Interactions in the Atmosphere of Droplets and Gases

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1 Introduction

There is an important class of chemical reactions in which initially gaseous substances produce suspended particles or droplets. The first part of this article is primarily concerned with the chemical and physical mechanisms which may contribute to the formation of such aerocolloids, and to the changes in size distribution as they develop or diminish. In the latter part the chemistry and kinetics of some specific aerosol-producing reactions will be considered. Because of their important contribution to particulate air-pollution, most attention will be given to reactions involving sulphur dioxide. In localities where fossil fuels are burned, it is of course a major gaseous pollutant in the atmosphere, and its interaction with other substances can frequently result in smogs, or in droplets of harmful acid.

More kinetic studies of gas–particle interactions should be encouraged, and not only because of their relevance to pollution and related problems of waste-gas cleaning. In some manufacturing processes major products are required in the form of fine particles. The ultimate median particle size may outweigh other considerations, as for instance with titanium dioxide pigment, where the radius has to be kept within a distribution close to 0.2 μm if the light-scattering quality is to be maintained. Again, if particles in the region 0.1 to 10 μm are to be collected by inertial or electrostatic precipitation, the efficiency will be improved by keeping the median size as high as possible.

The incorporation of water into the condensed phase of aerosols will be a major consideration. In humid atmospheres water will tend to condense to form droplets on any hygroscopic solid particle which may be present. For instance, with nuclei such as crystals of sodium chloride and ammonium sulphate, which are common in most atmospheres, relative humidities of only 78% and 73% respectively are required for droplets of solution to form. Now droplets of pure water are inherently unstable in that they grow spontaneously at any given relative humidity. This occurs because the vapour pressure at a small droplet falls as its curvature decreases. But droplets containing a solute also exhibit an opposing effect which predominates at smaller sizes. This is the raising, according to Raoult's law, of the vapour pressure as dilution proceeds. Thus any increment in growth is self-correcting and the droplet reaches a stable, equilibrium size.

Of course when growth becomes arrested in this way, droplets can stay suspended indefinitely, and this can be of enormous practical significance. Thus mists based on soluble air-pollutants may be stable and persistent in ill-ventilated atmospheres. Similar stability can be a troublesome feature of mists which are sometimes formed in sulphuric acid manufacture, and which cannot yet be consistently eliminated by design of the plant.

These examples should suffice to show that there will be considerable economic importance in understanding the factors which determine size distributions in aerosols, since it may allow effective control of their production and subsequent behaviour.

The kinetic processes which aerosol particles undergo can be briefly defined as follows. Nucleation is the initial establishment of a stable condensed phase and may occur either homogeneously, that is by spontaneous aggregation of the condensate, or heterogeneously—by association of the condensate with an already established nucleus of a foreign substance. Growth of particles and droplets is defined as accretion of gaseous molecules at their surface. Unless the number concentration is below about 10^{10} particles m^{-3}, growth will be accompanied to a significant extent by coagulation, the adhesion of particles as a consequence of random or induced collisions. At this level, coagulation would deplete their concentration by about 1 % h^{-1}.

After particles of moderate density have exceeded a certain diameter, they will fall in still air with appreciable speeds (about 10^{-3} cm s^{-1} for 10 μm diameter). Hence as an aerosol develops, removal of larger particles by sedimentation is a process which applies an effective upper limit to the ultimate size distribution in the suspension.

In the review which follows of the mechanisms of these processes some recent theories are summarized, and it is intended particularly to stress those cases where chemical reaction accompanies transfer of material across the phase boundary.

2 Mechanisms

Theoretical treatments of nucleation and of coagulation include fundamental difficulties and, perhaps as a consequence, have been more numerous than kinetic predictions for growth. In the latter process, the models have necessarily been rather specific, depending on variables such as the diffusion field, the number of components, and their reactivities.

A. Nucleation of Particles in Supersaturated Vapours.—The formation of a condensation nucleus in a homogeneous medium depends on fluctuations in the parent phase giving rise to an aggregate or cluster of molecules, and for the cluster to be stable a certain critical size must be exceeded.[1,2] In the thermodynamic approach to the frequency of such events a free-energy barrier is postulated, and variation of the rate of appearance of stable nuclei with the

[1] M. Volmer and A. Weber, *Z. phys. Chem. (Leipzig)*, 1926, **11** 9, 277.
[2] Y. I. Frenkel, 'Kinetic Theory of Liquids', Oxford University Press, 1946.

temperature (T) and with the supersaturation ratio (S) is predominantly exponential. The exponent W^* may be expressed by

$$W^* = -\frac{16\pi}{3}\left(\frac{m}{\rho_L \ln S}\right)^2\left(\frac{\sigma}{kT}\right)^3$$

where m = mass of molecule, σ = surface free-energy, ρ_L = density of liquid,

k = Boltzmann's constant, and $S = \dfrac{P_v}{P_\infty} = \dfrac{\text{vapour pressure at droplet surface}}{\text{vapour pressure at plane surface}}$

This follows immediately from consideration of the balance, as a droplet grows, between the free energy expended in the formation of the surface, and the free energy derived from the gas molecules which are condensed.

This form of the exponent was also used by Becker and Döring,[3] and more recent modifications to the theory have been reviewed by Wegener and Parlange.[4] The rate of nucleation is positive for all values of the supersaturation ratio, but in practice it increases very sharply around a certain value of S.[2,4] In terms of a given experiment, an observable amount of nucleation will occur in a practicable time interval only when this value, S^*, is exceeded.

Various authors have reviewed the agreement of experiments with these theories.[4—7] Whereas some experiments have been intended to measure the rate directly, others have measured the dependence of S^* on temperature. The latter test the rate equation in so far as it predicts that $\dfrac{\rho_L}{m}\left(\dfrac{T}{\sigma}\right)^{1.5} . \ln S^*$ should be a constant. Using an expansion cloud chamber, Powell[8] determined S^* for water vapour at a number of temperatures, and his results satisfy this relation to within about 6%.

So as to avoid significant depletion of the vapour concentration by growth on the nuclei, and to preserve the isentropic nature of the expansion, experiments have usually been designed to produce low concentrations of nuclei in brief experimental times. Typical values in cloud chambers would be 10—10^2 nuclei cm^{-3}, and 10^{-1}—10^{-2} s.[7,9,10] Besides cloud chambers,[7,8] devices used recently include rarefaction tubes,[11] jet quenching apparatus,[12,13] and supersonic nozzles.[4,6,14] With the latter, experimental times are in some cases about 10^{-5} s.

