Incidentally, having determined the primary salt effect, the decomposition of nitrosotriacetoneamine is readily adaptable to the estimation of Sörensen values between seven and ten at temperatures above 60°

The author is indebted to Professor F. O. Rice for his kindly criticism.

Summary

1. The catalytic decomposition of nitrosotriacetoneamine has been studied in solutions of sodium hydroxide and in alkaline buffer solutions.

2. The rates of reaction and the temperature coefficients have been determined from 20° to 80°.

3. The temperature coefficient is unaffected by neutral salt.

4. The results are in agreement with Brönsted's concept of secondary kinetic salt effect.

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THE CATALYTIC ACTIVITY OF DUST PARTICLES

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When a chemical reaction proceeds in a closed vessel it is subject to two influences which can ordinarily be neglected but which in some reactions completely determine the speed, because in the absence of the particular influence the reaction will not take place at a measurable rate. The first of these influences is the surface of the containing vessel; if, as is commonly the case, this is of glass, the reaction is surrounded by a thin envelope of condensed water containing many dissolved substances the most important of which is probably the hydroxyl ion. This film catalyzes many reactions between liquids, between dissolved substances and between gases; examples such as the interconversion of liquid keto-enol isomers,[1] the change of *n*-nitrocamphor to the pseudo form in different solvents[2] and the bromination of ethylene[3] illustrate the important chemical effects of this surface film, since none of these reactions takes place in a vessel with non-reactive walls.

The second influence arises from the presence of finely-divided dust particles which are always present unless special precautions are taken to exclude them. If an intense beam of light be passed through air or other gas and viewed at right angles against a dark background, the path of the beam is plainly visible owing to light scattering by the great numbers of

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[1] Meyer and Schoeller, *Ber.*, **53**, 1410 (1920). Meyer and Hopff, *Ber.*, **54**, 579 (1921).

[2] Lowry, *J. Chem. Soc.*, (a) **75**, 220 (1899); (b) **83**, 1316 (1903).

[3] Stewart and Edlund, THIS JOURNAL, **45**, 1014 (1923). Norrish, *J. Chem. Soc.*, **123**, 3006 (1923).

motes present; if a vessel of water or other liquid be held in the path of the beam, considerable scattering also takes place showing the presence of dust which is not removed even by careful distillation. Since distilled water contains about 25,000 suspended particles per cc.,[4] all of our chemical reactions occur in the presence of considerable amounts of suspended dust and it appeared not unlikely that these particles exert a catalytic influence which would explain a number of anomalous results in supposedly homogeneous reactions.

great number of studies have been made of systems[5] containing suspended dust particles, but almost without exception the work has been confined to light-scattering experiments and to the technique of dust removal; practically nothing has been done from the chemical point of view, probably because certain abnormal chemical phenomena that are due to dust have come into prominence only in comparatively recent years.

It soon became evident, however, that there are many reactions ordinarily considered homogeneous that are really catalyzed by solid surfaces and three representative reactions, namely, the thermal decomposition of hydrogen peroxide, the oxidation of sodium sulfite and the oxidation of benzaldehyde are now being investigated in this Laboratory. The thermal decomposition of hydrogen peroxide is an example of a reaction that is to some extent catalyzed by the walls of the vessel but mainly by suspended dust particles; when hydrogen peroxide, free from dust, is kept in a vessel of fused silica it is a remarkably stable substance and may be heated for several days to 60° without appreciable decomposition. There does not seem to be any evidence of a homogeneous decomposition, for when a solution of hydrogen peroxide free from preservative and organic matter is heated, the decomposition is a zero-order reaction, the rate being independent of the concentration of the hydrogen peroxide. The results of previous workers indicating a unimolecular reaction are due to the gradual destruction of solid organic matter in the solution.

The oxidation of sodium sulfite is almost entirely a dust reaction, since experiment shows that a dust-free alkaline solution of sodium sulfite may be left almost indefinitely in contact with dust-free oxygen without undergoing oxidation. The remarkable nature of this reaction may be gaged from an experiment in which we passed a dust-free mixture of sulfur dioxide and oxygen into a vessel, one bulb of which contained ordinary distilled water and the other bulb dust-free water; after 24 hours the former bulb gave a distinct test for sulfate but no sulfate was found in the clean bulb. The oxidation of benzaldehyde, on the other hand, is a wall reaction and the presence or absence of dust has a negligible effect.

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[4] Kenrick, *J. Phys. Chem.*, **26**, 72 (1922).

[5] A fairly complete bibliography is given by Martin, *Trans. Roy. Soc. Canada.*, **16**, 276 (1922).

