THE PRECIPITATION LAWS

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I. ON THE NUMERICAL DATA RELATING TO THE LAWS OF PRECIPITATION

The laws governing the precipitation of solid substances from solutions have received a detailed and systematic study in but comparatively recent times.

The law of precipitation according to which the mean magnitude of the individual crystals (subject to the condition that the process of direct crystallization has come to an end, and under exemption from consideration of the stably supersaturated solutions) of precipitates will progressively decrease as the concentration of the reacting solutions progressively increases, was formulated for the first time early in 1906 (2), on the basis of extensive approximately-quantitative investigations with about 60 different salts.

If we plot, along the axis of ordinates, the mean size of the precipitate crystals, and along the axis of abscissas, the concentration of the reacting solutions, we may accept, with a certain degree of approximation, the curves of the general equation: $y \cdot x^n = \text{const.}$ (n, being a positive integer or fraction), as the graphical expression of the above precipitation law.

Another law of precipitation, viz.: the law relating to the mean dimensions of the individual crystals prior to the completion of their growth through direct crystallization, was established somewhat later, though also in 1906 (3). This law may be formulated as follows: With progressively increasing concentration of the reacting solutions, the mean magnitude of the individual crystals of precipitates,—as determined after a given time interval, measured from the moment of mixing together the reacting solutions,—will pass through a maximum.

As the time interval selected becomes greater, this maximum is displaced to the left side and upwards.

Such a family of curves, with maxima moving leftwards and upwards, may be expressed analytically by an equation of the form

$$y = k_1 x^{-n} \left(\frac{k_2}{e^{x^{n} \cdot T} - 1} \right)^{-1}$$

where e, is the base of natural logarithms.

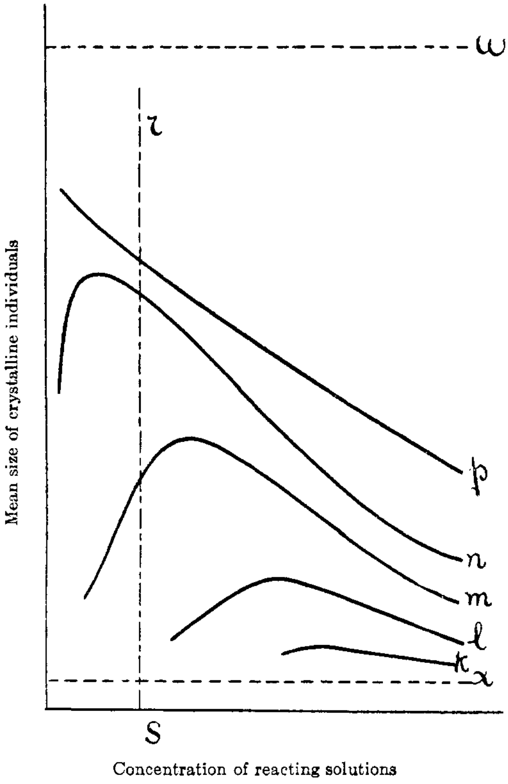
Since the precipitation curves with maxima are the first to occur (reckoning from the moment of mixing together the reacting solutions), and since only later (under the above mentioned condition of exempting from consideration the stably supersaturated solutions) do they go over into precipitation curves without maximum, the law given expression to by curveswith a maximum is conveniently called the first law of precipitation, and the law to which the curves without a maximum correspond—the second law of precipitation.

And the third law of precipitation reads as follows: For a set of dispersion media in which a solid substance X has different solubilities, the precipitation curves for that particular dispersion medium in which the solubility is least (assuming all other conditions during precipitation to be nearly—or exactly—the same for the whole set of dispersion media) will occupy the lowest position, beneath all other precipitation curves, and their beginnings will most of all be displaced to the left (4).

As a corollary of the second and the third laws of precipitation, we have the rule (or fourth law of precipitation), which reads as follows: On substituting for the absolute concentration of the reacting solutions (C) the relative concentration of the precipitating substance: $\frac{Q - L}{L}$ (where $Q = \frac{C}{2}$, since we are mixing together equal volumes of the reacting solutions), the precipitation curves without maximum for substance X precipitating from different dispersion media where $L = L_1, L_2, \ldots L_n$, will very closely approach each other, up to the point of sometimes almost merging into a single curve (4).

In view of the fact that some uncertainty prevails in the literature of dispersoidology in regard to the laws of precipitation, it should first of all be noted that theoretically the precipitation curves will begin—and terminate—with nearly straight lines (5), as shown in scheme A.

The dotted curve, α, corresponds to the instantaneous (for our limited perception powers) formation of the molecules of the precipitating substance, or to the sub-ultramicroscopic stage of precipitation (crystallization); the curves: k, l, m, n, p—to finite intervals of time, more and more prolonged, which have elapsed since the moment of mixing the reacting solutions; as regards the curve, ω, since all our measurements are confined to restricted, finite periods of time, and since this curve implies the



Scheme A

recrystallization of all the crystals belonging to each of the precipitates into one single macro-crystal (i.e., visible to the naked eye) for each precipitate, these macrocrystals being, in all precipitates, practically equal in size to one another,—it can never be attained in reality, for it would require, for its realisation, a period of time that would practically be infinitely-protracted.

In actual experiments, we are able to study only those parts of the precipitation curves which lie to the right of the vertical dotted line, rs, since precipitation from slightly supersaturated solutions will often begin only after very extended periods of time.

The whole experimental material so far available, pertaining to the processes of precipitation, includes accurate and complete data for the precipitation of only the five following salts: $BaSO_4$, $CaSO_4 \cdot 2H_2O$ ($CaSO_4$—at elevated temperatures), $SrSO_4$ ($SrSO_4 \cdot 2H_2O$—with high supersaturation, as the less stable phase), Ag_2SO_4, and $AgC_2H_3O_2$, the precipitation having been studied, for all these five salts, from aqueous, as well as from alcoholic-aqueous (ethyl alcohol) dispersion media (6).

The results obtained for the two last-mentioned salts, owing to the absence of any side-phenomena such as, for instance, hydration, formation of aggregate-particles out of the individual crystals, and the like, are especially valuable, being illustrations of the precipitation laws in their pure form, undisguised by any side-influences.

The numerical data for these salts can be duplicated with greater or less approximation, only if all conditions are accurately reproduced.

The study of the precipitation processes of $AgSO_4$ and $AgC_2H_3O_2$ has not been undertaken with the object in view of obtaining any ultra-exact quantitative data, but in order to study, with a degree of accuracy customary for this kind of dispersoidological investigation, the quantitative changes—both in form and in locus, that occur in the precipitation curves under the very same natural conditions under which research-work on dispersoidal synthesis has, so far, been commonly done; that is to say, within the ordinary range of fluctuations of temperature and pressure in the laboratory.

The variables the influence of which was purposely studied were: concentration of reacting solutions, solubility, and time.

Since the displacement of the precipitation curves is due to direct crystallization only at the very outset of the process (omitting from consideration the very slightly, and consequently—very stably supersaturated solutions), and since later this displacement is produced by the process of recrystallization—i.e., the growth of the larger crystals at the expense of the smaller ones, it is the average magnitude (notably the average length) of the large precipitate crystals[1] that was measured.

