LECTURE EXPERIMENTS ILLUSTRATING VARIOUS TYPES OF CATALYTIC ACTION.

A. A. NOYES AND G. V. SAMMET.

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INTRODUCTION.

THE experiments to be described in this article were devised as an accompaniment to two lectures upon the subject of catalysis.[1] It has been decided to publish them, as it is believed that the series as a whole may be of value in connection with lecture courses on theoretical chemistry, and that some of the separate experiments might be introduced into courses on inorganic and organic chemistry.

The experiments are presented in such a manner as to make their preparation and performance as easy as possible for the lecturer. As this involves the enumeration of many details, those who desire to obtain only a general view of the experiments here described are recommended to read, under each experiment, only the paragraphs entitled "Catalyzer", "Reaction Catalyzed" and "Observations", omitting those designated "Preparation" and "Experiment".

In accordance with the proposal of Ostwald, we understand the term *catalysis* to signify the *acceleration or retardation of a chemical reaction by substances which themselves undergo no permanent change as a result of their action.*

For convenience of consideration we distinguish the following important types or classes of catalytic agents:

1. Carriers; 2. Adsorbent contact agents; 3. Electrolytic contact agents; 4. Water; 5. Dissolved electrolytes; 6. Enzymes; 7. Inorganic colloids.

I. CATALYSIS BY CARRIERS.

By *carriers* are understood catalytic agents which are known to accelerate reactions through the formation of an intermediate compound with one of the reacting substances. Although it is

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[1] Delivered before the North-eastern Section of the American Chemical Society and the Society of Arts of the Massachusetts Institute of Technology.

probable that some of the other types of catalytic agents (for example, enzymes) are in reality carriers, the term is here confined to those agents which are known to be such.

The experiments here described illustrate the action of carriers in the three states of aggregation, gaseous, liquid, and solid.

The suggestion of Wagner[1] that carrier-actions be designated pseudo-catalyses, thereby implying that they are not true cases of catalysis, seems to us an unfortunate one. There has always been a tendency to attach to the term catalysis a mysterious significance, which would be continued if the term is still to be confined to *unexplained* accelerating actions. The advantage of Ostwald's definition is that it is a concrete, experimental one, having no reference whatever to the way in which the acceleration is brought about.

Experiment 1.

Catalyzer.—Nitric oxide.

Reaction Catalyzed.—$2SO_2 + O_2 = 2SO_3$.

Preparation of the Experiment.—Graduate roughly, a long, narrow bell-jar of about 500 cc. capacitv by marking lines upon it with a blue pencil at points corresponding to $^6/_{15}$ and $^{11}/_{15}$ of its total volume measured from the closed end of the jar. Rinse the jar with water so that the inner sides of it will be wet; fill it with mercury, and invert it over a long narrow trough, also filled with mercury, and having a deep longitudinal groove in the bottom. Introduce sulphur dioxide into the jar until the meniscus falls to the upper mark; then introduce, by means of a bent tube, enough water barely to cover the surface of the mercury. Connect the bent tube with a gasometer or cylinder of oxygen by means of a rubber tube. Fill two short, wide test-tubes with mercury, and invert them over the trough. Introduce into one of these tubes a volume of nitric oxide equal to 0.1 of the total volume of the bell-jar, and into the other tube one-half this amount of nitric oxide.

Experiment.—Introduce into the bell-jar oxygen from the gasometer or cylinder, until the mercury meniscus falls to the second mark. Place the mouth of the test-tube containing the larger amount of nitric oxide in the groove beneath that of the bell-jar,

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[1] *Ztschr. phys. Chem.*, **28**, 78.

and tip the tube until the gas has passed into the jar. After the mercury has nearly stopped rising, introduce in the same way into the jar the nitric oxide gas in the second tube.

Observations.—No change occurs on adding the oxygen to the sulphur dioxide. When the nitric oxide is introduced, the gas reddens and begins to contract and become filled with white fumes. A white deposit (nitrosylsulphuric acid) soon forms on the sides of the jar. The contraction nearly ceases after 30 to 40 seconds, but becomes rapid again when the second portion of the nitric oxide is introduced. The volume finally becomes constant at about 0.2 of the total volume of the jar.

Experiment 2.

Catalyzer.—Sulphuric acid.