Experiments have nearly always been done with water, and surprisingly the

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[3] R. Becker and W. Döring, *Ann. Physik*, 1935, **24**, 719.
[4] P. P. Wegener and J. Y. Parlange, *Naturwiss.*, 1970, **57**, 525.
[5] B. J. Mason, *Discuss. Faraday Soc.*, 1960, **30**, 20.
[6] P. P. Wegener and A. A. Pouring, *Phys. Fluids*, 1964, **7**, 352.
[7] L. B. Allen and J. L. Kassner, *J. Colloid Interface Sci.*, 1969, **30**, 81.
[8] C. F. Powell, *Proc. Roy. Soc.*, 1928, **A119**, 553.
[9] J. L. Kassner and R. J. Schmitt, *J. Chem. Phys.*, 1966, **44**, 4166.
[10] B. G. Schuster and W. B. Good, *J. Chem. Phys.*, 1966, **44**, 3132.
[11] P. P. Wegener and G. Lundquist, *J. Appl. Physics*, 1951, **22**, 233.
[12] A. G. Sutugin and N. A. Fuchs, *J. Colloid Interface Sci.*, 1968, **27**, 216.
[13] W. Higuchi and C. T. O'Konski, *J. Colloid Sci.*, 1960, **15**, 14.
[14] P. P. Wegener and L. M. Mack, *Adv. in Appl. Mech.*, 1958, **V**, 301.

original work of Volmer and Flood[15] on vapours of several aliphatic alcohols and esters has seldom been repeated.[16,17] Alkyl chlorides[18,19] and recently some n-alkanes[20] and even metal vapours have been experimentally investigated. Continued attempts are made to compensate for the depletion of available vapour which occurs in the course of rarefaction experiments,[21] and to overcome the fundamental problem that neither radius- nor surface-free-energy are well-defined quantities in the clusters of, say, tens of molecules which constitute most critical homogeneous nuclei.[7,22] The latter deficiency is more acute the higher the supersaturation ratio since the number in the critical nucleus is less.[2]

Solid particles of chemical salts are frequently found in the atmosphere and remain so as long as the relative humidity is low enough. They may originate not by direct transition from gas to solid phase, but either by subdivision of grosser matter or by evaporation of droplets of solution. Data on vapour condensation to form crystalline nuclei are few; for the interaction of ammonia and hydrogen chloride to form solid ammonium chloride classical nucleation theory appears to apply,[23] and Turkevich[24] has shown from electron micrographs of smokes of metals that the size-distribution curve can be used to deduce the distribution of nuclei formed from the gaseous state.

Many forms of heterogeneous nuclei are known, *e.g.* ions, foreign particles, or even foreign gas-phase molecules, such as the important pollutant molecules SO_2, SO_3, H_2SO_4, *etc.*[25] Dunning[26] and Mason[5] reviewed the agreement of experiments with theory for heterogeneous nucleation.

Experiments have been made on hundreds of nucleating substances to examine their propensity for nucleating water droplets and ice particles. The size of the nuclei is only influential in the range up to about 0.1 μm,[27,28] and below 10^{-2} μm efficiency is very low. The efficiency of porous particles as nuclei has been shown to be promoted by residual water previously frozen into their capillary pores,[29,30] a modification which could occur while particles are at high altitudes.

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[15] M. Volmer and H. Flood, *Z. phys. Chem. (Leipzig)*, 1934, **A170**, 273.

[16] W. G. Courtney, *J. Chem. Phys.*, 1962, **36**, 2009, 2018.

[17] J. L. Katz and B. J. Ostermeier, *J. Chem. Phys.*, 1967, **47**, 478.

[18] L. Scharrer, *Ann. Physik.*, 1939, **35**, 619.

[19] D. B. Dawson, E. J. Wilson, P. G. Hill, and K. C. Russel, *J. Chem. Phys.*, 1969, **51**, 5389.

[20] J. L. Katz, *J. Chem. Phys.*, 1970, **52**, 4733.

[21] L. H. Lund and J. L. Rivers, *J. Chem. Phys.*, 1966, **45**, 4612.

[22] J. Lothe and G. M. Pound, *J. Chem. Phys.*, 1962, **36**, 2080.

[23] S. Twomey, *J. Chem. Phys.*, 1959, **31**, 1684.

[24] J. Turkevichin, 'Proceedings of the 3rd Symposium on Fundamental Phenomena in the Materials Sciences', ed. L. J. Bonis, P. L. de Bruyn, and J. J. Duga, Plenum Press, New York, 1965, p. 195.

[25] Y. I. Kogan, L. E. Donetskaya, L. N. Pavlov, and E. N. Rubin, *Doklady Akad. Nauk S.S.S.R.*, 1968, **179**, 1145.

[26] W. J. Dunning, *Discuss. Faraday Soc.*, 1960, **30**, 9.

[27] N. H. Fletcher, *J. Chem. Phys.*, 1958, **29**, 572.

[28] I. Sano, Y. Fujitani and Y. Maena, *Mem. Kobe Marine Obs. Kobe, Japan*, 1960, **14**, 107.

[29] K. Higuchi, N. Fukuta, and J. Norihiko, *J. Atmos. Sci.*, 1966, **23**, 187.

[30] N. Fukuta, *J. Atmos. Sci.*, 1966, **23**, 741.

B. Growth and Evaporation of Droplets.—*Without Chemical Reaction.* Mason[31] gives a useful summary of the diffusion equations for mass transfer between a droplet and a surrounding vapour which is stationary relative to the droplet, and in which the concentration of the vapour varies smoothly right up to the interface:

(i) In evaporation, the mass, m, is lost at a rate proportional to the radius

$$\frac{\mathrm{d}m}{\mathrm{d}t} = -4\pi r\, D(\rho_{\mathrm{v,s}} - \rho_{\mathrm{v}}) \tag{1}$$

where r is the drop radius, D is the diffusion coefficient of the vapour, and $\rho_{\mathrm{v,s}}$ and ρ_{v} are its densities at the surface and at a large distance.

(ii) The rate of decrease of radius is inversely proportional to the radius

$$r \cdot \frac{\mathrm{d}r}{\mathrm{d}t} = -\frac{D}{\rho_{\mathrm{L}}}(\rho_{\mathrm{v,s}} - \rho_{\mathrm{v}}) \tag{2}$$

(iii) The surface area, A, falls off linearly with time (and thus the radius decreases parabolically with time)

$$\frac{\mathrm{d}A}{\mathrm{d}t} = -\frac{8\pi D}{\rho_{\mathrm{L}}}(\rho_{\mathrm{v,s}} - \rho_{\mathrm{v}}) \tag{3}$$

These three statements are equivalent and consist in Fick's diffusion equation, integrated under the assumption of a distribution of the vapour density which is independent of time. The error due to this approximation is of the order of only a few tenths per cent for water at room temperature.[32] With appropriate choices of the value of ρ_{v} further physical models can be considered:

(i) For evaporation into a vacuum

$$\frac{\mathrm{d}m}{\mathrm{d}t} = -4\pi r^2 \rho_{\mathrm{v,s}} \alpha \left(\frac{kT}{2\pi m}\right)^{\frac{1}{2}} \tag{4}$$

where α is the evaporation coefficient of the liquid.

(ii) For the growth of a droplet on a nucleus of soluble hygroscopic material ρ_{v} will be equivalent to the saturated vapour pressure, p_{∞}, above a plane surface of the solvent. The Kelvin equation[33] in combination with Raoult's law leads to the expression

$$\frac{\rho'_{\mathrm{v,s}}}{\rho_{\mathrm{v}}} = \frac{p'_{\mathrm{s}}}{p_{\infty}} = \left(\exp\frac{2\sigma' M}{\rho'_{\mathrm{L}} RTr}\right)\left(1 + i\,\frac{n_1}{n_2}\right)^{-\rho_{\mathrm{L}}/\rho'_{\mathrm{L}}} \tag{5}$$

where p'_{s} is the vapour pressure at the surface of the resulting droplet of solution.