In every precipitate we may always distinguish, without difficulty, the especially large individual crystals from the especially small individual crystals. It goes without saying that the especially large individual crystals are not equal to each other; nor are the especially small ones. It is convenient to designate as the category of especially large individual crystals of precipitates, such as do not differ in size by more than 20 per cent; the same may also conveniently be applied to the category of the especially small individual crystals. Evidently, those crystals which belong to neither of the above categories but are of an intermediate size, will constitute the average-size part of the precipitate.

In order to approach, to some extent, the ideal method of studying the precipitation process, this process should be graphically represented as follows (see scheme B).

Two curves of precipitation: one for the especially large individual crystals, and one for the especially small individual crystals should be given. Furthermore, for every experimentally obtained point in the curve, the corresponding content of especially large and especially small crystals should be indicated, in terms of per cent of the whole number of all individual crystals.

Now, in regard to the methods of expressing the mean dimensions of the individual crystals, i.e., whether according to their

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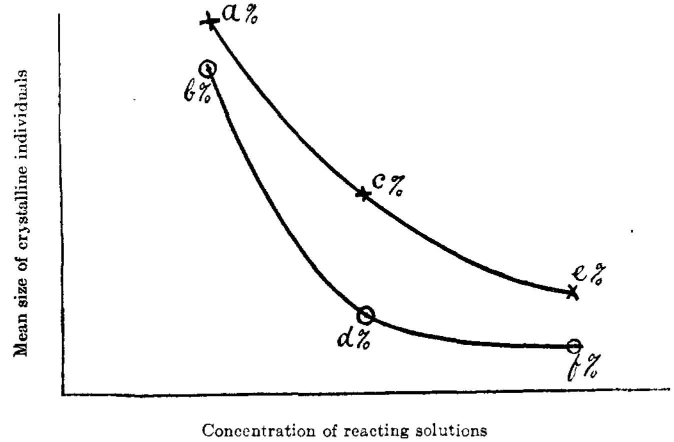
[1] Numbers of microphotographs of all precipitates are available, but these have not as yet been analysed.

mean magnitudes as calculated from their weights, or as calculated from their volumes, the best would be giving separate precipitation curves for each of the three dimensions: length, breadth, and depth, together with microphotographs showing the contours of the individual crystals; without the presentation of such microphotographs (as will clearly be understood from the microphotograph (P. 223) of a feathery skeleton-crystal of $BaSO_4$ obtained on mixing up boiling aqueous solutions of 1/10 normal concentration; magnification—1800-fold), the characterization of the precipitate, by means of its average linear dimensions, is far from being complete.



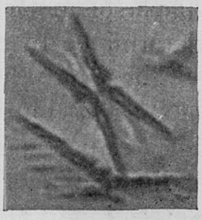
Scheme B

From the theoretical viewpoint, the best method would be to use as ordinates of the precipitation curves, the gramme-molecular surface of the precipitate; or else, the mean dimensions of the grains in terms of fractions of gramme-molecules.

The preparation of such curves would require, however, a great deal of meticulous and assiduous work; and so they have never been met with, so far, in the literature on dispersoids.

Since, in the course of time, the especially small crystals disappear, partially or wholly by solution and reprecipitation in the form of large crystals it was of particular interest to follow the process of growth of the especially large crystalline individuals.

For obtaining approximately reproducible results in precipitation it is extremely important always to mix the reacting solutions in exactly the same way; especially with respect to the direction in which the solutions are poured into one another, to the method of stirring applied, and to the volumes mixed.



In the experiments described here the reacting solutions were mixed by rapidly "dumping" the whole amount of one of the reacting solutions into the other, while shaking the vessel with the hand always in the same manner. No mechanical stirring devices have been used.

With respect to the volumes of the reacting solutions, the product: concentration × volume is kept approximately the same for a given dispersion medium (7).

The solubilities of Ag_2SO_4 at room temperature (20°C.) in the aqueous solutions of ethyl alcohol employed in the experiments were:

	gramme-equivalent in 1 litre
In 30 per cent (by volume) ethyl alcohol (average of seven determinations)	0.0106
In 60 per cent (by volume) ethyl alcohol (average of four determinations)	0.00106
Solubility, at 20° of Ag_2SO_4 in water	0.05
The solubility of $AgC_2H_3O_2$ was:	
In 50 per cent (by weight) of ethyl alcohol, at 20° (average of two determinations)	0.0088
In water at 20°	0.062

In view of the fact that, in all cases investigated, the lengths of the especially large crystalline individuals have never so diminished, as to fall into the ultramicroscopic domain, the measurement of the separate individual crystals has, in the vast majority of cases, been carried out with an accuracy of 0.001 mm. In most cases, an accuracy of 0.01 mm. is amply sufficient. All experiments were repeated at least two times, the results recorded being the average of all determinations.

II. ON THE NUMERICAL DATA RELATING TO THE VARIABLES REGULATING THE MEAN DIMENSIONS OF THE ULTRAMICROSCOPIC PARTICLES OF DISPERSE PHASES OF DISPERSOIDAL SOLUTIONS

The mean dimensions of the particles of disperse phases in dispersoidal solutions and in suspensions are, in the general case, determined by two superimposed influences.

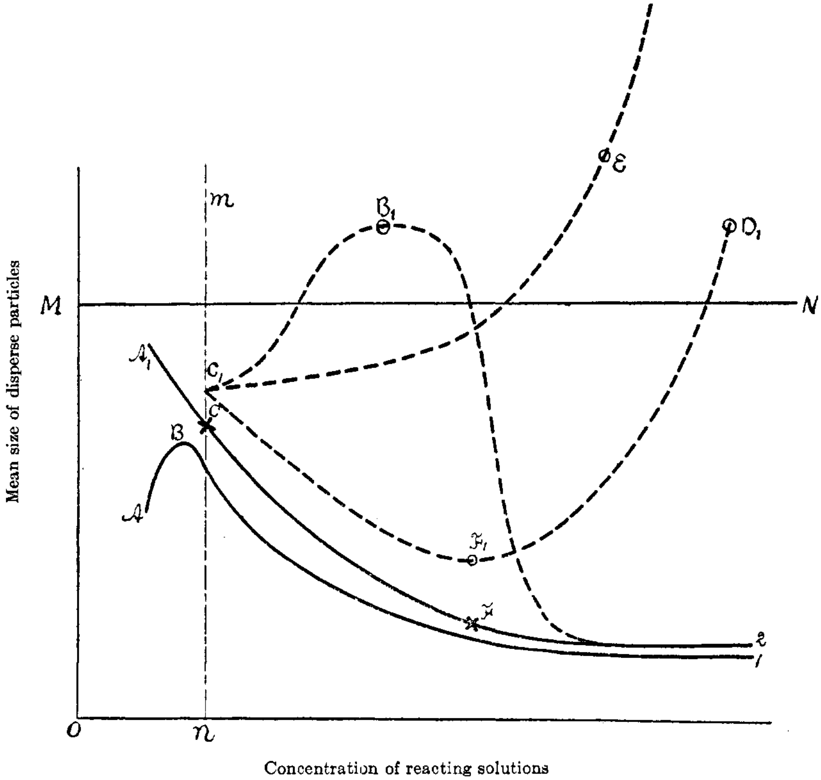
The first influence is the one determining the mean dimensions of the individual particles (this is a convenient term for designating the particles that represent individual ultramicrocrystals or individual microcrystals), and the second influence is the one determining the mean dimensions of the aggregate-particles (i.e., loose assemblies of individual ultramicrocrystals or individual microcrystals).