Reaction Catalyzed.—$2C_2H_5OH = (C_2H_5)_2O + H_2O$.

Preparation of the Experiment.—Connect a 500 cc. distilling flask with a Liebig condenser which is fitted with an adapter delivering into a 200 cc. graduate. Place in the flask 135 cc. of concentrated sulphuric acid, and add slowly 75 cc. of alcohol. Insert a 2-hole rubber stopper holding a thermometer and a 150 cc. drop-funnel, both of which reach nearly to the bottom of the flask. Fill the drop-funnel with alcohol, and, just before the lecture, heat the liquid in the flask to 140°-150°; then allow the alcohol to flow slowly into the flask at such a rate that the distillate drops rapidly into the graduate.

Experiment.—Add to the ether which has collected in the graduate 2 cc. of powdered potassium carbonate, and shake. After the layers have formed pour the top layer into a 200 cc. graduate which contains 75 cc. of water, and shake.

Observations.—The alcohol is continuously converted to ether, which comes over in the distillate and holds the water which is also produced by the reaction in solution; but on adding the potassium carbonate the distillate separates into two layers consisting of about 5 cc. of water to 100 cc. of ether. On pouring the upper layer into water, it does not mix with it, showing that the distillate is mainly ether, and not alcohol.

Experiment 3.

Catalyzer.—Ferric bromide.

Reaction Catalyzed.—$C_6H_6 + Br_2 = C_6H_5Br + HBr$.

Preparation of the Experiment.—Support a 250 cc. distilling flask upon a lamp-stand and connect its side-arm with a funnel whose mouth dips just below the surface of a caustic potash solution. Place in the flask 4 cc. of bromine. Provide a cork stopper for the flask, a long-necked funnel, a small wash-bottle, like that used in Experiment 2, containing strong ammonia, 30 cc. of benzene in a small bottle, and 0.5 cc. of powdered iron.

Experiment.—Pour into the distilling flask the 30 cc. of benzene; then add the 0.5 cc. of powdered iron. Blow ammonia gas from the wash-bottle over the neck of the distilling flask. Finally insert the cork.

Observations.—No action occurs between the benzene and bromine alone, but a vigorous boiling up and great clouds of white fumes are observed as soon as the iron is added.

Experiment 4.

Catalyzer.—Aluminum chloride.

Reaction Catalyzed.—$C_6H_6 + CH_3COCl = C_6H_5COCH_3 + HCl$.

Preparation of the Experiment.—Place a 250 cc. distilling flask in a clamp on a lamp-stand. Connect the side-arm with a funnel that dips just beneath the surface of a potash solution. Pour into the flask 10 cc. of acetyl chloride. Provide a cork stopper for the flask, a long-necked funnel, 50 cc. of benzene in a small bottle, 10 cc. of powdered sublimed aluminum chloride in a corked test-tube, and a small wash-bottle of strong ammonia with a rubber syringe bulb attached to the longer tube.

Experiment.—Pour into the flask through the funnel the 50 cc. of benzene, then add the 10 cc. of aluminum chloride. Blow from the wash-bottle ammonia gas over the mouth of the flask, and finally insert the cork.

Observations.—No action occurs between the benzene and acetyl chloride alone, but a vigorous effervescence and copious evolution of white fumes occur soon after the aluminum chloride is added.

Experiment 5.

Catalyzer.—Platinum foil.

Reaction Catalyzed.—$2CH_3OH + O_2 = 2CH_2O + H_2O$.

Preparation of the Experiment.—Pour into a 300 cc. beaker a layer of methyl alcohol 1 cm. deep. Cover the beaker with a perforated watch-glass in whose perforation is a cork stopper from which a star made of platinum foil hangs down by a platinum wire 2 to 3 cm. above the surface of the alcohol.

Experiment.—Ignite the methyl alcohol vapor in the beaker by applying the flame of a burner to it, and raise one side of the watch-glass a few millimeters by inserting a bit of wood or rubber tube.

Observations.—The platinum star glows brightly when the amount of air admitted to the beaker is properly adjusted.

2. CATALYSIS BY ADSORBENT CONTACT AGENTS.

By adsorbent contact agents we understand solid substances that accelerate reactions by the adsorption on their surfaces of one or more of the reacting substances. Whether the acceleration is due to an increase in the concentration of the reacting substances, or to an activation of them, or to a chemical combination constituting a carrier action, is not thereby taken into consideration.