It also seems likely that the anomalous results obtained in some photochemical reactions are to be ascribed to the presence of dust. Einstein's law of the photochemical equivalent fails for many of these reactions, one quantum of light of the characteristic frequency causing from 1 to 1,000,000 molecules to react. One of these reactions, namely, the photochemical decomposition of hydrogen peroxide, much more nearly obeys the law when suspended dust particles and inhibitors are removed from the solution; quantitative measurements are now in progress to test whether the law is followed exactly. It is evident, therefore, that the photochemical decomposition takes place on the surface of the dust and that the hydrogen peroxide is adsorbed in aggregates, the average size of these being given by some multiple of the quantum yield of the reaction. We may regard one of the molecules on the surface as absorbing a quantum of light, decomposing and the action then spreading throughout the whole adsorbed aggregate. We might expect the quantum yield on this basis to diminish with dilution because the amount of substrate adsorbed will also diminish with dilution; furthermore, only reactions that occur with liberation of free energy should give these large deviations from the equivalence law. All these conclusions are in accord with the results of photochemical investigations.

Several studies of the work described in this introduction have now been completed and the results will be published shortly; the work is being extended to other reactions, particularly those in the gaseous state, but it has not yet been determined whether dust is an appreciable factor in this type of reaction. An interesting field lies in the investigation of the character of catalyst surfaces; if some dust-free water be prepared by Martin's method[6] and the bulb containing the clean water be shaken violently, the water will be found to contain large numbers of motes detached from the surface of the vessel; the vessel may be filled again with clean water and the process repeated almost indefinitely.[7] We are now conducting these experiments using a platinum catalyst and comparing the catalytic activity of the old and the new surface as well as the catalytic activity of the platinum particles detached from the surface; similar experiments are in progress using a poisoned catalyst. Our results indicate that solid surfaces consist of loose, porous and scaly layers that are easily rubbed off; a freshly melted surface does not, however, behave in this manner, and only after more violent and long continued shaking does it yield any quantity of motes.

Some of the results obtained so far in this work, especially those dealing with photochemical decompositions, are only semi-quantitative and neces-

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[6] Martin, *J. Phys. Chem.*, **24**, 478 (1920).

[7] This has already been observed by Kenrick, Gilbert and Wismer, *ibid.*, **28**, 1305 (1924).

sarily, also, part of the discussion is somewhat speculative in character. However, it seems desirable to publish this preliminary paper because the work which has been in progress for the past two years has yielded results proving beyond doubt that suspended dust is an important factor in three reactions and may be the cause of anomalous results in a great many others.

Negative Catalysis

When a reaction is catalyzed by a weak acid, the addition of one of its salts lowers the velocity; similarly, a number of reactions occurring in absolute alcohol, such as the esterification of acids,[8] the formation of a lactone from an hydroxy acid,[9] the alcoholysis of amides,[10] etc., are very sensitive to the addition of small quantities of water, the reaction rate being greatly diminished in all cases; reactions that occur in 100% sulfuric acid, such as the decomposition of oxalic acid,[11] are also diminished in velocity by the addition of small quantities of water. All these are homogeneous reactions in which the negative catalyst such as the neutral salt or the water acts probably by diminishing the concentration of the hydrogen-ion catalyst. There is a second type of negative catalysis which consists of the inhibition of chemical reactions by minute traces of foreign substances. The oxidation of benzaldehyde is typical of a whole host of reactive organic substances which undergo slow oxidation in the presence of air, and reaction is inhibited or accelerated by minute traces of different substances; other examples are the decomposition of hydrogen peroxide and the oxidation of sodium sulfite.

It is convenient at this point to review briefly the subject of negative catalysis, noting that up to the present no attempt has been made to draw any distinction between the two types. The Luther-Titoff conception[12] of negative catalysis postulates that the phenomenon cannot occur in a reaction which is entirely free from positive catalysts, being due entirely to the destruction or inhibition of these by the negative catalyst. Recently Taylor[13] has criticized this view and advanced the hypothesis that the inhibitor combines with one of the reactants to form a double compound which subsequently dissociates, regenerating the inhibitor and reactant; the inhibitor is therefore a competitor for one of the reactants and owing to the probably high rate of double compound formation,[14] it is as-

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[8] Goldschmidt, *Z. Elektrochem.*, **15**, 4 (1909).

[9] Kailan and Neumann, *Z. physik. Chem.*, **101**, 63 (1922).

[10] Reid, *Am. Chem. J.*, **41**, 483 (1909).

[11] Bredig and Lichty, *J. Phys. Chem.*, **11**, 255 (1907).

[12] Luther, *Z. physik. Chem.*, **45**, 662 (1903). Titoff, *ibid.*, **45**, 641 (1903).