Each of these influences contains a considerable number of variables; this is why one meets with some difficulties in understanding the methods for the determinative regulation of the mean dimensions of particles of disperse phases in both dispersoidal solutions and suspensions.

It is extremely important—both for finding one's way in the confusion that prevails in the literature of dispersoidal synthesis, and also for correctly interpreting the graphs presented here—that it be well understood that the laws of precipitation stated above hold only for individual crystals, not for aggregated particles; and also, that the mean dimensions of the latter are determined by other laws and other variables.

In scheme C, the full lines represent the individual particles, the dotted lines, mixtures of individual and aggregated particles. (The content of the latter class in the disperse phase, *may* amount to 100 per cent.) The horizontal line, MN, is the boundary between the domain of ultramicroscopic dimensions and the domain of microscopic dimensions (larger than $200\mu\mu$).

For substances under conditions, such that their solubility in the dispersion medium is practically nil (e.g.: Au—in pure water; $Al(OH)_3$—in pure water; $BaSO_4$—in 70 per cent ethyl alcohol, etc.), the region of concentrations of the reacting solutions which lies to the left of the vertical line, mn (see scheme C) has, up to the present time, scarcely ever been studied; because, to the left of line, mn, the concentrations of the reacting solutions are only a small number of times greater than is the saturation-concentration of the precipitate; which substance is practically insoluble.[2]



SCHEME C

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[2] As regards such cases as $BaSO_4$ in water (solubility—2,4.10^{-4} gramme in 100 cc. water), the precipitation curve similar to the curve AB1 can actually be realized over its greater part; but, in the course of time, it will soon go over into a curve similar to A_1CF_2, except that, in its upper (left-hand) part, it will stretch out considerably beyond the boundary of the ultramicroscopic domain; we thus see that, in the present instance, the dispersoidal solutions will very rapidly turn into instable suspensions of microcrystals-individuals, on account of the rapid growth of the ultramicrocrystals.

In the case of the most typical dispersoidal solutions only the region to the right of the line, mn, say, beginning with the point C has been investigated.

Only when no powerful aggregators are formed as by-products of the reaction, or when, dispergators are formed, or introduced, may the line CF2 exist, over some definite interval of concentrations, for a sufficiently long time to make observations and in proportion as the aggregation of the individual ultramicrocrystals occurs, the curve CF2 will assume, after the lapse of a certain time, the position of the curve $C_1F_1D_1$.

It is quite obvious that, in the above case, over the range of concentrations between the points C_1, F_1 (respectively, C, F), the curve C_1F_1 (for a mixture of individual and aggregated particles) will portray the same mutual dependence between the mean dimensions of the particles of disperse phase and the concentration of the reacting solutions, as that expressed by the second law of precipitation, i.e., with increasing concentration of the reacting solutions, the mean dimension of the disperse particles will decrease.

In the above case, the aggregation has not yet gone so far as to mask the second law of precipitation.

If, however, the by-products of the reaction happen to be powerful aggregators, the precipitation curve will assume the form C_1E,—provided that the large microscopic and macroscopic flakes are aggregate-particles.

Since it is only the small aggregate-particles that are likely to be mistaken for individual ones, the large aggregate-flakes being easily recognized as possessing a very delicate grainy structure, the form C_1B_12, has been sometimes attributed to the precipitation curve under the erroneous impression that this curve was an example of the first law of precipitation for the individual crystals (8).

If any complicated aggregation (coagulation) processes are at play (see the curves illustrating the effect of electrolytes on the duration of life of the dispersoidal solutions (figs. 14 to 24) the precipitation curves which express the interdependence—not between the average size of the individual crystals and the concentration of the reacting solutions, but between this latter and the average size of particles in a mixture of individual and aggregated disperse particles—may also exhibit a more complicated form than that exhibited by the three (dotted) curves of scheme C.

The second misapprehension which is frequently met with in the literature devoted to dispersoidal synthesis consists in the erroneous method employed for expressing the concentration of the actual reacting molecules in the solutions used.

Thus, for example, in the case of (*a*) the preparation of dispersoidal solutions by means of hydrolysis of (*b*) the splitting up, with water or alcohol, of double salts of the type: $AgNO_3 \cdot$-AgX; $AgX \cdot KJ$,—where $X =$ a halogen and (*c*) in some measure, also of the reduction of Au by the formol-method, and many other instances, the principal reacting molecules are obviously the molecules of water, and it is by the ratio of their number to the number of the hydrolysing salt molecules that the velocity, as well as the degree of completeness, of the hydrolytic process is determined; it is quite plain that, in the cases now under discussion, the active mass of water is in inverse ratio to the concentration of the salts in the solutions used for the experiments.

Hence, the results obtained in dispersoidal synthesis by the method of hydrolysis—of $Fe(OH)_3$, $Al(OH)_3$, and so on—are not contradictory to, but rather confirm the general laws of precipitation. In the cases under consideration the precipitation curves will be of the types CF2 and $C_1F_1D_1$ (9), if the reciprocal of the concentration is plotted along the axis of abscissas.

Of all the cases of dispersoidal synthesis that up to now have been thoroughly studied quantitatively, the case which is the most easily reproducible (10) is the dispersoidal synthesis of selenium, by the method of pouring weak solutions of it in aniline or quinoline, into ethyl alcohol (93.5 to 90 per cent—by weight).

These dispersoidal solutions have moreover received the most thorough study, in connection with the effects produced on the mean magnitude of the disperse particles by the different variables.

This is the reason why the numerical data relating to this system have been selected for presentation here.

In order to facilitate the analysis of the dispersoidal synthesis, the coefficient expressed by the following formula (11):

$$\delta = J \frac{Q - L}{L},$$

is convenient. Q − L, is the concentration of the disperse phase produced; L, the ordinary solubility (i.e., the solubility of the large crystals) of the disperse phase, and J, the product of all other variables influencing the mean magnitude of the individual ultramicrocrystals, each of these variables being expressed in abstract numbers equivalent to that of the ratio $\frac{Q - L}{L}$.

For instance, if the viscosity of the dispersion medium is increasing, J will also increase; or if, independent of the variable L, the rate of the decrease of the concentration, from the value Q, down to the value L, is increasing, J will also increase; etc.

Since only very low concentrations of the selenium solutions are used, and since no powerful aggregators arise in the dispersion medium, it so happens that the fundamental precipitation laws for the individual ultramicrocrystals (though having undergone slight quantitative alterations due to aggregate-particle formation), remain unaltered in their essence.

