278. *The Reduction of Silver Ions by Ferrous Ions.*

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THE reduction of silver salts to metal by ferrous salts in solution, $Fe^{\cdot\cdot} + Ag^{\cdot} \longrightarrow Fe^{\cdot\cdot\cdot} + Ag$, has been studied by Dhar (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, **23**, 299), who, using silver nitrate and ferrous ammonium sulphate, found that the reaction was fast at 25°. The reaction was suggested as suitable for determining the hydrogen-ion concentration of a solution, since acids were found to exert a catalytic effect. As will be shown, however, other factors have an important influence so that the suggested method is inadmissible. The equilibrium constant of the reaction, which is reversible, has been studied by Noyes and Brann (*J. Amer. Chem. Soc.*, 1912, **34**, 1016), who found fair agreement with the requirements of electrode-potential data, if nitric acid were present to prevent hydrolysis of the ferric salt.

EXPERIMENTAL.

The course of the reaction was followed by estimation of the amount of ferrous salt present at various times. 25-C.c. portions of the mixture were rapidly filtered through asbestos in a Gooch crucible to remove the Ag particles, into excess of NaCl aq., which stops the reaction. If the particles are not first removed, they react with the ferric salt present at the end of the titration to form $Fe^{\cdot\cdot}$ and $Ag^{\cdot}$ ions which vitiate the estimation. The filtrate and washings containing the residual ferrous salt in excess NaCl were titrated with standard $K_2Cr_2O_7$, or alternatively, after treatment with $MnSO_4$ and H_3PO_4, with standard $KMnO_4$.

Examination of the Reaction between Ferrous Sulphate and Silver Nitrate in Aqueous Solution.—When aqueous solutions of the reagents were mixed so that their concn. was initially $M/50$, a period of induction was observed of some 15—20 mins. at 25°. The slow period is followed by one of rapid reaction until the system comes to equilibrium. The results of three such typical experiments are given below :

Time (mins.).	$[FeSO_4]$ × 50.	Time (mins.).	$[FeSO_4]$ × 50.	Time (mins.).	$[FeSO_4]$ × 50.
0·00	1·000	0·00	1·000	0·00	1·000
2·00	1·000	1·75	1·000	1·67	1·000
6·45	0·997	6·75	0·995	6·13	0·987
20·75	0·709	16·50	0·954	16·97	0·939
32·60	0·591	20·90	0·602	24·97	0·583
61·00	0·590	45·00	0·575	32·00	0·584

A possible explanation of the autocatalytic type of curve obtained is that the concn. of $H^{\cdot}$ ion, which catalyses the reaction, increases during the reduction owing to the formation of the extensively hydrolysed ferric salt.

Examination of the Reaction in Buffered Solutions.—NaOAc and HOAc were selected for the purpose of buffering the reaction mixture, for, although $Fe^{\cdot\cdot\cdot}$ ions are removed by the mixture to form ferric acetate, the buffer does not affect the concn. of the reacting ions provided the solubility product of AgOAc be not exceeded. Even in such buffered solutions, however, periods of induction were still obtained. A typical result at 25·0° is given below. (In the presence of the acetate mixture the reaction proceeds to completion, because of the removal of $Fe^{\cdot\cdot\cdot}$ ions as un-ionised ferric acetate.) It was thus apparent that other catalytic influences were operative and, as was shown by the incomplete reproducibility of the results, these were not under control.

$[FeSO_4] = [AgNO_3] = M/50$; $[AcOH] = 0{\cdot}096M$; $[AcONa] = 0{\cdot}1M$; $p_H = 4{\cdot}76$.

Time (mins.)......	0·00	1·75	3·17	4·45	6·20	8·67
$[FeSO_4]$ × 50 ...	1·000	0·943	0·848	0·300	0·060	0·000

Examination of the Effect of Colloidal Silver on the Reaction Speed.—Preliminary experiments on the effect of addition of a yellow Ag sol, prepared by Kohlschutter's method, on the speed of interaction in an unbuffered mixture showed that the period of induction was greatly shortened (compare the catalytic effect of silver halides on the interaction of $AgNO_3$ with halogens in org. compounds; Senter, J., 1910, **97**, 358). Owing to the coagulating effect of electrolytes on the sol, the number of Ag nuclei must decrease rapidly after the reaction mixture is made up, so that the effect of the sol in such experiments is probably fleeting. In the acetate mixtures, where the reaction is much faster, it might happen that the sol would retain its effectiveness over the period of reaction. Accordingly, the effect of addition of sol on the reaction speed in acetate buffers was examined, the sol being isolated from the salt solutions until the moment of mixing. The reaction speed was found to increase with the proportion of added sol up to 75% by vol., the highest proportion which could be used. The reaction curves for additions of 30, 50, and 75% sol are reproducible and are shown in Fig. 1. Details of one experiment for each different amount of sol added are given in Table I.

TABLE I.

$[FeSO_4] = [AgNO_3] = M/50$; $[AcOH] = 0{\cdot}096M$; $[AcONa] = 0{\cdot}1M$;
$p_H = 4{\cdot}76$; $T = 25{\cdot}0°$.

