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CLOUDS AND SMOKES

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BY

WILLIAM E. GIBBS, D.Sc.

CHIEF CHEMIST TO THE SALT UNION, LTD., LIVERPOOL

FOREWORD

BY

SIR OLIVER LODGE, F.R.S.

With 31 Illustrations



LONDON

J. & A. CHURCHILL

7 GREAT MARLBOROUGH STREET

1924

To

MY WIFE

Printed in Great Britain

PREFACE

THE investigation of matter in a highly disperse, or "colloidal," condition has largely been directed towards those disperse systems in which the dispersion medium is a liquid or a solid. In "Clouds and Smokes" we are concerned with disperse systems—for example, fog, smoke, flame, the atmosphere itself—in which a liquid or a solid substance exists in a highly disperse condition in a gas. Such disperse systems may conveniently be called aërosols.

A gas is the most attenuated form in which matter commonly occurs. It is characterised by a very low density and viscosity when compared with a liquid or a solid. At first sight, therefore, it would seem that, when liquid or solid particles are suspended in a gas, they would form a very unstable system, from which they would quickly become separated by the action of gravity. It must be remembered, however, that in a gas, owing to its relatively open structure—approximately 1,700 c.c. of steam at 100° C. condenses to 1 c.c. of water—Brownian motion can be imparted to very much larger particles, and can attain a greater amplitude than in liquids. Consequently, the particles, instead of being precipitated from the gas by the force of gravity, remain in suspension and are driven about the gas by the blows of the gas molecules. Further, the molecules of a gaseous dispersion medium are more readily adsorbed by the particles of the disperse phase than the molecules of a liquid dispersion medium would be. These adsorbed molecules form protective films that inhibit the coalescence or flocculation of the particles. A similar result is produced by the adsorption of gaseous ions of the same sign. Consequently, the particles remain small enough to continue in Brownian motion, and the stability of the system is enhanced.

Thus it is possible to prepare aerosols possessing a stability

that is comparable with that of many hydrosols. They are sufficiently stable to be investigated with precision. The movements of the particles under the influence of gravity or an electrical field, or when bombarded by the molecules of the dispersion medium, can be observed and accurately recorded. The optical and thermal properties can be determined and compared with those of the constituent phases. The manner in which, under certain conditions, an aerosol changes with time can be closely followed. In this connection it is interesting not only to investigate the stability of the aerosol and the causes that promote its decay, but also to investigate the closely related problem—frequently encountered in industrial operations—of separating quantitatively the particles of the disperse phase from the gases in which they are suspended.

. . . . . .

In this monograph I have attempted to give a clear and comprehensive account of the properties and behaviour of aerosols, and of their practical and industrial applications.

The contents of the book fall naturally into two parts. Part I. is devoted to a detailed consideration of the methods by which aerosols are formed, the general properties of such systems, the movements of the particles, the conditions that determine stability, and the methods by which all these properties can be determined experimentally. In Part II. this information is considered in its direct relation to the phenomena of meteorology, the problem of dust explosions, the industrial treatment of fumes and dusty gases, the manufacture of substances in a finely-divided condition, and, finally, the use of smoke in warfare.

In the present state of our knowledge I have thought it better to emphasise the general principles that underlie the subject, rather than to attempt to treat it in anything like an exhaustive manner. A list of references to papers giving more detailed information is appended to each chapter.

. . . . . .

My best thanks are accorded to Sir Oliver Lodge for contributing a Foreword.

My acknowledgments are due to the Controller of His Majesty's Stationery Office, and to the Editors of the *Chemical Age* and the *Journal of the Society of Chemical Industry*, for permission to quote—in Chapters III., IV., VII. and VIII.—extracts from my papers in the Fourth Colloid Report and in the journals mentioned.

My thanks are accorded :

For the loan of blocks—to Messrs. A. E. Harris, Russell Square, London, W.C. (Figs. 25 and 30) ; to the Secretary of the American Chemical Society (Fig. 19) ; to the Secretary of the Society of Chemical Industry (Figs. 23, 24, 26 and 27) ; to Messrs. J. & A. Churchill (Fig. 5).

For permission to reproduce illustrations—to Professor R. Whytlaw-Gray and the Secretary of the Royal Society (Figs. 7, 8, 9, 10, 11, 21 and 22) ; to Dr. H. J. Bush and Messrs. Longmans Green (Figs. 28 and 29).

Also for other illustrations that are taken from the original papers to which reference is made either in the text or at the end of a chapter.

I am grateful to Mr. R. Bennet for preparing drawings of these illustrations, and to Miss Margaret Gray for compiling the index and preparing the typescript for the press.

W. E. G.

RUNCORN.

FOREWORD

I HAVE been asked by Dr. W. E. Gibbs, the author of this book, to contribute a Foreword to the volume which Messrs. J. & A. Churchill are bringing out on the subject of Clouds and Smokes and Suspended Particles generally.

So far as I know, the chief writer hitherto on Dust in air has been John Aitken, and on Particles suspended in liquids M. le Professeur Jean Perrin. But there seems to be an immense literature on the subject of finely divided Particles in their innumerable forms ; and the author has assimilated and made accessible a great part of the information procurable, and, by giving copious and exact references, has enabled students to refer on special points to the original authorities. This seems to me an admirable piece of work. I am not reviewing the book, and do not pretend to have read it ; but I know its general scheme, and commend it heartily as a text-book or book of reference on a rather out-of-the-way subject, which, nevertheless, is of considerable practical importance. Few people have given it the attention it deserves. I have written and lectured on Dust myself, long ago, notably in the year 1884, at the Montreal Meeting of the British Association. References are given in a footnote.* But I never thought of

* Some references, as follows :

Dust-free Spaces, at Roy. Dub. Soc. See *Nature*, July 26th, 1883 ; April 24th, 1884.

Lecture on Dust to the Brit. Assoc. Reported in *Nature*, Jan. 22nd, 1885, and Abstracts in *Nature*, vol. xxix., p. 417, and vol. xxx., p. 54.

On Dusty Air near Illuminated Bodies (in conjunction with J. W. Clark).

See elaborate paper in the *Phil. Mag.* for March, 1885.

bringing together the whole series of facts in a comprehensive manner and exhibiting their inter-relations.

There is one part of the book in which I am sure to be specially interested, for I remember that it was in 1884 that I exhibited the effect of electrification in clearing a space of smoke, fume, or mist, a phenomenon which was afterwards found to have been casually observed and not developed by a Mr. Guitard so long ago as 1851, as recorded in the *English Mechanic* of that date. My sons, of the Lodge Fume Deposit Company, Great Charles Street, Birmingham, after long and continued trials, made the process really practicable, and have now combined with my friend Mr. F. G. Cottrell, who so successfully established it on a large scale in America. It is amazing to me to see the Lodge-Cottrell process at work continuously, night and day throughout the year, with a potential of hundreds of thousands of volts, giving a continuous current of sparks—or what Crookes more properly called a nitrogen flame—and, by the aid of great electrified chambers, clearing immense quantities of blast furnace gas of dust at Skinningrove, in Yorkshire, and elsewhere, and also depositing subliminated and previously wasted metallic ore, as, for instance, at the tin-smelting furnaces of Messrs. Williams, Harvey & Co., at Bootle, near Liverpool. The step from a laboratory experiment to a really practical and commercially continuous process is undoubtedly a great one, and the credit for it belongs to others than myself. It is, however, delightful to see the electrical process of clearing air gradually come into operation at manufactories all over the world, and I see that the author of this book has given an indication of the kind of arrangement employed. Short of inspection of the working operation, however, no adequate idea can be gained of the remarkable character of this engineering achievement.

Many other methods and processes for dealing with finely

divided suspended material are described in the book. And the vital subject of coal-dust, with its dangerous inflammability and methods of countering it, is, of course, not ignored.

The Brownian movement of fine particles has acquired special interest of late, from its quantitative illustration and enforcement of the kinetic theory of gases, for its application to emulsions, and its striking agreement with the notable theory of Einstein on that subject.

I expect to find a mass of little-known information conveniently here collected; and I commend the book to the notice of practical engineers and of workers in pure science.

OLIVER LODGE.

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CLOUDS AND SMOKES

PART I

CHAPTER I

INTRODUCTORY

The Molecular Structure of Matter

At the ordinary temperature and pressure a cubic centimetre of any gas contains about 10^{19} molecules. The diameter of each molecule is about 10^{-8} cm., and their average distance apart is about 10^{-6} cm. The molecules travel ceaselessly in straight lines, with a velocity of about 10^{-4} cm. per second. Each molecule collides with other molecules about 10^{9} times in every second.

It is difficult to form a mental picture of a system of such dimensions, but the following considerations[1] will probably be found of assistance in grasping something of the character of the extremely fine molecular structure of matter.

If all the molecules in 1 c.c. of a gas were ranged in a row, touching one another, they are so numerous that, in spite of their extremely small mass, they would form a line about three million miles long—that is, more than a hundred times round the earth. Even then all these molecules only fill about one three-thousandth part of the space that is actually occupied by the gas at ordinary temperatures and pressures.

Some conception of the relation between the diameters of molecules and the length of their mean free path may be obtained from the consideration that, if we could magnify the gas until each molecule was an inch in diameter, each cubic foot would contain about one molecule, and a molecule would travel about 25 feet before it collided with another.

Finally, the velocity of a gas molecule is approximately a quarter of a mile per second.

In a gas at ordinary temperatures and pressures, the mean free path of the molecules is equal to about three hundred times the diameter of the molecules themselves. It may be assumed, therefore, that the molecules of a gas are sufficiently far apart to be beyond the range of their mutual attractive forces. They move, therefore, in straight lines. Also, their kinetic energy is so great that even if, when they collide with one another, they unite, they will immediately separate again.[2] In other words, when the molecules of a gas collide they re-evaporate as rapidly as they condense. Owing to the tangential component of the force of impact, a rotary motion will be imparted to each molecule, and will probably vary in angular velocity and direction after each successive impact. The result of this irregular rotation will be that the attractive force that is exerted by the molecule will tend to be distributed uniformly, even although the field of force of the molecule itself may be definitely polar in character.

Owing to the vigorous movement of the molecules along their mean free paths and about their constantly changing axes of rotation, the properties of a gas are the same in all directions. The molecules being so far apart, the gas entirely lacks cohesion; in fact, owing to the kinetic energy of its molecules, it tends to expand uniformly in all directions, exerting a pressure upon the walls of the container.

As the temperature falls and, therefore, the mean kinetic energy of the molecules becomes less, they evaporate less readily, owing to the restraint that is imposed upon them by the force of molecular attraction. At a low enough temperature—the condensing point—the molecules condense upon each other more rapidly than they re-evaporate, and the gas becomes liquid.

In the liquid state, the molecules are separated by distances that are of the order of the length of the molecular diameter. The intermolecular force of cohesion, which approximately varies inversely as the fourth or fifth power of the distance, rapidly assumes high values. Consequently the liquid possesses

tensile strength, and, because of the pull of this cohesive force upon the surface molecules, it possesses surface tension, which distinguishes it from a gas or vapour. Molecules also now move in curved paths, and rotate less actively, so that, if polarised, they tend to exercise their mutual attractions more strongly in some directions than in others. Thus in the liquid state, we sometimes observe beginnings of a crystalline behaviour, as shown in the optical properties of liquid crystals.

With further cooling, the molecular velocity diminishes still further, and the force of cohesion draws the molecules more closely together. The intensity of this force increases rapidly as the intermolecular distance diminishes. Ultimately the molecules are so close together that they can no longer move freely past each other. The substance is no longer a liquid or even plastic, but now becomes a rigid solid. At the same time, the relatively sluggish movements of the molecules produce little or no rotary motion, and the molecules adopt a polarised arrangement, forming definite space-lattice arrangements. Such a crystalline substance will have properties that vary along different axes to an extent that depends probably upon the polar character of the forces exerted by the constituent molecules.

Thus the structure of matter depends partly upon the structure and character of the molecules of which it is made up, and partly upon the energy of their motion. The physical state, and in some cases the particular crystalline structure, of a substance, can be changed by modifying the movements of the molecules, through alterations of temperature or pressure.

Heterogeneous Systems

A heterogeneous system[3] consists essentially of one or more substances, co-existing in intimate contact in two or more different physical states or "phases," according to the temperature, and pressure, and the relative concentrations in which the substances occur in each phase. As these three factors—temperature, pressure and concentration—are altered, so the physical state of each substance will change. The conditions of equilibrium between the different phases can be defined by means of the phase rule. These conditions are determined ultimately

by the energy with which the molecules of each component are moving in the different phases. This molecular kinetic energy in its turn is dependent upon the temperature and pressure of the system and the concentrations of the different molecules in each phase. The more completely the values of these three factors are defined, the more restricted will the freedom of the system be.

So far we have assumed that the physical state of any substance can be completely defined by stating its temperature, its pressure, and its chemical composition. This is, however, only true so long as the surface of the substance is not unduly curved.

Molecules that are situated in the interior of a substance—that is to say, more than the distance of a molecular diameter from the actual surface—are completely surrounded by other molecules. On the other hand, molecules that are situated at the actual surface of a liquid or solid are only partially surrounded by the adjacent molecules. The force of attraction, therefore, between these surface molecules and their immediate neighbours will possess a resultant that will be directed inwards normally to the surface at that point. The attractive force of the molecule is only partially exercised, so that the balance is available for attracting to the surface of the substance liquid or gaseous molecules of the same substance that may come sufficiently close to it. Thus the substance possesses surface tension, and, by virtue of the residual attractive force exercised by the surface molecules, it can grow by the condensation of vapour upon it, or by crystallisation from the saturated solution in which it is immersed. The residual surface attraction may be exerted upon molecules of other substances to produce the phenomena of adsorption.

So long as the radius of curvature of the surface at any point does not approach molecular dimensions, the surface tension and the surface energy will vary only according to the intensity of the intermolecular force of attraction of the molecules of the substance—that is to say, will be directly proportional to the temperature, pressure and chemical composition of the substance —and will, therefore, not exercise any disturbing influence upon the conditions of equilibrium as they are defined by the phase rule.

When, however, the radius of curvature of the surface at any point approaches molecular dimensions, the spatial arrangement of the surface molecules and their immediate neighbours in the interior will be modified to an extent that will depend upon the actual radius of curvature. This can be seen from a consideration of the spatial arrangement of molecules at a plane surface and at a curved surface, in which the radius of curvature is a small multiple of the molecular diameter. If we assume the surface of a molecule to be identical with its sphere of attraction, and, further, assume the molecules to be unpolarised, so that their attractive force may be considered to be exercised uniformly in all directions, then we can see from the spatial arrangement of the surface molecules that the amount of the surface of each surface molecule that is free and unattached to the adjacent molecules is less at a concave surface, more at a plane surface, and greater at a convex surface, to an extent that clearly depends upon the relation between the radius of curvature of the surface and that of the constituent molecules. The difference is represented very diagrammatically in Fig. 1, where (A) represents the molecules of a convex surface, (B) those of a plane surface, and (C) those of a concave surface. Actually, of course, the arrangement shown in this diagram will be modified to some extent by the movements of the molecules, and by their shape and orientation.

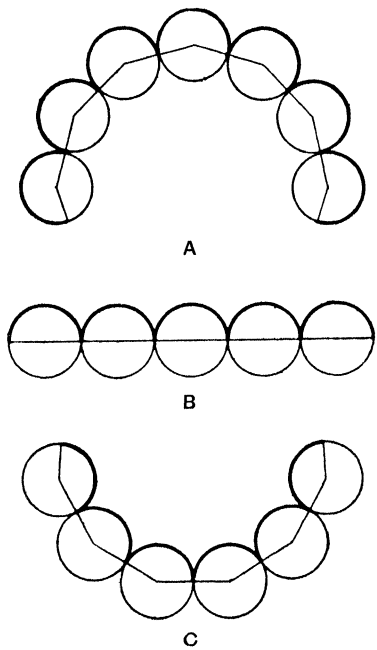


FIG. 1.—The arrangement of molecules at plane and curved surfaces.

Clearly, molecules situated in such highly curved convex surfaces tend, because of their spatial arrangement, to be more

loosely held to the substance. At a given temperature or pressure, therefore, they will pass the more readily from the solid into the liquid or from the liquid into the gaseous condition. Consequently a small particle or droplet, whose radius approaches molecular dimensions, will have a lower surface tension, a lower melting point and a higher vapour pressure. At the same time, because it will be correspondingly more difficult for condensation or crystallisation to proceed at such a surface, owing to the increased tendency to volatilisation, fusion or solution, the general result of this change in the distribution of the energy of the surface molecules will be that the conditions of equilibrium in heterogeneous systems, in which the phases are bounded by surfaces of such small radii of curvature, cannot be completely defined by the phase rule. Similarly at a highly curved concave surface of any substance the melting point and the boiling point will be correspondingly raised.

Such heterogeneous systems are extremely common both in natural and in industrial processes, and are generally produced by distributing one phase in a very finely divided condition in another phase, as, for example, the gold in ruby glass, the fat globules in milk, and the liquid or solid particles of a smoke. Such heterogeneous systems, in which one or more substances (known as the disperse phase) are distributed uniformly (dispersed) in another continuous phase (called the dispersion medium), are known as disperse systems. From the circumstance that the first disperse systems to be studied were of a gluey nature, disperse systems are commonly known as colloidal systems, or, more briefly, colloids (Greek, *kolla*, glue, and *eidos*, form, appearance).

Disperse Systems

The structure of a disperse system necessarily depends upon the physical character of the substances of which the two phases consist. In comparing the molecular structure of gases with liquids and with solids, it is convenient to speak of liquids as more " condensed " than gases, and less " condensed " than solids. The more condensed the molecular structure of a given

substance becomes—that is to say, the more closely its molecules are drawn together—the greater will be its density, surface tension and viscosity.

The absolute values of these properties will depend upon the characteristic mass and the force of molecular attraction of the molecules of the particular substance, as well as upon its degree of condensation.

If the dispersion medium is more condensed than the disperse phase, the structure of the disperse system will resemble that of a sponge—*e.g.*, pumice stone, in which the disperse phase is gas, and the dispersion medium is solid ; a jelly, in which the disperse phase is liquid and the dispersion medium solid ; or a foam, in which the disperse phase is gas and the dispersion medium liquid.

If the dispersion medium is less condensed than the disperse phase, the structure will be that of a suspension—*e.g.*, smoke, in which the disperse phase is solid and the dispersion medium a gas ; mist, in which the disperse phase is liquid and the dispersion medium gas ; muddy water, in which the disperse phase is solid and the dispersion medium a liquid.

If the degrees of condensation of the disperse phase and the dispersion medium are but little different from one another, the two may be interchangeable, and an emulsion type of structure will result, in which A may be dispersed in B, or B in A, according to their concentrations, without affecting the fundamental character of the structure—for example, lanoline (water in oil), mayonnaise (oil in water), frozen emulsions (solid in solid). It is practically impossible to obtain a gaseous emulsion, since gases are miscible in all proportions. Such a structure may possibly be obtained at high pressures and low temperatures, owing to the smaller intermolecular distances and the degree of association of the molecules.

It is impossible to define the equilibrium conditions of such disperse systems by ordinary phase rule methods, for, in addition to the three variants—temperature, pressure and concentration—it is found that the degree of dispersion and the electrical condition of the disperse phase profoundly influence the stability and the general properties of the system. In a

fine mist of water particles suspended in water vapour, for instance, the vapour tension of the water particles depends not only upon the temperature and pressure, but also varies with the size of the particles. It can also be modified by charging the particles electrically, or by surrounding each particle with a film of oil or with a layer of adsorbed gas.

Aerosols

Disperse systems, in which the dispersion medium is a gas or a vapour, may consist of one component—*e.g.*, a fine mist of liquid water suspended in water vapour—or of two or more components—*e.g.*, metallurgical fumes. The disperse phase may be liquid, as in cloud, mist or spray, or it may be solid, as in a dust-cloud, or a luminous gas flame.

Such familiar natural phenomena as dust, fog, cloud, mist, haze, fume, smoke, are essentially disperse systems in which a solid or liquid substance is dispersed in a gas—in most cases, the atmosphere. The use of so many different words to denote naturally or commonly occurring disperse systems, which differ in circumstance rather than in character, leads to a somewhat confused nomenclature. None of these terms is sufficiently comprehensive to include all disperse systems in gases. The term "gaseous dispersoid" suggests that the disperse phase is gaseous rather than the dispersion medium. "Aerosol" is the most satisfactory term, and is analogous to the accepted term "hydrosol," denoting disperse systems in water. Throughout this book it will be convenient to use this term and further to denote as "clouds," or "cloudy aerosols," those systems in which the particles are too large to exhibit Brownian motion at the ordinary temperature and pressure. The more highly disperse systems will be called "smokes," or "smoky aerosols."

The properties of aerosols differ in several important respects from those of disperse systems in liquids or solids. In the first place, owing to the relatively small viscosity and specific gravity of gases, the liquid or solid particles of the disperse phase tend to settle more readily from the system under the influence of gravity or centrifugal force. In the second place, the molecules

of a gas move with much greater freedom and in longer paths than do those of liquids or solids ; consequently the amplitude of the Brownian motion of the particles is very much greater in an aerosol than in other disperse systems. This tends to increase the rate at which particles collide to form aggregates. Finally, in a given aerosol some particles of the disperse phase may be electrically neutral, while at the same time others may be charged either positively or negatively. In a liquid or solid disperse system, all the particles are charged with the same sign. In all these respects, it would seem that an aerosol should be very much less stable than other forms of disperse systems. Experience has shown, however, that aerosols can be formed possessing a degree of stability comparable with that obtained in liquid systems.

Owing to the comparatively simple open structure of the gaseous dispersion medium, aerosols are structurally the simplest form of colloidal system with which we have to do. The relatively high specific gravity of the disperse phase and the greater amplitude of the Brownian movement make it impossible to obtain very concentrated systems. Such systems tend to flocculate readily to form a kind of aerogel.

Aerosols afford an almost ideal opportunity for studying the mechanism of Brownian movement. By increasing or diminishing the pressure of the gas, the concentration of the gas molecules and, therefore, the character and intensity of the molecular bombardment to which the suspended particles are subjected, can be varied throughout wide ranges.

From the ultramicroscopic investigation of very dilute aerosols, obtained by the interaction of two highly diluted gases—*e.g.*, NH_3 and HCl—or by the photochemical decomposition of a diluted vapour such as amyl nitrite, valuable information can be obtained relating to the condensation of vapours and the formation, motion and growth of the most minute liquid and solid particles.

The investigation of the electrical properties of aerosols is simplified by the relatively simple electrical character of ionised gases as compared with liquids or solids.

Similarly, in their optical, thermal and chemical properties,

aerosols, although in the main resembling other disperse systems, yet, owing to the low density and viscosity of the dispersion medium, possess properties that are peculiarly their own. The study of aerosols increases our knowledge of the colloidal condition of matter, and throws considerable light upon the properties and behaviour of gases and vapours.

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CHAPTER II

THE FORMATION OF AEROSOLS

THE methods by which aerosols can be formed may be divided conveniently into :—

I. Dispersion processes.
II. Condensation processes.

I. Dispersion Processes

In dispersion processes, the solid or liquid substance is disintegrated by mechanical means—by grinding or splashing, or by explosive disruption—and at the same time is projected into a relatively large volume of a gas, with which it becomes intimately mixed. In this way are produced the dusty air of a flour mill, the spray that drifts about a waterfall, and the fine dust cloud that is formed during a volcanic eruption.

(A) **The Mechanical Dispersion of Solids.**—In all processes of mechanical disintegration, the different particles into which the substance is divided have to be torn asunder against the force of cohesion. The amount of work that is performed against the force of cohesion is directly proportional to the area of new surface that is formed—that is to say, it is proportional to the increase in the specific surface of the product. In whatever way this work is performed, the energy that is expended appears as heat, and the temperature of the product is raised. It is not possible to obtain a high degree of dispersion—greater than 10^{-4} cm.—by ordinary grinding processes. Disintegration may be accomplished by shearing and tensile stresses gradually applied, as in attrition mills, or by a crushing pressure applied gradually by means of rolls, or by sudden blows, as in impact machines of the disintegrator type.

The efficiency with which the applied stress can act will depend upon the rigidity with which it is received by the pieces

of substance that are to be broken. As the particles gradually become smaller, they form a loose dust or paste, according to whether the grinding process is dry or wet, that yields more and more to the applied stress, so that the crushing effect is increasingly diminished. There comes a point, therefore, in all crushing operations at which the accumulated *débris* is fine enough to accommodate itself to the applied stress without the individual particles actually being stressed beyond their elastic limit. The rigidity of the mass is then too low for further crushing stresses to produce any effect.

The rigidity with which a fragment of material resists an impact depends also upon the velocity of the impact. When a stress is applied slowly, the yielding and fracturing of the substance absorbs the energy of the stress, and softens the force of the pressure, before it has extended to the more remote portions of the piece of material. If the velocity of the impact is such that the rate at which the stress is applied exceeds the rate at which deformation occurs, the substance possesses rigidity, by virtue of which the effect of the blow is transmitted to the most distant parts of the substance.

In most substances, the rate at which the stress is transmitted will not be equal in all directions, owing either to irregularities of shape—so that the blow itself is not uniformly distributed at the surface of impact—to abrupt changes in chemical composition, or to differences in the physical properties along different axes. Consequently the effect of the stress is concentrated in certain directions, producing cracks and splitting.

The more rapidly the blow is delivered, the more complete and far-reaching will be the shattering effect—that is to say, the higher will be the degree of dispersion of the product. The finest degree of disintegration is obtained with machines of the impact type. In an impact machine, the relatively coarse particles are subjected to a high velocity stress just when, owing to their size, they are best able to offer a rigid resistance to it. Thus a high shattering efficiency is obtained.

In the Plauson mill, an impact delivered at the rate of 40 metres per second effectively reduces most substances to colloidal proportions. In this mill, the disintegrating action

of the impact is reinforced by the presence of an excess of a suitable liquid, which, by reason of its rigidity, transmits the force of the impact to all parts of the surface of the particle, and also serves as a dispersion medium and effectively stabilises the disperse phase as it is formed. The liquid also absorbs the heat that is produced, and, owing to its greater mass, prevents the undue heating of the product. In the absence of such a liquid, the heating of the particles would tend to make them seize together, and thus reduce the degree of dispersion. With many substances the heating would destroy some particular quality.

Aerosols may be produced with the aid of a Plauson or other colloid mill by reducing the solid substance to colloidal proportions in a suitable volatile liquid, and then, by spraying this colloidal solution in warm air or other suitable gas, remove the dispersion medium by evaporation and obtain a solid-gas aerosol.[1] Similarly, solid-gas aerosols may be obtained in this way by the evaporation of finely atomised, molecular solutions of the solid in a suitable solvent.

With a perfectly rigid substance and a sufficiently rapid impact, uniformly applied, the kinetic energy of all the molecules should be increased almost instantaneously and by an equal amount, so that the substance should become plastic and yield, or melt and spread as a liquid spreads in such circumstances, and then congeal again as soon as the added energy had all been used up in performing the extension of surface. Something of this sort seems to occur when projectiles penetrate armour plate, the form that is assumed by the metal that is displaced by the projectile being identical with the form of the splash that is raised on the surface of a liquid, such as water, when a round, rough stone is dropped into it.[2]

Explosive Disruption.—Certain substances—*e.g.*, oxalates and salt crystals containing enclosed liquid, decrepitate when heated—that is to say, are blown to pieces by the accumulated pressure of the gas or water vapour that is generated within them.[3] When the solubility pressure of a saturated solution of a gas in a liquid is suddenly diminished—for example, when

molten silver saturated with oxygen solidifies quickly, or when molten volcanic magma saturated with steam at a high pressure is suddenly exposed to the ordinary atmospheric pressure—effervescence occurs with explosive violence, and the liquid or solid solvent is dispersed throughout the surrounding atmosphere. In some volcanic eruptions, a prodigious amount of fine dust is projected into the upper atmosphere, where it may remain suspended for years.

It has been shown that there is a close connection between the proportion of enclosed liquid and the degree of dispersion that is obtained.[4] When a sodium chloride crystal, containing 0·08 per cent. water, was decrepitated by heat, practically none of the resulting particles were able to pass a 30-mesh sieve. Salt containing 5 per cent. water gave a powder, of which 44 per cent. passed a 30-mesh sieve, 12 per cent. passing a 120-mesh sieve. With barytes crystals the effect was even more marked; with 0·04 per cent. contained water only 14 per cent. of the powder passed a 30-mesh sieve, while with 0·45 per cent. water 94 per cent. passed 30-mesh, of which over 30 per cent. was less than 120-mesh. This process has been employed to separate a decrepitating mineral, such as barytes, from impurities, such as blende, galena, pyrites and quartz, that do not decrepitate when heated.

The most complete dispersal of a dry solid is produced by detonation. An enormous amount of energy is applied, comparatively uniformly and practically instantaneously. The force of disintegration carries the particles apart, and tends to prevent their recombination.

A very fine smoke can be obtained by detonating a liquid or solid with a blasting cap. During the Great War substances such as diphenylchlorarsine were fired in a shell and detonated to produce a very penetrating toxic smoke.

Smoke clouds were frequently produced by the detonation of hygroscopic substances—*e.g.*, $SnCl_4$, $SiCl_4$, oleum. Atmospheric water vapour rapidly condensed upon the dispersed particles, producing a dense cloud.

When a substance, whether solid or liquid, is detonated, it is subjected to the impact of an extremely high velocity gas

pressure wave. It spreads violently in all directions, with sufficient velocity to overcome the force of cohesion, and the substance assumes the form of spray or dust.

(B) **The Mechanical Dispersion of Liquids.**—It is comparatively easy to disintegrate a liquid, owing to its relatively low viscosity. When a liquid is projected rapidly against a solid, liquid or gaseous surface, it is stretched from the point of impact, until the resulting tension exceeds the surface tension of the liquid. The specific surface of the liquid is enormously increased, and the condition of the liquid becomes unstable; consequently it breaks into numerous drops, each possessing a smaller specific surface and, therefore, greater stability. Similarly, if a liquid is distributed in the form of a number of fine threads—*e.g.*, by being forced through a perforated plate—the threads become unstable if their length exceeds three times the diameter, and they break up into a series of spherical drops.

Many sprays have been designed for reducing liquids such as water, oil, liquid metals, to a fine mist. These all depend for their action upon a sudden and violent collision between a jet of the liquid and either a solid surface (generally moving relatively at a high speed—*e.g.*, a rapidly rotating disc), a second jet of the liquid itself, or a jet of compressed gas. In a similar way, a bubble film breaks up into fine droplets when the bubble bursts, as in the formation of a mist during effervescence.

In all these methods, the degree of dispersion that is obtained with a given spray producer depends upon the velocity of impact—*i.e.*, the energy of dispersion—the viscosity of the liquid, and its surface tension and density. The success of any spraying action obviously depends upon the speed with which it can be completed. An increased viscosity not only delays the extension of the liquid, but also retards the action of surface tension in bringing about the segmentation of the extended liquid into drops. Long before dispersion has been completed the liquid may have fallen to the ground. Since relatively a much greater amount of energy is absorbed in extending the surface of a liquid of high viscosity, much greater pressures are required to produce a given degree of dispersion.

The lower the surface tension, the less will be the amount of energy that is used up in extending the liquid, and therefore, other things being equal, the further will the surface be extended by a given impact.

Similarly, the lower the density of a liquid, the further will it extend in response to a given impact.

The degree of dispersion that can be produced with a given expenditure of energy by spraying, therefore, can be increased by reducing the viscosity—*e.g.*, by raising the temperature, or by diluting with a liquid of comparatively low viscosity—or by lowering the surface tension—*e.g.*, by the addition of a substance like saponin to an aqueous salt solution. If these alterations are impracticable, it will be necessary to increase the velocity of impact at the surface of the jet.

II. Condensation Processes

When any substance is steadily heated, the amount of kinetic energy possessed by each molecule of the substance gradually increases. The molecules move more swiftly, and tend more and more to overcome the attractive forces that hold them together. The solid expands. The molecules become like ships that drag their anchors in a crowded harbour—the substance melts. The molecules put out to sea—the substance evaporates. In the gaseous state, all the molecules can be considered to be moving separately and freely along relatively long, mean, free paths.

In this condition, the substance occupies its maximum volume. Its total surface consists of the sum of the surfaces of all its molecules, and is thus the maximum surface possible. All molecules belong to the surface; none are internal and remote from the surface. In the gaseous state, therefore, the substance attains maximum chemical activity, partly because all the molecules are available almost simultaneously and partly also because each molecule in the gaseous state possesses a maximum content of kinetic energy. Further, the molecules are too far apart to be restricted by any of the intermolecular forces to which the characteristic surface condition of a liquid, or the tensile strength and rigidity of a solid, are due. This

change of state and increased activity are only made possible by increasing sufficiently the kinetic energy of the molecules.

If, now, we withdraw energy from a gas—for example, by cooling it gradually or by expanding it suddenly—we shall diminish the stock of kinetic energy possessed by each separate molecule. They will move more slowly, so that when they collide the attractive forces will tend more and more to overcome the force of rebound; ultimately, if the withdrawal of energy be carried far enough, the force of intermolecular attraction will reassert its ascendency, and throughout the whole volume of the contracting vapour there will be a strong tendency to liquefaction.

In a homogeneous system, it is very difficult to induce a change of state, as, for example, the crystallisation of a salt from a supersaturated solution. Some point of singularity, some nucleus or free surface, is necessery to act as a centre, from which the change can spread. A gas may be cooled until it has become a highly supersaturated vapour, and yet not condense to liquid if there are not suitable condensation nuclei present.[5] In such circumstances, progressive condensation occurs upon the walls of the containing vessel. In the presence of suitable nuclei, however, condensation occurs upon them simultaneously throughout the entire volume of the gas.

Such condensation nuclei may be dust particles, smoke particles, or complex or simple gaseous ions. They may be present in the gas before it is supersaturated, or they may be introduced or formed *in situ* during or after supersaturation. The condensation of a vapour upon such suspended nuclei produces a cloud or mist. The character of the cloud will vary very much according to the number, size and nature of the nuclei, and whether they are all present initially, or are produced during the reaction. In general, it may be said that a gas can readily be supersaturated, but that cloudy condensation will not occur in the absence of sufficient suitable condensation nuclei. In the absence of such nuclei, condensation will ultimately occur abruptly at a much higher degree of supersaturation, with the formation of large drops.

The formation of an aerosol by condensation may be accom-

plished by cooling either a pure vapour or a mixture of one or more vapours and gases; *e.g.*, dry steam as it expands may become wet steam—an aerosol of water in water vapour—or air saturated with water vapour may become a cumulus cloud or a fog—an aerosol of water in saturated air.

In every case, condensation is the spontaneous result of the withdrawal of energy from the system. Unlike dispersion processes, therefore, which are essentially forced processes, requiring the expenditure of energy, condensation processes occur spontaneously. When once a condensation process has begun, it is difficult to arrest it. The particles grow rapidly by further condensation or by coalescence, and, unless this can be arrested in some way, the aerosol will, if a liquid, soon rain itself out, or, if a solid, become flocculated.

In studying the formation of aerosols by condensation processes, it will be well to commence with a simple and familiar example, the condensation of water vapour in air.

The Condensation of Atmospheric Water Vapour.—A vapour may be cooled to saturation either by bringing it into contact with a relatively cold surface, whether solid, liquid or gas (surface cooling), or by expanding it adiabatically (volume cooling).

Surface Cooling is necessarily limited to the surface of contact with the cold substance. Condensation occurs upon the cold surface, and, therefore, if the surface be a continuous one—*i.e.*, solid or liquid—without the formation of an aerosol. If the cooling surface be gaseous, as, for example, when a mass of warm, humid air mixes with a mass of cold air, supersaturation may occur at the surface of contact, and spread gradually through the mass as the gases mingle. The vapour would condense upon any suitable nuclei that were present in either mass of gas.

Occasionally surface cooling may simulate volume cooling by occurring at many points simultaneously throughout the volume of the gas—for example, when warm, humid air is dried by being sprayed with ice-cold brine or water, water vapour condenses upon the minute droplets of the cold spray. Also when warm, humid air, containing suspended dust particles,

drifts slowly along the ground after a warm day, the dust particles lose heat by radiation more rapidly than the surrounding air, and become relatively cold, so that water vapour condenses upon them to form a mist. Actually these are both instances of surface cooling, but, occurring at many points simultaneously throughout the volume of the gas, might at first sight be mistaken for volume cooling.[6]

Volume Cooling by Adiabatic Expansion.—When the pressure upon a volume of air (V_1) is decreased, the air expands to a volume (V_2). To effect this expansion, which involves the performance of work, and, therefore, the expenditure of energy, a part of the heat energy of the air is utilised, and if the gas expands so slowly that heat energy flows in from outside as quickly as it is expended inside in doing the work of expansion, then the temperature of the air will remain constant throughout (isothermal expansion). If, however, the expansion be performed suddenly, or if the containing vessel be thermally insulated, then the temperature of the air will be lowered by the expansion by an amount that will be proportional to the amount of work done.

The degree of cooling will be directly proportional to the degree of expansion—that is, to the ratio $\frac{V_2}{V_1}$.

If, now, the air originally be saturated with water vapour, then this cooling of the air produces supersaturation to an extent which also is proportional to $\frac{V_2}{V_1}$.

Commencing with air saturated at a temperature $T_1 = 20°$ C., the degree of cooling $(T_1 - T_2)$ and the degree of supersaturation (S) produced by given expansion ratios $\frac{V_2}{V_1}$ are shown in Fig. 2.

$S = \frac{C_1}{C_2}$, where C_2 is the concentration of water vapour in the air at the final temperature T_2, and C_1 is the concentration of water vapour in the air immediately before expansion.

The initial pressures are chosen so that, after expansion, the pressure of the gas shall be 760 mm.

After the expansion is completed, and if suitable nuclei are present, vapour rapidly condenses upon the nuclei.

As condensation proceeds the degree of supersaturation diminishes and the temperature of the vapour steadily rises, owing to the liberation of the latent heat of condensation, until the vapour is just saturated at the temperature that is then reached, the equilibrium temperature. Condensation then ceases. This equilibrium temperature (t') for different degrees of expansion is also shown in Fig. 2.

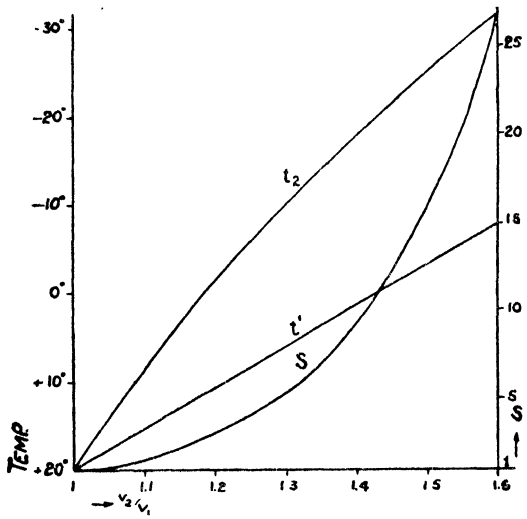


FIG. 2.—Variation of maximal cooling temperature t_2, equilibrium temperature t', supersaturation S, with ratio of volumes V_2/V_1 in the case of condensation of water vapour by adiabatic expansion.

Nuclei Necessary.—If the air and water vapour be entirely freed from condensation nuclei—for example, by filtration through a plug of cotton wool—no condensation occurs until the expansion almost reaches 1·25—*i.e.*, a supersaturation of nearly 4·2 times.

Ordinary unfiltered air contains an enormous number of condensation nuclei—dust particles, positive and negative gaseous ions, smoke particles, etc. Consequently condensation occurs readily at lower degrees of supersaturation.

If such dusty air be expanded once or twice, and the cloud that is formed be allowed to settle, it will deposit all the particles that served as condensation nuclei at these low expansions. It will then no longer be possible to obtain cloudy condensation at expansions below 1·25.

For expansions varying from 1·25 (S = 4·2) to 1·28 (S = 5·0) some condensation occurs in the form of fine rain.

Between expansions 1·31 and 1·34 (S = 5·8 to 6·8) more fine rain by condensation is obtained. The size of the drops in this condensate varies throughout the process of condensation, but in general it varies from 0·2 mm. radius (200μ), when S = 4·2, to about 0·02 mm. (20μ) radius, when S = 6·8 (1 mm. = 1,000μ = 1,000,000 $\mu\mu$). About one hundred drops are present per cubic centimetre at the moment of formation. Such drops sink to the bottom of the vessel in about one second.

When S = 8, $\left(\frac{V_2}{V_1} = 1{\cdot}4\right)$, the condensation becomes fog-like, and when S = 12, $\left(\frac{V_2}{V_1} = 1{\cdot}43\right)$, the condensation begins to become coarse again, and steadily becomes coarser as S increases. When S = 12, the radius of the drops is about 0·6 μ.

Influence of the Character of the Nuclei upon the Condensation Process.—These well-defined variations in the character of the condensation process are due to the specific action of different kinds of condensation nuclei. As these nuclei may differ in shape, in chemical character, or in electrical charge, the precise degree of supersaturation at which vapour will condense upon them will be determined by the properties of the particular nuclei that are present. In the absence of nuclei, it is impossible for condensation to occur, except at extremely high degrees of supersaturation.

It has been shown that the vapour pressure of a liquid may be greatly modified according to the curvature of the surface of the liquid. At a given temperature, the vapour pressure at a convex liquid surface of a sufficiently small radius of curvature is greater, while that at a concave surface is less, than that at a plane surface. Clearly, therefore, a vapour will condense more readily upon a porous nucleus—concave surface—than upon a convex one.

Little is known about the actual shape of nuclei, but it is reasonable to assume that liquid nuclei are spherical and, therefore, have a convex surface, while solid, crystalline nuclei may present a series of plane surfaces to the vapour, or, if irregularly crystalline or amorphous in structure, may at some point be concave. Vapour will condense more readily upon an irregular

particle—*e.g.*, a dust particle—than upon one more regular or continuous.

The vapour pressures (p) above a plane surface, and (p') above a curved surface whose radius of curvature is (r) are related to each other and to (r) by the expression [7]—

$$\text{Log.}\ \frac{p'}{p} = \frac{2\sigma}{r\rho \mathrm{RT}}, \quad . \quad . \quad . \quad . \quad (1)$$

where σ is the surface tension of the liquid,
ρ is the density of the liquid,
R is the gas constant,
and T is the absolute temperature.

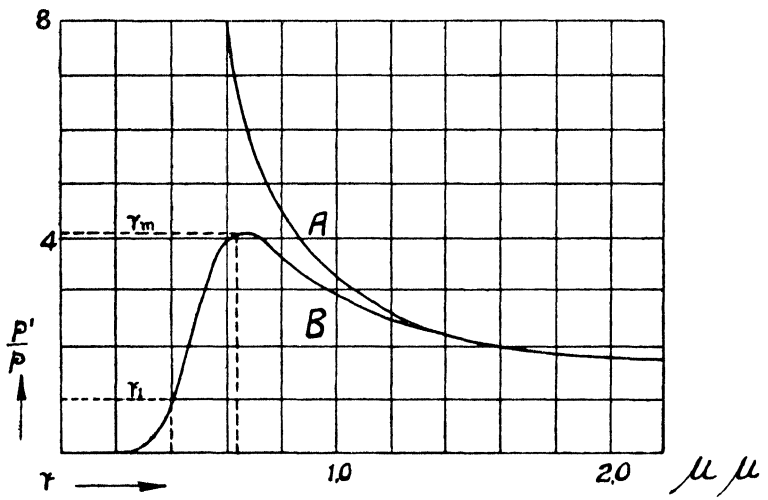


FIG. 3.—Vapour pressures of very small water droplets.

The values of $\frac{p'}{p}$ for different values of r are plotted in curve A, Fig. 3, assuming that the surface is convex, and that p', therefore, is greater than p. For a concave surface p' would be less than p, so that $\frac{p'}{p}$ would possess values less than 1, and the curve would be inverted.

At a plane water surface at 0° C. the vapour pressure p is 6,000 dynes per square centimetre. For a water droplet of radius μ, the vapour pressure at 0°C., p' is 6,007·3 dynes

per square centimetre—a negligible difference. We see from the curve, however, that, when the value of r has become 1·6 $\mu\mu$, $\frac{p'}{p} = 2$—that is, p' is twice as great as p. As the radius is further diminished p' increases with increasing rapidity.

Clearly, therefore, such small droplets would evaporate extremely rapidly at ordinary degrees of supersaturation. Conversely, it is impossible for vapour to condense upon them, unless the degree of supersaturation—that is to say, the density of the vapour—is very high. In the absence of nuclei, therefore, it is impossible for droplets to form, *i.e.*, for condensation to occur, unless, perhaps, at supersaturations of 8 or more, molecular aggregates exist of radius not less than 0·6 $\mu\mu$.

(At such extreme values of the curvature of the surface it is probable that the surface tension has a different value from that of a plane surface. If we assume that σ is diminished for a convex surface of such small radius of curvature, then $\log. \frac{p'}{p}$ is diminished, and consequently the value of $\frac{p'}{p}$ is smaller—that is, the increased vapour pressure of the droplet may not increase quite so rapidly at extremely small values of r.)

To induce condensation, therefore, it is necessary to introduce suitable nuclei that will reduce the pressure of the vapour at their surfaces. Such nuclei may be—

(*a*) Inert particles possessing plane surfaces, the vapour pressure at such a surface being equal to p, and, therefore, lower than the pressure of supersaturated vapour.

(*b*) Inert particles possessing porous surfaces, such that the radius of curvature of the pores is less than 1 μ—the value of r, at which for a concave surface, the pressure of the vapour begins to be less than at a plane surface. Clearly, once a film of vapour molecules has formed by adsorption, vapour will condense upon such a surface, even although it be unsaturated, and as the radius of curvature of the pores is further diminished it will condense readily upon the pore surfaces, even from vapour at pressures far below its saturation point.

(*c*) Inert particles carrying an electrical charge—*e.g.*, ionised

gas molecules. The presence of an electrical charge on the surface of a liquid opposes the surface tension, and, therefore, diminishes the vapour pressure, to an extent that is proportional to the fourth power of the drop.

For charged liquid surfaces

$$\log. \frac{p'}{p} = \frac{1}{RT\rho}\left(\frac{2\sigma}{r} - \frac{c^2}{8\pi r^4}\right), \quad . \quad . \quad . \quad (2)$$

where c is the quantity of charge per square centimetre of surface.[8]

The relation between $\frac{p'}{p}$ and r for charged droplets is shown in Fig. 3, curve B.

For a droplet of radius r, carrying unit charge, $\frac{p'}{p} = 1$, so that the vapour pressure of the charged drop is just equal to that of a plane liquid surface. If more vapour were to condense upon it, r would increase, and its vapour pressure would rapidly increase until, at a radius of 0·63 $\mu\mu$, the vapour pressure would reach a maximum, p' being about four times as great as p. Condensation is, therefore, impossible upon such charged droplets, if the radius is less than 0·63 $\mu\mu$.

Condensation is only possible if the vapour pressure diminishes as r increases—that is, when r is greater than 0·63 $\mu\mu$.

The pressure at which condensation to form a charged droplet first becomes possible, therefore, is that corresponding to radius r_m. This is 4·2 times that above a plane surface, a value which corresponds well with that obtained experimentally.

It is difficult to understand why, at a supersaturation of 4·2, water vapour condenses exclusively upon the negative ions, and, at a supersaturation of 6, upon positive ions. It would be more reasonable to expect that condensation would occur more readily upon positive ions, since these are generally the larger and condensation occurs more freely the larger the particle. Other vapours generally condense more readily upon positive ions. Apparently the anomalous behaviour of water vapour is due to some specific relationship between the character of the molecules of the vapour or of the "indifferent" gas and the size of the electrical charge. In this connection, it is

interesting to note that, when ultra-violet light passes through air, it ionises the constituent gases, and at the same time produces traces of such hygroscopic compounds as NH_3, H_2O_2, NO_2, etc. These form good nuclei for the condensation of water vapour.