The graphs for these systems are very explicit in showing that, with the increase of the dispersion coefficient δ, whatever the means by which this increase may have been produced, the mean magnitude of the particles of the disperse phase in the dispersoidal solutions and the suspensions of selenium, will decrease.

III. ON THE NUMERICAL DATA RELATING TO THE PROCESSES OF DISPERGATION OF THE PRECIPITATES IN STATU NASCENDI

Although the phenomena of dispergation of precipitates have been frequently investigated (12) (13), both as regards their exactitude (in comparison with other data) and their comprehensiveness, the best illustrative data are those obtained in studying the dispergation of $BaSO_4$ precipitates in statu nascendi, in 63 per cent. (by weight) ethyl alcohol.

Check experiments were carried out at room temperatures, the results obtained being practically identical.

IV. ON THE NUMERICAL DATA RELATING TO THE DEPENDENCE OF THE AMOUNT OF ADSORPTION ON THE SOLUBILITY, OF A GIVEN SALT FOR DISPERSION MEDIA IN WHICH THE SALT HAS DIFFERENT SOLUBILITIES

The numerical data illustrating the dependence between the solubilities of a given substance in different dispersion media, and the amount of adsorption of that substance, by a definite adsorbent, out of these media, are extremely scanty (14).

The only existing data for salts are displayed graphically below.

As adsorbent, $BaSO_4$ (Merck's extra pure, for x-ray diagnosis); in amounts of 20 grammes per 100 cc. of the solution of the salt to be studied, was employed. The salt solution was shaken, with a $BaSO_4$ precipitate, for ten minutes, after which the precipitate was allowed quietly to settle during twenty-four hours. The clear supernatant solution was then analysed.

Such was the procedure in studying the adsorption by $BaSO_4$ precipitates of all salts, except $BaCl_2$ from alcoholic-aqueous solutions. In these solutions the $BaSO_4$ became partially dispergated, under the influence of the $BaCl_2$ molecules, into suspensions (respectively—into dispersoidal solutions, in part) that took a long time to clear up completely.

These solutions were therefore centrifuged, in order to obtain a clear solution for analysis.

In table 1 below are given the concentrations of the salt solutions used for the experiments.

The concentrations of the salt solutions before and after adsorption (i.e., the initial and the resulting concentrations) were always determined by exact analytical methods; in the cases of the solutions of $Al_2(SO_4)_3$, Na_2SO_4, K_2SO_4, $NiSO_4$ and $CoSO_4$, the amount of sulphate ion was determined gravimetrically as $BaSO_4$; in the case of the $MnSO_4$, Mn was determined as pyrophosphate; and in the cases of $CuCl_2$ and $CuSO_4$, Cu was determined by the very exact method of De-Haën-Low (iodometry); in the case of $BaCl_2$ the Ba-ion was determined as $BaSO_4$.

TABLE 1

DISPERSION MEDIA	CONCENTRATIONS OF SALT SOLUTIONS IN GRAM-MOLECULES PER LITER								
	$Al_2(SO_4)_3$	Na_2SO_4	K_2SO_4	$MnSO_4$	$NiSO_4$	$CoSO_4$	$CuSO_4$	$CuCl_2$	$BaCl_2$
Pure water....	$1.0297.10^{-2}$	$1.3918.10^{-2}$	$0.9898.10^{-2}$	$0.9959.10^{-2}$	$1.0925.10^{-2}$	$1.1178.10^{-2}$	$0.9797.10^{-2}$	$0.9756.10^{-2}$	$0.9884.10^{-2}$
10 per cent ethyl alcohol.	$1.0364.10^{-2}$	$1.3807.10^{-2}$	$1.0597.10^{-2}$	$1.0016.10^{-2}$	$1.0478.10^{-2}$	$1.0546.10^{-2}$	$0.9731.10^{-2}$	$0.9728.10^{-2}$	$0.9937.10^{-2}$
20 per cent ethyl alcohol.	$1.0314.10^{-2}$	$1.3902.10^{-2}$	$1.0064.10^{-2}$	$0.9833.10^{-2}$	$1.0844.10^{-2}$	$1.0575.10^{-2}$	$0.9741.10^{-2}$	$0.9731.10^{-2}$	$1.0106.10^{-2}$
40 per cent ethyl alcohol.	$1.0229.10^{-2}$	$1.3743.10^{-2}$	$0\ 9932.10^{-2}$	$0.9774.10^{-2}$	$1.0585.10^{-2}$	$1.0475.10^{-2}$	$0.9722.10^{-2}$	$0.9678.10^{-2}$	$1.0029.10^{-2}$

In all the above cases of studying adsorption, the experiments were repeated two or three times, and the results recorded were the average results.

V. ON THE NUMERICAL DATA RELATING TO THE INFLUENCE ON THE DURATION OF LIFE OF DISPERSOIDAL SOLUTIONS, OF A PROGRESSIVE INCREASE OF THE CONCENTRATION OF ELECTROLYTES IN THE DISPERSION MEDIUM.

In spite of the fact that indications are not unfrequently met with in the literature on dispersoidology, to the effect that some dispersoidal solution or other has an "unlimited" stability, it is to be maintained that the life of every dispersoidal solution of any practically insoluble substance, is limited in time.

This should be noted first.

Second: the duration of life of dispersoidal solutions is determined by a very large number of variables among which the electrical conditions are by no means always the predominant. In fact, the influence of the electrolytes themselves is the resultant of quite a number of processes and consequently is far from being always so simple as sometimes represented (15).

Especially in those cases when the relative concentration of the disperse phase $\left(\frac{Q - L}{L}\right)$ is not large, the number of variables controlling the life of such kinds of dispersoidal solutions will so increase, that the phenomena will sometimes begin to acquire an accidental character.

Such cases, however, have so far received but very little study, and usually the relative concentration $\frac{Q - L}{L}$ of the dispersoidal solutions is expressed by very large numbers.[3]

Up to the present time, the influence of the electrolytes on the duration of life of dispersoidal solutions has, for the most part, been studied in instances of dispersoidal solutions resulting from chemical reactions.

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[3] For instance, if the concentration of the dispersoidal solution is equal to 1.10^{-2} gramme, and the true solubility of the substance—to 1.10^{-12} gramme, $\frac{Q-L}{L}$ will come to about 10,000,000,000.

But, under the above conditions, the different kinds of admixtures present in the dispersion medium would render the study of the influence exerted by the electrolytes extremely complicated, and the numerical data, difficultly reproducible.

In one isolated case, it is true, the effect of electrolytes (16) on a dispersoidal solution of sulphur prepared by a physico-chemical method (pouring alcoholic-aqueous sulphur solutions into water (17)) has been studied, but then only in the sense of determining the "Coagulating-Concentration" of the electrolytes.

Complete "Life-curves" of dispersoidal solutions, i.e., curves with the coördinates: concentration of electrolyte, duration of life, have but recently been realized, for the case of a dispersoidal solution of sulphur, prepared by the mechanical method of pulverizing sulphur together with grape-sugar.

