A NOTE ON NEGATIVE INDUCED REACTIONS.

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The rate of change of a chemical reaction may sometimes be greatly diminished in the presence of quite an independent chemical reaction, when they are carried out simultaneously in a same vessel. The phenomenon may probably be called negative induced reactions, corresponding to the term induced reactions, in the case of which a chemical reaction exhibits an accelerating action on quite an independent chemical reaction, whose reaction velocity is extremely small, when it is carried out separately.

The simultaneous oxidations of the two substances, given in the following equations, by means of air were studied by the author and it was reported that the experimental results obtained can be explained as examples of some kind of negative induced reactions.

$$\text{A.}\begin{cases} O_2+2Sn(OH)_2+2H_2O=2Sn(OH)_4 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ (1) \\ O_2+2Na_2SO_3=2Na_2SO_4 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (2) \end{cases}$$

in sodium hydroxide,[1] or in sodium carbonate solution.[2]

$$\text{B.}\begin{cases} O_2+4Fe(OH)_2+2H_2O=4Fe(OH)_3 \quad \ldots\ldots\ldots\ldots\ldots\ (1) \\ O_2+2Na_2SO_3=2Na_2SO_4 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (2) \end{cases}$$

in sodium hydroxide solution.[3]

The primary reaction in A or B exhibits a great inhibiting action on the velocity of the secondary reaction. It was also confirmed by the

(1) S. Miyamoto, this Bulletin, **2** (1927), 191; *Scientific Papers of the Institute of Physical and Chemical Research*, **7** (1927), 195.
(2) S. Miyamoto, this Bulletin, **3** (1928), 95; *Scientific Papers of the Institute of Physical and Chemical Research*, **8** (1928), 237.
(3) S. Miyamoto, this Bulletin, **4** (1929), 132; *Scientific Papers of the Institute of Physical and Chemical Research*, **11** (1929), 81.

previous studies[1] that each of these reactions proceeds a most at the same rate, when they are carried out separately under the conditions of the author's investigations.

The terms actor, inductor, and acceptor are usually employed for the specia ization of the reacting substances contained in ordinary induced reactions. For the oxidizing or the reducing agent, which is c. mmon in both reactions, the term *actor* can also be employed in negative induced reactions. In the place of the term inductor, the term *inhibitor* may be employed in the case of negative induced reactions for the substance, which can easily react with the actor, when the two reactions are carried out simultaneously. The substance, the reaction velocity of which with the actor is greatly diminished in the presence of the primary reaction, may be called *acceptor*.

In the cases, above described, oxygen may be called the actor, stannous hydroxide and ferrous hydroxide the inhibitors and sodium sulphite the acceptor respectively.

Corresponding to the term induction factor, which is used for the value of the ratio of the amount of the actor reacting with the acceptor to the amount of the actor reacting with the inductor, the term *inhibition factor* may be employed for the quantity,

$$\frac{A_{a.o} - A_a}{A_i}$$

where $A_{a.o}$ is the amount of the actor reacting with the acceptor in the absence of the inhibitor, A_a the amount of the actor reacting with the acceptor in the presence of the inhibitor, and A_i the amount of the actor reacting with the inhibitor.

W. D. Bancroft has given the following classification of induced reactions.[2]

(1) The inductor displays a catalytic action on the secondary reaction.
(2) The acceptor may react with a reduced stage of the actor.
(3) The acceptor may react with an oxidized stage of the inductor.
(4) The formation of a complex compound between the inductor and the acceptor.
(5) Combinations of the cases (1), (2), (3) and (4).

As for the classification of negative induced reactions, the following three cases were already described by the author[3] with examples.

(1) S. Miyamoto, this Bulletin, **2** (1927), 74; **2** (1927), 155; **3** (1928), 76; **3** (1928), 137; *Scientific Papers of the Institute of Physical and Chemical Research*, **7** (1917), 40; **7** (1927), 189; **8** (1928), 230; **9** (1928), 203.
(2) W. D. Bancroft, *J. Phys. Chem.*, **33** (1929), 1184.
(3) S. Miyamoto, this Bulletin, **4** (1929), 133; *Scientific Papers of the Institute of Physical and Chemical Research*, **11** (1929), 82.

(1) The inhibitor displays a negative catalytic action on the secondary reaction. In this case the reaction velocity between the actor and the acceptor will be extremely small in the beginning, but it will gradually increase with time as the concentration of the inhibitor decreases.

The simultaneous oxidation of stannous hydroxide and sodium sulphite in sodium hydroxide solution or sodium carbonate solution by means of air was found to be an example of this kind of negative induced reactions, as was already explained in the previous papers.

(2) The reaction product of the inhibitor exhibits a negative catalytic action on the secondary reaction. In this case the velocity of the secondary reaction will be un-affected at the starting point in the presence of the primary reaction, but it will decrease rapidly with time as the concentration of the reaction product of the inhibitor increases.

The simultaneous oxidation of ferrous hydroxide and sodium sulphite was found to be explained as an example of this type of negative induced reactions; ferric hydroxide, the reaction product of the inhibitor, acts as a negative catalyser on the oxidation velocity of sodium sulphide, the acceptor.

(3) Both of the inhibitor and its reaction product act as negative catalysers on the secondary reaction. This type of negative induced reactions can be regarded as a special case of the type (7), which will be described later, and it will scarcely occur in the actual cases, as the negative catalytic action should be regarded to depend upon the mutual specific nature of the two substances.

As the possible kinds of negative induced reactions, the following three cases may probably be added to the types above described, although the examples are not yet obtained.

(4) The reaction product of the actor of the primary reaction acts as a negative catalyser on the secondary reaction. It is quite clear that this case is only possible to occur, when the reaction product of the actor of the primary reaction is not the same as that of the secondary reaction, as the reaction product of the actor exhibits no inhibiting action on the velocity of the secondary reaction, when it is carried out separately.

(5) The inhibitor reduces the oxidation product of the acceptor. This is a kind of consecutive reactions and the induced reaction of the type (3) of Bancroft's classification may be regarded to be negative induced reaction of this type in special cases, if we consider the inductor as the acceptor and the acceptor as the inhibitor.

(6) Formation of a complex compound between inhibitor and acceptor.

(7) Combinations of the cases (1), (2), (4), (5) and (6).

The author has proposed, as a kind of possible mechanisms of catalysis, induced reactions[1] and negative induced reactions,[2] the process of the transference of active states. According to this idea, the transference of the active states of the molecules of the acceptor to the molecules of such substances as the inhibitor, the reaction product of the inhibitor and the reaction product of the actor of the primary reaction, may explain the mechanism of negative induced reactions of the types (1), (2) and (4), above described.

Summary.

(1) The possibility of the existence of negative induced reactions are described with examples, studied by the author.

(2) The definition of the terms actor, inhibitor and acceptor are given in the case of negative induced reactions.

(3) Corresponding to the term induction factor, the term inhibition factor was introduced in the case of negative induced reactions, although its value was not yet calculated in the actual cases.

(4) A classification of negative induced reactions was proposed. The classification will be unable to be confirmed thoroughly by experimental facts, as the examples of negative induced reactions are very few.

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(1) S. Miyamoto, *Scientific Papers of the Institute of Physical and Chemical Research*, **4** (1926), 259.

(2) Loc. cit.