

lation of hydrogen ions, when changes may be expected in the dissociation of cell substances. It may further be expected that a certain number of ions will be freed which, if the membrane is permeable to them, may leave the cell. In yeast cells potassium, calcium and phosphate ions may chiefly be concerned here.

Sodium fluoride enters the yeast cell as hydrogen fluoride⁴, which may cause an accumulation of hydrogen ions in the cell. At the same time, potassium leaves the cell⁵. For this reason it was of interest to examine the influence of fluoride on the charge of the yeast cell. This examination showed that the greater the concentration of sodium fluoride is in the surrounding solution, the lower is the electrophoretic mobility and the more apparent the agglutination of the cells. After the sodium fluoride has been washed out, the cells again behave as normal.

It seems that lower concentrations of sodium fluoride, which still cause stimulation of the respiration and fermentation of the cell, enhance the migration of the yeast cell toward the cathode.

It is interesting in this connexion to recall the tenacity with which erythrocytes⁶ and bacteria⁷ maintain their electrophoretic charge and mobility in spite of important changes both in the surrounding medium and, in the case of erythrocytes, even in the cells themselves (alterations in shape, haemoglobin content, etc.). However, with the aid of the weak acids carbon dioxide and acetic acid, Höber⁸ succeeded in changing the sign of the electrical charge of erythrocytes.

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Crack-Heal Mechanism of the Growth of Invisible Films on Metals

THE thickening of oxide or other films on metals according to the parabolic equation $y^2 = K_1 t + K_2$ (where y is the film thickness at time t and all K 's are constants) is generally attributed to lattice-defects, K_1 being related to the electrical constants of the film substance by Wagner's equations¹. Logarithmic thickening ($y = K_3 \log(K_4 t + K_5)$) is, in my view², associated with discrete mechanical breakdowns caused by the strains arising from the volume increase accompanying oxidation; evidence of such strains is provided by the wrinkling observed during film-stripping³.

In studying the invisible films formed on unheated iron exposed to air, a liquid giving conditions on the border-line between corrosion and passivity (preferably a sodium carbonate-bicarbonate buffer) has been used to show up major discontinuities as rust spots. The higher the concentration, the fewer the spots developed, since rust only appears if the outward effusion of metal exceeds inward diffusion of inhibitor, and at high concentrations this condition will only be fulfilled at exceptionally large discontinuities; thus the spots represent a 'selection' and not a 'sample', becoming increasingly 'select' with rising concentration. A scratch-line traced on heat-tinted metal serves conveniently as experimental area, steel being preferable to soft pure iron. A steel specially prepared for another research by the late Dr. Swinden⁴ was used. It was abraded, degreased, tinted by heating in air for 40 min. at 270° C. and engraved with a blunted gramophone needle loaded at 200 gm. on a modified Mears-Ward machine⁵. Prints were taken at intervals on filter paper wetted with the solution (0.011 M in each salt); the inconspicuous rust spots on the paper were afterwards darkened by conversion to Prussian blue or to a sepia image of metallic gold.



Fig. 1.

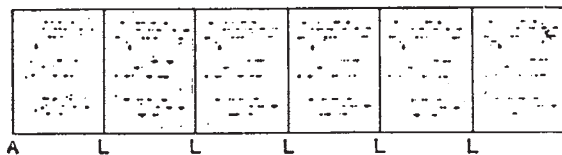


Fig. 2.

Fig. 1 shows the effect of 5-min. exposures at 25° C. alternately in air (A) and in the liquid (L) mentioned above. (Between each of these exposures there was a 5-min. contact with filter paper wetted with the liquid; the specimen was dried with filter paper before an air-exposure.) It will be noticed that after air-exposure most of the old spots disappear; but some new spots appear and still more arrive during the following immersion in liquid. This after-effect does not last long; Fig. 2 shows a single air-exposure followed by five liquid-exposures, and after the first, the pattern becomes nearly constant. These results have been obtained repeatedly, and other

experiments support the idea that the primary effect of air-exposure is to heal existing pores, and the secondary effect to introduce new ones; the two effects are evidently interconnected, and we are led to a mechanism for oxidation under conditions unfavourable to lattice-defect migration.