(*d*) Substances that have a strong chemical affinity for the vapour. With water vapour, for example, hygroscopic substances such as NaCl, SO_3, combine with molecules of the vapour to form droplets possessing a lower vapour pressure, upon which more vapour easily condenses, even at low degrees of supersaturation—in fact, from unsaturated vapour. Droplets so formed have a permanently lowered vapour pressure, although it increases slightly as the drop becomes diluted by further condensation. Such droplets, therefore, remain stable even when the air has become unsaturated. Atmospheric water vapour condenses to form a mist or cloud, because of the presence of hygroscopic nuclei—*e.g.*, NaCl, SO_3—in the atmosphere. The stability of a city fog, often in a highly unsaturated atmosphere, has been attributed to the lowered vapour pressure of the droplets, owing to the presence of H_2SO_4 dissolved in them.

Degree of Dispersion.—The actual *amount of water vapour* that is condensed as the result of a given expansion is determined by the degree of supersaturation. The *number of droplets* formed, and, therefore, their average size, will depend upon the number of nuclei present in the air. The greater the number of condensation nuclei, the larger the number of droplets produced, and, therefore, since the total amount of water formed is determined for a given expansion, the smaller is the average size. The highest degree of dispersion will be obtained when a small total amount of condensation takes place on a very large number of nuclei. Cloudy condensation results, since dust particles are numerous, in ordinary air at low expansions. In dust-free air, condensation must occur upon gaseous ions.

The " natural " ionisation of air is very small, and the negative and positive ions that serve as nuclei for expansions between 1·25 and 1·34 are not very numerous. The degree of dispersion, therefore, is correspondingly low—fine rain.

If the ionisation of the air be increased, *e.g.*, by X-rays or radioactive substances, the degree of dispersion will be greatly increased, and cloudy condensation will be produced instead of fine rain. This fact has been employed very ingeniously by C. T. R. Wilson to make visible the paths of α and β particles travelling through supersaturated and otherwise unnucleated air. The particle ionises the air as it passes through it, leaving behind it a trail of cloudy condensation.

The particular nuclei that commence to operate when S = 8

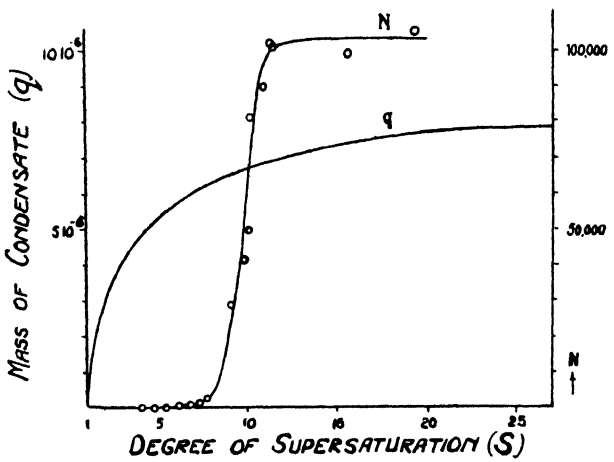


FIG. 4.—Variation of mass of condensate q and number of drops N per cubic centimetre with supersaturation S in the case of condensation of water vapour by adiabatic expansion.

are electrically neutral, and appear to be derived from the water vapour itself and not from the air. Similar results are obtained when other gases—for example, H_2 and CO_2—are used instead of air. According to P. Lenard, these nuclei are complex water molecules.

In Fig. 4 is shown the relation between the degree of supersaturation (S) and (1) the mass (q) of condensate produced (grammes per cubic centimetre) and (2) the number of droplets per cubic centimetre (N) for dust-free air and water vapour. The sudden increase in nucleation when S = 8 is well shown.

Influence of the Gaseous Dispersion Medium.—Experiments with different gases show that, within the region S = 4·2 to 6·8, N is to some degree dependent upon the nature of the gas.[9] This is no doubt associated with the fact that the extent to which the gas is naturally ionised is different in different gases.

The nature of the " indifferent " gas plays an important part in determining the conditions and character of the condensation process. Although the general character of the process is similar in O_2, N_2, CO_2, Cl_2, or H_2, yet there are characteristic differences.

In hydrogen, fine, cloudy condensation occurs at supersaturations above 1·37. Between S = 4·2 and S = 8·0, however, no rainy condensation takes place. This is evidently due to an unusually low degree of ionisation. At ordinary temperatures hydrogen is but little ionised by ordinary ionising radiation. At lower temperatures, however, it is ionised more readily, large ions being formed that persist when the gas is warmed again and will then serve as condensation nuclei. At supersaturations above S = 8 hydrogen appears to contain more nuclei than other gases. In this case, the nuclei are probably complex water molecules.

Chlorine normally contains more ions than many other gases, such as O_2, N_2, CO_2, H_2. Consequently between S = 4·2 and S = 8 the condensation in chlorine is more fog-like than in these other gases.

The observation of condensation processes in gases, such as CO_2 and Cl_2, that at ordinary temperatures are relatively near to their critical points, is complicated by the difficulty of calculating accurately the degree of supersaturation.

The vapours of other substances behave similarly to water vapour. The values of S, N, and q are found to be characteristic and different for each substance. For highly disperse, freshly formed aerosols of the following substances in air [10]—

	Methyl Alcohol.	Ethyl Alcohol.	Propyl Alcohol.	Benzene.	Water.
S =	4·0	2·5	3·5	11·0	8
N =	160,000	340,000	360,000	190,000	100,000

Stability.—Condensation, once commenced, proceeds continuously until the state of supersaturation disappears. If the number of nuclei is small, the droplets first formed continue to grow until, if the degree of supersaturation be sufficient, the cloud will rain itself out, or if the nuclei be introduced gradually into the supersaturated air, the droplets that form on the nuclei that are first introduced will grow to be much larger than those that are formed subsequently, so that the degree of dispersion of the cloud will be very irregular.

Generally speaking, the primary degree of dispersion becomes less with time, and much lower secondary and tertiary degrees of dispersion succeed it. It is often difficult to observe the primary degree of dispersion, so quickly does the cloud pass, by further condensation or by the coalescence of adjacent particles into a secondary or tertiary degree of dispersion.

When a vapour condenses in the presence of an indifferent gas, the character and stability of the resulting aerosol may also be profoundly modified by the adsorption of electrically charged or neutral molecules of the gas upon the particles of the disperse phase. The presence of electric charges of the same sign, or of adsorbed gas films, inhibits the coalescence and flocculation of the particles, and thus tends to increase the stability of the aerosol. If, however, the electric charges on different particles are of opposite sign or of different density, flocculation will be assisted.

Thus the stability of the cloud can be increased—

(*a*) By protecting the particles with a layer of adsorbed gas or oil, or with electrical charges of the same sign.

(*b*) By ensuring at the outset an adequate supply of suitable condensation nuclei of the same electrical sign, and so producing a uniform and regular cloud.

(*c*) By avoiding an excessive degree of supersaturation, having regard to the number of nuclei present.

(*d*) By keeping the cloud free from undue agitation.

The Temperature of Condensation.—If water vapour be condensed at temperatures below 0° C., a cloud of minute ice crystals is formed.[11] In these circumstances, water is typical of a large number of substances that, in cooling, give solid-gas aerosols.

When a cloud of any substance is formed by the condensation of the vapour at a temperature below the freezing point of the disperse phase, the particles of the cloud may consist either of sub-cooled liquid or of solid. If the concentration of the vapour be sufficiently high for the dew-point to be above the freezing point of the liquid, condensation will produce droplets of liquid, which, as the temperature falls below the freezing point, will become sub-cooled. Water droplets in a cloud may, in the complete absence of the solid (ice) phase, be sub-cooled to temperatures as low as − 30° C. If, however, the concentration of vapour is so low that the freezing point is passed before the dew-point is reached, then, instead of liquid droplets being formed, the molecules of the vapour will condense upon the nuclei that are present to form crystals of the solid phase. Instead of a dew-point we obtain a " hoar-frost " point.

At temperatures below 0° C. the vapour tension of ice is lower than that of liquid water. Consequently the relative humidity of air that is in equilibrium with ice at such temperatures is lower than the relative humidity of air that is in equilibrium with sub-cooled liquid water—*i.e.*, than 100 per cent. The actual values of the relative humidity of air in equilibrium with ice at various temperatures below 0° C. are shown in Table I.:

TABLE I.

Temperature, ° C. .	0	− 10	− 20	− 30	− 40	− 50	− 60
Relative humidity, per cent. . .	100	91	82	74	67	61	55

If we consider air of which the relative humidity at a given temperature—say, − 30° C.—lies between the ice value (74) and the water value (100), we see that such an atmosphere will be unsaturated with respect to a water surface and supersaturated with respect to an ice surface. Consequently, if suitable nuclei are present, condensation will occur to produce ice crystals.

The Condensation of Metal Vapours *in vacuo*.—The study of

other condensation processes throws considerable light upon the mechanism of the formation of aerosols.[12]

When a vapour—for example, a metal vapour—contained in a glass vessel, condenses upon the wall of the containing vessel at some point, the conditions that obtain in the vapour in the neighbourhood of the glass surface just before and during condensation can be regarded as being analogous to the conditions that must exist at the surface of any nucleus upon which vapour is condensing.

From a consideration of the behaviour of various metal vapours Knudsen and Wood have suggested that, when a metal molecule encounters a surface of the same metal, it always adheres to it, the intermolecular force of attraction being stronger than the force of rebound. When the metal molecule meets a surface of another material, however, it may adhere or rebound according to the temperature—*i.e.*, according to the velocity of rebound. For a given surface there will be a critical temperature of contact, above which the molecule will rebound, and below which it will adhere. For mercury molecules striking a glass wall the critical temperature is about — 135° C. For silver molecules striking a glass wall it is about + 575° C.

At temperatures above this critical point it is possible to obtain very high degrees of supersaturation, since all the molecules are reflected. If, however, condensation be induced at any point of the surface—for example, by touching the wall of the containing vessel with a cotton plug dipped in liquid air—so that a metal surface is formed, then condensation continues upon this metal surface, even after it has warmed up again. Cadmium, magnesium and zinc show this phenomenon readily in glass vessels. According to Knudsen, the critical temperature for these metals lies below — 78° C.

Silver, gold, platinum, tungsten, molybdenum, nickel, iron, copper, do not behave in this way. When wires of these metals are heated electrically *in vacuo*, the metal molecules are sent out in straight lines and adhere to the glass wall of the containing vessel. Owing to the complete absence of reflection from the glass surface, any obstacle that is placed between the

wire and the glass will cast a well-defined shadow, within which no metal will reach the glass at all.

Other metals, including cadmium, magnesium, zinc, behave similarly below the critical temperature.

Langmuir[13] assumes that all vapour or gas molecules that strike any surface condense upon it, no matter what the temperature of the surface may be. At the same time, molecules that have previously condensed upon the surface will re-evaporate after a definite interval of time, and at a rate that will depend upon their vapour pressure. This may be greater or less than the normal vapour pressure of the substance, according as the attractive force that exists between the condensed molecules and the surface upon which they are condensed is smaller or greater than that which exists between the condensed molecules and other molecules of the same substance. In most cases of adsorption, the condensed molecules of gas or vapour are held to the adsorbing surface by a relatively large attractive force. Consequently, an adsorbed layer of gas or vapour molecules can be formed at a solid or liquid surface at temperatures far above the normal boiling point of the adsorbed substance. Such an adsorbed layer of molecules would re-evaporate only with great difficulty.

Liquid cadmium and mercury do not wet glass. There is, therefore, very little attraction between their molecules and those of a glass surface. Consequently, when molecules of cadmium and mercury vapour strike a clean glass surface and condense upon it, the attractive force that is exerted upon them by the molecules of the glass surface is less than that which is exerted by the molecules of a cadmium or mercury surface respectively. They will evaporate, therefore, more readily from a glass surface than from one of cadmium or mercury.

Langmuir has shown that, at room temperature, there is practically no evaporation of molecules of tungsten, platinum, copper, gold, silver, molybdenum, carbon, iron, nickel and thallium from a glass surface. Cadmium and mercury molecules evaporate readily below room temperature.

The range of action of intermolecular forces is very small, so

that they act only between molecules that are practically in contact with one another. Consequently, a surface—*e.g.*, glass—that has become covered with a layer of cadmium molecules behaves, so far as further evaporation and condensation are concerned, like a surface of massive cadmium. If molecules of cadmium vapour condense upon such a cadmium surface, they will be held by the stronger attractive force of the cadmium molecules, and will re-evaporate much less readily. Once, therefore, the first layer has formed, evaporation practically ceases and further successive layers are formed upon it with ease.

We see, therefore, that, at any surface of condensation, a condition of dynamic equilibrium exists between molecules of the vapour that are condensing and molecules of the condensate that are evaporating. Above Knudsen's critical temperature, the rate of evaporation is greater than the rate of condensation. The molecules of the first layer do not linger long enough to become covered by others. At lower temperatures, evaporation is much slower and is overtaken by condensation, so that further layers of condensate readily form upon the first.

From these experiments it is reasonable to assume that the relationship between a vapour and the nucleus upon which it can condense is largely a specific one, depending upon the attractive force between the molecules of the vapour and those of the nucleus.

It will also depend upon the pressure of the vapour, since this will determine the rate of condensation ; and upon the temperature of the condensing surface, since this will affect the rate of re-evaporation.

The character of the metal condensate that is formed upon the glass is affected by the temperature of the vapour just before and during condensation. The highest degree of dispersion of the condensate is obtained when a very hot vapour is condensed upon a very cold surface, preferably below the critical temperature—that is, when the vapour is highly supersaturated. Highly refractory elements—*e.g.*, tungsten, molybdenum, platinum, nickel, iron, carbon—give condensates so highly disperse that they appear to be continuous even under the highest power of the microscope. In such cases, the tempera-

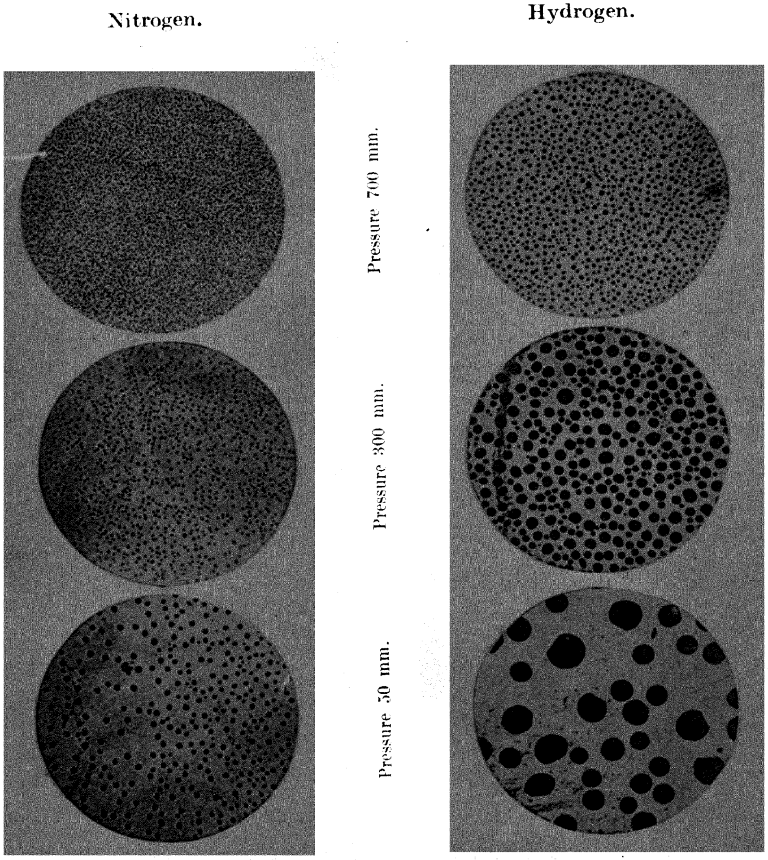


FIG. 5.—Condensation of zinc vapour. (According to Kohlschütter.)

ture gradient at the surface of condensation is very steep—3,000° C. for a tungsten wire and a cold surface. Under these conditions the condensate, when first produced, appears to be a film of amorphous metal. In time, however, this film undergoes further condensation, breaking up into discrete particles. This change is facilitated by heat, and appears to be analogous to the change that takes place in a metal during annealing.

Less refractory elements—*e.g.*, gold, silver, copper—give less highly disperse condensates, that rapidly disintegrate into discrete particles.

Metals such as magnesium, zinc, cadmium, give coarse, granular condensates, in which the larger grains grow rapidly at the expense of the smaller ones.

The presence of a thin film of some salt upon the glass surface prevents the formation of a coherent film. The granular film that is formed instead has a much lower light absorption. This fact is utilised in the manufacture of electric incandescent lamps to prevent the darkening of the glass by metal condensate from the filament.

Condensation of Metal Vapours in an Indifferent Gas.—When a metal vapour is allowed to condense in an atmosphere of an indifferent gas, the character of the condensate is greatly modified. The degree of dispersion of the condensate increases with the pressure of the gas and with the density of the gas. The more numerous the gas molecules and the heavier they are, the more likely they are to become adsorbed upon the surface of the newly formed particles and thus prevent them from coalescing. At the same time, the presence of a greater number of heavy gas molecules will tend to diminish the frequency with which the metal particles collide *with each other*.

In Fig. 5 are shown condensates formed from zinc vapour in gases of different densities and at different pressures.

The condensation of metal vapour in an indifferent gas can be conveniently studied by maintaining in the gas a direct current arc between two electrodes of the metal. When an electric arc or spark passes between electrodes of any suitable metal in a current of air, the metal vapour is diluted and cooled by the air stream, and a fine smoke is formed. Oxidisable

metals—for example, cadmium, lead, copper, manganese, chromium, magnesium, aluminium, antimony, iron—readily give oxides, whilst platinum, silver, and gold yield metallic smokes.

Ehrenhaft [14] has shown that such an arrangement produces rather a coarse condensate, which soon settles on the walls of the containing vessel. At the same time, the finest particles remain suspended in the gas for hours. Actually the initial or primary degree of dispersion is very high under such conditions, but the rate of coagulation is also so rapid that the originally high primary degree of dispersion is soon succeeded by much lower secondary and tertiary degrees of dispersion.

This rapid degradation of the aerosol is due partly to the further condensation of vapour upon the particles, and partly to coalescence of the particles with one another. The rapid coalescence of the particles is to be attributed to the frequency with which they collide with one another, on account of the Brownian movement imparted to them by the molecules of the gas. The rate of aggregation is most rapid at the time of formation, when the newly formed particles are moving most vigorously and are most numerous. The rate falls off rapidly, and, after a time, the size of the particles remaining in the gas becomes almost constant.

The rate at which the condensate grows coarser appears to depend very largely upon the density of the gas, a higher degree of dispersion being obtained in nitrogen than in hydrogen.

The degradation of the condensate can be arrested, to some extent, by condensing the vapour in close proximity to a cold liquid or solid surface. The condensate that is deposited upon such a surface generally is of a higher degree of dispersion than that formed freely in the gas. When the arc is immersed in a liquid, in order to produce a hydrosol or organosol of the metal in question, the liquid in immediate contact with the arc is volatilised, and the greater part of the metal vapour actually condenses in the vapour of the dispersion medium.

Similar results can be obtained by volatilising metal wire or foil, immersed either in an indifferent gas or liquid, by passing a sufficiently intense electric current through it.

Chemical Interaction in the Gas Phase.—A physical mixture of two gases is the most intimate mixture that can be obtained. If the gases react chemically with one another, they will, when mixed, combine sooner or later to produce a third substance, that may be either solid, liquid, or gas, and will have entirely different physical and chemical properties. Generally the product of this reaction has a very much lower vapour pressure than either of the original reactants, so that the resulting gas mixture is supersaturated with it, and some of it is precipitated. The degree of supersaturation of the final product is determined by the initial concentration of the reacting gases and the vapour pressure of the resulting compound. In this case, energy is removed from the original gases in the form of chemical energy —the heat of combination—and in general the difference between the molecular vapour pressure of the reactants and that of the resultant is a measure of the molecular heat of combination.

Since gases are molecularly disperse, it is clear that the reaction must be intermolecular, and the product, when first formed, must be in a molecularly dispersed condition. The newly formed molecules coalesce and condense to form liquid or solid particles at a rate which is determined by the degree of supersaturation of the products. The formation of a cloud or smoke by the chemical interaction of two or more gases, therefore, is essentially a condensation process.

The manner of condensation and the character of the resulting aerosol differ according to the extent to which the gases can be mixed before they react.

If the gases can be mixed completely before they react—for example, photochemical reactions, in which reaction is catalysed by light, *e.g.*, H_2S and SO_2—then precipitation takes place in and from a homogeneous medium, and a uniform aerosol results (volume condensation).

If, however, the gases react immediately they are brought into contact with one another—*e.g.*, NH_3 and HCl—then the formation and precipitation of the reaction product occurs at the surface of contact of the two gases, and only spreads as the gases mingle (surface condensation). This form of reaction

necessarily produces an aerosol of a lower and more uneven degree of dispersion.

In both cases, the more dilute the reacting gases are, the higher is the initial degree of dispersion of the resulting product. Ammonium chloride smokes can be prepared over a wide range of concentrations, for example from 0·02 to 1·2 mgm. per litre. Fine smokes of zinc oxide can be obtained by decomposing zinc ethyl vapour, highly diluted with an indifferent gas, in a rapid current of air.

In many cases, as in combustion processes, a gas reaction proceeds exothermically, and the reaction product, although gaseous at the temperature of formation, condenses as it cools.

Condensation is frequently the last and least obvious stage of a more complex process. Thus—

(*a*) A salt, introduced into a Bunsen flame, vaporises in the hot gases of the flame. The mixture of hot gases and salt vapour is cooled by mixing with the surrounding air, and the vapour is condensed.

(*b*) When a volatile solid—*e.g.*, NH_4Cl—is heated sufficiently, it volatilises ; the vapour mixes with cold air, and condenses to form a smoke.

(*c*) When a current of air passes over or through a hot solid or liquid that is only slightly volatile, the air becomes heated and saturated with vapour at the temperature of contact. A part of this vapour is precipitated as the air passes from the heated zone and cools. Such bodies as anthracene, acetanilide, diphenylamine, orthophthalic acid, paraffin wax, readily produce highly disperse smokes by this method. Other substances, such as benzyl benzoate, or clean mercury, produce either a coarse cloud or no detectable smoke.

(*d*) A hygroscopic substance does not fume in moist air at a given temperature—*e.g.*, the ordinary room temperature—unless either it, or one of the products of hydrolysis, possesses a considerable vapour tension at the given temperature. HCl, Al_2Cl_6, $SnCl_4$, fume in moist air at the ordinary temperature, but $CaCl_2$ and H_2SO_4 do not. The fume is produced by the condensation of atmospheric water vapour upon the hygroscopic vapour molecules.

The Law of Corresponding States. — Von Weimarn[15] has shown that, when any substance (*e.g.*, $BaSO_4$) is formed by double decomposition from solutions of two salts (in this case, for instance, $BaCl_2$ and Na_2SO_4) in a solvent (in this case, water) in which the substance is very slightly soluble, the physical characteristics of the resulting precipitate of the substance will depend upon (*a*) its solubility in the solvent used, (*b*) the amount of it that is formed per cubic centimetre in the reaction, and (*c*) the viscosity of the final solution. By choosing suitable solvents and adjusting the concentrations of the reacting solutions, the resulting precipitate may be obtained in states of aggregation as widely different as coarse crystals, colloidal solutions and jellies.

If (s) (in equivalents per litre) be the solubility of the substance in the selected solvent, (c) (in equivalents per litre) the amount of the substance that is potentially present in the mixed solution prior to precipitation, and (η) the viscosity of the solution, then the physical characteristics of the precipitate will be determined by what von Weimarn calls the dispersion coefficient of the substance (δ), which is equal to $\left(\frac{c}{s}\eta\right)$. It is found that the greater the value of (δ)—that is to say, the greater the degree of potential supersaturation—the finer will be the precipitate. A small value of (δ) corresponds to a coarse-grained precipitate.

Since the quantities concerned in this expression are only numerical, von Weimarn generalised the expression in the following way. The physical characteristics of *any* precipitate will be the same, provided that it has been precipitated under corresponding states or conditions—that is to say, when the quantity $\left(\frac{c}{s}\eta\right)$ has the same value for different reactions. It is reasonable, therefore, to assume that this law should hold for reactions between gases, and for the condensation of vapours, by adiabatic expansion.

The viscosity of water at 20° C. is approximately two hundred times as great as that of air at the same temperature. For approximately the same values of (c) and (s), therefore, $(\delta)_{\text{water}}$

$= 200\ (\delta)_{air}$. Consequently, to produce a precipitate of given grain, smaller degrees of supersaturation are required in gas reactions than in liquid reactions.

In any particular gas reaction, an increase in the value of (s) should produce a higher degree of dispersion. When water vapour is condensed in the absence of dust particles and gaseous ions, no condensation appears to occur until its supersaturation exceeds 8, except upon the walls of the container. At values of (s) greater than 8, the degree of dispersion rises rapidly, and, after reaching a maximum at ($s = 12$), diminishes again.

The existence of a critical degree of supersaturation below which no condensation occurs, but above which highly dispersed condensates are formed, appears to be characteristic of condensation in gases. It may correspond to the critical temperature that is observed when a vapour condenses upon a solid surface. Below the critical degree of supersaturation, vapour molecules that may have condensed upon each other or upon aggregates of the accompanying gas molecules will evaporate more rapidly than they condense. As the degree of supersaturation increases, the rate at which the molecules condense will also increase, whereas the rate of re-evaporation will not change appreciably since the temperature remains practically unaltered.

Upon the surface of the glass container, however, owing to the attraction that exists between the vapour molecules and those of the glass surface, the condensation of water vapour will occur more readily than re-evaporation.

Apparently, in all such condensation reactions, whether in liquid or gaseous media, the product is formed initially in a molecularly disperse condition. The final degree of dispersion will be the result of the gradual coalescence of these particles. Naturally, this will be influenced by the initial concentration of these particles and by the frequency and intensity of their Brownian movement—that is to say, by the viscosity of the dispersion medium. It will also depend upon the charges upon the particles, upon the presence upon them of adsorbed molecules of the dispersion medium, and upon the duration of time for which the particles are able to remain in suspension in the dispersion medium.

In gases, these molecularly disperse particles will diffuse comparatively rapidly to the walls of the containing vessel. Also, after reaching an appreciable size, they will speedily settle out of the system. Further, they are more likely to become protected by the adsorption of molecules of the dispersion medium. On the other hand, their collision frequency will be higher and, unlike the particles of disperse systems in liquids, they may carry unlike electrical charges, which will tend to promote coalescence or, at least, flocculation.

It would be interesting to study, in the light of von Weimarn's law, such physical and chemical methods of producing different substances from gases and vapours. If water vapour, for instance, were expanded adiabatically at different temperatures, thus giving different values of (s), the value of (c) could be varied at the same time by adjusting the degree of expansion. Similar experiments could be carried out with many other vapours of metals or other substances. Similarly, in flames, in cthe ondensation of gases and vapours, and in many gas reactions in which a non-volatile substance is produced, there would appear to be wide scope for the prosecution of an interesting investigation.

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CHAPTER III

THE MOVEMENTS OF THE PARTICLES

A PARTICLE suspended in a gas may move under the influence of—

(*a*) Forces which originate independently of the gas—*e.g.*, gravitation, centrifugal action, an electric field ;

(*b*) Forces which are the direct result of the molecular activity of the gas itself—*e.g.*, Brownian motion.

A gas is assumed to consist of molecules moving swiftly and ceaselessly in all directions in what is otherwise empty space. When the gas is in a condition of equilibrium, the molecules will have the same mass, the same kinetic energy and equal mean free paths. At constant pressure both the kinetic energy and the length of the mean free path will increase with rising temperature. At the critical temperature increased pressure will cause them both to diminish to minimum values.

In air at the ordinary pressure, λ, the mean free path of the molecules, (1×10^{-5} cm.), is more than 300 times the diameter of the molecules themselves, ($2{\cdot}86 \times 10^{-8}$ cm.). The molecules move with a velocity (u) equal to about 4×10^{-4} cm. per second. The collision frequency (number of collisions experienced by 1 molecule in a second) is equal to $\frac{u}{\lambda} = 4 \times 10^{9}$.

(a) Motion of Suspended Particles under the Influence of Forces external to the Gas

When a liquid or solid particle is suspended in a gas, it is subjected to a general bombardment by the molecules of the gas. If the particle is large when compared with the length of the mean free path of the gas molecules, the general effect of the molecular bombardment will be that of a uniform continuous pressure, exerted normally over the entire surface of the particle.

If the particle be moving through the gas—for example,

falling by gravity—the force of the molecular impacts will be greater in front of the moving particle than behind it by an amount which will depend upon the velocity of the particle. The particle will thus encounter a continuous uniform resistance to its motion, which will become greater as the velocity of the particle increases.

If the gas be moving bodily, as in a convection current, it will, by virtue of this resistance, impart to particles suspended in it a velocity which will depend upon the velocity and resistance of the gas and the mass of the particles. The particles will thus move along a path which will be the resultant of that due to gravity or any other external force, and that due to the motion of the gas.

When, however, the particle is small compared with the mean free path of the gas molecules, it will no longer encounter a continuously uniform pressure. It will tend to slip between the molecules, and will be driven hither and thither by the now irregularly distributed impacts of the gas molecules. It will also rotate about its axis. Such a particle moving under the influence of an external force—*e.g.*, gravity—in a gas at the ordinary pressure will pursue a zigzag course.

Its motion in a convection current will be correspondingly more complex.

It will be convenient to consider separately the behaviour of particles respectively larger than and smaller than 10^{-5} cm., the diameter of the mean free spaces of a gas at ordinary temperature and pressure.

Particles larger than the Mean Free Spaces of the Gas.—The velocity with which small spherical particles move through a uniformly viscous fluid (liquid or gas) under the influence of an external force—*e.g.*, gravity—or, if the particles be charged, an electric field—will be equal to $\frac{F}{K}$, where F is the strength of the force, and K is the frictional resistance encountered by the particle in passing through the gas.

It has been shown by Stokes [1] that $K = 6\pi\eta rv$, where η is the viscosity coefficient of the gas, r the radius of the particle and v its velocity. The resistance increases as the particle

becomes larger or moves more rapidly. It is also proportional to the viscosity of the gas.

A particle will be pulled vertically downwards by gravitation with a force which *in vacuo* will be equal to $\frac{4}{3}\pi r^3 pg$ dynes. In air or any other fluid, the force will be diminished by the buoyancy of the fluid, and will be equal to $\frac{4}{3}\pi r^3 (\rho - \rho')g$, where ρ is the density of the particle and ρ' that of the fluid.

When the velocity with which the particle is falling is such that the resistance it encounters just balances the weight of the particle, it will continue to fall at that velocity.

At this point—

$$6\pi\eta r v = \frac{4}{3}\pi r^3(\rho - \rho')g, \quad . \quad . \quad . \quad (3)$$

so that v, the ultimate constant velocity of the particle, will be equal to $\frac{2}{9}r^2 \frac{(\rho - \rho')g}{\eta}$. . . . . (4)

(For a particle moving in an electric field $F = Xe$, where X is the strength of the field in volts per centimetre, and e is the charge on the particle. Consequently $v = \frac{Xe}{6\pi\eta r}$. . . (5)

For particles of a given substance falling in air $(\rho - \rho')$ and η will have constant values, so that the velocity of the particle will be directly proportional to the square of its radius.

Stokes used this formula to calculate the rate at which the droplets of water of which clouds are formed sink in air. In this case, $\rho = 1$ and ρ' can be neglected, $\eta = 1{\cdot}81 \times 10^{-4}$ c.g.s. units, so that $v = 12 \times 10^5 \times r^2$ cm. per second.

For very small cloud particles of radius r cm. the rates of fall were found to be as follows :—

TABLE II.

Radius of Droplet, r cm.	Rate of Fall, V cm. per second.
10^{-2}	120 = 4,320 metres per hour.
10^{-3}	1·2 = 43·2 ,, ,,
10^{-4}	12×10^{-3} = 43·2 cm. per hour.
10^{-5}	12×10^{-5} = 4·32 mm. per hour.

Particles of greater or less specific gravity fall in air with correspondingly larger or smaller velocities.

Non-spherical particles fall in the position in which they will encounter maximum resistance. Fine crystals of ice fall through the air with their longer axis horizontal. Similarly, a cubic crystal falls point downwards, a plate or disc in a horizontal position.

Lord Rayleigh has shown that Stokes' law no longer holds when the radius of the water droplets exceeds 10^{-2} cm. Such droplets fall as rain.

In addition to the size of the particle, the viscosity of the gas determines the rate of fall of particles suspended in it. A given particle will fall twice as quickly in hydrogen or water vapour ($\eta = 0{\cdot}93$ and $0{\cdot}975 \times 10^{-4}$) as in air ($\eta = 1{\cdot}9 \times 10^{-4}$).

Particles that are smaller than the Mean Free Spaces of the Gas.—When a particle smaller than 10^{-5} cm. is suspended in a gas at the ordinary pressure, or when a larger particle is suspended in a rarefied gas, it will be smaller than the mean free spaces between the gas molecules. Consequently it will tend to slip between the molecules of the gas. The velocity with which it will be driven through the gas by a given force will, therefore, be greater than that given by Stokes' law. It has been shown by Cunningham [2] and Millikan [3] that—

$$V = V' \left(1 + K\frac{\lambda}{r}\right), \qquad . \quad . \quad . \quad (6)$$

where V is the true velocity and V′ the velocity according to Stokes' law, λ is the length of the mean free path of the gas molecules, and r is the radius of the particle. K is a constant approximately equal to 0·86.

Millikan [4] investigated the behaviour of charged oil droplets suspended in a gas, and exposed to the action of a vertical electric field. By an ingenious contrivance individual oil droplets could be introduced into an observation chamber formed between two parallel horizontal electrodes. The oil was sprayed in the form of a fine mist into a chamber situated above the upper electrode. The oil particles were found to be strongly charged by the spraying process. Individual particles

found their way into the observation chamber through a pin-hole in the upper electrode. By applying a force of some thousands of volts the gravitational force upon a given particle could be balanced, so that, after falling through a given distance under gravity, the particle could be brought back to its original position and the fall repeated as many times as desired. It was thus possible to observe accurately the rate of fall of a given particle. By diminishing the pressure of the surrounding gas the rate of fall of the particle for different values of λ could be determined. The relation between V and V′ for small oil drops, calculated from Millikan's observations, is shown in the following table [5] :—

TABLE III.

Stokes' Law.	Stokes-Cunningham Law.
1×10^{-4}	$1{\cdot}14 \times 10^{-4}$
1×10^{-5}	$2{\cdot}57 \times 10^{-5}$
1×10^{-6}	$4{\cdot}5 \times 10^{-6}$
1×10^{-7}	$17{\cdot}0 \times 10^{-7}$

(b) Brownian Movement

Very small particles not only move more readily through the relatively coarse gas network, but are also subjected to a vigorous buffeting by the rapidly moving gas molecules. Consequently they are driven hither and thither in a perpetual Brownian movement similar to, but more violent than, that described by particles suspended in a liquid.

According to the kinetic theory, the average kinetic energy of a particle in Brownian motion in a gas is the same as the average kinetic energy of the molecules of the gas ($\frac{1}{2}mv^2$). Owing to its greater mass, its velocity is correspondingly smaller than that of the gas molecules. For particles suspended in a gas Einstein assumes that $PV = \frac{n}{N}.RT$, where n is the number of particles into which 1 gram-molecule of the disperse phase is disintegrated and N is the number of gas molecules per gram-molecule of a gas. At constant volume (V) and constant temperature (T)

the pressure exerted by the particles increases as the degree of dispersion increases—that is, as the particles become more numerous and move more rapidly.

It has been shown by Einstein [6] and others that, for spherical particles in Brownian motion in a liquid, the amplitude (A) of the motion in a given direction in time (t) can be expressed by the formula—

$$A^2 = 2.\frac{RT}{N}.\frac{t}{K}, \quad . \quad . \quad . \quad . \quad (7)$$

where R is the ordinary gas constant, T the absolute temperature, N the number of molecules in 1 mole of a gas, and K the frictional resistance of the fluid ($= 6\pi\eta rv$). Consequently we can write—

$$A = \sqrt{\frac{RT}{N}.\frac{t}{3\pi\eta r}}. \quad . \quad . \quad . \quad (8)$$

In liquid suspensions, it has been shown experimentally that—

(a) A particle in Brownian motion moves with uniform velocity (Svedberg).[7]

(b) Smaller particles move more rapidly than larger ones (Exner).[8]

(c) Particles in a concentrated system move more rapidly than those in one more dilute (Zsigmondy).[9]

(d) Particles travel more rapidly as the viscosity of the medium is diminished (Svedberg).[10]

(e) At constant viscosity the amplitude of the motion is directly proportional to the absolute temperature (Seddig).[11]

(f) Owing to the small but continuous influence of gravity upon the motion of the particles, they gradually arrange themselves so that their concentration is greatest in the lowest layer and diminishes progressively upwards (Perrin).[12]

All these experimental observations are found to be in agreement with the Einstein general expression. Theoretically, this expression should hold equally well for particles suspended in gases.

A gas differs essentially from a liquid or solid in being more mobile. Its density and volume change very rapidly with temperature. It is almost impossible to obtain "still" air. Slight differences of temperature set up convection currents, so

that the whole mass of gas is constantly in motion. This property greatly modifies the behaviour of gas-liquid or gas-solid disperse systems. Particles that would settle comparatively quickly in still air are constantly being arrested in their descent and carried upwards by ascending masses of gas. It is correspondingly difficult to observe the Brownian motion of a particle in a gas for any length of time. Precautions should be taken to prevent disturbance due to heating and convection by placing a heat filter in the path of the beam.

" When a sample of smoke is viewed in the ultramicroscope, it appears like the starry heavens, except that the stars are dancing about violently, but aimlessly, due to the Brownian motion. At first little distinction is made between the particles, as there seems to be no order in their motion, but soon it becomes evident that the brighter particles are more sluggish than the dim ones. This is due to the greater mass of the brighter particles, for they are larger. The particles are all moving slowly away from the source of light, and eventually diffuse to the walls of the cell." [13]

Brownian Movement in Gases.—In 1881, Bodaszewski [14] studied the Brownian movement of smoke particles and other suspensions in air, and saw in them " an approximate image of the movements of the gas molecules, as postulated by the kinetic theory of gases."

In 1906, Smoluchowski [15] pointed out that very small particles suspended in gases ought to exhibit Brownian movement, and quoted Bodaszewski's observations. He calculated the amplitude of the mean displacements in the air for particles of radius $r = 10^{-4}$ cm.

The displacement of a particle suspended in air at the ordinary pressure is eight times as great, and in hydrogen fifteen times as great, as in water. At low pressures the displacements can easily be made from fifty to two hundred times as great in gases as in liquids.[16]

In the following year, Ehrenhaft [17] observed the displacements of the particles of cigarette smoke and ammonium chloride fume. He found that these displacements were of the order of magnitude calculated by Smoluchowski.

Ehrenhaft, however, was unable to test the validity of Einstein's equation as applied to the movements of these particles, as he did not measure the size of the particles and was thus unable to calculate the frictional resistance of the gas.

In 1908, De Broglie [18] studied the Brownian movement in the metallic smokes obtained by an arc or spark discharge between electrodes of zinc, platinum and silver. He arranged two parallel metal plates vertically, one on either side of the smoke, and found, on applying a potential difference to these plates, that some of the particles were positively charged, some negatively charged, while others were neutral. On holding radium near the chamber the charges carried by the particles were observed to change.

In 1909, De Broglie [19] made the first quantitative study of Brownian movement in gases.

(1) He determined the average rate at which tobacco smoke particles moved in a horizontal electric field.

For this movement $Xe = Kv$,

where X = the strength of the electric field ;

e = the charge on the particle ;

K = the frictional resistance of the gas ;

v = the velocity of the particle.

(2) He obtained the mean value of the displacements of the smoke particles from many measurements of the movements of a great many particles, and introduced this value into the Einstein equation—

$$A^2 = \frac{2RT}{N} \cdot \frac{t}{K} \cdot \quad . \quad . \quad . \quad . \quad (9)$$

By combining these two equations K was eliminated and e obtained in terms of N :—

$$A^2 = \frac{2RT}{N} \cdot \frac{vt}{Xe} \cdot \quad . \quad . \quad . \quad . \quad (10)$$

Introducing Perrin's value for N, he obtained for one series of experiments—

$$e = 4{\cdot}5 \times 10^{-10} \text{ e.s.u.}$$

With larger particles, he obtained values for e several times larger, and from this concluded that the larger particles carried more than one charge.

De Broglie's experimental method[20] was to illuminate the particles strongly in the ultramicroscope, and record their movements in a given time on a photographic plate. In addition to the particles that were large enough to be photographed in this way, he observed a number of much smaller particles, moving at higher velocities and unable to act upon his photographic plate.

De Broglie's work produced the first experimental evidence that Einstein's formula holds in gases. This evidence was the more valuable in that it involved no assumption as to the validity of Stokes' law in gases, or as to the size of the particles, except that they were all of the same radius and charge.

At the same time, the method had two faults. Smoke particles are not all of the same size, but vary within fairly wide limits. Also, owing to the tendency of the particles to diffuse out of the focal plane of the microscope during the exposure, the values obtained for the time (t) are liable to be too great.

A considerable number of observations of Brownian movement in different smokes were made by De Broglie, and also by Ehrenhaft, using De Broglie's method. De Broglie and Ehrenhaft's observations were not confined to one particle, but were made in succession upon a number of particles. Consequently the value of e obtained by them is really a mean value for the given smoke.

The velocities imparted to silver particles of different sizes (a) by gravitation and (b) by molecular impact are shown in Table IV.

TABLE IV.

Velocity due to Gravitation.	Velocity due to Molecular Impacts.	Radius of Particles.
12×10^{-8} cm./sec.	$6{\cdot}3 \times 10^{-3}$ cm./sec.	1×10^{-7} cm.
3×10^{-6} ,,	$2{\cdot}8 \times 10^{-3}$,,	5×10^{-7} ,,
12×10^{-6} ,,	$2{\cdot}0 \times 10^{-3}$,,	1×10^{-6} ,,
3×10^{-4} ,,	$8{\cdot}9 \times 10^{-4}$,,	5×10^{-6} ,,
12×10^{-4} ,,	$6{\cdot}3 \times 10^{-4}$,,	1×10^{-5} ,,
3×10^{-2} ,,	$2{\cdot}8 \times 10^{-4}$,,	5×10^{-5} ,,
12×10^{-2} ,,	$2{\cdot}0 \times 10^{-4}$,,	1×10^{-4} ,,

Ehrenhaft [17] found that particles larger than the mean free spaces of the gas (1×10^{-5} cm.) fell in a zigzag line, the velocity due to gravitation being greater than that due to molecular impacts. With small particles down to 1×10^{-7} cm. (near the limit of visibility in the ultramicroscope) the velocity due to molecular impacts is greater than that due to gravitation. These particles remain in active Brownian motion in the gas, the motion being increasingly rapid the smaller the particles.

In 1910, Millikan [21] began to investigate the Brownian movements of charged oil droplets suspended in a gas and exposed to the action of an electric field.

Observations of the Brownian movement of the particles were carried out at low pressure, since the Brownian movement of the droplets only became measurable when the pressure was diminished considerably—that is, when the mean free path of the gas molecules became as long as the diameter of the droplet.

The droplet was balanced between gravity and a vertically applied electric field. Several hundred determinations were made of the Brownian displacements of the particle in a given direction, and the mean square displacement (A^2) calculated. The electric field was then increased, and v_2, the upward velocity of the particle due to the force $Xe - mg$, measured. The electric field was then switched off, and the particle fell, under the force of gravity (mg), with a velocity v_1.

From
$$\frac{v_1}{v_2} = \frac{mg}{Xe - mg}, \quad . \quad . \quad . \quad . \quad (11)$$

$$e = \frac{mg}{Xv_1}(v_1 + v_2) = \frac{K}{X}(v_1 + v_2). \quad . \quad . \quad (12)$$

By combining this with the Einstein Brownian movement equation—

$$A^2 = \frac{2RT}{N} \cdot \frac{t}{K} \quad . \quad . \quad . \quad . \quad (13)$$

we get—

$$A^2 = \frac{2RT}{X} \cdot \frac{(v_1 + v_2)t}{Ne}. \quad . \quad . \quad . \quad (14)$$

Substituting from the Maxwell distribution law, which holds

for Brownian displacements as well as for molecular velocities, the relation $A = \sqrt{\frac{2\bar{A}^2}{\pi}}$,

we get—

$$A = \sqrt{\frac{4}{\pi} \cdot \frac{RT(v_1 + v_2)t}{X.Ne}} \quad . \quad . \quad . \quad (15)$$

From this

$$Ne = \frac{4}{\pi} \cdot \frac{RT}{X} \cdot \frac{(v_1 + v_2 t)}{A^2} \quad . \quad . \quad . \quad . \quad (16)$$

Thus we can obtain the product (N*e*) without any reference to the size of the particle or the frictional resistance of the medium. The value of N*e* is known with great precision from measurements of electrolysis. Consequently, by comparing the value for N*e* obtained by Millikan's oil-drop method with the known value from electrolysis, it is possible to subject the validity of the application of the Einstein equation to the Brownian movement of particles suspended in gases to a critical test.

In another method, Millikan [22] observed the length of time $(t + \Delta t)$ taken by a particle to fall a given distance (d) under the combined influence of gravity and Brownian movement, t being the time required for the particle to fall the distance (d) if there were no Brownian movement.

If Δt be small in comparison with t, we can assume that A, the Brownian path described by the particle in time Δt, equals $v_1.\Delta t$. Substituting in the equation 16, we get—

$$Ne = \frac{4}{\pi} \cdot \frac{RT(v_1 + v_2).tg}{Xv_1(\Delta t)^2.} \quad . \quad . \quad . \quad (17)$$

$(\Delta t)^2$ is the square of the average difference between an observed time of fall and the mean time of fall (tg).

Millikan found the value of N*e* to be $1{\cdot}698 \times 10^7$ e.s.u. This agrees very well with the value $1{\cdot}702 \times 10^7$ e.s.u., the quantity of current required to precipitate 1 gram-equivalent of silver from solution. Assuming that the charge on a gaseous ion is identical with that on an electrolytic ion, Millikan's experiments show definitely that Einstein's expression holds

satisfactorily for the Brownian movement of particles suspended in gases. This has since been confirmed by the work of Fletcher, Eyring, Weiss and Przibram.[23]

Radiation Pressure of Light.—Clerk Maxwell [24] has shown that a small particle is repelled by light rays with an intensity which is proportional to the surface exposed to the light. In this way he accounted for the formation of the tail of a comet as the comet approached the sun.

Nichols and Hull [25] have shown that fine soot, falling *in vacuo*, is displaced from its path by a strong light.

Solar Smoke.—It has been suggested by Arrhenius [26] and others that a considerable amount of very fine charged dust or smoke reaches the earth from the sun. These particles are probably driven from the sun to the earth by the radiation pressure of the sun's light. The photosphere is observed to be continually disturbed by explosions in the interior of the sun. Large masses of gas burst through the " reversing layer " of metallic vapours, carrying these vapours through the chromosphere with a velocity of 700 kilometres per second. These masses of vapour, projected in this way beyond the confines of the chromosphere, condense into smoke, the particles of the smoke varying in size and composition.

The smoke particles that are formed in this way will be subjected to two sets of forces : that of the radiation pressure of the sunlight and that of the gravitational attraction exerted by the mass of the sun itself. The radiation pressure P is proportional to the square of the diameter—*i.e.*, $P = kd^2$. The radiation pressure of light at the surface of the sun is equal to 2·75 dynes per square centimetre. The force of gravitation G, on the other hand, is proportional to the cube of the diameter—*i.e.*, $G = k'd^3$. Consequently, according to the value of d, the radiation pressure on a particle may be greater or less than the force of gravitation. As d diminishes P gradually overtakes G, until at the sun's surface, if the particle were a black body of unit density, P would just overbalance G when $d = 1{\cdot}5\ \mu$. If the density of the particle be 5·5, for example, then d will be equal to $0{\cdot}27\ \mu$. For a particle of diameter equal to $0{\cdot}16\ \mu$ of unit density at the sun's surface $P = 19 \times G$. As d

further diminishes the effect of G becomes relatively greater, until, when $d = \cdot 05\ \mu$, G is greater than P.