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[31] B. J. Mason, 'Physics of Clouds', Oxford University Press, 1971, p. 122.

[32] N. A. Fuchs, 'Evaporation and Droplet Growth in Gaseous Media', Pergamon, Oxford, 1959, p. 63.

[33] W. Thomson, *Proc. Roy. Soc. Edinburgh*, 1870, **7**, 63.

The other properties of the solution are σ' the surface free energy, M the molecular weight of the solvent, ρ'_L the density, i the van't Hoff factor, and n_1/n_2 the mole ratio.

Equation (5) can be written as follows, for dilute aqueous solutions with mass m of uni-univalent solute and mass S of solvent

$$\frac{p'_s}{p_\infty} = \left(\exp \frac{2\sigma' M}{\rho'_L RTr}\right)\left(1 - \frac{8.6m}{S\,r^3}\right) \tag{6}$$

Besides diffusion, the other main factor governing the rate of growth is the rate at which latent heat can be dissipated. This dissipation is limited by conduction in the gas phase and is thus expressed by

$$r\,.\frac{dr}{dt} = \frac{K}{L\rho'_L}(T_s - T) \tag{7}$$

where T_S and T are the temperatures at the droplet surface and in the surroundings, and K and L are respectively the thermal conductivity of the gas and its latent heat.

By combination of equations (1), (6), and (7) with the Clausius–Clapeyron equation for dp/dT, Mason gives the following useful rate expression

$$r\,.\frac{dr}{dt} = \frac{\left(S - 1 - \frac{2\sigma' M}{\rho'_L RTr} - \frac{8.6m}{S\,r^3}\right)}{\frac{L^2 M\rho'_L}{KRT^2} + \frac{\rho'_L\,R\,T}{DMp'_s}} \tag{8}$$

As the droplet grows, the curvature and strength of solution become no longer sufficient to affect the value of p'_s appreciably, and the equation (8) reduces to the reciprocal relation of radius with its rate of increase [equation (2)].

From equation (8) the time can be calculated for growth to specified radii for droplets containing given masses of nucleating material. A typical result, also quoted by Mason, is that under slight supersaturation water droplets will grow on a nucleus of NaCl of mass 10^{-13} g, to 5 μm radius in about five minutes, but will need a further 25 minutes to double this radius.

To turn from the growth to considerations of equilibrium between droplet and vapour, it was stated in the introduction that below a certain size droplets containing a solute can differ from those of pure liquid in possessing inherent stability with respect to growth. The transition to spontaneous growth comes when the size is such that the curvature term in (5) or (6), $\ln p'_s \propto 1/r$, dominates the Raoult's Law term, which for dilute solutions is of the form $\ln p'_s \propto 1/r^3$. The expression (6) can be used to calculate this transitional size, and predicts for instance that with a supersaturation of water of 0.05% and a nucleus of 10^{-14} g of NaCl, growth is spontaneous only after the radius has exceeded 2 μm.

As examples of the size range in which solution droplets are stable, Vohra and

Nair[34] quote that aqueous sulphuric acid droplets at 90% relative humidity will be stable at a radius of 25.4 nm. when the mole fraction is 0.09, whereas at mole fraction 0.33 the equilibrium radius is 2.1 nm.

It must be repeated that the expressions quoted above for the growth and evaporation of droplets have all been based on assumptions of control by molecular diffusion in a stagnant gas phase containing no discontinuity of concentration near the surface. This continuum model becomes invalid when droplets are small enough to give values greater than about 10^{-2} for the Knudsen number, K_n, which is the ratio of molecular mean-free-path to droplet radius. At atmospheric pressures, this means any droplet of radius below about 7 μm. The consideration of deviations for droplets smaller than this will be limited here to some practical cases. The simplest correction is valid to some limit near $K_n = 0.25$, *i.e.* for particles of radius down to about 0.3 μm. In the theory it is assumed that the vapour concentration gradient is continuous only at distances from the surface in excess of some 1—5 gas mean-free-paths. In other words a sharp discontinuity exists at that distance. The consequent ratio of d*m*/d*t* [equation (1)] in a continuum to that in this 'slip flow' regime is

$$1 + \frac{D}{\alpha}\left(\frac{2\pi m}{kT}\right)^{\frac{1}{2}}$$

The second term depends critically on the evaporation coefficient α, and in fact predominates when the latter is significantly less than unity. Some empirical results for dibutyl phthalate, quoted by Fuchs,[32] indicate that the correction to equation (1) is nearly linear with K_n, and even at $K_n = 0.75$ it amounts to only about a factor of two. A different theoretical model with minimal intermolecular collisions is already becoming necessary when K_n has risen to such high values.

Considering now water droplets, the $1 + \frac{D}{\alpha}\left(\frac{2\pi m}{kT}\right)^{\frac{1}{2}}$ correction amounts to a factor of two even at radii of about 10 μm if the conventional value of 0.04 is taken for α. Such a low value of α is suspect for pure water but values as low as 10^{-4} have been observed for water surfaces where evaporation is inhibited by contamination. Hence for droplets which contain surfactant contamination the discontinuity correction would be vital at a much larger radius than for droplets of pure water.

It is not the purpose here to review experimental tests of the above rate equations for single substances, but materials and sizes of droplets tested range from water of diameter about 1 mm (ref. 32) to lead and bismuth at less than 30 nm (ref. 35).

Chemically Reacting Aerosols. When chemical reaction at a particle is involved, the rate of its growth or shrinkage may again be limited by diffusion in the gas

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[34] K. G. Vohra and P. V. N. Nair, *J. Aerosol Sci.*, 1970, **1**, 127.
[35] M. Blackman, N. D. Lisgarten, and L. M. Skinner, *Nature*, 1968, **217**, 1245.

phase, or by diffusion inside the droplet. Alternatively, and particularly in the initial stage, some reaction in the interface may be the rate-limiting step. Following the latter model, Cadle and Robbins[36] give the following upper limit to the initial rate for the general case of gas molecules A, interacting with particles B:

$$-\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = \frac{3k[\mathrm{A}]_0[\mathrm{B}]_0}{r_0} \tag{9}$$

where k is a rate constant, and $[\mathrm{A}]_0$ and $[\mathrm{B}]_0$ are the original concentrations of A and of particles with radius r_0.

If a steady state of reaction is achieved, which is frequently the case under diffusion control, the time-independent equations for the diffusion are, for the interior of the spherical droplet

$$D_\mathrm{i}\left(\frac{\mathrm{d}^2C_\mathrm{i}}{\mathrm{d}r^2} + \frac{2}{r}\cdot\frac{\mathrm{d}C_\mathrm{i}}{\mathrm{d}r}\right) + q = 0 \tag{10}$$

with a reaction rate q, diffusion coefficient D_i, and reactant concentration C_i.