The experiments to be here presented refer mostly to gaseous mixtures, but include one dissolved substance (hydrogen peroxide).

Experiment 6.

Catalyzer.—Platinum.

Reaction Catalyzed.—$2xNH_3 + yO_2 = 3xH_2O + zN_2 + wNO$.

Preparation of the Experiment.—Place in a wide-necked bottle of about 250 cc. capacity, 75 cc. of concentrated ammonia-water (sp. gr., 0.90). Insert a delivery tube, which is connected to a tank of oxygen, so that it dips below the surface of the ammonia-water. Wind one end of a platinum wire (about 0.5 mm. diameter) around a match, leaving the other end so long that, when the match is supported across the mouth of the bottle, the end will be about 1 cm. above the surface of the liquid.

Experiment.—Heat the platinum wire in a flame, and insert it while hot into the flask. After a few seconds turn on a moderately rapid current of oxygen.

Observations.—Almost immediately after introducing the platinum wire into the flask, it begins to glow. When the oxygen is bubbled through the ammonia, the platinum glows more brightly, and the flask becomes filled with white fumes; and after a few seconds an explosion is produced.

Experiment 7.

Catalyzer.—Platinum.

Reaction Catalyzed.—$2SO_2 + O_2 = 2SO_3$.

Preparation of the Experiment.—Place about 5 grams of loose asbestos on a filter plate and pour through it a 10 per cent. hydrochlorplatinic acid solution until the asbestos is saturated with it. Transfer it to a large porcelain crucible, and ignite strongly for thirty minutes, disintegrating the mass from time to time. Pack loosely with the platinized asbestos a piece of combustion tubing about 45 cm. long, to within 4 or 5 cm. of one end and 20 cm. of the other. Place the tube in a short furnace with 2 or 3 burners, and connect one end by means of rubber stoppers and a delivery tube to one of the necks of a three-necked Woulff bottle which is charged to a depth of 2 or 3 cm. with concentrated sulphuric acid. The other two necks of the Woulff bottle are connected by means of rubber stoppers and delivery tubes which dip below the surface of the sulphuric acid in the Woulff bottle, to an oxygen cylinder and a sulphur dioxide generator, respectively. The sulphur dioxide is produced by dropping strong sulphuric acid from a drop funnel into a flask containing strong commercial sodium bisulphite solution. The other end of the combustion tube is fitted with a rubber stopper carrying a T-tube, of which the perpendicular arm is closed by a piece of rubber tubing and a pinch-cock. The straight end of the T-tube is joined to a condensation-tube (such as is used for sulphur dioxide), the bulb of which is placed in a dish of ice. The outlet of the condensation-tube is connected to a funnel, the mouth of which dips only a little below the surface of a potash solution.

Experiment.—Pass the oxygen and sulphur dioxide at a moderate rate through the tube so that the sulphur dioxide bubbles through the sulphuric acid about twice as fast as the oxygen. Light the burners beneath the empty part of the tube, and heat it to just below redness; after a minute or two, open the pinch-cock momentarily to show that no combination is taking place. Then push the tube along so that the platinized asbestos is brought over the flame, and, after the tube has become hot, open the pinch-cock on the T-tube for a moment. Continue the experiment for fifteen minutes or more, and then remove the condensation-tube from the ice-bath.

Observations.—No white fumes are seen on opening the pinch-cock until the platinized asbestos is heated. After about fifteen minutes the condensation-tube will be coated with white crystals.

Experiment 8.

Catalyzers.—Platinum black and bone-black.

Reaction Catalyzed.—$2H_2O_2 = 2H_2O + O_2$.

Preparation of the Experiment.—Place in each of two lecture test-tubes 25 cc. of commercial, concentrated hydrogen peroxide solution which has been made very slightly alkaline by the addition of ammonia. Soak two 9-cm. filter-papers in a 10 per cent. hydrochlorplatinic acid solution; dry the filter papers and ignite them in a large porcelain crucible until the carbon is all burned off. Place the reduced platinum in a small test-tube. Provide also 1 cc. of bone-black and a splinter of wood.