In Fig. 6 is shown the relation between the forces P and G for particles of unit density and various diameters.

Hence with particles of different sizes, and possibly of different densities, some will be drawn back into the sun (G being greater than P), some will remain suspended in space, possibly forming the solar corona (G being equal to P), and others will be repelled (G being less than P). Fleming has calculated that particles of unit density, and of diameters, say, equal to 0·16, 0·50 and 1·0 μ, projected from the sun at the velocity of 200 kilometres per second, would reach the earth in 22 hours, 42 hours, and 76 hours respectively, their final velocities being 1,700, 780 and 350 kilometres per second.

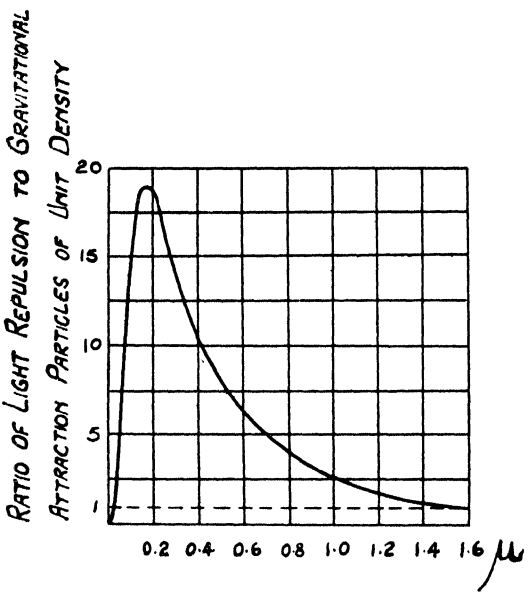


FIG. 6.—Curve showing the variation of the ratio of light pressure (P) to gravitation (G) for particles of unit density and various diameters.

These particles will be electrically charged, on account of the high temperature and intense ultra-violet radiation that will exist at the surface of the sun. Some will be positively charged, owing to the loss of electrons, others negatively charged, owing to condensation of gas or vapour molecules upon free electrons; others may be neutral, owing to the recombination of charged particles of opposite sign.

As this stream of solar smoke enters the earth's magnetic field the positively and negatively charged particles will

separate into two streams. Also the positive particles will be larger than the negatively charged particles, and will, therefore, penetrate the outer atmosphere or stratosphere of the earth more deeply before being arrested by the viscosity of the gas. Probably all will be arrested, and will accumulate and recombine above a height of 100 kilometres above the earth's surface to form a layer having a well-defined under-surface; the negative particles will proceed towards the magnetic poles.

This hypothesis is supported by the following observations :—

(*a*) The existence of light from the sky on clear, moonless nights in excess of that produced by the stars.

(*b*) The presence of a green line spectroscopically visible in all parts of the tropical sky on moonless nights, corresponding to the green line that is characteristic of the spectra of the aurora.

Photophoresis.—According to Ehrenhaft,[27] particles of various substances of the order of magnitude of 10^{-4} and 10^{-6} cm., suspended in a gas, are attracted or repelled by the intense light of an electric arc. Spherules of gold, silver and mercury, produced in pure nitrogen, and particles of the smokes of turpentine and camphor, are repelled. Sulphur and selenium particles distilled in argon, droplets of nitric acid and its decomposition products in air, water mist, cigar smoke and wood smoke, are attracted. Fine droplets of water, suspended in oxygen or hydrogen, are not affected. The velocity of the displacement is increased by increasing the intensity of the light, or by diminishing the pressure of the gas.

The existence of positive and negative photophoresis can be attributed to the same cause as that to which the action of the Crookes radiometer is due.[28] Whether a particle will be attracted or repelled will depend upon its capacity for absorbing or transmitting radiant energy. In the case of a strongly absorbing particle, the illuminated side will be heated more than the other side; thus the impact between the gas molecules and the heated surface will be more vigorous than on the other side of the particle, so that the particle moves away from the source of light. Weakly absorbing particles—for example, sulphur and selenium—will permit the light to pass freely

through them, so that the far side of the particle becomes warmed more than the illuminated side. Such particles, therefore, would move towards the source of light.

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CHAPTER IV

GENERAL PROPERTIES OF AEROSOLS

Mechanical Properties

WHEN a liquid or solid is dispersed in a gas to form a cloud or smoke, its character and properties are greatly altered.

(a) **It occupies a much larger volume.** In a sense, it may be said to be masquerading as a gas, or rather as a very coarse vapour. In the following table are compared the dimensions of a number of typical aerosols. In estimating the number of particles and the total surface area per gram of the disperse phase, it is assumed that the particles are spherical and that their specific gravity is not changed by dispersion. Neither of these assumptions is really justified, except, perhaps, sometimes when the disperse phase is liquid, but the figures obtained give a general indication of the extent to which the character of the substance of the disperse phase is modified by dispersion.

TABLE V.

Aerosol.	Per Gram of Disperse Phase.		
	Volume (litres).	Number of Particles per c.c.	Av. Diam. of Particles (μ).
Tobacco smoke	5,000	3×10^7	0·25
NH_4Cl smoke	10,000	5×10^6	0·1
H_2SO_4 mist	100	$2\times10^7-1{\cdot}6\times10^5$	0·8—5·5
ZnO smoke	10,000	$2\times10^6-5\times10^6$	·05
Coal mine air	15	10^5	10
Flour mill air	40	$2\times10^4-6\times10^3$	15—20
Cement mill (kiln exhaust)	8	$1{\cdot}2\times10^5$	10
Grain elevator air	1	4×10^5	15

(b) Its surface area is enlarged. The total area of surface possessed by 1 gram of the disperse phase is called its *specific surface.* Some conception of the extent to which the specific surface of any substance can be increased by subdivision may be obtained from the following consideration.

A centimetre cube of any substance has a total surface area of 6 sq. cm. If it be divided into 1,000 mm. cubes each possessing a surface area of 6 sq. mm., the total surface area of the substance becomes 60 sq. cm. If each millimetre cube be further subdivided into 1,000 cubes of 0·1 mm. side, the total surface area of the substance will be 600 sq. cm. After three further such subdivisions there will be 10^{15} particles, each 10^{-5} mm. in diameter and possessing a total surface area of 600,000 sq. cm. —that is to say, 60 sq. metres. This is equivalent to the total wall area of a large room measuring 20 feet long, 13 feet wide and 9 feet high. Thus the number of molecules of the substance that are at the surface, and, therefore, immediately available for any physical or chemical reaction, will be enormously increased. This increase represents approximately the extent to which the chemical activity of a substance is increased by this subdivision.

Similarly, a gram of water falling as heavy rain would be made up of 30 drops, each 4 mm. in diameter, the total surface area of the drops being 15 sq. cm. A gram of water falling as fine drizzle would consist of 30 million droplets, each 0·4 mm. in diameter ; the total surface area of these droplets would be 1,500 sq. cm. Finally, a gram of water in the form of a cirrus cloud would be made up of 30,000 million droplets, each 0·004 mm. in diameter, and would, therefore, possess a total surface area of 1,500,000 sq. cm.

As a direct result of this increase in the specific surface, the properties that depend upon the activity of the surface molecules are greatly enhanced. Consequently—

(c) The chemical activity is greater. Any physical or chemical reaction that takes place between two adjacent phases necessarily consists of an exchange of surface molecules of the two phases at the surface of contact. The rate at which such a reaction takes place will, therefore, depend upon the rate at

which the molecules of the substance become available—that is to say, the rate at which they come to the surface. Apart altogether, therefore, from actual changes produced in the available surface energy of a substance by increasing the curvature of its surface, the very fact of two phases existing in the intimate degree of contact afforded by the structure of a disperse system will, owing to the enormously increased area of the surface of contact, greatly accelerate physical or chemical reactions, such as evaporation and condensation, or actual chemical combination once a reaction is initiated. Thus, even if the degree of dispersion or the shape of the particles of the disperse phase does not produce extreme degrees of curvature, the chemical activity of the disperse phase is enormously increased.

In an aerosol, a great proportion of the molecules of the disperse phase are situated at the surface, so that the rate at which the disperse phase can react with the dispersion medium will be very high. The higher the degree of dispersion, the more nearly will the reaction velocity approach to that of a gas reaction, for, in addition to the greatly extended surface of contact, the Brownian motion of the particles themselves will facilitate the transference of ignition throughout the reaction volume. Many substances that in a massive condition, or in the form of coarse powder or drops, are almost unaffected by air, for example, or react so slowly with it that the heat produced in the reaction is dissipated by radiation and conduction as fast as it is formed, react with such vigour when highly dispersed in air as to become incandescent. Finely divided iron or lead, prepared by the ignition of the oxalates in the absence of air, are spontaneously inflammable when scattered in air. Substances that ordinarily burn easily in air—for example, sugar, coal, starch—will, if ignited, explode violently when dispersed in air in the form of fine dust (200—300 mesh).

In some cases, this increased chemical activity is further modified by the presence of a film of adsorbed gas on the surface of each particle. This adsorbed gas may be oxygen, for example, and may still further accelerate combustion, or it may be an inert gas—*e.g.*, nitrogen or carbon dioxide—and may retard or prevent ignition.

When an inert dust is dispersed in an explosive gas mixture—for example, of oxygen and hydrogen—it may, by adsorbing one or both of them strongly, so lower the temperature of ignition that they may combine spontaneously, and with explosive violence, if present in suitable proportions.

(d) It possesses increased physical activity. The enormously increased total surface of the disperse phase also leads to a greatly increased rate of physical interchange of molecules between the disperse phase and the dispersion medium, as, for example, in the processes of evaporation and condensation. Although this is largely due to the greater total surface, it is further affected—particularly in the case of very small liquid particles—by the increased curvature of the surface of these particles. The vapour pressure at the surface of a droplet increases as the radius of the droplet becomes smaller. This effect only becomes apparent, however, when the radius of the particles is less than 10^{-4} mm. In the practice of spray evaporation, for example, in which a liquid to be evaporated, *e.g.* milk, is warmed and sprayed into a mass of warm air, the efficiency of the process is due almost entirely to the large total surface of contact between the air and the sprayed liquid. The spray particles are never small enough to possess a perceptibly increased vapour pressure.

In dealing with the opposite problem, however, the condensation of a vapour, the extraordinarily high vapour pressure of the minute droplets that would be first formed makes condensation impossible, except with very high degrees of supersaturation, unless suitable nuclei are present, that by their size or shape, or by their electrical or chemical character, will lower sufficiently the pressure of the vapour in contact with the liquid to make the existence of such small droplets possible.

The presence of an electrical charge on a small droplet greatly diminishes its vapour pressure. An electrically charged gas molecule, although so small, will so lower the vapour pressure in its immediate vicinity that some of the vapour will condense upon it to form a stable droplet. Conversely, when a charged droplet is gradually reduced by evaporation, it ultimately reaches a size at which the effect of its increased curvature just neutra-

lises the opposed effect of the electric charge. Such a droplet is then stable, and it is practically impossible to reduce it further by evaporation. Further drying of a gas, for example, can only be effected by removing the charged droplets by electrostatic precipitation.

In addition to actual chemical combination, the molecules of two adjacent phases may attract each other sufficiently to form a condensed layer of the molecules of the phase having the least cohesion, and, therefore, surface tension, upon the surface of the phase possessing the higher surface tension. All solids tend to adsorb gas or vapour with which they are in contact. The amount of gas that is adsorbed upon a given area of surface will depend upon the nature of the solid and gas. Since adsorption is essentially a surface phenomenon, the extent to which one phase is adsorbed by another is necessarily proportional to the area of the surface of contact. Thus adsorption plays a much more important part in disperse systems than in other heterogeneous systems that are not so highly dispersed.

Since adsorption is a specific phenomenon, depending upon the nature of the adsorbing and adsorbed substances, the particles of the disperse phase may adsorb molecules of the dispersion medium or of a particular constituent of the dispersion medium. They may also adsorb positive or negative ions from the gaseous dispersion medium. The existence of such films of adsorbed molecules or ions profoundly affects the behaviour and stability of the system. Such adsorbed films may be protective, and, by preventing the coalescence or the adhesion of the particles, they may greatly increase the stability of the system. On the other hand, if ions of opposite sign are adsorbed by different particles of the disperse phase, the electrical forces that are set up between the oppositely charged particles would rapidly cause coalescence or flocculation, and so diminish the stability of the system.

In some cases, the evaporation of the liquid particles of the disperse phase is arrested by the presence of an oil film or a film of adsorbed gas on the surface of each particle.

(e) **The particles may exhibit Brownian movement.** If the degree of dispersion is sufficiently high, the chemical and

physical activity of the disperse phase is further increased by the mobility of the particles. In air, for example, at normal temperature and pressure, the mean free path of the air molecules is about 10^{-5} cm. If the particles of a substance dispersed in air are of this order of magnitude or less, they will be driven to and fro incessantly by the irregular impacts of the molecules of the air. They will acquire a kinetic energy equivalent to the average kinetic energy of the air molecules, but, owing to their much greater mass, they will move correspondingly more slowly.

An important factor in determining the combustible character of a dust cloud is the rate at which ignition can be communicated through the cloud. Clearly, this will depend upon the intensity of combustion of each particle and the distance that separates it from its neighbours. Particles much larger than 10^{-5} cm. do not exhibit any Brownian motion, but drift bodily with the gas under the influence of pressure or temperature gradients. If, however, the particles are in active Brownian motion, it is reasonable to suppose that their frequent collisions will facilitate the spreading of ignition through the aerosol. A smoke is much more readily and violently explosive than a cloud. In many cases, a cloud is made more explosive by the presence of a small proportion of combustible gas, or of a proportion of smoke particles. The greater mobility of the molecules of the combustible gas, or of the fine smoke particles, greatly increases the flame velocity and explosion pressure. The mobility of these finer particles probably plays an essential part, also, in promoting the coalescence of smoke or cloud particles, and the flocculation of the corresponding aerosol.

Thermal Properties

Gases are very transparent to radiant heat. Cloud or smoke particles suspended in a gas diminish its thermal transparency, and absorb the heat radiation. The particles become warmed, and communicate their heat by conduction to the gas immediately surrounding them. If the heat rays be intercepted, the suspended particles quickly cool by radiation, and assume a lower temperature than that of the gas. If the gas contains

sufficient water vapour to saturate it at the temperature of these cooling particles, some of it will condense upon them. In this way ground fogs and mists are sometimes formed.[1] A cloud or smoke is thus more sensitive to thermal radiation than a pure gas.

A luminous gas flame radiates more heat and light than a Bunsen flame, because the luminous flame contains incandescent particles of carbon.

Thermal Precipitation

When an electrically neutral particle, too large to exhibit Brownian motion, is suspended in a thermally and electrically uniform gas, the molecular bombardment will be uniform in all directions, and will produce no displacement of the particle. If, however, a thermal gradient be set up in the gas—for example, by introducing a hot rod into it—the gas molecules in the neighbourhood of the rod become "warmed" and move more energetically than those more remote. Any such particle, therefore, suspended in the gas in the immediate vicinity of the rod, will be repelled from it. Smaller particles in Brownian motion will pursue a zigzag path away from the hot rod. The rod thus becomes surrounded by a region of warm, dust-free air, streaming upwards.[2]

A cold rod gives rise to a down-streaming current of dust-free air.[3] In this case, the dust is deposited upon the rod as the warm, dusty air streams downward over its cold surface.

Solid particles present in flames are deposited more easily upon a cold surface than upon a hot surface.[4] A flame of burning magnesium will deposit magnesium oxide soot upon a cold flask held in the flame, but not upon a similar flask containing boiling water.

In rooms that are heated by direct radiation—*e.g.*, by an open fire—the walls and furniture of the room are warmer than the air. Consequently the dust in the air remains in suspension.[5] In rooms that are heated by convection—*e.g.*, by steam-pipes or hot water "radiators"—the air is warmer than the objects in the room, and therefore deposits the suspended dust upon them. This dust deposition is very pronounced upon walls and ceilings

above a radiator or lamp, and more particularly on those portions of the ceiling that are cooled by contact with air pockets between the laths and rafters.

Tolman [6] has shown that tobacco smoke, passed between two concentric tubes maintained at a temperature difference of from 50° to 80° C., will be quantitatively deposited upon the cold surface.

The repulsion of suspended dust particles from a hot surface is assisted by the evaporation of a liquid from the surface. When dusty air is inhaled, the dust is largely prevented from being deposited upon the walls of the lungs, partly by reason of the higher temperature of the lungs and partly because of the evaporation of moisture from the surface of the lungs.

Optical Properties

Gases are very transparent to light, the spectrum of the transmitted light usually being crossed only by a number of fine absorption lines. The absorption spectra of some vapours exhibit broad bands resembling those shown by liquids and solids. Many gases and vapours only exhibit absorption lines when great thicknesses are used. The absorption spectrum of dry steam shows absorption lines if the layer of steam be 37 metres thick.

The presence of a disperse phase in a gas or vapour reduces the transparency to an extent which depends upon the concentration of the disperse phase, its degree of dispersion and the optical constants of the dispersed substance.

Aitken [7] has calculated the number of dust particles suspended in the atmosphere that are necessary to render a distant object invisible. Total extinction is produced by fewer particles when the air is humid than when it is dry, owing to the condensation of water upon such of the particles as are hygroscopic.

An absorption band for any disperse system moves towards the violet end of the spectrum as the degree of dispersion increases.[8]

Reflection and Refraction.—Cloud particles that are large

when compared with the wave-length of light (656 $\mu\mu$—433 $\mu\mu$) reflect and refract light in a regular manner.

Smoke particles that are small when compared with the wave-length of light—*i.e.*, too small to reflect or refract light—scatter the incident light in all directions, each particle becoming the source of a new wave front.[9] The scattered light is more or less completely plane polarised.

Clouds.—Cloud particles may be opaque or transparent. If the particles are opaque, the light will partly undergo diffuse reflection, partly be absorbed by the particles and to a small extent by the gas or vapour, and partly be transmitted.

When the cloud particles are transparent, the light, in addition to being reflected at the surface of each particle, may be refracted and dispersed. In the formation of rainbows or fog-bows, the incident light is refracted, reflected, and refracted again inside each particle. Secondary bows are produced by a further internal reflection and refraction. Rainbows of richest colour are produced by drops of from 0·2 to 0·4 mm. diameter.

Such meteorological phenomena as solar and lunar haloes and parhelia are due to the reflection and refraction of the light from the sun or moon by small crystals of ice suspended in the atmosphere.

The light reflected by cloud particles is partially plane polarised. It is difficult, however, to detect the polarisation of the diffused reflected light that has been reflected many times, and in many different directions, by the particles of the cloud.

Wood [10] has shown that the cloud formed by the condensation of iodine vapour scatters deep red light, which is plane polarised in a plane parallel to the direction of the incident beam. The particles of this cloud were of an average diameter of 0·003 mm. By transmitted light the cloud appeared colourless. This abnormal polarisation is attributed to the transparency of the particles. A part of the incident beam will be reflected from the surface of the particles, will be colourless, and will be polarised quite normally in a plane perpendicular to the direction of the incident ray. The other part of the incident beam will be refracted and reflected inside the particles. It therefore undergoes absorption, and emerges highly coloured

and polarised in a plane parallel to the direction of the incident ray. Similar behaviour was observed with a cloud of nitroso-dimethylaniline.

Diffraction.—In addition to reflection and refraction, light passing through a cloud may be diffracted. Diffraction haloes are observed when the sun or moon is viewed through a cloud of opaque or transparent particles. The angular diameter of a halo is inversely proportional to the size of the particles producing it.[11] The order of the colours in a diffraction halo is the reverse of that in a rainbow, red being outermost.

Young has devised an ingenious apparatus for measuring the diameters of fibres or small particles of any sort by observing the diameter of the diffraction halo produced by such particles under standard conditions of illumination.

The diffraction of light by fine clouds of condensing water vapour has been investigated by Kiessling,[12] Aitken [13] and Barus.[14] Barus allowed low pressure steam to be discharged into warm air contained in a suitable observation tube. As condensation takes place the light transmitted by the resulting cloud exhibits a magnificent display of colour changes. The succession of diffraction colours can be obtained either by gradually diminishing the pressure of the steam—*e.g.*, from 156 cm. of mercury down to the atmospheric pressure—or by using a large amount of low pressure steam and admitting varying amounts of dusty air. The size of the particles is determined from the colour and order of the spectrum. Barus observed particles ranging in diameter from 0·01 mm. to 0·0025 mm.

Tolman [15] has shown that the intensity of the light reflected by cloud particles is equal to $\frac{R'C}{d}$, where C is the concentration (mass of disperse phase per unit volume), and d the diameter of the particles. For a given degree of dispersion the intensity of the reflected light increases with increasing concentration. For a given concentration the intensity diminishes as the particles increase in size—*i.e.*, diminish in number.

Optical Resonance.—For most substances the intensity of the reflected light is almost independent of the wave-length.

Some substances, however—for example, the metals and certain dyestuffs—show markedly selective reflection. They reflect waves of lengths approximately equal to those which they absorb. This selective reflection is attributed to the optical resonance of the particles at the surface of the substance. Optical resonance is a special case of fluorescence. If the resonating particles are separated by distances much larger than their diameters, as, for example, the particles of a cloud, the light may be absorbed and re-emitted on the further side from the source of light. Sodium vapour absorbs yellow light and transmits blue. Wood [16] has shown, however, that the metallic fog produced by the condensation of sodium vapour scatters violet light, and transmits yellow. This appears to be due to the optical resonance of the metal cloud particles.

A potassium cloud behaves similarly, but scatters longer waves than those scattered by the corresponding sodium cloud. By regulating the conditions it is possible to get potassium clouds which will scatter red, yellow, and green rays, and transmit blue. Changing the nature of the dispersion medium greatly modifies the optical character of the cloud.

Smokes.—Particles that are too small to reflect or refract light cannot be said to be opaque or transparent. The incident light, depending upon its wave-length, is either scattered by the particles or is unaffected. Tyndall found that very fine smoke particles scatter blue light and transmit orange-red. This is well seen with freshly formed cigar smoke, or with producer gas escaping from the poke-hole of the producer. These appear blue against a dark background, and orange-red against the light. The scattered light is plane polarised, the direction of maximum polarisation being perpendicular to the direction of the incident beam. As the particles increase in size the blue colour gradually disappears, the scattered light ultimately appearing white. At the same time, the direction of maximum polarisation shifts towards the origin. The intensity of this Tyndall beam depends upon the degree of dispersion, the concentration of the disperse phase, and the wave-length of the incident light.

Lord Rayleigh [9] has shown that the intensity (I_s) of the light

scattered in a direction making an angle β with the incident beam is proportional to

$$\frac{I(D' - D)^2}{D^2}.(1 + \cos^2\beta).\frac{n.\pi.T^2}{\lambda^4} \quad . \quad . \quad (18)$$

where I is the intensity of the incident light, D' is the optical density of the particle, D of the dispersion medium, n is the number of particles per unit volume, T the volume of a particle, and λ is the wave-length of the scattered light.

For a given disperse system we can write—

$$I_s = \frac{A.n.r^6}{\lambda^4}, \quad . \quad . \quad . \quad . \quad (19)$$

where n is the number of particles of radius r, scattering light of wave-length λ.

It follows, therefore, that—

(1) For a given degree of dispersion the intensity with which light of a given wave-length is scattered is proportional to the concentration of the disperse phase.

(2) For a given degree of dispersion light of different wave-lengths will be scattered with an intensity which is inversely proportional to the fourth power of the wave-length.

(3) For monochromatic light the intensity is proportional to the sixth power of the radius.

Since the intensity is inversely proportional to the fourth power of the wave-length of the incident light, it follows that, when white light falls upon smoke containing particles of a given radius, the longer red rays will be scattered with only one-twelfth of the intensity of the shorter violet rays. For some wave-lengths, not necessarily in the visible region of the spectrum, there will be a maximum intensity.

Rayleigh's expression has been tested experimentally by Bocks.[16A] High pressure steam was charged with condensation nuclei by the addition to it of a small quantity of hydrochloric acid. On being released through a narrow orifice the steam condensed to form a blue jet. Bocks then measured spectrophotometrically the intensities of the scattered light of different wave-lengths, and compared the experimental results with those that were calculated according to Rayleigh's theory.

The relative intensities are compared in Table VI.

TABLE VI.

Wave-length ($\mu\mu$).	Relative Intensity.	
	Observed.	Calculated $\left(\frac{1}{\lambda^4}\right)$.
700	1·0	1·0
590	1·5	2·0
540	2·9	2·8
470	4·4	4·9
410	9·8	8·5

Better agreement was obtained when monochromatic light was used instead of a band of the spectrum, probably because the degree of dispersion of the cloud was not uniform, and larger droplets would affect the intensity to a different extent in different parts of the spectrum.

Tolman and Vliet [17] have devised a Tyndallmeter for measuring the intensity of the Tyndall beam. It consists essentially of a glass-sided cell in which a sample of smoke or any other transparent disperse system can be illuminated transversely by a light of known intensity. The intensity of the scattered light is measured photometrically.

Tolman has studied the relation between the intensity of the Tyndall beam and the concentration of the disperse phase. For ammonium chloride smokes, varying in concentration from 0·005 to 0·12 mgm. per litre and from 0·25 to 1·2 mgm. per litre, the Tyndallmeter reading in foot-candles is found to be directly proportional to the concentration of the smoke in milligrams per litre, provided that—

(*a*) The concentration is not high enough to cause appreciable opacity, and

(*b*) The size of the particles remains practically unaltered.

As the result of a very large number of experiments with many different smokes, Tolman finds that, at a given concentration, the intensity of the Tyndall beam increases as the degree of dispersion increases.

attached to a neutral or positively charged molecule. Gaseous ions, unless in a rarefied gas, may, therefore, be regarded as consisting of molecules of the gas which have lost or gained one or more electrons. The number of ions formed in a gas is very small compared with the number of ions formed when a salt is dissolved in water. The number is rapidly diminished by the collision and recombination of oppositely charged ions with one another. The rate at which oppositely charged ions recombine to form neutral molecules is increased by the presence in the gas of suspended solid or liquid particles that adsorb the ions. Ions are also removed by diffusion to the walls of the containing vessel, although this effect is generally small enough to be negligible.

When an ionised gas is exposed to the influence of a uniform electric field of strength X, the positive and negative ions will move with velocities u and v respectively, where $u = K_1X$ and $v = K_2X$.

K_1 and K_2, the mobilities of the ions, are constant for a given gas under given conditions of temperature and pressure. The mobilities of positive and negative ions of different gases are shown in the following table [21] :—

TABLE VII.

Gas.	$K_1(+)$.	$K_2(-)$.
Hydrogen	6·70 cm. per sec.	7·95 cm. per sec.
Hydrogen (moist)	5·30 ,, ,,	5·60 ,, ,,
Air	1·36 ,, ,,	1·87 ,, ,,
Air (moist)	1·36 ,, ,,	1·51 ,, ,,
Carbon monoxide	1·10 ,, ,,	1·14 ,, ,,
Carbon dioxide	0·81 ,, ,,	0·85 ,, ,,
Sulphur dioxide	0·44 ,, ,,	0·41 ,, ,,
Pentane	0·35 ,, ,,	0·35 ,, ,,
Ammonia	0·74 ,, ,,	0·80 ,, ,,

The greater mobility of the negative ion is due to the fact that for the first part of its path it is a free electron, moving with a relatively high velocity, until it becomes attached to a neutral

molecule. As the pressure of the gas is reduced, or as its temperature is increased, the mean free path of the gas molecule becomes longer, so that the time spent by the electron in the free state is considerably increased. Consequently it is observed that, under such conditions, the mobility of the negative ion rapidly becomes greater.

All the ions that are produced in gases by radioactive bodies, X-rays, canal rays, or ultra-violet light, are apparently identical. Langevin [22] calls them " small ions," and assumes them to consist of an ionised molecule, to which one or more neutral molecules are attached by electrostatic forces. In unit field, at the ordinary temperature and pressure, these small ions move with a velocity of about 1 cm. per second.

" Large ions " [23] are produced in the cool part of a flame, or in a dusty gas or smoke, or when gases are produced electrolytically or chemically, or are bubbled through salt solutions, or when liquids are sprayed or splashed in a gas. They move much more slowly than " small ions," the mobility being of the order of 0·003 mm. per second, in unit field. These " large " ions vary in size up to microscopic dimensions. They are assumed to be large clusters of neutral molecules round a charged molecule, and, if liquid particles, may be considered to be small charged droplets. Their low coefficient of diffusion retards recombination, and tends to stabilise the conductivity of the gas in which they are formed. As the gas cools or ages the mobility of these large ions decreases, probably because their mass is increased by further condensation, or by coalescence. These large ions are apparently identical in character with charged smoke particles. The mobility of charged dust and smoke particles will, in many cases, be considerably less than 0·003 mm. per second.

The Charge on an Ion.—If an ionised gas, saturated with water vapour, be subjected to a sudden adiabatic expansion, it becomes supersaturated. The excess water vapour condenses upon the gas ions to form a cloud. The degree of expansion required to produce this cloud condensation is less for negative ions (1·26) than for positive ions (1·30).[24]

J. J. Thomson [25] carried out this expansion so that condensa-

molecule. As the pressure of the gas is reduced, or as its temperature is increased, the mean free path of the gas molecule becomes longer, so that the time spent by the electron in the free state is considerably increased. Consequently it is observed that, under such conditions, the mobility of the negative ion rapidly becomes greater.

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J. J. Thomson [25] carried out this expansion so that condensa-

tion occurred only on the negative ions. By observing the rate at which the cloud droplets settled (the droplets being all of the same size) it was possible to calculate the size of the droplets, using Stokes' law. The amount of water precipitated and the total quantity of electricity brought down with it were then measured. The charge on each droplet was assumed to be equal to the charge originally present on the ion, and was found by dividing the total quantity of electricity by the number of drops.

H. A. Wilson [26] applied to the falling droplet an electric field of strength X, just sufficient to balance the force of gravity, so that the cloud remained stationary. The charge on each droplet was equal to $\frac{mg}{X}$, where m is the mass of a droplet calculated by observing the rate of free fall of the droplets under gravity. In both these methods, m tends to diminish during the experiment, owing to re-evaporation, as the gas gradually warms up after the expansion.

Millikan [27] has overcome this defect by his oil-drop method, already described on p. 50. He found that the charges acquired by small droplets of various sizes of various liquids suspended in air, and using different ionising agents, were always a multiple of $4{\cdot}774 \times 10^{-10}$ e.s.u., the accuracy being of the order of one part in a thousand. It was found that the charge acquired or lost by an oil drop at each collision was almost invariably a single electronic charge, although, of course, a number of charges may be present on a single drop simultaneously.

The Value of e, the Electronic Charge.—When the gas in which the oil droplet is suspended is exposed to an ionising radiation, the charge upon the droplet constantly changes as individual positive or negative gas ions attach themselves to it. From the magnitude of the change produced by each arriving ion the charge (e) upon the ion can be determined. In this way Millikan made hundreds of observations of the magnitude of the charges carried by the ions of the gas. He found that "the electrical charges on the ion all have either exactly the same value or else small exact multiples of that value." The

value of this electronic charge (e) is $4{\cdot}774 \times 10^{-10}$ e.s.u. He showed that the resistance of the medium to the motion of a drop through it is exactly the same whether the particle is highly charged or uncharged. A very small droplet of almost molecular magnitude would encounter more resistance if it were charged, since the charge upon it would drag an increased number of gas molecules into collision with it.

From observations of the movements of many charged drops under gravity and also in an electric field, it is evident that the drops are not distorted by the electric field, but behave throughout like rigid spheres. It is possible that very small particles, consisting of only a few molecules, would become polarised and distorted in an electric field.

Ehrenhaft and others [28] using Millikan's method, but working with much smaller droplets of gold, silver and mercury, obtained values for e which were considerably smaller than those obtained by Millikan. They concluded that the unit electrical charge is considerably smaller than 10^{-10} e.s.u.

Millikan has pointed out that the number of observations, from which they calculate the statistical average $(\Delta t)^2$, is too small to give a reliable result. Dust particles becoming attached to a particle of silver, gold or mercury would greatly modify its apparent density. The accuracy of the observations may also be impaired by the evaporation of the drop during the experiment. Millikan carried out further experiments with oil drops and mercury drops even smaller than those used by Ehrenhaft, and suspended both in air and in hydrogen. He found no indication of any variation in the value of e with the size of the drop. He concluded that the apparent value of the electron is independent of the nature of the gas, or of the material of the drop, or of the size of the drop.

More recently various workers have shown that observations made upon very small particles, such as those used by Ehrenhaft, give variable results.

In making repeated measurements of the rate of fall of the given particle, the apparent mass of the particle is observed to diminish. According to Targonski,[29] this is due to bombardment of the particle by the gas molecules, causing disintegration

of the surface of the particle, some of the surface molecules of the particle being replaced by gas molecules. With mercury droplets he finds that the decrease of mass per unit surface per unit of time becomes less as the pressure of the gas is diminished, and is, in fact, proportional to the number of gas molecules present. The mass of a mercury droplet diminishes more rapidly and more regularly if the mercury be pure and if the droplet be positively charged. He considers that particles formed at high temperature—*e.g.*, in the electric arc—probably have too small a density, owing to enclosed or adsorbed gas.

Schidlof [30] and McKeehan [31] find the density of the particle to vary with the nature of the surrounding gas, and attribute this variation to the adsorption of gas at the surface of the particle.

The Brownian movement of a particle, unlike its movement under the influence of an external force, is independent of its form or density. Measurements of the Brownian movement give a more uniform value of e, but lower than those given by the oil-drop method, and higher than those obtained with arc particles. Targonski [32] finds, from his results and Fletcher's, that the value of e obtained from observations of Brownian motion approaches nearer to Millikan's as $\frac{\lambda}{r}$ increases.

Targonski and Schidlof consider that the theory of Brownian motion only applies rigorously when r is small compared with λ.

Fürth [33] suggests that the discrepancy between Millikan's and Ehrenhaft's results can be explained by assuming (1) the existence of a fundamental unit quantum of electricity of charge $e = 4{\cdot}77 \times 10^{-10}$ e.s.u., and (2) the existence of a continuously variable positive charge which approximates to an average equal to the charge on a positive ion in electrolysis.

Regener [34] considers that Ehrenhaft's particles, being so much smaller than Millikan's, should be corrected for adsorbed gas.

De Broglie [35] observed the Brownian motion at different pressures of the particles of a smoke made by burning a mixture of phosphorus and vaseline. Einstein's formula holds satisfactorily at pressures from 760 mm. to 10 mm. of mercury, but

at pressures between 10 mm. and 1 mm. there is a considerable increase in speed and amplitude.

It is generally found that the electrically charged particles of a smoke carry only a single electronic charge, the number of particles with two or more charges being very small. This is due to the number of particles being greater than the number of available ions in the gas, and also to the greater probability of a highly charged particle acquiring oppositely charged ions, so that its charge becomes partially or completely neutralised.

Conductivity of Flames.—Flames conduct electricity. The mobility of the negative ions in a flame is about a hundred times that of the " small " ions produced by the ordinary ionisation of a gas.[36] The positive ions are apparently ordinary " small " ions ; the negative ions are assumed to be electrons. The current (i), passing between two electrodes immersed in the flame, is related to the voltage (v) by the expression—

$$i^2 = a \times v,$$

where a is a constant ; i is independent of the distance between the electrodes, since, throughout the greater part of the field, the rate of recombination of the ions exactly balances the rate of ionisation. Near the electrodes ions of one kind only will accumulate, so that the rate of recombination will be very low. There will thus be an increased conductivity in the neighbourhood of the electrodes, particularly of the cathode.

The conductivity of the flame is greatly increased by the presence of salt vapours, notably those of the alkali metals, provided that the vapour of the salt comes into contact with the cathode. The salt is ionised, particularly in the neighbourhood of the cathode. A sodium electrode only gives a yellow Bunsen flame when it is made a cathode—*i.e.*, when there is a sufficient concentration of sodium ions. H. A. Wilson [37] has shown that the same quantitative relationships hold for the passage of a current through a salt vapour as through a corresponding aqueous solution of the same salt. The recombination of the ions of the salt vapour can be checked by a sudden cooling. Thus, many metals can be deposited upon a cold surface from flames containing their salts.

The luminosity imparted to a Bunsen flame by metallic salts is attributed to the recombination of the dissociated salt vapour.[38] A flame may be rendered luminous by the presence of incandescent solid particles in it—*e.g.*, carbon particles in a luminous gas flame.

The cool gases of the flame also contain ions. If the products of combustion are gaseous at the ordinary temperature—for example, the combustion of carbon monoxide in air—" small " ions only are present in the gases.[39] " Large " ions are produced when the products of combustion are liquid or solid at the ordinary temperature—for example, a hydrogen flame, or flames in which metal oxides or chlorides are formed. The " large " ions produced from flames cannot be seen in the ultramicroscope, possibly because they consist of a loose grouping of molecules too diffuse to give an ultramicroscopic image.[40]

Clouds and Smokes.—In practically all clouds and smokes, a proportion of the particles are electrically charged.

(1) **The particles may become charged by contact with the dispersion medium,** possibly on account of the specific adsorption of gas ions at the surface of the particles.

(*a*) Dust becomes charged electrically when blown about in the air. Rudge [41] has shown that the charge acquired by the dust particles varies according to their chemical composition. Generally speaking, from experiments carried out in air,—

(1) Non-metallic dust becomes positively charged.

(2) Metallic dust becomes negatively charged.

(3) Dust of acid-forming oxides becomes positively charged.

(4) The dust of basic-forming oxides becomes negatively charged.

(5) With salts the charge depends upon the relative strength of the acid and basic ions.

The electrification of the dust during dust storms in South Africa is invariably positive, the dust being usually of a siliceous character. In England, on the other hand, clouds of calcareous dust raised by motor cars have been found to be negatively charged. The air in the neighbourhood of the dust cloud becomes oppositely charged.

(*b*) When liquid splashes or is atomised in a gas, the increase

of specific surface is generally associated with the electrification of the droplets.[42]

When large raindrops, in falling, are flattened and broken by the resistance of the air, the drops become positively charged, the surrounding air being negatively charged.[43] Similarly, in waterfalls, the water becomes positively charged, the air in the neighbourhood of the waterfall being negatively charged. When water is sprayed in air, the size of the ions produced depends upon the humidity of the air.[44]

(*c*) When a vapour—*e.g.*, steam—expands suddenly into the air through a narrow orifice, the particles of the resulting cloud are found to be electrically charged.[45]

With steam the water droplets acquire a positive charge. This fact forms the basis of Armstrong's hydro-electric machine.[46] The phenomenon was investigated by Faraday, who found that, with perfectly dry steam, no electricity was produced. He ascribed it to the friction of the water globules against the walls of the orifice. The addition of acids, salts or fatty matter to the water, even in minute quantity, prevents the development of electricity. The kind of electricity produced with pure steam depends upon the material of which the orifice is formed. With an ivory orifice little or no electricity is produced. If turpentine is added to the boiler, the steam becomes negatively charged. Similar effects are obtained with a current of moist air.

(*d*) When a gas containing neutral nuclei is bubbled through certain ionising liquids, the nuclei become electrically charged.[47]

Water, salt solutions, alcohols, are ionising liquids ; benzene, ether, mineral oils, are not.

(2) **Cloud or smoke particles may acquire their charge by direct dissociation, or from the ions produced by the ionisation of the dispersion medium.** Particularly is this the case when smokes are formed at high temperatures—*e.g.*, by combustion—or when clouds are formed by the condensation of vapour upon gaseous ions.

An ionised gas, when bubbled through water, forms a cloud. This cloud disappears when bubbled through H_2SO_4, but reappears in moist air.[48]

(3) **The particles may become electrically charged by the**

direct action of an ionising agent—*e.g.*, ultra-violet light or radioactive substances.

De Broglie [49] has shown that uncharged smokes and clouds become charged when exposed to radioactive substances, both negative and positive ions being produced.

Neutral nuclei may be produced when gases from flames or when certain liquids—*e.g.*, benzene—are sprayed, or when damp substances are heated. They can be ionised directly by any ionising radiation, or by contact with a carbon monoxide flame.[50]

According to De Broglie and Brizard,[51]—

(*a*) Fumes produced by chemical action without rise of temperature do not contain charged particles—for example, the action of moist air upon $SnCl_4$, SiF_4, HCl, HNO_3, $H_2S_2O_7$, PCl_5, $AsCl_3$, etc.

(*b*) Fumes produced by violent chemical action contain charged particles of both signs—for instance, the action of water upon H_2SO_4, P_2O_5, PCl_5, metallic sodium, etc.

Fumes produced by flaming combustion contain charged particles—*e.g.*, powdered arsenic or antimony projected into chlorine, or the spontaneous combustion of PH_3.

NH_4Cl smoke consists of particles of one sign, travelling with a relatively high velocity.

The proportion of charged particles in a smoke or cloud will not only depend upon the way in which the cloud or smoke is produced, but, since smoke particles accelerate the recombination of gaseous ions, it will depend also upon the age of the smoke.

The presence of these charged particles greatly affects the stability of a gas-liquid or a gas-solid disperse system. If all the particles are charged with the same sign, the system will be very stable, as the particles will mutually repel each other. In some cases, however, the system will contain some neutral particles, and these will be attracted by the charged particles by reason of the opposite charge induced upon them. Where the system contains negatively and positively charged particles, collision and coalescence will take place readily.

The flocculation of a smoke is accelerated by exposing it to

the influence of an alternating electric field. Lodge [52] has shown that when various smokes—tobacco, camphor, turpentine, MgO, NH_4Cl, $(NH_4)_2SO_3$, P_2O_5, steam, brown paper, lead fume, zinc fume—are subjected to an electric discharge of some few thousand volts, the smoke particles form in masses or flakes along the lines of force and then precipitate on the floor of the vessel. He shows that positive or negative electricity acts in the same way, that point electrodes are more efficient than knobs, and that a brush discharge—*i.e.*, anything that electrifies the air itself—is the most effective flocculating agent.

With liquid disperse particles the presence of an electric charge reduces the effect of the surface tension of the liquid, and also its vapour tension, to an extent which is inversely proportional to the fourth power of the diameter of the drop. It is well known that, when a charged stick of sealing wax is held near to a fine spray of water, the water drops coalesce, and the spray changes into a coarse rain.

In the absence of suitable nuclei, the condensation of a vapour is difficult and only occurs when the supersaturation of the vapour is sufficiently intense to bring about the condensation of the vapour upon the vapour molecules themselves. Condensation is facilitated if the condensation nuclei be charged. Most vapours condense more readily on positive ions, water being an exception.

The vapour tension of a charged droplet is lower than that of a neutral droplet of the same size.[53] Consequently the neutral droplet will tend to evaporate and condense upon the charged droplet. It is very difficult to dry completely a gas containing charged droplets or nuclei. As the gas is dried and the drop evaporates r diminishes, Q, the amount of electricity on the drop, remaining constant. Thus the electrical energy of the droplet $\left(\frac{Q^2}{2r}\right)$ increases. As the drop gets smaller its vapour tension will increase. Ultimately the two forces balance each other, and the drop persists. Water droplets formed on gaseous ions in the atmosphere at the ordinary temperature persist when the radius has reached 3×10^{-7} cm. To reduce the radius by half by simple evaporation, it would

be necessary to reduce the relative humidity of the air to 3×10^{-14} per cent.

Probably the only way in which such a gas can be completely dried is by removing these droplets by electrostatic precipitation.

Behaviour in an Electric Field.—A charged particle in an electric field will move under the direct action of the field. Assuming Stokes' law, the velocity imparted to a charged particle by a field of X volts per centimetre equals $\frac{Xe}{6\pi r\eta}$, where e is the charge on the particle, and r its diameter.

At sufficiently high voltages particles that originally are uncharged acquire a considerable mobility, even when they are relatively large.[54] This fact forms the basis of the electrostatic process of smoke precipitation.

When smoke or dusty gas is passed through an earthed cylinder in which a highly charged wire is fixed axially, any gas ions or charged particles present in the gas will be acted upon by the field, and will either move towards the wire or towards the surface of the cylinder, according to the sign of the charge they carry. The intensity of the field in this case is inversely proportional to the distance from the axial wire. It is intense near the wire and small near the cylinder. If the wire be negatively charged, positively charged particles present in the gas will be attracted towards the wire, and, owing to the increasing intensity of the field, their velocity will rapidly accelerate as they approach the wire. Negatively charged particles or ions will be attracted towards the cylinder.

The velocity acquired between two successive collisions by an ion of mass (m) and charge (e), moving under the action of a field of strength (X), is—

$$\frac{Xe\lambda}{m\overline{V}}, \quad . \quad . \quad . \quad . \quad . \quad (20)$$

where λ is the length of the mean free path of the ion, m its mass, and V its mean velocity (thermal agitation).[55] Its velocity on striking another molecule of the gas is thus, for a given pressure of the gas, proportional to the intensity of the field. If the field be so intense that the velocity of the ion is

sufficient to produce ionisation by collision with the molecules of the gas or of the electrode, ionisation will occur in the neighbourhood of the wire electrode. The negative ions formed will be repelled by the negatively charged electrode, and will move at a high velocity from it towards the surface of the cylinder. These streams of rapidly moving ions charge the suspended particles, and also, by their impact, drive the particles to the surface of the cylinder, the mechanism of the action being similar to that of the electric wind.

Negatively charged dust or smoke particles will also move towards the cylinder under the direct action of the electric field. Since the actual mobility of such a particle in unit electric field is probably considerably less than 0·003 cm. per second, and the potential gradient used in electrostatic precipitation rarely exceeds 5,000 volts per centimetre, the mobility imparted to the particle by the direct action of the field will not exceed 1 cm. per second. Considering the velocity with which the gas streams through the precipitator, it is clear that this mobility is altogether too small for effecting precipitation of the particles. Actually, therefore, the particles are deposited mainly by the electric wind that is set up between the two electrodes.

Some positively charged particles are deposited upon the wire electrode, forming irregular deposits which, if not removed, produce an uneven distribution of the current.

When charged smoke particles pass in close proximity to an uncharged wire or metal plate, they are seen to change their direction, and fly to the wire, probably on account of an opposite charge induced on the plate or wire.[56] It is found in practice that metal plates (Freudenberg) or wires (Roesing), suspended in any flue or settling chamber through which metallurgical smoke is passing, rapidly become coated with a thick deposit of dust.

When hot gases stream over suitable surfaces, both gas and surface become electrically charged. Conceivably a smoke could be treated by passing it first of all between a number of " charging " baffles set fairly close together, and then over a series of " depositing " baffles.

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CHAPTER V

THE STABILITY OF AEROSOLS

THE equilibrium conditions of a disperse system are not completely determined by the factors,—temperature, pressure and chemical composition of the phases—that define the equilibrium conditions under which the disperse phase and dispersion medium can exist together simply as separate phases. They also depend upon the degree of dispersion and the precise manner in which the particles of the disperse phase are distributed throughout the dispersion medium.

The stability of the system can be upset by changing the temperature, pressure or composition of the two phases, as, for example, when the disperse phase evaporates or dissolves in the dispersion medium as the temperature rises.

These changes may be greatly modified by the presence of films of adsorbed gas or liquid, or of electric charges upon the particles of the disperse phase.

The peculiar character of a disperse system is also destroyed if the particles of the disperse phase diffuse out of the gas—for example, to the walls of the container, or to the surface of a filtering medium—or if they settle from the gas, assisted possibly by a preliminary coalescence or flocculation.

The stability of an aerosol is chiefly determined by the rate at which the particles either diffuse or settle. Naturally, owing to the relatively low density and viscosity of the dispersion medium, the particles of the disperse phase of an aerosol tend to settle more rapidly than do the particles of a disperse phase in a liquid dispersion medium. Thus spherical particles of unit density and of radius 0·4 μ settle in air at normal temperature and pressure at the rate of 0·003 cm. per second. In water, they would only settle 0·003 cm. in three days.