Unfortunately, for "positive" dispersoids, the only part of the "Life-curves" that has so far been realized is their right-hand, descending branch; and this notably for dispersoidal solutions of the hydroxide of aluminium, prepared by the same mechanical method as mentioned for the case of dispersoidal solutions of sulphur.

The numerical data relating to the above disperse systems are presented graphically.

The dispersoidal solutions of sulphur were prepared as follows: 0.1 gramme of purest rhombic sulphur, specially recrystallized, was treated by grinding, for one hour, in an agate mortar, together with 0.9 gramme of grape-sugar (Merck's anhydrous, extra-pure); of the resulting mixture, 0.2 to 0.3 gramme were taken, and ground again, in small portions, in an agate mortar, for two hours more; from this last grinding, 0.15 gramme was taken, and quickly introduced, under vigorous stirring, into exactly 100 cc. of specially purified, freshly re-distilled (using a silver condenser) water.

The disperse systems of sulphur prepared in the above described manner were then filtered off from the coarsely-disperse parts, through a filter (S. and S. No. 602, "extra-hart").

The resulting dispersoidal solutions of sulphur prepared at different times after the manner described above (at temperatures between 30° to 20°C.; in the summer months), were of a concentration between 30 to 20 mg. sulphur per litre, and of an average size of particles between 90 to 80$\mu\mu$.

The duration of life was expressed in terms of days (1 day = 24 hours) elapsed from the moment of preparation of any given dispersoidal solution, up to the moment when the sedimentation of the whole of the disperse particles present was practically completed. In the case of the dispersoidal solutions of sulphur now under consideration, this latter occurrence is easily recognized from the complete disappearance of opalescence which, in the cases under consideration, exactly coincides with the practically complete disappearance of any Tyndall cone produced by the rays of an arc lamp, whenever the experiments are carried out in a dark room. The temperature varied during the experiments, between 30° and 20° (in the summer months). In the winter months (at temperatures fluctuating between 10° to 4°) the dispersoidal solutions of sulphur had a considerably greater stability.

The preparation, by the mechanical method, of dispersoidal solutions of aluminium hydroxide was done in exactly the same manner as in the case of sulphur, except that, of the material resulting from the last grinding, 0.3 gramme were introduced into 200 cc. of water. The alumina used was composed of microcrystals of $Al_2O_3 \cdot 3H_2O$ (obtained by the method Shulten-Weimarn from a dilute solution of $Al(OH)_3$ in strong aqueous NH_4OH). Since a positive dispersoid was desired filtration could not be used; and consequently after settling, the supernatant liquid was pipetted off and used for the experiments. The concentration of the dispersoidal solutions employed varied between 50 to 60 mg. of $Al_2O_3 \cdot 3H_2O$ per litre of the solution, and the average size of the disperse particles was 85 to 95$\mu\mu$. The dispersoidal solutions of aluminium hydroxide contained particles of a variety of different dimensions as evident from the initial rapid sedimentation of the coarser particles.

The duration of life was measured in terms of days (1 day = 24 hours), from the moment of preparation of the dispersoidal solution, up to the complete disappearance of any Tyndall cone.

The temperature during the experiments was varying between 10° to 4° (winter months).

The duration of life of the dispersoidal solutions of aluminium hydroxide without the addition of electrolytes amounts to a few (e.g., 2 to 3) months; and therefore, the left-hand parts of the "Life-curves" have not yet been determined.[4]

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(7) von Weimarn, P. P.: e.g., Kolloid-Zeitschr., **4**, 134 (1909).

(8) Trivelli, A. P. H., and Sheppard, S. E.: The Silver Bromide Grain of Photographic Emulsions, pp. 36–37. Eastman Kodak Company. Rochester. 1921. Sheppard, S. E.: Colloid Symposium Monograph, pp. 353–354. Wisconsin. 1923.

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[4] The investigation is now in progress, so that complete life-curves may be expected to be established in this case also.

(10) The colloidal synthesis of gold by the formol-method (R. Zsigmondy) has received, in certain directions, a very thorough study; but, when in its classical form, it is difficultly reproducible; see, e.g.: Ostwald, Wo.: Kleines Praktikum der Kolloidchemie. VI. II Auflage. 1921. Verlag von Theodor Steinkopff. Dresden.; P. P. von Weimarn. Koll.-Zeitschr., **33,** 74–81; 228–247 (1923).

(11) von Weimarn, P. P.: Kolloidchem. Beihefte., **18,** 44–76 (1923).

(12) Graham, Thomas: In Ostwald's Klassiker der exakten Wissenschaften, No. 179, p. 77–78 (1864–1865).

(13) Lottermoser, Alfred: Jour. für praktische Chemie (2) **72,** 39–56. (1905); **73,** 374–382 (1906). Koll.-Zeitschr., **2,** Suppl.-Heft I (1907). Zeitschr. für physikal. Chemie., **60,** 451 (1907); **62,** 359 (1908). Compare: von Weimarn, P. P.: Koll.-Zeitschr., **4,** 123 (1909).

(14) van Bemmelen, J. M.: Die Absorption. 426. Verlag von Theodor Steinkopff. Dresden. 1910. von Weimarn, P. P.: Journ. Russ. Chem. Soc. **42,** 646 (1910). Lundelius, E. F.: Koll.-Zeitschr., **36,** 145 (1920).

(15) Ostwald, Wo.: Koll.-Zeitschr., **36,** 28, 69 (1920). This is the best critical work on the numerical data relating to the "Coagulating Concentration" of the electrolytes, and the laws connected therewith.

(16) Freundlich, H., and Scholz, P.: Kolloidchem. Beihefte., **16,** 234 (1922).

(17) von Weimarn, P. P., and Malyschew, B. W.: Journ. Russ. Chem. Soc., **42,** 484 (1910). Koll.-Zeitschr., **8,** 216 (1911).

EXPLANATION OF FIGURES

(*1*) The dispersion medium is indicated thus (93% C_2H_5OH); (*2*) The direction of pouring is indicated by the arrow. (*3*) The time, t_o, represents the period (*ca.* 10–15 min.) required for the operations of sampling and photomicrographing. (*4*) All data shown are the average of at least two independent experiments.

1. Precipitation of Ag_2SO_4.—Reaction: $AgNO_3 + MnSO_4 = Ag_2SO_4 + Mn(NO_3)_2$. Figs. 1–7, incl. Per liter of final solution, $C = Ag_2SO_4$ produced by the reaction and $S =$ its solubility, both in g-equivalents.

2. Precipitation of $AgC_2H_3O_2$.—Reaction: $AgNO_3 + KC_2H_3O_2 = AgC_2H_3O_2 + KNO_3$. Figs. 8–9.

3. Precipitation of Se.—Reaction: (a) 5 cc. of aniline containing m milligrams of Se are poured into 100 cc. of 93.5 wt. % C_2H_5OH; or (Fig. 13) mixtures thereof with An. or glycerol. $t = 20°$. Figs. 10–13, *a*-curves.

(b) As in (a) but with quinoline instead of aniline and using 90 wt. % C_2H_5OH. Figs. 10–13, *b*-curves.

