AN INVESTIGATION INTO THE ACTION OF FEED WATER UPON THE METAL OF BOILERS

with Special Reference to CAUSTIC CRACKING.

by

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INTRODUCTORY NOTE.

The work described in this report was, at the outset, intended to comprise a short investigation of corrosion problems in general as they affect steam generating plant. It soon became evident, however, that the particular type of boiler corrosion known usually as "caustic cracking", or "caustic embrittlement", provided a particularly attractive field of study and virtually the whole of the investigation has been devoted to an attempt to clarify certain aspects of the problem presented by failures due to this cause.

Those who are acquainted with the subject of caustic cracking will agree that there is as yet no indisputable explanation of the fundamental causes of it, and the present writer has given much of his attention to a search for such an explanation.

It is because of this that a discussion has been introduced at the end of each relevant part of this report and a general discussion has been embodied in Part VII. The practical and experimental work done in the course of this investigation is described in Parts III, IV, V and VI. Part III includes a statistical analysis of extant observations. One paper dealing with this part of the work has already appeared and another is in print. A relationship between hydrogen overpotential and hydrogen embrittlement has been tentatively established in Parts IV and V. The writer was encouraged by results which he obtained with the apparatus described in Part VI. This apparatus, which is of his own design, is, so far as he knows, the only one of its kind in this country. Care has been taken to accredit data and information taken from outside sources to the proper authorities. Since ideas and concepts normally result from a series of associations, the origins of which may be forgotten, the writer may not have been able to cite the source of every item, but he has endeavoured to do so to the best of his ability.

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PART I

THE OCCURRENCE OF CAUSTIC CRACKING IN PRACTICE.

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1. INTRODUCTION.

The failure of boilers in service due to cracking within the riveted seams, and at other similar locations has for a great many years engaged the serious attention of those responsible for the manufacture and operation of steam generating plant. The extent of the problem will become apparent when it is realised that the presence of such cracks, because of their position, will not be detected in any normal inspection of the boiler unless they have reached disastrous proportions. This state of affairs implies at least the replacement of the affected plates, and not infrequently of the complete boiler shell. Such economic considerations are, however, of minor consequence in comparison with the very real danger of complete disruption of the boiler, with the attendant danger to human life and to neighbouring plant.

Failures attributable to cracking of the seams are rather infrequently met with in this country, though occasional cases do occur, especially in Scotch marine boilers. In America, the trouble would appear to be rather more prevalent, and its occurrence in locomotive boilers is a matter of some concern. In consequence, research has been carried out in the U.S.A. much more vigorously than here.

Despite its comparative rarity as a mode of boiler failure, this form of cracking has been responsible for a disquieting number of explosions. The case of the Dutch East Indian steamship "Pahud" 1) 2)[X], and that of the disastrous explosion of a water-tube boiler at Reisholz, in Germany, may be specially mentioned. The Reisholz explosion, which resulted in the loss of 27 lives and caused much material havoc 3) led to the formation of the Vereinigung der Grosskesselbesitzern, an organisation which has done much in investigating not only this problem of boiler operation but many others as well.

Occasionally failures superficially of the nature outlined above may be attributed to more or less obvious causes as, for example, excessive stresses set up during fabrication, fatigue, or (more rarely) faulty material. In most cases, however, none of these factors is operative to the requisite extent, and the cause of failure must be sought elsewhere.

It was suggested early in the present century by Stromeyer 4) 5) and by Parr 6), that the cracks might be due to the action on the boiler metal of caustic alkali formed by the hydrolysis of the sodium carbonate frequently added to the boiler feed. This view has come to be generally accepted, and consequently failures of this type are frequently referred to as "caustic cracking", or on account of the apparently brittle nature of the cracks,

[X] The figures refer to a bibliography to be found at the conclusion of the report.

"caustic embrittlement". In subsequent sections these ideas will be examined in more detail, but in the meantime it is necessary to inquire more closely into the nature of the problem by an examination of the features typifying such failures.

2. LOCATION AND MACROSCOPIC CHARACTERISTICS OF CAUSTIC CRACKS.

On the gross scale, caustic cracking presents a number of well-defined characteristics which, while not necessarily unique, permit us, when taken in conjunction with the results of a micrographical study, to arrive at several important conclusions regarding the mechanism whereby the cracks are produced. These distinguishing features are summarized below.

(i) The cracks are confined to regions where cavities may exist in the boiler structure, and to which the main body of feedwater has but limited access. Typical locations are the riveted seams of the shell-plates and the rolled-in ends of fire-tubes.

(ii) They only occur at areas where a considerable degree of asymmetrical stressing, accompanied by plastic deformation of the metal, is present; as, for example, in the vicinity of rivet holes.