Also, for outside the droplet

$$\frac{\mathrm{d}^2C_\mathrm{e}}{\mathrm{d}r^2} + \frac{2}{r}\frac{\mathrm{d}C_\mathrm{e}}{\mathrm{d}r} = 0 \tag{11}$$

and at the interface where $r = r_0$

$$D_\mathrm{i}\frac{\mathrm{d}C_\mathrm{i}}{\mathrm{d}r} = D_\mathrm{e}\frac{\mathrm{d}C_\mathrm{e}}{\mathrm{d}r} \tag{12}$$

Now several predictions of absorption rate can be distinguished:

(i) If diffusion in the gas phase is rate-controlling, the solution of the equations for the growth of a stationary droplet is simply equation (1) with reversed sign and ρ representing the density of the gas A.

(ii) When the controlling factors are internal diffusion and the reaction rate, different solutions arise according to the kinetic order of the reaction.

For a zero-order reaction with a rate constant k_0, the solution for the case where C_i still has a finite value at the centre of the droplet is

$$\frac{\mathrm{d}m}{\mathrm{d}t} = \frac{4\pi}{3}k_0r_0^3 \tag{13}$$

If, however, C_i falls to zero at some point in the interior where the radius is r_1, then

$$\frac{\mathrm{d}m}{\mathrm{d}t} = \frac{4\pi}{3}k_0\,(r_0^3 - r_1^3) \tag{14}$$

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[36] R. D. Cadle and R. C. Robbins, *Discuss. Faraday Soc.*, 1960, **30**, 155.

Consequently if C_0 is the value at the interface, the concentration falls according to the profile

$$C_{\mathrm{i}} = C_0 - \frac{k_0}{6D_{\mathrm{i}}}(r_0^2 - r^2) - \frac{k_0 r_1^3}{3Dr_0} + \frac{k_0 r_1^3}{3Dr} \tag{15}$$

A convenient kinetic parameter is the rate of absorption per unit area of drop surface,

$$R = \frac{1}{4\pi r_0^2} \cdot \frac{\mathrm{d}m}{\mathrm{d}t}$$

Substitution of this into equation (15) eliminates r_1 and gives a relationship between R and the other measurable variables

$$C_0 = \frac{(k_0 r_0^2)}{6D_{\mathrm{i}}}\left\{1 - 6\left[\frac{1}{2}\left(1 - \frac{3R}{r_0 k_0}\right)^{\frac{2}{3}} - \frac{1}{3}\left(1 - \frac{3R}{k_0 r_0}\right)\right]\right\} \tag{16}$$

If the distance of penetration is small, however, *i.e.* the reaction is all occurring in a thin outer shell of the particle,

$$R = \sqrt{2C_0 D_{\mathrm{i}} k_0} \tag{17}$$

or

$$\frac{\mathrm{d}m}{\mathrm{d}t} = 4\pi r_0^2 \sqrt{2C_0 D_{\mathrm{i}} k_0} \tag{18}$$

For a reaction which is first order with respect to A, and has a rate constant k_1,

$$\frac{\mathrm{d}m}{\mathrm{d}t} = 4\pi r_0 D_{\mathrm{i}} C_0\left[\frac{\sqrt{k_1 r_0^2}}{D_{\mathrm{i}}} \,.\, \coth\frac{\sqrt{k_1 r_0^2}}{D_{\mathrm{i}}} - 1\right] \tag{19}$$

Also, when the dimensionless quantity $\sqrt{k_1 r_0^2/D_{\mathrm{i}}}$ is large,

$$\frac{\mathrm{d}m}{\mathrm{d}t} = 4\pi r_0^2 C_0 \sqrt{D_{\mathrm{i}} k_1} \tag{20}$$

In the review of experiments which follows the next section, the applications of these solutions will be discussed where they have proved feasible.

C. Coagulation of Particles by Brownian Motion.—The most important experimental facts of coagulation are simply expressed as follows:

(i) A second-order decay is observed[37] in n, the total number of particles in unit volume,

$$-\frac{\mathrm{d}n}{\mathrm{d}t} = K_0 \,.\, n^2 \tag{21}$$

(ii) The value of K_0 increases if the system becomes more polydisperse and

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[37] R. Whytlaw-Gray and H. S. Patterson, 'Smoke', Arnold, London, 1932, p. 8.

decreases as the particle size increases. Both the effects contribute as coagulation proceeds and the net result is that equation (21) is a good approximation if K_0 is assumed to be constant throughout.

(iii) It is hard to deduce the original population of a decaying aerosol from counts made a significant time after coagulation has commenced. This is because of the reciprocal relationship between n and t, and the magnitudes of K_0, generally about 10^{-15} m^3 s^{-1} for aerosols.

The rate of change of concentration as a result of collisions of spherical particles of radii r_1 and r_2 is theoretically predicted[38] to be

$$-\frac{\mathrm{d}n_{1,2}}{\mathrm{d}t} = \frac{(2n_1n_2kT)}{3\eta}s(r_1 + r_2)\left[\frac{(1 + (Al/r_1)}{r_1} + \frac{1 + (Al/r_2)}{r_2}\right] \qquad (22)$$

This prediction includes Einstein's expression for diffusivity in the Stokes regime, together with Cunningham's correction for the similarity, in aerosols, of the particle size r and the gas mean free path l. The other variables are:

$s(r_1 + r_2)$ = the radius of spheres of influence
A = Cunningham constant (*ca.* unity)
η = viscosity of the gas.

By making the simplification that $r_1 = r_2$, a comparison between polydisperse and monodisperse coagulation-constants is possible. The two constants are distinguished by containing two different factors which are respectively $X = D_1r_1\,(r_1 + r_2)(1/r_1 + 1/r_2)$ and $Y = 4D_1r_1$. Hence, since $X = D_1r_1[4 + (\sqrt{r_1/r_2} - \sqrt{r_2/r_1})^2]$, therefore $X > Y$. Gillespie[39] and others[40] have shown that the difference is never more than 2% for the skewed particle-size distributions encountered, for instance in atmospheric aerosols. In addition, Gillespie has shown[39] that the number of collisions induced by shear will be decreased by polydispersity.

Since the largest particles disappear from an aerosol suspension by sedimentation, there is a tendency for the size distribution to become self-preserving. This will be the practical consequence of the interaction of nucleation, growth, and coagulation.