Experiment.—Add the reduced platinum to one portion of hydrogen peroxide solution and the bone-black to the other portion. Ignite the wood-splinter in a flame until one end of it glows when removed from the flame, and insert it in turn into each of the test-tubes.

Observations.—When the platinum black and the bone-black are added to the hydrogen peroxide a violent effervescence ensues and the glowing splinter becomes ignited.

3. CATALYSIS BY ELECTROLYTIC CONTACT AGENTS.

Electrolytic contact agents are those catalytic agents which accelerate reactions in which metals are involved through the formation of a voltaic couple. They are themselves in all cases metallic substances. Two experiments are given below, illustrating their action in case of an inorganic and of an organic reaction, respectively.

Experiment 9.

Catalyzer.—Platinum.

Reaction Catalyzed.—$Sn + 2HCl = SnCl_2 + H_2$.

Preparation of the Experiment.—Fit a 300 cc. Erlenmeyer flask with a rubber stopper provided with a thistle-tube and a delivery-tube, the end of which dips into a beaker of water. Cover the bottom of the flask to a depth of 2 cm. with a layer of pure feathered tin. Provide a medicine dropper, some hydrochloric acid of 1.12 sp. gr., and a little 10 per cent. hydrochlorplatinic acid solution.

Experiment.—Pour into the flask through the thistle-tube enough hydrochloric acid to entirely cover the tin; then add 5 or 6 drops of the platinum solution and shake.

Observations.—Only a very slight action occurs between the tin and acid alone; but a vigorous effervescence and rapid evolution of gas occur soon after the platinum solution is added.

Experiment 10.

Catalyzer.—Copper.

Reaction Catalyzed.—$C_2H_4Br_2 + Zn = C_2H_4 + ZnBr_2$.

Preparation of the Experiment.—Place 20 cc. of absolute alcohol and 20 cc. of ethylene bromide in a lecture test-tube whose mouth is fitted with a cork carrying a straight piece of (5 mm. wide) delivery tubing. Provide 2 cc. of granulated zinc in a test-tube, a little saturated solution of crystallized copper chloride in alcohol, and a beaker of ice water.

Experiment.—Pour the zinc into the test-tube, then add 3 cc. of the copper chloride solution, insert the cork, and shake. As soon as the effervescence becomes very vigorous, so that the air has been completely expelled, light the gas issuing from the tip of the delivery tube. When the action becomes too violent, place the test-tube in the beaker of ice water.

Observations.—No action occurs between the ethylene bromide and zinc alone, but a vigorous effervescence begins in about ten or fifteen seconds after the addition of the copper chloride, and a large jet of flame is produced when the gas is ignited.

4. CATALYSIS BY WATER.

Water is a substance whose presence in at least minute amounts seems to be essential to the occurrence of most chemical reactions. Moreover, its method of action is probably unique, consisting either in a hydration or electrolytic dissociation of the reacting substance. It is therefore not inappropriate that it alone constitutes a type of catalytic agent.

Four experiments illustrating its action on gaseous, liquid, and solid reacting mixtures, and on a solid-gaseous mixture, are here described.

Experiment 11.

Catalyzer.—Water.

Reaction Catalyzed.—$2H_2S + SO_2 = 2H_2O + 3S$.

Preparation of the Experiment.—Fit a thoroughly dry glass balloon with a cork stopper with four holes carrying two dry delivery tubes leading to the bottom of the balloon and a third one terminating just below the stopper. All of these tubes should be bent at right angles above the stopper. Connect one of the long tubes with a tower filled with calcium chloride, which in turn is connected with a gas wash-bottle containing dilute sulphuric acid (1:3), which last is connected with a Kipp hydrogen sulphide generator. Connect the other long tube through two gas wash-bottles containing concentrated sulphuric acid, with a sulphur dioxide gasometer, or a generator in which sulphur dioxide is made by dropping concentrated sulphuric acid into a strong solution of commercial acid sodium sulphite. Connect the third delivery tube with a funnel whose mouth dips a little below the surface of a strong caustic potash solution. Close the fourth hole of the stopper with a piece of glass rod. Pass the two gases into the balloon for ten to fifteen minutes, running the hydrogen sulphide about twice as fast as the sulphur dioxide. (The experiment may fail if the sulphur dioxide is in considerable excess.) Place a 250 cc. flat-bottom flask upon a tripod with a burner beneath. Fill it one-third full of water and fit it with a rubber stopper provided with a delivery tube, so bent that its outer end can be easily inserted in the fourth hole of the stopper of the balloon. Regulate the flame of the burner so that the water is kept barely boiling.