(iii) The cracks appear to be brittle in character, in that they are not associated with any appreciable elongation of the metal. Nevertheless, tests carried

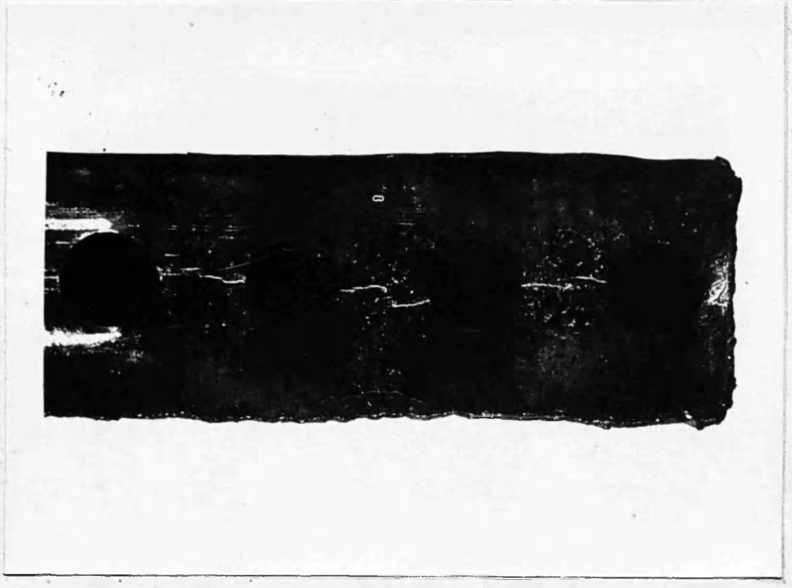


Fig. 1.

out on specimens taken from the region of the cracks do not reveal any appreciable reduction in the ductility of the metal (7) [X].

(iv) In riveted seams the cracks are frequently found to pass from rivet hole to rivet hole, though not always in a continuous fashion, as will be clear from the accompanying photograph (Fig.1), of an embrittled shell plate. Sometimes they are found to be distributed radially round the circumference of the rivet holes. They do not always traverse the supposed lines of maximum stress. Cracks are also in many cases present in the rivets themselves, and in severe cases the heads may be broken off by a blow from a hammer. This test is sometimes applied in routine inspections of the boiler.

(v) Failures are not invariably confined to plates of poor chemical or physical properties, nor are they always associated with faulty workmanship or design. Variations in the operational conditions (temperature distribution, frequency of on-and-off loading, and so on) are apparently without material influence. It is true that in particular cases the trouble may be aggravated by faulty material or workmanship (such as excessive riveting pressure or insufficient caulking of inside seams), or to exceptionally severe operating conditions; but proper attention to these

[X] Compare, however, the work of White and Schneidewind. (infra p.156)

100x Etched.

Fig. 2.

550x. Etched.

Fig. 3.

500x. Unetched.

Fig. 4.

matters will not necessarily render the boiler immune from attack.

3. MICROSCOPIC CHARACTERISTICS OF CAUSTIC CRACKS.

Though on the macroscopic scale caustic cracks exhibit certain unusual features it is only on the examination of specially prepared microsections that their peculiarities are fully revealed. The Photomicrographs reproduced in Figs 2, 3 and 4 were taken from a microsection cut from the boiler plate of Fig 1 at the region marked by the chalked square. These may be taken as typical of this mode of failure, of which the salient features are set out below.

(1) Frequently there is one large fissure in each region, which is filled with the products of corrosion. These are mainly ferroso-ferric oxide, associated with smaller quantities of ferrous oxide (8) (Fig 2).

(ii) Associated with each of these fissures is an extensive network of extremely fine subsidiary cracks, some of which may be discerned in their relation to the main fissure in Fig 2.

(ii) The subsidiary cracks are peculiar in that they are predominantly intercrystalline (Fig 3); that is, they tend to follow the boundaries of the individual crystals of which the metal is composed in preference to a path passing through the body of the crystals. Occasionally the fracture may become transgranular over a short distance, as is shown towards the right-hand edge of Fig 3, but this behaviour would appear to be somewhat exceptional.

(iv) Many of the finer cracks appear to be entirely free from corrosion products, as is particularly clear in the unetched microsection of Fig 4. In Fig 3, however, there is some evidence of attack at the edges of the grains bordering the crack, which in some cases has resulted in the development of short branch cracks. This may possibly indicate the presence of a corroding medium.

(v) It cannot be said that the cracks show any particular association with inclusions, or with pearlite as has sometimes been stated (9); an apparent association with these features of the microstructure is a natural consequence of their intergranular path.