[13] Taylor, *J. Phys. Chem.*, **27**, 322 (1923).

[14] The rate of collision of two gases may be calculated on the basis of ordinary kinetic considerations; assuming that in such a mixture of two gases every collision results in chemical combination, a velocity constant $k = 10^{15}$ is obtained; this would be an upper limit for the rate of double compound formation.

sumed that one molecule of inhibitor is able to prevent many molecules from reacting. This hypothesis is supported by some recent work[15] in which it was shown that double compound formation and inhibitory power are related. A third hypothesis to explain catalysis has been advanced by Christiansen[16] who assumes that negative catalysis is really due to the presence of chain reactions; when two reacting molecules combine, the resulting "hot" molecule is supposed to be able, on the first collision, to activate a molecule of reactant which combines forming a second hot molecule, thus starting a chain reaction in the system. The rate of such a reaction is proportional to the number of chains starting per minute multiplied by the average length of the chain; the action of the inhibitor is explained by assuming that it breaks the chains, the energy of the hot molecules being dissipated on collision with an inhibitor. This concludes the review of the previous work.

We may now consider the second type of negative catalysis and, in particular, certain peculiarities that are common to these reactions. They are extremely sensitive to the most minute traces of impurities which may either accelerate or retard the reaction; a wide variety of substances, especially organic compounds, retard the reactions; finally, there seems to be something erratic connected with the phenomenon which makes duplication of results impossible in spite of most careful work. Comments on this erratic character of the results appear in many of the publications in this field, the following comment being a translation from a paper[17] by Moureau and Dufraisse on the oxidation of benzaldehyde.

> In the course of these studies, we have occasionally noted strange, capricious and even anomalous effects. Thus, we have noticed that the retarding of the oxidation, at first quite sharp, suddenly stopped. Furthermore, after a sort of incubation, there is sometimes an inversion of the phenomenon, the oxidation being accelerated and not retarded. We can only call attention to the facts here, but the conditions underlying the results remain to be determined.

The three experimental observations just recorded provided the clue that the phenomenon is really heterogeneous catalysis, the catalyst being suspended dust,[18] its action being promoted or poisoned by minute traces of foreign substances—a behavior very common among heterogeneous catalysts; the erratic nature of the phenomenon also becomes quite clear.

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[15] Underwood, *Proc. Nat. Acad. Sci.*, **2**, 78 (1925).

[16] Christiansen, *J. Phys. Chem.*, **28**, 145 (1924).

[17] Moureau and Dufraisse, *Compt. rend.*, **175**, 127 (1922). This is one of a series of papers published in *Compt. rend.* for 1922–1925. ("Au cours........préciser.")

[18] Certain of these reactions such as the benzaldehyde oxidation are catalyzed mainly by the walls of the vessel and only to a minor extent by dust particles. The oxidation of benzaldehyde will not be dealt with further in this paper, because Dr. Reiff, working in this Laboratory, has now completed a study of it which will be published shortly.

Thermal Decomposition of Hydrogen Peroxide.[19]—Most of the investigations in this connection deal not with the rate in pure aqueous solution but with the effect of acids, alkalies, metals and conserving agents on the stability. In two recent papers,[20] however, the thermal decomposition has been extensively studied. Most of the workers agree that the reaction is unimolecular but the constants obtained show the widest variations. Lemoine considers that the surface of the containing vessel is an important factor in determining the rate, whereas Clayton considers that colloidal organic matter is of primary importance. Both of these workers used peroxide containing inhibitor, since both observed "une certaine inertie au début" and this is a phenomenon which we find does not occur when pure hydrogen peroxide is used. It does not seem worth while to discuss this work further, because the results were obtained in presence of an unknown inhibitor at an unknown concentration; indeed we find that by a proper selection of the nature and concentration of an inhibitor the reaction rate may be varied over an extremely wide range and the concentration-time curve can assume a great variety of shapes.

It seems desirable at this point to discuss the application of the term "unimolecular" to this change since, as has been previously pointed out,[21] "unimolecular" is commonly used when "pseudo-unimolecular" is meant. At ordinary temperatures it is not possible for any unimolecular thermal decomposition of hydrogen peroxide to occur because this would mean the production of a molecule of water and an atom of oxygen, a reaction which *absorbs* about 50,000 calories of free energy; the reaction could be dimolecular but there is no evidence for this in any published work. Actually, we find that the decomposition of hydrogen peroxide prepared by ourselves and kept quite free from any preservative is a zero-order reaction which is, of course, characteristic of reactions at solid surfaces. The active surface in this case is mainly suspended dust particles because when these are removed by Martin's method[6] the rate of decomposition falls enormously. The remaining slow rate is due mainly to catalysis by the walls of the vessel; this effect may be almost entirely removed by collecting the dust-free peroxide in a freshly fused quartz or Pyrex vessel. We have found empirically that a freshly fused glass surface is comparatively inactive, whereas glass which has been "roughened" by some such treatment as immersing in hot cleaning solution is very active catalytically. Material prepared in this way is extremely stable, far more so than commercial samples, even those heavily loaded with preservative; it is quite

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[19] The experiments described in this section were made in collaboration with Dr. O. M. Reiff; a full account of this work will be published shortly.

