*Kolloid Z.*, 1922, **31**, 15), however, the insoluble material first forms as a metastable colloidal dispersion, and precipitation occurs as a result of coagulation of this sol by excess of the diffusing ion. The latter theory received quantitative proof by Matalon and Packter (*J. Colloid Sci.*, in the press).

Although rhythmic precipitation has been generally observed in set gels, no colloid is necessary for its occurrence. Morse (*J. Phys. Chem.*, 1930, **34**, 19554), investigating the phenomenon in aqueous solution, showed that substances of all degrees of solubility and crystal habit formed periodic precipitates, when the rate of diffusion of the cation into a solution of reacting anion was sufficiently slow: the " supersaturation " or cation–anion concentration ratio at which the precipitation occurred varied from system to system. The substances showing this behaviour were all " coarsely crystalline " when precipitated in aqueous solution, and did not absorb appreciable amounts of reacting ion.

Similar results obtained by other workers have been summarised in von Weimarn's laws of precipitation (*Chem. Reviews*, 1926, **2**, 1). The average crystal size of a precipitate varied inversely as a function of the " supersaturation " of the solution from which the salt was precipitated; and crystals were not formed until the supersaturation exceeded a certain critical value. For salts such as the silver halides, a stable sol may be the most common system, obtained over a wide range of concentration of the reacting ions, and such materials do not form crystalline precipitates in aqueous media (Tezak, *Discuss. Faraday Soc.*, in the press). The crystallinity of a material is thus a decisive factor in determining the rate of growth and final form of the precipitate over a wide range of " supersaturation."

In this work, Morse's experiments have been extended, and the two-dimensional precipitation of a series of insoluble metal salts has been studied in cellulose filter-papers, which have proved to be an excellent medium for such an investigation, since the high values of k obtained may be measured by simple experimental techniques; while crystalline and non-crystalline gelatinous precipitates may be readily differentiated.

The results substantiate the recent hypotheses proposed to explain the rhythmic precipitation of insoluble metal salts in set gels, and indicate clearly the importance of crystallinity in this phenomenon. A number of techniques that improve the crystallinity of gelatinous precipitates have been examined; and in all cases, improvement in this property leads to more rhythmic precipitation.

Experimental.—The following method was adopted, Whatman's No. 1 (coarse) filter-papers being used throughout. The papers (11·0 or 12·5 cm. diam.) are dipped in the anion solution (N/100—N/10), freed from excess of solution by blotting, and dried for 5 or 10 min. on a steam radiator (at 40°) to give " half-dry " or " dry " papers, respectively. A drop (0·05 ml.) of 2N-cation solution is then added at the centre of the paper, held in position, by clips, on top of glazed non-absorbent white paper, to prevent spreading. Every 2 min., a drop of distilled water is added at the same central spot. This displaces the solution, and causes the cation to travel radially through the filter paper. Under these conditions, the metal salt sol is coagulated by the cation, at cation : anion concentration ratios in the range 50 : 1.

A series of concentric rings of precipitate is generally obtained, separated by clear annuli of sol. When diffusion is complete (after 8—12 rings have been formed), the papers are dried at 40° and, where necessary for clearer definition, are developed by exposure to moist hydrogen sulphide or ammonia vapour, or sprayed with dilute solutions of these reagents. The radius of the rings is measured by reading off their distance from the centre of the paper with an accurately graduated ruler.

(I) *Direct precipitation.* The precipitation behaviour of several series of insoluble metal salts has been examined : and two main types of precipitate may be distinguished by the above technique. (*a*) Crystalline : definite crystalline particles of average size $>1\ \mu$. The excess of cation is readily washed out from the centre, and diffusion of the cation outwards leads to rhythmic precipitation. (*b*) Gelatinous : " flocculent " or " gelatinous " non-crystalline particles of average size $<1\ \mu$. The excess of cation is strongly absorbed by such a precipitate and is not readily washed out by addition of water.

With many such materials the excess of cation may itself peptise the precipitate; *e.g.*, in the precipitation of silver or cuprous iodide, the addition of distilled water leads to outward diffusion of the cation peptised sol through the paper. The results obtained are summarised in Table 1.