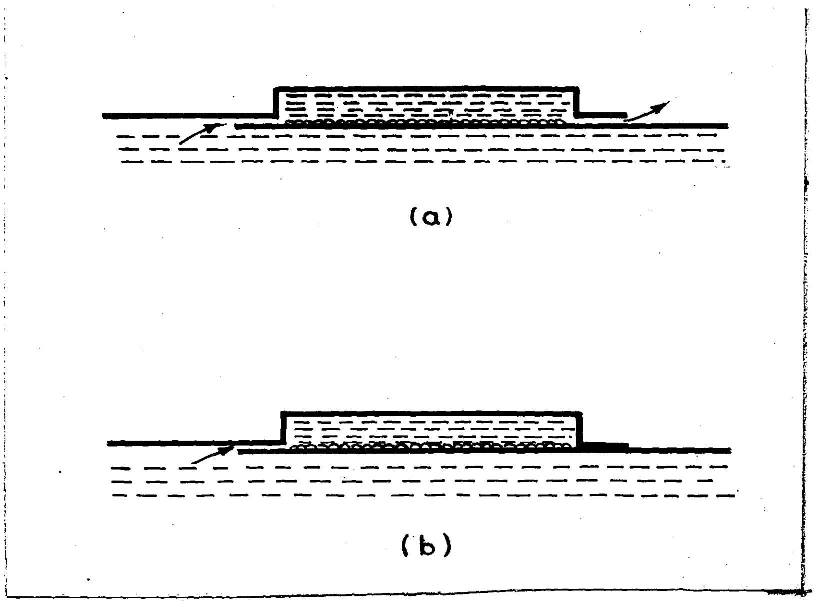
The marked tendenc~~e~~y of caustic embrittlement cracks to follow an intergranular course distinguishes them sharply from most normal modes of failure in mild steel. Cracking which is attributable to brittleness of the material (whether on account of chemical composition, heat treatment, or cold work), normal fatigue, or corrosion fatigue exhibits in general no particular regard for the grain boundaries. Occasionally cracks originating from these causes may pass along the boundary of one or two individual grains, while a certain amount of intergranular pitting on the flanks of a corrosion-fatigue fissure is not uncommon (10). But such cases are readily distinguishable from the type of failure in question.

It must not be supposed, however, that intergranular failure of steel is only found under such circumstances as have been outlined in the preceding paragraphs. Numerous examples are well known, each assignable to certain specific causes. Nor is it a phenomenon peculiar to mild steel; many other ferrous and non-ferrous alloys exhibit (under certain conditions) the same susceptibility. A discussion of some of the more important examples of intergranular failure is undertaken in Part II, since it is only by this means that the particular type under review may be placed in its proper perspective.

4. THE INFLUENCE OF THE FEEDWATER.

So far, any mention of the part played by the chemical composition of the boiler feedwater in the production of caustic cracks has been avoided. The relationship is an involved one and, as yet, by no means fully understood. Full consideration has therefore been postponed to Parts III and VII, but it is convenient to discuss here certain practical aspects of the matter.

As has already been mentioned, it was determined by the earliest investigators that cracking identical with



(a)

(b)

Fig. 5.

that occurring in practice could be obtained by severely stressing mild steel in hot caustic soda solutions. A difficulty immediately arose in attempting to correlate these results with practice, in that the concentration of alkali required to produce failure exceeded by many times that found in the feedwater of embrittled boilers. It is possible, however, to suggest a mechanism whereby the necessary concentration may be attained at those regions susceptible to attack.

Fig 5(a) represents, diagrammatically, a boiler seam which has been badly caulked internally and externally so that an internal cavity is in limited communication both with the interior of the boiler and with the atmosphere. It is easy to envisage that feed seeping into the seam will be rapidly concentrated by evaporation into the atmosphere, and that ultimately a deposition of solid salts will occur in the cavity. This condition has been ingeniously reproduced by Dr. Schroeder in his "Embrittlement Detector" to which we shall have occasion to refer later.

By means of a simple but instructive experiment, Straub 7) has shown how concentration of the feedwater may take place even in cases where the seam is tightly caulked externally. Referring to Fig 5(b), water enters the seam and evaporates either partially or completely, the vapour being ejected into the body of the feedwater.

Due to temperature variations the vapour remaining in the inner cavity is condensed, thus permitting the entry of a fresh portion of feedwater; or it may be that opening and closing of the cavity through operational pressure fluctuations serve the same end. By this process a high concentration of salts is soon attained.

It has been shown by Pfleiderer 3) that the deposition of salts may readily occur even under conditions much less severe than those implied in the above discussion, and it seems doubtful if riveted seams can be rendered entirely immune by even the most lavish care in fabrication. The occurrence is no doubt closely connected with the remarkable powers of seepage possessed by alkaline solutions.

