

The Process of Coagulation in Smokes.

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OF the various classes of disperse system known to colloid chemistry, that in which the medium is a gas has until recently attracted little attention. This is the more remarkable because aerial types are of such common occurrence and they should be relatively simpler than hydrosols and easier to interpret. Systems of this type, though presenting certain analogies with true colloids, differ from them sharply and definitely by one outstanding characteristic, *viz.*, their instability.

The ultramicroscopic particles in gold sols, for instance, remain in suspension for indefinite periods, and it is only by experiments at strictly controlled temperatures that it is possible to detect a separation by sedimentation of the two phases. Further, the particles in such a sol, though in active Brownian movement, never approach close enough to collide but are held apart by ionic forces. It is only when, by the addition of electrolytes, the isoelectric point is approached, that coagulation takes place and the sol precipitates.

Aerial disperse systems behave in a totally different manner: not only do the particles sediment more rapidly, but collisions under Brownian movement cause them to cohere so that the system rapidly becomes coarser and finally flocculates out.

No instance has been discovered of an aerial or gaseous disperse system which is not undergoing spontaneous coagulation. This difference is fundamental, and sharply differentiates the two types. It is clearly due to the difference between the media, water and air. Not only do these differ widely in density and viscosity, but even in the purest water the concentration of the ions is very much greater than in air. In consequence, the Brownian motion and rate of sedimentation in gaseous media are very much more rapid than in liquids, and no counterpart of the ionic micelle with its electric double layer has been detected. Indeed, in smokes and many aerosols, oppositely charged as well as un-electrified particles can exist for long periods in the same system and in many cases the electrification has little influence on the rate of coagulation. The particles in smokes are on the average about ten times larger than in colloids and, in general, have radii between 5×10^{-6} and 5×10^{-5} cm. (0.05—0.5 μ).

The one property, then, which determines to a large extent the behaviour of all aerial or gaseous systems such as smoke, fume, dust, or fog is this property of continual coagulation, and a study of the process is important because all the properties dependent on particle size are determined by it.

The first clear indication that smokes coagulate was obtained by Tolman and his co-workers in 1919 (*J. Amer. Chem. Soc.*, **41**, 297, 575, 587) by the measurement of the variation with time of the intensity of the Tyndall beam. Various smokes were dispersed thermally in a large metal chamber, and it was found that for any one smoke the tyndallmeter readings decreased with time more rapidly than the weight of smoke material in suspension. Now, by independent experiment, it was found possible to correlate the tyndallmeter readings with (a) mass concentration, and (b) average size of particle, and it was evident that the decrease noted could only be explained by coagulation.

These experiments, however, gave no information about the number of particles present or their actual size, and afforded no means of comparing different smokes. The first attempt to apply Zsigmondy's slit ultramicroscope to the counting of smoke particles was made in 1923 (Whytlaw-Gray, Speakman, and Campbell, *Proc. Roy. Soc., A*, **102**, 600), and it was soon found that dense smokes similar to those used by Tolman, of a mass concentration of the order of 1 g. per cubic metre, were unsuitable because the particles were too large and too heterogeneous. A suitable mass concentration proved to be about 20 mg. per cubic metre. This weight was dispersed quickly inside a cubic-metre glass chamber by volatilisation either from an electrically heated boat, in the case of substances like ammonium chloride, resin, paraffin, etc., or from an arc, when oxide or metal smokes

were used. During dispersal, the smoke was mixed rapidly with air by means of an electric fan in the chamber.

In the first experiments of this kind, when organic substances of high boiling point were used to produce the smoke, it was found that the number of particles, initially about 1—2 million per c.c., diminished very rapidly for the first hour and thereafter at a slowly decreasing rate, but after 7 hours the air of the chamber still contained many thousands per c.c., and even after 24 hours the presence of particulate matter was usually clearly visible in the Tyndall beam. In normal light these smokes were quite transparent and no haze was noticeable.

In order to determine what fraction of the material originally dispersed remained in suspension at different periods during the life of the smoke, one litre was filtered off from time to time through small asbestos filters which were weighed on a microbalance (Whytlaw-Gray and Speakman, *ibid.*, p. 615). It was then found that the change in mass was small during the early period when the decrease in number was very rapid. This observation proved clearly that, unless the particles were disappearing by evaporation, coagulation was taking place. An examination of a series of oxide smokes set these doubts at rest: there could be no possibility of the evaporation of smoke particles of the oxides of magnesium, copper, or zinc. From these data, too, the average weight of the particle could be calculated and an estimate made of its size.

Knowledge of the form and degree of complexity of the aggregates was obtained (Whytlaw-Gray, Speakman, and Campbell, *ibid.*, p. 613) by exposing glass slides to the smoke and examining the deposits with the microscope under dark-ground illumination. In fine smokes, only minute diffraction discs were visible at first, but later, the discs became brighter and increased in size just as did the suspended particles seen in the slit ultramicroscope. When, however, much denser smokes were used, the increase in complexity of the aggregates with time was clearly marked, and these in many oxide smokes exhibited a remarkable chain-like structure; this was particularly noticeable with the oxides of zinc, cadmium, magnesium, aluminium, and antimony. At high concentration these oxides aggregate finally to loose and flock-like complexes composed of a vast number of irregular strings and chains. As Kohlschütter and Tüscher (*Z. Elektrochem.*, 1921, 27, 1) have shown, these, when collected in bulk by electrical precipitation, have a remarkably low density, much smaller than that of the oxides prepared in the usual way; further, when treated with water or dilute alkalis, the complexes often disintegrate and form colloidal solutions or fine suspensions. This is especially marked with smokes composed of the oxides of tin, iron, antimony, and silicon.