4. Effects of salts dissolved in the dispersion medium.—Reaction: (a) $BaSO_4$.—50 cc. ($= 2a + 2x$ equiv.) BaH_2 + 50 cc. ($=2a$ equiv.) $MnSO_4 = a$ equiv. $BaSO_4$ + a equiv. $MnR_2 + x$ equiv. BaR_2. Dispersion medium, 63 wt. % C_2H_5OH. Figs. 14–17.

(b) S.—Dispersoidal solutions of sulphur prepared by the method of grinding with sugar. *Ca.* 25 milligrams S per liter of H_2O; particles *ca* 85 $\mu\mu$.

Figs. 18–28. $C =$ millimols salt per liter. The dotted horizontal is for $C = 0$. To the right of the dotted vertical (fig. 23) the disperse phase begins to dissolve by chemical action.

(c) $Al(OH)_3$.—Prepared as in (b) *supra. Ca.* 55 milligrams $Al_2O_3 \cdot 3H_2O$ per liter of H_2O; particles *ca.* 90 $\mu\mu$. Fig. 24. The dotted horizontal is for $C = 0$. Dissolving begins at points marked with crosses.

5. Adsorption and Solubility of Salts.—Fig. 25.

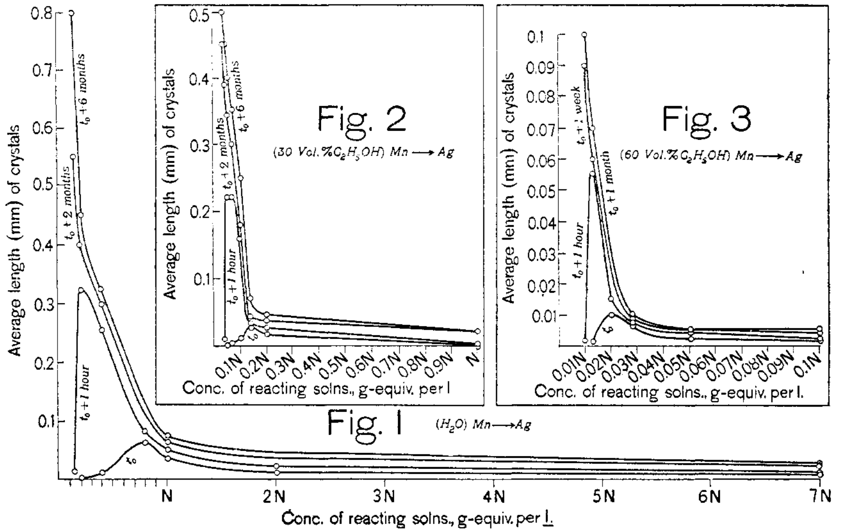


Fig. 1 (H_2O) Mn → Ag

Fig. 2 (30 Vol.% C_2H_5OH) Mn → Ag

Fig. 3 (60 Vol.% C_2H_5OH) Mn → Ag

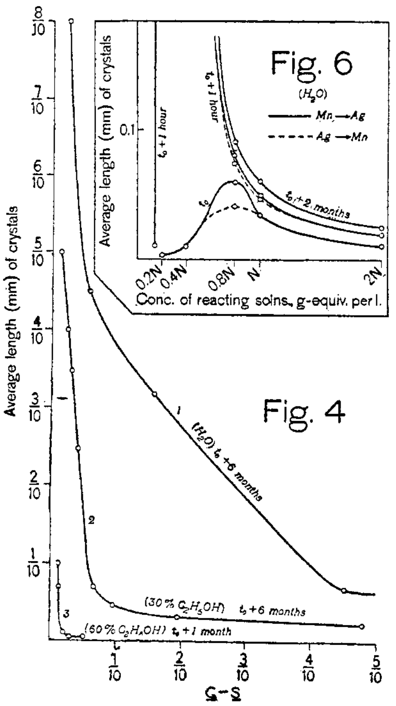


Fig. 6

Fig. 4

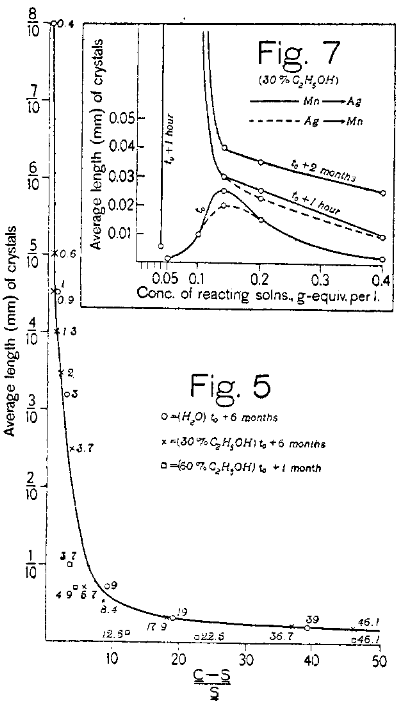


Fig. 7

Fig. 5

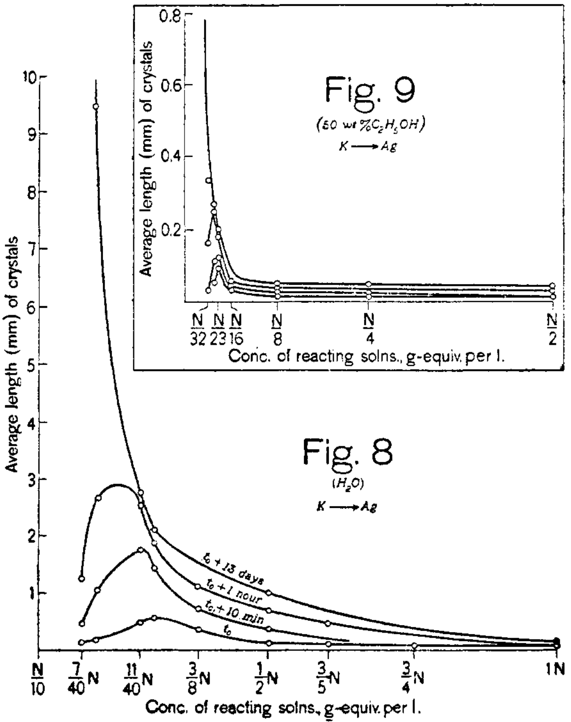


Fig. 9

(50 wt $\%C_2H_5OH$)

$K \longrightarrow Ag$

Fig. 8

(H_2O)