PART II

THE NATURE OF THE CRYSTAL BOUNDARY, AND INTERCRYSTALLINE FAILURE IN METALS AND ALLOYS.

II THE NATURE OF THE CRYSTAL BOUNDARY, AND INTERCRYSTALLINE FAILURES IN METALS AND ALLOYS.

In this part of the work it is proposed, first, to discuss the nature of the boundary layer separating the crystals of metallic aggregates, and second, to give an account of some of the circumstances under which metals and alloys are found to fracture in an intercrystalline manner. In order to avoid lengthy digressions at a later stage, and to preserve a logical sequence it is desirable to include in this brief review material which may not be unfamiliar. The treatment is, on the whole, objective, but on some matters of dispute the writer has ventured to submit his own opinion, Where this has been done, the fact is explicitly stated.

NATURE OF THE GRAIN BOUNDARY.

1. NOTE ON CRYSTAL STRUCTURE.

The individual crystals of a metal (or indeed of any true solid) are built up by the regular disposition in space of atoms or groups of atoms so as to generate a space lattice. Such a lattice may be represented by a network of points in space so arranged that each point possesses identical surroundings. This condition imposes a severe restraint on the number of possible arrangements: there are indeed only fourteen.

In the simplest case only one atom is associated with each point of the lattice. Thus α- iron (ferrite) the allotropic modification stable at normal temperatures has a body - centred cubic structure in which there are iron atoms at each cube corner and at the cube centre and nowhere else. Similarly γ - iron (austenite) stable between 912°C and 1400°C has a face-centred cubic structure, there being atoms at each corner of the unit cube and at the centre of each cube face. Much more complicated arrangements are, of course, possible in which symmetrically arrayed groups of atoms (or other units of structure, such as asymmetrical atom groups) are associated with each point of the space lattice. Crystallographers have shown that 230 such space-groups are possible, each of which is associated with one or other of the 14 space-lattices. These space groups are generated by the operation of certain symmetry elements in space in a manner analogous to the generation of the 32 classes of macroscopic crystal symmetry by the operation of symmetry elements at a point. [X]

[X] The relevant references are:-
F.C. Phillips, "An Introduction of Crystallography", London (1946). Ch. VI and Pt. II:
(Sir) W.L. Bragg, "An Introduction to Crystal Analysis" London (1928). Ch. IV.

2. FORMATION OF THE GRAIN BOUNDARY IN PURE METALS.

When a pure metal crystallizes from its melt numerous minute crystallites (nuclei) of solid are first formed, in each of which the atoms are disposed in regular array, as outlined above. The crystallite as a whole, however, possesses a random orientation with respect to its neighbours. As crystallization proceeds the nuclei continue to grow in certain preferred directions with respect to its internal structure, the random orientation of each with respect to the others is, however, still maintained. This process of growth continues until only a thin film of molten material separates each developed crystal from its neighbours. It is the mode of solidification of this film which determines the nature of the intercrystalline boundary.

Two suggestions have been advanced. The older is that the inter-atomic stresses set up during the solidification of the intergranular film are sufficient to disrupt completely the regular arrangement of the atoms and produce an amorphous layer. This intergranular "amorphous cement", as it is frequently called, is regarded as being similar to the flowed layer of amorphous metal (Beilby Layer) produced by metallographic polishing. Because the regular crystalline structure is the most stable arrangement of the atoms of a metal in the solid state, it will possess the minimum free energy of all possible states at the temperature in question. The amorphous state existing at the boundary will therefore possess a higher free energy and on this account might be expected to exhibit an enhanced propensity to change; its presence has thus frequently been invoked to explain changes which commence at or are confined to the grain boundaries. For example, structural changes occurring in the solid state which commence at the grain boundaries, such as the transformation of austenite to pearlite (11), are sometimes ascribed to their increased activity as is also the tendency shown by certain metals to fail intergranularly at elevated temperatures. In the latter case it is supposed that the intergranular metal being, in effect, a glass, will possess a certain capacity for viscous flow, thus facilitating rupture between the drystal grains (12). The hypothesis that an amorphous layer possessing the properties attributed to it above exists has been vigo~~u~~rously defended by Rosenhain (13).

Recently the notion of an amorphous film extending to several hundred atomic layers in depth such as the above considerations would appear to imply has fallen somewhat into disfavour. It is known now that the stresses set up by the relatively displaced positions of the atoms in the approaching crystal faces become negligible beyond a few atomic diameters and it is widely held that the distorted layer cannot exceed this thickness. It is now supposed that the contiguous crystals preserve their regular atomic arrangement to within a few atomic layers of the interface, while across the remaining distance a gradual rearrangement of the atoms takes place as each crystal face strives to attain the structure of the face which the other presents to it. A compromise is thus attained, and it is such a thin, distorted layer which is believed to constitute the interface.