In an electric field, the particles which are highly charged in the arc smokes build up on the electrodes long strings or chains which often take the shape of tree-like growths. In a gentle stream of air some of the branches can be made to rotate continuously, the trunk and other branches remaining stationary. This behaviour, and also the peptisation in dilute alkalis, was regarded as lending support to the view that the single particles composing the chains are separated from each other by films of adsorbed air. By using a more elaborate technique, it has been found possible to examine the particles in dilute clouds at high magnification by transmitted light: those in arc smokes consist largely of small chains, sometimes with invisible material between the links.

Much more compact aggregates, roughly spherical, are formed by substances which volatilise at a lower temperature, such as arsenic trioxide, mercuric chloride, resin, stearic acid, and many organic dyestuffs. The density and radii of the complex smoke particles can be determined by an inversion of Millikan's method for finding the charge on the electron (Patterson and Whytlaw-Gray, *Proc. Roy. Soc.*, 1926, A, 113, 302). The particle carrying a known number of electrons is balanced against gravity in an electric field of known strength, and then its velocity under gravity alone is measured. The electronic charge being assumed, the density and radius can be calculated. It was found that, whilst minute droplets of paraffin oil gave a normal value for the density, yet the particles in arc clouds were on the average about one-tenth of the normal, though occasionally, even in these smokes, particles approaching a normal density were found, especially among the very small ones.

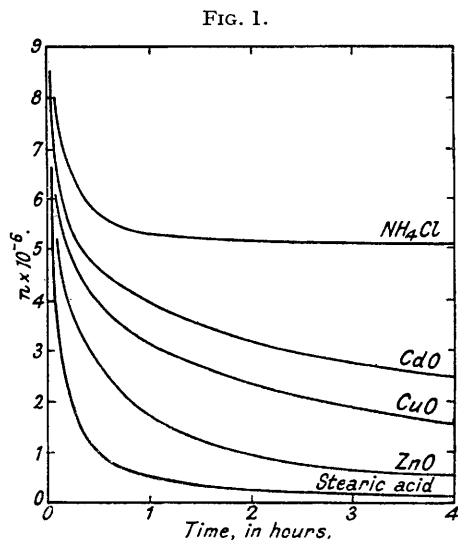
Of the easily volatilised substances only mercuric chloride was examined in this way. Its mean density was found to be about one-quarter of its bulk density, an observation in close accord with its compact structure under the microscope.

It might be thought that the high charges carried by these particles determine to some extent the structures we have described. This, however, is certainly not the case for zinc oxide, for unelectricified clouds of this substance, prepared by the interaction of the vapour of diethylzinc with air, give complexes and chains of exactly the same character and appearance under the microscope as those just described. It seems probable that the particles in the chains and strings are minute crystals too small to be resolved by the microscope, which are held together by polar forces acting along crystal axes or even by amicroscopic threads of crystalline material. The crystalline nature of many smoke films has been proved by Finch (*Proc. Physical Soc.*, 1934, **46**, 148) by means of an electron-diffraction method, and he has established the structure of films of zinc oxide. Walmsley,

too, has studied cadmium oxide complexes by an X-ray method and has determined the probable orientation of the crystals in the chains (*ibid.*, 1928, **40**, 7).

Returning now to coagulation, it is of importance to determine the true course of this process, to find out if it varies with the size and nature of the particles, and if it is analogous to the corresponding process in colloids. Before this can be done it is essential to be able to determine the true variation with time of the number of particles, *i.e.*, the form of the coagulation curve.

With the object of improving the ultramicroscopic method, the original instrument was replaced by one of improved design provided with a lens system of higher optical aperture and illuminated by an automatic arc instead of a pointolite lamp. A number of dilute smokes were then examined and counted, and the number-time or "particulate number" curves plotted (Fig. 1). These showed the same features as the earlier graphs, but indicated that the



Slit ultramicroscope curves compared with standard curve for stearic acid.

course of coagulation varies from smoke to smoke, especially in the later stages. At the time it was believed that these graphs were at least approximately correct, but subsequent experience has proved that they present a totally erroneous picture of the coagulation process.

In order to check the accuracy of these counts, a sedimentation method was developed, in which a small sample of smoke could be enclosed between two glass plates without causing disturbance. This was done by sliding the plates along the upper and lower surfaces of a horizontally placed rectangular sheet of brass 2 mm. thick, which was pierced by a hole of about 1 cm. in diameter. When the glass plates were pushed over the hole a small cylindrical segment of smoke was enclosed, and on standing, the particles settled out on the under plate in the form of an even deposit; usually a few particles were caught on the upper surface by diffusion. The particles in the deposit could be easily counted with the microscope when illuminated suitably.

A series of these "collector slides," as we have called them, were constructed and placed inside the smoke chamber, and the plates drawn at any suitable time. The method gave numbers in close agreement with the counts obtained with the first ultramicroscope, but very much smaller than those with the improved instrument.

It was thought that small particles might become invisible on settling on a glass surface. A direct experiment in which the particles could be observed as they settled showed that they vanished from sight only if they were liquid—solid particles remained clearly visible

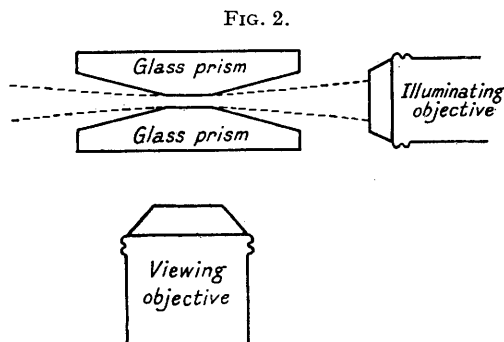
down to very small dimensions. Thus, many of the particles in tobacco smoke disappear as they settle, others diminish in brightness, but cadmium oxide particles even in fine smokes are easily seen after settling, provided the glass surface is clean and free from dots and striæ. One of the great difficulties of the method is to obtain glass surfaces so perfectly polished that even in intense illumination they show no imperfections simulating particles.

