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## ON THE ASSUMPTION OF A SPECIAL "NASCENT STATE."

BY LAUNCELOT ANDREWS, PH. D.

The assumption frequently appears in chemical literature that elements at the moment of being set free from their compounds exhibit properties which the same elements do not ordinarily possess. This alleged specific condition is designated as the "nascent state" or *status nascendi*. The hypothesis of such a condition dates back to the time when the dualistic theory held sway and, so far as I am aware, has not been subjected to criticism in the light of modern views.

It is my purpose in the present paper to consider the following pertinent questions concerning this hypothesis:

*First.* Is it necessary to our understanding of any known facts?

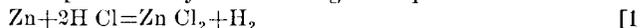
*Second.* Does it offer a simpler explanation of any facts than can be given without its aid?

*Third.* Is it inconsistent with known facts?

*Fourth.* Can it be consistently applied to any class of phenomena without the aid of additional auxiliary assumptions?

One of the classes of chemical reactions which is most often explained by the assumption of a nascent state is that in which reduction is effected by metallic zinc in acid solutions or by sodium amalgam in aqueous neutral alkaline or acid solution or by other oxydizable metals. Here the metal is said to act upon the water or the acid, setting free hydrogen which in turn, by virtue of the peculiar properties it is supposed to possess in the nascent state, effects the reduction.

Thus the reducing of ferric chloride to ferrous chloride by zinc in acid solutions would be represented by the following two equations:



The reduction of a copper sulphate solution would be represented thus:

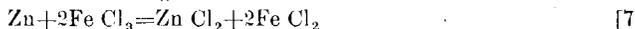


And in the same way the reduction of metallic Cu at the negative electrode during the electrolysis of a Cu SO<sub>4</sub> solution would be represented as *secondary* and due to the nascent hydrogen appearing there. In the familiar process of preparing sulphurous anhydride by the action of copper on concentrated hot sulphuric acid we find it assumed that hydrogen is first produced as in equation 3 and then in *statu nascendi* immediately reacts on the sulphuric acid,



forming water and sulphurous anhydride.

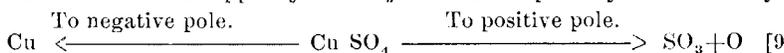
Many other cases might be cited of simple reactions in which it is considered necessary by some authors to employ the nascent hypothesis, but I shall, for the present, confine myself to these and in the light of the facts seek an answer to our four crucial questions. If we dispense with the hypothesis we must assume in each case a direct action of the metal on the salt; thus zinc and ferric chloride would give zinc chloride and ferrous chloride.



Zinc and copper sulphate would simply present a case of direct interchange of metals.

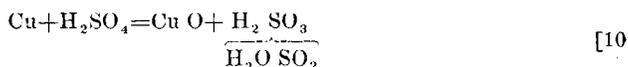


The reduction of copper by electrolysis would be primary not secondary.



This view in the latter case will not be seriously questioned by any student of the recent work of Arrhenius and Ostwald and their followers.

Lastly, we can simply represent the reduction of hot concentrated sulphuric acid as consisting in the first stage in an oxidation of the copper at the expense of the acid.



The sulphurous acid becoming dehydrated of course at the high temperature of the reaction; and the copper oxide being soon converted into copper sulphate.

In the cases named it is clear that the nascent state hypothesis is not necessary and does not lead to a simpler explanation of the facts than can be had without it. Is it inconsistent with any of the facts? Considering first the reduction of sulphuric acid by copper, the following phenomena may be observed: When metallic copper, carefully cleaned, is heated gradually with concentrated sulphuric acid until sulphurous anhydride begins to be evolved, the surface of the copper becomes coated with a black crust. If the metal is now removed from the acid, then washed and placed in hydrochloric acid, the coating dissolves, forming a solution of copper chloride. In fact, this crust consists of copper oxide. Its formation is not explained by the hypothesis in question (eqs. 5-6) but is a direct confirmation of eq. 10. If the acid is reduced by hydrogen some of the hydrogen might be expected to escape unoxidized. In order to test this point pure sulphuric acid was heated with copper which was obtained by electrolysis from a recrystallized specimen of copper sulphate and subsequently ignited in an atmosphere of carbon monoxide. The gases evolved were collected over mercury and about 50 c. c. were treated with caustic potash. All was absorbed except a small bubble, which consisted essentially of oxygen. No hydrogen could be detected.

In order to demonstrate, however, that none had been formed it was necessary to show that if formed it would not be wholly oxidized by the hot acid. To get direct evidence upon this point, a quantity of nearly pure zinc was heated with the same acid that had served for the copper experiment and in the same way. Fifty c. c. of the evolved gas was only partly

absorbed by potash, a residue of about 3 c. c. being left. This residue consisted essentially of hydrogen.

The chain of evidence now appeared complete, for unless there were two kinds of nascent hydrogen it would be all oxidized in both cases *if in either*, the conditions being the same, and the fact that none was found in the copper experiment must be taken for valid proof that none was formed.