It is extremely difficult to obtain reliable experimental evidence which would enable one to decide between the two alternatives advanced above, since the presence of even minute amounts of impurities may profoundly influence the behaviour of the boundaries. This matter is discussed in the ensuing section.

3. INFLUENCE OF IMPURITIES AND OF ALLOYING ELEMENTS.

As an example of the manner in which the addition of a second component (not forming a continuous series of solid solutions) to the melt of a pure metal may influence the behaviour of the crystal boundaries, the system iron-sulphur may be considered. This is a case of considerable practical importance.

Pure iron crystallizes in the δ form at 1537°C;

the addition of sulphur to the melt causes a progressive lowering of the initial freezing point until a eutectic is formed between γ - iron and iron sulphide at 985°C and 31% sulphur. Solidification of an alloy containing less than the eutectic proportion of sulphur takes place by the separation of pure iron (the solubility of sulphur in solid iron being negligibly small) until the remainder of the melt attains the eutectic proportions, when simultaneous precipitation of iron and FeS occurs. In commercial iron and steel sulphur is present only in small quantities as an impurity, consequently the eutectic solidifies not as well-defined grains, but as thin films in the interstices between the iron crystals. The presence of these thin films results in intergranular brittleness at normal temperatures, and because of the low melting point of the eutectic, in weakness at hot-working temperatures: a condition known as "hot-shortness".

This behaviour is typical of several alloy systems in which a secondary phase forms a brittle intergranular film. Another example is provided by the system gold-bismuth. Pure gold, one of the most malleable and ductile of metals, is rendered extremely brittle by the addition of as little as 0.1 per cent. of bismuth.

In the examples cited above, the intergranular component is deposited from the melt, but its presence may also result from changes occurring in the solid state. An example is the formation of intergranular cementite in low carbon steels (carbon content 0.10% or less) by separation from austenite at the eutectoid temperature. Similarly the phenomenon of age-hardening (notably in mild steel, aluminium-copper and copper - beryllium alloys) is regarded as being due to the separation of a new phase at the grain boundaries and along certain crystallographic planes from a supersaturated solid solution.

INTERCRYSTALLINE FAILURE.

4. CLASSIFICATION.

Failures of metallic materials by intergranular fracture fall, as a general rule, into one or other of four main classes;

(1) Those attributable to the leaching out of the grain boundary material by some (usually specific) corrosive medium. The presence of mechanical stress, either internal or external is frequently a necessary adjunct to failure of this type.

(ii) Those which result from the reaction of gases dissolved in the metal with the grain boundary material to form products whose self-adhesion or adhesion to the contiguous metal is inferior to that of the grains themselves.

(iii) Those due to the penetration of liquid metal between the grains.

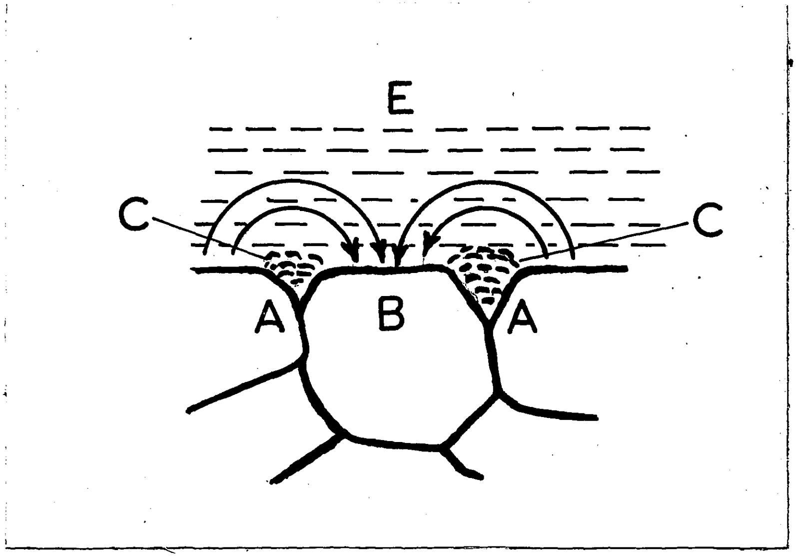


Fig. 6.

(iv) Those due to inherent intergranular weakness resulting from the composition or heat treatment of the metal.

In subsequent sections each of the above classes will be examined in some detail.

5. CORROSION AT GRAIN BOUNDARIES.

Failure of a metallic aggregate by the separation of individual grains is an exceptional state of affairs and can seldom be attributed solely to the structure of the metal and the effect of mechanical stress. Certain corrosive media exert a profound effect in this connection.