$K \longrightarrow Ag$

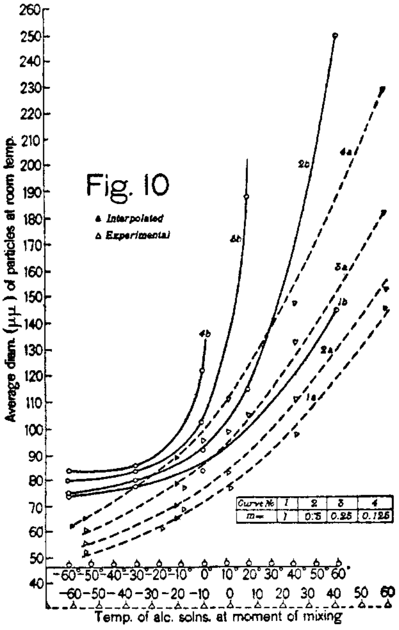


Fig. 10

▲ Interpolated
△ Experimental

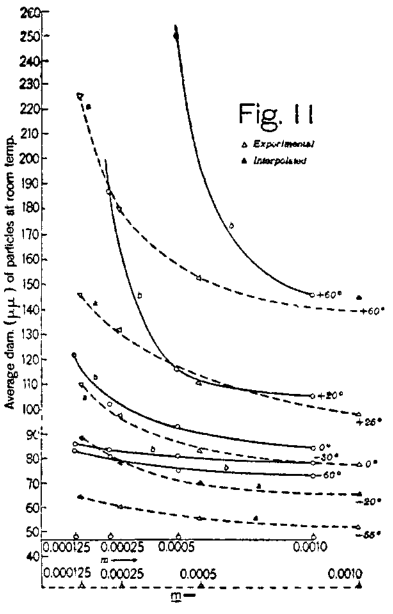


Fig. 11

△ Experimental
▲ Interpolated

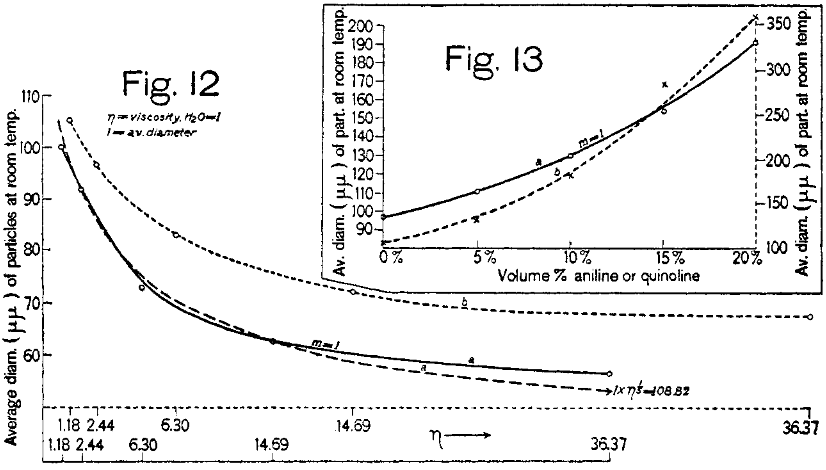


Fig. 12
η = viscosity, H₂O = 1
l = av. diameter
Average diam. (μμ) of particles at room temp.
110
100
90
80
70
60
m=1
a
b
l×η^{1/5}=108.82
1.18 2.44 6.30 14.69 36.37
1.18 2.44 6.30 14.69 36.37
η →
Fig. 13
Av. diam. (μμ) of part. at room temp.
200 190 180 170 160 150 140 130 120 110 100 90
350 300 250 200 150 100
0% 5% 10% 15% 20%
Volume % aniline or quinoline
m=1
a
b

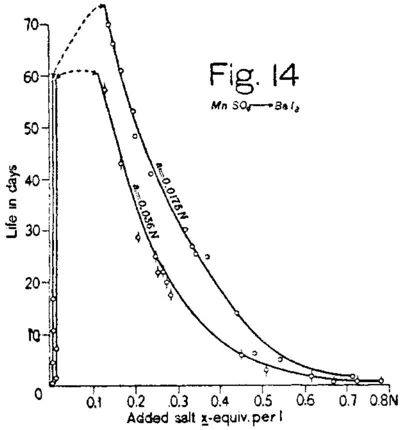
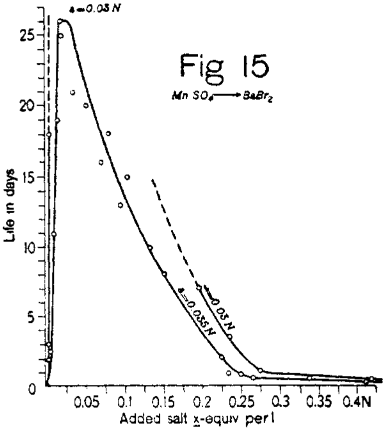


Fig. 14
Mn SO₄ → BaI₂
Life in days
70 60 50 40 30 20 10 0
a=0.0175 N
a=0.035 N
0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8N
Added salt x-equiv. per l


a=0.03 N
Fig 15
Mn SO₄ → BaBr₂
Life in days
25 20 15 10 5 0
a=0.055 N
a=0.03 N
0.05 0.1 0.15 0.2 0.25 0.3 0.35 0.4N
Added salt x-equiv. per l