Experiment.—Cause the two gases to flow into the balloon for half a minute. Then remove the piece of glass-rod, insert the delivery tube leading from the flask of boiling water, and allow the steam to flow into the balloon for a few seconds.

Observations.—Nothing occurs on mixing the two gases in the dry state. After introducing the steam, sulphur at once begins to deposit on the walls of the balloon, and, in the course of half a minute, completely covers them.

Experiment 12.

Catalyzer.—Water.

Reaction Catalyzed.—$I_2 + H_2S = 2HI + S$.

Preparation of the Experiment.—Place 250 cc. of commercial sodium-distilled ether in a 500 cc. glass-stoppered bottle. Dissolve in this 0.35 gram of iodine and saturate the solution with hydrogen sulphide by passing through it for ten minutes a slow current of gas, generated in a Kipp generator and dried by being passed first through a gas wash-bottle containing dilute sulphuric acid (1:3) and then through a drying tower filled with calcium chloride. Place the hydrogen sulphide apparatus upon the lecture table. Measure out 3 cc. of water in a small graduate.

Experiment.—Pass a slow current of hydrogen sulphide into the ethereal solution of iodine for half a minute. Add 3 cc. of water to the ether solution and shake thoroughly.

Observations.—Decolorization of the dry ethereal solution of iodine is caused only very slowly by the hydrogen sulphide, but takes place very rapidly when the water is added.

Experiment 13.

Catalyzer.—Water.

Reaction Catalyzed.—$Zn + I_2 = ZnI_2$.

Preparation of the Experiment.—Place 4 cc. of powdered iodine in a test-tube and 2 cc. of zinc dust in a 25 cc. glass-stoppered wide-mouthed bottle. Place a carbon-funnel in the mouth of a 4-liter glass balloon supported on a suitable ring. Provide a wash-bottle delivering a fine stream.

Experiment.—Pour the iodine into the bottle containing the zinc dust and shake. Then pour the mixture onto the bottom of the balloon and direct a stream from the wash-bottle upon it.

Observations.—On the addition of water to the dry mixture of the zinc dust and powdered iodine, a violent action takes place attended by a sizzling and evolution of violet vapors of iodine, which entirely fill the balloon.

Experiment 14.

Catalyzer.—Water.

Reaction Catalyzed.—$2Na + Cl_2 = 2NaCl$.

Preparation of the Experiment.—Fill a piece of combustion tube 100 cm. long, which has been dried by flashing with a flame, quickly with phosphorus pentoxide for $^2/_3$ of the distance from one end of the tube, using ignited asbestos plugs to hold it in place. The delivery tube from a gasometer of chlorine is joined to a T-tube, one branch of which is connected with a rubber tube (provided with a pinch-cock) long enough to reach to the empty end of the combustion tube; the other branch of the T-tube leads through two gas-wash-bottles containing sulphuric acid to the filled end of the combustion tube, which is fitted with a rubber stopper carrying a Y-tube, of which the third branch leads through a rubber tube provided with a pinch-cock to a funnel dipping under strong caustic potash solution. Fit the empty end of the combustion tube with a perforated stopper carrying a small delivery tube. Pass chlorine at a slow rate for half an hour through the sulphuric acid bottles and the combustion tube, which is inclined somewhat so that the gas enters at the lower end.

While the chlorine is passing, flash the empty part of the combustion tube for some minutes with a flame in order to dry it completely. Provide a Bunsen burner, a small porcelain boat, a pair of pincers, several pieces of sodium of the size of a pea, and a stout wire with a hook at one end for removing the boat from the combustion tube.

Experiment.—Start a slow current of chlorine through the combustion tube. Place in the porcelain boat three or four pieces of sodium. Ignite the sodium by heating the boat in the flame of the burner and push it into the empty part of the combustion tube. Draw the boat back into the air for a moment, and again push it into the tube; then insert the stopper, connect the delivery tube in it with the rubber tube leading directly to the chlorine generator, and open the pinch-cock upon it. Open the pinch-cock on the tube leading into the potash solution, and pass a rapid current of the undried chlorine over the sodium through the tube in the reverse direction to that of the previous current.