As has been pointed out earlier, the metal in the region of the grain boundaries, being more or less distorted, has an enhanced free energy content. In consequence of this, the exposed boundaries of the surface crystals might be expected to be anodic towards the remainder of the surface when the metal is immersed in an electrolyte. This is, indeed, frequently found to be the case, and in many metals and alloys corrosion is initiated in that region. Due, however, to the accumulation of corrosion products, polarisation sets in, and the attack becomes more general. This can perhaps be made clearer by reference to Fig 6. The anodic areas at the grain boundaries, AA, begin to corrode first, the accompanying flow of positive ions in the solution being indicated by the arrows. As the products of corrosion begin to accumulate, the potential difference between A and the remainder of the grain surface B, is reduced. The attack therefore becomes less intense, and ultimately is spread uniformly over the entire surface.

The sequence of events outlined above may be somewhat modified when the metal is simultaneously subjected to a tensile stress, the tiny intergranular pits initially formed are extended and widened, thus permitting access of the electrolyte to their roots, which, in view of the intense distortion existing there, are invariably anodic towards the remainder of the surface. Under these conditions, and provided polarisation is comparatively weak, serious intergranular <u>pitting</u> may result. It is at least doubtful, however, if these conditions alone are sufficient to account for intergranular <u>cracking</u>. As a matter of fact, because of macroscopic areas of differing electrochemical potential (due, for example, to differential aeration) intergranular pitting is comparatively rare in practice, though the phenomenon is sometimes observed on the sides of corrosion fatigue cracks where the conditions existing at the surface are naturally of minor importance. Intergranular cracking, though more commen, is a much more subtle occurrence, and the problem is perhaps best approached through the medium of specific cases.

Perhaps the best known example is provided by the cracking of cold-worked brass in an atmosphere containing ammonia. In this case the formation of (probably) the complex cuprammonium ion, $Cu.\ 4NH_3^{\cdot\cdot}$,[x] prevents polarisation by free cuprion, while the residual stresses resulting from cold work facilitate the propagation of the attack. Thus far, however, the explanation is very probably incomplete. There is evidence that only the β-constituent of brass is attacked by ammonia, while it is only the mono-phase α-brass which is susceptible to intercrystalline attack (14). On this account, it has been suggested that failure is due to traces of the β-constituent existing at the grain boundaries.

Certain nickel-chromium steels, and notably the alloy containing 8 per cent nickel and 18 per cent chromium are susceptible to intergranular attack under certain conditions. These steels are quenched from 1000 - 1200°C and are austenitic at room temperatures, for although the solid solution is thermodynamically unstable the rate of decomposition is immeasurably slow. If, however, the steel is heated in the region 600 - 900° C the austenite breaks down with the precipitation of chromium carbide. The reaction proceeds most rapidly at the grain boundaries, which become impoverished in

[x] It appears to be sometimes overlooked that cuprammonium hydroxide is only stable in concentrated solutions of ammonia. This fact may invalidate the argument in some cases.

chromium and so more liable to attack. It is this decomposition of the austenite which is responsible for the well known phenomenon of weld decay.

The trouble may be averted in several ways. The maintenance of an extremely low carbon content (less than about 0.02 per cent) is hardly practicable on the commercial scale but it is quite usual to add some substance having an affinity for carbon superior to that of chromium, such as titanium, niobium, vanadium, or tantalum. The carbides of these elements are then preferentially precipitated, leaving the chromium in solution. Another method is to produce an α-iron phase by the addition of molybdenum. Chromium carbide is then precipitated at the α-phase boundaries, and provided the α-iron masses are isolated no serious damage results. Similar results can also be achieved by reduction of the grain size through cold working. The consequent increase in grain boundary area prevents the formation of a continuous "foam" of deposited carbide. A rather spectacular illustration of the protective effect of cold working was exhibited recently in the form of an 18 per cent Cr, 8 per cent Ni alloy bolt in which the body had crumbled away through intergranular corrosion, leaving the cold-worked threads in the form of a coiled helical spring. Sensitivity to intergranular attack may be detected by reheating the steel to 650°C and subsequently subjecting to the action of a boiling acid copper sulphate solution.

Intergranular corrosion in light alloys is of frequent occurrence. An important example is provided by duralumin, an~~d~~ aluminium - rich alloy containing about 4 per cent copper. This alloy possesses the property of age-hardening to a remarkable extent, and it is the resultant increase in hardness and tensile strength which gives it its great technical importance. Age-hardening (and temper-hardening), as the phenomenon is understood nowadays, ~~is~~ are due to the precipitation of a second phase in sub-microscopic quantities along certain crystallographic planes and at the grain boundaries. The distortions set up in the lattice by the nuclei of the second phase tend to toughen the alloy in a manner analogous to work-hardening. As precipitation of the second phase proceeds the distortions in the lattice decrease, and by the time the quantity precipitated has reached microscopic proportions the hardness and other properties affected by the process have passed their maxima (15). This latter state may readily result from adverse quenching conditions (i.e. from too low a temperature, or too slowly) and, if the accumulation of the second phase at the grain boundaries is sufficient, the material is rendered seriously susceptible to intergranular attack.

