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THE INCREASE IN POTENTIAL WHEN SOME REDUCING AGENTS ARE ADDED TO CERTAIN OXIDANTS¹

W. S. HENDRIXSON

Several years ago Forbes and Bartlett² found that ferrous sulfate caused an increase in potential when added to dilute chromate in dilute sulfuric acid, and that chlorides were fatal to this rise. Arsenious acid and ferrocyanide produced much the same effect. Of the oxidizing agents only dichromate showed this rise when treated with reducing agents. So far as known to the writer this subject had received no further systematic study when he took it up near the beginning of the current year. So far as his study has extended, the phenomenon observed by Forbes and Bartlett seems to be by no means an isolated one.

In this work due care was taken to use only "highest purity" chemicals which were carefully tested, or those prepared by him for other researches. The essentials of the apparatus was a student's potentiometer, and a galvanometer of 2000 megohms. To prevent diffusion between the normal calomel electrode and the solution under examination, the siphon of the electrode vessel, provided with a stop-cock, was drawn out to a fine capillary and connected with a second electrode vessel of identical form, filled with a saturated solution of pure potassium sulfate which was renewed before each experiment. The galvanometer was so sensitive that the potentials could be read to a few millivolts with the stop-cocks closed. They were opened only for final readings, thus restricting further the chance of the mixing of the solutions. In the early part of the work it was carried out in the atmosphere of carbon dioxide, but this precaution was found to be unnecessary. In the experiments here recorded two to six platinum electrodes, some bright and some platinized, were used.

It was soon realized that to get trustworthy results the platinum electrodes must be left for several hours, even for days, in the solutions of concentration and acidity as they were to be titrated, until the electrodes became "saturated" and the potentials con-

¹ Contribution from the Chemical Laboratory of Grinnell College.

² Forbes and Bartlett, *Journ. Am. Chem. Soc.* vol. 35; p. 1527. 1913.

stant. To illustrate this necessity and also as an instance of higher potential on adding a reducing agent to an oxidizing agent, the curves in a paper published by the writer several months ago are cited.³ The rises shown when titanous ion was added to solutions of iodate, bromate, chlorate are real but much exaggerated, because the electrodes were taken from dilute sulfuric acid and used at once.

Taking the precautions stated, several titrations of 5 to 20 cc normal 0.05 dichromate in 200 cc 2 to 4 normal sulfuric acid were made by adding 0.1 normal ferrous sulfate in 1 cc portions. In all cases when the platinum electrodes had been in the solution till they showed constant voltage the additions of ferrous sulfate caused normal falls in potentials. One cannot assume the electrodes saturated since saturation requires more time in very dilute solutions. The following data show this fall and also the effect of adding at the point indicated one gram of solid salt.

In this experiment three closely agreeing bright electrodes, and two platinized electrodes were used after they had been in the solution five hours. The readings were taken twice for each electrode in rotation, five to ten minutes after portions of iron had been added. Opposite P. (1) are the average potentials of the bright electrodes, and opposite P. (2) the average of the platinized electrodes.

$FeSO_4$, cc.	0	1	2	3	4	6	8	9	10	11
P. (1)	0.867	0.826	0.796	0.777	0.814	0.893	0.912	0.916	0.784	0.405
P. (2)	0.905	0.881	0.863	0.847	0.791	0.836	0.803	0.751	0.655	0.402

The salt caused a fall in potentials which was nearly overcome by the platinized electrodes, on adding more iron, while the bright electrodes gave an average potential exceeding that shown at the beginning.

Several experiments were carried out on the effect of adding ferrous iron to chromate in 2-normal hydrochloric acid. The following results are those of a typical titration. The temperature did not vary more than 0.2 of a degree. Opposite P. (1) are the average potentials of two bright electrodes, and opposite P. (2) the potentials of one platinized electrode, all of which had been in the solution sixty hours. Other experiments

$FeSO_4$, cc.	0	0	0	0	2	4	6	8	10	12	13
P. (1)	0.888	0.888	0.887	0.886	0.896	0.896	0.898	0.899	0.900	0.899	0.420
P. (2)	0.888	0.888	0.887	0.887	0.895	0.896	0.895	0.896	0.899	0.885	0.421

showed the same remarkable uniformity of potential, and it

³ Hendrixson, Journ. Am. Chem. Soc. vol. 45, p. 2013, 1923.

suggests the formation of some substance which a little more than compensated for the dichromate destroyed, for example the ferric ion formed. The same ferric ion was formed in sulfuric acid solution and produced no such compensation. Moreover, my experience agrees with that of Forbes and Bartlett that adding ferric iron to the dichromate solution causes no change in potential. To test this point further the experiment was repeated with the difference that hydrogen peroxide was used as the reducing agent. This substance when added to dichromate in dilute sulfuric acid gave decreasing potentials, if the electrodes were saturated, even under conditions that gave very evidently the blue color usually ascribed to perchromic acid. Bubbling oxygen around the electrode gave no evident change in the potential.