There have been numerous experimental confirmations of this self-preservation mechanism.[41—43] Several theoretical approaches have been adopted to model it, and the most comprehensive allow for growth both by coagulation and by single-molecule condensation, and for diminution in size both by splitting into

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[38] M. Smoluchowski, *Z. phys. Chem. (Leipzig)*, 1917, **92**, 129.
[39] T. Gillespie, *J. Colloid Sci.*, 1963, **18**, 582.
[40] S. E. Devir, *J. Colloid Sci.*, 1966, **21**, 9.
[41] C. E. Junge, *Ber. Deut. Wetterd.*, 1952, **35**, 261.
[42] D. K. Swift and S. K. Friedlander, *J. Colloid Sci.*, 1964, **19**, 621.
[43] W. E. Clark and K. T. Whitby, *J. Atmos. Sci.*, 1967, **24**, 677.

smaller aggregates and by evaporation of single molecules.[42—54] Formally all such steps can be represented as follows:

$$\frac{\mathrm{d}n_k}{\mathrm{d}t} = \tfrac{1}{2}\sum_{i+j=k} N_{i,j} + \sum_{i=1}^{i=\infty} S_{i,k} - \sum_{i=1}^{i=\infty} N_{i,k} - \tfrac{1}{2}\sum_{i+j=k} S_{i,j} \tag{23}$$

Here, in unit time, $N_{i,j}$ is the number of collisions between i and j clusters which achieve coalescence, and $S_{i,j}$ is the number of splittings into i and j clusters. The older theories of nucleation and coagulation are special cases of (23). For instance, the Volmer and Becker–Döring theories express the process of nucleation under supersaturation by selecting only the terms where a single molecule and a cluster are interacting

$$\frac{\mathrm{d}n_k}{\mathrm{d}t} = N_{1,k-1} + S_{1,k} - N_{1,k} - S_{1,k-1} \tag{24}$$

Smoluchowski's approach to coagulation[38] includes only terms such as are represented in equation (22), and Friedlander[44] has pointed out that it ought to be extended as follows to take account of the reverse processes, splitting and evaporation:

$$\frac{\mathrm{d}n_k}{\mathrm{d}t} = \pi\Big[\tfrac{1}{2}\sum_{i+j=k}(D_i + D_j)s_{i,j}(r_i + r_j)n_i n_j - n_k \sum_{i=1}^{i=\infty}(D_i + D_k)s_{i,k} \times (r_i + r_k)n_i\Big] \tag{25}$$

Using the generalized theory, Friedlander *et al.*[46] have shown that a dimensionless parameter can be used to describe the relative rates of condensation and coagulation and to define the point where they compensate one another to produce a surface-area per unit gas-volume which does not vary with time. If the said parameter, which depends on the supersaturation, does not take the unique value mentioned, the supersaturation must vary with time in a specific way for the distribution still to be self-preserving. Numerical evaluations over the whole size spectrum fitted well to this theory and analytical solutions were obtained at the upper and lower ends, which are the influential regions for the preservation mechanism.

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[44] S. K. Friedlander, *Phys. Fluids*, 1960, **3**, 693.
[45] S. K. Friedlander and C. S. Wang, *J. Colloid Interface Sci.*, 1966, **22**, 126.
[46] J. Pich, S. K. Friedlander, and F. S. Lai, *J. Aerosol Sci.*, 1970, **1**, 115.
[47] S. E. Devir, *J. Colloid Sci.*, 1963, **18**, 744.
[48] G. M. Hidy, *J. Colloid Sci.*, 1965, **20**, 123.
[49] W. A. Mordy and E. X. Berry, *J. Atmos. Sci.*, 1965, **22**, 340.
[50] S. Twomey, *J. Atmos. Sci.*, 1964, **21**, 553.
[51] V. I. Smirnov, *Trudy Tsentr. Aerolog. Observ.*, 1964, **55**, 86 (*Ref. Zhur. Khim.*, 1965, 11B1018).
[52] M. V. Buikov, *Kolloid Zhur.*, 1967, **29**, 42.
[53] M. V. Buikov, and A. V. Silaev, *Kolloid Zhur.*, 1967, **29**, 34.
[54] G. Zebel, *Staub*, 1959, **19**, 381.

3 Discussion of Reactions

The reactions to be discussed here are classified according to chemical nature without attempting to separate laboratory studies from designed production of aerosols in manufacture, or from their inadvertent production in the atmosphere.

In the low-altitude atmospheric chemistry which is relevant to air pollution, certain variables may be hard to measure at the true site of a reaction. Examples of such variables are the intensity of incident sunlight and the concentration of water vapour, or indeed of any reactant in so far as it might be subject to spatial and temporal variations which are not due to chemical conversion. In the laboratory, values of these variables can be set, but there is always some doubt about extending the conclusions to a more general environment.

A. Aerosols involving Sulphur Dioxide.—Particles and droplets composed of sulphates form an important part numerically of the atmospheric aerosol.[55,56] For instance, at a site in 'rural' England, in a typical sample of all particles in the size range 0.08—1.0 μm, ammonium sulphate formed 90% of the number, and 99% of the mass. Sulphur dioxide also plays a crucial role in the condensation of the aerosol known as photochemical smog. The chemistry of the involvement of sulphur dioxide in both these aerosols must include its oxidation to sulphur trioxide, and it is useful to distinguish at least three possible mechanisms for this reaction in the atmosphere:

(i) in the gas phase, by photochemical oxidation,

(ii) in water droplets either with or without catalysis by other solutes which may be present, such as metal or ammonium ions.

(iii) on the surface of suspended solid particles.

There are recent experimental studies of all these modes of reaction, and a useful summary is given by Urone and Schroeder.[57]

(i) *Gas-phase Photochemical Oxidation.* (*a*) *Sulphur dioxide photo-oxidation.* Few experiments have been carried out in the complete absence of water. Hall[58] observed a rate of conversion to sulphur trioxide of only $8 \times 10^{-4}\%$ min^{-1} under sunlight, which is ten times slower than values found in the presence of water vapour. Gerhard and Johnstone[59] used moist air, illumination equivalent to noon sunlight, and concentrations of sulphur dioxide of the order of 10 p.p.m., and found a rate of $2 \times 10^{-3}\%$ min^{-1}. They detected no marked influence of ambient humidity, foreign nuclei, or of nitrogen dioxide added up to 2 p.p.m. The results of Schuck and Doyle[60] were two orders of magnitude higher, using only about 0.5 p.p.m. of SO_2; even at the lower rate the conversion

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[55] C. E. Junge and G. Scheich, *Atm. Env.*, 1969, **3**, 423.

[56] M. J. Heard and R. D. Wiffen, *Atm. Env.*, 1969, **3**, 337.

[57] P. Urone and W. H. Schroeder, *Environmental Sci. and Technol.*, 1969, **3**, 436.

[58] T. C. Hall, jun. Ph.D. Thesis, UCLA, 1953.

[59] E. R. Gerhard and H. F. Johnstone, *Ind. and Eng. Chem.*, 1955, **47**, 972.

[60] E. A. Schuck and G. J. Doyle, Report No. 29, Air Pollution Foundation, San Marino, California, 1959.

is significant on the time scale of a day, *e.g.* with a concentration of 10^{-2} p.p.m. SO_2 the yield of H_2SO_4 in about one hour is 10^{-5} p.p.m., and according to calculation[61] the nucleation rate for the condensation of the sulphuric acid would be high at such a partial pressure of acid. Cox and Penkett[62] have also estimated about $10^{-2}\%$ min^{-1} conversion in moist air using p.p.m. quantities and sunlight.

If smog were to form by this means alone, a reduction of visibility to 2 km. would take about ten[63] or one hundred[59] hours of bright sunlight.

