

REACTION VELOCITY AND THE "EQUI-VALENCE-CHANGE PRINCIPLE"

Sir:

For some time I have been searching for cases of oxidation-reduction reactions suitable to test an hypothesis concerning a factor which it is thought may be an important one affecting reaction velocity, and which appears not to have been considered heretofore. The hypothesis, which may be called the equi-valence-change principle—if it prove to be a principle—may be briefly stated in simplest form as follows. It is reasonable to suppose that chemical reactions are more likely to result from bi-molecular collisions (or a sequence of such), than from simultaneous collisions of larger number. True tri-molecular or higher order reactions, if such occur, would be expected to be much slower processes because such collisions are statistically less probable events. If, then, in the case of oxidation-reduction reactions, a reductant molecule in an active state collides with an active oxidant molecule, reaction will occur if there results a decrease of free energy, and provided the *number* of electrons which the reductant *may* lose (or share) is the same as the number the oxidant may accept or share. It is assumed that only certain valence states, represented by known compounds, are "possible." If the number of electrons which may be lost or shared is not the same as the number required by the oxidant—if the possible valence change of reductant does not satisfy a possible valence state of oxidant—it would seem logical to expect that bi-molecular reaction could not occur, regardless of activity or free energy decrease, except as a result of less frequent tri-molecular collisions. (The idea is perhaps not applicable to some gaseous reactions.) According to this view "permissible" equivalence of valence change should be a factor affecting the fraction of collisions which are successful. And, where this factor inhibits reaction velocity, the introduction of third reactants able to mediate the first "odd" reaction into consecutive "even" steps should markedly catalyze the process.

Many cases seemingly in support of this idea have been surveyed in a preliminary way, and will be reported in due time, though few cases are found which are not open to several interpretations. The following case, called to my attention by Dr. P. W. Preisler, appears to be free from this objection, and is here recorded from the desire of securing criticism of my interpretation of it, and of the hypothesis.

Ceric-cerous sulfates, and thallos-thallic sulfates are known to be reversible, electromotively active couples, both the oxidants and reductants being almost instantly reactive with many substances in *N* sulfuric acid solution at room temperature. If a half cell is made of each couple in any finite ratio, using platinum electrodes, the potential difference between them is promptly registered and determinable by potentiometer, and corresponds with that expected from their recorded normal potentials

($Tl^{3+} - Tl^{1+}$, 1.2 v.; $Ce^{4+} - Ce^{2+}$, 1.5 v.)

It is therefore surprising to find that when ceric sulfate and thallosulfate in *N* sulfuric acid are mixed, there is virtually no reaction, even on boiling. At 25° the half period is longer, perhaps much longer, than a thousand hours. The observed potential difference indicates the possibility of reaction and performance of work *when separated*, but when together reaction fails to take place. Mellor's Treatise (Vol. V, p. 662) cites the existence of a double salt of thallosulfate ceric sulfates, $2Tl_2SO_4 \cdot Ce(SO_4)_2$. The most probable explanation of this unreactivity is that oxidation of thallosulfate ion requires the loss of *two* electrons (Tl^{2+} being unknown) while ceric ion can accept only *one* (Ce^{2+} being unknown).

The addition of $MnSO_4$ (0.001 *M*) to a mixture of ceric and thallosulfates (0.01 g. atomic in *N* H_2SO_4 at 25°) so catalyzes the reaction that the half period is about one hour. The probable mechanism of the catalysis follows from the facts that (a) ceric sulfate rapidly oxidizes Mn^{++} to Mn^{3+} and then to Mn^{4+} (MnO_2), and (b) MnO_2 oxidizes Tl^{1+} to Tl^{3+} . Platinum black, also, rather more rapidly catalyzes the reaction. The halide ions show slight catalytic activity.

These and other reactions, including oxidations involving oxygen, and their catalysis are being studied from the point of view of the hypothesis stated. There are many apparent contradictions, some of which already appear capable of resolution; whether it will be possible to establish the hypothesis as a general rule, future work will decide.

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EXCHANGE ADSORPTION AND ITS INFLUENCE UPON THE SOLUBILITY OF PRECIPITATES WITH IONIC LATTICES IN ELECTROLYTE SOLUTIONS

Sir:

In a previous communication [I. M. Kolthoff and Charles Rosenblum, *THIS JOURNAL*, **55**, 851 (1933)] it was reported that in the adsorption of the sodium salt of Ponceau 4R only dye ions were adsorbed, no sodium ions being removed from the solutions. Other experiments have shown that this "exchange" adsorption at the water-solid interface of pure ionic precipitates may occur quite generally. Finely divided calcium oxalate monohydrate was precipitated and purified by intermittent shaking and washing for several months. In the determination of the adsorption of alkali iodates, sulfates and sodium hydroxide, it was found that only the anions were adsorbed, or at least ten times more strongly than the alkali ions. On shaking with very dilute barium and manganese chloride solutions only the cations were adsorbed. Therefore cation as well as anion exchange occurs