On the other hand, the greater amplitude of the Brownian

movement of smoke particles delays the settling of the particles. Cloud particles do not exhibit Brownian movement; they, therefore, do not diffuse, but settle steadily in still air. Their fall may be retarded or prevented altogether by vertical convection currents, set up in the relatively very mobile gaseous dispersion medium.

When the particles of a cloud or smoke come into contact with a solid surface—*e.g.*, the walls of the containing vessel—they tend to adhere to the surface or to each other, to form coarse flocks or aggregates, and so become removed from the system. The rate at which a smoke will be cleared in this way, as we have seen, is very low. The process can be accelerated by agitating the gas, so that more particles are brought into contact with the surface per second. It can also be accelerated by increasing the area of the surface. In a filter, the gas is drawn through a porous diaphragm—*e.g.*, a cotton or woollen fabric, a loose plug of asbestos fibre, or a canister filled with small carbon granules. Thus it is broken up into a large number of small eddy currents, and it is brought into contact with a relatively enormous surface. Consequently the diffusion of particles to a surface upon which they can be deposited is very greatly facilitated.

The efficiency and, therefore, the capacity of a given filter clearly depend upon the rate at which the particles diffuse towards the filtering surfaces as the smoke passes through. Owing to the much higher diffusion velocities of gas molecules, it is much easier to remove a gas from a gas mixture by filtration through a charcoal filter than it is to remove smoke particles.

To some extent the particles, particularly the larger ones, are deposited in the filter by centrifugal force, due to the eddy currents that are set up in the smoke as it passes through the filter. Owing to the relatively low density and viscosity of gases, this effect is probably more important in filtering an aerosol than a disperse system in a liquid. It is more effective with clouds than smokes.

A thin layer of wood charcoal granules of about 1 mm. diameter will remove chlorine quantitatively from a mixture of chlorine and air, but tobacco smoke, sulphuric acid mist, clouds

and smokes obtained by the detonation of various organic liquids will pass through it with their composition absolutely unchanged.

During the war it was found that filters made of felt or paper gave far more efficient protection against smokes and clouds than the granular charcoal filter that had served so successfully against gas. A paper filter made of a felted mass of long fibres loosely packed was more efficient than one made of short fibres that were tightly packed. Probably, in the former, there were longer spiral ramifications through the paper, so that, as the cloud passed through it, the particles would be deposited upon the walls of these passages by centrifugal action. This action would be stronger the larger the particles were.

When a cloud of diphenylchlorarsine, obtained by detonation, is passed through such a filter, it is found that the efficiency of the filter reaches a minimum when the radius of the particles is between 0·1 and 0·2 μ. Probably, at lower values of r, the velocity of diffusion is the determining factor, while, for larger particles, the efficiency depends upon the effect of centrifugal force, which increases with the radius, that is to say, with the mass of the particles.

The relation between the permeability of the filter and the radius (r) of the particles of the aerosol [1] is shown in Table VIII.

TABLE VIII.

Relation between Permeability of Paper Felt Filter and Size of Particle.

Radius $\mu\mu$.	Percentage of Aerosol passing through Filter.
Below 50 . . .	52·4
50—100 . . .	87·6
100—200 . . .	93·9
200—400 . . .	30·4
400—800 . . .	4·2
Above 800 . . .	0·0

Diffusion.—Owing to their Brownian motion, smoke particles

diffuse in all directions, thus tending to distribute themselves uniformly throughout the medium. Completely uniform distribution is checked by the action of gravity. Although the effect of gravity is more pronounced in gases than in liquids, actually its action is often masked by convection currents. If convection currents be prevented, it is found that, after a time, the particles are more closely packed in the lower layers of the gas, on account of the small but continuous disturbing action of gravity upon the direction of their movements.

The rate at which smoke particles diffuse through the gas depends upon the size of the particles, the viscosity of the gas, and the temperature.

From equation 8 we see that—

$$r = \frac{RT}{N} \cdot \frac{t}{3\pi\eta A^2}. \quad . \quad . \quad . \quad (21)$$

Putting $R = 8{\cdot}316 \times 10^7$,

$N = 6{\cdot}06 \times 10^{23}$,

$T = 293$,

we get—

$$r = \frac{4{\cdot}7 \times 10^{-11} t}{A^2}. \quad . \quad . \quad . \quad (22)$$

For particles of a given size the time required for the particle to travel a given distance (A) is directly proportional to the square of the distance. Consequently the rate at which particles diffuse through the gas to the walls of the container is generally too slow to be effective.

Einstein [2] and Smoluchowski have shown that the rate of diffusion is related to the amplitude of the Brownian motion of the particles by the expression $D = \frac{1}{2}A^2/t$, where A is the length of the Brownian path described by the particles in time (t). Combining this with equation 21, we get—

$$D = \tfrac{1}{2}\frac{A^2}{t} = \tfrac{1}{2} \cdot \frac{RT}{N} \cdot \frac{1}{3\pi\eta r}. \quad . \quad . \quad . \quad (23)$$

If the dispersion medium, temperature and viscosity remain unchanged, we find that $D = K/r$. From this it is clear that the smaller the particle, the more rapidly will it diffuse. The finest smoke, however, will diffuse less rapidly than a pure gas.

Thin wisps of tobacco smoke preserve their outline for a considerable time when rising slowly through the still air of a room. Cloud particles appear hardly to diffuse at all. A fog will remain stable for days unless it is stirred by a breeze.

Flocculation of the Particles

The chief effect of diffusion is to increase the chance of collision between the particles. When an aerosol is first formed, the degree of dispersion may be very high. When the aerosol is viewed in the ultramicroscope, the particles are seen to be very numerous and in rapid Brownian motion. The collision frequency of the particles possesses a maximum value. In many cases, this value is further increased by the relatively high temperature of the system just after dispersal.

As the direct result of this initially high collision frequency, the aerosol is very unstable, and the particles begin to form aggregates. The primary degree of dispersion is rapidly succeeded by a lower secondary degree of dispersion. As the degree of dispersion decreases the stability of the system increases, since, as they become larger, the particles become fewer and further apart, and more sluggish in their movements. Ultimately they reach a state of comparative equilibrium, corresponding to the secondary degree of dispersion, after which further flocculation takes place slowly, or not at all. The collision frequency of the particles diminishes to a minimum, or, if the secondary degree of dispersion is such that the radius of the particles is of the order of 0·1 μ or more, collisions due to Brownian movement practically cease to occur at ordinary pressures. In most cases, however, the secondary degree of dispersion is still that of a smoke, so that collisions between the particles still occur with considerable frequency, and the secondary degree of dispersion is slowly succeeded by a tertiary degree of dispersion.

Whytlaw-Gray,[3] working with smokes of NH_4Cl, CdO, CuO, ZnO, observed that the life history of such systems can be separated into three periods :—

(*a*) An unstable period, lasting for five hours or more, in which the decrease in the *number* of particles with time is very

rapid. This is due to the aggregation of the particles and corresponds to an increase in the average mass of the particles.

(*b*) A stable period, in which the number of particles dimi-

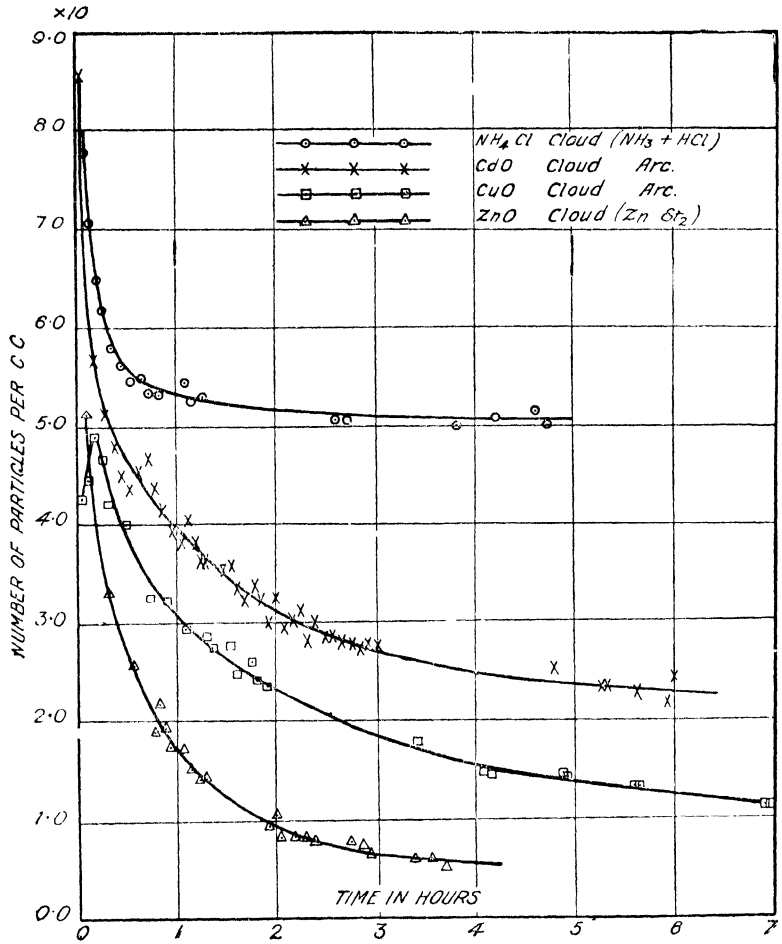


FIG. 7.—Relation between number of particles per cc. and age of smoke.

nishes very slowly, chiefly as a result of sedimentation. This stage may last for twenty-four hours or more, even in a chamber of only 1 cubic metre capacity.

(*c*) These two stages overlap to produce an intermediate stage, in which both flocculation and settling operate.

The course of these changes is indicated in the curves of Fig. 7, in which is shown for different smokes the relation between the number of particles per cubic centimetre and the age of the smoke.

When an aerosol is first formed—for example, by the condensation of a vapour in the presence of a sufficient number of suitable nuclei—the primary degree of dispersion is very high. The diameter of the particles will be of the order of 10^{-7} cm. The particles tend to coalesce by reason of the intermolecular attraction that exists between their surface molecules. They will also tend to adsorb molecules or ions of the dispersion medium. Which tendency will be the stronger will depend upon the nature of the disperse phase and the dispersion medium, upon their concentrations, and also upon the temperature. Which action will have the greater opportunity will be determined by the frequency with which the particles collide with one another and with molecules of the dispersion medium, and the closeness with which they come into contact at the moment of collision.

The aerosol particles, owing to their greater mass, move with much smaller velocities than the molecules of the dispersion medium. Consequently the frequency of collision between the particles of the disperse phase is very much less than the collision frequency of the molecules themselves. If, therefore, the particles tend to adsorb the gas molecules, it is very probable that they will become surrounded by films of adsorbed gas before they collide with each other.

In the absence of any so-called indifferent gas, or if the indifferent gas that is present is not adsorbed by the particles, the particles will coalesce readily, and coarse secondary degrees of dispersion will rapidly ensue.

If the gas molecules are adsorbed to an extent sufficient to form a film of adsorbed gas, for example, 1 molecule thick, then, when two such particles approach each other sufficiently closely for the two adsorbed gas films to touch each other, the particles will be attracted to one another by the force of cohesion between the adjacent molecules of the two gas films, and also by the force of cohesion between the two particles, the latter being greatly diminished in intensity by the increased distance

that separates the particles. This distance will be equal to twice the thickness of the adsorbed gas films, which may each be 1 molecule thick. In most cases, this would still permit strong forces of cohesion to come into play between the particles, particularly as the surface molecules, owing to the high degree of curvature of the particles, exercise a more intense attractive force than the molecules of a plane surface.

Owing to the presence of the adsorbed gas film, such colliding particles would not be able to coalesce, but would become loosely attached to one another, forming flocks.

If the gas molecules are adsorbed strongly, even flocculation might be prevented, and the aerosol would then remain with a high degree of dispersion, the particles gradually being removed by diffusion to the walls of the containing vessel.

When a metal vapour is condensed, it is found that the coarsest condensates are formed in the entire absence of any indifferent gas. When such a gas is present—*e.g.*, nitrogen, carbon dioxide, hydrogen, bromine—then, according to the nature of the metal, finer condensates are obtained. The degree of dispersion is higher the greater the density and pressure of the gas. Thus finer condensates are obtained in nitrogen than in hydrogen, and at 760 mm. pressure than at 30 mm. pressure.

In many—possibly in most—cases, the effect of adsorption is further complicated by the presence of gaseous ions in the dispersion medium. These will be adsorbed by the particles. They may be adsorbed indiscriminately, in which case they will impart charges of opposite sign to different particles, and thus promote flocculation. On the other hand, the particles may adsorb ions of one sign only, and thus, becoming charged with the same sign, exhibit no tendency towards flocculation.

In some cases, the particles, either because of ion adsorption or because of their intrinsic structure and configuration, may be electrically polarised. Such particles will become attached to one another by their unlike poles, and thus tend to form peculiar thread-like aggregates.

Whytlaw-Gray found that the particles of CdO and ZnO smokes form flexible, string-like aggregates. The tendency to form such string-like complexes seems to be weakest with oxides

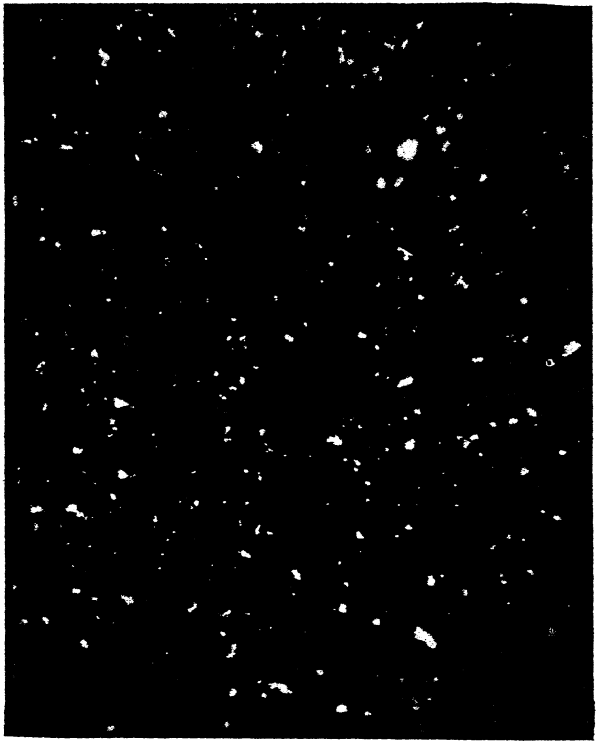


FIG. 8.—ZnO smoke particles 9 minutes after formation.

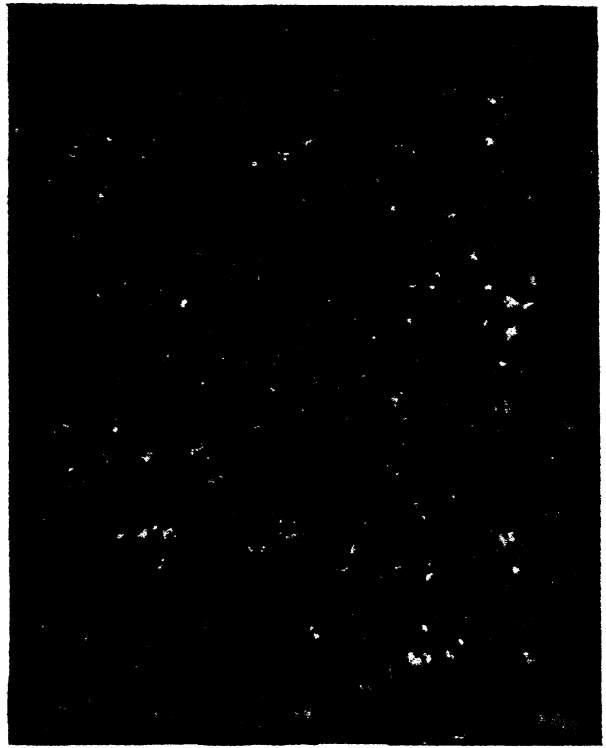


FIG. 9 —ZnO smoke particles 29 minutes after formation.

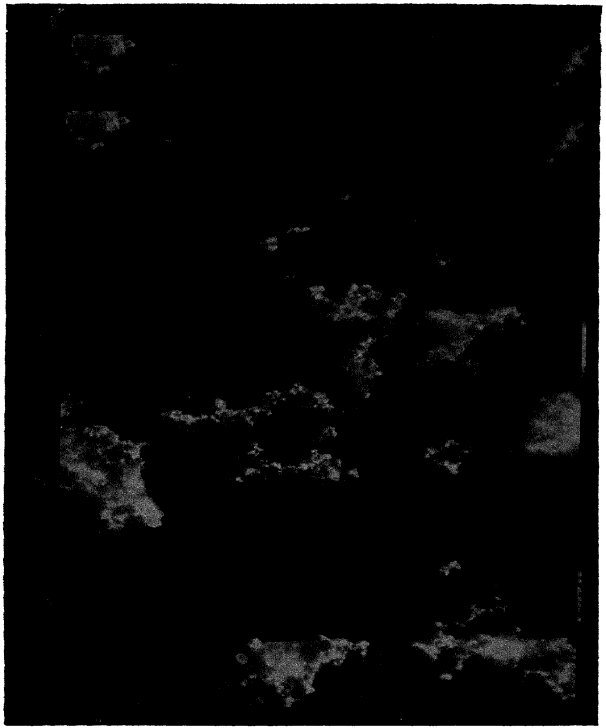


FIG. 10.—ZnO smoke particles 49 minutes after formation.



FIG. 11.—ZnO smoke particles 244 minutes after formation.

of lead, manganese, copper, chromium. It is slightly greater with iron, whilst magnesium, aluminium, antimony, resemble zinc and easily form loose, flock-like aggregates.

The particular structure of the aggregates that are formed by the particles of a given smoke appears to depend upon the nature of the substance of which the individual particles are composed rather than upon the influence of electrical charges on the particles. In the case of zinc oxide smokes, the formation of thread-like complexes, for instance, must be attributed to the intrinsically polar character of the particles themselves, since precisely similar complexes are formed in smoke that is formed by the decomposition of zinc ethyl in which very few charged particles are produced.

In Figs. 8, 9, 10, 11, the gradual formation of these aggregates is shown in the case of a zinc oxide smoke. The samples were obtained by exposing microscope slides to the smoke at intervals, respectively, of 9 minutes, 29 minutes, 49 minutes and 244 minutes after the formation of the smoke. These photographs show very well the gradual aggregation of the particles to form string-like complexes, which subsequently join together to form a network "flock." The network structure of these flocks resembles that of certain gels. It has been suggested by Donnan that the term "aerogel" might be applied to such structures.

The flocculation of an aerosol is facilitated by anything that will displace the protective electric charge, or film of adsorbed gas. This may be done by charging the aerosol electrically. This may neutralise an electric charge, or it may displace a film of adsorbed gas. An electric charge acts so as to oppose the effect of surface tension.[4] It will thus tend to diminish the force of attraction between the adsorbed gas and the surface of the particle, and may displace the gas film sufficiently for contact to occur between colliding particles. It is found that water drops, colliding in air, rebound from one another, probably owing to the presence of such a surrounding film of gas. If the air in the immediate vicinity of the drops is charged, the particles become charged by adsorption of ions, and then coalesce when they collide with one another.[5]

Similarly, a smoke or cloud can be flocculated by mixing with it a smoke or cloud containing oppositely charged particles.

Recently light fogs and clouds have been flocculated by scattering charged sand over them from an aeroplane.[6]

Even if the original aerosol contains only neutral particles the addition of charged particles may produce flocculation, since mutual attraction will exist between a charged particle and a neutral particle, on account of the induced opposite charge that is produced on the neutral particle.

If a smoke is subjected to a high tension discharge, so that the molecules of the dispersion medium are charged, the particles of the disperse phase will become charged by ion adsorption. They will then be brought together by the force of the electric field, to form thread-like aggregates along the lines of force. These aggregates speedily settle to the floor of the container.

The stability of a P_2O_5 or SO_3 smoke, when bubbled through water, is partly to be attributed to the presence of a film of adsorbed gas (air) surrounding the particles.[7] The stability of the blue ZnO smoke from a brass foundry can be similarly explained. When the ZnO is collected—*e.g.*, with woollen filters—it is very light and mobile. It flows and surges in a bottle like a limpid liquid, and has an apparent density of 0·1, the normal density of ZnO being 5·78. The ZnO smoke is rapidly flocculated by steam. Possibly the steam displaces adsorbed gas from the surface of the particles.

A smoke can be flocculated by alternating electrical discharge,[8] or by mixture with a smoke or gas containing oppositely charged particles or molecules.[9] A mutual attraction exists between an electrically charged particle and a neutral particle, owing to the production of an induced charge upon the neutral particle.

According to Bjerknes,[10] high frequency sound waves promote the attraction and repulsion of particles in suspension in a gas or liquid.

Particles may grow by further condensation from the vapour phase as the system cools. Aitken has shown that minute dust particles in humid air become surrounded by a film of water.

Cooling vapours of aluminium chloride or ammonium chloride produce minute crystalline nuclei which, as long as they remain in suspension, grow rapidly at the expense of the vapour phase.

Tolman and others [11] have investigated the stability of smokes of acetanilide, benzoic acid, resin and petroleum oil. They find that—

(1) Stirring or agitation accelerates the rate of disappearance of the smoke by bringing the particles more completely into contact with the walls of the containing vessel, to which they adhere.

(2) Increasing the concentration of the smoke—the size of the particles remaining constant—accelerates the rate of disappearance by increasing the frequency with which the particles collide with each other and with the walls of the vessel.

(3) Fine particles (blue smoke) disappear more rapidly than large particles (cloud), owing to the greater velocity with which they diffuse, and consequently the greater frequency with which they collide.

Mists or fogs, in which the particles are too large to diffuse, are rapidly dispelled by a breeze. This is probably due to the fog or mist particles being brought into contact with one another, so that larger and heavier aggregates are formed.

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CHAPTER VI

THE CHEMICAL AND PHYSICAL EXAMINATION OF AN AEROSOL

FULLY to describe a given aerosol it is necessary to define its chemical composition, its physical structure and its degree of stability. Since a freshly formed aerosol is generally a very unstable and rapidly changing system, it is always essential to record carefully the temperature and the age of the sample at the time of observation. For a given concentration of disperse phase the primary degree of dispersion may be very high. The smaller the particles are, the more numerous they will be and the more rapidly they will move. Consequently the frequency with which the particles collide with one another will approach a maximum value. Thus they may coalesce rapidly to produce a much lower secondary or tertiary degree of dispersion. As the particles become larger and further apart and move more slowly, the frequency of collision and coalescence becomes very much less, and the system becomes relatively stable.

(A) The Chemical Composition

To determine the chemical composition and the concentrations of the different constituents of an aerosol, it is necessary to work upon a large sample—for example, a cubic metre. This can be collected in a suitable sampling vessel thermally insulated or capable of being kept at a constant temperature, or a known volume of the aerosol may be drawn through a suitable filter or precipitator, in which the disperse phase can be quantitatively separated from the dispersion medium. The dispersion medium can then be collected separately in any form of gas-collecting apparatus for examination by the ordinary methods of gas analysis. In obtaining or filtering a sample of an aerosol it is frequently necessary to maintain a constant temperature throughout the whole of the operation to prevent any change of

concentration due to the evaporation or condensation of the disperse phase.

The operation should be carried out in as short a time as possible to minimise any loss of the disperse phase through settling upon the walls of the apparatus.

Various methods have been devised for separating and collecting the disperse phase from a known volume of an aerosol. Most of them were devised to determine the amount of smoke in furnace gases, or in the atmosphere, or the dustiness of mine or factory air. More recently other methods have been worked out to determine with greater accuracy the concentration of the disperse phase in various smokes and clouds of high degrees of dispersion and of correspondingly low stability.

It will be convenient to consider first those methods that can be used when the degree of dispersion is relatively low and the concentration relatively high.

(1) **Coarse Suspensions : Clouds.**—Three kinds of methods are used : deposition, filtration and precipitation.

Deposition.—The simplest form of deposition is to expose a plate or open vessel of a definite surface area to the dusty air or gas for a known length of time, and weigh the accumulated deposit. This method is in general use for determining the amount of impurity that settles from the atmosphere per square metre per mensem or per annum.

By this means it is possible to obtain a quantity of material sufficient for a complete microscopical and chemical examination. The result gives in no sense a measure of the total amount of suspended matter in the air or gas, but only an approximate mean figure for the amount that is deposited upon the collecting surface during the given period of time. In determining the amount of atmospheric impurity it is difficult to prevent the sample from being contaminated with foreign matter, particularly in windy weather.

When an aerosol impinges upon a solid or liquid surface the particles of the disperse phase are deposited upon it to an extent that depends upon the velocity and direction of impact, the temperature of the aerosol and of the depositing surface, and the chemical and physical character of the surface. Deposi-

tion is largely due to the centrifugal force that is produced when the gas stream suddenly changes its direction as it approaches closely to the depositing surface. Probably the action is to some extent a specific one and depends first of all upon the degree of contact that can be obtained between the particles and the depositing surface, and then upon the force of attraction that exists between them when they are brought into such close contact. Generally the particles adhere to the surface more readily when it has become coated with a film of the disperse phase. In some forms of trap the aerosol impinges upon or passes between glass plates that are coated with glycerine, oil or vaseline.[1] Theoretically, if the surface be extensive enough, all the suspended particles will ultimately be trapped provided that they can be wetted.

The deposit that is obtained in this way can be examined microscopically or compared with standards, or, if large enough, it can be weighed. In some forms of apparatus a known volume of gas is passed through the apparatus, and the liquid film, with its adhering dust particles, is dissolved in a suitable solvent, and either the particles are collected upon a filter and weighed, or a small volume of the liquid is taken, and the number of particles that it contains are counted.

The accuracy of such methods is very restricted, because—

(1) It is difficult to bring every particle into contact with the collecting surface ;

(2) The particles may not be wetted easily, particularly if the liquid be water ;

(3) Some of the particles may be soluble in the liquid or may form finer or coarser particles when they are suspended in it.

In some instances the final colour or shade of the collecting surface or of the resulting suspension is compared with standards.

A method has been devised by G. T. Palmer[1] in which a known volume of air is drawn through a washing vessel, in which it is intimately mixed with a fine water spray. The number of particles in a given volume of water is then determined, and the weight of collected matter can be ascertained by evaporating the water and weighing the residue. Such a method, also,

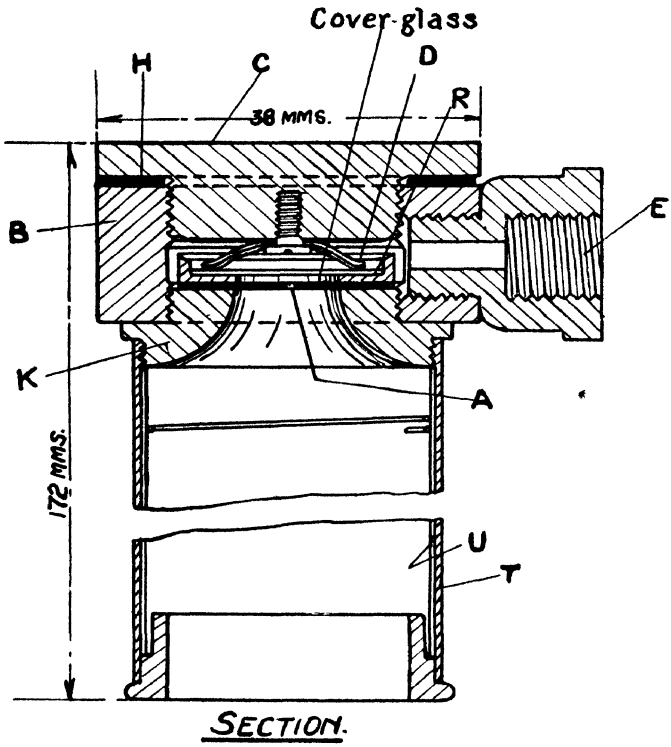
clearly depends upon the wetting of the particles by the water. It is useless for substances like tar, carbon, soapstone, talc or zinc oxide. Even if wetting can occur, the degree of contact between the particles and the water droplets is far from being complete. The method has been examined critically,[2] and has been shown to have an efficiency of only 13 per cent. with tobacco smoke, while for air charged with fine silica dust the efficiency was 30 per cent. when the air passed through the apparatus at 4 cubic feet per minute, and 20 per cent. at 3 cubic feet per minute. The efficiency increases the coarser the particles and the fewer particles there are per unit volume of air. Possibly the wetting efficiency could be materially improved by lowering the surface tension of the liquid, for example, by using a soap solution instead of water.

All these methods have the further disadvantage that they are slow and somewhat inconvenient for field work.

A most convenient and relatively accurate method of determining the amount of suspended matter in a gas is with the Owens jet apparatus.[3] In this apparatus a jet of the dusty air is caused to impinge at a high velocity upon a glass surface, for example, a microscope slide. Under suitable conditions of humidity and velocity, the dust particles adhere to the glass surface, and form a record that can be removed and examined microscopically and microchemically.

The construction of the apparatus is shown in Fig. 12. A slot (A) is formed by the parallel straight edges of two half-discs of hard brass or copper sheet. By means of four screws, these two half-discs are attached to a brass ring and adjusted to the required width of opening. The internal diameter of the ring determines the length of the slot. A microscope cover-glass is held in position above the ring—that is, above the slot—and distant from it to the extent of the thickness of the ring. By means of the connection E a given volume of air can be drawn through the slot at a definite velocity and caused to impinge directly upon the cover-glass. The apparatus can be arranged so that the actual deposition of the particles upon the glass can be watched with a microscope.

A brass tube (T), lined with moist blotting paper, serves to



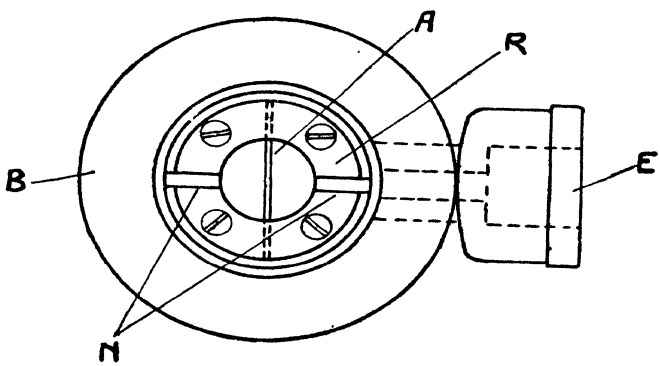


FIG. 12.—The Owens jet apparatus.

saturate the incoming air with water vapour. As the saturated air passes through the slot its pressure is suddenly lowered, so that it expands and therefore cools. Water vapour condenses upon the dust particles, so that when they impinge upon the glass they adhere more readily to it.

The length of the slot can be adjusted according to the dustiness of the air that is to be examined. For use with city air a slot 1·0 cm. in length and 0·1 mm. wide is used, the volume of air being 50 c.c. In very clean air, a shorter slot may be used —say 2 mm.—or a greater volume of air may be drawn through the slot.

The air passes through the jet with a velocity of about $2{\cdot}5 \times 10^4$ cm. per second—about ten miles per minute. As the jet, on striking the plate, is deflected, the particles are projected against the glass and adhere to it. To obtain the greatest efficiency, it is necessary to keep the velocity of the jet as high as possible. If the velocity be low—for example, about 8×10^2 cm. per second—the dust particles tend to form loose, flocculated masses instead of a discrete, particulate deposit.

The volume of air that is used should be so chosen that the number of particles deposited is not too numerous. They can then be counted by using a net-ruled micrometer eyepiece.

The deposits that are obtained can be preserved in Canada balsam to form permanent records.

The efficiency of the apparatus, as tested by passing the air in succession through two such deposition cells and comparing the two deposits that are obtained, is about 90 per cent.

In addition to its use in determining the amount of impurity in the atmosphere, the apparatus is well adapted for the examination of such dusty gases as factory air, mine air, smelter fumes, etc.

By allowing the dusty air to impinge upon a moving strip of paper it is possible to obtain a continuous record of the quantity and character of the atmospheric dust.

Filtration.—Filtration is essentially a special form of deposition. The particles are not held in the interstices of the

filter as on a sieve, but are deposited upon the surface of the fibres of which the filter is made. The particles are deposited very largely by the centrifugal force of the eddy currents that are set up in the gas as it passes through the various passages in the filter. The accumulation of particles of the disperse phase at the filtering surface leads to the formation of flocks, which, by forming an extensive and irregular surface of the actual substance of the disperse phase, greatly increase the efficiency of the filter. The linear velocity of the gas through the filter is generally high, and contributes to the efficiency of deposition.

It is very difficult to obtain a filter that will completely separate the disperse phase from the dispersion medium. An aerosol can easily pass through a filter that will absorb a gas completely. This is because the relatively slow moving particles of the aerosol come into contact with the walls of the filter passages very much less frequently than the swiftly moving molecules of the gas.

The filtering efficiency of a porous paper depends very much upon the texture of the paper. A paper that is made up of long fibres loosely packed is much more effective than a paper that is made up of short fibres that are tightly packed together. This appears to be due to the existence of spiral passages in the long-fibred paper, in which, as the aerosol passes through them, the particles are deposited by centrifugal force.

Quantitative determinations by filtration methods can only be regarded as satisfactory for relatively coarse aerosols, and preferably those in which the concentration of the disperse phase is high—for example, the dusty air of mines and factories and certain metallurgical fumes.

Filtration Methods.—The choice of a suitable filter medium will be determined by the character of the aerosol, the concentration and the degree of dispersion of the disperse phase, and whether the particles are liquid or solid. A known volume of the aerosol is drawn through the filter, and the amount of deposit is determined either by weighing, by matching the coloration that is produced on the filter, or by using a filter of soluble material—for example, collodion or sugar—and dissolving

the filter and its contents in a suitable solvent and counting the number of particles in a given portion of the solution.

The accuracy with which the deposit can be determined gravimetrically, using a paper filter, is diminished by incomplete filtration and by the absorption of moisture by the filter paper. It is often very difficult to examine a deposit on a filter paper microscopically or to remove it for chemical analysis.

Filters made of blotting paper, in which the stain that is produced by a known volume of the aerosol is compared with standard stains, have long been used for recording the amount of suspended matter in the air in different localities.[4] Mechanically driven filter recorders are used in which a disc or strip of paper is caused to move regularly over a small aperture connected with an air-pump. At regular intervals of time an amount of air corresponding to a single stroke of the pump is drawn through the area of the paper that is situated just over the aperture. The paper is graduated in hours or fractions of an hour, so that a continuous record of the amount of suspended matter in the gas is obtained. In recording the dustiness of factory air in which white or light-coloured dusts are suspended, black filter paper is sometimes used.[14]

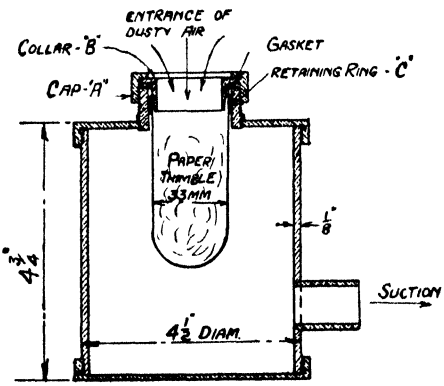


FIG. 13.—Paper filter for dusty gas.

A convenient form of paper filter [5] is shown in Fig. 13. The dusty gas is drawn through the paper thimble at a rate of about 32 litres (1·1 cubic foot) per minute. The volume of gas is determined by counting the number of strokes of the pump. The thimble is weighed before, and again after, the passing of the gas.

The thimble used is the ordinary single thickness Whatman

extraction thimble that is used for Soxhlet extractions. About 0·1 gram of cotton wool is well fluffed out and placed inside the thimble to catch some of the dust and prevent it from clogging the pores of the paper.

Before use the filter is dried for two days at 95° C. and weighed. After sampling is complete the filter and its contents are again dried for two days at 95° C. It is then placed in a weighing bottle and cooled in a desiccator. The increase in weight gives the dry weight of the dust accumulated. The filtering efficiency of the thimble was found to be about 100 per cent. for particles of diameter greater than 1 μ. With finer particles—for example, those of tobacco smoke—averaging 0·25 μ in diameter, the efficiency was only 43 per cent.

Such a filter is admirably adapted for determining the concentration of dust in factory or mine air.

Precipitation.—The particles of a coarse suspension can also be deposited conveniently and accurately by the method of electrostatic precipitation that is about to be described for use with systems of a high degree of dispersion.

(2) **Fine Suspensions : Smokes.**—By far the most satisfactory method of separating smoke particles from the gas in which they are suspended is that of electrostatic precipitation. A convenient form of precipitator for use in the laboratory has been described by Tolman.[6] The apparatus consists essentially of a cylindrical anode made of platinum or aluminium foil and an axially arranged wire which forms the discharge electrode. The aerosol is drawn through the apparatus at a known rate, and the particles of the disperse phase are precipitated upon the foil by a high voltage direct current. The concentration is determined by measuring the volume of the aerosol that passes through the apparatus and the weight of the foil before, and again after, precipitation is complete. The method is suitable for liquid or solid particles. The deposit can readily be examined microscopically. The apparatus can be arranged so as to permit the observation of the particles as they are being deposited.

A combined electrostatic precipitator and filter, in which the precipitating action of a high tension discharge is combined with

the large collecting surface of a fibre filter, has been used by R. W. Gray.[7] It consists of a light glass tube containing a plug of asbestos fibre. A wire discharge electrode is introduced into the centre of the asbestos plug, and is connected to a source of high potential current. A known volume of the aerosol is passed through the filter, and the increase in the weight of the filter is carefully determined by means of a micro-balance. With this apparatus Gray was able to determine with an accuracy of about 3 per cent. the concentration of the disperse phase in rapidly changing smokes of ZnO, CdO, etc., of very high degrees of dispersion.

Strong [8] has devised a smoke recorder in which the smoke is precipitated electrostatically upon a moving strip of paper.

Thermal Precipitation.—When a smoke passes between two concentric tubes that are maintained at sufficiently different temperatures the particles of the smoke are deposited quantitatively upon the surface of the colder tube. It is conceivable that a serviceable form of precipitator could be devised in which the particles of the disperse phase would be thermally precipitated upon the surface of a cooled tube, in which a suitable temperature gradient could be maintained by means of an electrically warmed wire or rod.

The principle of thermal precipitation is utilised in the design of certain forms of smoke recorder.[9] Paper, mounted on a water-cooled drum, moves at a constant rate across a small opening through which it is directly exposed to the smoke. The intensity of the smoke stain that is produced is roughly proportional to the concentration of the smoke.

After the disperse phase has been separated from the dispersion medium by any of these methods a chemical examination of the gas can be made by any of the standard methods of gas analysis, supplemented, where necessary, by special tests for any uncondensed constituents of the disperse phase that may be present.

Optical Methods of Examination.—Frequently the chemical identity of a given aerosol is already known, and it is only necessary to determine the concentration of the disperse phase.

This can be determined without separating the two phases by observing the optical constants of the aerosol, either (*a*) the intensity of the Tyndall beam or (*b*) the opacity of the aerosol to a standard source of light.

Tolman [10] and Vliet have devised a useful instrument—the Tyndallmeter—for measuring the intensity of the Tyndall beam. The instrument was used extensively during the war to determine the concentrations of various screening and toxic

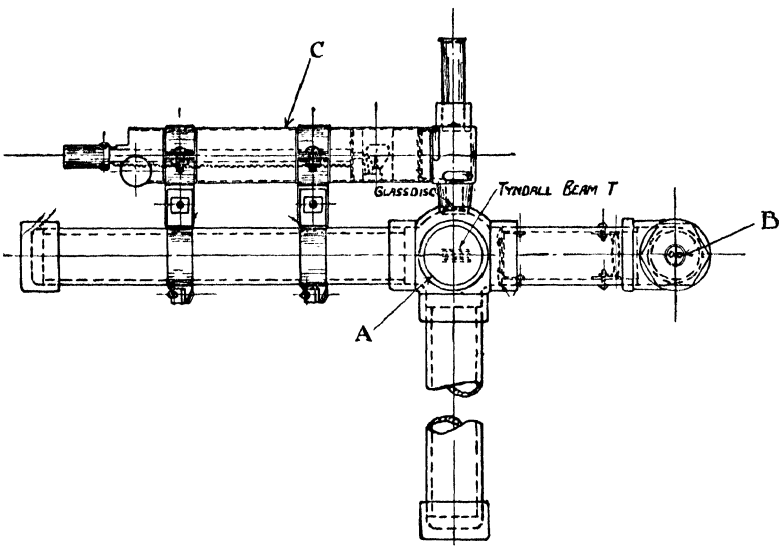


FIG. 14.—The Tyndallmeter for measuring the intensity of a Tyndall beam.

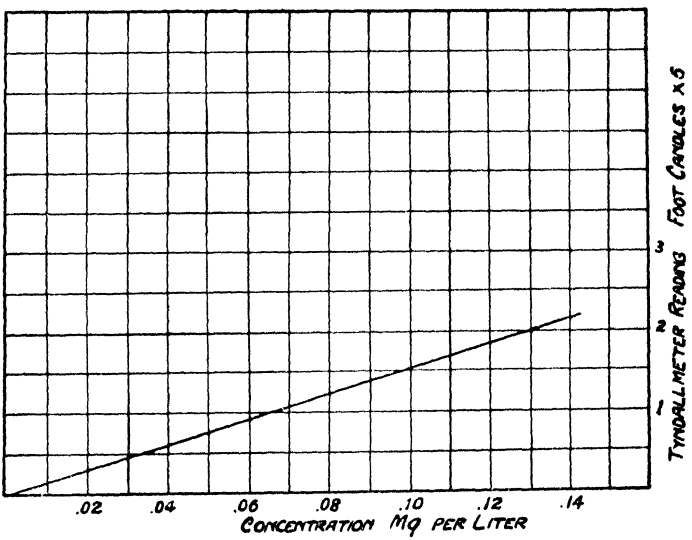
smokes, and also to study the manner in which their concentrations changed with time.

The apparatus is shown in Fig. 14. A glass-sided cell (A) contains the aerosol. This is illuminated by a light (B) of standard intensity, and the intensity of the resulting Tyndall beam in a direction at right angles to that of the incident light is measured by comparison with an illuminometer (C).

The instrument is calibrated using a standard liquid suspension—for example, of quartz in water—that is contained in a small rectangular glass vessel that is introduced into the observation cell. Alternatively a piece of turbid glass can be

used by simply inserting it in the observation chamber. The intensity of the Tyndall beam is measured in foot candles.

With NH_4Cl smokes, ranging in concentration from 0·02 mgm. per litre to 1·2 mgm. per litre, a very good relation was obtained between the concentration of the NH_4Cl and the intensity of the Tyndall beam. The results are shown graphically in Figs. 15

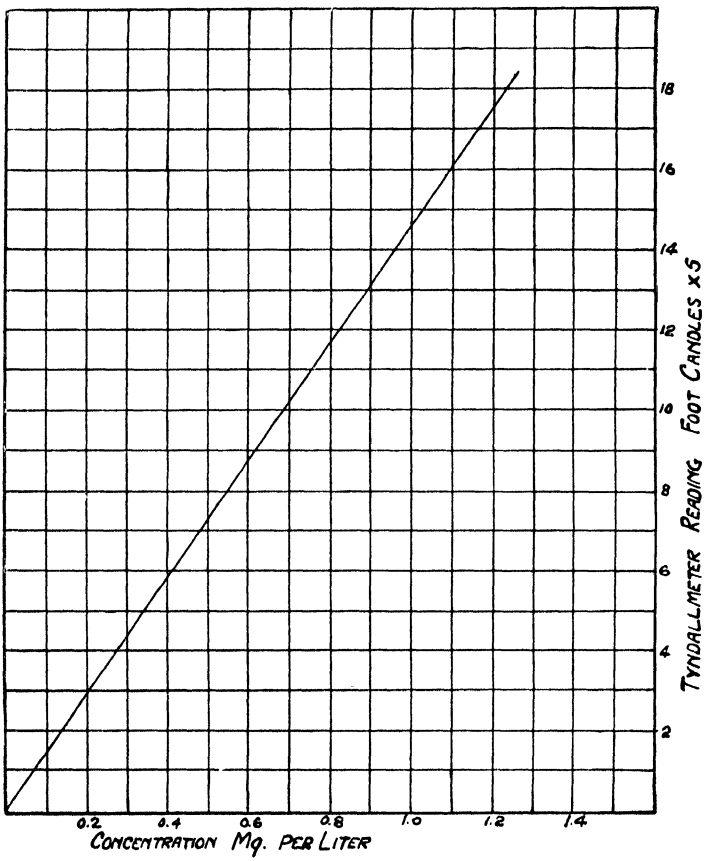


RELATION OF DILUTE CONCENTRATIONS OF NH_4Cl SMOKE TO TYNDALLMETER READING.

FIG. 15.

and 16. These measurements indicate that, in general, the intensity of the Tyndall beam that is produced when an aerosol is illuminated by light of a given intensity will be proportional to the concentration of the disperse phase, provided that (*a*) the concentration is not high enough for the opacity of the aerosol appreciably to affect the result, and (*b*) the degree of dispersion at the different concentrations remains unaltered.

Particles that are larger than 1 μ will reflect the incident light, so that the intensity of the Tyndall beam that is produced, for example, by a cloudy aerosol, will be proportional to



RELATION OF CONCENTRATION OF NH_4Cl SMOKE TO TYNDALLMETER READING.

FIG. 16.

the area of the reflecting surface (d^2) and the number of particles per cubic centimetre (n).

That is, $I_C = k.n.d^2$, where k is a constant.

With smoky aerosols the light is scattered by the particles, and the intensity of the Tyndall beam will be proportional to the sixth power of the diameter (d^6) and to the number of particles per cubic centimetre (n).

That is, $I_S = k'.n.d^6$.

Since the concentration (c) is proportional to nd^3, we can write

$$I_C = \frac{k.c}{d} \quad . \quad . \quad . \quad . \quad (24)$$

and

$$I_S = k.c.d^3. \quad . \quad . \quad . \quad . \quad (25)$$

For a given concentration, therefore, the intensity of a cloudy aerosol will vary inversely as the diameter of the particles (the degree of dispersion), while for a smoky aerosol it will vary directly as the third power of the diameter of the particles.

This means, of course, that in the case of a cloudy aerosol a large number of small particles will reflect more light than a smaller number of larger particles. On the other hand, the light scattered by a smaller number of relatively large particles of a smoky aerosol is more intense than that scattered by a larger number of smaller particles. This is supported by direct observation with an ultramicroscope, in which the intensity of the scattered light is seen to diminish rapidly as the size of the particle decreases.

When different clouds are compared, it is found that the shape of the particles also greatly influences the intensity of the Tyndall beam. Flat plates, for example, in certain positions, will offer a larger reflecting surface than spherical particles. Such flat particles will set themselves in the gas so that they encounter greatest resistance to their motion—*e.g.*, under the influence of gravity. They will thus tend to become orientated, and the aerosol will reflect a Tyndall beam of high or low intensity, according to the angle of reflection.

The total obscuring power of an aerosol has been used during the war as a measure of concentration.[11] It is defined as the

number of square feet of landscape that can be obscured by 1 lb. of cloud-producing material. Actually, it is measured by dividing the volume of cloud (in cubic feet) produced by 1 lb. of cloud-forming material by the depth of the cloud layer (in feet) at which it is impossible clearly to distinguish the filament of a 40-watt Mazda lamp. It is found that, with a given concentration, a large number of smaller particles obscure more effectively than a smaller number of larger particles.

For estimating the density of coal smoke issuing from a stack Ringelmann [12] introduced a graduated series of smoke charts (six in all), ranging from white through increasingly dark shades of grey to black. The charts are hung about 50 feet from the observer, and are compared directly with the appearance of the smoke issuing from the chimney.

Optical methods are not very reliable when applied to highly disperse systems, owing to the rapidity with which such systems change by flocculation.[13]

Examination of the Disperse Phase.—The chemical examination of the precipitated disperse phase should be preceded by a careful microscopical examination of the particles to determine their size, shape, texture, and degree of uniformity. The deposit, if a powder, is then examined in bulk for specific gravity and mobility.