The reaction is generally agreed[59,62] to be first order with respect to sulphur dioxide and some rate constants have now been quoted.[59,60,62]

The mechanism of the photo-oxidation was uncertain in 1961[64] and still is. It has a low, concentration-dependent quantum yield at 313 nm,[62] which wavelength of course cannot dissociate SO_2 but can excite it with a high absorption coefficient to a singlet upper state.[65]

In view of the strong hygroscopicity of the sulphuric acid produced in the oxidation, it is to be expected that water droplets which are nucleated by it will grow fairly rapidly in diurnal terms. There is some evidence for this in the strong dependence on ambient relative humidity of the optical extinction, which can be correlated with the size distribution of droplets.[63]

Coutarel *et al.*[66] have passed a stream of air containing an aerosol of pure sulphuric acid over a bath of more dilute acid and observed a 3% increase in average radius in a contact time of 10^{-1} s. After about 100 s sufficient water was absorbed for the sub-micron-sized droplets to reach the size at which their vapour pressure was equal to that of the solution. It could be important in the context of inhalation by mammals of such droplets if their growth in humid conditions is as slow as it appears to be from these results. The author's observation that the growth rate of the particles (presumably on a volume basis) is proportional to their volume is not discussed, although it implies that water-vapour diffusion to the droplets is not the controlling mechanism [*cf.* equations (1)—(3) above]. Perhaps the factor giving rise to such slow growth is the raising of the vapour pressure at the drop by the considerable heat of solution which is involved.

(*b*) *Sulphur dioxide photo-oxidation in impure systems.* The rate of photo-oxidation is greatly enhanced in the presence of other trace gases, notably ammonia, and combinations of olefins with nitrogen oxides.

Conversely, it has often been shown in the laboratory that chemical involvement of sulphur dioxide is crucial in the production of photochemical aerosol from certain other air pollutants. In particular it enables the formation of such

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[61] G. J. Doyle, *J. Chem. Phys.*, 1961, **35**, 795.
[62] R. A. Cox and S. A. Penkett, *Atm. Env.*, 1970, **4**, 425.
[63] J. A. Garland, *Atm. Env.*, 1969, **3**, 347.
[64] P. A. Leighton, 'Photochemistry of Air Pollution', Academic Press, N.Y., 1961, p. 235.
[65] J. H. Clements, *Phys. Rev.*, 1935, **47**, 224.
[66] L. Coutarel, E. Matijevic, M. Kerker, and Huang Cheo-Ming, *J. Colloid Interface Sci.* 1967, **24**, 338.

smogs from any olefin, whereas in its absence the effect is limited to cyclohexene,[55] other higher cyclic olefins, and diolefins.[67]

Even with saturated hydrocarbons, sulphur dioxide at partial pressures of up to 7 kN m^{-2} is capable of forming dense aerosols.[68,69]

A copolymer of olefin and sulphur dioxide has been produced in photo-oxidation[67] and a tendency has been noted for SO_2 to form polymers with traces of free radicals in discharges.[70] The formation of aerosol from sulphur dioxide–alkane mixtures might thus be a consequence of the production of radicals from the hydrocarbon which, as Ogata[69] *et al.* have suggested, can be effected by excited molecules of SO_2 which absorb u.v. light with ample energy for fission of a carbon–hydrogen bond.

(*c*) *Sulphur dioxide photo-oxidation with nitrogen oxides.* Photochemical activation of SO_2 is not in practice the important primary process in photochemical-smog formation. Nitrogen dioxide is a key component of pollution by automobiles, although the mechanism of its formation from the NO in the exhaust gas is not clearly understood quantitatively. Nitrogen dioxide is much more readily dissociated by photolysis than is SO_2, and it has been shown[71] that the products can accelerate the oxidation of SO_2 to SO_3.

The pattern of the chemical involvement of SO_2 in the formation of aerosols is complicated. In the above-mentioned aerosols formed in the presence of alkanes, [68,69] sulphur has been found in the form of sulphonic and sulphuric acids. Even with nitrogen dioxide also present, aqueous sulphuric acid was the major constituent of some aerosols from olefins,[72] and stronger acid, which resulted from lower ambient humidity, altered the proportions of the product in favour of inorganic nitrates. Very little organic material was incorporated and certainly none bonded to sulphur. As Altshuller[73] has expressed it, the oxidation of SO_2 to particulate sulphur compounds is efficiently aided by participation in the smog-forming reactions.

(*d*) *The photochemical-smog mechanism.* It is still not possible or useful to generalize about the chemical nature of the typical atmospheric smog resulting from photo-oxidation of hydrocarbon–nitrogen oxides–SO_2–air mixtures. The constitution depends on conditions such as humidity,[74] identity of the hydrocarbons,[75] and the presence of foreign nuclei. Collateral indicators of the level of severity of smog which are commonly used are eye irritation and ozone or

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[67] M. J. Prager, E. R. Stephens, and W. E. Scott, *Ind. and Eng. Chem.*, 1960, **52,** 521.

[68] H. S. Johnston and K. Dev Jain, *Science*, 1960, **131,** 1523.

[69] Y. Ogata, Y. Izawa, and T. Tsuda, *Tetrahedron*, 1965, **21,** 1349.

[70] D. H. Fraser, personal communication.

[71] S. Jaffe and F. S. Klein, *Trans. Faraday Soc.*, 1966, **62,** 2150.

[72] N. Endow, G. J. Doyle, and J. L. Jones, *J. Air Pollution Control Assoc.*, 1963, **13,** 141.

[73] A. P. Altshuller, *J. Air Pollution Control Assoc.*, 1970, **20,** 390.

[74] W. E. Wilson, jun. and A. Levy, *J. Air Pollution Control Assoc.*, 1970, **20,** 385.

[75] A. P. Altshuller, S. L. Kopczynski, D. L. Wilson, W. A. Lenneman, and F. P. Sutterfield, *J. Air Pollution Control Assoc.*, 1969, **19,** 787.

'oxidant' concentration.[75—77] The essentials of a reaction scheme which includes these factors are given by Agnew:[76]

Nitrogen dioxide can be dissociated by all solar radiation below 390 nm.

$$NO_2 + h\nu \rightarrow NO + O; \ \Delta H_{298}{}^0 = 307 \text{ kJ mol}^{-1} \qquad \text{(I)}$$

and ozone can accumulate as a result of

$$O + O_2 + M \rightarrow O_3 + M; \ \Delta H_{298}{}^0 = -96.6 \text{ kJ mol}^{-1} \qquad \text{(II)}$$

In turn NO may remove O_3

$$O_3 + NO \rightarrow NO_2 + O_2 \qquad \text{(III)}$$

but in the presence of hydrocarbon this would suffer competition from

$$RO_2^{\cdot} + NO \rightarrow RO^{\cdot} + NO_2$$

Reactions (I), (II), and (III) may comprise the basic photochemical equilibrium, with atomic oxygen then attacking the hydrocarbon:

$$O + RH \rightarrow R^{\cdot} + OH^{\cdot}$$
$$R + O_2 \rightarrow RO_2$$

followed by

$$RO_2^{\cdot} + NO \rightarrow RO^{\cdot} + NO_2$$
$$RO + NO_2 \rightarrow RONO_2$$

