reduction system. The case of alloxantin is thus analogous to that of quinhydrone. Richardson and Cannan[2] extended the potentiometric study over a wide pH range and performed oxidative potentiometric titration experiments which, in spite of difficulties with respect to the lack of stability of the potentials, led to reasonable results.

The reproduction of Biilmann's experiment is easy, provided one works with rather concentrated solutions of alloxantin (about 0.3 per cent.), best in saturated solution with an excess of solid alloxantin. In this case, of course, oxidative or reductive potentiometric titration experiments can not be performed.

On the occasion of our own potentiometric study of alloxantin it appeared to us striking that the potentials become erratic, inconstant in time and irreproducible, when a somewhat diluted solution of alloxantin is used instead of a saturated one, a fact which has never been mentioned anywhere. A further study showed that on the addition of a small amount of an iron salt the potentials become reproducible and are rapidly established, even in very dilute solutions of alloxantin (1:10,000 and even more dilute). Mere traces of iron are not sufficient to establish the full effect, but well-measurable amounts are requisite. About 0.1 to 1.0 milligram of iron, as sulphate, added to a volume of 25 cc of the solution is necessary. On the other hand, in a concentrated solution of alloxantin, Fe is not requisite. On working with all precautions as Fe-free as possible and adding such powerful Fe-combining reagents as alpha, alpha'-dipyridyl, or alpha, alpha'-phenantrolin the potentials are quickly established in concentrated solutions.

Alloxantin can be reduced in the electrode vessel by hydrogen and colloidal palladium to dialuric acid, and after replacing the hydrogen by nitrogen an oxidative titration experiment with bromine can be performed. The oxidation product is alloxan. The establishment of the potentials is sluggish and erratic. When, however, a small amount of $FeSO_4$ had been added to the mixture, the potentials are immediately established, just as with any reversible dyestuff. The shape of the titration curve is precisely the one of an ordinary organic dyestuff system, with no indication of any intermediary step of oxidation being shown. This intermediary form, known as alloxantin in the crystalline state, does not exist to any appreciable extent in the solution, just as the substance called quinhydrone in its crystalline state does not exist in solution. The titration curve is not influenced at all by the adding even of a great excess of iron.

The effect of the iron is most evident between pH 4 and 6. At lower pH the effect is small and at pH about 1.0, where Biilmann and Lund worked, no ap-

preciable effect of iron can be seen any more. At so low a pH only a concentrated solution of alloxantin establishes a reproducible potential, and this is not influenced at all by iron.

Iron can not be replaced by copper, manganese, cobalt, nickel or organic dyestuffs.

As for the explanation of this effect, it should be recalled that dialuric acid gives a complex compound with iron. This can be shown, however, only in an alkaline solution. Dialuric acid plus $FeCl_3$, plus ammonia, produces a deep violet color. At the pH range 4 to 6, where the effect of iron on the potential is strongest, no evidence of any complex formation can be shown. No color and no precipitate is produced by the iron. If there exists, at pH 4–6, a Fe complex at all, this complex can represent only a very slight fraction of that part of the substance not combined with Fe. Yet, this minute trace of the complex may be considered as the intermediator for the establishment of the potential. Without emphasizing too much this hypothesis, at any rate, this is another case of the catalytic establishment of a potential in a system which is thermodynamically reversible but sluggishly reactive without a catalyst.

It should be recalled[3] also that Fe acts as a catalyst for the oxidation of dialuric acid by molecular oxygen. The pH optimum of this effect is around pH 7, whereas the effect described above has its optimum at pH 4–6.

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