Observations.—When the burning sodium is inserted in the dry chlorine, it is extinguished. When drawn back into the air, it becomes again ignited, and is again extinguished on pushing it back into the dry chlorine. When the moist chlorine is passed over it, it burns with great brilliancy.

5. CATALYSIS BY DISSOLVED ELECTROLYTES.

Dissociated substances in aqueous solution exert a variety of catalytic actions. The most important of these is that exerted upon reactions of hydrolysis by acids in virtue of their hydrogen ions.[1] This is illustrated by an experiment on the saccharification of starch by sulphuric acid.

Another variety of catalytic action by electrolytes is the great retardation of reactions involving weak acids, by their neutral salts,—a phenomenon explained by the Ionic Theory and the Law

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[1] We desire to take this opportunity to suggest what seems to us a plausible hypothesis in regard to the action of hydrogen ions: that is, that these ions are hydrated and that the water in combination with them is more reactive than ordinary water; in other words, that the hydrogen ions act as water-carriers. While there is at present no experimental evidence in favor of this hypothesis (or of any other), the fact that it is an entirely reasonable one shows that one of the purest types of catalytic action may be in reality only a carrier action.

of Mass-Action. A lecture experiment illustrating this has been already described in detail in this Journal.[1]

Still another variety of such catalytic actions is the highly specific influence on reactions of oxidation and reduction of certain dissociated substances, especially of those which are themselves capable of undergoing oxidation or reduction. An experiment on a reaction of this kind has been earlier presented.[2]

Finally is to be mentioned a type of action which electrolytes exert apparently as a direct consequence of the electric charges upon the ions, namely, the coagulation of colloidal solutions and fine suspensions. Although this is not in a strict sense a catalytic action, since according to recent experiments[3] a minute quantity of the electrolyte is decomposed and precipitated with the colloid, yet the coagulative effect produced is so great in comparison with the quantity of electrolyte consumed that it has, from a practical standpoint, the characteristics of a catalysis. We have therefore included an experiment showing both the coagulation of colloidal arsenic sulphide by salts and the much greater coagulating effect upon it of bivalent than of univalent positive ions.

Experiment 15.

Catalyzer.—Sulphuric acid.

Reaction Catalyzed.—$(C_6H_{10}O_5)_x + xH_2O = xC_6H_{12}O_6$.

Preparation of the Experiment.—Place 2 cc. of starch in each of two lecture test-tubes. Measure out in small graduates two 5 cc. portions of Fehling's solution, 25 cc. of a 5 per cent. sulphuric acid solution and enough strong caustic potash solution to neutralize this acid (9 cc. of 50 per cent. potash).

Experiment.—Add the 25 cc. of acid to the starch in one of the test-tubes and 25 cc. of water to that in the other, and boil both for about half a minute. Neutralize the acid solution with the potash. Bring the contents of both test-tubes to a boil, then add 5 cc. of Fehling's solution to each, and bring to a boil again.

Observations.—On addition of the Fehling's solution a heavy

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[1] This Journal, **22**, 744.

[2] *Ibid.*, **22**, 742.

[3] Linder and Picton: *J. Chem. Soc.*, **67**, 63 (1895); Whitney and Ober: This Journal, **23**, 842 (1901).

red precipitate is thrown out in the tube in which the starch was boiled with the acid, but the blue color of the solution is not discharged in the other tube containing only starch and water.

Experiment 16.

Catalyzers.—Barium chloride and sodium chloride.

Reaction Catalyzed.—As_2S_3 (colloid) = As_2S_3 (precipitate).

Preparation of the Experiment.—Saturate 250 cc. of cold distilled water with hydrogen sulphide, and add to it gradually (that is, within two or three minutes) a solution of 5 grams of arsenious oxide in 250 cc. of water, keeping the hydrogen sulphide passing into the solution during the addition. Filter this solution. Place 200 cc. of it in each of two lecture jars provided with glass stirring rods. Prepare 100 cc. of a half-normal solution of barium chloride and also of one of sodium chloride.