The principal eye-irritants are peroxyacylnitrates, of the form $R{\cdot}CO_3{\cdot}NO_2$, which are in fact mixed anhydrides of nitric and peroxycarboxylic acids.[78] These may be formed as follows:

$$O_3 + R^1H \rightarrow R^2CO_2^{\cdot} + R^3CHO$$
$$R^2CO_2^{\cdot} + NO \rightarrow NO_2 + R^2CO$$
$$R^2CO^{\cdot} + O_2 + NO_2 \rightarrow R^2{\cdot}CO_3{\cdot}NO_2$$

This scheme is open to two criticisms:

(i) Alkyl nitrates are not experimentally found[72] and

(ii) the molecular singlet $O_2(^1\Delta_g)$ may play a more significant role than atomic oxygen.[79—81] Several feasible routes for the photochemical formation of $O_2(^1\Delta_g)$ in adequate yield have been proposed, and its direct addition to olefins would be a simple route to alkenylhydroperoxides:

$$O_2(^1\Delta_g) + C_nH_{2n} \rightarrow C_nH_{2n-1}OOH$$

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[76] W. G. Agnew, *Proc. Roy. Soc.*, 1968, A307, 153.

[77] E. R. Stephens and M. A. Price, *Atm. Env.*, 1969, **3**, 573.

[78] E. R. Stephens, *Adv. Env. Sci.*, 1969, **1**, 119.

[79] J. N. Pitts, jun, A. V. Khan, E. B. Smith, and R. P. Wayne, *Environmental Sci. and Technol.*, 1969, **3**, 241.

[80] R. H. Kummler, M. H. Bortner, and T. Baurer, *Environmental Sci. and Technol.*, 1969, **3**, 248.

[81] R. P. Steer, P. L. Sprung, and J. N. Pitts, jun, *Environmental Sci. and Technol.*, 1969, **3**, 946.

These in turn may be oxidized further and release sufficient energy to effect, for instance, the conversion of nitric oxide to NO_2.[79] The bulk of the nitrogen oxide emitted in the automobile exhaust is NO, but its conversion to NO_2 must precede the absorption of the solar-radiation energy. Thus both the schemes, involving atomic and molecular oxygen respectively, will satisfactorily explain the ozone and irritant levels which accompany smog, but neither includes consideration of any of the sulphur compounds referred to in the previous section.

(ii) *Reactions in Droplets.* (*a*) *Chemical oxidation of sulphur dioxide in the droplet phase.* It has been mentioned above that ammonium sulphate aerosol is of considerable practical importance in the atmospheric chemistry in geographical areas where substantial amounts of sulphur dioxide and ammonia have been released into a poorly ventilated atmosphere. The particles which would normally remain suspended for an appreciable time lie in the size range 0.2—1 μm,[56,82—86] and by this criterion are known in the context of meteorological precipitation as 'large nuclei'. The proportions of NH_3^+ and SO_4^{2-} generally indicate the presence of NH_4HSO_4 and $(NH_4)_2SO_4$, and the comparatively small size of the stable particles enables them to spread widely, upwards to reach the stratosphere,[86] and outwards over oceans far from the centres of origin.[82]

Ammonia strongly accelerates the oxidation of SO_2 in aqueous bulk solution[87] and in macroscopic droplets,[88] and so it is probably an important aid to the process in cloud droplets in the appropriate geographical areas mentioned above.[84] In laboratory studies[88] of uptake of sulphur dioxide in droplets of diameter 10^2—10^3 μm the ammonia-catalysed mass-increase was found to be proportional both to droplet surface area and to exposure time. Reference to equation (19) indicates that diffusion in the liquid phase was the overall controlling factor.

Manganese sulphate in p.p.m. concentrations is one of several salts which have considerable catalytic effect on the solution-phase oxidation.[89,90] With droplets of 500—10^3 μm diameter Johnstone and Coughanowr[89] found that equation (18) was obeyed for catalyst concentrations of 500—1000 p.p.m., whereas with only 250 p.p.m. equation (16) was obeyed, and it appeared that oxidation was slow enough for sulphur dioxide to penetrate into the centres of the droplets.

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[82] C. E. Junge, 'Proceedings of the Conference on the Physics of Cloud Precipitation', Wood's Hole, 1955, p.3.

[83] E. Eriksson, *Tellus*, 1952, **4**, 215, 280.

[84] H. N. Georgii, *Umschau*, 1968, **68**, 565.

[85] H. R. Byers, J. R. Sieves, and J. T. Tufts, 'Proceedings of the Conference on the Physics of Cloud Precipitation', Wood's Hole, 1955, p. 47.

[86] J. P. Friend, *Tellus*, 1966, **18**, 465.

[87] C. E. Junge and T. G. Ryan, *Quart. J. Roy. Meteorol. Soc.*, 1958, **84**, 46.

[88] A. P. Van den Heuval and B. J. Mason, *Quart. J. Roy. Meteorol. Soc.*, 1963, **89**, 271.

[89] H. F. Johnstone and D. R. Coughanowr, *Ind. and Eng. Chem.*, 1958, **50**, 1169.

[90] R. C. Hoather and C. F. Goodeve, *Trans. Faraday Soc.*, 1934, **30**, **1149**.

Extrapolation of the observed rates to an atmospheric fog containing 20 μm diameter droplets of reasonable manganese content and 1 p.p.m. of sulphur dioxide predicted a conversion of 1% min^{-1}, *i.e.* 500 times that found in the photochemical oxidation by Gerhard and Johnstone.[59] It is interesting that the same reaction, with hydrogen peroxide in the droplets instead of $MnSO_4$, is only some ten times faster, but is controlled by diffusion in the gas-phase rather than internally.

Rates of acid formation were measured by Johnstone and Moll,[91] using sub-micron-sized droplets of aqueous manganous sulphate in a fog chamber containing sulphur dioxide—physical conditions which approximate to those in chimney plumes. With the latter practical situation in mind, Foster[92] interpreted their results, using a theoretical rate of growth for the droplet radius expressed by

$$\frac{\mathrm{d}r}{\mathrm{d}t} = r \cdot \frac{R_{\mathrm{H_2SO_4}}}{3[\mathrm{H_2SO_4}]\left[1 + \dfrac{r}{3[\mathrm{H_2SO_4}]} \cdot \dfrac{\mathrm{d}[\mathrm{H_2SO_4}]}{\mathrm{d}r}\right]}$$

Here $R_{\mathrm{H_2SO_4}}$ is the rate of formation and can be represented, at least for low acid concentrations, by a zero-order rate constant. Although the equation is in broad agreement with equation (13), it contains the implication that the acid produced inhibits the oxidation, so that the latter is faster at higher relative humidity where more dilute droplets are concerned. Complexing of the manganese catalyst may be the reason for the inhibition, a question which is further considered by Matteson *et al.*[93] The conditions on which equation (13) are based are valid for most of Johnstone and Moll's experiments, except at very low partial pressures of sulphur dioxide, and more particularly when an iron salt is the catalyst. Under the latter conditions the rate is dependent on the pressure of sulphur dioxide, which may be due to less complete penetration of the droplets [see equation (14)]. Foster predicted rates of conversion in plumes of about 0.1% min^{-1} with manganese as catalyst, and 0.15—1.5% min^{-1} with iron, which is typically ten times the more abundant in pulverized fuel ash.