For the detection of the finest particles, we have found that the most effective dark-ground illumination is furnished by a convergent beam of light from an arc directed on to the deposit at an angle of 30°. Through the kindness of Sir Herbert Jackson, we were finally able to procure nearly perfect glass surfaces. A comparison of the two methods again indicated a similar divergence, as shown in the following table.

Comparison of counts on the same smoke made by collector slide and slit ultramicroscope methods.

Time, minutes	4	10	20	40	60
Number per c.c. × 10 ⁻⁶ { Slit ultramicroscope...	2.75	2.15	1.63	1.15	0.9
{ Collector slide	2.15	1.47	0.78	0.45	0.32

In the meantime the possibility of particles being counted outside the illuminated ribbon of light in the slit ultramicroscope was investigated. With intense illumination, an error of this kind may arise from stray light reflected from the walls of the cell itself or from smoke particles outside the field of vision, especially in the later stages when the complexes are bright. Any extraneous light would extend the visibility outside the measured zone and give rise to counts which are too high. Westgren (*Arkiv Matem. Astron. Fys.*, 1918, 11, No. 8), in counting gold sols, drew attention to this error, and more recently Tuorila (*Kolloid-Z.*, 1926, 38, 16), who checked the readings of the slit instrument against a cardiod ultramicroscope, found a constant difference between the two, the former giving counts four times as great as the latter. In smokes, with their much larger particles, this error appears to be of greater significance than in sols.



Our experiments cast grave doubts on the reliability of the counts made in smokes with the slit ultramicroscope, and led us (Nonhebel, Colvin, Patterson, and Whytlaw-Gray, *Proc. Roy. Soc.*, 1927, A, 116, 542) to design a cell in which the depth was strictly defined, as in the cardiod, by the distance between the cell walls instead of by the optical boundaries of the image of the slit.

The essential features of the cell will be clear from the accompanying diagram (Fig. 2). The count is made when the smoke is between the parallel portions of the two glass surfaces, the distance between which can be as small as 0.1 mm. A current of smoke is passed through the cell and stopped intermittently by means of a slowly rotating tap so that the small element of smoke to be counted only remains in the narrow part for a small fraction of a second. The proportion of particles diffusing to the walls in the narrow space before the count is made is inconsiderable. Full details of the method have been described elsewhere.

After gaining experience with the new cell by counting a number of smokes and improving the experimental technique, we were in a position to compare the data it furnished with those given by the collector-slide method. When a fine cadmium oxide smoke was used for a series of clouds, a good agreement was obtained, which was quite satisfactory in view of the fact that the experimental errors in the two methods differ widely. Below are given the data obtained from a single experiment :

Cadmium oxide smoke.

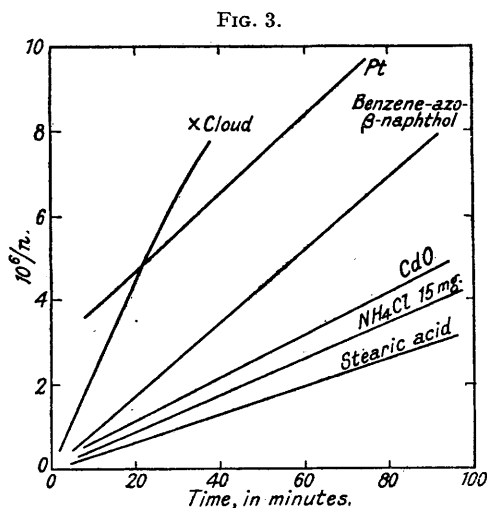
Time, minutes	8	24	43	62	84
Number per c.c. × 10 ⁻⁶ { New cell.....	0.88	0.51	0.34	0.26	0.20
{ Collector slides	0.92	0.47	0.33	0.24	0.21

A further confirmation of the reliability of the data obtained with the new cell is afforded by the results of an extremely elegant method of counting smoke particles, devised independently by Green (*Phil. Mag.*, 1927, 4, 1046), in which a modified Wilson expansion apparatus is used. A cell similar to that employed in the slit ultramicroscope is arranged so as to form the upper part of the cylinder of a small expansion apparatus, and on expansion the smoke particles are instantaneously loaded with moisture and grow to a comparatively large size, whereupon they can be easily photographed. Since the droplets are large and bright, a narrow beam of light of low intensity can be used; moreover, it is easy to exclude particles outside the depth of focus of the microscope, and the error inherent in counting diffraction images with the slit ultramicroscope does not arise. The method, too, has the advantage of being able to detect and enumerate amicroscopic particles, and also small ultramicroscopic ones which, on account of their vivid Brownian motion and low visibility, are very difficult to perceive when using the direct ultramicroscopic method.

Green's method was found to agree satisfactorily with the two methods just described. Hence, there are now three independent ways of counting the particles in smoke clouds, and

they all yield substantially the same result, account being taken of the comparatively large errors inherent in work of this character.

The agreement between these different ways of counting smoke particles has been emphasised because the form of the particulate-number curve is of importance for the correct interpretation of the process of coagulation. For instance, if the graphs in Fig. 1 were assumed to be accurate, it would be concluded that coagulation ceased or became very slow when the complexes reached a certain size depending on the nature of the smoke substance; e.g., the ammonium chloride smoke apparently becomes stable after an hour, when the number of particles is about 5×10^6 per c.c., whilst cadmium oxide seems to stabilise at a much lower figure. If, however, the curves obtained by counting with the new cell are compared, we find that they are all closely similar to each other and



Particulate-volume graphs for various smokes.

show no sign of stabilisation. The type of curve is at once evident if, instead of the number of particles per c.c., its reciprocal is plotted against time, whereby in nearly all cases a straight line is obtained.