Experiment.—Add to the colloid in one jar 3 cc. of the barium chloride solution, stirring constantly. To the other colloid, add 25 cc. of the sodium chloride solution, and after waiting about a minute, add 40 cc. more.

Observations.—On addition of the salt solutions to the colloid, immediate coagulation of arsenious sulphide takes place in the solution to which the barium chloride was added, and on waiting a minute or so, the precipitated sulphide settles in this solution, while no change takes place in the colloid to which the sodium chloride was added. On the addition of the second portion of sodium chloride, however, this solution also coagulates.

6. CATALYSIS BY ENZYMES.

Enzymes are complex organic substances of animal or vegetable origin which exert a variety of catalytic actions. Enzymes may be classified as hydrolyzing, oxidizing, molecule-splitting, synthesizing, and coagulating, according to the nature of the reaction which they catalyze. Experiments are described below illustrating the first, third, and fifth of these classes; namely, the hydrolysis of starch by ptyalin and of a glucoside by emulsin, the decomposition of hydrogen peroxide by blood, and the coagulation of casein by rennet. The decomposition of hydrogen peroxide is produced by enzymes of all kinds, and is therefore not a good example of a specific molecule-splitting enzyme. A far better one would be the decomposition of sugar into alcohol and carbon dioxide by zymase, the recently discovered enzyme to which the action of yeast has been shown to be due; but its separation from the yeast-cells is a matter of some difficulty.[1] The hydrogen peroxide experiment is introduced here partly for the sake of illustrating the retarding effect which poisons exert on enzyme-action.

Experiment 17.

Catalyzer.—Ptyalin.

Reaction Catalyzed.—$(C_6H_{10}O_5)_x + xH_2O = xC_6H_{12}O_6$.

Preparation of the Experiment.—Place in a lecture test-tube an amount of corn-starch of the volume of a split pea. Provide 25 cc. of fresh saliva and a little 1 per cent. iodine solution. (Secretion of saliva in the mouth may be greatly promoted by chewing a piece of paraffin.)

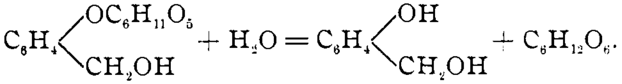
Experiment.—Add 10 cc. of water to the starch and heat it to boiling. Add 10 cc. more of cold water and 2 or 3 drops of the iodine solution; then add the 25 cc. of saliva. When decolorized, add a few more drops of iodine.

Observations.—The starch solution becomes of a deep blue color on the addition of the iodine, and this disappears almost immediately on addition of the saliva and is not restored when the second portion of iodine is added.

Experiment 18.

Catalyzer.—Emulsin.

Reaction Catalyzed.—



$$C_6H_4\begin{cases}OC_6H_{11}O_5\\CH_2OH\end{cases} + H_2O = C_6H_4\begin{cases}OH\\CH_2OH\end{cases} + C_6H_{12}O_6.$$

Preparation of the Experiment.—Dissolve 10 cc. of powdered salicine in 75 cc. of water. Place half of this solution in each of

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[1] See Effront: "Enzymes and their Applications," Prescott's Translation, p. 277.

two lecture test-tubes. Rub 0.25 gram of emulsin to a fine powder in a mortar and treat it with 20 cc. of warm water; allow it to stand for some hours and then filter it. Pour one-half of the emulsin solution into each of two small test-tubes. Measure out two 5 cc. portions of Fehling's solution.

Experiment.—Add to one of the test-tubes containing the salicine one-half of the solution of emulsin, warm gently (not above 50°), and allow to stand for more than a minute. In the meantime, heat the rest of the emulsin to boiling for half a minute, add it to the other half of the salicine, and heat the mixture to boiling. Then heat the other tube of salicine and emulsin to boiling, add 5 cc. of Fehling's solution to each tube, and bring to a boil again.

Observations.—On boiling with Fehling's solution, scarcely any change takes place in the salicine solution to which the emulsin destroyed by boiling was added, but decolorization and formation of a red precipitate take place in the other salicine solution which was treated with the unboiled emulsin.

Experiment 19.

Catalyzers.—Blood and blood + potassium cyanide.

Reaction Catalyzed.—$2H_2O_2 = 2H_2O + O_2$.

