

## NASCENT STATE OF THE ELEMENTS.

BY J. H. RANSOM AND R. A. STEVENS.

It is well known that some of the elements at the instant of liberation from their compounds or when in contact with certain other materials are more chemically active than under other conditions. This so-called "nascent state" has for more than sixty years been assumed to be due to the atomic as distinguished from the molecular condition of the elements. In some of the more recent texts this explanation has been replaced either by one based upon thermodynamics or by that known as "contact or catalytic action."

The principle of thermodynamics is that those reactions will be most apt to occur which are accompanied with the greatest degradation of energy. On this principle is explained the fact that hypochlorous acid is a better oxidizing agent than free oxygen. The former decomposes with the evolution of heat and therefore the total energy evolved during oxidation with it is that much greater than would be produced with the use of free oxygen. Or as Mellor (*Inorganic Chem.*, p. 460) says regarding nascent hydrogen, "Its greater activity is ascribed to the energy of the reaction being available for inaugurating another reaction rather than being frittered away as heat." This is a fundamental principle and no doubt influences if it does not determine the course of reactions. But it does not seem to explain why iodic acid, which decomposes with the absorption of almost as much heat (per atom of oxygen) as hypochlorous acid evolves, oxidizes hydrogen iodide, in solution, much more rapidly than does free oxygen.

The contact explanation assumes that the presence of certain substances in contact with reacting materials increases the velocity of the action between those materials *solely* by its presence. According to this theory the increased activity of nascent hydrogen is due to its contact with the metal at the instant of liberation. If the presence of the contact agent forms the only difference between the active and inactive hydrogen then it would seem that intimate contact of the latter with the more positive metals should cause it to become active. This explanation of activity appears less fundamental than that due to the atomic condition of the

elements, but it is claimed that it offers a better explanation for the varying degrees of activity of hydrogen obtained from different sources and that it also explains the activity of hydrogen absorbed in metals.

The experiments described in this paper are designed to study the activity of hydrogen from various sources as shown in its action on chromic acid and chromates as well as on hydrogen peroxide and permanganates. These were chosen because they are not the most readily reduced or because their disappearance may be easily determined by color reactions. The attempt was made to study the effect of each of the substances which would need to be present for the reduction of the substance by nascent hydrogen. In the preparation of free hydrogen for use care was taken to remove any foreign material which might act as an oxidizing or reducing agent. Very dilute solutions of the oxidizing agents were used in order that a slight color change might be the better noticed. The acid was 30% C. P. sulphuric. Pure stick zinc was used, a dozen or more being bound together so that the lower end of the pile was concave, thus allowing hydrogen to collect and work its way up between the sticks. The results with potassium dichromate solution were as follows: Purified hydrogen passed into the aqueous or acidified solution caused only a very slight reduction in several hours of time. With zinc rods in the aqueous solution a very slight reduction could be noticed at the end of eight hours passage of the hydrogen. Nascent hydrogen generated in the solution caused a much more rapid reduction of the chromate.

Next a solution of chromium trioxide was made, the zinc rods were suspended in the solution and especially purified hydrogen caused to pass up around the bundle of rods several hours a day until the time amounted to 205 hours. During the time the air was excluded and the space above the liquid (the rods were only partly submerged) was an atmosphere of hydrogen. At the end of this time the solution was still distinctly yellow though slightly lighter in color than at the commencement.

The same kind of an experiment was repeated with potassium dichromate but platinum foil was substituted for the zinc rods. In order that the hydrogen might be divided into small bubbles and come into contact with as much platinum as was possible a platinum filtering cone was sealed into the end of the delivery tube and just above this was fastened a rosette made of strips of platinum foil. The hydrogen bubbles bumped against this foil as they rose through the liquid. Connection was made so that this platinum might be made the negative electrode for the production of nascent

hydrogen. In this series the hydrogen passed through the solution for only four hours. Little or no reduction occurred except when the platinum was made the negative electrode from a battery. Then reduction was quite rapid.

When zinc dust or platinum black was suspended in the liquid and hydrogen passed in the reduction approached the rapidity due to nascent hydrogen.