If n is the number of particles per c.c. at any time t , and n_0 the number present immediately the smoke is formed, then

$$1/n - 1/n_0 = Kt, \text{ or, if } 1/n = \sigma \text{ and } 1/n_0 = \sigma_0, \sigma - \sigma_0 = Kt,$$

where σ has a definite physical meaning and represents the volume on the average inhabited by a particle in the smoke. It is conveniently termed the "particulate volume," and as coagulation proceeds it increases linearly with time. For ordinary smokes of a mass concentration of the order we have used, the lines are straight or almost so within the limits of accuracy of the experimental points. Their slopes provide a means of classifying or comparing different smokes. The equation is of the same form as that established by Rutherford in 1897 for the rate of combination of small ions, and was later shown by Kennedy to be valid for the combination of large atmospheric ions, and also by Nolan for the rate of disappearance of nuclei, but naturally, on account of the smaller mobilities, the constant K is smaller for smokes than for ions.

It is remarkable that the coagulation constants for different smokes all lie fairly close to each other. In the table below are collected the constants for a variety of smokes

which we have determined. The weight concentrations (mg./cu.m.) are given in parentheses.

Coagulation constants for various smokes (in cm.³/sec. $\times 10^9$).

	<i>K.</i>		<i>K.</i>
Magnesium oxide	0.8	*Stearic acid (15 mg.), blown	0.51
Cadmium oxide (50 mg.)	0.8	*Oleic acid (15 mg.), blown	0.51
*Ferric oxide (16 mg.)	0.66	Paraffin oil (15 mg.), blown.....	0.50
Ammonium chloride (15 mg.)	0.60	<i>p</i> -Xyleneazo- β -naphthol (15 mg.)	0.63
*Resin (15 mg.), blown	0.49	Antipyrine (40 mg.)	0.57

Some of these numbers are only approximately correct. The well-established ones are marked with an asterisk.

The rate of coagulation depends on the method used for dispersal: some methods give smokes which initially may consist of even-sized particles; others tend to yield dispersions which are widely heterogeneous. Again, the rate of coagulation depends considerably on the average size of the particle. It is possible, however, to a large extent, to determine experimentally the influence of these factors. Thus, with ammonium chloride dispersed under strictly controlled conditions of temperature and rate of admixture with air, the initial number of particles does not vary much when the mass of the material volatilised is changed considerably. It is, hence, possible to determine the influence of size on the rate of coagulation.

Numerous careful experiments have been made with this object. Thus with ammonium chloride (Patterson, Whytlaw-Gray, and Cawood, *Proc. Roy. Soc.*, 1929, *A*, **124**, 504), a series of six different concentrations was investigated, *viz.*, 60, 30, 15, 7.5, 3, and 1 mg. per cubic metre, and a number of clouds at each concentration counted. Equality of numbers at the start being assumed, the average radii are roughly in the proportion of 4 : 3 : 2.5 : 2 : 1.4 : 1. The actual mean radii when the smokes contained 1 million particles per c.c. range from 21×10^{-6} cm. for the 60 mg. concentration to 5.4×10^{-6} cm. for the 1 mg. smoke.

These sizes are calculated on the assumption that the density of the particle is normal, which for this substance in the early stages of coagulation is not far from the truth. A series of six particulate-volume graphs was obtained of gradually increasing slope as the concentration diminished; the lines for the two lowest concentrations were distinctly curved towards the time axis. The *K* values, which in the case of the two lowest concentrations were computed from the earlier points, were 0.55, 0.61, 0.70, 0.87, 1.30, and 1.70×10^{-9} . Although no accuracy is claimed for these figures, and probably the last two are much too great, they do show clearly that the coagulation rate increases rapidly as the average particle size falls. These smokes were heterogeneous and the values for *K* were abnormal. Considerable difficulty was experienced at first in counting the very fine particles in the 1 mg. cloud, for although they could be seen, it was not easy to enumerate them. It was found possible to transform them into minute droplets before they entered the counting cell by lining the entrance tube with damp filter-paper; the particles then grew to a size which was easily visible.

A confirmation of the greater coagulation rate of small particles can be deduced from the work of Flower (*Phil. Mag.*, 1928, **5**, 1084) on the fine particles given off by a heated platinum wire. These were just on the limit of visibility in the ultramicroscope, and at first only the larger were visible, the numbers increasing as coagulation proceeded. Finally, they were counted by Green's method. The graph of the particulate volumes against time was a straight line, the constant of which was 1.5×10^{-9} cm.³/sec.

In some of our experiments we found that a very fine smoke was obtained when a stream of carefully filtered air was passed through an electrically heated metal tube. No matter what precautions were taken to clean the tube or to purify the air, Green's apparatus showed the presence of a large number of particles ("X smoke") which, however, were quite invisible in the ultramicroscope. A strong Tyndall beam did, however, indicate faintly the presence in the chamber of particulate matter. The cloud coagulated very rapidly, and the graph showed a slight curvature. The constant was found to be 3.2×10^{-9} cm.³/sec. Collecting together the results for these very small particles, we have:

Coagulation rates for very small particles ($K \times 10^9$, cm.³/sec.).

Particulate system.	Size, cm. $\times 10^{-6}$.	$K \times 10^9$.	Particulate system.	$K \times 10^9$.
NH ₄ Cl (1 mg. per cu. m.)	5	1.7	Atmospheric nuclei (Kennedy)	1.3
Platinum	2.2	1.5	Small ions	1600
X Smoke	—	3.2	Small ions and nuclei (Nolan)	5000

It is of interest to compare these values with those of Kennedy (*Proc. Roy. Irish Acad.*, 1916, A, 33, 66) for large ions and of Nolan for the rate of combination of small ions and nuclei.