[20] Lemoine, *J. chim. phys.*, **12**, 1 (1914). Clayton, *Trans. Faraday Soc.*, **11**, 164 (1915). See also Spring, *Z. anorg. Chem.*, **10**, 161 (1895).

[21] "Treatise on Physical Chemistry," Ed. by Taylor, Van Nostrand Co., New York, **1925**, vol. 2, p. 874 (1924).

simple by this method to prepare a sample of say 50% aqueous hydrogen peroxide which has a half life of several months at 60°; the best sample prepared by Clayton using peroxide *containing inhibitor* had a half life of about five days. The whole of this work leads to the conclusion that the ordinary thermal decomposition of hydrogen peroxide is a heterogeneous reaction taking place mainly on the surface of suspended dust particles, that the action of inhibitors is to poison the active surface of the dust, and finally that the ordinary thermal decomposition in the presence of preservatives consists first of oxidation and destruction of the adsorbed inhibitor, which corresponds to the initial inhibition usually observed, and second of a competition between the hydrogen peroxide and dissolved inhibitor for the active surface of the dust; this second reaction in some cases gives a curve very approximately resembling that of a first-order reaction.

Thermal Oxidation of Sodium Sulfite.—The early studies of Bigelow[22] and Young[23] showed that this reaction is a typical example of negative catalysis of the second kind, the reaction being inhibited sometimes to an extraordinary degree by traces of organic compounds. It seemed possible that these experiments, as well as those of Titoff,[12] could be readily explained by catalysis due to suspended dust; thus Titoff's experiments with copper sulfate and mannitol indicate that he was simply copper plating the dust particles and then poisoning the copper with mannitol. The reaction is usually considered to be unimolecular with respect to the sodium sulfite[24] but here again we meet the same difficulty as in the decomposition of hydrogen peroxide, that such a process requires the production of atomic oxygen and therefore cannot occur; it appears that the oxidation of sodium sulfite must be either dimolecular with respect to the sulfite or a heterogeneous reaction like the decomposition of hydrogen peroxide. Our experiments show that the oxidation of sodium sulfite is almost entirely a dust reaction, the walls of the vessel having a negligible effect. Using Spring's method,[25] the dust was removed by envelopment by a gelatinous precipitate, the resulting solution of sodium sulfite being optically clear and giving no absorption of oxygen over a period of several hours; if this clear solution is poured into a beaker and then poured back into the apparatus, the resulting solution contains great numbers of motes and oxidizes at a rapid rate. It may easily be shown that copper alone has no catalytic activity because the sulfite solution may be freed from dust by precipitating in it copper hydroxide; the resulting clean solution does not oxidize in the presence of oxygen. The

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[22] Bigelow, *Z. physik. Chem.*, **26**, 493 (1898).

[23] Young, This Journal, **24**, 297 (1902).

[24] See Mack, Osterhof and Kraner, *ibid.*, **45**, 617 (1923).

[25] Spring, *Rec. trav. chim. Pays-Bas.*, **18**, 153 (1899).

experimental part of this work, done in collaboration with Mr. George I. Lavin, is still in progress and will be reported in a later communication.