Similar experiments were carried out using carbon instead of platinum. New arc-light carbons were purified by first soaking them in acid and then heating them to redness for twenty minutes. They were then placed in a solution of acidified potassium dichromate until no reduction of the latter was observed. After thorough washing they were bound into a bundle and used in the same way as were the zinc rods. In the aqueous solution containing the carbons hydrogen produced little or no reduction of the dichromate in four and one-half hours. When the carbons were made the negative electrode from a battery reduction was complete in from fifteen to thirty minutes.

Finely divided carbon suspended in the solution of dichromate did not increase the reducing power of hydrogen led into the solution.

An attempt was made to duplicate the conditions for the production of nascent hydrogen by having both zinc and acid in the dichromate solution and then to prevent the formation of nascent hydrogen at the surface of the zinc by connecting the latter by wire to a piece of platinum placed in a different part of the solution and prevent diffusion of hydrogen by surrounding the zinc with a porous cup. The zinc was also made the positive electrode from a weak battery. But local action around the zinc produced a small amount of nascent hydrogen so that a slow reduction always occurred. It is still hoped that this may be made successful.

In this connection it is interesting to note that in order to eliminate local action amalgamated zinc rods were tried. But in the presence of these hydrogen caused a more rapid reduction of the dichromate than when they were made the negative electrode from a battery. The reason for this has not been determined and will be the subject of further inquiry.

The reduction of hydrogen peroxide was attempted using the platinum rosette as contact agent. No change in the amount of the peroxide could be detected with the usual tests for that substance after hydrogen had passed for four and one-half hours. But when the platinum was made the

negative electrode complete reduction occurred in about one-third the time.

In order further to compare the activity of nascent hydrogen made in contact with different metals pieces of sheet copper, tin and platinum as nearly equal in exposed area as possible were each made the negative electrode from a battery giving practically the same current. The cell contained the same quantity, in solution, of acidified dichromate. The hydrogen in all cases reduced the solution in about the same time.

Finally a glass tube about five feet long and one centimeter bore, sealed at one end, was filled with a good grade of granulated zinc whose surface had been cleaned by washing, in turn, with acid, water, ammonium hydroxide and large quantities of distilled water. A solution of chromic acid was made by dissolving a small quantity of chromium trioxide in water which had been purified by re-distilling ordinary distilled water from alkaline permanganate and using only the middle fraction which was again brought to boiling for a few minutes immediately before using. The tube containing the zinc was filled with this solution and then one-half of it replaced by well purified hydrogen free from air. The open end of the tube was connected to a smaller tube leading to a vessel of mercury to prevent the escape of hydrogen and to indicate any change in the volume of the latter. The tube was then placed on a table in a horizontal position so that one-half of the zinc was in the liquid and one-half in contact with the hydrogen. The tube remained in this position from January ninth to October seventeenth last. Except for two months during the summer the tube was observed daily. No change in pressure occurred except that due to changes of temperature, and no amount of hydrogen was evolved. The solution perhaps, became slightly lighter in color. On opening the tube the hydrogen burned quietly. A little sulphuric acid added caused the solution to become as dark as at the beginning. A little sediment was found in the tube which looked like zinc oxide. Acid and zinc added to the solution caused rapid reduction.

In connection with the same subject some preliminary work has been done on the reduction of potassium permanganate. Purified hydrogen passed into a dilute aqueous solution of the permanganate decolorized the solution in less than twelve hours forming a brown deposit. In the presence of platinum foil the reduction was more rapid, sometimes being complete in one hour. If the platinum were allowed to remain in contact with the solution for some time the reduction with hydrogen seemed to be even

more rapid. To get some idea of the part the metal might be playing a strip of platinum foil about a foot long was thoroughly cleaned and put into a glass tube. A dilute solution of permanganate was poured in to cover the metal, and the tube stoppered. Gradually a brown deposit appeared on the platinum and floating in the liquid. In twelve days the color was discharged. Treated with hydrochloric acid the brown solid gave the odor of chlorine. The same result was obtained when hydrogen was passed into a solution of permanganate containing granulated zinc. The colorless filtrate from the zinc was strongly alkaline, contained potassium, but only a trace of manganese.

In order to study this action more in detail some granulated zinc was allowed to stand in contact with a solution of the permanganate. Gradually reduction occurred the zinc becoming covered with a gold-yellow deposit. The reduction became slower as the deposit on the zinc increased. Finally the solution became colorless and gave an alkaline reaction.