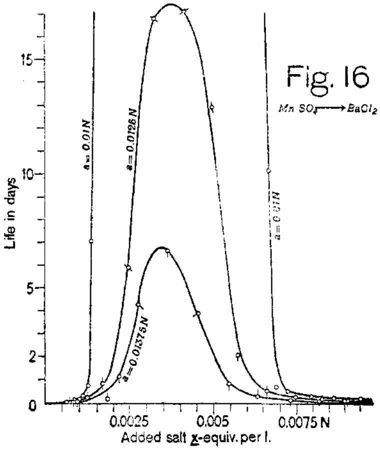


Fig. 16

$MnSO_4 \longrightarrow BaCl_2$

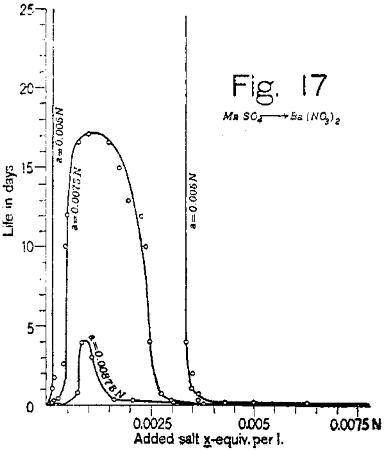


Fig. 17

$MnSO_4 \longrightarrow Ba(NO_3)_2$

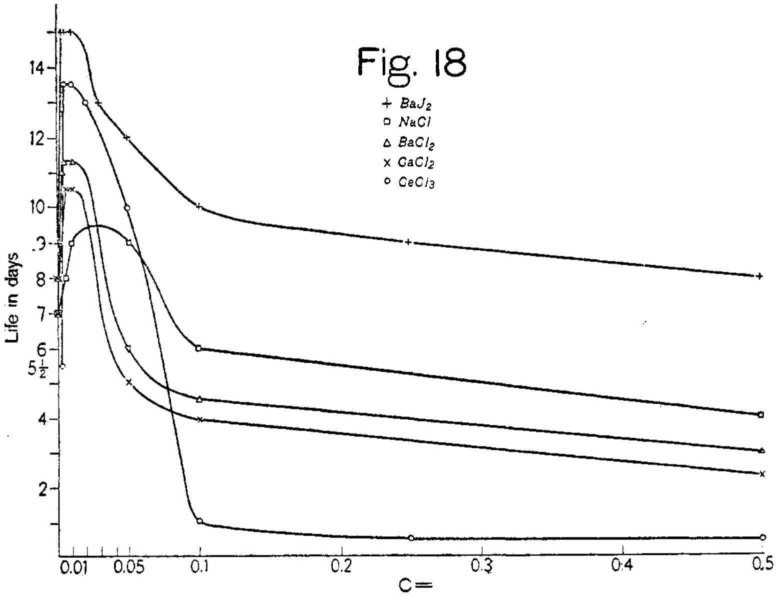


Fig. 18

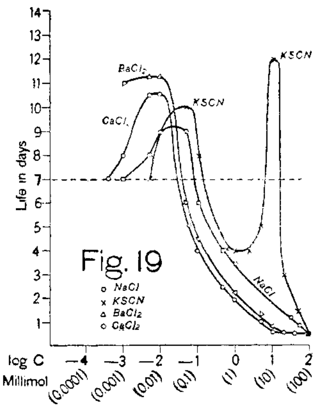


Fig. 19
Life in days
14
13
12
11
10
9
8
7
6
5
4
3
2
1
BaCl₂
CaCl₂
KSCN
KSCN
NaCl
○ NaCl
× KSCN
△ BaCl₂
○ CaCl₂
log C
Millimol
−4
−3
−2
−1
0
1
2
(0.0001)
(0.001)
(0.01)
(0.1)
(1)
(10)
(100)

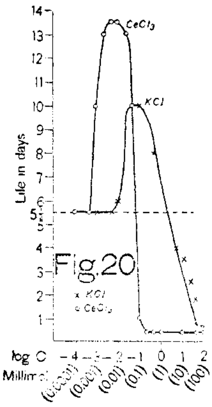


Fig. 20
Life in days
14
13
12
11
10
9
8
7
6
5
4
3
2
1
CeCl₃
KCl
× KCl
○ CeCl₃
log C
Millimol
−4
−3
−2
−1
0
1
2
(0.0001)
(0.001)
(0.01)
(0.1)
(1)
(10)
(100)

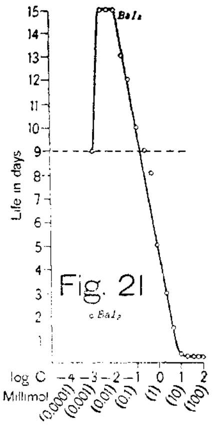


Fig. 21
Life in days
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
BaI₂
○ BaI₂
log C
Millimol
−4
−3
−2
−1
0
1
2
(0.0001)
(0.001)
(0.01)
(0.1)
(1)
(10)
(100)

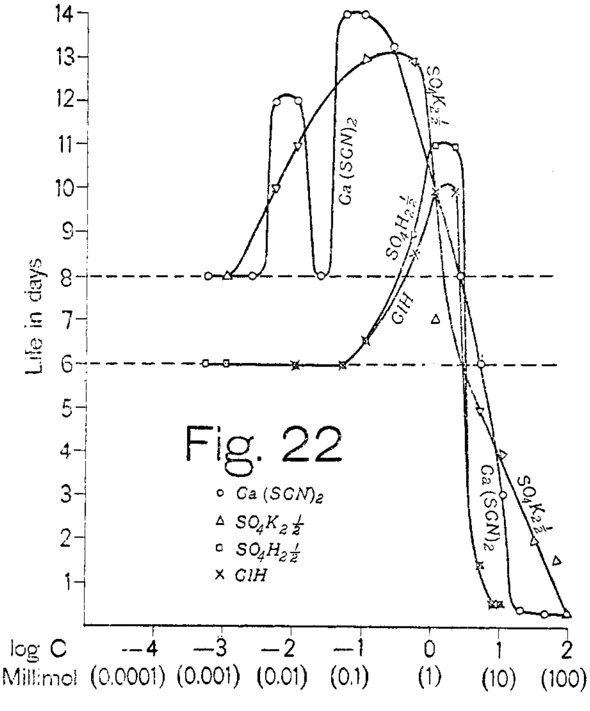


Fig. 22
Life in days
14
13
12
11
10
9
8
7
6
5
4
3
2
1
Ca (SCN)₂
SO₄K₂ ½
SO₄H₂ ½
ClH
Ca (SCN)₂
SO₄K₂ ½
○ Ca (SCN)₂
△ SO₄K₂ ½
□ SO₄H₂ ½
× ClH
log C
Millimol
−4
−3
−2
−1
0
1
2
(0.0001)
(0.001)
(0.01)
(0.1)
(1)
(10)
(100)

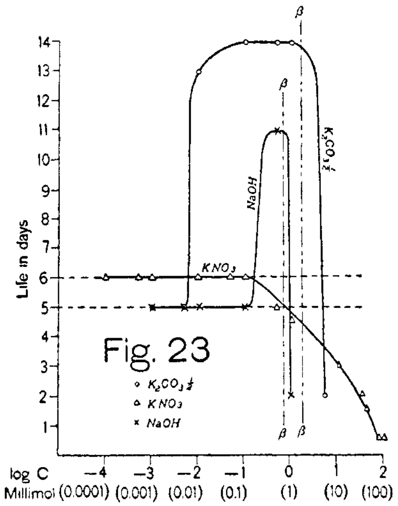


Fig. 23

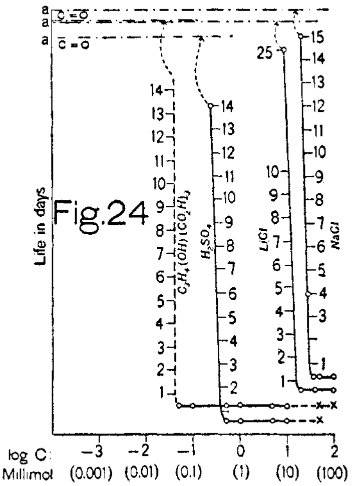


Fig. 24

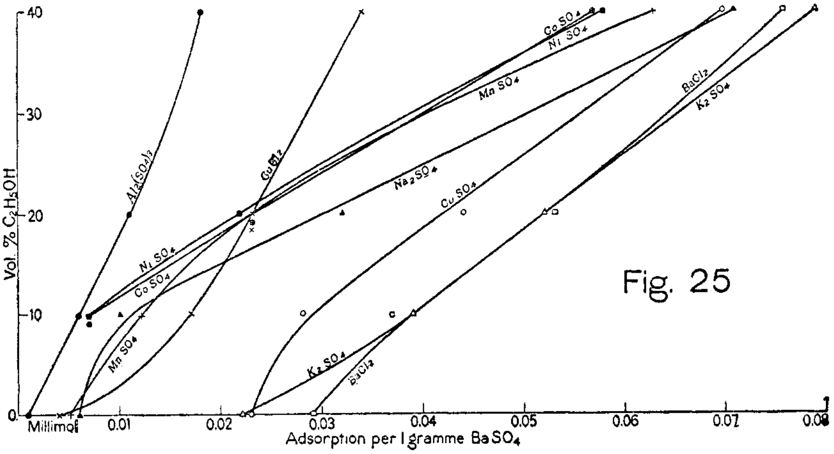


Fig. 25