On the basis of the examples described above, and on others, the conditions favourable for intergranular attack (as envisaged by the writer) may be set down as follows:-

(a) The reaction must not stifle itself, that is, its progress must not be hindered by the accumulation of solid reaction products. This is naturally a prerequisite of any continuous corrosion process, but it is to be remembered that the intensely localised intergranular attack may be much more readily stifled by solid corrosion products than a more generalised attack. To achieve this end the products must be soluble in the electrolyte or if solid, be deposited at some distance from the seat of the attack.

(b) Electrochemically the process must be efficiently anodically depolarised. In some cases the reaction may be self-depolarising through the removal of free cations by the formation of complexes while in others a suitable depolariser may be present in the electrolyte. In any event, the depolarising agent must be capable of functioning efficiently in the restricted intergranular fissures.

(c) It seems highly probable that a grain boundary phase, anodic towards the bulk phase, must exist in sufficient quantity to permit the initiation and propagation of the attack.

(d) While the presence of tensile stress is not invariably necessary (it is not, for example, in the case of "18 - 8" stainless steel) it is very frequently an important contributory factor.

Surprise has sometimes been expressed that intercrystalline corrosion is not the rule rather than exception, the idea being based on arguments similar to those advanced at the beginning of this section. It is seldom however, that the conditions laid down above are operative to the requisite extent. Conditions (a) and (b) are in themselves, in fact, sufficient to restrict corrosion to the metal surface except under the most exceptional circumstances.

6. INTERGRANULAR FAILURE DUE TO DISSOLVED GASES.

Several examples of intergranular attack may probably be placed in this category [x], but for the purposes of the present discussion it will suffice to give a brief account of the behaviour of mild steel when subjected to the action of electrolytic hydrogen.

Under certain circumstances hydrogen evolved at the surface of mild steel is found to penetrate the metal, rendering it brittle and thus extremely susceptible to cracking. The trouble is most frequently

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[x] For example; "Green rot" in nickel-chromium alloys - a complicated process (Cf. U.R. Evans, "Metallic Corrosion, Passivity and Protection", London (1946), p.116); intergranular oxidation of alloy steels at elevated temperatures; and the intergranular weakening of copper steels in atmospheres containing sulphur.

met with in industrial pickling processes, and is thus frequently referred to as "pickling brittleness" (Beizsprödigkeit). A somewhat similar phenomenon, met with in steel plant employed in ammonia synthesis by the Haber process, at temperatures in the region of 500°C, is known as "hydrogen sickness" (Wasserstoffkrankheit); in this case decarburisation of the pearlite accompanies the general brittleness of the ferrite grains (16). Hydrogen is also frequently invoked as a cause of hair-line cracks in ingots and of "fish-eyes" in welds; it is also responsible for the blistering sometimes encountered in enamel coatings . An account of these matters, together with very complete bibliographies will be found in the papers by Zapffe and Sims (17) and Zapffe (18).

The rate of diffusion of hydrogen through steel sheets has been investigated by several workers, among whom may be specially mentioned Morris (19), Edwards (20) and Bardenheuer and Thanheiser (21). The last mentioned workers have shown that diffusion is much more rapid when the steel is attacked by sulphuric acid than when hydrochloric acid is used. Possibly this is due to the presence of stimulating impurities in the former (see below). While increase in temperature or in acid concentration resulted in an increased rate of diffusion, expressed as a proportion of the total amount of hydrogen produced the amount diffusing was less. Increase in the carbon content of the steel was found to decrease the rate of diffusion in agreement with the known fact that hydrogen embrittlement is only troublesome in hypo-eutectoid steels. By allowing hydrogen produced electrolytically at the outer surface of a closed steel bomb to diffuse into the interior, Bardenheuer and Thanheiser were able to show that quite phenomenal pressures could be developed. They regard this experiment as duplicating the conditions existing at the discontinuities in the metal structure resulting from non-metallic inclusions, where pressures sufficient to cause cracking or, if the site of the inclusion be near the surface, severe blistering may be developed. The trouble may be very considerably mitigated by "killing" the steel in the ingot by the addition of aluminium, a process which markedly reduced the segregation of impurities.