Photochemical Reactions

From the results obtained with thermal reactions it appeared extremely likely that the abnormalities of photochemical reactions are in part at least due to suspended dust, and two reactions, the photochemical decomposition of hydrogen peroxide and the combination of hydrogen and chlorine, are now under investigation in this Laboratory; this work is in collaboration with Mrs. M. L. Kilpatrick but only some preliminary results with reference to the hydrogen peroxide decomposition are now available. Both these reactions show large deviations[26] from Einstein's photochemical law, one quantum of light in the case of a 2% hydrogen peroxide solution decomposing about 80 molecules. The effect of dust on this reaction may be illustrated in a striking manner by a qualitative experiment; two quartz flasks are placed equidistant from a mercury lamp and protected from heat rays by a water screen. A 2% solution of peroxide is then made up and part is poured into one flask and the remainder is placed in the second flask and freed from dust by Martin's method;[6] when the flasks are near the lamp the first flask shows a rapid evolution of gas so that the solution appears to be boiling vigorously whereas the second flask shows a very slow and hardly perceptible gas evolution. Many experiments such as this have been performed in which the rate of decomposition of the peroxide has been followed both by gas evolution and by titration, and there is no doubt that the presence of dust is the main factor in the ordinary photochemical decomposition of peroxide. When a dust-free solution of peroxide, which a test shows to decompose extremely slowly, is poured out of the flask into a beaker and then back to the flask, the rate of decomposition greatly increases, attaining practically the same value as the blank which had not been freed from dust; in the process of pouring a dust-free liquid from one vessel to another in laboratory air, it acquires practically the same dust content as untreated liquid. Owing to the great ease with which a clean liquid picks up dust, a special technique has to be followed in handling and preserving such liquids in a dust-free condition; the ordinary chemical method of cleaning a vessel by hot dichromate solution has no effect so far as the dust is concerned because on pouring out the cleaning solution, the vessel becomes filled with ordinary air and the washing with distilled water completes the process of re-introducing the motes; indeed, by roughening the glass surface, the dichromate works mischief in two ways, first by making it easy to detach motes from the surface by shaking the vessel and second by increasing any catalytic activity which the surface may have had originally.

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[26] See Ref. 21, Chap. 18.

We find that the rate of decomposition of hydrogen peroxide by ultraviolet light is roughly proportional to the dust content as measured by the light-scattering power of the solution and it remains, therefore, to find whether the dust-free solution obeys the photochemical equivalent law. The measurements are difficult because low-voltage arcs do not decompose hydrogen peroxide at a rate convenient for measurement. If the dust-free material obeys the law, its rate of decomposition will be only about 1% of the ordinary rate;[27] it requires about 90 minutes' exposure to a mercury-vapor lamp to obtain a quantitative measurement on an ordinary dusty solution, so that we may expect that a dust-free solution would require a week's exposure both day and night to give sufficient decomposition. The reaction is now being investigated, using a high-tension spark as source of light with a monochromator and standard thermopile.

It is evident, therefore, that dust may act as a photocatalyst and is perhaps the only one; substances which change the rate of a photochemical reaction act by promoting or poisoning the catalytic activity of the dust. The term photocatalyst as ordinarily used is therefore applied to substances which promote the action of the dust, probably by bringing about increased adsorption, whereas negative photocatalysts poison the dust, probably by being adsorbed themselves instead of the substrate. If this is true it is evident that an inhibitor must be placed in the solution, since its use in a separate solution as a screen can only bring about absorption of the active radiation. Anderson and Taylor have shown[28] that the same substance is much more effective as an inhibitor when added directly to the solution than when used in a separate solution as a screen. It is, of course, possible for a substance not adsorbed by the dust to act as an inhibitor merely by absorbing the active radiation.

On the basis of these views it may be no longer necessary to postulate the existence of reaction chains[29] as a mechanism for photochemical changes in which the quantum yield is very high; the substrate is supposed to be adsorbed on the surface of the dust and on the walls of the vessel, in isolated aggregates, the average size of which is given by a multiple of the quantum yield of the reaction; one quantum of light of characteristic frequency is absorbed by one of the molecules which decomposes and the action spreads throughout the whole aggregate. In order for such a process to occur it is obvious that the free energy of the system must diminish, and on this basis the heat change of the reaction is not important since it is conceivable that an endothermic reaction could give a high quantum yield. Some such

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[27] See Henri and Wurmser, *Compt. rend.*, **151**, 1040 (1910). Kornfeld, *Z. wiss. Phot.*, **21**, 66 (1921).

[28] Anderson and Taylor, THIS JOURNAL, **45**, 650, 1210 (1923).

[29] In the discussion of photochemical reactions that follows, individual references to the various points will not be given because two very recent reviews are now available. See *Trans. Faraday Soc.*, **21**, 438 (1926); *Ann. Repts. Progress Chem.*, **22**, 333 (1925).

explanation as this appears to be very likely for the hydrogen peroxide decomposition and may apply to other photochemical changes of high quantum yield.

The results now obtained in this work provide additional confirmation of Taylor's concept[30] of a catalytic surface in which the Langmuir active areas are shown to occupy only a small fraction of the surface; the quantum yield of a reaction enables us to measure the average number of molecules adsorbed by these active centers and suggests several lines of investigation that are now in progress; it is possible to free a system from dust and then introduce various materials in the form of dust and measure the quantum yield in each case; the effects of poisons, temperature and dilution are also being investigated. In this connection it is interesting to consider the temperature coefficients of photochemical processes because the change in rate with temperature will depend, for those reactions of high quantum yield, upon the change of adsorption of the substrate with temperature; since the heat of adsorption is in general positive, the effect of rise in temperature will be to diminish the size of the cluster of molecules at an active point on a dust particle, which would have the effect of causing abnormally low or negative temperature coefficients for photochemical reactions of high quantum yield; doubtless the conflicting results obtained in these measurements are due to differences in composition of active suspended material.