A low specific gravity and a high mobility are generally associated with the presence of adsorbed gas upon the particles. A known weight of the powder is heated *in vacuo*, and the adsorbed gas pumped off and examined. The condition of the powder after doing this is then noted, and compared with its character when first precipitated. If adsorbed gas has been removed by this treatment, the powder should shrink, and increase in specific gravity. Frequently a low specific gravity is due to the particles possessing the very open, spongy structure of an " aerogel."

By this means are determined the chemical composition of the disperse phase and the dispersion medium, and the relative concentrations of the two phases, and, to some extent, the character of the particles of which the disperse phase is made up.

(B) The Physical Structure

The physical structure of an aerosol is determined by the size of the particles of the disperse phase (the degree of dispersion), the number of particles per cubic centimetre, and the nature and velocity of their movements in the dispersion medium.

The Number of Particles per Cubic Centimetre of the Aerosol.—If we know the concentration of the disperse phase, and also the average size of the particles, it is possible, assuming that the density of the dispersed substance is not altered by dispersion, to arrive at a close estimate of the number of particles per cubic centimetre. Actually, this is not a reliable procedure, since the density does alter, particularly at high degrees of dispersion. Further, it is generally comparatively easy to count the actual particles with a fair degree of accuracy by direct observation in an ultramicroscope.

With particles of microscopic size—that is to say, of cloud aerosols—*the degree of dispersion* and the number of particles per cubic centimetre can be determined by collecting on a microscope slide all the particles contained in a known volume of the aerosol. They can then be measured and counted. This can best be done with the Owens apparatus, or with the dust counter designed by Aitken [15] for determining the number of dust particles per cubic centimetre of air.

Owens' apparatus has already been described. Aitken's dust counter is shown diagrammatically in Fig. 17. It consists essentially of a glass globe (A), in which the air to be examined is first saturated with water and then cooled by being expanded suddenly with the pump (B). Water vapour then condenses upon dust particles or other nuclei present in the air, and the water droplets that are formed settle slowly under the action of gravity. O is a micrometer, 1 cm. square, made of polished silver and ruled into square millimetres. It is illuminated by a light (R), focussed by a water lens (Q), which also serves to absorb the heat rays. The volume of air immediately above O is exactly 1 c.c. Consequently the droplets that settle on O correspond to the number of condensation nuclei that were

originally present in 1 c.c. of the air. They are counted with the help of a lens (S).

In making an observation with a given sample of air, the globe (A) is first filled with dust-free air, drawn in through the filter (D). This air is then tested for nuclei by expansion, and

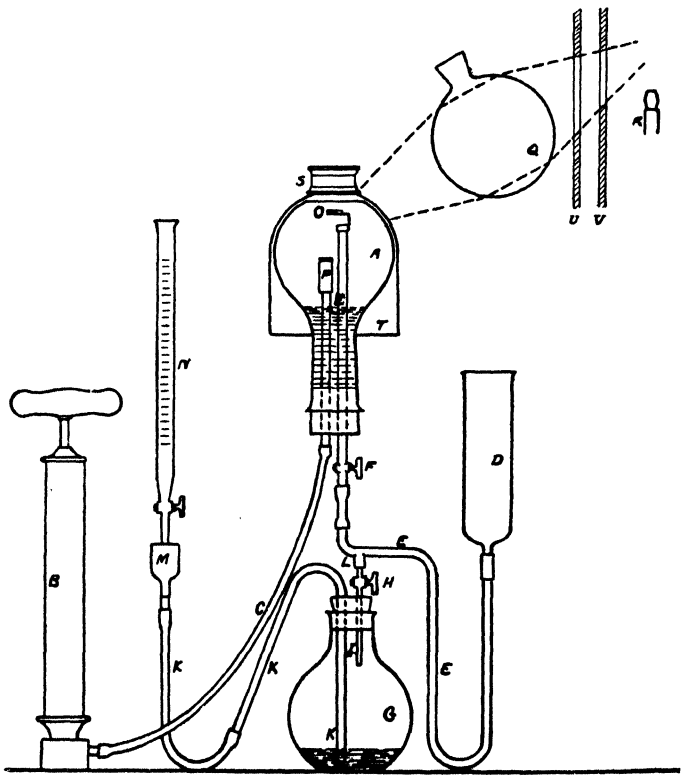


FIG. 17.—Aitken's dust counter.

the globe is exhausted and refilled, until the air in it is free from all condensation nuclei. The sample of air to be examined is contained in the flask (G). One cubic centimetre of this air is displaced from G into the globe (A) by the following procedure :—

One cubic centimetre of water is added from the burette to the graduated funnel (M), the taps ((H) and (F)) being closed.

The tap H is then opened until the water level in M falls again to the graduation mark. F is then opened, and the dusty air is swept into the globe (A) along with a quantity of dust-free air from D.

Sufficient time is allowed for the air to become thoroughly mixed and saturated with water vapour. It is then expanded, allowed to settle, and the number of droplets on O counted. The number of drops formed should not exceed five per square millimetre of the plate ; otherwise it is possible that the nuclei were too numerous for all to have been precipitated. For very dusty air it is necessary to dilute the sample with a large volume of pure air before introducing 1 c.c. of the mixture into the expansion chamber.

The number of condensation nuclei per cubic centimetre of the air to be tested is given by multiplying the number of droplets counted per square millimetre by 100, by the volume of the original sample in cubic centimetres (and by the ratio of dilution, if mixed previously with a volume of pure air), and also by the expansion ratio—final volume to original volume—in the expansion chamber.

If the degree of expansion be large—that is to say, $\frac{v_2}{v_1}$ is greater than 1·25—gaseous ions may also serve as condensation nuclei, so that a count of the number of drops formed would yield too high a result. By restricting the expansion to smaller values this error will be avoided.

Neither Aitken's nor Owens' method is applicable to aerosols of a high degree of dispersion. Such systems frequently have to be examined immediately after they are formed, or during their subsequent development. Further, it is impossible to separate the disperse phase from the dispersion medium in such a system without completely changing the size and character of the particles by aggregation. Such systems, therefore, must be observed *in situ* with the help of an ultramicroscope.

The Ultramicroscope.—An ultramicroscope is an ordinary microscope on the stage of which is fitted a small, glass-sided cell, which contains the aerosol or other colloidal solution that is to be examined. Light from an intense source, the sun or an

arc lamp, is focussed upon the contents of the cell, the axis of this illuminating beam being perpendicular to the axis of the microscope. The background of the cell is dark, and all extraneous light is carefully kept out of the system. If the particles forming the disperse phase are larger than 10^{-5} cm.—the order of magnitude of a wave-length of light—they will reflect and refract the light in a regular manner, and will move relatively slowly in the field of view. Such particles are above the limit of resolution of the microscope, and their shape and size will easily be seen.

If the particles are smaller than 10^{-5} cm.—that is to say, form smoky aerosols—they will be too small to reflect or refract light waves, but instead will scatter some of the light that falls upon them in all directions. They are below the limit of resolution of the microscope, and, consequently, it is impossible to see their shape or size. Such particles also are in rapid Brownian motion.

The amount of incident light that is scattered by the particles varies as their size; the larger particles, therefore, appear brighter. They do not appear to be larger, the only difference between large and small particles being their brightness and the velocity with which they move in a given gas. Even the smallest particles, however, are made visible by using a dark background, since any object, however small, which emits enough light to affect the retina, is visible provided the background is sufficiently dark. Thus stars are visible at night, and dust particles are easily seen in a sunbeam in a darkened room.

The form of ultramicroscope cell that was used by Wells and Gerke [16] in their investigation of certain aerosols is illustrated in Fig. 18.

The cell is cubical, and consists of two stout copper plates, each 15 mm. square and connected at the corners by four square brass rods, each 15 mm. long, the form, or frame, to which four cover glasses, each 15 mm. square, are attached with glue. Two thick copper lugs project from the copper side plates, and serve to carry the supporting clamps and the entrance tubes for the sample. These entrance tubes were made to rotate in a tapered bearing, so that, in a certain position, a small hole in the wall of

the tube communicated with the cell through a passage bored through the copper block. This arrangement formed an effective and convenient stopcock. When closed, the entire cell could be immersed in a thermostat, to bring the sample to temperature equilibrium.

The microscope was fitted with a 16-mm. objective, and two 16-mm. objectives served to focus the light from an arc upon the particles in the cell after passing through a water cell to remove the heat rays.

The particles could be photographed directly by fitting the microscope draw tube with a plate-holder. No eyepiece was used, the microscope objective itself serving as the photographic lens. A magnification of 11 was obtained.

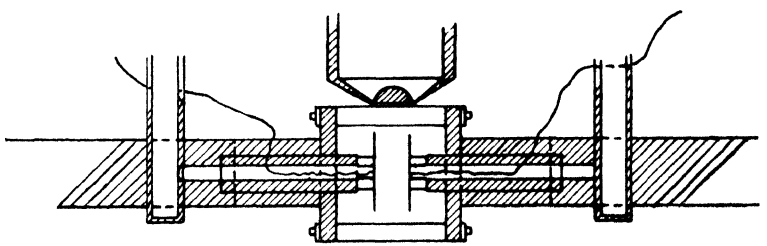


FIG. 18.—Ultramicroscope cell for smokes.

Such an apparatus is well adapted for the direct examination of aerosols.

The Degree of Dispersion.—To determine the size of a particle, it is necessary to measure the rate at which it is moving in a given direction. If the particle is large enough, it will settle at a constant velocity, following Stokes' law. The rate at which it falls under the influence of gravity can be determined, using a micrometer eyepiece and a stop-watch, and correcting for the magnification of the microscope. A large number of separate observations are necessary, and the mean value for v is then substituted in Stokes' formula [17]: —

$$v = \frac{2}{9} \frac{r^3(\rho - \rho')g}{\eta}.$$

If the particles are small enough to exhibit Brownian motion, the problem is rendered more difficult by the more rapid and

erratic character of their movements. The path traced by the particle during a given interval of time, as measured by a stop-watch, is traced on squared paper by means of a camera lucida. The mean displacement of the particle in the observed time along a given axis is then calculated.

Einstein has shown that the Brownian displacement (A) of a particle, measured along a given axis in an interval of time (t), is related to the diffusion constant by the expression—

$$A = \sqrt{2Dt}. \quad . \quad . \quad . \quad . \quad (26)$$

Combining this with Sutherland's diffusion formula—

$$D = \frac{RT}{N} \cdot \frac{1}{6\pi\eta r}, \quad . \quad . \quad . \quad . \quad (27)$$

we get

$$r = \frac{RT}{N} \cdot \frac{t}{3\pi\eta A^2}. \quad . \quad . \quad . \quad . \quad (28)$$

Since r varies as the *square* of A, the accuracy of this method is not very high. The accuracy increases as A increases—that is to say, as the degree of dispersion rises.

This method is also slow and laborious, and the measurements may be vitiated, owing to the particle altering in size, diffusing out of the field of view, or being carried away by convection currents, which, for very small particles, are generally more important than their Brownian motion.

De Broglie [18] attempted to record the paths of the particles photographically, but, owing to the liability of the particles to diffuse away from the field of view during the exposure, the measurement of the time of displacement was rendered uncertain.

In nearly every aerosol, a number of the particles are electrically charged. By observing their velocity in a known electrical field it is possible to calculate their size, assuming that each particle carries a single electrical charge. The number of particles in the aerosol that carry two or more charges is negligible.

Assuming Stokes' law, Von Hevesey has shown that the velocity (V) that is imparted to a charged particle by an electrical field of X volts per centimetre is given by—

$$V = \frac{Xe}{3\pi\eta d'} \quad . \quad . \quad . \quad . \quad (29)$$

where e is the charge on the particle, and d its diameter.

Putting $e = 1{\cdot}59 \times 10^{-20}$,

$$d = \frac{9{\cdot}3 \times 10^{-10}}{V} \quad . \quad . \quad . \quad . \quad . \quad (30)$$

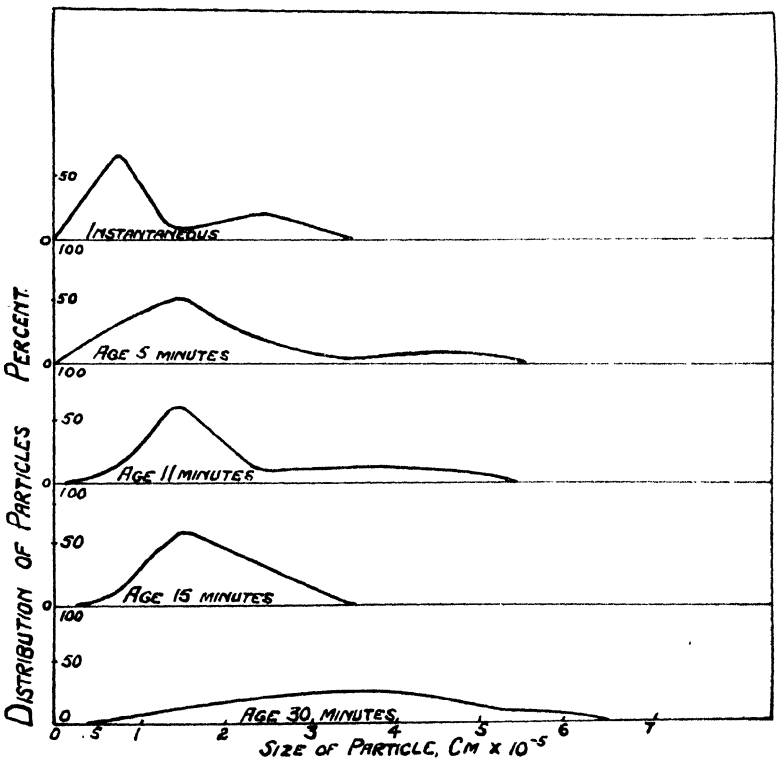


FIG. 20.—Distribution of particle size in a smoke after various intervals of time

Wells and Gerke [16] have devised a greatly improved method, in which the particles are subjected to the influence of a rapidly alternating electric field. The particles are thereby made to oscillate in a direction perpendicular to the convection movement due to the source of light, so that they describe regular zigzag paths. The amplitude of these oscillations is an accurate measure of the

distance traversed by a given particle in a definite small interval of time under the influence of the known electrical force.

A photographic record, showing curves of different amplitudes corresponding to particles of different sizes (assuming that the particles all carry unit charge), is reproduced in Fig. 19. The particles represented vary in radius from 1×10^{-4} cm. to 5×10^{-6} cm.

A great advantage of this method is that particles of different sizes can be measured simultaneously. Also it is possible in

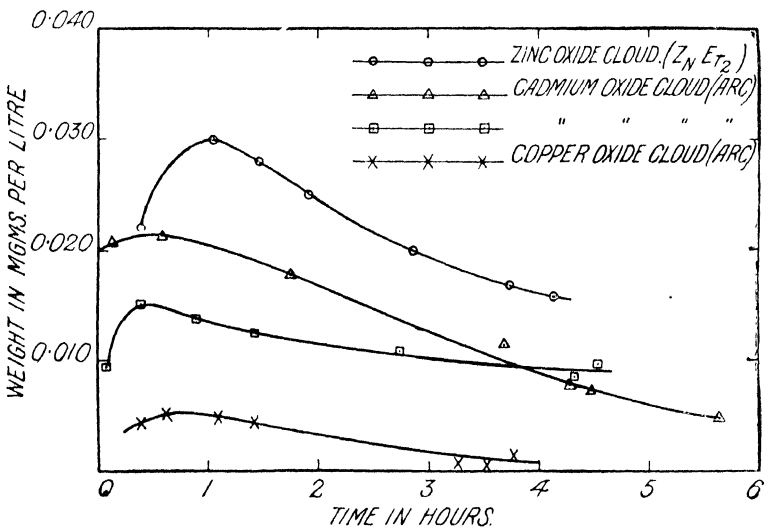


FIG. 21.—Variation of the concentration of different smokes with time.

this way to determine the range and distribution of the sizes of the particles forming a given aerosol at a given moment of time.

The curves in Fig. 20 show the distribution of the particles of a smoke, obtained by detonating oil in air, according to their size at different intervals of time.

Individual particles have been weighed by applying a vertical electrical force to the particle, thus imparting to it a velocity greatly in excess of either its gravitational or Brownian movements.[19] The mass of the particle is obtained by applying Stokes' law to the difference between the observed upward and downward velocities of the particle.

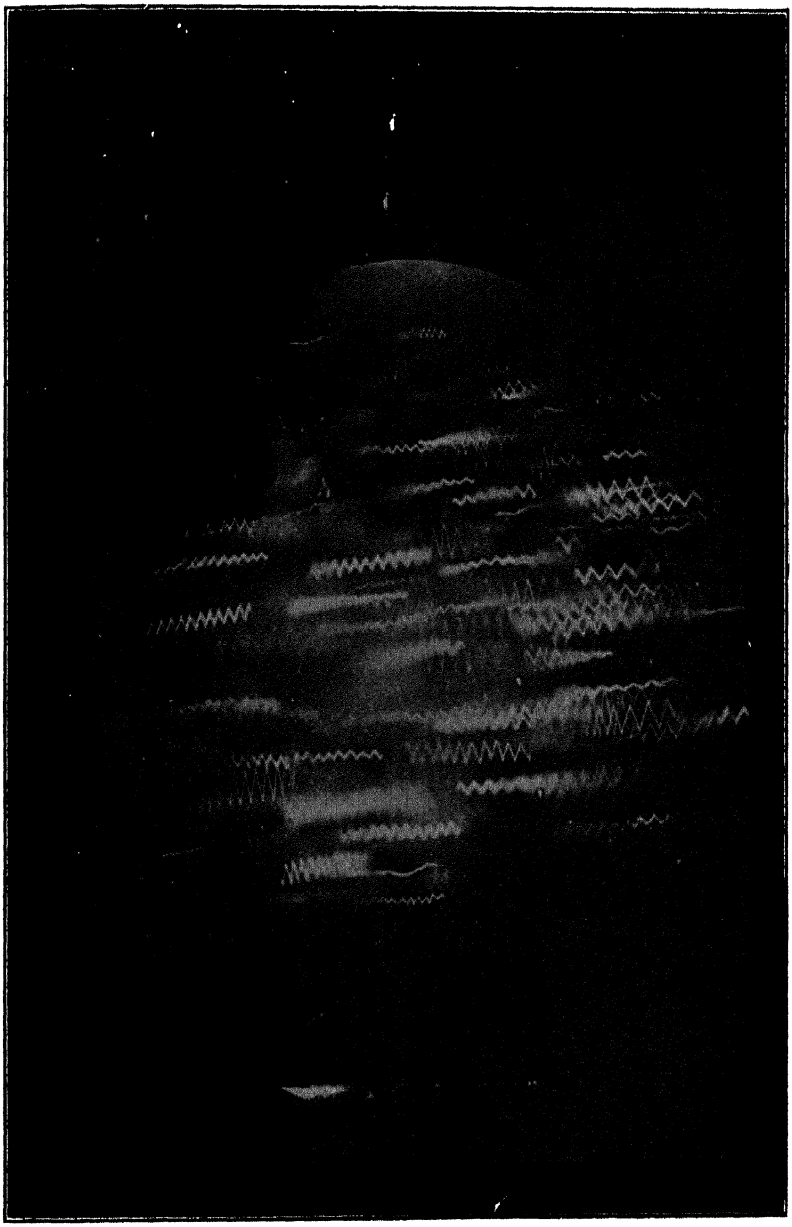


FIG. 19.—Paths traced by smoke particles in alternating electric field.

Millikan's oil-drop method [20] makes it possible to weigh a suspended particle by solving for mg the equation of the equilibrium of the drop between gravity and a vertical electrical field :—

$$\frac{V_1}{V_2} = \frac{mg}{Xe.mg} \quad . \quad . \quad . \quad . \quad . \quad (31)$$

Whytlaw-Gray,[7] using the special precipitation filter described on p. 107, determined, for a number of different aerosols, the concentration of the disperse phase, and, using an ultramicroscope, counted the number of particles per unit volume. He was thus able to calculate the average mass of a particle, and, assuming its density to be identical with that of the undispersed substance, he was able to obtain a value for the radius of the particle.

By this method he was further able to trace the gradual growth of the particles by flocculation or coalescence. In Fig. 21 are shown, for a number of different smokes, the concentration of disperse phase, in milligrams per litre, over periods of up to six hours' duration. In their general characteristics, the curves resemble one another fairly closely.

In Fig. 7 (p. 92) are shown the number of particles per cubic centimetre in such clouds. Considering a zinc oxide cloud as typical, the corresponding numerical observations are given in Tables IX. (*a*) and (*b*).

TABLE IX. (*a*).

Zinc Oxide Cloud. Number Curve.

Time.	Particles per c.c.	Time.	Particles per c.c.	Time.	Particles per c.c.
h. m.		h. m.		h. m.	
0 4	$4{\cdot}54 \times 10^6$	1 51	$1{\cdot}68 \times 10^6$	2 47	$0{\cdot}88 \times 10^6$
0 26	2·99	1 53	1·42	2 49	0·77
0 29	2·89	1 55	1·31	2 51	0·69
0 51	2·09	1 58	1·59	4 7	0·56
0 53	2·25	2 28	0·91	4 10	0·48
1 21	1·68	2 33	0·81	4 16	0·56
1 24	1·65	2 34	0·92		

TABLE IX. (*b*).

Zinc Oxide Cloud. Microbalance Curve.

Time.	Weight (mgrm. per litre).	Time.	Weight (mgrm. per litre).
h. m.		h. m.	
0 10	0·0172	2 46	0·0124
0 35	0·0187	4 23	0·0081
1 3	0·0171	4 36	0·0079
1 33	0·0141	4 50	0·0076
2 11	0·0147		

By dividing the smoothed values for the concentration, taken from the curve (Fig. 21), by the corresponding value for the numbers of particles (Fig. 7), a series of values is obtained of the average weight of a particle at different periods. These values are shown in Table IX. (*c*).

TABLE IX. (*c*).

Table showing the Average Weight of a Particle at Different Periods.

Time.	Average Weight per Particle, grm.	Time.	Average Weight per Particle, grm.
h. m.		h. m.	
0 4	$3{\cdot}62 \times 10^{-15}$	3 0	$15{\cdot}1 \times 10^{-15}$
0 30	6·60	3 30	16·4
1 0	8·37	4 0	16·9
1 30	9·82	4 30	16·9
2 0	11·7	5 0	16·8
2 30	13·6		

Fig. 22 (*a*) shows the change of concentration of such a cloud with time. Fig. 22 (*b*) shows the gradual growth of the particles in the same smoke during the same period. After four hours the weight of the particles became constant.

The degree of dispersion can also be deduced from the ob-

served optical behaviour of the aerosol. Rayleigh [21] (1871) has shown that the intensity (I) of the light scattered by very small particles of radius (r) is equal to $\frac{A.n.r^6}{\lambda^4}$, where λ is the wave-length of the incident light. If, therefore, a given aerosol is illuminated by light of various wave-lengths, the intensity of

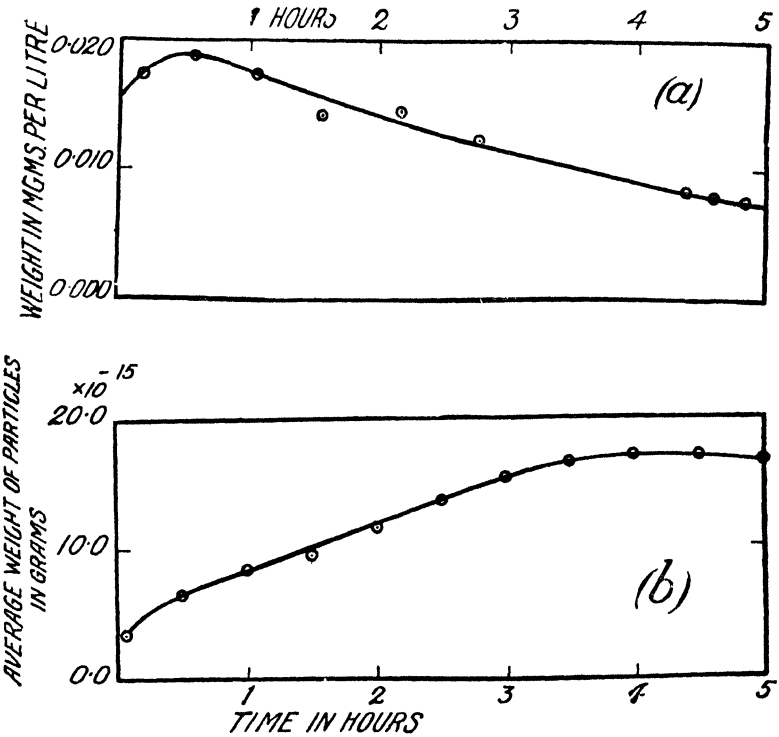


FIG. 22.—Concentration and size of particles of ZnO smoke.

the light that is scattered in a direction at right-angles to the incident beam will vary for the different wave-lengths according to the size of the scattering particles.

The spectrum of the light that is diffused by the aerosol in a direction at right-angles to the incident beam is photographed. The intensity of the light for each wave-length is measured photometrically from the spectrogram. From the distribution

of intensity, it is possible to calculate the size distribution of the particles of the aerosol.

When a small source of light is viewed through a cloud of fine particles, it is seen to be surrounded by a halo. The angular diameter of the halo is inversely proportional to the size of the particles.[22]

This fact has been utilised by a number of workers—notably Barus [23]—to determine the size of the particles forming an aerosol. Barus discharged low pressure steam into warm air contained in a suitable observation tube. As condensation takes place the light that is transmitted by the resulting cloud exhibits a magnificent display of colour change. A succession of diffraction colours can be obtained either by gradually diminishing the pressure of the steam—*e.g.*, from 156 cm. of mercury down to the atmospheric pressure—or by using a large amount of low pressure steam and introducing into it varying amounts of dusty air. The size of the particles is determined from the colour, and the order of the spectrum. Working with atmospheric air, Barus observed the presence of particles varying in diameter from 10^{-3} cm. to 2×10^{-5} cm.

McKeehan [24] measured the diameter of mercury droplets, when only equal to two or three wave-lengths of light, by illuminating the droplet from both sides. The reflected images of the sources of light appeared as point-source diffraction patterns. The diameter of the droplet was determined by measuring the distance between the centres of the centre discs of these patterns.

(C) The Stability of Aerosols

Aerosols are probably the least stable of all disperse systems. This is largely on account of the relatively great molecular activity of the dispersion medium, which, especially at high degrees of dispersion, imparts a correspondingly vigorous movement to the actual particles of the disperse phase. The frequency with which the particles of a smoky aerosol collide is, therefore, very high, and consequently the rate at which coalescence and flocculation occur is correspondingly great.

The particles of a cloudy aerosol, whether originally formed

as such or produced by the condensation or flocculation of a smoky aerosol, settle rapidly on account of the great difference of density between the disperse phase and the dispersion medium. They do not exhibit any Brownian motion, and, therefore, do not diffuse. They may be buoyed up for a time by a rising convection current, but in a comparatively still gas they steadily settle to the floor of the containing vessel. This can well be observed without a microscope in a tall, flat-sided rectangular glass cell, preferably painted dead black except for a narrow, vertical slit down the centre of two adjacent sides, If such a vessel be filled with a cloudy aerosol, and illuminated by a strong side-light, and observed through a hand lens or low power microscope, the particles of the disperse phase will be observed, settling gradually towards the bottom of the vessel, until the gas is quite clear. If the slit be ruled into millimetres, the rate of sedimentation of the surface of the cloud can conveniently be followed with the aid of a stop-watch. In such an aerosol, there is practically no tendency for the particles to coalesce, unless the aerosol is agitated or stirred.

The particles forming the disperse phase of a smoky aerosol are in active Brownian motion; consequently they do not settle, but tend to diffuse to the walls of the containing vessel, and also coalesce to form larger particles that, when they become large enough, behave like cloud particles and settle slowly to the floor of the vessel.

To observe the movement of such particles, it is necessary to place the aerosol in the cell of the ultramicroscope.

The amplitude and velocity of the Brownian movement of the particles is determined in the manner that has already been described (p. 118). The rate at which the particles diffuse through the aerosol can be measured in a precisely similar way.

The change in the degree of dispersion, assuming that the concentration remains constant, is accompanied by a reduction in the number of particles per cubic centimetre. It can best be followed by determining at regular intervals of time the number of particles of the disperse phase per cubic centimetre.

The concentration of the disperse phase should be determined

at intervals throughout the experiment to determine to what extent, if any, the change in the degree of dispersion is due to further condensation of disperse phase from the dispersion medium. This can conveniently be done with a large volume of the aerosol in a separate vessel, a measured volume of the aerosol being drawn off from time to time and passed through a suitable separator.

The movements of the particles can be recorded photographically, as shown by Wells and Gerke.

As the mass of the particles increases their motion becomes more sluggish. It is thus possible to follow the change in the degree of dispersion by recording this gradual change in the velocity.

Wells and Gerke [16] recorded the movements of the particles in an alternating electric field at intervals of fifteen minutes. They then plotted against different values of the diameter the number of particles of each diameter that were present in the aerosol at each interval. Using an oil smoke, obtained by detonating a medium mineral oil in air—1 gram oil per cubic metre—they obtained the curves shown in Fig. 20. It will be noticed that the proportion of larger particles, as well as the actual maximum diameter of the particles, steadily increases from curves 1 to 5.

The motion of the particles can also be modified by setting up a temperature gradient across the observation cell. This can easily be done by introducing two plates, one warmed, the other cooled by water. All the particles will be seen to travel towards the cold plate.

If two wires be inserted in the cell, and a potential gradient be maintained between them, the particles will be seen to travel some to one and some to the other. Even if a neutral wire only be introduced, some of the particles will be seen to travel towards it and become deposited upon it, probably because of an induced charge of opposite sign being formed on the wire by the charge on the particle.

Such an ultramicroscopic examination of the movements of the particles under different controlled conditions affords a very important method of determining the behaviour of aerosol

particles, whether moving freely in the dispersion medium or in a constrained manner—for example, at the surface of a filter.

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PART II.

CHAPTER VII

THE INDUSTRIAL TREATMENT OF FUMES AND DUSTY GASES

INDUSTRIAL smokes and fumes and dusty gases are aerosols in which the dispersed substance may be solid or liquid, and the dispersion medium a gas—either the atmosphere (*e.g.*, the dusty atmosphere of mines and mills), flue gases from furnaces (*e.g.*, metallurgical fume and sulphuric acid mist), or fuel gases (blast furnace gas and producer gas).

Any particle suspended in a gas is subject to two sets of forces. It is pulled downwards by gravity with a force (F), and the resulting movement downwards is resisted by the viscous friction of the gas (R). In general, for particles larger than 10^{-2} to 10^{-3} cm., according to the density of the particle, F is greater than R at all velocities, and the particle settles with increasing velocity. For smaller particles the resistance of the gas increases with the velocity of the particle until R becomes equal to F. The particle then continues to fall at a constant velocity (v).

Values of v for spherical particles of unit density, falling in still air, are given in Table X.

TABLE X.

Diameter of Particle.	Rate of Settling (v).	
cm.	cm./sec.	metres/hr.
10^{-2}	30	1080
10^{-3}	0·3	10·8
10^{-4}	0·003	10·8 cm.
10^{-5}	0·00003	1·08 mm.

From this it is clear that effective settling from air or gases in motion can only be obtained with particles of more than

10^{-3} cm. diameter. Smaller particles settle so slowly that they are carried up again by the least upward movement of the air. For particles of diameter smaller than 10^{-5} cm., the mean free path of the gas molecules, the impacts of the gas molecules drive the particles hither and thither about the gas in ceaseless Brownian motion. For such particles the force of gravity has but little effect compared with that of the individual molecular impacts.

It is convenient to distinguish between three kinds of industrial aerosols according to the size of particle (degree of dispersion) :—

(*a*) **Dusts,** in which the particles are larger than 10^{-3} cm. diameter. Such particles settle in still air with increasing velocity. They do not diffuse.

(*b*) **Clouds,** the particles of which range in diameter from 10^{-3} to 10^{-5} cm. Such particles settle in still air at a constant velocity, depending upon their size, according to Stokes' law. They, also, do not diffuse.

(*c*) **Smokes,** the particles of which range from 10^{-5} to 10^{-7} cm. diameter. Such particles are in active Brownian motion, and diffuse fairly rapidly. They do not settle at all in still air.

The degree of dispersion of a number of industrial dusts, clouds and smokes is shown in Table XI.

TABLE XI.

Substance.	Diameter of Particles. cm.
Milk powder (by evaporation of fine spray)	$1{\cdot}4 \times 10^{-2}$ to $0{\cdot}7 \times 10^{-2}$
Fine powder (300-mesh)—*e.g.*, cement	1×10^{-2} ,, $0{\cdot}7 \times 10^{-2}$
Smelter fume	1×10^{-2} ,, 1×10^{-5}
Atmospheric fog particles	$1{\cdot}4 \times 10^{-3}$,, $3{\cdot}5 \times 10^{-3}$
Cement kiln flue dust	6×10^{-3} ,, $0{\cdot}8 \times 10^{-3}$
H_2SO_4 mist from concentrators	$1{\cdot}1 \times 10^{-3}$,, $1{\cdot}6 \times 10^{-4}$
NH_4Cl fume	1×10^{-4} ,, 1×10^{-5}
Oil smoke	1×10^{-4} ,, 5×10^{-6}
Rosin smoke	1×10^{-4} ,, 1×10^{-6}
Tobacco smoke	$1{\cdot}5 \times 10^{-5}$,, 1×10^{-6}

These industrially important aerosols are formed either—

(1) By the condensation of vapours of metals (mercury, silver, copper, lead, zinc, arsenic, antimony) or of metallic compounds (oxides, sulphates, chlorides) that are formed in the hottest parts of the smelting furnace, and condense in the fume after it leaves the furnace, or by the condensation of non-metallic vapours—for example, of tar vapours in producer gas;

(2) By chemical action between metallic vapours and the furnace gases (oxygen, chlorine, sulphur trioxide) to form compounds that are not volatile at the temperature of the furnace—*e.g.*, SnO_2 from a tin-smelting furnace, or ZnO fume from a brass foundry—or that are volatile at the furnace temperature, but condense as the fume passes away and cools—*e.g.*, chloride vapours from a chloridising roast, and As_4O_6 from an oxidising roast;

(3) By mechanical disintegration and dispersion of solid or liquid substances—*e.g.*, ore dust carried over from a furnace; the dust in the air of grinding mills and mines.

In many cases, substances are manufactured in powder form by being dispersed in a gas and subsequently collected—for example, milk powder, carbon black, zinc dust.

Liquid or solid matter dispersed in a gas, whether in the form of dust, cloud or smoke, is generally separated from the gas industrially for one or more of the following reasons:—

(1) **It may be obnoxious.** (*a*) Smelter fumes contain, in addition to SO_2, considerable quantities of finely divided ore particles, and also smoke particles produced by the condensation of metal, or metal compounds volatilised in the furnace. The greater proportion of this dust consists of particles of diameter greater than 10^{-3} cm.

Most non-ferrous smelter fumes also contain considerable quantities of acid gases (SO_2, SO_3) which seriously damage vegetation over large areas surrounding the works. In such fumes, it is necessary to render the waste gases innocuous by neutralising or absorbing their acid constituents with lime dust.

In localities where smelting operations are carried out on a large scale—*e.g.*, in certain parts of the United States—fumes from these smelters constitute a serious public nuisance. In

one smelter, as much as four million cubic feet of fume are produced per minute. The fume has to be freed from its suspended matter before it is discharged into the open air. Generally speaking, if the amount of suspended matter in the fume is enough to be obnoxious, it will pay for recovery.

(*b*) Acid fumes. When weak sulphuric acid is concentrated by contact with hot gases in Gaillard towers or Kessler concentrators, the gases carry away a considerable quantity of H_2SO_4 in the form of fine mist, varying from 4 to 10 grams of real SO_3 per cubic metre. The particles vary in diameter from 0·8 to 5·5 μ.

A similar acid mist is formed when SO_3 smoke is bubbled through water, or when hot gases, containing steam and SO_3, are cooled.

(2) **It may be injurious to the workers.** (*a*) Some dusts—for example, the arsenical dust that is formed when certain kinds of insecticide are being packed, or the zinc oxide fume from a brass foundry—are directly poisonous when they are inhaled by the workers.

(*b*) In many grinding mills and packing rooms, the suspended dust, when inhaled by the workers, may be directly harmful to the lungs.

The dust that is produced when certain alkaloid-containing barks are disintegrated is extremely irritating to the eyes, nose and throat of the workers, and causes considerable distress.

The hard, insoluble dust from quartz and other rocks, that is formed in gold and other metal mines, may make it physically impossible for the workers to work at more than one-third of their normal capacity, and may in a very short period—frequently less than five years—completely incapacitate them for work by causing chronic bronchitis, miners' asthma or miners' phthisis.

In many industries—*e.g.*, cement, textiles, flint and steel grinding, asbestos, felt hat, pottery—injurious dust is produced, the particles ranging in diameter from 1 μ upwards.

A great deal has been done in this country by the Home Office and the Ministry of Health, and in other countries—notably in America by the Bureau of Mines and the Public

Health Service—to minimise this form of dust hazard, either by the removal of the dust at the point of formation or, where possible, by keeping the work damp, preventing the formation of dry dust, or, where these methods are impracticable, by introducing the use of gas masks by the workers.

(3) **It may be valuable.** (*a*) Smelter fumes, particularly those from copper, silver, tin, arsenic and mercury furnaces, contain suspended matter worth many times more than the cost of recovery.

(*b*) Blast furnace potash. Blast furnace gas contains from 5 to 6 grams per cubic metre of dust. This dust may contain from 2 to 30 per cent. K_2O, depending upon the composition of the charge. By suitable choice of charge materials as much as 50 lbs. of potash can be obtained from the gas per ton of iron produced.

(4) **It may be an undesirable impurity.** (*a*) Iron blast furnace gas leaves the furnace mouth at a temperature of from 200° to 300° C. It contains a considerable amount of dust from the charge, some of which is relatively coarse and settles readily. The remainder, however, is very fine, and passes on with the gas. This dust contains from 40 to 100 lbs. of potash per million cubic feet of gas, according to the composition of the furnace charge.

Unlike non-ferrous metallurgical smoke, iron blast furnace gas possesses, in addition to its sensible heat, considerable calorific value, on account of its content of CO (about 24 per cent.). It is passed through regenerators, generally constructed of firebrick chequerwork, and is burnt in stoves or under boilers ; some of it is also used in gas engines. As the gas leaves the downcomers of the blast furnace it may contain up to 7 grams of dust per cubic metre. This dust will soon accumulate in the flues, and choke the regenerators. Owing to its alkaline character, it corrodes the brick construction work. Dusty gas is useless for gas engines.

Blast furnace gas or producer gas, when used for internal combustion engines, should contain less than 0·01 gram per cubic metre of dust. If more dust be present, and, therefore, probably coarser dust, the gritty particles wear out the cylinders

of the engines. Blast furnace gas for stoves and boilers should not contain more than 1 gram per cubic metre of dust; otherwise the flues and chequerwork become choked and require frequent cleaning. Also the walls of the flues become corroded by the hot alkaline dust.

Since blast furnace gas is to be used as a fuel, it is necessary not only to recover the suspended impurities in it, but also to conserve, as far as possible, the sensible heat and the calorific power of the gas.

(*b*) Sulphur dioxide from pyrites burners commonly contains up to 5 grams of dust per cubic metre. This dust, unless removed, will choke the Glover towers and scrubbers in the chamber process, or, in the contact process, will speedily choke the catalyst and render it useless.

(*c*) The gases obtained by the distillation or partial combustion of bituminous coal contain vapours of tar oil and CS_2, which, although volatile at the temperature of formation, condense as the gas cools, and form a very stable mist. It is difficult to remove this tar completely, and it accumulates in pipes and valves, and, becoming carbonised, fouls the ports and cylinders of gas engines.

(*d*) When soft wood—*e.g.*, pine—undergoes destructive distillation, a considerable quantity of tar is driven off with the vapours of water and pyroligneous acid. This tar condenses as the vapour cools, and forms an emulsion in the pyroligneous acid. Unless it is separated from the acid, the liquid froths badly during the subsequent distillation process.

(*e*) Air conditioning. In the mechanical ventilation of public or private buildings, mills, factories, hospitals, etc., it is often necessary to free the ventilating air as completely as possible from dust, bacteria, and mould spores. In many industries, fine dust is produced, which, floating in the air, may be explosive or injurious to health. This dust must be removed as quickly as it is formed. Many manufacturing processes—*e.g.*, textiles, photographic films, gas mantles—must be carried out in dust-free air.

Air compressors and air-cooled turbo-generators must be supplied with cool, dust-free air; otherwise dust collects in the

air passages or on the windings, impairing the cooling efficiency, and causing a risk of breakdown due to possible short-circuiting.

In many ventilating systems, the outgoing warm air is returned to the building continuously, in order to avoid an undue loss of sensible heat. Such conditions favour the growth of mould spores and pathogenic bacteria. Mould spores are a continual source of trouble in margarine and other foodstuff factories and stores and in breweries. In some industries, it is necessary to maintain the air at a particular degree of humidity.

(5) **It may be explosive.** (*a*) Mills. In many mills, in which combustible substances such as flour, starch, sugar, coal, are ground, the fine particles are caught up into the air and retained in suspension. Unless the air is circulated and filtered continually, the concentration of this suspended dust may reach the explosive limit. Thirty-five grams of flour dust per cubic metre of air are explosive.

(*b*) Mines. In coal mines, fine coal dust is formed by the firing of the shots, and by the traffic along the workings. Thirty grams of coal dust per cubic metre of air are explosive.

Dust explosions are never spontaneous, but always the result of ignition. They can be inhibited (*a*) by diluting the explosive dust with an inert dust—*e.g.*, fine shale or stone dust in coal mines; (*b*) by diluting with an inert gas the air in which the dust is suspended—*e.g.*, flue gas; or (*c*) by humidifying the air and, therefore, the dust suspended in it.

(6) **The manufacture of substances in powder form.** (*a*) When liquids, such as milk, egg yolk, fruit juices, are sprayed into hot gases, the particles evaporate, thus producing a fine dust of the evaporated product. In this way evaporation is carried out rapidly, and at a temperature that will not damage the material.

(*b*) Carbon black is manufactured by the combustion of oil vapour, or naturally occurring hydrocarbon gases such as methane, in a limited supply of air. The finely divided carbon particles so produced are allowed to settle, or are filtered or precipitated from the gaseous products of combustion.

(*c*) High grade zinc dust is manufactured by projecting a finely divided spray of molten zinc into an inert gas, in which it cools and is condensed in the form of powder.

Methods of Treatment

The method to be adopted for the purification of a particular metallurgical smoke will depend very much upon the character of the gases, their temperature, volume and composition, the nature of the suspended matter, its physical and chemical composition and economic value, and the immediate destination of the purified gases, whether to be used for power purposes or to be discharged into the air.

All smoke-treating or dust-recovery processes should be continuous in action, and should offer as little resistance as possible to the passage of the smoke. One of the inherent difficulties associated with the filtration of smelter smoke is the enormous volume of smoke that has to be treated ; frequently as much as a million cubic feet of smoke has to be treated per minute, from 20 to 30 tons of material being recovered per day. It is a matter of first importance, therefore, that any process of filtration or condensation be rapid ; otherwise the dimensions of the plant will be prohibitively large.

(1) **Settling : Gravity.**—In many metallurgical furnaces, the flame comes into direct contact with the charge, so that a considerable amount of finely divided material is caught up by the gases and carried away mechanically. The amount of this dusty matter present in the smoke will depend upon the density and fineness of the charged materials, and the velocity of the gases. These dust particles, ranging in diameter from 1 mm. to 0·01 mm., are not to be regarded as true constituents of the smoke. The true smoke particles are much smaller, and are often electrically charged.

The density of fume particles (varying, say, from 1 to 10) is much higher than that of the gas (·001 to ·003) in which they are suspended. Given the opportunity, therefore, such particles should settle from the gas under the action of gravity. Even in still air, however, only particles greater than 10^{-5} cm. can settle at all, and of these only those that are coarser than 10^{-3} cm. can settle at all rapidly.

The separation of dust particles by settling is facilitated by the following methods :—

(*a*) **By retarding the rate at which the gas is travelling**—for example, by passing it through settling chambers of which the cross-sectional area is many times that of the fume. Such settling chambers are used for smelter fume, and it is found that the maximum speed at which the fume can travel, and at the same time permit settling of the suspended dust particles, is about 6 feet per second. To deal with a million cubic feet of gas per minute, therefore, will involve a settling chamber of about 3,000 square feet cross-sectional area. For copper blast furnace fume satisfactory settling at 300° C. is only obtained at a velocity of $3\frac{1}{2}$ feet per second.[1] It is found that 200-mesh dust—*i.e.*, ·009 cm. diameter—settles at 125 feet, if the velocity is not greater than $2\frac{1}{2}$ feet per second. These settling chambers require to be designed and constructed with special baffles across the floor and sides, to distribute the flow of the fume through them ; otherwise the fume flows straight through the centre of the chamber with practically undiminished velocity.

Where the gases are very hot as they leave the furnace, the velocity can be greatly diminished by cooling them. The volume, and hence the velocity, of a fume can be reduced to about one-fourth of its original value by cooling it from 1,000° C. to 100° C. This cooling can be brought about either by passing the gas through air-cooled sheet-iron flues, designed to produce the maximum amount of cooling by radiation and convection, or by spraying water into the fume.

(*b*) **By shortening the vertical path that has to be traversed by the particles.** In the Howard dust chamber,[2] this is done by inserting in the settling space a large number of horizontal shelves, spaced a few inches apart, one below the other, so that the gas passes between them in parallel, the dust being deposited upon the upper surfaces of all the shelves simultaneously. In this way the actual distance through which the dust particle has to settle is reduced from many feet to a few inches.

(*c*) **By centrifugal action.** A fume can be submitted to centrifugal force either by causing it to enter tangentially a fixed cylindrical vessel[3] (Fig. 23) or by introducing it axially into a rapidly rotating cylindrical vessel.[4] Assuming that the density of the suspended solid or liquid particles is of the order of one

hundred times the density of the gas molecules, it would seem that the centrifugal force method should offer considerable scope. It is found, however, that such methods, although useful for coarse dust particles, are of little use for clouds or smokes, owing to the frictional resistance of the gas against the particles. The rotating cylinder is more efficient than the stationary vessel, but is much too expensive for dealing with large volumes of gas.

Another method in which centrifugal force is utilised consists in submitting the gas to a sudden change of direction when travelling at a considerable velocity.[5] This method is in use in the form of zigzag flues, and in many types of separator, in which a change of direction is imparted to the gas current by means of baffles. In some cases, the gas approaches the baffle at a high velocity, so that, as it changes its direction at the surface of the baffle, the suspended particles are thrown against the baffle by centrifugal force and caused to impinge upon it.

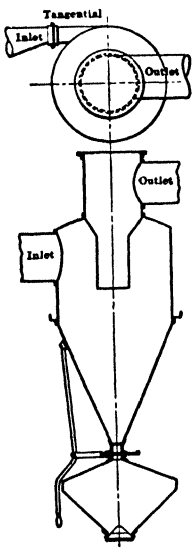


FIG. 23.—Centrifugal dust catcher.

In the Calder-Fox scrubber,[6] which is largely used for the elimination of sulphuric acid mist from concentrator gases, the acid-laden gas passes successively through three uniformly perforated plates, placed one behind the other. The diameters of the perforations in the three plates are respectively $\frac{1}{4}$, $\frac{1}{8}$, and $\frac{1}{16}$ inch. The plates are from 2 inches to 3 inches apart. The number of perforations in each plate is so arranged that the gas passes through them with a velocity of from 40 to 80 feet per second, according to the concentration and the degree of dispersion of the mist.

While actually passing through the perforations, the gas is momentarily compressed, so that many of the mist particles are forced into contact and may coalesce. To some extent, the coalescence is inhibited by the presence of absorbed gas upon the particles.