The same electrodes as in the last experiment were used after they had been in the solution of dichromate and normal hydrochloric acid five hours. The temperature was kept practically constant. The hydrogen peroxide was about 0.1 normal.

H_2O_2 , cc	0	0	0	3	5	7	9	11	13	16	17
P. (1).	0.901	0.900	0.899	0.913	0.916	0.918	0.919	0.920	0.920	0.916	0.68
P. (2)	0.896	0.896	0.896	0.907	0.908	0.910	0.913	0.915	0.913	0.908	0.590

Here the peroxide gave about the same rise as ferrous iron under the same conditions. In other experiments in which more concentrated hydrochloric acid was used the fall in potential at the end point became smaller, and with the acidity 5-normal no fall was obtained. In the absence of chromate merely adding hydrogen peroxide to 5-normal hydrochloric acid raised the potential to 0.9 volt. It seems quite possible that the fall that should mark the disappearance of the dichromate is prevented by the formation of traces of chlorine, due to the action of the excess of peroxide and the hydrochloric acid. Of course the oxidation of hydrochloric acid by chromate with amounts of chlorine set free which are evident to the senses and ordinary tests, is only a matter of concentration and temperature. Experiments of my own, which consisted of aspirating air or carbon dioxide through the vessel containing the mixture, and through an iodide solution, showed that 5-normal hydrochloric acid and either dichromate or hydrogen peroxide gave evident chlorine, and more when both were added to the acid. Even 2-normal acid seemed to show traces of chlorine under the same conditions, and only traces would be necessary to increase potentials perceptibly between 0.9 and 1 volt, as experiments of my own have shown. Of course it may be said in general that, when a halogen is set free on add-

ing a reducing agent to any oxidant there is sure to occur a rise in potential at first, if the potential of the halogen is decidedly higher than that of the oxidant. Examples are bromate, chlorate and titanous ion; the same oxidants and hydrobromic or hydrochloric acid in larger amounts.

Persulfuric acid in relation to rise of potential on adding reducing agents was also studied. A bright and a platinized electrode were left 24 hours in a dilute solution of persulfate and 2-normal sulfuric acid, after which their potentials were 1.080 and 1.133 volts. The addition of 1 cc. ferrous sulfate raised the former potential to 1.128 and lowered the latter to 1.127 after which further additions caused parallel decreases. The facts seem to show that the bright electrode was not saturated even after 24 hours, and the iron performed its usual role in such cases, of greatly increasing the rate of charging. Platinized electrodes, possibly because they carry their own catalyst as spongy platinum, far more quickly assume normal charges. The behavior of persulfate in hydrochloric acid was not studied, since in this acid of moderate concentration it soon sets free amounts of chlorine evident to the senses.

Two experiments illustrated the extreme slowness of electrode saturation in dilute solutions of even the strongest oxidants. In one of them four bright and two platinized electrodes, which had been 40 hours in a solution 2-normal with sulfuric acid and 0.002 normal with respect to permanganate gave an average rise of 0.011 volt on adding ferrous iron. The second solution with the same acidity but 0.01 normal permanganate gave after the electrodes had been in it only 12 hours falls in potential from the beginning to the sharp drop at the end-point.

To the present time ferrous ion is the only substance tried which greatly hastens the saturation of electrodes in sulfuric acid solutions of oxidants. This action is not limited to dichromate, but seems to apply generally to dilute solutions of oxidants in which the electrodes have not reached equilibrium. Nickel, cobalt, manganase, titanium and some others seem to have no such effect. Others will be investigated.

SUMMARY

1. Ferrous iron has the appearance of causing rises in the potential of electrodes when it is added to dilute solutions of oxidants in sulfuric acid for the reason that it greatly accelerates the speed with which the electrodes take up their full charges.

In all but extremely dilute solutions the electrodes reach saturation after several hours, and normal falls of potential are then produced by adding ferrous sulfate.

2. Several other instances of rises in potential when reducing agents are added to oxidants are pointed out, in some cases evidently due to free halogens, and in others it seems probable that the cause is the same though the amounts of the halogens are too small to be detected in such combinations by ordinary tests.

3. It is suggested that the slow saturation of electrodes in dilute solutions may lead to erroneous potential curves, want of sharpness and even delays in the indication of end-points.

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