Metal exposed (unwetted) to cold air must suffer oxidation at any pores present in the invisible film; the effect will be to block the original pores but introduce strains capable of cracking the film and producing new pores elsewhere. Thus the sequence crack - heal - crack - heal is set up, and it might be expected that the oxidation-rate would settle down to that constant value at which the cracking caused by oxidation balanced the oxidation produced by cracking ($dy/dt = K$). But in addition to (chemical) blockage connected with conversion of metal to oxide at the base of a pore, there may be some alternative (physical or mechanical) type of blockage which can occur anywhere on a pore; (to give just one example, the pore might 'weld up'). The oxidation-rate should then fall off as the film thickens, the pores lengthen, and the proportion of pores suffering physical blockage increases; for physical blockage contributes nothing to oxidation. If the chance of physical blockage in thickness-element dy is defined as py , the chance of escaping it in the full film-thickness y is $\exp - py$, and the equation becomes $dy/dt = K \exp - py$, which is just the relation ($y = K_6 \log(K_7 t + K_8)$) found by Vernon, Akeroyd and Stroud⁶ on zinc exposed to fairly pure air; apparently p is small in polluted air, since Vernon⁷ found a rectilinear law ($dy/dt = K$) for zinc in the London atmosphere.

This treatment is in many respects an over-simplification. It is hoped to publish later a more detailed discussion, taking account of the manner in which corrosion at any point depresses the probability of attack in the vicinity—as found by Mears and me⁸. Means of overcoming this statistical complication suggest themselves, and it may be possible to obtain curves showing how the frequency of pores of each size-class diminishes with time, and thus obtain detailed knowledge of the oxidation process.

Meanwhile, it appears unnecessary—in the case of iron and zinc—to postulate *ad hoc* mechanisms for the film growth, since the known facts are explained by the heal - crack - heal sequence, of which these experiments provide ocular evidence.

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Combustion of Carbon

It was pointed out by Nicholls¹ in 1933 that when an attempt is made to set up a heat balance from data relating to temperature measurement and gas composition within a fuel-bed in active combustion, there is an anomalous disappearance of energy at the point in the bed where the oxygen concentration becomes insignificant and the carbon dioxide concentration attains its maximum value. This observation has been confirmed by later workers², who have also shown that the 'missing' energy reappears as the gases further traverse the bed.

The conditions in a burning bed of solid fuel particles represent a departure from those of refined laboratory experiments in two main respects: (a) irregularity and time-dependence of the geometry of the surfaces of the fuel particles; (b) complexity of the chemical nature of the fuel and of the processes leading to ignition and combustion.

In order to study problems of energy release and the mechanism of oxidation reactions occurring in such systems without the above complications, it was found useful to employ a tube of elementary carbon, the conditions within which would approximate to those obtaining in a single channel in a fuel-bed. A slow air stream was passed through the tube, which was also electrically heated to an effectively steady state in which the electrical energy input was very large compared with the heat released by its combustion.

It was considered probable that the main cause of the above energy discrepancy lay not in the temperature measurements but in the technique of sampling the gases which, if they still contain oxygen and carbon monoxide, may continue to react after being drawn into the sampling probe. Attempts were therefore made to achieve more effective quenching by the use of very fine probes which were water-cooled to the extreme tip.

With the aid of these sampling tubes, it was established that the gas within a fraction of a millimetre of the carbon wall contained appreciable carbon monoxide (0.5-2.0 per cent), thus justifying in some measure the suggested cause of the energy discrepancy (unless drastic quenching is achieved, virtually no carbon monoxide is found so long as there is surviving oxygen). Away from the wall, however,