TABLE 1. *Type of precipitate.*

	Cation (added as central drop)	
Anion	Crystalline	Gelatinous
Chromates	Ag^+, Cu^{++}, Pb^{++}, Hg_2^{++}, Hg^{++}	Cu^{++} ($<$N/50)
Iodides	Cu^+, Pb^{++}, Hg_2^{++}, Hg^{++}	Ag^+, Cu^+ ($<$N/50)
Arsenates	Ag^+, Pb^{++}, Hg^{++}	Cu^{++} ($<$N/50)
Sulphides	Ag^+, Cu^+, Hg^+, Fe^{++}, Fe^{+++}	—
Hydroxides	Ag^+, Hg_2^{++}	Cu^{++}, Pb^{++}, Fe^{+++}, Co^{++}, Ni^{++}
Silicates and thiocyanates	—	Ag^+ (N/50)

Some typical values of x_n for crystalline salts are presented in Table 2. In all cases, the spacing obeys the geometric progression law found by previous investigators, as shown by the values of x_{n+1}/x_n. It is seen that precipitation occurs at some particular cation : anion concentration ratio that may vary from salt to salt; and that rhythmic precipitation is observed only when this "supersaturation" lies within the range for which crystalline precipitates are formed.

TABLE 2. *Rhythmic precipitation in cellulose.*

Lead iodide						Silver chromate					
0·1N-I′ and 2N-Pb^{++}						0·01N-CrO_4'' and 2N-Ag^+					
n	x_n, cm.	x_{n+1}/x_n	n	x_n, cm.	x_{n+1}/x_n	n	x_n, cm.	x_{n+1}/x_n	n	x_n, cm.	x_{n+1}/x_n
3	0·60	—	8	1·35	1·18	3	1·50	—	7	2·80	1·17
4	0·70	1·16	9	1·65	1·22	4	1·80	1·20	8	3·30	1·18
5	0·80	1·14	10	1·95	1·18	5	2·15	1·19	9	4·05	1·21
6	0·95	1·19	11	2·30	1·18	6	2·40	1·15	10	4·80	1·19
7	1·15	1·20	12	2·70	1·17					Average	1·182
				Average	1·186						

The spacing coefficients (values of k) may, however, vary from experiment to experiment by a factor of $\pm 5\%$, owing to small variations in the drying process. The values of $(k - 1)$ obtained for crystalline precipitates are presented in Table 3. Despite the greater rate of diffusion, the spacing is in all cases very much greater than that observed for the same materials precipitated in gelatin or carbohydrate gels (in two dimensions), where the values of $(k - 1)$ are generally $<0{\cdot}005$. Furthermore, the spacings observed for a series of salts of a particular metal are in no way related to the solubilities of these salts in water. Similar results have been observed for three-dimensional precipitation in gelatin gels (Matalon and Packter, *loc. cit.*).

TABLE 3. *Values of* $(k - 1)$: *two-dimensional precipitation in cellulose (excess of cation).*

	0·01N-Soln.	0·1N-Soln.		0·01N-Soln.	0·1N-Soln.
Silver chromate	0·186	$<0{\cdot}050$	Cupric pyridine thiocyanate	$>0{\cdot}500$	0·148
,, arsenate	$>0{\cdot}500$	0·200	,, arsenate	,,	0·200
Mercurous iodide	$>0{\cdot}500$	0·198	Cuprous iodide	,,	0·250
,, chromate	0·094	$<0{\cdot}050$	Lead iodide	$>0{\cdot}500$	0·190
Ferrous ferricyanide	$>0{\cdot}500$	0·167	,, arsenate	,,	0·150
			,, chromate	0·390	$<0{\cdot}050$

(II) *Modification of crystallinity.* The crystallinity of the gelatinous precipitates has been modified by a number of methods.

Complexing with organic bases. Certain metal salts form highly crystalline complexes with pyridine and this fact is utilised in certain analytical methods.

(*a*) Hydroxides. Whereas papers impregnated with N-sodium hydroxide give a gelatinous central spot with most metal ions, excess of pyridine (20—30N) leads to rhythmic precipitation of, *e.g.*, ferric hydroxide as a yellow-brown precipitate : $(k - 1) = 0{\cdot}400$.

(*b*) Thiocyanates. Pyridine forms complex salts, which give crystalline precipitates, even at high "supersaturation." $Cu(CNS)_2py_2$ is rhythmically precipitated as a series of clear green rings, $(k - 1) = 0{\cdot}148$, from dry papers 0·1N with regard to CNS′ and 5—10N with regard to pyridine.

Pyridine can also modify the crystallinity of many silver and copper salts by stabilising the sol against rapid coagulation at high "supersaturation" (Packter, unpublished). Silver iodide has been rhythmically precipitated as a series of pale, clear yellow rings, $(k - 1) = 0{\cdot}110$, from dry papers 0·1N with respect to I′ and 10N to pyridine; and cupric chromate and cuprous iodide give series of diffuse rings from papers 0·1N with respect to anion and 10N to pyridine.