In interpreting these figures, it must be borne in mind that the value of K depends on the rate at which the particles disappear, and the disappearance may be the result of evaporation as well as of coagulation. Small particles of substances of vapour pressure as low as 1×10^{-5} mm. of mercury evaporate at a noticeable rate when suspended in air. Evaporation can be followed conveniently by determining on the same particle the change with time of the rate of fall, and finding the radius by the Stokes-Cunningham law. A large number of observations (Whytlaw-Gray and Patterson, "Smoke," p. 169) were made in this way on droplets of various substances, and it was found that the rate of evaporation is given by the expression $-ds/dt = \text{constant}$, for both small and large droplets; *i.e.*, the rate of change of surface of the droplet on evaporation is independent of its size. This result shows, as might be expected, that diffusion is the determining factor, and that when, as is the case with small droplets, the diffusion gradient is steep, evaporation is accelerated. For instance, droplets of triphenylmethane of about 2×10^{-4} cm. radius were observed to evaporate markedly in 15 minutes, although the vapour pressure of this substance at room temperature is about 2×10^{-5} mm. of mercury. It can be calculated that a particle of this material of radius 1×10^{-5} cm. would disappear in about 5 seconds, provided the same law holds down to very small dimensions.

The coagulation of smokes formed from azobenzene, α -naphthylamine, phenanthrene, and benzil cannot be determined, for although on volatilisation a dense cloud is formed, the particles disappear quickly by evaporation. A steep particulate-volume curve may hence be produced by the joint effect of evaporation and coagulation. Such is the case with mercuric iodide smoke, which gives a steep and straight line for which $K = 2.7 \times 10^{-9}$ cm.³/sec., and evaporation may be the explanation of the abnormal value $K = 1.4 \times 10^{-9}$ found for homogeneous clouds of benzeneazo- β -naphthol of the usual weight concentration.

To gain a clear impression of the process of coagulation, it is worth while considering the time taken to halve the original number of particles. This is easily found from the formula $\sigma - \sigma_0 = Kt$ by putting $\sigma = 2\sigma_0$, whence $t = \sigma_0/K$ or $1/n_0K$. A smoke of cadmium oxide containing initially 5×10^6 particles per c.c. will have its numbers reduced to a half after coagulating for 250 secs., whilst a 15 mg. stearic acid cloud starting from the same number will take 392 secs. All ordinary smokes, provided their particles are not much smaller than 2×10^{-5} cm. radius, coagulate at rates between these limits. When the initial number is increased by powers of ten, the time taken to halve the number decreases in the same proportion; *e.g.*, a system of cadmium oxide containing 5×10^{10} particles per c.c. will halve its numbers in 0.025 sec., and to reach by coagulation a value of 2.5×10^6 , a number 20,000 times smaller, will take only 500 seconds.

It follows, therefore, that when the number concentration is high, coagulation is so rapid that the number per c.c. present after a few minutes is practically independent of the initial number. For instance, using as before the constant for cadmium oxide, *i.e.*, $K = 0.80 \times 10^{-9}$ cm.³/sec., whether we start with a system of 5×10^{12} or of 5×10^8 per c.c., the time taken to form by coagulation a system containing 2.5×10^6 per c.c. is nearly the same. This explains why it is that, on forming a smoke from different quantities of material, the number, by the time the cloud is ready to examine, is the same though the average size is different.

Now all smokes, in contradistinction to dusts which arise by true dispersion of some kind or another, are in reality formed by a process of condensation, and the particles grow from molecular dimensions. The coagulation constant for very small particles is, as we

have seen, distinctly greater, so that in the early stages coagulation will proceed faster. Usually, too, the smokes we have used have been formed by diluting rapidly with air the very concentrated smoke first produced, so that the process before dilution must be extremely fast. In the early stages it is certainly incorrect to assume, as in the above calculation, that the value of K remains the same; it is certainly much greater, and the same stage of the process will undoubtedly be attained earlier. The true particulate-volume curve in the first stages is probably of the form shown in Fig. 4, but is too steep to be followed.

When the formation of a smoke is observed carefully inside the cubic-metre chamber, it is easy to see that the vapour arising from the heated boat condenses immediately, either partially or entirely, to smoke before it is mixed by fanning with excess of air. The volume of this smoke cannot be much greater than the volume of the vapour; in the case of 16 mg. of stearic acid, it can hardly exceed 100 c.c. and is probably much less, so that at a maximum it is one ten-thousandth of the volume of the air with which it is subsequently mixed. But it is not possible to make counts until after some five minutes have elapsed, so, supposing that then 5×10^6 particles per c.c. are present, over 10^7 per c.c. must have been in the smoke immediately after dilution, and the number in the smoke arising from the boat before mixing must have been of the order of 10^{11} or 10^{12} per c.c.

FIG. 4.

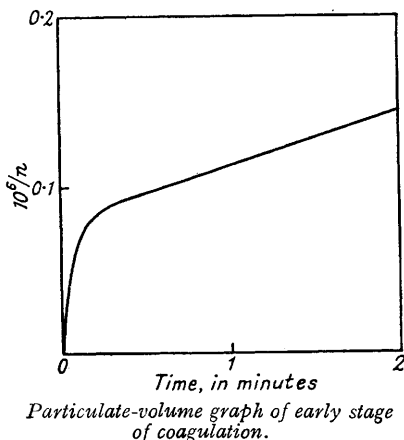
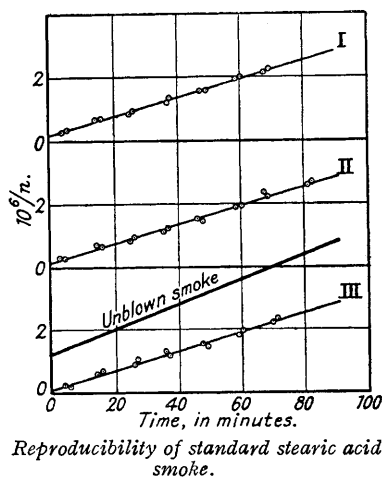


FIG. 5.



