

Letters to the Editor.

[The Editor does not hold himself responsible for opinions expressed by his correspondents. Neither can he undertake to return, nor to correspond with the writers of, rejected manuscripts intended for this or any other part of NATURE. No notice is taken of anonymous communications.]

Lecture Experiments on the Hydrogen Ion Concentration Changes in the Rusting of Iron.

For the rusting of iron, oxygen, water, and a trace of acid are required. In the process oxygen is used up, also a certain amount of water, but the acid may be said to act as a catalyst. It is, in fact, regenerated when the ferrous salt first formed is oxidised to the ferric state, as was shown previously (*Trans. Faraday Soc.*, 18, 310-317; 1923). This is at once evident when we consider that, on making solutions of ferric or ferrous salts less acid, ferric hydroxide is first precipitated, at pH 3.5 to 5.5, and ferrous hydroxide comes down later, at pH 5.1 and onwards, a trace being still in solution at pH 7.6. Oxidation, therefore, must result in a liberation of acid, accounted for by the ferric being hydrolysed to a greater extent than the ferrous salt.

The reaction may be demonstrated as follows: Adding four drops of 0.04 per cent. brom phenol blue to each 10 c.c. of a dilute solution of a ferric salt, the yellowish colour of the indicator denotes acidity equivalent to pH 3.2 or less, namely, equivalent to a solution at least as acid. A similar solution of ferrous sulphate gives a purple colour with this indicator and can accordingly be no more acid than pH 4.2. It is in reality at about pH 4.8. On standing for some days the change to the ferric condition is accompanied by a change in reaction, as shown by the indicator. For lecture demonstration, however, it may be brought about instantaneously. By adding a few crystals of 'hyperol' to distilled water, a solution of hydrogen peroxide may be prepared which is no more acid than pH 5.6. It is accordingly alkaline towards the indicator mentioned and gives with it a good purple colour, as does also the freshly prepared ferrous solution. On mixing these two alkaline solutions, the result is a solution acid to the indicator, namely, at about pH 3.2, which is a clear yellow. This somewhat paradoxical behaviour is accounted for by the regeneration of acid from the hydrolysis of the ferric salt. Were metallic iron present, this acid would be free to attack it.

The action of carbon dioxide in solution can also be demonstrated. Bright iron wire is carefully washed free from the lime in which it is stored, being finally dipped in dilute acetic acid and thoroughly washed with distilled water. It is then placed in a test tube with distilled water to which brom thymol blue (0.04 per cent.) has been added. The full yellow colour of the indicator denotes the presence of free carbonic acid, so that the water is at least as acid as pH 6. This indicator changes to a clear green at pH 7.0 and is blue by pH 7.3. To demonstrate the rapidity of the change, one must work near the neutral point and in an unbuffered solution; the water is therefore brought to a yellowish green colour, pH 6.6-6.8, by the addition of either a trace of pure sodium bicarbonate or a few drops of sea water. On standing, the very low acidity, pH 6.8, is reduced by the attack on the iron; within two minutes the reaction has become noticeably less acid; within five minutes the change is readily recognised. For lecture demonstration the experiment may be started an hour beforehand, when the green colour of the indicator will have been changed to an intense blue

round the wire. On shaking up, the whole tube becomes blue, but on allowing to stand, a green colour reappears in the parts remote from the wire, especially near the surface, owing to the oxidation of the ferrous salt, with regeneration of acid. Inasmuch as increase in acidity appears to slow down the rate, there are reasons for thinking that the constituent most readily oxidised is the fraction of the ferrous salt which is hydrolysed to hydroxide. By its oxidation the equilibrium is upset and more ferrous bicarbonate hydrolysed to hydroxide, the equivalent of acid being set free. The changes occurring round the wire may be projected on a screen and so made visible to the audience.

With solutions which are alkaline at the start, namely, those containing fewer hydrogen ions than does pure water, the change proceeds, though more slowly. Using 0.02 per cent. phenol red, a pink colour may be obtained, increasing to a good red, indicating pH 8. Using xylenol blue, a light blue may be obtained, showing a reaction as alkaline as pH 8.4-8.6. Beyond this I have not succeeded in going, for the change being much slower, the liberation of acid through oxidation prevents further increase in alkalinity. Were care taken, however, to remove all oxygen, it seems likely that a greater alkalinity could be reached.

On standing in a tube with distilled water, iron wire in rusting continues to absorb carbon dioxide from the air to such an extent that when the acid is set free by 'hyperol' solution, as previously described, the solution, originally no more acid than pH 5.6-6.0, will give a good red colour with methyl red, showing that it is nearly saturated with carbon dioxide and is somewhere near pH 4.6.

Control tubes without the iron wire were used throughout and the tubes were of British resistance glass. The water was freshly distilled in a room free from chemical fumes.

The explanation given here of the mechanism of the rusting of iron is, I believe, that which is now generally accepted, and the hydrogen ion changes revealed by the indicators support it. It naturally follows that the experiments described are against the view that an oxidation of the iron is the first stage in rusting.

W. R. G. ATKINS.

Marine Biological Laboratory,
Plymouth, Mar. 13.

The Disintegration of Radium E from the Point of View of Wave Mechanics.

ELLIS and Wooster (*Proc. Roy. Soc.*, A, 117, p. 109) have shown recently that in the disintegration of radium E the single β -particle emitted has an initial energy which may vary from 40,000 to 1,050,000 volts. This means that the result of disintegration is in some way indeterminate, a conclusion difficult to reconcile with the usual ideas of radio-activity.

Some such result, however, is to be expected on the new wave mechanics, if the ejection of a β -particle is produced by anything like a sudden explosion. In such a case one would expect that the wave-group which accompanies, and on some views actually constitutes, the electron, would be of the nature of a single pulse, that is, the damping factor of the amplitude would be of the order of the wave-length. Such a wave-group, being very far from monochromatic, would spread rapidly lengthwise owing to the large dispersion of the phase waves, and so the distance within which the electron may occur becomes large, implying a marked 'straggling' in velocity. Similarly, if the waves pass through a magnetic field,