10% Sol.		30% Sol.		50% Sol.		75% Sol.	
Time (mins.).	$[FeSO_4]$ × 50.	Time (mins.).	$[FeSO_4]$ × 50.	Time (mins.).	$[FeSO_4]$ × 50.	Time (mins.).	$[FeSO_4]$ × 50.
0·00	1·000	0·00	1·000	0·00	1·000	0·00	1·000
1·17	0·861	0·92	0·842	1·50	0·556	0·53	0·764
2·20	0·589	2·67	0·400	3·00	0·256	1·58	0·220
3·43	0·326	4·58	0·135	4·50	0·074	2·67	0·073
4·92	0·164	6·92	0·017	6·17	0·010	3·92	0·010
10·00	0·000	10·00	0·000	15·00	0·000	5·30	0·000

The reaction speed thus appears to be governed by factors affecting the ease of separation of Ag from solution and may be compared to the reduction by H_2O_2 of $HAuCl_4$ to colloidal Au (Svedberg, "Formation of Colloids," London, 1931, p. 61). It is suggested that the initial period of induction is due to atomic Ag in solution balancing the reaction

$$Ag^{\cdot} + Fe^{\cdot\cdot} \xrightarrow{\text{fast}} Fe^{\cdot\cdot\cdot} + Ag\ (\text{solution}) \xrightarrow{\text{slow}} Ag\ (\text{solid})$$

until a sufficient number of nuclei are formed to act as centres of deposition. The effect of providing Ag nuclei is to facilitate the separation of metal and, if present in sufficient amount, to eliminate the induction period.

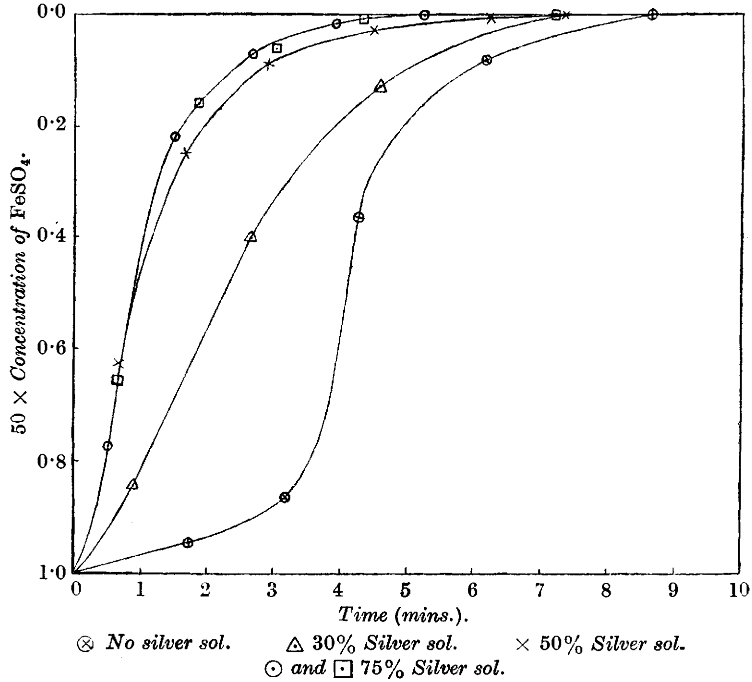
The effect of $H^{\cdot}$ ions, which undoubtedly increase the measured rate of reaction, may thus be due, not to an acceleration of the reaction between reagent ions, but rather to their influence on the speed of separation of atomic Ag on the surface of the nuclei. In order to secure further data, the effect on the reaction speed of varying the $[H^{\cdot}]$ at constant ionic strength was examined in the presence of 75% Ag sol. Results at p_H 5·063 and initial ionic strength the same as in the experiments summarised in Table I are given below.

$[FeSO_4] = [AgNO_3] = M/50$; $[AcOH] = 0{\cdot}048M$; $[AcONa] = 0{\cdot}1M$;
$T = 25{\cdot}0°$.

Time (mins.)	0·00	1·42	2·86	4·50	7·82	20·15	50·50
$[FeSO_4]$ × 50 ...	1·000	0·892	0·970	0·715	0·547	0·316	0·147

Comparison with the figures in the last two columns of Table I shows that the effect of halving the [H˙] (*i.e.*, from p_H 4·76 to p_H 5·063) is to increase the time of half-decomposition from 1 to 10 mins. The effect of the H˙ ion, even allowing for an effect due to the change in the un-ionised AcOH concn., must therefore be considerably greater than simply proportional to its concn. and, presumably, is an effect on the rate of separation of Ag on the nuclei. Further, it was found that, at constant [H˙], increase in ionic strength causes a marked enhancement of the reaction speed, much greater than that anticipated for a reaction between ions of like sign. Here also the salt effect appears to be connected with the rate of separation of Ag rather than with the rate of the homogeneous reduction. The results obtained with 50% Ag sol at 25·0° and [H˙] = 0·865 × 10^{-5} are shown below.

FIG. 1.



Ionic strength 0·16.

Time (mins.).	[$FeSO_4$] × 50.
0·00	1·000
1·05	0·930
3·28	0·833
11·00	0·604
40·55	0·330
75·00	0·161

Ionic strength 0·26.

Time (mins.).	[$FeSO_4$] × 50.
0·00	1·000
0·93	0·870
2·92	0·676
6·05	0·196
10·00	0·005
16·00	0·000

The conclusion drawn is that the homogenous reaction between silver and ferrous ions is a rapid one which cannot be measured from a study of the rate of disappearance of ferrous ions. The initial induction period in the rate of disappearance of these ions and appearance of silver, is due to the time required for the formation of silver nuclei, and the subsequent speed, which is accelerated by salts and by hydrogen ions, is a measure of the rate of condensation on these nuclei of atomic silver.

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