It is evident, then, that in smokes formed in this way, coagulation will proceed to an advanced stage, and on dilution a heterogeneous system will be formed containing a large variety of particles of different sizes. It is easy to see that a difference of a small fraction of a second before mixing may alter considerably the character of a smoke. The difficulty of obtaining by this process of formation, systems which coagulate at the same rate is now explained. For a long time we could not get reproducible results with the same smoke formed under the same conditions until the extreme rapidity of the coagulation process in its early stages was recognised. Clearly, in order to get the same result on successive occasions it is necessary to arrange the initial process so that the smoke is diluted instantly. For substances which volatilise at moderate temperatures this can be achieved by passing a very rapid current of hot, dust-free air over the heated boat from which the material is volatilising. The details and experimental conditions for success by this method have been carefully studied by Patterson and Cawood (*Proc. Roy. Soc., 1932, A, 136, 358*) for stearic and oleic acids and also for a number of other substances.

Smokes formed in an air blast in this way, which it is convenient to call "blown smokes," invariably coagulate at a slower rate than smokes produced inside the chamber and mixed by means of a fan, and are reproducible to a marked degree. In a recent paper, these authors give examples of fourteen different stearic acid smokes of the same weight con-

centration, in which the constant K varied only from 0.50 to 0.53×10^{-9} cm.³/sec., and also of thirteen others formed in a much larger chamber (3.3 cu. m.) which gave values ranging between the same extremes. The reproducibility of these smokes is shown in Fig. 5, where the experimental points are given and for comparison an unblown smoke is included. The difference between the blown and the unblown type can only be due to the former being more homogeneous. This is supported by the appearance of the particles in the ultramicroscope, which appear initially of equal brightness and mobility. The use of these blown smokes makes it easier to determine the effect of particle size on coagulation rate. As an example, a series of concordant results obtained with blown smokes of stearic acid of weight concentrations of 10, 15, and 30 mg. may be quoted: the respective K values were 0.56, 0.51, and 0.48×10^{-9} .

As Winkel and Jander have pointed out (*Kolloid-Z.*, 1933, **63**, 5), the conception of homogeneity and heterogeneity in a smoke is purely statistical. No coagulating smoke can be really homogeneous, although at the start it may be nearly so. Its particles may fall within either a narrow or a wide range of sizes according to its past history.

In this sense dusts, in particular, and many industrial smokes are widely heterogeneous, whilst country fogs and clouds approximate to homogeneous systems.

Town fogs are of the heterogeneous type, for the smoke particles of which they are composed coagulate to a considerable extent before they emerge from chimneys and are diluted by the atmosphere. The particles are hygroscopic and readily grow to a comparatively large size, whereupon their opacity is great although the actual number concentration is small. On this account the diminution of fogs by coagulation is slow, although the actual coagulation constant is normal. Experiments made in Leeds show that the number per c.c. in a dense fog is about $1-2 \times 10^5$.

The particles are highly charged electrically and contain approximately equal numbers of both signs. To halve by coagulation the number of particles would take about $3\frac{1}{2}$ hours, and about 16 hours would be required to reduce the total to 2.5×10^4 , a number comparable with the usual dust content of town air.

A very interesting smoke which approximates to the monodisperse or homogeneous type has recently been discovered and investigated by Jander and Winkel (*loc. cit.*). The system is composed of particles of ferric oxide, and is formed by exposing a mixture of iron pentacarbonyl and air to the action of light of short wave-length, a quick photochemical decomposition producing ferric oxide and carbon monoxide. Since the smoke can be formed by uniform radiation throughout the whole volume and no dilution is necessary, a highly homogeneous system can be obtained. Dr. Cawood and I have recently determined its coagulation constant and have examined the complex particles microscopically; the latter are markedly of chain structure and resemble the complexes of cadmium oxide. As was expected, the particulate-volume curve is straight for a 16 mg. cloud, and shows no sign of the curvature found by Jander and Winkel, which we think was due to an error in counting inherent in the slit ultramicroscope they used. The constant found, *viz.*, 0.66×10^{-9} cm.³/sec., lies close to that of a 15 mg. ammonium chloride smoke, and is distinctly smaller than the value for cadmium oxide. This is an important piece of evidence, for it is the first measurement made of the constant of a homogeneous smoke forming chain-like complexes: the arc smokes previously examined were probably more or less heterogeneous.

It appears as if the particle structure has no considerable influence on the coagulation rate, for there is no great difference between this smoke and the standard stearic acid which forms compact aggregates. For sols, however, of very long rod-shaped particles, a large increase in coagulation rate has been found (Wiegner and Marshall, *Z. physikal. Chem.*, 1929, **140**, 1).

So far, coagulation has been considered entirely from the experimental standpoint. It remains to be seen whether a theoretical formulation of the process, similar to that derived by Smoluchowski and applied to sols, is possible for smoke systems.

Assuming that the particles are spherical, are all of the same size, and that Brownian motion alone is responsible for their impacts, Smoluchowski deduced the expression $1/n - 1/n_0 = \frac{2}{3} \cdot RTst/\eta N$ for the change with time of the total number of particles in a

sol undergoing quick coagulation. In this formula, n and n_0 have the usual significance, R is the gas constant, T the absolute temperature, N the Avogadro number, η the viscosity of the medium, and s the ratio of the radius of the sphere of influence of the particle to the actual radius.

If it is supposed that the particles only cohere when they hit, *i.e.*, when they approach within two radii, s becomes equal to 2, and the expression becomes $1/n - 1/n_0 = \frac{4}{3} \cdot RTt/\eta N$ which, for any one medium at a constant temperature, is $1/n - 1/n_0 = Kt$, identical in form with that found experimentally for smokes.

The value of K so calculated, however, though in agreement with the experimental data for sols, as the comprehensive investigations of Tuorila (*Koll. Chem. Beih.*, 1926, 22, 192—394) and Wiegner (Wiegner and Tuorila, *Kolloid-Z.*, 1926, 38, 3) have recently shown, diverges considerably for smokes. For instance, using the appropriate value for η for air at 20°, the calculated K value is 0.29×10^{-9} cm.³/sec. instead of 0.51×10^{-9} found experimentally for standard stearic acid smoke.