As the gas approaches the perforations in the first plate, it

necessarily undergoes a sudden change of direction as it separates into a number of small streams. The centrifugal force that is set up near each perforation flings the acid particles against the surface of the plate with sufficient force to make them coalesce. The perforations in the second plate are in staggered relation to those in the first and third, so that the process is repeated as the gas approaches each plate in turn.

The principle upon which this and other similar scrubbers—*e.g.*, Pelouze's tar eliminator [6]—operate is closely akin to that of the Owens jet. Their efficiency depends upon the velocity with which the gas passes through the perforations.

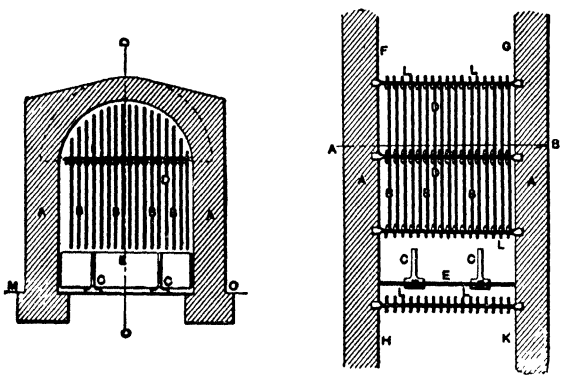
The Calder-Fox scrubber reduces an acid content of 20 grams of real SO_3 per cubic metre to 2 grams per cubic metre, with an efficiency of from 90 to 97 per cent.

An interesting case of deposition by impact is afforded by the Schoop metal spray, in which finely atomised molten metal is caused to impinge upon the surface to be coated. It is found that lead coatings formed in this way become, when treated with cold distilled water, disintegrated to form a fine suspension of metallic lead in the water. Microscopical examination shows that these minute lead particles are, in nearly every case, round discs. It would appear that the particles of the lead spray were surrounded by a film of adsorbed gas, so that the coating formed in this way is not continuous, but consists of an accumulation of minute, flat plates of lead, separated from one another by films of adsorbed gas.

(*d*) **By loading the particles with water.** This is done by cooling the gas below the dew-point, so that the water vapour present in the gas condenses upon the particles. Cooling can be obtained by passing the hot gases through a sheet-iron flue suspended above the ground, so that a maximum surface is exposed to the cooling effect of the air. The gas also may be cooled by causing it to expand adiabatically into a large settling chamber, where the deposition of moisture on the suspended particles reinforces the increased settling efficiency that results from the diminished velocity. In some cases, water is introduced into the fume in a finely atomised con-

dition, in quantities sufficient to cool the gas and also to moisten the particles.

(*e*) **By contact with solid surfaces.** When smokes or dusty gases are driven against or along solid or liquid surfaces, the particles tend to adhere to the surface, and to unite with one another to form coarser aggregates. Freudenberg [7] found that by suspending in the gas a large number of sheet-iron plates ($\frac{1}{32}$ inch thick and 4 to 5 inches apart) (Fig. 24) parallel to the gas current the suspended matter was deposited upon them up to a thickness of about $1\frac{1}{4}$ inches, and then fell away. He found that the amount of dust deposited was proportional to the surface area of the plates. Roesing [8] obtained similar results, using No. 10 gauge iron wires 1 inch apart.



Elevation. Plan.

FIG. 24.—Freudenberg plates in flue.

(*f*) **By thermal precipitation.**[7a] An interesting form of precipitation is obtained when a warm, dusty gas or smoke comes into contact with a relatively cold surface. If tobacco smoke be passed through the annular space between two concentric tubes, of which the inner one is steam-heated and the outer one air-cooled, it is found that very quickly the whole of the suspended matter is deposited upon the surface of the cold tube.[9]

This principle has been made use of to some extent in removing dust from smelter fume.[10] In this case, the fume is passed over a number of water-cooled tubes, the dust being deposited upon the outside of them and scraped off from time to time. A similar action is obtained upon the outside surfaces of the economiser tubes in boiler plants, in which the feed-water, on its way to the boiler, passes through the inside of the tubes, the hot

waste gases from the furnace, on their way to the stack, passing over the outside of the tubes. The whole question of deposition upon surfaces, as the result of impact between the dusty gas and the surface, necessarily depends very much upon the velocity and direction of the gas current, and the form of the surface.

(*g*) **By flocculation.** Spontaneous flocculation, producing coarser fume, only occurs to any marked extent in the case of smokes, and is due to the contact of the particles with one another, brought about by diffusion, or by the action of electrical charges of opposite sign on different particles.

Flocculation of smokes is greatly facilitated by agitation.[11] With coarser suspensions frequent contact between the particles can only be obtained by agitation, by compression, or by contact with solid surfaces. A fog is stable in still air, but is soon flocculated and deposited by wind. The flocculation of many smokes is inhibited by the protective action of films of adsorbed gas surrounding the smoke particles. This is particularly marked in such smokes as the blue zinc oxide smoke from a brass foundry, the $SnCl_2$ smoke from the chlorination of tin ores, and the SO_3 smoke or mist from catalyst chambers.[12] In some cases, this adsorbed gas film can be displaced by altering the composition of the dispersion medium—for example, by introducing steam.

Why does a suspended particle tend to adhere to a solid surface with which it is brought into contact? In many cases, it is probably due to the fact that the layer of dusty gas in close contact with the surface is travelling very slowly, and the particles are arrested and held by the roughness of the surface. To some extent, also, possibly, gravitational forces, acting under these conditions, draw the particles to the surface. Where the local irregularities of the surface are such as to maintain local eddy currents at the surface, these eddy currents will tend to deposit dust by centrifugal action. In some cases, electrically charged smoke particles are attracted to the surface by reason of the electric charge induced at the surface. When a smoke is viewed through an ultramicroscope, particles in the neighbourhood of a wire are seen to change their direction as they come

near the wire, and fly to it.[13] With certain surfaces an electrostatic charge can be produced at the surface by the friction of the gas passing over it. The nature and intensity of this charge will depend upon the nature of the surface and the gas.

(2) **Filtration.**—Considerable attention has been directed, particularly in Germany and the United States of America, to the dry filtration of metallurgical smoke. Owing to the enormous volume of smoke to be handled and the low permeability of an effective filtering medium, the filtering area has to be very great. Large fans are necessary to draw or drive the gases through the filters. In most cases, also, the filtering material is an animal or vegetable fibre, and will char or catch fire unless the gases are cooled.

Some of the earliest filters were simply towers filled with dry coke. They soon became choked and were troublesome to clean. They have been superseded by bag filters.[14] The bags are made of wool or cotton, and sometimes asbestos. The smoke is drawn through the walls of the bag, the dust being collected on the surface of the fabric. To remove the dust, the bags are shaken or beaten periodically, or treated with compressed air. The gases must be cooled below 90° C. for cotton, and below 120° C. for wool; otherwise the bags are charred. On the other hand, the temperature of the gases must not fall below the dew-point of the smoke (50° C.), or the acid will condense on the fabric and rot it.

Bag filtering is really a special form of separation by surface contact. The filter does not behave altogether as a fine sieve, for the interstices of the fabric are much larger than the smoke particles. The particles are first deposited on the fibres, and gradually built up until the bags become choked. Wool is found to be about 50 per cent. more efficient than cotton, possibly on account of the scaly surface of its fibres. Also it is much more durable, although initially it is considerably more expensive. Camel's hair has been used of recent years, and is said to be even better than wool. From 3 to 4 square feet of filtering area are necessary per cubic foot of gas per minute, 0·5 square foot if the bags are cleaned mechanically.[15]

Fig. 25 illustrates a bag filter fitted with a mechanical

cleaning device. When the filter is in operation, (A), the gases are drawn through the bags in the direction shown by the arrows, so that the pressure in the bags is below that of the atmosphere. When the dust has accumulated to a sufficient extent, the damper (*g*) is thrown over to the position indicated in Fig. 25 (B), so that the filter is cut off from the fan suction. At the same time, on account of the reduced pressure in the bags and

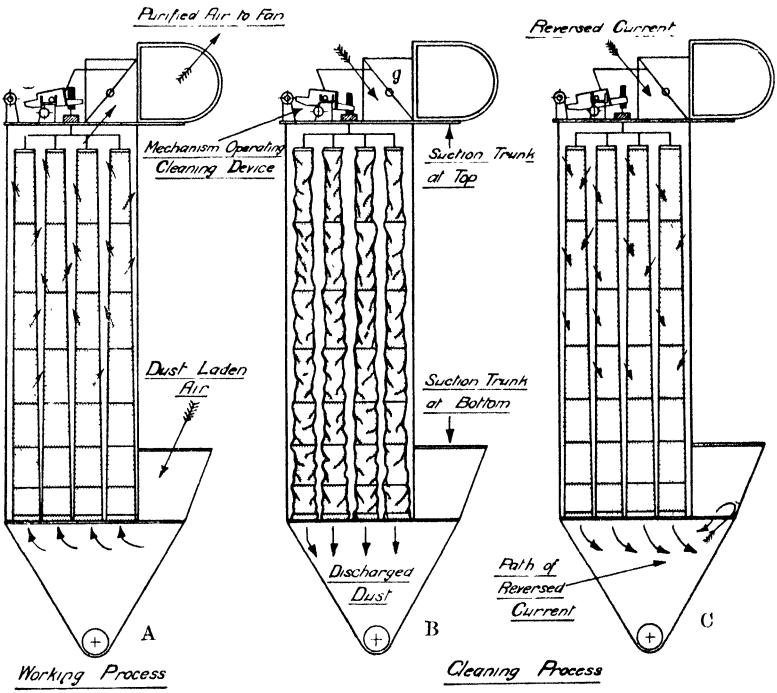


FIG. 25.—Mechanically cleaned bag filter.

container, air is drawn into the container and through the walls of the bags (C). In this way the bags become partially collapsed, and the dust is dislodged and falls into the hopper. The whole operation takes but a few seconds.

The danger of rotting the fabric with acid gases is sometimes avoided by neutralising the gases with lime or zinc oxide dust before being filtered.[16] The life of a bag will depend very much upon the kind of dust for which it is used; the sharp dust

particles from grinding and buffing shops, for instance, cut the bag and quickly wear it out.

Bag filters are generally less expensive than a washing plant to construct and maintain. They have the additional advantage that they collect the material in a dry state. Their application is limited, however, by the difficulty of obtaining a sufficiently resisting fabric. Also the power required to draw such large volumes of gases through the bags is very large, particularly when the bags become choked with dust. Asbestos bags and screens are expensive, and become brittle when exposed to hot acid gases. By means of a bag filtering plant the dust content of blast furnace gas at 50° C. can be reduced to from 0·01 to 0·001 gram per cubic metre.[17] Bags last from six to twelve months, and the power expended amounts to 1 h.p. per 10,000 cubic feet. For ordinary bag filters, without mechanical cleaning, 1 h.p. is consumed per 3,000 cubic feet of fume.

In some blast furnaces, the gases are filtered by passing them through filter mattresses, consisting of metal framework packed with metallic wool.[18] The gas passes in succession through a number of such filters, the texture of the filters becoming progressively finer the more remote they are from the gas inlet. By this means the dust content of blast furnace gas can be reduced to 0·5 gram per cubic metre. In some cases dusty gases or smokes are filtered through loose granular materials, such as sand.[19] It has also been proposed to use froths and foams in a similar way.

(3) **Washing.**—Many methods have been devised for removing the particles from metallurgical smoke by bringing them into contact with water. The smoke is either driven against a water surface, bubbled through water with violent agitation, drawn or driven through a scrubbing tower against a stream of water, or treated with fine water sprays. It is difficult to clean a gas efficiently with water. This difficulty is reflected in the enormous number of processes that have been devised for improving gas washing.

In the first place, it is difficult to make certain that every particle of the smoke will come into contact with the water. Townsend [20] has shown that when an ionised gas is bubbled

through water, and then through a drying agent, 20 to 25 per cent. of its charge is lost, representing the fraction of the gas that actually comes into contact with the water.

The efficiency of a washer is improved by increasing the intimacy of contact between the smoke and the water. This can be done—

(*a*) **By bubbling the smoke through the water.** Originally the gas was forced through the water by means of pump or Archimedean screw. This proved to be inadequate, and the gas was finely subdivided by forcing it through superimposed fine wire gauze. This was still inefficient, and very soon became choked. Also it involved a disproportionately high power consumption.

(*b*) **By spraying the water into the smoke.** This either cools the gas to the dew-point, causing condensation of water upon the particles, or wets the particles by contact. The spray particles and dust are finally removed by eliminator plates. It is difficult in the time and space available to obtain complete contact between the water and all the particles of the smoke.

(*c*) **By passing the smoke upwards through an absorption tower through coke, gravel, slag wool, coarse sand, asbestos, etc., against a descending stream of water.** Both smoke and water are broken up. In this arrangement, there is a contest between wetting efficiency and power consumption.

If the filter is coarse enough to allow the gas to pass freely, the dust or smoke is not effectively wetted. If the filter is fine enough to bring about intimate contact between the suspended particles and the water, the openings soon become clogged and require frequent cleaning. Even when complete contact is possible, it does not necessarily follow that the smoke particles will be wetted by the water. Generally speaking, wetting is easier the lower the interfacial tension between the particles and the water. Possibly, in some cases, soap solutions would be more effective than water.

Some smoke particles are extremely difficult to wet.[21] The blue zinc oxide smoke from a brass foundry, which is generally diluted with a considerable quantity of air, will pass right through an absorption tower packed with wet coke practically

unaffected. This is conceivably due to the presence round each particle of an adsorbed film of gas (air).

The difficulty of wetting smoke particles can be overcome by humidifying the hot gases with water sprays or waste steam to such an extent that when they are subsequently cooled (for example, by expanding into a large settling chamber, or by passing through a surface condenser) the excess water vapour will condense upon the particles and carry them down with it. In many cases, the amount of water vapour originally present in the gas will be sufficient to supersaturate it when it is cooled below 50° C.

Sulphur trioxide mist is difficult to catch with water or weak acid, but can be caught readily with sulphuric acid. The mist is more stable and difficult to catch the more quickly the SO_3 gas has been cooled. It is probable that each SO_3 particle is protected by an adsorbed gas film. In a mist formed by quick cooling, the particles will be smaller, and therefore the gas film will be relatively thicker. Apparently this gas film is readily displaced by H_2SO_4, although not by water.

In addition to the relatively high power consumption required for thorough gas washing, the process is often costly and troublesome in practice, owing to the acid gases in the fume. This necessitates the use of expensive acid-resisting plant.

For certain processes in which the volume of gas is relatively small, washing processes are economically practicable and are well established. They are used successfully with coal gas, producer gas, and for the small proportion of iron blast furnace gas which is used for gas engines.

Such gas washers are of three types: stationary washers, consisting essentially of absorption towers, up which the gas passes against a descending stream of water, and slow-moving and high speed rotary washers.

Fig. 26 illustrates the construction and action of a slow-moving rotary washer, the Bian gas washer.[22] It consists essentially of a stationary cylinder (B), 10 feet in diameter, and from 10 to 16 feet long, with closed ends and open bottom, standing in a trough of water. A horizontal shaft (D) carries a number of parallel discs of $\frac{3}{8}$-inch mesh wire gauze. These

are rotated at from 10 to 12 revolutions per minute, and carry a film of water in their meshes. The gas—for instance, blast furnace gas—enters at A at about 200° C., and as it passes through the first screens it becomes cooled and saturated with water vapour. Cold water is admitted near the gas outlet (C), so that the last screens of the washer are the coldest. These cool the humid gas still further, and the water vapour condenses upon the dust particles and precipitates them. The washer absorbs about 1 h.p. per 10,000 cubic feet of gas per hour, and reduces the dust content of blast furnace gas from 10 grams per cubic metre to 0·5 gram per cubic metre.

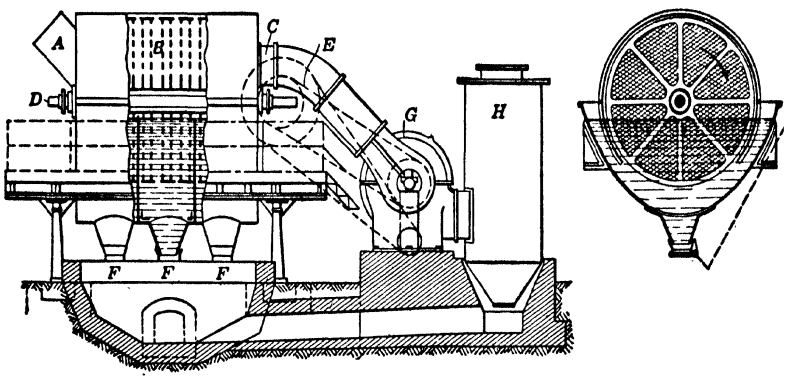


Fig. 26.—Bian gas washer.

Fig. 27 illustrates a high speed rotary gas washer, the Theisen washer.[23] It consists of a horizontal drum (D), revolving at from 300 to 450 revolutions per minute, inside a fixed conical casing (A). Spiral vanes are attached to the surface of the drum, so that the gas follows a spiral path in passing through the washer. The inner surface of the casing (A) is lined with fine gauze, through which water, admitted by the ports (F), bubbles continually. The gas travelling from right to left is thus brought into intimate contact with a film of water travelling in the opposite direction. A Theisen washer absorbs 1·5 h.p. per 10,000 cubic feet of gas per hour, and reduces the dust content to 0·4 gram per cubic metre.

After passing through Bian or Theisen washers, the dust con-

tent of the gas can be further reduced to 0·02 gram per cubic metre by passing it through a dry filter or scrubber.

Suspended particles are removed from air either by filtration through bag filters, or filter chests stuffed with fibres or shavings, or by washing with fine water sprays, the fine water droplets being removed subsequently by eliminator plates or baffles. Dry filtration does not remove the finer particles efficiently; it offers high resistance to the passage of large volumes of air, and it requires attention and cleaning.

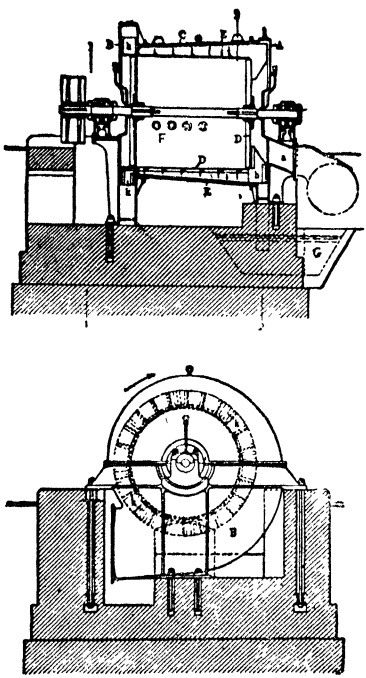


Fig. 27.—Theisen gas washer.

In washing processes the air becomes saturated with water vapour at the temperature of the washer, and although the washer offers less resistance to the passage of the air, and is self-cleaning, yet its efficiency is impaired by the difficulty of obtaining complete contact between the suspended particles and the water droplets. In many cases, washing devices are unsuccessful because the dust is difficult to wet—*e.g.*, coal dust, graphite dust and soapstone dust.

(4) **Electrostatic Precipitation.**—As early as 1824 Hohlfeld [24] suggested that electricity might be used for precipitating smoke.

In 1850 Guitard [25] observed that if a wire connected with an electrifying machine were introduced into the neck of a cylinder filled with smoke, "the air would immediately become charged with electricity, which would cause each portion of the smoke to fly to the sides of the cylinder. The effect produced was perfectly magical. It was astounding to see how small a quantity of electricity produced a most powerful effect."

In 1883 the matter was investigated more fully by Lodge.[26] He observed that at charges of up to 200 volts the electrification of a rod suspended in a box full of smoke exerted practically no effect. When, however, the voltage was increased to some thousands, and a brush discharge became possible, the " dark coat of dust-free air surrounding the rod widened enormously and tumultuously, and the box was rapidly cleared of smoke."

The following smokes were examined : tobacco, camphor, turpentine, MgO and NH_4Cl, $(NH_4)_2SO_3$, P_2O_5, steam, burning brown paper, lead fume, zinc fume.

It was found—

(*a*) That the smoke particles formed into masses or flakes along the lines of force, and then precipitated on the floor of the vessel ;

(*b*) That positive and negative electricity act similarly ;

(*c*) That point electrodes are more effective than knobs ;

(*d*) That a brush discharge is the most effective.

In all these experiments, Lodge had to rely for high voltage currents upon electrostatic machines.

In 1886, Lodge, in conjunction with Mr. Walker, of Messrs. Walker, Park and Company, lead smelters, applied the process to the lead smoke discharged from their works in Bagillt, North Wales. Electrodes were arranged in the flue along which the lead smoke travelled, and were charged from two Wimshurst machines, constructed with glass plates 5 feet in diameter and driven by an engine of 1 h.p. The experiment was unsuccessful, owing, no doubt, to the available current being much too small. It was not until the technical development of high voltage generators made larger currents possible that the problem was successfully solved.

In the meantime, however, the problem was attacked independently by various workers in Germany and America.

In 1903, Lodge patented the use of the mercury arc for rectifying high voltage alternating currents. Apparently this device was not actually employed successfully.

In 1905, F. G. Cottrell[27] in America, whilst studying the removal of the H_2SO_4 mist which is formed in the contact

process, began the experiments which led to the development of the Cottrell process of electrostatic precipitation.

The electrostatic precipitation of smoke is possible with either alternating or direct current. When a smoke is subjected to a high voltage alternating current discharge, the gas is ionised, and the smoke particles become electrically charged by the adsorption of ions from the gas. Owing to the rapidly alternating polarity of the particles, they agglomerate to form large flakes. If the gas is still, or moving very slowly, these flakes will settle. To obtain effective precipitation with an alternating current, it is necessary to have the electrodes very close, and the gas path long, and the gas velocity low.

In practically all industrial problems, however, we have to deal with very large volumes of gas, necessarily travelling at a considerable velocity along flues. In these circumstances, it is found that direct current is vastly more effective, since it drives the suspended particles to the surface of the depositing electrode.

When a highly charged wire is fixed opposite to a flat plate at some distance from it the intervening air space becomes highly charged with electricity of the same sign as the wire, whether it be positive or negative. The intensity of the field between the wire and the plate varies inversely as the distance from the wire. Of the gas ions or charged particles originally present in the air space some will be attracted by the wire. As they approach the wire their velocity will increase rapidly, owing to the increasing strength of the field, and if the voltage be high enough, their velocity will be so great that they will ionise the intervening gas and the wire itself by the force of their collision with the molecules of the gas and the wire.

In general, the wire is negatively charged, so that it is the positively charged ions originally present in the gas that produce this ionisation by collision. The negative ions so formed are repelled from the wire, and travel rapidly towards the plate. Any gas molecules or smoke particles present in this intervening space become charged by these ions, and are, therefore, driven by electric force towards the plate. The suspended particles are also driven mechanically by the rush of ions from wire to plate.

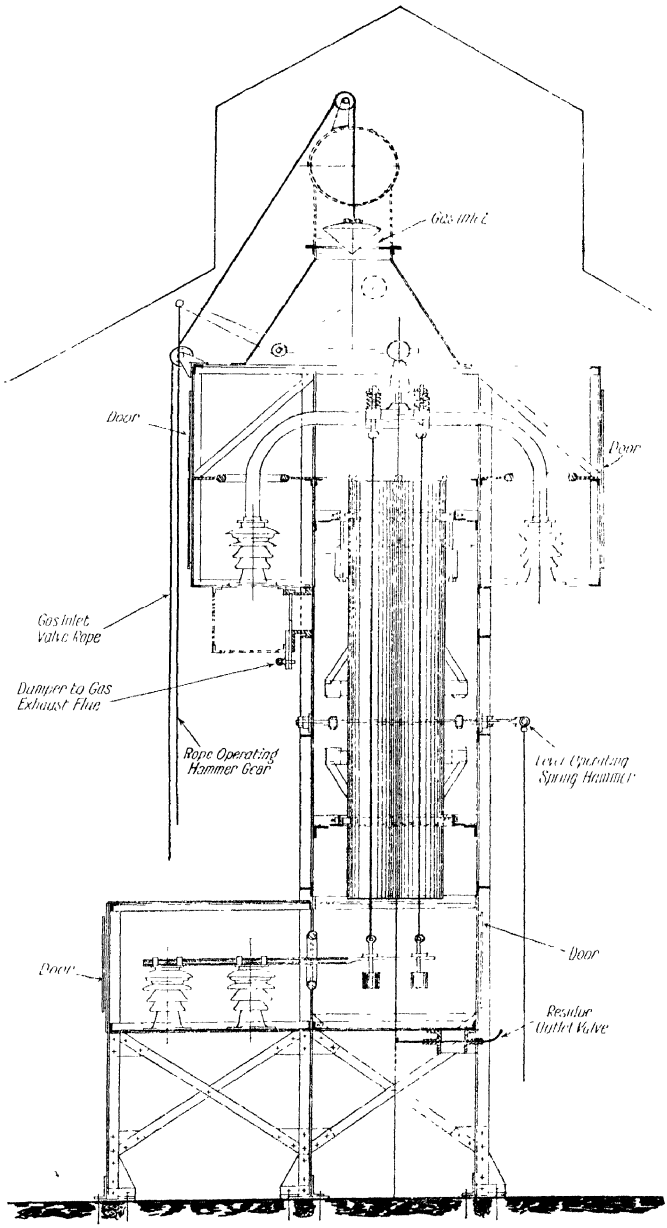


FIG. 28.—Sectional elevation of pipe type electrostatic precipitator.

The essential unit of the Lodge-Cottrell precipitator consists of a wire passing down the centre of a long metal pipe (Fig. 28). The wire is charged negatively, the pipe is earthed, and the gas to be treated passes through the pipe. It is found that when the wire is charged negatively the treater can sustain a higher potential gradient without spark discharges and arcing occurring, so that the capacity of the treater is proportionately greater. In practice, pipes up to 36 inches in diameter and 20 feet long are in use, although, in general, 6 or 9-inch diameter pipes are used. A number of parallel pipes are arranged vertically, and connected by headers, the lower header opening into a hopper in which the dust is collected. The voltage employed varies from 20,000 to 100,000 according to the nature and velocity of the fume. The potential gradient across the treater pipe varies from 4,000 to 5,000 volts per centimetre. The velocity of the gas varies from 3 to 10 feet per second, and averages from 5 to 6 feet per second.

To obtain efficient precipitation, it is necessary to maintain unimpaired the conductivity of the collecting electrode and the deposit that forms upon it. If the collecting electrode becomes coated with a deposit of non-conducting dust, then, instead of a point to plate discharge, a series of discharges are obtained simultaneously from the central wire and from points upon the collecting electrode at which the dust layer is perforated, or is sufficiently thin to permit the passage of the current. Thus the gas adjacent to *both* electrodes is ionised by the high velocity ions associated with these point discharges, and the fume particles, instead of being driven steadily from wire to plate, are buffeted about by the two streams of ions without being precipitated on either electrode.

This is prevented by treating the fume with water vapour, or with sulphuric acid mist, before it enters the precipitator, so that the deposit is damp and therefore electrically conducting.

To obtain efficient precipitation and at the same time a deposit that is damp enough to conduct well, but dry enough to be easily dislodged, the relative humidity of the fume should be between 40 and 70 per cent. This is generally attained by cooling the gases on their way to the precipitator. When

H_2SO_4 mist is used, the temperature of the gases, and therefore the draught, can be much higher, nearly as high as 300° C., the boiling point of H_2SO_4. Efficient precipitation and a dry deposit are obtained with an addition of up to 5 per cent. H_2SO_4. Larger amounts of H_2SO_4 give a sticky deposit, which is troublesome to remove.

Some fumes—for example, certain metallurgical fumes—have too high a conductivity, owing to their high degree of ionisation, so that it is practically impossible to maintain a high potential gradient across the treater. Such fumes have to be partially neutralised before they can be treated.

It is difficult to construct direct current generators to give such high voltage current, chiefly owing to the difficulty of securing satisfactory insulation. On the other hand, ordinary low voltage alternating current (200 to 500 volts) can be satisfactorily transformed up to 100,000 volts. This high tension alternating current can be rectified to give an intermittent direct current.

In practice it is found that when the wire—the discharge electrode—is charged negatively the whole arrangement is more stable, and can be run at higher voltage without the danger of destructive discharge occurring, than if the wire is charged positively.

Where a fume contains more than one dispersed constituent, differing appreciably from one another in volatility, it is possible to precipitate these constituents separately by taking advantage of this difference. Thus, when burner gases are treated while hot, the more refractory dust particles are precipitated. If the gases are then cooled, the arsenious oxide, which up to then has been present as vapour, condenses to a white cloud, which can then be precipitated separately. Some smoke particles—for instance, ZnO and $SnCl_2$—appear to reflect the gas ions, and are little affected by the electric field through which they pass. Such fumes have to be humidified before they can be successfully treated.

The behaviour of the deposited dust differs considerably for different substances. The deposit from blast furnace gas, for instance, clings to the electrodes, and is discharged only by

vigorous tapping, whereas the dust collected from burner gases drops freely from the electrodes of its own accord. Liquids dispersed in a gas are successfully treated by this process just as much as solids, the process being used extensively for the precipitation of sulphuric acid mist from concentrator gases, and also for the removal of tar fog and oils from the vapours from wood distillation and from producer, coke oven and illuminating gas. The process is also in active operation for the cleaning of air drawn from buildings and rooms in which grinding, buffing and similar operations are carried on.

Three types of installation are in general use : the pipe type, in which an axial wire forms a discharge electrode in an earthed pipe which forms the collecting electrode ; the plate type (Fig. 29), in which a star section rod forms the discharge electrode, and parallel earthed plates constitute the collecting electrode (this type, constructed of iron and heavily coated with lead, is used for the precipitation of sulphuric acid mist) ; the grid type, in which a metal grid, set transversely to the fume, forms the discharge electrode, the dust being deposited upon baffles placed parallel to the discharge electrodes and alternately with them along the flue.

During the last twenty years the Lodge-Cottrell process has been applied to a variety of industrial smokes and fumes. The earliest experiments were carried out with contact gases from a Mannheim sulphuric acid plant. It was found that with a voltage of 6,600, and a power consumption of 1/6 kw., it was possible to obtain 100 per cent. efficiency (*i.e.*, precipitation of all the suspended sulphuric acid mist) if the gases were passing at the rate of 100 to 200 cubic feet per minute.

At the Balaklala Smelter in America from quarter to half a million cubic feet of fume containing copper and zinc travels per minute through a flue 18 feet by 20 feet, with a linear velocity of from 10 feet to 20 feet per second. This fume is treated with a battery of nine precipitators. The voltage varies from 25,000 to 30,000. The discharge electrodes are made by inserting asbestos or mica strips between two iron wires and then twisting them all together. In this way a large and uniform distribution of point discharges is obtained.

From 6 to 8 tons of dust are precipitated per twenty-four hours, the precipitating efficiency being from 80 per cent. to 90 per cent. The total power consumption is at the rate of 120 kw. The temperature of the gases varies from 100° C. to 150° C.

Where the precipitated fume particles are liquid—*e.g.*, sulphuric acid—the condensing electrodes are sometimes made of

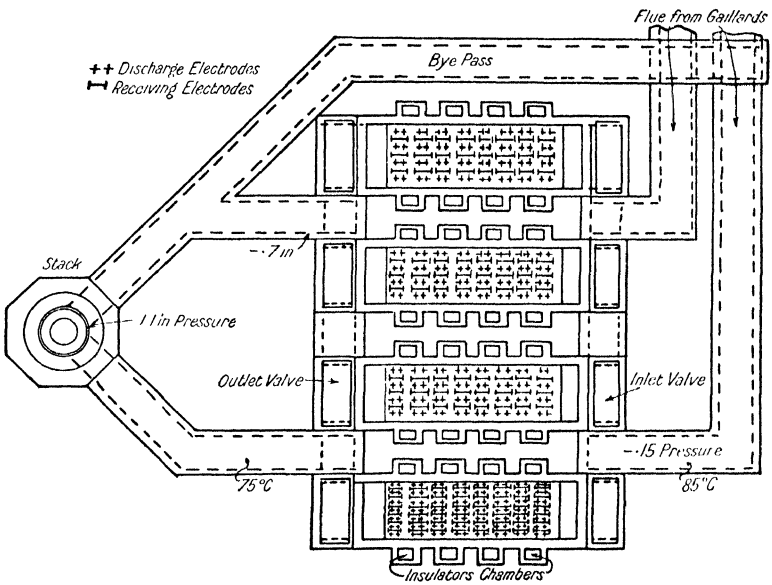


FIG. 29.—Section, in plan, of plate type electrostatic precipitator for precipitating sulphuric acid mist, showing arrangement of electrodes.

wood staves, or of pipes of vitrified terra cotta. These latter have been used up to diameters of 2 feet.

The Lodge-Cottrell process has been used in this country, as well as in America, for the precipitation of sulphuric acid mist, and for cleaning blast furnace gas. For the former purpose both discharge electrodes and condensing electrodes are constructed of lead—generally in the form of points and plates respectively. In a recent plant, 25 tons of 40° Bé. acid are produced per day from 30,000 cubic feet of gases per minute at a temperature of 180° F. Electrostatic precipitation is also

used to remove dust from the gases entering the catalyst chambers of contact plants.

The process has been used for the fractional precipitation of the constituents of a smoke. Thus, if a dusty arsenic smoke is treated at a temperature above the condensing point of the As_2O_3, the dust only is precipitated. On cooling the smoke the As_2O_3 is condensed, and can be precipitated separately.

Chlorine-bearing gases from bleach chambers have been treated with $Ca(OH)_2$ dust, the finely divided bleaching powder formed being precipitated electrostatically.

Condensed milk or other solutions or emulsions can be atomised into warm, dry air, and the fine powder produced by their evaporation precipitated electrostatically.

The metal in low grade oxidised ores is volatilised as chloride. The chloride smoke is recovered by electrostatic precipitation.

Phosphate rock is heated with coke and silica in an electric furnace. The P_2O_5 is volatilised and precipitated electrostatically as H_3PO_4.

The nitric acid cloud formed in the nitrous gases from the Haber process is precipitated electrostatically.

Lampblack is manufactured by burning hydrocarbons in a limited supply of oxygen, the smoke being collected in settling chambers. The best product, carbon black, is manufactured in America by the partial combustion of natural gas. Irvine [28] has shown that the smoke produced by burning coal or oil consists of carbon particles, each surrounded by a film of oil. A gas smoke carbon particle is surrounded by a water film. The finest quality black is formed by condensing the smoke at temperatures above the dew-point of the oil or water. In modern plants, the smoke is precipitated electrostatically at a temperature of 250° to 300° C.

Electrostatic precipitation provides the most satisfactory method of air purification, for it not only precipitates bacteria, but actually kills them.

Until the introduction of electrostatic precipitation the industrial treatment of fumes and dusty gases was restricted to purely empirical methods. During the war many systematic

investigations were made into the characteristic properties and into the conditions of stability of the various disperse systems in gases that were employed in chemical warfare. It is suggested that the knowledge and experience obtained then might usefully be applied to the study of those industrial smokes and fumes the successful treatment of which is a matter of such wide industrial importance. Such research work should seek to determine—

(*a*) The physical properties of such disperse systems, the concentration of the disperse phase, the degree of dispersion, the motion and diffusion of the particles ;

(*b*) The factors that cause and destroy the stability of the system ;

(*c*) The methods that can be adopted for flocculating smokes into coarse clouds or dusts ;

(*d*) The industrial possibility of such processes as thermal precipitation and directed impact.

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CHAPTER VIII

DUST EXPLOSIONS

Explosive Combustion

WHEN any substance burns in air, the rate of combustion depends, *cæteris paribus*, upon the surface area that is freely exposed by the substance to the air. There is no comparison, for example, between the rate of combustion of a block of wood and that of the same weight of wood shavings. An equal weight of sawdust would burn even more rapidly provided that all the particles had free access to the air throughout the combustion process, and at the same time were near enough to one another to communicate ignition to each other.

The maximum possible surface of contact between a combustible and air is attained when a combustible *gas* is mixed with air. In such a mixture, provided that the gas and air are mixed in suitable proportions—approximately their combining proportions—combustion spreads through the mass with such velocity as to cause an explosion.[1] The combustion of such a gas-air mixture takes place in at least two stages: ignition and propagation. To ignite the mixture, it is necessary to raise its temperature sufficiently at some point for combustion to take place. The heat produced by this combustion, except for any that is lost by radiation, will raise the temperature of the adjacent layer of unburnt gas. If the amount of heat be sufficient to raise the temperature of this unburnt gas to the ignition point, the gas will burn, and, in its turn, will ignite the next layer of unburnt gas. In this way a wave of ignition will spread through the gas, to be followed by a wave of combustion—that is to say, a flame. In a suitable gas mixture the flame velocity will easily exceed 2,000 feet per second.

Where combustion occurs, the gas in the immediate locality will be suddenly expanded, owing to the rise of temperature, so that a wave of pressure travelling with the velocity of sound will

overtake the wave of combustion. The effect of the compression wave under certain conditions is to compress the gas immediately in front of it, and so to raise its temperature. If the amount of this compression is sufficient to raise the temperature to the ignition point, combustion occurs with very much greater velocity and violence, producing detonation.

Anything which lowers the rate of combustion of the gas—for example, a reduction of pressure, or dilution with an inert gas—or anything which may absorb any of the heat of combustion—for instance, inert gases, water vapour, inert dust or an excess of either reacting gas—will diminish the heating effect of the primary ignition, and may make it impossible to raise the temperature of the adjacent unburnt gas to the ignition point. Combustion will not then spread through the gas.

To obtain explosive combustion of a gas mixture, therefore, it is necessary to have (*a*) a sufficient proportion of inflammable gas, and (*b*) an adequate means of ignition. The most explosive mixture is that which consists of the pure gas and oxygen in their combining proportions. The mixture becomes less explosive as the proportion of either constituent is increased, until, beyond an upper and lower limit of concentration of the inflammable gas, the mixture ceases to be explosively inflammable. The propagation of combustion through the gas mixture can be arrested also by diluting the gas with an inert gas or with inert dust, with liquid water—*e.g.*, fog—or by surrounding the source of ignition with a mass of metal able to absorb the heat of combustion sufficiently to prevent the spread of ignition, as in the Davy safety lamp.

In a mixture of gas and air, the molecules of each constituent are not only intimately mixed, but are in rapid and ceaseless thermodynamic motion, each molecule colliding with its neighbours many thousand million times per second. This intimate dynamic contact probably plays an important part in facilitating the propagation of ignition through the gas mixture.

Dust Exp'osions

The particles of a dust cloud, although many million times larger than molecules, are yet very small. Dust particles that

float in the air for any length of time cannot be much larger than 10^{-3} cm. diameter. Such particles, however, are too large to respond to molecular bombardment by the air at ordinary pressures—that is, they do not exhibit Brownian motion. They simply drift in the air in response to convection currents and draughts. In practically all dust clouds, however, there is a proportion of finer dust particles that are in active Brownian motion. They are, therefore, less than 10^{-5} cm. in diameter. It is reasonable to expect that these particles would facilitate the propagation of ignition, and so help to promote explosive combustion.

A dust-air mixture, therefore, differs essentially from a gas-air mixture in the degree of intimacy of contact between the two constituents, regarded both statically and dynamically. The specific surface of the dust, however, is still enormous when compared with the same substance in massive form, and, under suitable conditions of concentration, it can, when ignited, burn with explosive violence. One hundred grams of starch dust, distributed in a cubic metre of air, constitute a very explosive mixture. If we assume the dust particles to be spherical, and of an average diameter of 10^{-3} cm., there will be about 100,000 particles per cubic centimetre of air. The particles will be about 0·02 cm. apart, and the total surface area of 100 grams of dust will exceed 30 square metres. A small proportion of finer dust particles of, say, 10^{-5} cm. diameter, would effectively occupy the intervening spaces, and, by their ceaseless agitation, would form a connecting link between the coarser particles. In much the same way, a small amount of inflammable gas would serve to communicate ignition from one particle to another.

In such a system, the possibility of ignition would be determined, in the first place, by the ease of oxidation of the particles themselves. This is indicated by the relative temperature at which the dust particles ignite. In a dust cloud, the ignition of the particles may be facilitated by the presence of a film of adsorbed oxygen upon the surface of the particles.

It has also been suggested that certain forms of inert dust, suspended in inflammable gas mixtures, may catalyse the combustion of the mixture by adsorbing one or both of the con-

stituents,[8] and so produce a greatly increased local concentration. It is probable that in a number of instances of so-called photochemical reactions between two gases—*e.g.*, SO_2 and H_2S—the action of the light rays is to form nuclei in the gas mixture which then catalyse the reaction between the two gases by adsorbing one or both of them.

The propagation of ignition through the dust cloud will be determined by the quantity and intensity of the heat given out by the ignited particles after allowing for loss by radiation and by the absorption of heat by inert gas or inert dust—that is to say, it will be determined by the rate of combustion of the inflammable dust and the specific heat and thermal conductivity of the dust cloud. The rate of combustion of each individual particle clearly depends upon the area of contact between it and the oxygen : the smaller the particle, the larger will be its specific surface, and the more rapidly will it burn. Also, the higher the partial pressure of oxygen, the more rapidly will combustion proceed. Some of the heat of combustion may be absorbed by liquid water on the dust particles, or, to a less extent, by water vapour in the gas, by inert gas or by inert dust. The presence of incombustible matter—ash—in the combustible dust itself will retard the combustion of the combustible part of the dust by diluting it, and will also absorb some of the heat of combustion. Heat may also be lost by radiation from the incandescent particles, whether combustible or incombustible. The amount of heat lost by radiation in this way will depend upon the surface area of the particles, and upon the radiating efficiency of the substances of which they consist.

If the heat of combustion is generated at a sufficient rate, so that, after all losses by absorption and radiation have been incurred, it is still sufficient to raise the temperature of the adjacent unburnt gas to the ignition point, combustion will spread. The velocity of propagation will depend upon the distance between the particles ; it is necessarily lower in a dust cloud than in a gas mixture, for (*a*) the dust particles take longer to ignite and to burn than the gas molecules, and (*b*) they are further apart, and not undergoing frequent collision. The velocity of propagation can conceivably be accelerated by

the presence of (1) inflammable gas, or (2) very fine dust particles in active Brownian motion.

Experimental Results.—In 1911, R. V. Wheeler [2] conducted a valuable series of experiments on sixty-six different samples of dust, collected from factories that would come under the jurisdiction of the Factories and Workshops Acts. Wheeler investigated :—

(*a*) The relative temperatures at which the various dusts could be ignited freely, thus discriminating between harmless and dangerous dusts ;

(*b*) The lowest temperature at which ignition could be effected, from which the possibility of ignition by such common causes as electric sparks, a match flame, heated metal, etc., could be inferred.

The relative temperature of free ignition was determined by passing the dust over platinum heated electrically and observing the temperature at which combustion occurred.

The lowest temperature at which ignition could occur was determined by passing the dust through a small, electrically heated glass tube containing a copper spiral, and observing the lowest temperature at which ignition of the dust occurred.

As a result of these tests, he arranged the various dusts in three classes, as follows :—

CLASS I.

Dust.	(*a*) Relative Temperature of Ignition, Deg. C.	(*b*) Lowest Ignition Temperature, Deg. C.
Sugar	805	540
Dextrine	940	540
Starch	1,035	640
Cocoa	970	620
Rice, meal and cake refuse	970	630
Cork	1,000	630
Soya bean (unextracted)	975	630
Wood flour	985	610
Malt	990	600
Oat husk	990	620
Grain (flour mill)	995	630
Maize	1,010	645

CLASS I.—*continued.*

Dust.	(*a*) Relative Temperature of Ignition, Deg. C.	(*b*) Lowest Ignition Temperature, Deg. C.
Tea	1,010	640
Compound cake	955	620
Grain (storage)	1,050	630
Rape seed	1,050	650
Cornflour	1,060	620
Flour (flour mill)	1 060	650
Chicory	1,070	660
Briquette	1,090	800
Gramophone record	1,100	750
Soya bean (extracted)	1,140	630

These dusts ignite and propagate flame readily. The source of heat required for ignition is comparatively small—for example, a match flame. The dusts are arranged roughly in the order of their inflammability. The most dangerous are sugar, dextrine, starch and cocoa, particularly sugar. Sugar ignites when projected as a cloud against a surface heated to below red heat, and when ignition has taken place, the flame travels through the dust cloud with great rapidity.

CLASS II.

Dust.	(*a*) Relative Temperature of Ignition, Deg. C	(*b*) Lowest Ignition Temperature, Deg. C.
Copal gum	1,010	750
Leather	1,050	740
" Dead " cork	1,100	740
Cocoanut oil milling	—	640
Rice milling	—	630
Sawdust	970	635
Castor oil meal	1,100	655
Oilcake	945	660
Offal grinding (bran)	980	640
Grist milling	—	600
Horn meal	—	670
Mustard	1,050	680
Shoddy	—	690
Shellac composition	—	780

These dusts are readily ignited, but, for the propagation of flame, they require a source of heat, either of large size and high temperature—*e.g.*, an electric arc—or of long duration—*e.g.*, a Bunsen burner.

CLASS III.

Dust.	(*a*) Relative Temperature of Ignition, Deg. C.	(*b*) Lowest Ignition Temperature, Deg. C.
Organic ammonia	—	690
Tobacco	—	680
Spice milling	—	680
Bone meal	—	700
Coal (foundry blacking)	—	830
Lampblack	—	—
Sack cleaning	—	—
Retort carbon	—	—
Rape seed (Russian)	—	640
Blacking	—	—
Drug grinding	—	690
Cotton seed	—	—
Charcoal	—	760
Foundry blacking	—	810
Brush carbon	—	—
Stale coke	—	—
Plumbago	—	—
Bone charcoal	—	—
Mineral and ivory black	—	—

These dusts do not appear to be capable of propagating flame under ordinary factory conditions, either (*a*) because they do not readily form a cloud in air, or (*b*) because they contain a large quantity of incombustible matter, or (*c*) because the material of which they are composed does not burn rapidly enough. Of these dusts the first ten are all inflammable, but the samples tested were not capable of propagating flame. It is possible, however, that other samples of the same materials, containing less incombustible matter, or in a finer state of division, might be capable of propagating flame.

It is found experimentally that for a given dust-air mixture there is an optimum concentration of dust at which the combustion is most rapid and complete—that is to say, most explosive. As in a gas-air mixture, this composition corresponds approximately to the combining proportions of the dust and the oxygen in the air, although it is modified considerably according to the fineness of the dust and the amount of incombustible material present in it. 123 grams of coal dust per cubic metre, and 220 grams of starch dust per cubic metre, are found to give a maximum explosion. Generally speaking, the finer the dust and the purer the substance, the more closely it approximates in behaviour to a gas.

In dusts such as coal dust, the optimum concentration is also found to depend to some extent upon the nature of the coal—its content of volatile matter and ash. It has been suggested that the explosive character of coal dust is to be attributed to the rapid production of inflammable gas by the heated dust. There is no doubt that the presence of even small amounts of inflammable gas greatly facilitates the explosion of coal or other inflammable dusts, but there is no reason to suppose that the presence of inflammable gas is necessary to produce a dust explosion. Many dusts are explosive which, when heated well above the ignition temperature, do not give off any inflammable gas—for example, aluminium, starch. The explosion of a dust-air mixture is evidently initiated and maintained by the direct combustion of the dust itself. Its violence is directly due to the high velocity of combustion, consequent upon the very large specific surface of the dispersed combustible.

Concentration of Dust.—As the concentration of dust departs from the optimum concentration the mixture becomes less inflammable. The relation between the concentration of dust in grams per litre and the pressure developed by the combustion of the corresponding cloud is shown in Table XII.[3] The inflammability of the dust cloud, as measured by the pressure generated by its combustion, diminishes as the concentration of dust is increased or decreased beyond the optimum value. Beyond a lower and an upper limit of concentration the dust cloud is no longer inflammable.

TABLE XII.

Relation between Concentration of Lycopodium Dust and Inflammability of Cloud.