In a roughly quantitative experiment two grams of permanganate were dissolved in especially purified water and this solution placed with a large quantity of zinc. The mixture was shaken periodically. In a month the liquid had become colorless. The liquid was filtered from the zinc and the latter thoroughly washed. Titration of this liquid with methyl orange, against a standard acid, gave 89 per cent. of the theory for the hydrolysis of the permanganate. As much as possible of the yellow solid was removed from the zinc and this with the finer particles was treated with nitric acid to dissolve any zinc. On treatment the solid darkened. Its weight was .9077 grams, and it gave chlorine with hydrochloric acid.

In order to understand what was the reducing agent in the above reaction a quantity of well cleaned zinc was placed in a flask with especially purified water. The flask was connected with a eudiometer filled with the same kind of water. The eudiometer was arranged so that the water might be displaced by a gas. Gradually hydrogen was formed. By stirring the zinc about the hydrogen passed into the eudiometer. In 35 days twenty-five cubic centimeters of hydrogen had collected. This burned quietly showing no admixture with oxygen. The experiment was then discontinued.

The results of the experiments with permanganate indicate that its solution is hydrolized and that the free acid is then reduced either directly by the zinc or by the nascent hydrogen produced by the action of zinc on

water or on the acid. The instability of the acid apparently plays a part especially in the presence of something which can combine with the oxygen or absorb it (in the case of platinum) and thus prevent equilibrium.

Very little work seems to have been done to determine the cause or causes of the increased activity of nascent elements. Most of the workers have assumed the atomic state as a sufficient explanation. Pattison Muir (*Prin. of Chem.*, p. 105) points out the need of considering all the reacting substances rather than that of the element only, and cites the work of Tommasi (*Pogg. Beiblätter* 2,205) who found that sodium amalgam would not reduce a solution of potassium chlorate but that hydrogen from zinc and dilute sulphuric acid would do so. Muir afterwards found that magnesium, sodium and even a copper-zinc couple would reduce (presumably slowly) an aqueous solution of potassium chlorate; but he seems to have overlooked the fact that with zinc and acid the substance reduced is not the chlorate but chloric acid, a much less stable material and consequently more easily reduced. Thorpe has found (*C. S. Journ. Trans.* 1882, 289) that the rate of reduction of ferric sulphate varies with the chances which hydrogen has of coming in contact with the material, and that the rate of reduction in unit time decreases with increased rate of hydrogen evolution. He also observed that the presence of certain salts, as zinc sulphate, decreased the rate of reduction, and that the nature of the metal used influenced the rate. Perhaps the most enlightening results were obtained by Traube (*Ber.* 15, 659, 2421, 2434; 16, 1201) in his work on the constitution of hydrogen peroxide. He found that when palladium is charged with hydrogen and made the positive pole of a battery no peroxide is formed but the nascent oxygen is reduced to water. But when such palladium is made the negative pole and molecular oxygen is bubbled around the pole peroxide is produced. If non-hydrogenized palladium is used the greatest amount of the peroxide is formed (only at the negative pole) when all the hydrogen produced is absorbed by the palladium, and the amount decreases as the amount of hydrogen more than this increases. With carbon poles no peroxide was produced at either pole. There seems to be no evidence, however, that hydrogen evolved from carbon poles did not reduce the oxygen, and it is probable that it was reduced to water either directly or through the peroxide as an intermediate product. The latter is the more probable since nascent hydrogen rapidly reduces the peroxide.

From the foregoing experiments the following conclusions appear justifiable. First, nascent hydrogen obtained from varying sources and in contact with different substances has about the same reducing power. And, second, gaseous hydrogen in contact with metals used to make nascent hydrogen is not made more active by that contact. If these conclusions *are* justifiable the argument upon which the "contact" explanation is based becomes greatly weakened. And it becomes still weaker when the first part of the work of Traube, described above, is considered. For if contact with palladium is the only cause of the activity of nascent hydrogen there is no reason why the same substance should not have formed at the two poles. It remains to show that the activity of absorbed hydrogen is not due to contact action.

