FERRYL ION, A COMPOUND OF TETRAVALENT IRON

Sir:

Several independent kinetic investigations in this Laboratory have furnished evidence that a compound of tetravalent iron, FeO^{++}, is formed as an intermediate. The results are in agreement with the theory that

$$2Fe^{+++} + H_2O = Fe^{++} + FeO^{++} + 2H^+$$

is a reversible and fairly rapid reaction. The equilibrium constant has the form $K = (Fe^{++})(FeO^{++})(H^+)^2/(Fe^{+++})^2$.

If H_2O_2 reacts with both Fe^{++} and "ferryl ion" but not directly with Fe^{+++}

$$Fe^{++} + H_2O_2 \longrightarrow FeO^{++} + H_2O,\ -d(Fe^{++})/dt = k_1(H_2O_2)(Fe^{++})$$
$$FeO^{++} + H_2O_2 \longrightarrow Fe^{++} + H_2O + O_2,\ d(Fe^{++})/dt = k_2(H_2O_2)(FeO^{++})$$

then a steady state will be reached in which $(FeO^{++})/(Fe^{++}) = k_1/k_2 =$ a constant, and the above equilibrium is maintained. The rate of catalytic decomposition of H_2O_2, $-d(H_2O_2)/dt$, is then equal to

$$2k_1(Fe^{++})(H_2O_2) = 2(\sqrt{Kk_1k_2})(H_2O_2)(Fe^{+++})/(H^+) = k(H_2O_2)(Fe^{+++})/(H^+)$$

This rate law was determined by von Bertalan in 1920 and has been confirmed in this Laboratory [Bray, *Chem. Rev.*, **10**, 171 (1932), $k = 0.125$ (not 125) at 40°]. The proposed mechanism explains also the decomposition of H_2O_2 during the very rapid oxidation of Fe^{++} to Fe^{+++}.

If in the reduction of Fe^{+++} by a stannous salt Sn^{++} reacts with FeO^{++} but not with Fe^{+++}, and the equilibrium between 2, 3 and 4-valent iron is established relatively rapidly, the rate law will be $-d(Sn^{++})/dt = k'(Sn^{++})(Fe^{+++})^2/(Fe^{++})(H^+)^2$. This has now been established as a limiting law in solutions in which the only negative ion is ClO_4^-. Also, by raising the temperature and lowering the concentration of Fe^{++}, another limiting condition has been found where the rate is independent of the concentration of Sn^{++}, and the indicated rate-determining reaction is $2Fe(OH)^{++} \longrightarrow Fe^{++} + FeO^{++} + H_2O$.

Other investigators have already observed and studied the retarding effect of ferrous salts during the reduction of ferric salts by hydroxylamine and by iodide. The results of Mitchell [*J. Chem. Soc.*, 336 (1926)] with hydroxylamine and Fe^{+++}, published in 1926, are in accord with the ferryl ion mechanism. In the case of the reactions of iodide with ferric salt and with ferricyanide, Wagner [*Z. physik. Chem.*, **113**, 271 (1924)] in 1924 postulated the formation of I_2^- as an intermediate. There seems, however, to be no supporting evidence for the existence of this compound.

In order to obtain more information about the reaction between Fe^{++} and I^-, Bray and Hershey are studying the reverse reaction between Fe^{++} and I_2. The first experiments, in the presence of AgI, AgBr and Br^-, *i. e.*, at very low concentrations of I^-, are in agreement with the rate law, $-d(I_2)/dt = k''(Fe^{++})(I_2)/(I^-)(H^+)$. This result and the analogy with other reactions of iodine in aqueous solution have led to the conclusion that the rate-determining reaction is $Fe^{++} + HIO \longrightarrow FeO^{++} + H^+ + I^-$.

Additional experiments have been planned which, it is hoped, will furnish further information about the properties of ferryl ion.

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THE EXISTENCE OF NEUTRONS IN THE ATOMIC NUCLEUS

Sir:

In my article on the Arrangement of Protons and Electrons in the Atomic Nucleus [THIS JOURNAL, **53,** 981 (1931)] the discussion was limited to nuclei in which the numbers of protons and electrons are multiples of four and two, respectively. These atoms are by far the most abundant and in terms of the proposed coupling pattern represent the highest symmetry attainable. Although it is not yet possible to make a definite extension to the other nuclear series, it is of interest to discuss the problem briefly in reference to recent investigations.

It appears significant that the next most abundant nuclear type is that which resembles the symmetrical or $4n$ proton type most closely and may be derived from it by the removal of a single proton. This series, *i. e.*, with $4n-1$ protons, follows very closely the $4n$ series: the first and second "extra electron pair" enter at the corresponding atomic numbers. All other nuclei, *i. e.*, those with $4n-2$ and $4n-3$ protons and those with uneven numbers of electrons constitute but a fraction of one per cent. of the atoms of the earth's crust and appear in general to owe their instability to the presence of incomplete or unsaturated groups. More information about nuclear spins and a knowledge of the coupling rules in these cases are necessary before definite conclusions can be drawn regarding these structures. At present we can only discuss certain possibilities.

As an illustration we may consider carbon 13. In the accompanying figure, this nucleus is pictured in the same symbols formerly employed, a proton, or the direction of the proton spin vector, by a bar and an electron pair by a ball. The structure is the same as that of carbon 12 plus one proton and one electron (half ball). Of course we do not know where the extra proton is coupled but we do know that such a bond of two protons and one electron as suggested in the figure (two bars and the half ball) is stable from the existence of the hydrogen isotope [Urey, Brickwedde and Murphy, *Phys. Rev.*, **39,** 154 (1932)] of mass 2. Beryllium 9 must also contain such a group and when it captures a high speed alpha particle to form carbon 13 it is not difficult to imagine that occasionally the loosely bound