It is evident that photosensitization processes may occur with large quantum yields, if an excited atom or molecule collides with aggregates adsorbed on the surface of the dust, and this explanation is suggested for such experiments as those of Bonhoeffer[31] on the decomposition of ozone using bromine as sensitizer; 30 molecules of ozone are decomposed for each quantum of energy absorbed and no completely satisfactory mechanism for such an abnormal yield has yet been found.

The existence of induction periods in photochemical reactions is doubtless related, as in thermal reactions, to the presence of adsorbed materials either on the walls of the vessel or on the dust particles; in a recent paper Norrish[32] has shown that ammonia poisons the surface of the vessel in the hydrogen-chlorine combination but he did not examine for the effect of suspended dust. On the basis of the views put forward in this paper the hydrogen-chlorine reaction provides an extraordinary example of the variation in size of these adsorbed aggregates since the number of molecules of hydrochloric acid formed per light quantum varies from 1,000,000 when the reaction occurs at ordinary pressures to 20 when the reaction occurs at 0.01 mm.[33] It seems desirable, therefore, to discuss the mech-

[30] Taylor, *Proc. Roy. Soc.*, **108A**, 105 (1925).

[31] Bonhoeffer, *Z. Physik*, **106**, 403 (1923).

[32] Norrish, *J. Chem. Soc.*, **127**, 2316 (1925).

[33] Marshall, *J. Phys. Chem.*, **29**, 1453 (1925).

anism of such reactions because it must be quite different from those discussed by Born and Franck[34] and by Franck.[35] When a quantum of light strikes an adsorbed aggregate of chlorine molecules or hydrogen peroxide molecules, it is absorbed by one of them with consequent excitation; since the excited molecule is in combination with the rest of the aggregate, the reaction can pass throughout the adsorbed mass *via* either molecular bonds or the surface of the dust particle. If we imagine ten quanta of absorbable light entering a solution of hydrogen peroxide, nine of them may collide with molecules in solution whereas the tenth may collide with a molecule attached to an aggregate on a dust particle and thus decompose the whole aggregate; for practical purposes we may therefore regard the size of the aggregate as being some multiple of the quantum yield. For hydrogen peroxide the multiple is probably very small because the scattering power of the dust is probably comparable with the absorptive power of the peroxide. An important point comes up in this connection because the absorption spectrum of the adsorbed material may not be the same as when it is in solution; the effect of double-compound formation is in general to move the absorption spectrum towards the longer wave length so that it may be possible to decompose a substance by light which it does not absorb in the homogeneous condition. It appears probable also that the degree of excitation required is less for an adsorbed molecule than for one in the free state because Coehn and Jung[36] showed that after intensive drying of a hydrogen-chlorine mixture (which would destroy the activity of the surface) it reacts only to ultraviolet light and not to blue light which affects the ordinary moist gases. An experiment is now in progress to test the reactivity of the dust-free gases to visible light.

Gas Reactions

Owing to the contradictory results obtained in the studies of some of these reactions it seems desirable to test whether the anomalies are to be ascribed wholly or in part to suspended dust; not only does there seem to be no work in which precautions were taken to remove the dust, but the usual technique of drying the gases with phosphorus pentoxide just before entering the decomposition chamber ensures a great plenitude of suspended particles.[37] Two gas reactions are now under investigation in this Laboratory, namely, the thermal decomposition of ozone and the thermal decomposition of nitrogen pentoxide; although results are not yet available

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[34] Born and Franck, *Z. Physik,* **31,** 411 (1925).

[35] Franck, *Trans. Faraday Soc.,* **21,** 536 (1926).

[36] Coehn and Jung, *Ber.,* **56,** 696 (1923).

[37] See Hartung, *J. Chem. Soc.,* **127,** 2697 (1925). In his study with the microbalance the author notes that "the presence of phosphorus pentoxide has been found to be most objectionable because of the fine dust which arises from it with changes of pressure."

it seems desirable to give a preliminary discussion of these reactions. Published results show that many gas reactions occur partly on the wall of the containing vessel and it is certainly reasonable to infer that the supposed homogeneous part of the reaction occurs on the surface of suspended particles. There is conflict of opinion in the case of the thermal decomposition of ozone, Chapman and Clarke[38] believing that the reaction is practically entirely homogeneous whereas Perman and Greaves[39] consider that the reaction occurs mainly on the surface of the vessel. In a very recent paper Griffith and McKeown state:[40] "We are unable from the results of the present work or from the results of previous workers to arrive at a definite conclusion on this point. All that may safely be inferred is that some part at least of the measured rate is due to a heterogeneous change." The decomposition of chlorine monoxide[41] is usually accepted as a homogeneous dimolecular change but the concentration-time curves show a period of inhibition and closely resemble the curves obtained for the decomposition of aqueous hydrogen peroxide, a typical dust reaction. Several other examples of such anomalous results might be quoted, which seems to indicate that until gas reactions have been investigated in the dust-free condition we cannot afford to neglect the possibility that there are no real examples of homogeneous uncatalyzed gas reactions.