Concentration of Dust, gms. per 100 c.c.	Pressure, lbs. per sq. in.
0·2	33
0·3	52
0·5	60
1·0	33
1·5	19
3·5	9
5·0	7

The minimum concentration at which coal dust becomes explosive is from 23 to 40 grams per cubic metre, according to the nature of the coal. A bituminous coal is generally more easily ignited than anthracite. A coal of high ash content is less easily ignited than one with little ash. Some dusts—for example, certain kinds of starch—are more readily ignited than coal dust, and produce a more violent explosion. The relative inflammability of a number of dusts, as indicated by the pressure produced by their combustion, is given in Table XIII. It is found that a cloud of flour dust ignites and burns very similarly to coal dust. Starch dust burns with twice as high a flame velocity as coal dust, and generates from eight to ten times as much pressure.

TABLE XIII.

Dust.	Pressure generated, lbs./sq. in.	Dust.	Pressure generated, lbs./sq. in.
Lycopodium	17·5	Pittsburgh standard coal	10·1
Dextrine	14·6	Cocoa	9·1
Wheat starch	14·0	Sulphur flour	8·8
Tan bark dust	13·3	Rice bran dust	8·7
Wood dust	12·8	Ground cork dust	7·4
Wheat dust	12·6	Powdered milk	7·1
Wheat elevator	12·5	Charcoal	3·6
Sugar	12·2	Flax dust	3·2
Linseed meal	11·7		
Fertiliser dust (grinding dry tankage)	10·5		

Fineness of Dust.—It has been shown experimentally that the inflammability of a given dust increases with its fineness. This is illustrated in Table XIV., in which various samples of dust, separated into fractions of different degrees of fineness, are compared. It will be noticed that in practically every case the finer dust is more inflammable than the coarser dust, although the difference is hardly as great as might be expected. The order of inflammability of the coarser fractions of the six dusts examined is very different from that of the finer fractions.

TABLE XIV.

Dust.	Pressure, lbs. per sq. in.						
Maximum Size Particles.	·02	·025	·03	·04	·05	·06	·11 mm.
Wood dust . .	18·3	—	18·1	—	15·5	—	10·6
Oat and corn .	15·7	—	—	14·2	—	—	8·7
Potato starch .	14·5	—	14·0	—	12·8	—	11·1
Pittsburgh coal .	—	—	12·5	—	10·3	—	3·9
Wheat flour .	—	14·9	—	13·9	—	12·5	9·6
Cocoa . . .	—	—	7·3	11·3	—	10·7	10·2

It is probable that the shape of the particles is also an important factor in determining the amount of surface exposed to the air by a given weight of the dust, and hence its inflammability.

Effect of Ash.—In Table XV., the retarding influence of the incombustible portion of the dust is illustrated with various samples of rice dust. Although, for a given dust, an increase in the percentage of incombustible matter reduces the inflammability, yet the percentage of ash that can be present in an explosive dust varies within very wide limits. Thus rice dust may contain 57 per cent. of ash and still be inflammable; while carbon dust may contain only 4 per cent. of ash and be incapable of ignition.

TABLE XV.

Effect of Ash on Inflammability of Rice Dusts.

Dust.	Explosion Pressure, lbs./sq. in.	Ash, per cent.
Rice polish dust from polisher .	10·1	8·06
Rice polish dust from collector around polisher . . .	9·3	7·05
Rice bran dust	8·7	21·49
Rice dust from cleaning . .	7·9	29·33
Rice dust	7·1	35·52
Rice dust from shaker . .	4·8	53·40
Rice dust from bins above cyclone from receiving aspirator . .	4·8	56·77
Rice dust from clippers . .	3·9	50·40
Cyclone dust from rough rice receiving aspirator . . .	0·0	47·66

Volatile Matter.—During the temperature rise that precedes ignition any constituent of the dust that is volatile at temperatures below the ignition point will be set free, the more readily the finer the dust. If the dust is damp, this volatile matter will not be evolved until the water has been driven off. The volatile matter may be inflammable—coal dust—or it may be non-inflammable—starch or cellulose. With coal dust it is generally agreed that the liberation of inflammable gas and vapours from the dust may lower the ignition temperature, and facilitate the explosion of the dust.

The formation of inflammable vapour or gas from the dust is clearly not essential to the propagation of a dust explosion, since starch and cellulose explode very readily, and even finely divided metal dusts, such as aluminium, have been known to explode violently.

Moisture.—Moist dust has a higher ignition temperature than the same dust when dried. This is because some of the heat of ignition is absorbed by the evaporation of the water. The extent to which the ignition point is raised by the moisture differs with different substances. It is impossible, by adding

moisture, to render coal dust absolutely and theoretically incombustible, since it would require six or seven times its weight of water. Potato starch dust, after drying at 100° C., will explode violently, but is quite incombustible if it contains 10 per cent. of moisture. On the other hand, wheat smut dust, containing 35 per cent. moisture, has been ignited easily. Generally speaking, if a dust is not too wet to form a cloud in the air, it is not too wet to explode, provided the concentration is high enough.

Ignition.—From a practical standpoint, the possibility of the ignition of the dust is perhaps the most important. The temperature of ignition of a given dust cloud varies according to the character of the source of ignition. Some dust clouds require a large source of heat of some duration—for example, a gas flame. Others are easily combustible, and can be ignited by an electric spark. The inflammability of a given dust cloud is greatly modified according to the temperature of the source of ignition. In Table XVI. the pressure developed by the combustion of different kinds of dust is compared for different ignition temperatures. It will be noticed that the order of inflammability of the dusts in the first column differs very markedly from the order in the second column.

TABLE XVI.

Effect of Ignition Temperatures on Inflammability.

Dust	Pressure, lbs. per sq. in.	
	Ignition Temperature, 1200° C.	Ignition Temperature, 800° C.
Stinking smut of wheat	21·4	0·6
White dextrine	15·5	7·6
Canary dextrine	14·9	7·9
Wheat starch	14·1	8·5
Corn starch	12·6	6·7
Sugar, lump pulverised to pass 200-mesh	13·0	7·5
Dark canary dextrine	15·1	7·3
Potato flour	10·4	6·2
Rice starch	12·3	5·3

Ignition tests with an arc lamp, an oil lamp and a candle flame, carried out with various dusts, show a wide variation in the ease of ignition and the violence of the resulting explosion. A sample of rice dust that is easily exploded by a candle flame could not be ignited by an electric arc. A coal dust that ignited weakly with an arc exploded violently with a candle flame. Flour exploded readily with each source of ignition. Corn elevator dust that was not ignited by an arc or candle flame could burn round the flame of the oil lamp, but combustion was not propagated. In the classification on p. 166, the lowest temperatures are given at which various dust clouds will ignite when allowed to fall through a small porcelain tube heated to a definite temperature, and containing a roll of copper gauze. In this case, propagation is facilitated, since the whole of the cloud is heated. Higher ignition temperatures will be required to ignite such dusts at a single point.

Effect of Inert Dust.—An explosion of a dust cloud can be restrained, or entirely prevented, by mixing with it a suitable proportion of inert dust, such as shale or limestone. Starch dust, for example, is easily exploded by a candle flame or arc, but a dust mixture of 30 per cent. starch and 70 per cent. shale cannot be ignited by either. Similarly, a mixture of 40 per cent. flour and 60 per cent. shale dust cannot be exploded by an arc. A dust cloud consisting of 40 per cent. sulphur and 60 per cent. shale can be exploded easily by a candle flame, but 30 per cent. sulphur mixed with 70 per cent. shale dust cannot. A mixture of 50 per cent. flour dust with 50 per cent. shale dust can be exploded by a candle flame, but is not ignited by an arc.

Fine shale and limestone dust are used in coal mines to check the propagation of a coal dust explosion. The dust is contained on shelves or in boxes that are suspended from the roof of the mine galleries at various points, high enough to be clear of traffic. They are tripped by the advancing explosion wave, and discharge the dust into the air beneath, thus diluting the coal dust that is present in the air, and effectively checking further propagation of the explosion.

Flame Velocity.—The maximum velocity of flame propagation that has been observed during experiments with gas

mixtures ranges from 5,000 feet per second for a mixture of carbon monoxide and oxygen to 9,000 feet per second for a mixture of hydrogen and oxygen. During experiments with coal dusts at different times flame velocities of over 3,000 feet per second have been observed, while in certain tests there were indications that the velocity exceeded 6,000 feet per second. The flame velocity is increased by increasing the fineness of the dust, or by mixing a small amount of inflammable gas with the dust, and is higher and more dry the more free the dust is from ash and moisture.

Explosion Pressures.—Experiments made with coal, flour, starch, etc., indicate that the pressures that are developed when these dusts are exploded are of the same order as those developed in gas explosions. In large scale experiments with coal dusts, pressures have been obtained as high as 270 lbs. per square inch.

When starch and other factory dusts, that are more inflammable than coal dust, are exploded in a closed gallery or tunnel, they are found to burn with as much as twice the velocity of coal dust, and may produce eight or ten times as much pressure. In an actual factory explosion, these maximum values of flame velocity and pressure are never approached, for factory buildings are not constructed to withstand explosions, and collapse long before the pressure has risen to these values.

The Practical Problem

There is only one way by which dust explosions in a factory can be absolutely avoided, and that is by removing the dust as soon as it is formed. In a modern factory, all grinding and disintegrating appliances are, wherever possible, enclosed in casings. The dusty air inside these casings is drawn away by suction, and passed through an air filter of the bag or other suitable type. In this way the dust is recovered, effecting an economy in proportion to its value, the factory air is kept clean, and the physiological and explosion hazards are eliminated. When installing such a dust removal system, it is necessary to place the fan on the exhaust side of the air filter, so that only dust-free air comes into contact with it. Explosions have

occurred in dust-extracting systems, owing to spark formation in the fan itself, through pieces of metal or other foreign material striking the fan blades.

In many factories, much can be done to reduce the risk of explosion by diluting the air in the neighbourhood of the machines with flue gas. This also involves the necessity for enclosing the machines, but where the dust is not valuable and where the introduction of a dust-extraction system would be difficult and costly, dilution with flue gas has certain advantages.

These methods, however, are of only limited application, and there still remains a variety of plants and processes and machines in which other methods must be adopted. The risk of explosion will depend upon the possibility of forming an explosive mixture, and the occurrence of a suitable means of ignition. Adequate ventilation may do much to check the concentration of dust in the air beyond a safe limit, but there are always places where the air is relatively stagnant, and where dust can accumulate. It frequently happens that dust accumulates on roof beams and girders, from which it may become dislodged, to form an explosive cloud in the air beneath. Similarly, dust that has accumulated on the floor may be stirred up by the breaking of a belt. A disastrous explosion in Liverpool in 1911 [4] was attributed to the blowing of an uncovered fuse on a temporary switchboard at the very moment when a large belt broke, and stirred up a dense cloud of accumulated dust. The accumulation of dust on walls, windows, floors and roof should be prevented by frequent sweeping, or, better still, by suction cleaning.

There are many possible sources of ignition in a factory. There is always the possibility of criminal carelessness on the part of employees and staff through smoking and the use of matches and other forms of open flames or lights. Such practices should be rigidly prohibited in any factory in which explosive dust is produced. In most modern factories, electric light and power are used, and although this eliminates the danger from gas flames and oil lamps, it introduces the possibility of ignition by electric sparks. Such a spark may be formed at the brush of a motor, or by the blowing of a fuse or

the breaking of a switch or cut-out, by short-circuiting or by the breaking of an electric light bulb.

Dust may be directly heated to its ignition temperature by settling on an electric light bulb, or on a hot metal surface, heated, for example, by friction. Instances of the latter have occurred frequently in grain elevators in America, where the elevator has become choked at the top, and the pulley, rotating in the mass of grain, has generated sufficient heat to ignite it. This danger has been eliminated largely by the introduction of a non-chokable elevator head.

Sparks may be formed in grinding machines and disintegrators by nails and bolts and other foreign matter getting into the machine along with the material to be ground. This accidental intrusion of foreign matter can be prevented by installing pneumatic or magnetic separators.

In dry climates—for example, certain parts of America and Australia—ignition has been traced to electric sparks that result from the generation of static electricity by the friction between belts and pulleys,[5] and between grinding machines and the dry material that is being ground. This has been shown to be a common cause of fires and explosions in cotton gins and in grain-threshing machines. It is said that, in certain parts of America at threshing time, the relative humidity of the atmosphere falls as low as 10 per cent. In this country, owing to the much greater atmospheric humidity that ordinarily prevails, the danger from the accumulation of static electricity would appear to be much less. This possible source of ignition is satisfactorily eliminated in practice either by humidifying the atmosphere in the neighbourhood of the machines, so that the frictional electricity leaks away instead of accumulating, or, better still, by introducing earthed collectors to remove the electricity from the belts and machinery as it forms.

Coal Dust Explosions.—A considerable amount of work has been done in this country, and also abroad, on the causes and mechanism of dust explosions in coal mines. In this country during the last twelve years the subject has been investigated experimentally at Altofts, in Yorkshire, by the Mine-owners' Association, and at Eskmeals, in Cumberland, by a committee

of experts appointed in 1911 by the Home Secretary. Beginning in 1907, valuable work has been carried out at Liévin, in France, under the direction of a committee appointed by the French Government. In 1907, also, the Technological Branch of the United States Geological Survey commenced the investigation of explosions in coal mines. An experimental station was established at Pittsburgh. In 1910, this division became a separate bureau, the United States Bureau of Mines.

As a result of these investigations, it has been shown [6] that—

(*a*) 0·2 oz. per cubic foot of air (1 lb. of dust per linear foot of an ordinary mine gangway) will propagate an explosion.

(*b*) Blasting a single hole, using a long flame explosive (black powder or dynamite), may cause the ignition of the dust cloud.

(*c*) Dust-laden air will explode whether it be quiescent or moving to or from the source of ignition.

(*d*) The air may be saturated with moisture, but the dust will explode, provided enough dust be present.

(*e*) The force of a coal dust explosion usually increases in violence as it is propagated through a mine working, and may reach its maximum after travelling from 500 to 800 feet from the place of origin.

(*f*) Pressures as high as 120 lbs. per square inch have been measured at right-angles to the direction of propagation, the pressure in the line of advance, doubtless, being much greater.

It was found that the propagation of an explosion could be effectively arrested by the introduction of rock-dust barriers [7] which are tripped mechanically by the advancing force wave, and discharge from three to four tons of stone dust in a dense cloud in front of the advancing explosion wave. This dust dilutes the coal dust in the air of the gangway, and prevents the propagation of the explosion.

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CHAPTER IX

METEOROLOGY

THE earth's atmosphere consists of two distinct layers. The lower extends from the surface of the earth to an altitude of about 10 kilometres, and is known as the troposphere. Above it is the stratosphere, extending outwards to a distance estimated to be as much as 200 kilometres. The density of the atmosphere decreases with increasing altitude until, at a height of 50 kilometres, the atmosphere must be too tenuous to manifest any measurable pressure. Yet, even at this extreme tenuity, it can scatter an appreciable amount of the sun's rays at sunrise and sunset, thus prolonging the duration of twilight. It can also resist the passage of meteorites ; they have been observed to become incandescent even at a height of 200 kilometres.

The stratosphere is apparently a region of perpetual calm. In the absence of convection currents and water vapour, no cloud formation, rain or wind disturbs its tranquillity. The average temperature of the atmosphere diminishes vertically at an approximately uniform rate, from about 11° C. at the surface of the earth to — 55° C. at 10 kilometres, and beyond this altitude it appears to remain constant. The composition of the atmosphere remains constant throughout the troposphere, owing to the continuous action of convection currents, but beyond the tropopause, at an altitude of 10 kilometres, the composition greatly changes with increasing altitude. At first it consists roughly of a layer of nitrogen, containing progressively less oxygen, and then, at a height of from 90 to 100 kilometres, this is succeeded by practically pure hydrogen.

The troposphere is a region of storm and constant commotion. Warmed here and there by contact with the earth, the air becomes rarefied, and rises with greater or less rapidity, its place being taken by denser, colder air, flowing in from the vicinity. In this way convection currents are set up, that may

produce a light breeze, the steady trade wind, or an equinoctial gale. The vertical temperature gradient near the ground necessarily varies according to the locality, being determined chiefly by the warming of the ground by the sun.

• Upon this continual circulation in the lower part of the atmosphere depend all the phenomena that collectively we describe as " the weather." It will help us to understand them if we regard this portion of the atmosphere as a vast aerosol,[5] in which water functions both as a constituent of the disperse phase and of the dispersion medium, according to the conditions of temperature and pressure that obtain at the time and in the place of observation. In addition to water and water vapour, the atmosphere contains an incredibly large quantity of highly dispersed solid matter, consisting of smoke particles, and dust of all kinds from the surface of the earth and from outer space.[24] This suspended dust is a determining factor in nearly all atmospheric phenomena.

Atmospheric Dust

The atmosphere is continually receiving large quantities of dust and smoke. Soil particles and the dust of roads and deserts are swept up into the air by winds. Of this dust the coarser particles (of diameter greater than $1\,\mu$) soon settle again, but the finer particles may remain in suspension in the air for a long enough time to travel great distances. The fine particles of coal ash and soot that are discharged into the atmosphere above an industrial area are carried by a favourable wind many hundred miles across country. Sea-water spray, carried by a dry wind, evaporates to form a salt haze that may extend inland for many miles. Fine dust discharged from the crater of a volcano may remain suspended in the upper air for years. During the eruption of Krakatoa,[1] in 1883, enormous quantities of fine dust and water vapour were projected to a great height into the atmosphere. The dust gradually formed a layer from 5 to 15 miles above the surface of the earth, and extending round the world. This dust layer persisted for over five years.

Many million tons of fine coal ash and soot are discharged

hail, the falling particles are charged positively or negatively, and, therefore, carry a convection current of electricity from air to ground (if they be positively charged), and from ground to air (if negatively charged). Such currents rarely exceed 1• milliampere per square kilometre, and, on the whole, carry more positive than negative electricity from the air to the ground.

Water droplets may be electrified :

(1) By adsorption of ions. Owing to their greater mobility, more negative ions will be adsorbed than positive ions.

(2) By the action of ultra-violet light, especially in the upper air.

(3) By friction between water drops and ice crystals, or dust particles.

(4) By collision between large and small drops.

(5) By the breaking up of large drops by the resistance of the air through which they are falling at high velocity. The ruptured drop acquires a positive, the air a negative charge.

During a thunderstorm a lightning flash may carry a positive charge from cloud to ground or *vice versâ*. Generally, it is the latter. The potential of a thunder cloud must approach 30,000 volts per centimetre to produce a lightning flash. The average current during a lightning flash is about 1 ampere.

A thunder cloud functions as an electrical machine.[26] It is very lofty, its base being from 1 to 2 kilometres, and its summit from 5 to 10 kilometres above the ground. The upward rush of air, produced in the cloud by the powerful convection current, carries the fine charged cloud particles upwards. The oppositely charged large drops and hailstones settle to the lower portion of the cloud. The E.M.F. between the summit and base of a thunder cloud is probably of the order of 10^9 volts. This is very much greater than the potential of the ground or of the upper air (10^6 volts), so that discharge may take place from pole to pole of the cloud, either directly, through the cloud, or *viâ* the ground. The cloud may also discharge partly to the conducting upper layers of the atmosphere.

In addition to a direct discharge between a thunder cloud and the ground, the greatly increased potential gradient in the air

There appear to be four well-defined dust layers in the atmosphere.[7] The first of these is the relatively dense dust layer near the ground. It consists of comparatively coarse particles, and extends upwards for rather less than a kilometre. It can be well seen from the top of a mountain, covering the valley or plain below. The second layer extends above the first to a height of about 4 kilometres. It consists of finer particles, carried up by convection currents. A third layer extends from the 4-kilometre level to 10 kilometres, the altitude at which convection effects cease. This layer consists of very fine particles, carried up from lower layers by powerful convection currents—*e.g.*, cyclones. The fine dust that exists in the stratosphere is probably of cosmic origin, reinforced sometimes by volcanic dust that, during an unusually violent eruption, may be projected into these high altitudes.

Chemical Composition.—The chemical composition of atmospheric dust varies according to its origin. In the neighbourhood of large towns and industrial areas, it consists largely of the products of the incomplete combustion of coal—viz., soot particles, ranging between 0·25 μ and 1·0 μ—accompanied by tarry oils and very fine particles of coal ash. Minute crystals of sulphate are also found, probably as the result of the sulphur in the coal. The composition of the suspended matter at a large number of places in Great Britain has been recorded continuously during the past eight years.[4]

The blue haze that is found all over England in certain types of warm, dry weather cannot be due to the condensation of water vapour. It is due to the presence of black smoke particles of about 0·5 μ diameter, that have been carried from the towns. Thus the purity of the air, even in a country district far removed from any town, depends very much upon the direction of the prevailing winds in relation to the nearest industrial localities. Smoke from the industrial Midlands is found in the atmosphere of Devon.

The presence of haze, however, is not necessarily an indication of coal smoke pollution. The atmosphere may contain, in addition to coal smoke, the smoke from prairie and forest fires, also soil particles, bacteria, pollen, salt from sea spray, as

well as volcanic and cosmic dust. At sea, for example, haze may be caused by sulphates and chlorides. At Algarve, in South Portugal, a persistent blue haze was shown to be caused entirely by particles of sodium chloride.[2]

In a humid atmosphere, the intensity of an existing haze may be greatly intensified by the condensation of water upon the suspended particles. Particles of a soluble salt will promote the condensation of water from such an atmosphere, by reason of the lowered vapour pressure of water at their surfaces. Thus, at the ordinary temperature, water vapour will condense upon particles of common salt from an atmosphere of which the relative humidity is only 80 per cent. The condensation of water vapour upon smoke particles, to produce a fog, is largely due to the hygroscopic action of sulphur trioxide or sulphates associated with the soot particles.

Volcanic dust consists of minute spheres and fragments of spheres, varying in diameter from 1·5 μ downwards. Many of them are colourless and transparent. They appear to consist of calcium, magnesium, sodium and potassium silicates, probably in a sub-cooled, vitreous condition. Heavy metals—for example, lead and iron—are present only in very small proportions.

Dust from clouds or hailstones, or in sleet or rain, has been examined spectroscopically and analytically, and is found to be remarkably regular in composition.[6] Iron, nickel, calcium, copper, sodium and potassium occur in all specimens examined, and in the same proportions. Dust from sleet or snow contains more lead than that from hail. The amount of carbonaceous matter present is small.

Cosmic dust probably contains sodium, potassium, calcium, silver, copper, gallium, thallium, iron, nickel, lead, and is free from rubidium, strontium, magnesium. It is magnetic.

The Quantity of Dust.—The quantity of dust that is present in the air in a given locality at any time depends not only upon the rate at which it is being produced—for example, by volcanoes or chimneys—but also upon the direction and velocity of the wind. Generally speaking, dust is produced in industrial localities or in naturally arid regions, is distributed over great distances by winds, and gradually deposited again by rain and

snow. It is estimated that between the hours of 6 and 9 every morning during the winter months 200 tons of coal smoke are poured into the air over London. If the smoke rises well and is carried away by a steady breeze the concentration of smoke in the air does not exceed 1 milligram per cubic metre. This is sufficient to produce the ordinary haze that is characteristic of a bright winter day.[4]

On a calm morning this smoke is not carried away, and accumulates in the air, until it may reach a concentration of 4 milligrams per cubic metre. If the upper air is colder than the warm chimney gases they will rise, and in so doing, will expand and become cooler. They will rise no further after their temperature has become equal to that of the surrounding air. With a well-marked temperature gradient, such as ordinarily exists, smoke rises well above the city and becomes dissipated by air currents in the upper air. If, however, the temperature gradient is reversed, and the air near the ground is cooler than the air higher up, the chimney gases will not rise far before they reach air as warm as themselves. They will then rise no higher. In such circumstances, the smoke accumulates, to form a fog either overhead or on the ground, according to the distribution of temperature that prevails. It is estimated that the output of smoke from the chimneys in London between 6 a.m. and 9 a.m., if accumulated in this way to form a layer 400 feet high, is sufficient of itself to form a dense smoke fog. The increasing substitution of gas and electric heating for coal fires during recent years has resulted already in a marked diminution of the amount of solid impurity in the air of London, and has also reduced the number and density of its fogs.

In certain places, the air becomes charged locally with an enormous quantity of temporary impurity. This may be swept up by traffic into the air above a dusty road, or it may be distributed throughout the air in the neighbourhood of a disintegrating machine, or it may be due to the passage of a dust storm in the desert. In general, this dust is not sufficiently highly dispersed to remain in suspension in the atmosphere, and soon settles.

Probably the chief constituents of the permanent impurity

are salt crystals formed by the evaporation of sea spray, smoke particles from industrial and domestic fires, forest and prairie fires, and volcanic and cosmic dust.

The Number of Particles.—Many observations have been made of the size of the particles that are normally present in the atmosphere. They are found to be singularly uniform in size, ranging from 0·25 μ to 1·0 μ, and averaging about 0·5 μ. This is, no doubt, a natural result of the selective action of the air in supporting the finer particles and allowing the coarser ones to settle. The number of particles in a given volume can, therefore, be regarded as an approximate measure of the relative amount of impurity that is present. In the following table,[2] the number of particles per cubic centimetre is given for various localities, under different weather conditions.

TABLE XVII.

Number of Dust Particles in Air at Different Localities.

Sept., 1922.	Place.	Time.	No. of Smoke Particles/cc.	Remarks.
2nd, Sat. .	Holme (Norfolk).	12 noon.	152	Country air—no chimneys near.
5th, Tues.	Brighton .	12.10 p.m.	1,380	Wind N.E./N.
7th, Thurs.	Hull (near Victoria Pier).	7.30 a.m.	4,830	Thick water fog.
8th, Fri. .	Do.	7.15 a.m.	8,100	Wind N.E./N. Smoke haze.
10th, Sun. .	Do.	6.30 p.m.	3,080	Wind N.E./N. Air obviously clearer.
11th, Mon..	Do.	7.30 a.m.	13,800	Wind W. Thick smoke haze.
11th, Mon..	Do. (off Spurn Point).	4.30 p.m.	140	Haze visible over land.
March, 1922.				
18th . .	Cheam (Surrey)	Afternoon	1,200	
20th . .	Westminster .	4.30 p.m.	8,450	

The Optical Effects of Atmospheric Dust

The Transparency of the Atmosphere.—Pure air is almost completely transparent to light of all wave-lengths. This trans-

parency is diminished slightly by the presence of water vapour. It is very much reduced by the presence of dust particles or water droplets ; consequently, the intensity of direct insolation at the surface of the ground is less than at the summit of a high mountain, above the dust layer, by an amount that is proportional to the concentration of dust in the intervening atmosphere.

This diminished transparency is almost entirely due to the diffuse scattering of the incident light by the suspended particles. The composition of the light is altered, light of short wave-length being more completely scattered than that of longer wave-length. The extent to which the shorter wave light is scattered by the atmospheric dust can be seen clearly from a consideration of the equation for the intensity of monochromatic light at the surface of the earth,[8] $I = I_0 a^m$, where I_0 is the intensity of sunlight outside the earth's atmosphere, a is the transmission coefficient of the atmosphere—*i.e.*, the proportion that would be transmitted to the earth's surface if the sun were in the zenith—and m is the length of the path of the solar ray through the atmosphere, the unit path being the length of the path when the sun is in the zenith.

On Mount Whitney, practically above the dust layers of the atmosphere, the average value of a for wave-length 0·39 μ is 0·763, while for Washington the corresponding average value is 0·445.[9] In the smoky atmosphere of an industrial area, the value of a is much less. Consequently, in winter, when for latitudes equal to or greater than that of Washington, the value of m always exceeds 2, the factor (a^m) becomes very small.

For the wave-length 1·0 μ, the average value of a on Mount Whitney was 0·980, and for Washington 0·901. Clearly, therefore, longer wave light is much less affected than short wave light, and possesses a relatively greater intensity at all seasons of the year.

The intensity of direct insolation is greatly diminished after a great volcanic eruption, owing to the scattering of the solar rays when passing through the unusually dense dust layer. After the eruption of Katmai Volcano [1] in Alaska in 1912, the intensity of solar radiation was diminished by from 15 to 20 per cent. Bolometric observations showed that the diminished

intensity of insolation during the following year was several per cent. greater in the short wave-lengths than in the long ones.

The average intensity of sunlight in the centre of a large manufacturing town (Leeds) is less than 50 per cent. of that in the surrounding country.[10]

Diffusion of Sunlight.—One of the most important effects of atmospheric dust is the diffusion of sunlight. Without dust, there would be no diffused light from the sky, except for such of the shorter rays that are scattered by the molecules of the air. The dust particles scatter or, if large enough, reflect the sunlight in all directions, thus illuminating the air itself, and also objects that are in the shade and not receiving direct sunlight. This scattering is more complete the shorter the wave-length of the light. Thus, the ratio of blue to red in diffuse sky light is six times the ratio of blue to red in direct sunlight.

Visibility.—The visibility of distant objects is very much reduced by the dust in the air. The visibility of a distant object depends mostly upon the amount of contrast that exists between it and its surroundings. Dust or mist in the air not only cuts off direct light from the object, but also, by diffusely reflecting the sunlight that falls upon the suspended particles themselves, adds to the total amount of light that is received by the eye, thus reducing the effective contrast.

The light that is scattered or reflected in this way by the particles is generally polarised, and can be eliminated by viewing the hazy landscape through a Nicol prism, held at such an angle that the polarised light that is scattered by the dust particles is extinguished. Distant objects then become clear and distinct.

The true extent to which a haze diminishes the transparency of the air is best observed at sunset, when the air is no longer directly illuminated by the sun.

It has been shown that, owing to the condensation of water vapour upon the dust particles, the hazing effect of dust is intensified by an increased atmospheric humidity. Aitken[11] determined the mean limit of visibility, in miles, of air at Falkirk, for winds from different directions, and for different degrees of relative humidity. West to north winds blow from regions having less than fifty inhabitants per square mile, while southerly and

easterly winds come from regions having a population ranging from 100 to 12,000 per square mile. The results are given in Table XVIII.

TABLE XVIII.

Direction of Wind.	Depression of Wet-Bulb Thermometer.						
	2°	3°	4°	5°	6°	7°	8°
West to North	50	100	132	132	198	193	191 miles.
All other directions	8	11	14	18·5	16·4	19	26 miles.

In London in winter the average limit of visibility on a clear day does not exceed half a mile. This is in marked contrast to the amazingly clear atmosphere that prevails in the warm air of a tropical or semi-tropical maritime climate.

Atmospheric dust enhances the intensity and duration of twilight. For some time before sunrise and after sunset, the sun's rays fall upon the upper air, but too obliquely to be refracted to the earth. The light is scattered by the dust particles and gas molecules in the upper air, and irradiates the earth with a relatively faint, soft light. Twilight would probably be very different and much less bright if the upper air were completely free from particles of dust and water.

The Colours of the Sky.—The blue colour of the sky, although due mainly to the scattering of sunlight by the molecules of the air, is also due in part to the scattering action of suspended dust. If it were entirely due to scattering by air molecules, there should be no glare or excess of brightness of the sky in the vicinity of the sun. This excess is attributed to the diffraction of the sunlight by dust particles and ice crystals.

After the eruption of Krakatoa in 1883, a faint reddish corona of large radius was observed surrounding the sun. Its inner edge was 12 degrees, its outer edge 23 degrees from the sun. From the observed angular diameter of this ring, the diffracting particles were calculated to be 0·002 mm. in diameter. The ring persisted for many months.

At sunrise and sunset the level rays of the sun pass through

a layer of air almost twice as thick as at noon ; also the lower levels of the atmosphere through which the light is then passing are more dusty than the upper air. Consequently, when the sun is low the extent to which the blue light is scattered by the atmosphere reaches a maximum. The residual red-orange light illuminating atmospheric haze or clouds produces the typical sunrise and sunset colours.

Four well-marked phenomena attend the setting of the sun [12] :

(*a*) The counterglow—a ruddy glow in the eastern sky ;

(*b*) The over-sun glare—a white, luminous area in the western sky, well above the sun ;

(*c*) The twilight arch—a bright red or gold segment across the western sky after the sun has set ;

(*d*) The purple light, succeeding the over-sun glare after the sun has set. On mountains this produces the well-known Alpine after-glow.

Frequently a second similar series of phenomena succeed the first, and in the same order.

The counter-glow and the twilight arch are attributed to the scattering of the light by the air molecules. The over-sun glare and the succeeding purple light and after-glow, however, are due to diffraction by the dust particles.

These phenomena become greatly enhanced after a great volcanic eruption—for example, Krakatoa. The distance from the sun of the brightest region of the over-sun glare corresponds to the distance of Bishop's ring.

The brighter, more vivid colours of sunrise and sunset are probably due to the atmospheric dust and water particles, the softer, more delicate shades and gradations being caused by the scattering of the light by the gas molecules.

The Thermal Effects of Atmospheric Dust

The presence of dust and smoke particles in the atmosphere increases its capacity for absorbing and radiating heat; and thus reduces its transparency to heat rays. This affects the atmospheric temperature in three ways :—

(*a*) The heat rays are partly absorbed by the dust particles, which then warm the surrounding air by conduction.

(*b*) The intensity of the transmitted rays is diminished, so that the temperature rise at the ground level during the day is checked. Consequently, the diurnal temperature range is decreased.

(*c*) Radiation from the ground and from the dust particles that are suspended in the lower air is restrained. This tends to give higher minimum temperatures.

This principle is extensively employed to protect small fruit and garden crops from injury by frost. A smoke cloud is formed by kindling a suitable fire, and serves to check the loss of surface heat by radiation from the ground or crops.

By their action in absorbing and radiating heat energy, and communicating their resulting change of temperature to the surrounding air, the dust particles promote thermal changes in the air, to which the formation of certain forms of fog and mist are due.

Duration of Sunshine.—A black or brown city fog, that is formed by the condensation of water vapour upon the particles of the smoke cloud, is very much more opaque than a white mist. Consequently, the heat rays from the sun are unable to penetrate it to any appreciable depth, so that in a great city like London the fog persists all day, while in the surrounding country it may have evaporated by midday.

As a result of this greater stability of the city fogs, the observed hours of sunshine in the heart of a large city are frequently much less than in the adjacent country districts. The monthly average duration of bright sunshine (per cent. of total possible) at places increasingly distant from the centre of London are compared in Table XIX. The figures are derived from figures extending over a period of twenty years.[13]

TABLE XIX.

Station.	November	December.	January.	February.
Bunhill Row .	22·8	7·5	14·1	30·6
Westminster .	27·7	13·1	18·4	32·8
Kew . .	50·8	38·1	40·3	54·6
Cambridge .	61·0	40·6	48·9	73·8

use of efficient combustion processes, so that to-day the city is " as clean as Bath " (Saleeby).

Similar investigations have been carried out in this country, although up to the present they have not borne much legislative fruit. Very valuable investigations have been carried on during the past nine years by a special committee on atmospheric pollution, appointed by the Meteorological Office. The results of this work to date are embodied in eight annual reports.[4]

Atmospheric Water

Water evaporates into the atmosphere continually from the surfaces of oceans, rivers, lakes and ice-fields, and from moist ground and vegetation. The rate of evaporation depends upon the temperature of the surface water, and the temperature, humidity and wind velocity of the air that is actually in contact with the water.

In spite of this continual evaporation, the atmosphere remains unsaturated, owing to convection currents that carry the warm, humid air up into colder air, where much of its contained water vapour is precipitated as rain or snow. At the close of the cycle the air returns to the surface relatively dry again.

The amount of water vapour in the air varies from a fraction of 1 per cent. by weight in arid regions to 5 per cent. of the air in warm, humid regions.

The capacity of air for absorbing and holding water vapour is practically the same as that of an equal volume of empty space. This capacity increases with rising temperature, being doubled by a rise of from 10° to 11° C. On a very cold day in winter ($t = -8°$ C.), the air will be saturated if it contains 0·2 per cent. water vapour. On a hot day in summer ($t = 45°$ C.), it will, if saturated, contain 5 per cent. Under suitable conditions of temperature and pressure, this water vapour will condense to form cloud, rain, snow or hail.

Cloudy Condensation.—When a mass of air, saturated with water vapour and containing a sufficient number of suitable nuclei, is cooled below its dew-point, some of the water vapour

condenses upon the nuclei to form a cloud. At temperatures above the freezing point, the particles of the disperse phase will be liquid. At lower temperatures they will be solid, or sub-cooled liquid.

In the absence of nuclei, condensation can only occur if the air is very highly supersaturated, and would then produce fine rain. It is unlikely that the degree of supersaturation ever approaches such high values in the atmosphere.

A mass of air may be cooled to its dew-point :—

(*a*) By contact with a cold surface, which may be either solid, liquid or gaseous. (Surface condensation.)

(*b*) By the expansion of the air, either by a vertical convection current or by rotation, as in a tornado or the funnel of a water-spout. (Volume condensation.)

(*a*) **Surface Cooling.**—During clear nights, the surface of the earth loses heat by radiation, so that its temperature and that of the air adjacent to it are lowered. The cooling effect is the most pronounced on a calm night. After the air has been cooled to the dew-point, all further loss of heat results in the deposition respectively of dew or hoar-frost at temperatures above or below the freezing point. At the same time, the latent heat that is set free by the condensation of this water vapour diminishes the rate of cooling of the surface of the earth and of the adjacent air.

Similarly, when a mass of relatively warm, moist air comes into contact with any colder surface—for example, a bank of snow, or a mass of colder air—water or ice is formed at the surface of contact.

The quantity of vapour that is condensed will depend upon the specific heat of the cooler surface —*i.e.*, upon its capacity for absorbing heat from the air. As condensation proceeds, latent heat is set free, and if the specific heat of the cooling surface be low—if, for example, it is a gas—its temperature will rise rapidly, and condensation will be arrested. For this reason very little condensation can be effected by mixing masses of air.

It has been shown [15] that, if equal masses of saturated air, at 0° C. and 20° C. respectively, and at normal pressure, be mixed

—a very extreme case—the resulting condensation, after allowing for the subsequent warming of the mixture by the latent heat of condensation that is set free, amounts to 0·6 grams water per 1,000 grams of air. This corresponds to a concentration of 0·74 gram per cubic metre, a quantity capable of producing only a light cloud, through which objects could be seen at a distance of 70 metres. Assuming the diameter of each cloud particle to be 0·033 mm., there would be thirty-nine such particles per cubic centimetre.

From such a cloud 1 kilometre thick, complete precipitation would produce a layer of water only 0·074 cm. deep.

In certain circumstances, the effect of surface condensation may closely resemble that of volume condensation. Particles of atmospheric dust, owing to their greater surface area, radiate heat more rapidly than the molecules of air in which they are suspended. Consequently, they become colder than the surrounding air, and when the temperature of the dust particles reaches the dew-point of the water vapour in the air, some of the water vapour condenses upon them, forming a mist or fog. In this way a ground fog is formed on a clear evening, as the air drifts along the ground after a warm day.

(*b*) **Volume Cooling.**—In the atmosphere, cloudy condensation is nearly always brought about by expansion.

A warm, humid mass of air, carried upwards by a convection current, expands as the pressure of the surrounding air decreases. The rate at which it expands depends upon the velocity of ascent—that is to say, it depends upon the strength of the convection current. The more rapidly it ascends, the more nearly does the expansion become adiabatic. In any case, the gas can only expand by performing work against the surrounding air, and is, therefore, cooled uniformly throughout its mass.

When it has become cooled as far as its dew-point, water vapour begins to condense upon the nuclei that are present, and a cloud is formed. The form of the cloud and the altitude at which it is formed depend upon the initial temperature and humidity, and the vertical temperature gradient in the surrounding air.

Condensation Nuclei in the Atmosphere.—The number of

condensation nuclei per cubic centimetre of air in different localities was shown by Aitken [16] to vary widely, from less than 100 per cubic centimetre on the summits of the Alps and in mid-ocean to thousands per cubic centimetre in many country districts, and reaching as many as 100,000 to 150,000 per cubic centimetre in the air above cities such as London and Paris.

Aitken assumed that supersaturated water vapour condensed upon the dust particles, on account of their relatively large size, and that, therefore, a determination of the number of condensation nuclei indicated the number of dust particles present per cubic centimetre. It has been shown, however, more recently [17] that when the number of actual dust particles per cubic centimetre is enormously increased, it does not necessarily increase the number of water droplets per cubic centimetre that form when the vapour condenses. Further, in humid air at a temperature some degrees above its dew-point, the hazing effect, due to dust particles, grows in intensity, owing to the progressive condensation of further water vapour from the air.

It would appear, therefore, that only dust particles that are chemically or physically hygroscopic actually function as condensation nuclei.[17] These "dust" particles may be solid or liquid —*e.g.*, NaCl (from the evaporation of sea spray), or SO_3 (from the action of ultra-violet light upon SO_2, formed by the combustion of sulphur in coal). NO_2, H_2O_2, NH_3, also are produced by the direct action of sunlight upon the oxygen, nitrogen and water vapour of the atmosphere.

Ordinary gaseous ions—small ions—cannot possibly be regarded as condensation nuclei, as there is no evidence that supersaturations of four and upwards are obtained in the atmosphere. Ions consisting of electrically charged, hygroscopic particles, however, will serve as nuclei, but only because of their hygroscopic nature.

It is not possible to calculate the amount of water that is condensed for a given rise in altitude or for a given drop in temperature, simply from the initial temperature, humidity and pressure.

The rate of cooling with elevation is decreased by the latent heat set free by condensation, and the amount of condensation is also diminished by the increase of volume, which itself is a function of the temperature and pressure. Unsaturated air cools through 1° C. during an ascent of 100 metres. Saturated air, owing to the liberation of latent heat, only cools through 0·54° C. At temperatures below 0° C., the problem is further complicated by the latent heat set free by the solidification of ice.

As the cloud rises further, the droplets steadily grow as further condensation continues. Also, because of their greater density, they tend to rise more slowly than the air itself—particularly as they become larger than 0·1 mm. (drizzle).

Now adiabatic expansion implies that all the products of condensation—cloud particles, raindrops, snowflakes—are carried along with the identical mass of air from which they were condensed. Actually, the more highly dispersed portion of the condensate is carried along with the air, while the coarser droplets are gradually left behind.

The character of the resulting cloud formation will depend upon the humidity, temperature and velocity of the ascending air current. Warm, humid air will soon reach its dew-point, and will produce a copious cloud at no great height from the surface of the earth. Fairly dry air may ascend to a great height before reaching its dew-point, which may be considerably below 0° C. The water vapour will then condense to form ice crystals. These ice crystals fall slowly through the atmosphere, the longer axis horizontal, rotating or oscillating slightly about their horizontal axes. Lunar and solar haloes are produced by the diffraction of light by a cloud of these crystals. Snow is formed by the coalescence of fine ice crystals.

When a cloud of water droplets descends through a layer of very cold air, the particles become supercooled, possibly to as low a temperature as — 20° C. These supercooled water droplets solidify the moment they touch each other or any other liquid or solid object.

Summary.—It will be seen that, according to the temperature

and rate of condensation, the products of condensation may assume many different forms. These may be :—

(*a*) **Dew,** formed by the condensation of water vapour upon cooled surfaces—generally cooled by radiation.

(*b*) **Frost**, formed similarly to dew but upon surfaces at a temperature below freezing point.

(*c*) **Free drops**, formed by the cloudy condensation of water vapour upon free nuclei at temperatures above 0° C. These drops may range in size from cloud or fog particles to large raindrops.

Frequently, when a cloud is cooled to temperatures below 0° C., it consists of subcooled drops of water.

(*d*) **Hoar-frost**, formed by cloudy condensation, occurring at temperatures below 0° C. to produce ice crystals instead of water droplets.

(*e*) **Rime**, an accumulated feathery deposit of ice, often many inches thick, on the windward side of exposed objects. It is formed by the impinging of subcooled fog particles, and, therefore, develops on the windward side of an object.

(*f*) **Glaze**, a smooth coating of clear ice on trees, ground, etc., generally due to rain falling on surfaces cooled below 0° C.

(*g*) **Snow**, a flocculated cloud of ice crystals.

(*h*) **Sleet**, rain frozen by passage through a cold layer of air near the surface of the earth, sometimes consisting of melted snowflakes refrozen.

(*i*) **Hail**, rounded lumps of ice, consisting of a core of frozen snow, surrounded by a number of concentric layers of ice. They are only produced during thunderstorms, and are due to the violent and extensive convection currents that may prevail in hot weather carrying them round alternately up into cold air (below 0° C.) and down through warm, humid air. Each time the hailstone passes through the warm air, it becomes coated with a layer of condensed water, which freezes as the hailstone is carried through the cold region. This continues until the hailstone becomes too heavy to be carried up again, or it may be thrown from the convection current by centrifugal force.

Precipitation.—It has been suggested that rain is formed :

(*a*) By the progressive condensation of water vapour. This is unlikely, since the condensation nuclei that are present in the air are sufficiently numerous to support all the water in the atmosphere in the form of fog.

(*b*) By the coalescence of cloud particles. If cloud particles collide, they will probably behave like the drops of two colliding jets of water, and rebound from one another owing to the presence either of a film of adsorbed air or of electrical charges of the same sign and surface density.

(*c*) By the growth of the larger drops at the expense of the smaller ones, owing to the higher vapour pressure of the smaller drops. It is conceivable that some drops are larger than the others, but at diameters of 10 μ (a fog particle) or 33 μ (a cloud particle) the excess vapour pressure over the saturation pressure is only of the order of 1 part in 44,000. This factor is, therefore, negligible.

(*d*) By further condensation from the slightly warmer surrounding atmosphere. This effect is very small, and is speedily checked by the liberation of latent heat at the surface of the drop.

Rain is only formed in an ascending air current. Vertical convection does not usually occur in a fog or an ordinary cloud, so that rain is not generally produced by the flocculation of a cloud. Cloudy condensation first occurs, and then, as the air still rises, the cloud particles begin to lag behind. Thus, the rising air contains progressively fewer nuclei or droplets. It is at this stage, presumably, that a high degree of supersaturation, combined with relatively few condensation nuclei, leads to the formation of a relatively coarse condensate, of the order of a drizzle. These droplets fall through the ascending cloud, and grow through coalescence, since they may be assumed to be electrically charged but of different sign or density from the cloud particles. Colliding droplets will coalesce if they are electrically charged with charges of opposite signs, or of the same sign but of different density.

The dimensions of the different forms of precipitation are compared in Table XXI.

TABLE XXI.

Precipitation Values.

(*Air density as at 0° C. and 740 mm. pressure.*)

Popular Name.	Precipitation intensity, mm. per hour.	Diameter of drop, mm.	Velocity of fall, m. per sec.	Milligrams of liquid water per cub. metre of air.	Height of cloud above surface, metres.
Clear	0·00	—	—	0·00	—
Fog	Trace	0·01	0·003	6·0	0
Mist	0·05	0·1	0·25	55·5	100
Drizzle	0·25	0·2	0·75	92·6	200
Light rain	1·00	0·45	2·00	138·9	600
Moderate rain	4·00	1·0	4·00	277·8	600
Heavy rain	15·00	1·5	5·00	833·3	1,000
Excessive rain	40·00	2·1	6·00	1,851·9	1,200
Cloudburst	100·00	3·0	7·00	5,401·4	1,200

From this table it will be seen that clouds and fogs remain suspended in air simply because their particles are so small that the attraction of gravity is almost completely balanced by the frictional resistance of the air. The least upward movement of the air serves to check any tendency to settle that they may possess.

Raindrops fall more rapidly the larger they are. When the drops are larger than 0·2 mm. diameter the rate of fall is proportional to the diameter.

Large drops—above 4·0 mm.—are flattened as they fall by the resistance of the air, and become broken up into two or more smaller drops.

Fog Dissipation.—From time to time, attempts have been made to influence the formation or precipitation of clouds. It was thought that clouds could be precipitated as rain by means of a loud noise—for example, thunder or cannonading, or even the ringing of bells. This was supposed to agitate the cloud particles and cause them to collide and coalesce. Experiments made by the United States Government, in which heavy charges were exploded in the interior of clouds without any result, disproved this theory.