Kolthoff (*J. Phys. Chem.*, 1932, **36**, 860) has shown that mixed crystals may be formed when two insoluble salts are coprecipitated. The crystalline structure of a gelatinous material may be markedly modified on cellulose by coprecipitation with a second crystalline material. Two methods have been adopted.

(i) *Coprecipitation.* A mixed cation solution is diffused through papers containing the anion; or, alternatively, the cation solution may be diffused through papers soaked in a mixture of two anions. On half-dry papers, 0·1N with respect to I′, for example, outward diffusion of a mixed lead nitrate–silver nitrate solution leads to rhythmic precipitation of a very close series of clear rings of silver iodide, starting at 3·5 cm. from the centre, $(k - 1) = 0{\cdot}100$, and accompanied by the usual lead iodide rings, when the Ag^+/Pb^{++} concentration ratio $<2{\cdot}5$.

The concentration ratios of crystalline to gelatinous precipitate required to produce crystallinity and rhythmic precipitation of the latter are presented in Table 4, for a number of systems examined. (All concentrations are expressed in g.-equiv./l.) It is seen that the more crystalline lead iodide is more efficient than silver chromate in inducing crystallinity (Packter, *loc. cit.*).

TABLE 4. *Ratios of concentrations of crystalline to gelatinous precipitate required for crystallinity.*

Silver iodide:
  Coprecipitated with PbI_2 : $Pb^{++}/Ag^+ = 4{\cdot}0$—$0{\cdot}4$.
  ,, ,, Ag_2CrO_4 : $CrO_4''/I' = 10{\cdot}0$—$1{\cdot}0$.

Copper chromate:
  Coprecipitated with Ag_2CrO_4 : $Ag^+/Cu^{++} = 2{\cdot}5$—$1{\cdot}0$.

(ii) *Displacement.* A series of papers containing 8—10 rhythmically precipitated silver chromate, lead iodide, etc., rings are prepared and half dried at 40°. A third solution (N/100 cation or anion) is then diffused outwards from the centre, 0·05 ml. every 2 min. By this method silver iodide, copper chromate, etc., can be rhythmically precipitated on existent "nuclei" of a crystalline material.

Conclusions.—The above results show that cellulose is a very suitable medium for following the precipitation of many insoluble metal salts. Previous workers have already reported the use of carbohydrate media for the rhythmic precipitation of certain copper (Roy, *Kolloid Z.*, 1931, **54**, 190), lead (Hatschek, *Proc. Roy. Soc.*, 1921, *A*, **99**, 496), and magnesium (Fricke, *Z. physikal. Chem.*, 1926, **124**, 359) salts: but the protecting power of cellulose-fibre membranes is exceptionally high, and clear rhythmic precipitation with large spacing coefficients has been obtained in this medium despite the high rate of diffusion, even with such highly insoluble lead salts as the chromate. This high protection shown for such a range of metal salts allows of a quantitative investigation of precipitation behaviour by very simple techniques, and without the need for high-power optical magnification or photoelectric instruments as used by other investigators (Morse, *loc. cit.*; Veil, *Compt. rend.*, 1930, **191**, 611).

Morse's conclusion that crystallinity of the precipitated material is of fundamental importance for rhythmicity has been fully confirmed. The crystal size of precipitates of insoluble metal salts will vary inversely as the degree of supersaturation (von Weimarn, *loc. cit.*), and for "crystalline salts" such as silver chromate, lead iodide, and dipyridine-copper thiocyanate, it may be greater than 1 μ over a wide range of cation–anion concentration ratios. Precipitation that occurs at a "supersaturation" within this range then leads to formation of rings of crystalline precipitate, separated by clear peptised sol.

It also appears that the gel or membrane medium may itself affect the crystallinity of a particular insoluble salt. Gelatinous precipitates generally tend strongly to adsorb the diffusing ion as it travels through the gel or membrane. In set gels, such a material will be precipitated as a series of thick diffuse rings separated by a concentrated opaque peptised sol, and the distances cannot be measured quantitatively by simple means; while in cellulose membranes, the insoluble material tends to be distributed throughout the medium as a peptised sol, and may hinder the displacement of the cation solution from the centre.

The crystallinity of such materials is shown to be improved by complexing with organic bases or coprecipitation with a highly crystalline material. They can then be rhythmically precipitated in cellulose, over a wide range of " supersaturation."

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