We may now consider the most interesting of all the gas reactions, namely the decomposition of nitrogen pentoxide. The generally accepted view[42] is that "there seems to be no reason for doubting the unimolecular homogeneous character of this reaction," although one may well demur in view of the difficulty of finding a reasonably satisfactory theoretical treatment, as well as the unexplained result of Daniels, Wulf and Karrer.[43] It appeared possible that the decomposition was of the usual pseudo-unimolecular type, suspended dust being the catalyst, especially as the technique used by Daniels, Wulf and Karrer would probably free the gases from dust; however, preliminary experiments in collaboration with Miss D. Getz indicate that the rate of decomposition is not affected by dust; the work is still in progress because the experiments are not quite conclusive, in that our filters would not remove very fine dust. Also, there are other hypotheses that it is desirable to test, in particular, that the reaction is due to the presence of a small amount of catalyst. Lowry[44] suggested some time ago that all reactions are catalytic in character although presumably he had in mind that all *slow* reactions are catalytic since, as pointed

[38] Clarke and Chapman, *J. Chem. Soc.*, **93**, 1638 (1908).

[39] Perman and Greaves, *Proc. Roy. Soc.*, **80A**, 353 (1908).

[40] Griffith and McKeown, *J. Chem. Soc.*, **127**, 2086 (1925).

[41] Hinshelwood and Prichard, *ibid.*, **123**, 2730 (1923).

[42] *Ann. Repts. Progress Chem.*, **22**, 16 (1925).

[43] Daniels, Wulf and Karrer, THIS JOURNAL, **44**, 2402 (1922).

[44] Lowry, *Trans. Faraday Soc.*, **17**, 596 (1922).

out by Perrin,[45] the former suggestion leads to an obvious absurdity. The problem is then to find whether nitrogen pentoxide is likely to contain any small amount of impurity present in constant amount. One of these impurities is nitric acid as may be seen from the following considerations: the nitrogen pentoxide before entering the reaction chamber passes over phosphorus pentoxide, so that we have the following equilibrium: $2HNO_3 + P_2O_5 \rightleftarrows N_2O_5 + 2HPO_3$. The heat of this reaction for gaseous nitric acid and gaseous nitrogen pentoxide is approximately 13,800 cal.; the equilibrium concentration of the nitric acid will not, therefore, vary very much, since the phosphorus pentoxide is used at ordinary laboratory temperatures. Experiments are in progress to test this by drying with the phosphorus pentoxide at different temperatures which also would indicate the presence of any other catalytic impurity introduced in constant amount *via* the drying agent.

Other Reactions

Periodic reactions have been the subject of several extensive investigations recently. Among other reactions, Hedges and Myers[46] investigated the periodic decomposition of hydrogen peroxide by metals, metallic oxides and other substances; Firth and Watson[47] found that with sugar charcoal at higher temperatures the decomposition is periodic. None of these workers, however, state the source of their hydrogen peroxide although this is far more important than the particular substance used to decompose the peroxide; some commercial samples when merely diluted with distilled water give a periodic decomposition curve but we find that the periodicity is due to traces of inhibitor, because the phenomenon is not observed with pure hydrogen peroxide. The periodic reaction observed by Bray[48] also is due apparently to the presence of dust; by varying the amount of dust and inhibitors present in the reaction its periodic character can be increased or suppressed at will. The phenomenon of periodicity appears to be due to a competition between the substrate and an inhibitor for the surface of the vessel, suspended dust or an added solid substance.

Induced reactions probably in some cases at least are examples of heterogeneous catalysis taking place on dust particles. Thus a solution of sodium arsenite alone does not oxidize[49] in air or oxygen but does so in the presence of sodium sulfite, this reaction being typical of a great number of others.[50]

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[45] Perrin, *Trans. Faraday Soc.*, **17,** 605 (1922).

[46] Hedges and Myers, *J. Chem. Soc.*, (a) **125,** 604, 1282 (1924); (b) **127,** 445, 1013 (1925).

[47] Firth and Watson, *ibid.*, **123,** 1750 (1923).

[48] Bray, THIS JOURNAL, **43,** 1262 (1921).