The above expression is not really applicable to gaseous or aerial systems, for in these media the mean molecular free path is of the same order of magnitude as the particles themselves, and their mobility is greater than it would be were the medium truly homogeneous. In other words, the smoke particles in Brownian motion move through the spaces in the medium, and the simple resistance law of Stokes, $F = 6\pi\eta rv$, no longer expresses their mobility, but must be modified by a correction factor $(1 + Al/r)$. The validity of this correction term, first proposed by Cunningham, has been proved experimentally within wide limits by Millikan. In this expression, l = mean free path, r = radius of particle, and A = constant.

For the simplest case, then, of a truly homogeneous smoke of spherical particles in the initial stage of coagulation, the expression $\frac{1}{n} - \frac{1}{n_0} = \frac{4}{3} \frac{RT}{\eta N} \left(1 + \frac{Al}{r}\right) t^*$ should apply.

From the form of the equation, it is evident that K is not a constant but grows smaller as coagulation proceeds and the radius of the average particle increases. The experimentally determined graphs, however, are straight lines within the limits of experimental error except for the case of very small particles, for which there is indication of curvature.

Inserting in the above equation the appropriate numerical values at 20°, *i.e.*, $\frac{4}{3} RT/\eta N = 0.292 \times 10^{-9}$ cm.³/sec. and $Al = 9 \times 10^{-6}$, and taking as the radius of the particle the value calculated from the weight in a standard stearic acid smoke of number concentration of 2×10^6 per c.c. when the density of the particle is assumed to be normal, we get $K = 0.510 \times 10^{-9}$ cm.³/sec., whilst the mean value from a large number of concordant experiments is $K = 0.523 \times 10^{-9}$ cm.³/sec.

This agreement between theory and experiment is to some extent misleading. In reality, the experimental value of K is determined by drawing a mean line through all the experimental points, and what is really wanted for a strict comparison is the K value in the early stages which, if there is a slight curvature, would be different. Patterson and Cawood (*loc. cit.*), who have discussed this question in detail, conclude that actually the two values would agree closely if account could be taken of the size distribution of the smoke, and the true mean radius used to compute K at various stages of coagulation. The mean of these values for K should be truly comparable with the experimental value. At present, the only way of arriving at the size distribution in these smokes is by calculation, using Smoluchowski's equations for the numbers of 1, 2, 3, 4 n -fold particles present in a sol after given intervals and applying the result to smokes. This, as the authors point out, must lead to a result which is somewhat inaccurate, but until a method of determining experimentally the size range in smokes is available, it is the only possible approximation.

That there is agreement at all is sufficiently striking considering that the Smoluchowski expression contains no arbitrary constant and depends only on Brownian motion and the theory of diffusion. It is satisfactory, too, to note that only those smokes which approximate to uniformity and the particles of which coagulate to compact aggregates,

* For a derivation of this equation and its application to heterogeneous systems, see "Smoke," pp. 63, 64.

such as oleic and stearic acids, give a good agreement. Heterogeneous smokes and those composed of chain-like particles coagulate too rapidly. The only case investigated of a smoke coagulating to spheres is that of paraffin oil and perhaps resin. Heavy paraffin oil when dispersed inside the chamber gives a typically heterogeneous smoke and coagulates much at the same rate as ammonium chloride dispersed in a similar manner. When, however, it is produced in a blast of heated air, it coagulates at the same rate as the stearic acid smokes. Unfortunately, the data for this smoke are not sufficiently numerous to allow its constant to be known to the same accuracy as that of stearic acid.

Smoluchowski's theory, which has been shown by many workers to be valid for sols, thus finds strong additional support from work with aerial systems. It is interesting to compare the rates of coagulation of the two classes of system. The following two values of the constants of monodisperse systems in water are taken from the results of Tuorila :

Suspension.	Radius of particle, cm.	Coagulation constant, cm. ³ /sec. $\times 10^{11}$.
Kaolin	3×10^{-5}	0.53
Coarse gold sol	9.7×10^{-6}	0.56
Theoretical value at 20°	—	0.52

For comparison the theoretical value calculated from the formula on p. 277 is given. With these may be compared the value $K = 0.52 \times 10^{-9}$ cm.³/sec. found for stearic acid smoke; and it is evident that the constant for smokes is about 100 times greater than for sols and aqueous suspensions. There is, however, an important difference between the quick coagulation of sols and suspensions and the coagulation of smokes, for in sols the process is independent of the size of particle, whilst in smokes coagulation increases rapidly when the particle is smaller than 1×10^{-5} cm. radius. Both these deductions from theory have been confirmed experimentally, but from the experimental evidence with very fine smokes it appears as if the calculated values for K are too high. This point would be worth investigating.

Another important effect foreseen by theory is the greater rate of coagulation of heterogeneous smokes. It is easily shown that the probability of collision between particles of unequal size must be greater than that between those of equal dimensions. The effect is, however, small unless the size difference is great. Smoluchowski assumed in his calculations that the chances of encounter were equal. Whilst this is a close approximation for systems which are uniform at the start, it leads to a coagulation rate which may be much too small when, as in the later stages of coagulation, a large range of sizes is present.

Müller (*Kolloid-Z.*, 1926, **38**, 1) has extended Smoluchowski's equations to include systems which are highly polydisperse, and Tuorila has tested them experimentally for sols and obtained a satisfactory concordance with theory.

When the theory for smokes is examined, it is easy to see that heterogeneity must lead to an increased rate, but it is difficult to apply it quantitatively, and on the experimental side the coagulation of mixed systems consisting of particles of different sizes has not been investigated so far.

In view then of these theoretical considerations and of the experimental evidence, we can form a rough picture of the course of coagulation during the life history of a blown smoke. Any small particles will disappear rapidly from the system, for they will unite with the larger units and with each other at a rate much exceeding the normal.