In laboratory experiments, ammonia was found to react rapidly with sulphuric acid aerosol droplets of 0.2—1 μm diameter,[94] and in interpreting the rate of uptake, an empirical modification of equation (9) such as

$$-\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = \frac{3k[\mathrm{A}][\mathrm{B}]}{r_0}(1 - Fx)$$

was found adequate. This allows for the departure from the initial rate in terms

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[91] H. F. Johnstone and A. J. Moll, *Ind. and Eng. Chem.*, 1960, **52**, 861.

[92] P. M. Foster, *Atm. Env.*, 1969, **3**, 157.

[93] M. J. Matteson, W. Stoeber, and H. Luther, *Ind. and Eng. Chem.* (*Fundamentals*), 1969, **8**, 677.

[94] R. C. Robbins and R. D. Cadle, *J. Phys. Chem.*, 1958, **62**, 469.

of x, the fraction of the droplet that has reacted, and F, which is dimensionless and expresses both the diffusion rate of products and the change in surface area. (*b*) *Sulphur dioxide–ammonia reaction at low humidity.* The products when two such commonplace chemicals as sulphur dioxide and ammonia react in dry conditions without oxygen are surprisingly not yet identified clearly, but even well below room-temperature they take the form of an aerosol. A yellow solid adduct, formed at temperatures below −10 °C with excess sulphur dioxide, was described by Goering[95] by the empirical formula H_3NO_2S, probably being $H\cdot SO_2\cdot NH_2$. On the other hand ammonia in excess produces a red adduct $H_6N_2O_2S$, which is probably $NH_4\cdot SO_2\cdot NH_2$. The i.r. spectra of the products at room temperature[96] indicated gas-phase HNSO and particles of $(NH_4)_2S_2O_5$, formed by the reaction

$$3SO_2 + 3NH_3 \rightarrow HNSO + (NH_4)_2S_2O_5$$

X-Ray and further i.r. identifications of the initial solid aerosol[97] formed at room temperature have been attempted[98] but the results are so far ambiguous. The hygroscopic product(s) progressively change to $(NH_4)_2SO_4$ in moist air.

In the presence of water the possible reactions are more straightforward, although their occurrence in droplets is as yet unconfirmed by experimental proof:

$$NH_3 + SO_2 + H_2O \rightarrow NH_4\cdot HSO_3$$

On the question of the transition from solid particles of $(NH_4)_2SO_4$ to droplets, the critical humidity for this, at 15 °C, appears to be about 73%, compared with 78% for sodium chloride. The numerous solid particles of ammonium sulphate found probably result from evaporation of atmospheric droplets[88] but the most probable sequence of events is hard to specify in a given case and is obviously under control of meteorological factors. Heard and Wiffen[56] found no positive signs of any insoluble nuclei in the particles they collected from the atmosphere. This is not conclusive proof that the ammonium sulphate was not formed in droplets, but it is useful fragmentary evidence, typical of investigations of atmospheric chemistry when performed at ground level.

A related reaction of ammonia, with the sulphur trioxide produced by catalytic oxidation, is the basis of a dry method[99] for cleaning flue gases of their sulphur content.

(iii) *Oxidation of Sulphur Dioxide on Particles.* We have seen[89] that the rate of oxidation in fog droplets containing metals such as iron and manganese can be considerable, of the order of 1% min^{-1}, and hence several times faster than the

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[95] M. Goehring and H. W. Kaloumenos, *Z. anorg. Chem.*, 1950, **263**, 137.
[96] T. Hata, *Bull. Chem. Res. Inst. Non-aqueous Solns. Tohoku Univ.*, 1964, **14**, 5.
[97] M. D. Carabine, J. E. L. Maddock, and A. P. Moore, *Nature Phys. Sci.*, 1971, **231**, 18.
[98] M. D. Carabine and A. P. Moore, unpublished work,
[99] R. Kiyoura, *Staub*, 1966, **26**, 524.

photochemical oxidation.[59] Urone *et al*,[100] after confirming the latter photochemical rate at 50% relative humidity, measured the rates over powdered salts and oxides, with and without both u.v. irradiation and water vapour. Substances known to be effective catalysts at high temperature, *e.g.* V_2O_5 and Cr_2O_3, surprisingly produced rates of only about $10^{-2}\%$ min^{-1}, which were not greatly enhanced by irradiation or moisture. A key factor may be moisture in the particles themselves; the relative humidity (50%) employed here was quite insufficient to induce deliquescence in any of the substances, except for calcium oxide which did increase the rate and which was suspected of inadvertent moisture content.

When the levels of promotion on albeit relatively coarse particles are so insignificant, it is clear that no substantial measure of atmospheric oxidation can occur on dry airborne particles, the more so since in these experiments the mass ratio of particles to sulphur dioxide was two orders of magnitude higher than typical values in even heavily polluted atmospheres. This assertion must be viewed with reservation until experiments are made with particles of surface to mass ratios comparable to those of atmospheric particles: an unexpectedly high degree of promotion by iron oxide may have been connected with its mode of preparation. Commins[101] has found interesting correlations between conversion of sulphur dioxide to particulate sulphate and the ambient concentrations of smoke or ash containing traces of various catalytic metals.

Let us now summarize the chemical fate of sulphur dioxide in various atmospheric environments. In hydrocarbon-polluted atmospheres with intense sunlight, and in laboratory simulations of these, it will predominantly go into the sequence of reactions leading to photochemical smog. In the absence of such radiation, and if droplets are present, oxidative reaction in the liquid phase is bound to predominate. The rate may be greatly increased if iron, or manganese, vanadium, *etc.* has entered the environment as a component of smoke or ash.

Ammonia is a key participant in the global cycle of sulphur reactions. On this scale its emission, mostly from natural sources, relative to that of man-made sulphur dioxide satisfies the stoicheiometry of neutralization to ammonium sulphate. However on the local scale the proportions are frequently vastly disparate, and in any case ammonium sulphate is not entirely innocuous since it can impair visibility by stabilizing mist droplets. The interaction of these two gases in the absence of water may be slow, but could be important in arid atmospheres.

In conclusion, it may be said that whereas many examples have been quoted [32,36,88,89] of the kinetic study of the growth of particles and droplets which are well above 1 μm in size, studies on particles which are smaller and can hence survive in aerosol suspension are only beginning.[66, 97] For observing changes in submicron sizes and their distributions, light scattering with laser sources is one of the more promising current techniques.[97]

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[100] P. Urone, H. Lutsep, C. M. Noyes, and J. F. Parcher, *Environmental Sci. and Technol.*, 1968, **2**, 611.

[101] B. T. Commins, M.R.C. Air Pollution Unit, London, personal communication.