Preparation of the Experiment.—Place in each of two lecture test-tubes 25 cc. of hydrogen peroxide. Provide 2 cc. of saturated potassium cyanide solution, some fresh blood, and a medicine dropper.

Experiment.—To one tube of hydrogen peroxide add 5 or 6 drops of the potassium cyanide solution, then add to each tube 4 or 5 drops of blood.

Observations.—A very vigorous effervescence and a voluminous frothing occur in the tube of hydrogen peroxide to which blood alone was added, while in the one to which the cyanide was added only a slight action takes place.

Experiment 20.

Catalyzer.—Rennet.

Reaction Catalyzed.—Casein (colloid) = Casein (precipitate).

Preparation of the Experiment.—Place 200 cc. of skimmed milk in a lecture jar. Provide some commercial liquid rennet.

Experiment.—Add 30 cc. of the rennet to the milk, and stir.

Observations.—Almost immediate coagulation of the milk occurs.

7. CATALYSIS BY INORGANIC COLLOIDS.

Experiment 21.

Catalyzers.—Colloidal platinum and colloidal platinum + potassium cyanide or iodine.

Reaction Catalyzed.—$2H_2O_2 = 2H_2O + O_2$.

Preparation of the Experiment.—Prepare some colloidal platinum solution as follows:[1] Attach each of two short platinum wires 1 mm. in diameter, to a stout copper wire, covered with insulating material, by binding the ends of the copper and platinum wire together with thin copper wire. Slip a small glass tube over each platinum wire so as to cover it within 1 cm. of its free end. Connect the wires with the terminals of a 110-volt-direct-circuit, having a 32-candle-power lamp in series. Place pure distilled water, best that distilled from alkaline permanganate, in a crystallizing dish 10 cm. in diameter, and surround this dish, in a larger one, with cracked ice and water. Grasp the glass tubes firmly in the hand, bring the two platinum points together beneath the surface of the pure water, and immediately separate them so as to form an arc. Maintain this arc for about ten minutes, pulling the platinum points apart when they fuse together and touching them momentarily when the arc disappears as a result of too great separation of the wires. Filter the black solution thus obtained and keep it in a stoppered bottle. Place in each of two lecture test-tubes 25 cc. of hydrogen peroxide made slightly alkaline with ammonium hydroxide. Provide 2 cc. saturated potassium cyanide solution, 2 cc. 5 per cent. solution of iodine in potassium iodide, two 10 cc. graduates, and a medicine dropper.

Experiment.—Measure out two 10 cc. portions of the colloidal platinum solution, and add to one portion about 5 drops of the

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[1] According to Bredig's directions. See *Ztschr. phys. Chem.*, 31, 271 (1900).

potassium cyanide solution. Pour one of these two portions into each of the tubes of hydrogen peroxide. After a vigorous effervescence has started in the solution which contains no cyanide, add about 5 drops of the iodine solution to it.

Observations.—After the hydrogen peroxide has stood about a minute with the colloidal platinum solution, a vigorous effervescence occurs in the solution which contains no potassium cyanide, while in the solution in which the cyanide is present no appreciable evolution of gas occurs. Immediately after adding the iodine to the effervescing tube, the reaction slackens, and in the course of a few seconds the evolution of oxygen almost entirely ceases.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY.

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THE POLARIZATION OF FRUITS, JELLIES, JAMS, AND HONIES.

BY L. M. TOLMAN.

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LARGE amounts of sucrose are added in the preparation of jellies and jams, some of which is inverted in the process by the action of the organic acids, such as citric, malic, or tartaric. As a rule the jams which are cooked the longest[1] show the largest amount of inversion as would be expected. In working with a large number of these products, however, the rather curious fact was noted that apparently complete inversion rarely if ever took place, or, at least, in polarizing before and after inversion there was always an increase in the minus reading on the sugar scale, often not more than from 1° to 2°, which calculated as sugar by the Clerget formula showed from 1 to 1.5 per cent. of cane sugar. The usual explanation of the phenomenon is that it is due to cane sugar, but it is probable that this change is due to an entirely different cause.

It must be remembered that the cane sugar in these products has been inverted by the action of the fruit acids and it is possible

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[1] Tolman, Munson, and Bigelow: This Journal, **22**, 351 (1901).