[49] Jorissen, *Z. physik. Chem.*, **23,** 667 (1897).

[50] Shilow, *ibid.*, **42,** 641 (1903). Luther, *ibid.*, **46,** 777 (1903). Jorissen and van den Pol, *Rec. trav. chim.*, **43,** 582 (1924).

It seems likely that the oxidation of sodium arsenite also takes place on the dust which is activated, so far as the arsenite oxidation is concerned, by the sodium sulfite; it is interesting to note in this connection that Chapin[51] found that arsenite could be oxidized easily by oxygen when finely-divided carbon is used as a catalyst.

The possibility that dust is a factor in change of state was suggested by Baker's work on the boiling points of highly dried liquids, in particular by his remarkable observations[52] that dried benzene, b. p. 106°, may be poured onto water and the water boiled through it without the benzene undergoing change; the benzene regains its normal boiling point only after several days' contact with the water. This experiment suggests that the dust and not the water is the actual catalyst and that the drying process simply diminishes the catalytic activity of the dust. In order to test this hypothesis, some carefully purified benzene dried by calcium chloride was freed from dust by distillation without ebullition[6] and the boiling point determined.[53] The temperature of the benzene was raised very slowly to 100°, but at this point boiling commenced and the temperature fell to 80°, the normal boiling point. This experiment is not, however, decisive because the benzene was found to contain a large quantity of motes apparently detached from the glass by the violent ebullition. Further work along these lines indicated that the dust alone is not the deciding factor in the boiling and evaporation of liquids; measurements showed that the rate of evaporation or condensation in the dust-free condition is the same as when dust is present. It may be, however, that the change of state from a liquid to a gas is a catalytic phenomenon which requires a *moist* surface; if this is so, Baker's results become explicable because not only must the liquid and the surface of the vessel be dry but the dust particles also; undoubtedly the last process would be very slow.

Summary

All chemical reactions proceeding under the usual conditions do so in the presence of great numbers of suspended dust particles; these are the cause of a number of anomalous results in certain supposedly homogeneous reactions.

The thermal decomposition of hydrogen peroxide occurs mainly on dust particles but partly on the surface of the vessel; there is no evidence of any homogeneous decomposition. The thermal oxidation of sodium sulfite

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[51] Chapin, *J. Ind. Eng. Chem.*, **6**, 1002 (1914). See also Reinders and Vles, *Rec. trav. chim.*, **44**, 29 (1925).

[52] Baker, *J. Chem. Soc.*, **121**, 568 (1922).

[53] This experiment was performed at New York University with Mr. W. A. Wesolowski in January, 1924. Recently a very comprehensive study of this phenomenon has been published in which a similar experiment with ether yielded negative results. See Kenrick, Gilbert and Wismer, *J. Phys. Chem.*, **28**, 1297 (1924).

is almost entirely a dust reaction, for when the dust is removed the rate of oxidation is immeasurably slow.

The photochemical decomposition of hydrogen peroxide occurs largely on the surface of suspended dust; when this is removed, the quantum yield is very greatly diminished. It seems likely that when reactions of large quantum yield are studied in the dust-free condition the Einstein photochemical equivalence law will hold. We may explain this by assuming that the substrate is adsorbed in isolated aggregates, the average size of which is given by some multiple of the quantum yield of the reaction; a single quantum of light absorbed by one molecule of the aggregate is supposed to "explode" the whole aggregate.

There are two classes of reactions in which the phenomenon of negative catalysis appears. The first class is homogeneous and consists mainly of those reactions which occur in anhydrous organic solvents or 100% sulfuric acid and are inhibited by small amounts of water. The second class is heterogeneous and inhibitors or accelerators simply poison or promote the catalytic activity of dust particles or the walls of the containing vessel.

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PARAMETERS IN CRYSTAL STRUCTURE. THE MERCUROUS HALIDES

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In the analysis of crystal structure by means of X-rays it is necessary to make a calculation of the intensities of X-ray reflection from different crystal planes for various atomic arrangements and to compare the calculated intensities with those observed. Unless the atomic positions are completely determined by the symmetry of the crystal, there will be one or more undetermined parameters which can be evaluated only with the aid of the intensity data; the values obtained for the parameters will be correct if the method of calculating the intensity of reflection is correct. Unfortunately, the expression that is used in the calculation of the intensity of reflection contains an empirical factor called the "structure factor," depending upon the atomic and electronic arrangement in the crystal, which is but vaguely understood. The two points about which most uncertainty exists are: (1) the relation between the intensity of reflection and the structure factor and (2) the correct method of calculating the structure factor from any given atomic arrangement.

The purposes of this paper are: (1) to discuss the bearing of recent

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