The dissipation of fog is a matter of direct practical impor-

tance to the shipping and flying industries, and to all who dwell in cities or industrial areas. The stability of an ordinary sea or ground fog is due to the inability of the water droplets to settle, or to coalesce with one another. This may be due to the protective action of films of adsorbed air, or to the presence upon the droplets of electric charges of the same sign and density.

Following upon his experiments upon the electrostatic precipitation of lead fumes, Sir Oliver Lodge endeavoured to dissipate fogs at Liverpool by means of powerful high-tension discharges, similar in character to those that were used in electrostatic fume precipitation, but of greater magnitude. The fog was successfully dissipated or repulsed throughout a space of a few yards from the discharge electrode. Lodge suggests that fog may be successfully dissipated on a large scale, if sufficiently powerful discharges are employed.

Recently [18] attempts have been made in America to dissipate clouds and fogs by sprinkling an electrically charged dielectric—for example, sand—over the surface of the cloud from an aeroplane. In these experiments, a single aeroplane succeeded in dissipating a cloud a mile or two long, and over 1,000 feet deep, in a few minutes by using 100 lb. of sand (150 mesh), charged to 14,000 volts.

It is possible that this method may be applied also to the dissipation of the smoke fogs of industrial areas. It is not certain that rain can be produced in this way, since the formation of rain appears to depend upon the condensation of water vapour in the presence of relatively few nuclei.

In some of the vine-growing districts of Europe, vortex rings of smoke are projected upward, with the object of preventing hail by breaking up the convection currents to which the formation of hail is due. It has been clearly shown that the vortex rings, even if they reach the clouds, cannot have any appreciable action upon the formation or fall of the hailstones.

Rain can only be prevented by cutting off the supply of moisture by preventing vertical convection, or by greatly increasing the number of nuclei present in the upper part of a convection current, and so promoting cloudy instead of rainy condensation.

It is frequently observed that after a prairie or forest fire no rain is precipitated for a long time, owing to the increased concentration of smoke particles in the upper air.

Optical Effects of Atmospheric Water [19]

When sunlight falls upon the droplets of a cloud or fog about 6 per cent. of it is reflected backward and 94 per cent. of it passes on through the drop. As the light penetrates more deeply into the cloud its intensity rapidly diminishes. It is found that, when the sun is just visible through a stratus cloud, the intensity of the transmitted light is only one ten-thousandth part of its original value.

The brightness of the sun when seen through a haze or fog is similarly diminished by scattering. The short wave light is more completely scattered than the longer wave light; consequently, the disc of the sun appears yellow or red when viewed through a haze or fog.

The proportion of the incident light that is reflected by a cloud to an observer depends upon the angle made by the sun and the observer at the surfaces of the drops. At an angle of 165 degrees, the intensity of the reflected light is six times that of the light that is reflected when the angle is 10 degrees. The mean reflecting power of a cloud is about 65 per cent.

Rain falling through the air greatly reduces its transparency. Large drops cut off more light than small drops do, but owing to their greater rate of fall, the apparent diminution of the intensity is lessened by the persistence of vision. For a given rate of precipitation (amount of water precipitated per hour), the obscuring power of the rain is proportional to the square root of the volume of the drop.

Refraction Phenomena.—Rainbows are seen when an observer stands with his back to the sun and looks at falling rain, provided that the angle that is subtended at the drops by the sun and the observer lies between 40 degrees and 42 degrees. Rays from the sun, entering the raindrops, are refracted and, after undergoing internal reflection, are refracted out again to the eye of the observer. During this double refraction, the sunlight is dispersed into a spectrum.

The form and colours of the bow depend upon the angle made by the sun and the observer at the surface of the drops, and also upon the size of the drops. If the drops are above 1 mm. in diameter, they produce a well-defined single spectrum. The colours are brightest when the diameter of the drops is from 0·2 to 0·4 mm.

With very small drops less than 0·1 mm. in diameter, the emergent light is very much less dispersed—the maxima for the different colours of the spectrum almost coincide—so that the bow is nearly white.[20] Such white rainbows are observed when sunlight, falling upon the face of a fog or cloud, is reflected to an observer standing near to the cloud—for example, upon the cloud-wreathed summit of a mountain. These cloud or fog bows also differ from rainbows in their dimensions. The diameter of a bow, whether caused by rain or cloud, becomes greater as the drops become larger. Consequently, cloud or fog bows have a smaller diameter than rainbows. The breadth of the band of colour in a rainbow is about 1·5 degrees. The breadth of a cloud bow is much larger, and may be as much as 6 or 7 degrees.

White bows are also produced by subcooled droplets of rain or cloud.

Diffraction Phenomena.—When light falls upon small drops of water, less than 0·01 mm. in diameter, it is absorbed by the drop, secondary rays being emitted, some forward and others backward. When a bright source of light is viewed through a cloud of such droplets, it is seen to be surrounded by a coloured circle or corona. If the source of light be behind the observer, and the cloud be in front of him, his shadow will be cast upon the cloud and will be seen to be surrounded by a bright halo or glory, made up of the light rays that are scattered backward by the droplets towards the observer.

Lunar or solar coronas [21] are seen surrounding the moon or sun respectively when the moon or sun is viewed through a light cloud. The diameter of a corona is very much less than that of a rainbow, rarely exceeding 15 degrees. It is inversely proportional to the size of the droplets. A corona, of which the angular diameter is 15 degrees, is produced by droplets of

0·002 mm. in diameter. The average size of the droplets of a cloud can be estimated from the diameter of the solar or lunar haloes that such a cloud produces. The colours of a corona are arranged in the reverse order to those of a rainbow, the blue being innermost.

Fragments of large diameter coronas are sometimes seen in the sky in the form of detached luminescent clouds.

Glories are seen surrounding the observer's shadow when it is cast by the sun upon a cloud or bank of mist. The well-known "spectre of the Brocken" is formed in this way. Similar effects are noticed when the shadow of an aeroplane is cast upon the upper surface of a cloud.

Other striking optical phenomena are produced by the reflection and refraction of light by ice crystals in the atmosphere. Naturally these phenomena are most frequent in the polar regions, and are a familiar feature of all descriptions of the polar skies.

A ray of light, passing through a crystal of ice, may be refracted through two edges inclined to one another at an angle either of 60 or 90 degrees. The crystals may be disposed in the air with their edges all vertical or all horizontal, or they may all be nearly vertical. They may also be disposed at random, with no common orientation. Depending upon the particular set of conditions that exist at the time, the resulting phenomenon may be a halo of 22 or 46 degrees angular diameter, a parhelion of similar diameters, or a parhelic sun pillar, etc.

Other arcs, parhelia, sun pillars, haloes, etc., are formed as a result of the *reflection* of light by ice crystals in the atmosphere.

Atmospheric Electricity [22]

In fine weather the atmosphere is charged positively, the ground negatively. The vertical potential gradient near the ground is about 100 volts per metre. At increasing altitudes, the potential gradient falls off, being less than 1 volt per metre at altitudes considerably less than 10 kilometres. At greater altitudes than 10 kilometres, it appears to be constant.

In fine weather, the potential at any point in the stratosphere (above 10,000 metres) is probably less than 10^6 volts. It would

appear, therefore, that the atmospheric charge resides in the lower layers of the atmosphere—lines of force starting from the negatively charged ground, and terminating upon positively charged dust particles or positive ions suspended in the troposphere.

Vertical Potential Gradient.—The vertical potential gradient reaches a maximum value in mid-winter, and a minimum value in mid-summer. It varies also during the day, showing in winter a minimum value in the early morning and a maximum in the late afternoon. These annual and diurnal variations differ considerably in different localities, according to local meteorological conditions. In some localities, particularly in summer, a second minimum is shown in the early afternoon. At Simla, in June, the minimum is so marked that the potential gradient becomes negative for an hour or two every afternoon. Such very low or negative values are associated with great dustiness of the air.

The potential gradient is greatly affected locally by the presence of dust or fog. In a fog, the potential gradient is generally several times its normal value, owing to the adsorption of ions by the fog particles. Dust clouds produce very large changes, depending upon the character of the dust. In Bloemfontein (South Africa), the normal and fine-weather charge at a height of 4,500 feet seldom exceeds a maximum value of 200 volts per metre. It was shown that the charge on the dust itself was positive. Consequently, the strong negative charge produced by the dust must reside upon the molecules of the air itself.

In England, dust (limestone) above a busy road became charged negatively, and increased the positive charge of the air.

The charge that is acquired by any particular kind of dust appears to depend upon the chemical character of the dust,[23] as follows :

(1) Non-metallic dust gives positively charged clouds.
(2) Metallic dust gives negatively charged clouds.
(3) Acidic oxide dust gives positively charged clouds.
(4) Basic oxide dust gives negatively charged clouds.

(5) Salts give charges depending upon the relative strength of the constituent acidic and basic ions.

When ice crystals collide, they become negatively, and the air positively, charged. Fine snow, driving in a cold, dry atmosphere, exercises a large influence upon the potential gradient.

During rain, there is a large exchange of charges between the air and the ground. The potential gradient near the ground fluctuates rapidly, and may be either positive or negative, and may reach values of the order of 10,000 volts per metre during the passing of a thunder cloud.

Air-Earth Current.—The normal vertical electrical field tends to drive positively charged ions, dust particles, and water droplets down to the earth, and negatively charged particles upwards.

The electrical conductivity of the air at any point will depend upon the number of such charged particles present, the rate at which they move under the existing vertical forces, and the charge that is carried by each.

"Small ions," consisting of gas molecules which have lost or acquired one or more electrons, possess a mobility of about 1 cm. per second at a potential gradient of 1 volt per centimetre. "Large ions," consisting of dust particles, water droplets, etc., to which a small ion has become attached, move with only about one three-thousandth of this velocity.

Although the large ions may greatly outnumber the small ions, yet, because of the enormously greater mobility of the small ions, they will carry most of the current.

The conductivity, therefore, depends upon the number of small ions that are present per cubic centimetre of air. It will be diminished if fewer small ions are produced per second, or if more are lost by recombination with each other, or by conversion into the slow-moving large ions. Generally speaking, the dustiness of the air is the most important factor. A high dust content means fewer small ions and a lower conductivity.

Small ions are produced by the action of :

(1) Radiations from radioactive material in the earth and the atmosphere (emanations from radium and thorium).

(2) A penetrating radiation from outer space.

The air above the sea only receives ions due to the radiation from outer space. On the other hand, owing to the dustiness of the air over the land converting small ions into large ions, the rate of ionisation over land and sea is practically the same.

At higher levels, the conductivity increases, owing to the lower dust content. Owing to the much lower density of the air, the small ions have greater mobility and a lower rate of recombination. Also, the rate at which ions are produced by the radiation from outer space is greater.

At levels above 60 to 100 kilometres, the air is probably ionised directly by the action of sunlight. This ionisation will diminish rapidly during the night, owing to the cessation of the photoelectric action and the recombination of the ions that already existed. At higher levels, probably above 80 to 100 kilometres, the air appears to be permanently ionised with negative ions. The transmission of wireless waves round the curved surface of the earth has been attributed to the reflecting action of such a highly-ionised, conducting ceiling in the upper atmosphere, having a specific resistance of about 0·75 megohm per cubic centimetre. The specific resistance of ordinary air at normal temperature and pressure is about 10^9 megohms per cubic centimetre. The existence of this highly ionised layer is attributed to the ionising action of negatively charged solar dust.

The average air-earth current is about 2×10^{-16} amps. per square centimetre. This is equivalent to 2 micro-amperes per square kilometre, or 1,000 amperes for the whole surface area of the earth.

Assuming that this current flows uniformly from air to earth all over the world, it would convey to the ground every minute a positive charge that is equivalent to one-tenth of the total negative charge on the ground. Yet the negative charge upon the ground remains practically unchanged. Clearly, at some points on the earth's surface, a current must flow from ground to air.

Wet Weather.—During the precipitation of rain, snow or

hail, the falling particles are charged positively or negatively, and, therefore, carry a convection current of electricity from air to ground (if they be positively charged), and from ground to air (if negatively charged). Such currents rarely exceed ½ milliampere per square kilometre, and, on the whole, carry more positive than negative electricity from the air to the ground.

Water droplets may be electrified :

(1) By adsorption of ions. Owing to their greater mobility, more negative ions will be adsorbed than positive ions.

(2) By the action of ultra-violet light, especially in the upper air.

(3) By friction between water drops and ice crystals, or dust particles.

(4) By collision between large and small drops.

(5) By the breaking up of large drops by the resistance of the air through which they are falling at high velocity. The ruptured drop acquires a positive, the air a negative charge.

During a thunderstorm a lightning flash may carry a positive charge from cloud to ground or *vice versâ*. Generally, it is the latter. The potential of a thunder cloud must approach 30,000 volts per centimetre to produce a lightning flash. The average current during a lightning flash is about 1 ampere.

A thunder cloud functions as an electrical machine.[26] It is very lofty, its base being from 1 to 2 kilometres, and its summit from 5 to 10 kilometres above the ground. The upward rush of air, produced in the cloud by the powerful convection current, carries the fine charged cloud particles upwards. The oppositely charged large drops and hailstones settle to the lower portion of the cloud. The E.M.F. between the summit and base of a thunder cloud is probably of the order of 10^9 volts. This is very much greater than the potential of the ground or of the upper air (10^6 volts), so that discharge may take place from pole to pole of the cloud, either directly, through the cloud, or *viâ* the ground. The cloud may also discharge partly to the conducting upper layers of the atmosphere.

In addition to a direct discharge between a thunder cloud and the ground, the greatly increased potential gradient in the air

between the cloud and the ground and the increased ionisation produced by the evaporation of charged drops and the splashing of large drops on the ground increases the conductivity of the air, so that a continuous current is conducted between the cloud and the ground. The direction of this current will be determined by the character of the vertical electrical force. The electric field at the ground may be strong enough to produce numerous point discharges—for example, from blades of grass—that collectively may carry a current larger than 1 ampere.

It is probable that the electric charge that normally exists in the atmosphere in fine weather is maintained partly by such currents passing from the earth to the air during thunderstorms, and partly by the existence in the neighbourhood of the poles of a negative potential gradient, due to ionisation that is produced by particles of solar dust in the upper polar atmosphere.

It is estimated that a current of about 1 ampere passes from the ground to the air during a thunderstorm, and that approximately one thousand such clouds are always in action at any given moment.

The upper atmosphere is sufficiently ionised to be a good conductor. It will, therefore, distribute charges received from thunder clouds, or by the earth-air current in the polar regions to fine weather regions of the earth.

Light clouds and mists diminish the conductivity of the air by adsorbing ions, thus increasing the vertical electrical force within the cloud and diminishing that in the air above and below the cloud. A very thick cloud layer may reduce the vertical current, and hence the potential gradient at the ground, almost to zero.

Cumulus clouds do not appreciably affect the potential gradient at the ground level.

The charges carried by raindrops appear to depend upon the rate of precipitation. Positively charged rain is more frequent, the heavier the fall. If the rate of precipitation exceeds 1 mm. in two minutes, the droplets are always charged positively. The electrical convection current due to rain is often as much as a thousand times as great as the normal fine-weather current.

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CHAPTER X

THE INDUSTRIAL PREPARATION AND UTILISATION OF SUBSTANCES IN A FINELY DIVIDED CONDITION

For many industrial purposes, it is necessary to prepare substances in a very finely divided condition. The covering power of a paint pigment, for example, is a function of the degree of dispersion of the particles of the pigment.

Finely divided materials are required for use as catalysts for gas reactions, as absorbents for clarifying liquids, as precipitates for dissolved substances, as opalising agents for glass and enamels and as medicines.

The chemical activity of a reducing agent, such as zinc dust, depends upon its specific surface and its freedom from oxide.

Many organic liquids that cannot readily be evaporated by ordinary methods without spoiling the product can be evaporated successfully by spraying them in a very finely divided condition into a quantity of hot gas.

Certain fuels—*e.g.*, oil and various grades of coal—are efficiently and conveniently burned in the form of spray or fine powder.

Condensation Processes

Metallic Powders.—Finely divided zinc and aluminium are used extensively as reducing agents, and in the manufacture of special paints. These are best prepared by condensing the vapour of the metal in a suitable, non-oxidising atmosphere. The vapour may be produced by heating an ore with a suitable reducing agent, or by heating the metal itself.

A very convenient method is to volatilise the metal by means of an enclosed electric arc. The vapour, diluted with an indifferent gas[1]—for example, nitrogen—is drawn from the furnace and cooled quickly, thus producing a very fine powder, free from oxide. The degree of dispersion that is obtained will

be higher the greater the density of the gas, the higher its pressure, and the more rapid the cooling of the vapour. A very high-grade zinc dust, averaging 99 per cent. zinc, can be obtained in this way in an atmosphere of nitrogen. Generally speaking, if the vapour is cooled rapidly so that condensation occurs at a temperature well below the melting point of the metal, dust will be produced.

If, as in the condensation of zinc vapour that comes from the retorts during the smelting process, the formation of dust is to be avoided, the vapour must be cooled slowly, so that condensation occurs at temperatures well above the melting point —*i.e.*, between 430° and 560° C.[2]

The Schoop Process.[3]—In this process, a coating of a metal is formed on all kinds of solid surfaces by spraying them with the molten metal. A jet of compressed air impinges upon an arc between two wires of the metal, atomises the molten metal, and projects it forward in the form of a fine spray. Smooth, well-adhering deposits of metal are obtained with compressed air at a pressure of five atmospheres. Aluminium or copper, sprayed on a glass surface at a distance of a few inches, adheres so tenaciously that it is impossible to remove the film without destroying the glass surface. Microscopic examination reveals the fact that the surface of the glass is penetrated by the metal.

At greater distances, the metal can be sprayed safely upon flowers, paper, textiles, even the hands, owing to the small heat capacity of the particles, and therefore the rapid cooling effect of the air jet.

An alternating current is necessary to ensure equal consumption of the two wires.

Using wires of copper and zinc, a coating of brass can be formed, the composition of the brass being determined by the relative speeds at which the two wires are fed to the arc.

Refractory metals, such as molybdenum and tungsten, are sprayed by maintaining an arc between a stout wire of the metal and the edge of a metal disc, rotating at from 10,000 to 20,000 r.p.m. The wire is inclined to the edge of the disc at an angle of about 30 degrees, and the molten globules of metal

are sprayed into the surrounding gas, on account of the high velocity of the edge of the disc.

When certain metals—for example, lead—are sprayed, the particles apparently become surrounded by a film of adsorbed gas. Consequently, the deposit is not coherent, and in contact with water may separate from the surface to form a coarse metal suspension in the water.

Metal paints are conveniently made by spraying a metal into a suitable oil.

Carbon black, or lamp black, is used as a pigment in the preparation of paints and printers' inks. It is prepared by burning a hydrocarbon in an insufficient supply of oxygen—for example :

$$CH_4 + O_2 \rightarrow 2H_2O + C.$$

The carbon condenses in the form of a dense smoke that is passed into a large chamber, in which it cools and settles.[4]

In this country the hydrocarbon is generally a mineral oil. In America natural gas is used, from 0·8 to 1·5 lb. of carbon black being obtained per 1,000 cubic feet of gas—CH_4—consumed. This is less than 5 per cent. of the total carbon in the gas. If the gas can be more completely decomposed by some other means, or if the heat generated by the combustion of a part of the gas can be applied more efficiently to the decomposition of the remainder, then a better yield of carbon would be possible. Owing to the continually increasing demand for natural gas for other purposes, the manufacture of carbon black by this process is prohibited in many of the States.

It is now proposed to decompose the hydrocarbon—gas or oil vapour—by the application of a high-tension, intermittent arc.[5]

The recovery of carbon per unit volume of gas depends upon the current, and the rate of gas flow. The maximum yield per kilowatt hour is obtained with 6 amperes flowing in the primary circuit, and a consumption of 41 kilowatts per pound of carbon black made.

In some plants, the carbon black is collected in bag filters, or is precipitated electrostatically.

In an alternative process, the gas is decomposed by forcing

it through a molten metal.[6] A cloud of carbon in hydrogen is obtained, from which the carbon is precipitated electrostatically, the hydrogen being obtained as a by-product. The quality of the product and the efficiency of the process will depend upon the intimacy of contact between the gas and the metal.

A microscopical examination shows that when the carbon black is made from oil, the particles are frequently coated with a film of oil, owing to the condensation of unburnt oil vapour. If made from gas, the particles may be coated with a film of water. A finer product, free from oil or water, can be obtained by condensing the carbon on a hot surface, and removing it from the accompanying gases at a temperature above the dew-point of the oil or water.[7]

Carbon black adsorbs gases very markedly. As little as 5 per cent. of the apparent volume may be due to actual solid, the remainder being adsorbed gas. A litre of carbon black may contain 2·5 litres of adsorbed air, measured at 0° C. and 760 mm. The adsorbed air is readily displaced by water, unless the carbon black be oily. The presence of mineral oil also interferes with the drying of a paint that is made with it.

Zinc oxide, prepared in great quantities, either by the oxidation of zinc sulphide, or by the combustion of zinc vapour, is also used as a pigment.

When zinc sulphide is roasted at a bright red heat in a small reverberatory furnace in the presence of an excess of air, it oxidises to form zinc oxide and sulphur dioxide. These form a dense smoke, from which the zinc oxide is separated in a settling chamber, or better, by passing the smoke through a bag filter.

Specially fine grades of zinc oxide, of good covering power, are prepared by burning highly preheated zinc vapour in an excess of air, rapidly cooling the fume, and collecting the product in a bag filter. The diameter of the particles of zinc oxide prepared in this way is 0·25 μ and less. The flocculation of the fume can also be inhibited, and a fine product obtained, by diluting the smoke with carbon dioxide immediately after it has formed.[8]

Zinc oxide also adsorbs gases strongly, and forms a very

light, limpid powder, from which the adsorbed gas can be displaced by steam or water.

Oxides of arsenic, tin, bismuth, etc., are formed by similar methods from the metal, or compounds such as sulphide or carbide. They are frequently obtained as by-products in a smelting process.

Catalytic substances, such as nickel and iron oxides, in conjunction with carriers such as oxides of aluminium, titanium, tin, silicon or vanadium, may be obtained by electrically vaporising compounds or alloys of the metals with aluminium, titanium, tin, silicon, vanadium, etc., in a current of air, subjecting the vapour and air to a whirling action in a large chamber, and then collecting the oxide smoke by electrostatic precipitation. When ferro-titanium or ferro-vanadium is treated in this manner, and the product reduced in hydrogen, a pyrophoric product is obtained.[9]

Spray Evaporation

Certain substances—*e.g.*, milk, white of egg, phosphoric acid, Na_2SiO_3—cannot be evaporated to dryness by ordinary processes of evaporation, on account of their liability to undergo some chemical or physical change that makes them unfit for the particular purpose for which they were intended. Dried milk, or blood, for example, are no longer water-soluble. Sodium silicate becomes gelatinous and insoluble.

Such substances may generally be evaporated to dryness by the spray process without it in any way reducing their solubility or other desirable properties. By this process, also, any substance may be obtained in the form of a fine, dry powder, provided that it can first be brought into solution or colloidal solution in a suitable solvent.[10]

In this process the solution or emulsion, previously concentrated as far as possible by ordinary methods, is discharged in a finely divided condition (atomised) into a chamber, through which a current of warm, dry air is passing. In this way an enormous surface is exposed to the air, the drops rapidly evaporate and the resulting powder is carried by the air stream to a suitable settling chamber or filter.

Since the heat is applied directly to the surface of each drop, where the evaporation actually occurs, it is almost as quickly lost again as latent heat of evaporation, so that practically no heating effect is communicated to the liquid inside the drop, the drop evaporates very quickly, and without being decomposed or coagulated.

Fig. 30 is a diagrammatic representation of a spray evaporation plant.

The liquid to be evaporated may be a solution in any suitable solvent or a colloidal solution, prepared, for example, in a colloid mill.

The extent to which the solution can be concentrated before spraying will depend upon the nature of the substance. If the solution becomes very viscous, it may be more economical to spray a less concentrated solution of low viscosity than a highly viscous solution, containing considerably less water, owing to the disproportionately high-power consumption required for such highly viscous solutions. A concentrated solution of sodium silicate ($Na_2O.2SiO_2$) of 140° Tw. (50 per cent. silicate) is very viscous and can only be sprayed with great difficulty and at pressures of many hundred pounds per square inch. At a concentration of 100° Tw. (30 per cent. silicate), however, the solution can be sprayed easily, with a comparatively small consumption of power.

The temperature at which a liquid can be sprayed will depend upon the nature of the substance, and must not exceed the temperature at which it would be decomposed or coagulated. The air temperature can be considerably higher than the actual temperature of decomposition or coagulation, since the actual heating effect at the surface of the droplets is restricted by the loss of latent heat, and is only of very short duration. The air must not be hot enough to change the chemical or physical properties of the dried product during the short time that they are in contact. Albumen coagulates at 65° C., but may be dried at 75° C. and higher. Bacterial cultures can be dried at temperatures well above their thermal death points, without being destroyed.

The degree of dispersion of the sprayed liquid should not

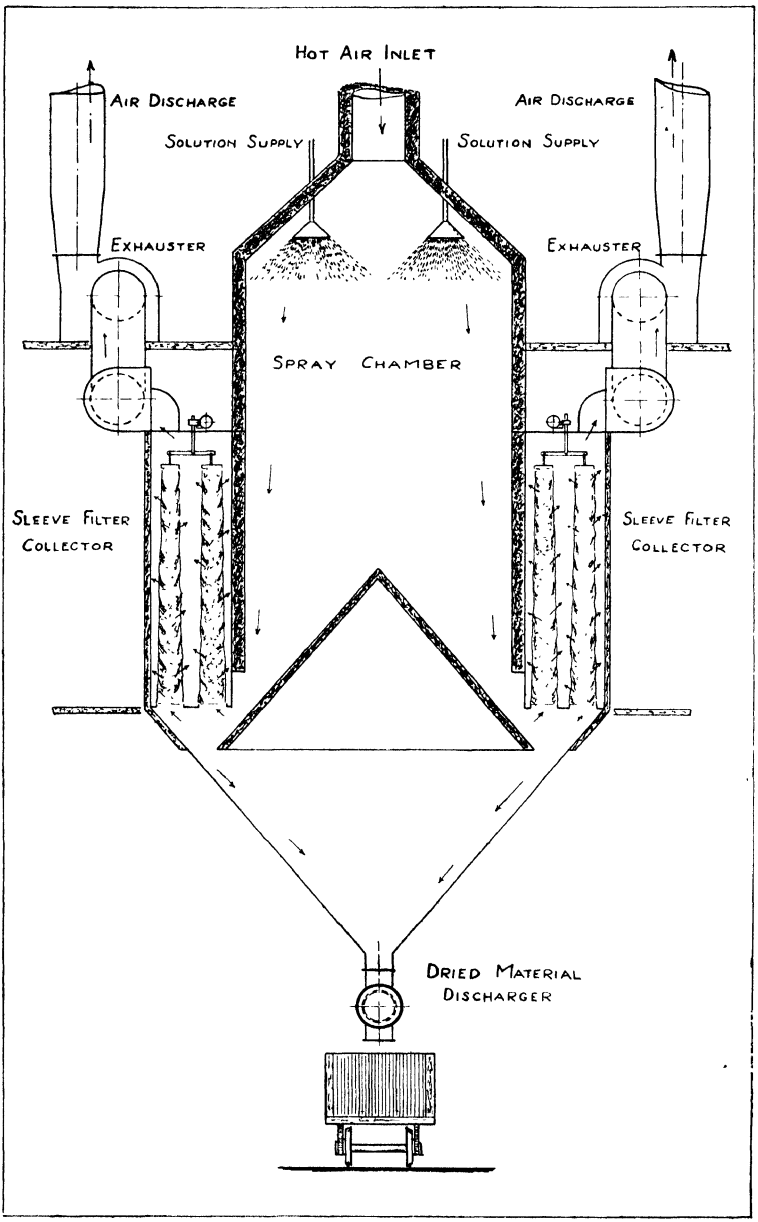


FIG. 30.—Diagrammatic representation of plant for spray evaporation.

necessarily be too fine. It will depend upon the kind of product that is required. The finer the spray the more rapid will be the evaporation, owing to the greater surface of contact, and the finer will be the product. It is frequently found, however, that if the degree of dispersion is too high, the particles become coated with a film of adsorbed gas, and are then difficult to collect. Subsequently, when mixed with water, they may be very difficult to wet and dissolve. Coarser particles may be collected on the floor of the spray chamber itself.

When a solution is evaporated in this way the size of the resulting particles of the solute will depend upon the concentration of the solution, the degree of dispersion of the spray, and the temperature at which evaporation takes place. At temperatures above the boiling point of the solvent, the particles of solute may be dispersed into yet smaller particles. If substances of higher boiling point than the solvent are added to the solution, they will be found, after evaporation, to be attached to the particles. Such substances may act as stabilising agents.

Spray evaporation is a comparatively expensive process, for in addition to the cost of spraying there is a great loss of sensible and latent heat in the outlet air. Whether it is the best method to use for a particular substance will depend upon the nature of the substance and the character of the product that is required.

In general, it is found that substances that are dried by the spray process retain their natural properties unimpaired. When dried milk is mixed with water, it again becomes normal milk. There is no sediment. It has the true milk flavour. The albumen and casein are not coagulated. The butter fat is in the form of an emulsion. The enzymes and vitamines are active.

The Combustion of Finely Divided Fuel

Of recent years a great deal of attention has been devoted to the combustion of mineral oils and coal, dispersed in the form of a fine cloud in air.

In fuel oil installations, the oil is forced under pressure

through an atomising nozzle, and enters the combustion chamber as a very fine mist. Combustion is rapid, complete and smokeless, and a very high flame temperature can be obtained.

A cloud of powdered coal (200—300 mesh) is projected into the combustion chamber of a boiler or other furnace. It burns very rapidly and completely, and produces an intense heat.

The coal is crushed, dried and then pulverised, so that 95 per cent. will pass a 100-mesh, and 85 per cent. a 200-mesh screen. In this finely divided condition, the coal particles appear to become surrounded by a film of adsorbed air. The powder flows like a liquid, and can be pumped and piped for considerable distances.

The powder, mixed with the primary air, is projected through the burner into the combustion chamber, secondary air being drawn in through a separate channel of the burner by the "injector" action of the main dust-air stream.

The system has the following advantages [11] :—

(1) Combustion is rapid, complete and smokeless. The CO_2 content of the gases is high, since much less excess air is required than in the combustion of coarse coal, whether with mechanical or hand stoking. In many boiler plants, this excess air amounts to from 50 to 100 per cent. With pulverised coal, it rarely exceeds 20 per cent.

(2) It resembles gas-firing in the ease with which combustion can be controlled. The intensity and character of the flame can be accurately determined by adjusting the proportions of fuel and the primary or secondary air. This flexibility makes powdered fuel eminently suitable for variable loads.

(3) Low-grade coals can be used efficiently. When coarse coals are fired in an ordinary furnace, the accumulation of ash in the fire seriously interferes with efficient combustion. When the coal is pulverised, the effect of the ash is reduced to a minimum. Coals containing as much as 40 per cent. ash can be fired successfully in this way. In comparing the combustion of pulverised coal with ordinary mechanical stoking, the relative advantage of the pulverised fuel rapidly increases as the ash content of the fuel rises.

(4) Labour charges, particularly in large installations, are found to be less than with mechanical stoking.

The system may have the following disadvantages :—

(1) **The Cost of preparing the Fuel in a suitable, Dry, Powdered Form.**—This amounts to not more than 1 per cent. of the total steam production of the plant, and, therefore, compares not unfavourably with the best mechanical-stoker practice.

(2) **Effect of High Combustion Temperature.**—In the early types of furnace, serious trouble was caused by the very intense combustion temperature that resulted from the rapid combustion of the fuel. The ash fused, and became deposited upon the furnace walls, so that they were slagged and corroded, and speedily wore out. This is now avoided by making the combustion chamber larger, by constructing the furnace linings of hollow firebricks, and lining the back and bottom of the combustion chamber with steel tubes, through which a part of the boiler water circulates. About 25 to 50 per cent. of the ash is deposited in the combustion chamber as a hard, dry powder—from 25 to 35 per cent. accumulates at the base of the chimney, and about 12 to 25 per cent. passes up the stack.

(3) **The Risk of Explosion.**—There is practically no risk of explosion in a properly designed plant. The original coal-air mixture is too rich in coal to be explosive. It may form an explosive mixture when stirred up by air in a draughty bin. For this reason, it is better to avoid storage of the dust, only using it as it is prepared. Secondary air may blow back into the system, owing to a stoppage of the primary air blower, but even then explosion cannot occur unless a spark also enters.

Powdered fuel installations on a very large scale are well established in America and in France. In one instance, a large boiler plant is equipped for burning powdered fuel and blast furnace gas, either together or separately. In this way, the varying outputs of blast furnace gas can be used efficiently.

Probably in the near future, other combustible dusts, at present collected as dangerous waste products, will be used as powdered fuel.

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CHAPTER XI

SMOKE IN WARFARE

GUNPOWDER and all other explosive mixtures or compounds that contain metallic salts produce smoke when they are exploded. The smoke is due to the violent dispersion of the non-gaseous reaction products. Atmospheric water vapour condenses upon these highly dispersed particles, so that the density of the smoke is rapidly increased. Practically all so-called smokeless powders produce a slight haze, due to the condensation of steam and small amounts of hydrocarbon vapours.

Before the development of smokeless powder, battles were fought amidst a general fog of gunpowder smoke. During the recent war, the production of smoke clouds became an important and highly specialised military art. Smoke clouds were used for concealing the position or movements of an attacking force both on land and at sea. Aeroplanes concealed themselves behind clouds, and dirigibles (especially Zeppelins) frequently produced their own smoke screens. Smoke was also used to carry and conceal poison gas. Finally, actual smokes of toxic substances were projected upon the enemy, with the object of incapacitating him.

In the early gas offensives, in which chlorine or phosgene were released from cylinders, the gas formed a dense, white cloud, owing to the condensation of atmospheric water vapour upon the gas particles, cooled by rapid expansion from the compressed vapour or liquid.[1]

Gas diffuses rapidly, and is fairly easily filtered by passing it through a canister containing granules of carbon and soda lime. Smoke particles, however, diffuse much more slowly, and cannot be filtered readily by such means. Consequently, irritant smoke—*e.g.*, $SnCl_4$—was added to the gas. Diphenylchlorarsine (sneezing gas), when fired in shells and detonated,

produced an exceedingly fine smoke which easily penetrated masks that relied upon the absorption of gases by granules of charcoal or soda lime. It cannot be kept out completely, even by filter paper or other similar materials.

Tolman [2] has devised a mask in which smokes can be precipitated electrostatically.

Smoke clouds were used to carry and conceal the gas. It was found that, owing to the low rate of diffusion of the particles, a smoke cloud moves bodily and carries with it the gases that are entangled in it.

Screening Smokes

Smoke screens were thrown out by merchantmen and warships to conceal their movements. A dense black smoke was produced by shutting off air from the fires. The smoke was intensified by adding wood, high in pitch or resin, to the fires.

This black funnel smoke possessed poor obscuring power. It showed frequent rents and holes, and was difficult to standardise. Also, it involved a loss of speed. It was soon abandoned in favour of a white smoke, that could be produced by chemical means.

Smoke screens soon came into use on land for concealing the movements of troops.

A screening smoke must be cheap, dense (possessing maximum screening properties), and stable. Within limits, both the density and stability can be increased by increasing the degree of dispersion.

Smokes are mostly produced by the dispersion of suitable hygroscopic substances—*e.g.*, $SnCl_4$, $SiCl_4$, oleum and S_2Cl_2—either by detonation or by combustion. Water vapour condenses upon the hygroscopic particles of the smoke, so that the density of the smoke rapidly increases, particularly in a humid atmosphere. The density of the cloud is increased by the addition of ammonia gas. Some of the earliest smoke clouds were produced by the combustion of white phosphorus.

Richter [3] has investigated the conditions necessary for satisfactory smoke formation, using $SiCl_4$ and $TiCl_4$. When these substances are dispersed in the air, they are hydrolysed

by the water vapour to give HCl and a residual oxide or hydroxide. In dry air, no cloud is formed. When NH_3 is added, it reacts with the HCl to form NH_4Cl, and greatly increases the density of the smoke.

Combustion Smokes

When a metal high in the electromotive series—*e.g.*, zinc or aluminium—reacts with an organic chloride—*e.g.*, CCl_4—a metallic chloride is produced, which is sublimed by the heat of the reaction. An effective combustion mixture devised by the United States Bureau of Mines [4] consists of :—

		Per cent.
A metal giving a readily volatile chloride	Zinc dust	34·5
A chlorinating agent	CCl_4	40·8
An oxidising agent	$NaClO_3$	9·3
A cooling material	NH_4Cl	7·0
An absorbent for the CCl_4	Precipitated magnesium carbonate	8·3

For screening purposes it is important that the smoke shall not be too warm ; otherwise it will rise and much of its effect will be lost. The smoke produced by the detonation of oleum is cooler, and has much less tendency to rise, than that produced by the combustion of phosphorus.

Total Obscuring Power

For screening purposes, the most important property of a smoke is its obscuring power. The total obscuring power (T.O.P.) is determined directly as follows :—

A large box, measuring 6 feet × 6 feet × 8 feet in length, is filled with the smoke. A 25-watt "Mazda" lamp is supported at one end of the box in such a way that it can be moved backwards and forwards along the axis of the box. At the other end of the box is a window through which the lamp can be viewed through the smoke. The smoke is kept thoroughly mixed up by means of an 18-inch fan, and the position of the lamp is adjusted until it is just distinguishable. The depth of smoke that is necessary to obscure the light gives a measure of the T.O.P. of the smoke.

Gradually the smoke clears, owing to diffusion, flocculation

and settling, at a rate that depends upon its stability. Such an arrangement, therefore, also affords a means of comparing the relative stability of different smokes.

In forming smokes the reacting gases are diluted with from 50 to 400 volumes of air to produce fine, stable particles of high obscuring power.

The total obscuring power of a number of different smokes is given in Table XXII.

TABLE XXII.

Smoke.	Total Obscuring Power.
Phosphorus . . .	4,600
$NH_3 + HCl$ . . .	2,500
$SnCl_4 + NH_3 + H_2O$.	1,590
Combustion mixture .	1,250
$SnCl_4 + NH_3$ . . .	900
$SO_2 + NH_3$ . . .	375

The total obscuring power of phosphorus smoke varies from 3,000 to 6,000, depending upon the humidity of the atmosphere, and is taken as a standard. HCl gas and NH_3 produce a smoke of obscuring power up to 2,500.

The obscuring power of $SiCl_4$ smoke is greatly increased by the addition of ammonia. The greatest total obscuring power is obtained when :—

(1) Liquid NH_3 and $SiCl_4$ are atomised into the atmosphere ;

(2) Both ingredients are well diluted with air before mixing, thus producing a large number of very fine particles ;

(3) The atmospheric humidity is sufficient to hydrolyse the $SiCl_4$ completely before the HCl produced comes into contact with the NH_3, otherwise $SiCl_4.6NH_3$ is formed, which is not readily hydrolysed.

All smokes give greater T.O.P. in cold, damp weather than on a warm, dry day. Excessive moisture, rain or steam, gives a low T.O.P., owing to the formation of large droplets of HCl.

$TiCl_4$, although giving about 50 per cent. more T.O.P. than $SiCl_4$, is little used in practice, owing to its relatively slow evaporation. The smoke that is produced by these substances

is inferior to the smoke that is produced by phosphorus, $ZnCl_2$ combustion mixture, or $SnCl_4$.

The maximum total obscuring power of the combustion mixture smoke varied between 900 and 1,400, according to the temperature and the humidity.

Production of Smoke Screens

Smoke screens were produced by the following different methods according to circumstances.

(*a*) **By the Combustion of a Smoke Mixture.**—The mixture, combined with a suitable ignition device, was made up into "candles" or drums, and ignited as required. Smoke floats, containing 100 lb. of smoke mixture, were used by the Navy for producing smoke away from the ship.

(*b*) **By the Detonation of a suitable Hygroscopic Substance.**—High explosive shells and grenades were filled with hygroscopic substances that, when detonated, were dispersed to form a fine smoke. The relative values of different materials for smoke shells were :—

White phosphorus . . .	100
SO_3	60—75
$SnCl_4$	40
$TiCl_4$	25—35
$AsCl_3$	10

With a 4·5-inch howitzer, a complete smoke barrage could be established and maintained over a front of 200 yards in bright sunshine, in from 40 to 60 seconds, by firing a salvo, followed by battery fire of 3 seconds. In moist, cool weather, the smoke was so much more stable that a battery fire of 15 seconds was sufficient to maintain the barrage.

(*c*) **By the Chemical Interaction of two or more Gases.**—In the Navy, a smoke trail was produced from the stern of a vessel by discharging $SiCl_4$ and NH_3 from a specially constructed "funnel" 7 feet long × 2 feet in diameter. Liquid $SiCl_4$ and NH_3, contained in cylinders, were forced by CO_2 through sprays into the smoke funnel, where they were mixed by a fan and ejected as a dense, white cloud of high total obscuring power. Two pounds of $SiCl_4$ were used to 1 lb. of NH_3. A set of cylinders lasted for about 30 minutes. Smoke knapsacks,

similarly equipped with $SiCl_4$ and NH_3, were also used by land troops.

(*d*) **By the Vaporisation of Acid.**—Oleum or HCl were sprayed into the exhaust pipes of aeroplanes, tanks or motor boats, or into the smoke-stacks of ships.

Toxic Smokes

Various irritating or toxic substances were highly dispersed by detonation in high explosive shells, to form a fine smoke, the particles of which were slow to settle and easily penetrated the ordinary gas mask.

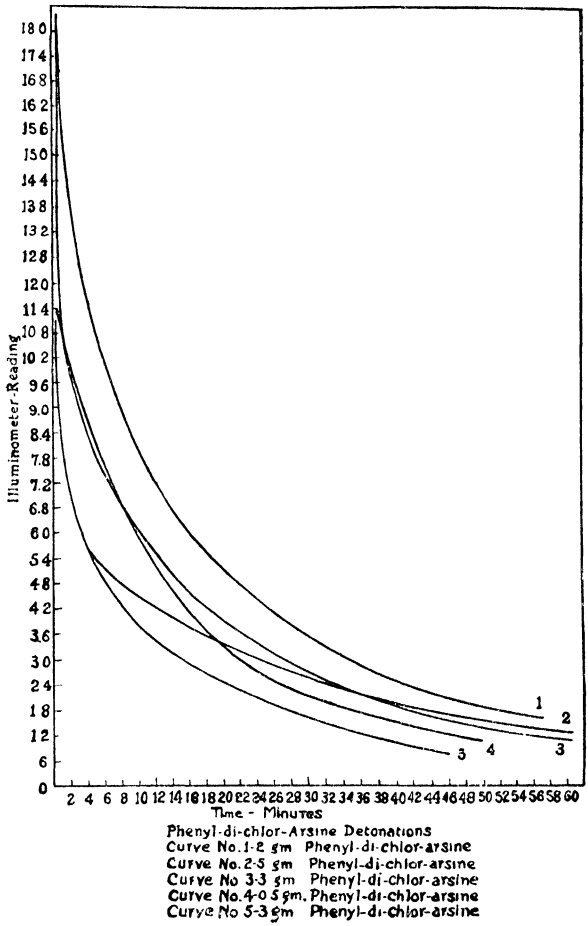
The following substances were used :—

Substance.	Character.	Persistence.
Diphenylchlorarsine Diphenylcyanarsine	Cloud of solid particles.	Non-persistent (10 mins. in open).
Diphosgene Phenylcarbylamine chloride Phosgene + diphosgene + diphenylchlorarsine. Chlorpicrin, 75 per cent. ; $COCl_2$, 25 per cent. Diphosgene and chlorpicrin Chlorpicrin, 80 per cent. ; $SnCl_4$, 20 per cent. Ethyldichlorarsine + dichlormethyl ether.	Moderately high B.P. Penetrating smokes of liquid or solid particles of about 1μ in diameter. Slowly settle on ground.	Semi-persistent (3 hours).
Bromacetone Bromketones Brombenzylcyanide Dichlorethyl sulphide (mustard gas).	High B.P. partly dispersed ; greater portion scattered over the ground.	Persistent (3 days).

To test toxic smokes for penetrating power and stability, 1 gram of the substance is dispersed in 1,000 litres of air in a sheet-iron box of that capacity. A steady concentration was generally attained after about five minutes. A sample of the smoke is then withdrawn, suitably diluted with air, and passed through a standard felt filter. The Tyndallmeter reading before and after passing through the filter indicates the penetrating power of the smoke, or, alternatively, the efficiency of the filter.

The smoke-producing power of toxic substances varies according to their volatility. Most materials that boil below 130° C. do not produce smoke ; they simply evaporate as soon as they are dispersed. 500° C. appears to be the maximum boiling point for satisfactory smoke production ; substances of higher boiling point do not form good smokes. The best smoke-producing substances are various arsenic compounds.

If for a given smoke the Tyndallmeter readings are plotted against the age of the smoke (in minutes), the curve generally



TYPICAL CURVES SHOWING THE DECREASE IN CONCENTRATION OF SMOKE CLOUD WITH TIME.

FIG. 31.

descends sharply at first, gradually reaches a more stable secondary degree of dispersion, after which it changes comparatively slowly. It is found that the area enclosed by the

axes and the portion of the curve between $t = 0$ and $t = 30$ is a rough measure of the relative stabilities of the different smokes. The more slowly the initial concentration changes the greater the area enclosed between the curve and the axes. Curves for phenyldichlorarsine smokes of different concentrations are shown in Fig. 31. The values of the significant area for a number of different substances are compared in Table XXIII.

TABLE XXIII.

Phenyldichlorarsine	181
Triphenyldichlorarsine . . .	178
Diphenylcyanarsine	137
Diphenylchlorarsine	101
Cyanogenbromide	94
Methyldichlorarsine	70
Phenylimidophosgene . . .	69
Mustard gas	38

Signal Smokes

Certain coloured smokes were used for signalling purposes :—

Rouge and ultramarine were fired in shells and detonated at the top of their trajectory.

HI, Cl and NH_3, when mixed together, produced a smoke that appeared purple from above and white from below.

Neither of these methods proved to be satisfactory for signalling purposes.

The best results were obtained with smoke torches, consisting of—

Red As_2S_3 . . .	55 per cent.
S	15 ,,
KNO_3	30 ,,

The heat of combustion of the sulphur volatilised the As_2S_3.

Other colours were obtained satisfactorily by the careful volatilisation of suitable dyestuffs :—

Red . . .	Paratones.
Yellow . .	Chrysoidine and auramine.
Green . .	Auramine yellow and indigo.
Blue . .	Indigo.
Purple . .	Indulin.

Smoke Filters

The use of toxic smokes necessarily led to the introduction of suitable filters. The two most successful filtering media were felt and paper. The theoretical considerations that underlie efficient smoke filtration have already been described (p. 88).

Smoke filters were tested against detonated diphenylchlorarsine, NH_4Cl, SO_3 smoke (air charged with SO_3 vapour mixed with air of 50 per cent. humidity), and tobacco smoke.

Of these smokes, the NH_4Cl smoke consisted of particles of different sizes, and tended to clog the filter.

The SO_3 smoke was readily analysed, did not clog the filter, and its concentration could readily be determined by optical methods.

The tobacco smoke, obtained by the combustion of sticks of a mixture of tobacco (63 per cent.), rosin (30 per cent.), KNO_3 (7 per cent.), consisted of very uniformly sized particles. Chemically, it was relatively inert, and therefore not altered by moisture or by further dilution with air. It did not clog the filter.

Smoke appears likely to become one of the great elements of war in the future. "The smoke will be generated in candles, or two- or three-pound cans, that can be thrown out in front of trenches; by knapsacks that can be carried, and which will give off dense white smoke in large volume for many minutes; by grenades which, while they may be thrown by hand, will generally be fired from rifles; by artillery shells reaching ten, fifteen, twenty miles back of the main battle line; and finally from aeroplane bombs, whose radius of action is limited only by the size of the earth." [1]

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