At a certain stage, depending on the relative dimensions of the units as well as on the actual size of the small ones, a maximum degree of uniformity will be reached, and afterwards the normal rate of coagulation will render the system less and less homogeneous as time goes on. The degree of heterogeneity reached by a homogeneous smoke in the time over which it is usually studied is not great. For example, the number of particles in a stearic acid smoke will have been reduced to one-tenth at the end of an hour, which means that the average radius will be only a little more than twice as great as it was initially, a difference which would produce a very small effect on the coagulation rate. It would be of interest to study the coagulation of smokes over much longer periods.

The expression $K = 4RT(1 + Al/r)/3\eta N$ enables the influence of changes of pressure,

viscosity, and temperature on the coagulation rate of smokes to be predicted. It is evident that in gases of a large mean free path and a low viscosity coagulation should be rapid. Lowering of pressure should produce a change in the same direction, K increasing in proportion with the $(1 + Al/r)$ term, the viscosity remaining constant. A rise in temperature should, however, be partly balanced by the increased viscosity and have only a small effect on K . Up to the present, no smokes formed in gaseous media other than air have been studied. The effect of pressure on the coagulation rate of ferric oxide aerosols produced as described on p. 276 has been investigated by Jander and Winkel (*loc. cit.*), who find that the number of particles remaining after 1 hour in systems of the same initial concentration varies linearly with the pressure. This is not in agreement with the predictions of theory and needs confirmation. It would be interesting if it were established.

An extension of these methods of investigations to coarser systems such as dusts would be of great interest, for in these the size distribution can be measured microscopically with some accuracy, as the researches of Green (*J. Indust. Hyg.*, 1934, 16, 29) have shown. Also, it appears from his preliminary observations that these suspensions coagulate faster than smokes, which may be due to the larger particles falling past the smaller and so increasing the chances of a collision. This has been proved to be the case for aqueous suspensions by Wiegner and Tuorila (*Koll. Chem. Beih.*, 1927, 24, 1) in their investigation of what they term "orthokinetic" coagulation.

A factor which so far has not been considered in discussing coagulation in smokes is electrification. The particles in smokes produced at a high temperature, such as arc smokes, smokes from flames, etc., are as might be expected highly charged, though usually the smoke as a whole is electrically neutral. In these, the number of charged particles of opposite sign remains constant for long periods during coagulation, owing probably to the large number of electrons each particle carries and to the rarity of collisions between units carrying equal and opposite charges. Smokes formed by volatilisation at low temperatures and also by many chemical reactions contain at first few charged particles, but as coagulation proceeds the proportion of these increases and may rise in a few hours to 75% of the total. This effect is due to the catching of ions from the surrounding air, and the ions so caught do not easily escape again.

Patterson (*Phil. Mag.*, 1931, 12, 1175) has shown how the change in the proportion of charged units with time can be calculated from the coagulation constant of the smoke and the rate of formation of ions in the surrounding air. Whether the presence of electrified particles in a smoke influences the rate of coagulation has not been determined. It is, however, certain that the presence of charges produces no very marked effect. Rough experiments on the coagulation rates of charged and uncharged smokes of zinc oxide showed no clear distinction in their behaviour. Similarly, no clear difference could be detected in the coagulation rate of uncharged ammonium chloride and a highly charged smoke of the same material formed in the presence of X -rays. Smokes containing a large percentage of particles charged to one sign can be formed by means of the silent electric discharge, but these in course of time lose their unipolar character and after a few hours contain equal numbers of positive and negative units. It might be expected that coagulation in a unipolar smoke would be arrested or its rate at least diminished. Although experiments have been made on this, the evidence so far is confused and no certain conclusions can be drawn.

It is evident that the coagulation of smoke and other disperse systems in air presents a close analogy to the process of quick coagulation in sols. In both the particles collide as a result of Brownian motion and the agreement between theory and experiment renders it probable that in smokes as in sols every collision between particles is effective.

In aerial systems the greater velocity of the process is a consequence not only of the much smaller viscosity but also of the discontinuous nature of the medium, air, which for the smoke particle of average size is far from homogeneous. As a result, coagulation of particles of radius 1×10^{-5} cm. or 0.1μ is about twice as fast as it would be in a continuous medium of the same viscosity as air, and it increases rapidly as the particle size falls, whilst in sols it is independent of size. At present, on account of the paucity of experimental data a correlation of coagulation velocity and particle size is only possible with

the help of theory. Although there is no doubt whatever that the effect is real, further experimental work would provide an interesting test of current theories.

Another factor which affects the coagulation process in both sols and smokes is the degree of uniformity in size of the particles. Whether it is possible to form a smoke which in this sense is really homogeneous may be questioned, but theoretically it is easy to see that a small degree of heterogeneity must have little effect and experimentally it is found that the more nearly a smoke approaches uniformity the slower it coagulates.

These two effects, the greater probability of encounter (*a*) when the particles are small and (*b*) where they vary considerably in size, determine the course of the coagulation process during the life history of smokes. Initially the so-called coagulation constant K is large on account of the small size of the particles; it decreases rapidly at first and afterwards more slowly, but as the smoke becomes heterogeneous the second effect (*b*) becomes operative and tends to make K increase again. The result is that these two effects often partially neutralise each other, with the result that K found experimentally is a constant and the particulate volume curve is a straight line.

As far as this field has been explored at present no counterpart to the process of slow coagulation in sols has been discovered, nor has any definite indication been found of the possibility of arresting coagulation and obtaining a stable smoke.

In the reverse direction, since, apparently, smoke particles always cohere on impact and do not rebound, there is little possibility of accelerating the coagulation rate except by processes which increase the sphere of influence of the particles, such as turbulence, sound waves, or electrical forces.

Although the investigations described here have thrown some light on the properties of a class of disperse system about which little is known, much remains to be done, and it is hoped that this preliminary survey may attract attention to the importance of further studies in this field.