Much work has been done in investigating the phenomena of absorption of gases by metals. From the volume of gas absorbed by different metals, as platinum, silver and nickel, Sieverts (*Zeit. für Phys. Chem.* LX, 129 and LXVIII, 115) concluded that the absorbed element was in the atomic state. Richardson (*Phil. Mag.* VII, 266 and VIII, 1), in his studies on the diffusion of gases through metals came to the same conclusion, saying "This result can be explained by supposing that the hydrogen is dissociated and that the dissociated atoms pass freely through the platinum." Gladstone and Tribe in their work on "The Action of Substances on Nascent and Occluded Hydrogen" (*C. S. Journ.* 1879, 179, *Trans.*) say "Among other results of this investigation we may claim to have established still more fully the close likeness of character and therefore of condition between hydrogen usually denominated nascent and hydrogen occluded by metals." Also Bain in his work on the absorption of hydrogen by carbon (*Zeit. für Phys. Chem.* LXVIII, 471) concludes that the absorbed hydrogen is in the atomic state. If these conclusions are justified the activity of absorbed hydrogen need not be longer considered as due to "contact" action. But if it still be found that contact does modify the activity of elements is it not a condition of chemical activity or a means of altering the velocity of a chemical change rather than an explanation? Does not the question remain, "Why, and in what manner they do so? Manganese dioxide accelerates the decomposition of potassium chlorate, but this fact does not throw any light on the mechanism of the reaction nor does it explain why the oxygen at the instant of separation is a better oxidizing agent than ordinary oxygen at the same temperature. Heat is a necessary condi-

tion for the rapid reduction of copper oxide by gaseous hydrogen, but it is in no sense an explanation of the chemical changes. To explain these it may be said that at the high temperature the molecules become unstable or actually begin to decompose into the various atoms and that these then combine to form molecules more stable at the temperature. The presence of acids makes possible the decomposition of water by electricity. The ionic theory offers a satisfactory explanation.

In contradistinction to the "contact explanation" stands the atom-molecular idea. It is based upon established and almost universally accepted theories involving atoms and molecules, the relations between which have been used to explain differences in properties, and to account for constitutional and space isomerism, unsaturation and chemical activity. Assuming molecules then the atoms follow as a perfectly logical deduction. And if atoms they must separate from molecules as such during chemical reactions, for in many cases there is less than a molecule of the element in a molecule of the compound and even if there is they are not often united in the molecule. Moreover the ionic condition of the elements necessitates that the atoms exist at the instant of discharge of the electricity. Likewise combinations must often, if not always be preceded by decomposition of molecules into the constituent atoms. The addition of hydrogen to unsaturated molecules, as ethylene, must be preceded by the formation of atoms of hydrogen for these are found in different parts of the new molecule. The combination of sulphur dioxide with oxygen in the presence of platinum black must be preceded by the formation of atoms of oxygen for the new molecule contains but a half molecule of oxygen and at the high temperature the double molecule,  $S_2O_2$ , is probably not formed. Even the formation of the molecules of water from hydrogen and oxygen must be preceded by the decomposition of both kinds of molecules, for in the molecule of water there is but half a molecule of oxygen and the atoms of hydrogen are not united to each other. The combination of ammonia with hydrogen chloride may be cited as another example for the hydrogen and chlorine are not united in ammonium chloride. It is doubtful if any molecules as such ever have any tendency to combine or to interact in any way. The conditions under which material is placed in order to stimulate chemical action is conceivably for the purpose of starting the decomposition of molecules into atoms which by combining evolve the energy to continue the decomposition. The ther-



mochemical change would not be affected by such a process because it depends only on the initial and final products.

Objection is made to the atomic-molecular explanation (Smith Inorganic Chemistry, p. 424) because it is used to explain the oxidizing activity of hypochlorous acid but is not often used to explain that of sulphuric acid or of double decompositions, as the action of sulphuric acid on salt. Concerning the former it may be said that it should be applied as rigidly in one case as the other. The pre-heating in the case of sulphuric acid may be considered as necessary for the decomposition of the acid to form atomic oxygen, and is often so considered. Concerning such actions as that of acid on salt it may be replied that they are explained by as "fairy" a theory, viz., the electron modification of the ionic theory.

Even if the activity of nascent hydrogen is finally found to vary greatly with the sources of its production the atomic-molecular explanation will still be sufficient. For the absorbing or atomizing power of the elements varies greatly; and for those having little atomizing power the smoothness and other characteristics of the superficial surfaces must determine the relative chances of the atoms meeting to form molecules or of acting on the other material present.

The investigation of the subject will be continued as opportunity offers.