In reality the correct view would appear to be that at the temperature of the reaction the acid is for the greater part dissociated into  $H_2O$  and  $SO_3$ , the copper being oxidized by the latter only. The zinc acts upon the  $SO_3$  forming  $SO_2$ , and also upon the undissociated part of the acid, setting free hydrogen which escapes.

Further light may be thrown upon this matter by a consideration of the reduction of the sulphuric acid by carbon. This reaction takes place at about the same temperature as that with copper, in accordance with the equation



Here there can be no question of nascent hydrogen unless by assuming the existence of a sulphate of carbon, thus



which is wholly unwarranted, and there is no ground for supposing the mechanism of the action of carbon on sulphuric acid to be entirely different from that of copper on the same compound.

A favorite field in which nascent hydrogen often disports itself lies in the extremely complex reactions between nitric acid on the one hand and various metals on the other. Here the nitric acid may be reduced to ammonia, hydroxylamine, free nitrogen, nitrous acid, any of the oxides of nitrogen, and possibly still other products. Often many of them are simultaneously formed. Of these, ammonia and laughing gas and  $N_2$  are never formed by the action of mercury, Bi., Cu. and Ag.<sup>1</sup> Iron, on the other hand, may reduce the whole of the nitric acid to ammonia. Montemartini, who has made a special study of this group of reactions<sup>2</sup>, and others have shown that the various metals reduce nitric acid in various ways, giving reaction products in different proportions and of different kinds. The bearing of this upon the subject of the present paper is evident. If, for example, iron, zinc and copper all reduce nitric acid indirectly through the primary formation of nascent hydrogen, we would expect the ultimate products to be the same in kind and in relative amount, the absolute amount depending simply upon the quantity of hydrogen formed. Since this is not so, the conclusion is inevitable that the nascent hydrogen is not the reducing agent but the action of each metal is immediate and specific, removing oxygen from the acid and forming unstable intermediate products which elude direct observation but which, by their reactions, give rise to the products characteristic of each case.

I have endeavored, in this discussion, to select the fairest instances of the application of the nascent condition hypothesis and find myself forced to the conclusion that it is the survival of an obsolete doctrine; that it explains nothing which cannot be as well or better explained without it; that it cannot be reconciled in certain cases with known facts, and that,

<sup>1</sup> Ber. 92, 616, 898 f.

<sup>2</sup> Loc. cit.

therefore, we are not at present justified in the assumption that elements at the moment of formation or liberation from their compounds possess properties in any way different from those they commonly exhibit.

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## SOME PECULIARITIES OF SOLUTIONS OF FERRIC SULPHOCYANATE

BY LAUNCELOT ANDREWS, PH. D.

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The deep blood-red color of solutions of ferric sulphocyanate has frequently been taken advantage of for the determination of small quantities of iron in river or spring water, in blood, in alloys, in alumcake, etc.

The earliest method of this kind, so far as I have been able to ascertain, is due to T. L. Herapath, who proposed to determine minute quantities of iron by the addition of potassium sulphocyanate to the acidified solution containing an unknown amount of iron, and also to a standard iron solution of known strength, the latter being then diluted until both showed the same tint.

Very similar methods have been employed or devised by A. Thomsen (*Ch. Soc. Jour.*, 47, 493), Ad. Joles (*Arch. f. Hygiene*, XIII, 402), L. Lapique (*Bull. Soc. Chim.*, 2, 295, and by R. R. Tatlock (*Jour. Soc. Ch. Ind.* 6, 276).

Vierordt (*Quant., Spektralanalyse*), suggested a fundamental modification of Herapath's colorimetric method, in that he dispensed wholly with a standard comparison solution, substituting for it a direct spectrophotometric determination of the amount of light of given wave length, transmitted by a layer of the ferric sulphocyanate solution one c. m. thick. In this method the assumption, based upon analogy, is made that the light absorbing power of the solution is directly proportional to the amount of iron contained therein; or in other words, *that the negative logarithm of the fraction of light transmitted is proportional to the concentration of the solution*, and the assumption seems to be confirmed by Vierordt's observations.

Subsequent investigations by Krüss and Moraht (*Lieb. Ann.*, 260, 193; *Kalorimetrie, u. Spektral analyse*, 1891, p. 125), and by Magnanini (*Zeit. phys. Ch.* 8,1) have shown the assumed proportionality to be non-existent in fact. If aqueous solution of ferric sulphocyanate be diluted its color fades away in a much more rapid ratio than corresponds to the diminishing concentration of the solution. The depth of color is much enhanced by an excess of either generatrix, *i. e.*, of KSCN or of Fe Cl<sub>3</sub>, and as Magnanini has shown the change follows the laws of mass action qualitatively and quantitatively.

Magnanini dismisses the affair at this point as a *res adjudicata* assuming that the sulphocyanate is subject, in its solution in water, to a progressive electrolytic dissociation in the ions, Fe and S C N. In accordance with well