Certain impurities in the pickling acid exert a profound influence on the rate of diffusion into the metal and on the resultant embrittlement. Aten (22), employing an apparatus in which a constant current density was maintained, showed that mercuric chloride and arsenious trioxide when present in small quantities caused a very marked increase in the rate of diffusion of hydrogen through a steel sheet. The phenomenon is accompanied by a considerable rise in overpotential. Somewhat similar experiments were carried out by Bablik (23) in hydrochloric acid, but in which no external e.m.f. was applied. This worker found that the addition of a small quantity of hydrogen sulphide to the acid increased the amount of hydrogen diffused, while arsenic and mercuric chloride had the opposite effect.

Alekseew and his co-workers (24)(25), in an extensive series of experiments, have examined the embrittling effect of minor constituents of the electrolyte in some detail, by subjecting loaded wires to cathodic polarisation. In (analytically) pure sulphuric acid little or no brittleness of the wires ensued, but the addition of small quantities of arsenious trioxide, hydrogen sulphide, and sulphur dioxide among other substances[x] resulted in quite spectacular embrittlement, accompanied by a very considerable lowering in tensile strength. Similar results were obtained in 1N. sodium hydroxide solutions containing

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[x] Telluric and selenic acid and certain compounds of phosphorous.

small quantities of mercuric chloride, but the present writer has been unable fully to confirm this (p.101).

Several workers have examined the influence of these "poisons" (as they are frequently called) on the hydrogen overpotential. Their results are superficially contradictory but to the writer appear amenable to a reasonable interpretation; it is, however, convenient to postpone discussion to a later stage (p.91). It is worth while noting here, however, as has been pointed out by Evans (26), that the results of experiments carried out under an applied e.m.f. must be carefully distinguished from those arising from tests in which no external potential is employed. In the first case hydrogen is discharged at the cathode at the rate independent of internal potential changes which may result from the addition of a poison to the electrolyte, while in the second the reaction rate, being dependent on the internal potential, will be profoundly affected by changes induced in it.

The effect of dissolved hydrogen on the mechanical properties of mild steel and iron has been investigated by many workers. Bardenheuer and Ploum (27) have shown by means of a bend test, that the brittleness of the metal decreases steadily with time, recovery being almost complete after a few weeks[x]

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[x] Alekseew (loc.cit) reports a case in which considerable brittleness persisted even after a lapse of three years.

at room temperature, or after a few minutes at 100°C. It is important to note, however, that a complete restoration of the original ductility is never attained. A conventional tensile test, modified to permit cathodizing of the specimen, was employed by Pfeil (28) with interesting results using specimens of iron, obtained by the decarburisation of mild steel, he found a very considerable loss in ductility (elongation 1/6 normal) in commercial sulphuric acid at 25°C, though the ultimate strength of the specimen was but little reduced. On raising the temperature to 40°C the original properties of the material were almost completely restored, though the effect of diffused hydrogen was still obvious in the form of surface cracks. Single crystal specimens showed very little loss of ductility even at 25°C, indicating that the occluded gas has very little influence on the slip of the crystal.

A metallographic approach to the problem has been adopted by Zapffe and Sims (17) and Zapffe and Moore(29). These workers examined micrographically the facets of the fractured surfaces of ferrite embrittled by hydrogen, and obtained evidence of a series of structures which they believe to play an intimate part in the embrittling action of the occluded gas. The coarsest of these is a "lineage" structure of rifts in the surface of the facets, and the finest a "mosaic", exhibiting a statistical regularity, which they believe to be identical with the mosaic structure generally associated with the name of Buerger [x]. Between the two extreme types exists a continuous series of "transition structures". Zapffe and Sims regard these discontinuities in the crystal structure as being largely inherent, though only revealed by the action of the dissolved hydrogen. It is supposed that hydrogen, existing in the atomic form in the interstices of the lattice, can combine at the site of the discontinuities to form a molecular fluid at a high pressure, which widens the rifts and thus renders them visible. Because of the block form of the discontinuities a tri-axial stress is set up by the fluid which largely precludes the normal process of slip, and brittle failure occurs by cleavage through the rifts.

This explanation is not entirely satisfactory. It has been pointed out (30) that the existence of a block structure surrounded by fluid would lead to spontaneous disintegration and a more localised

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[x] An account of these lattice imperfections (mosaics) will be found in Hume-Rothery "The Structure of Metals and Alloys", London, (1945) Ch.V1

accumulation has been suggested. The significance of the gross lineage structure is also doubtful. It has been shown (31) that many of the supposed rifts are in fact Neumann bands, and apparently similar structures in normal fracture have been noticed by the present writer. The argument is not entirely invalidated by these criticisms, however. The existence of the finer mosaic structure is little in doubt, and it seems quite reasonable to suppose that it plays an intimate part in the brittle failure induced by hydrogen. The mode of failure in hydrogenized iron will be further discussed later (p 117) in relation to some of the writer's own results.

The addition of any one of a wide group of organic compounds to the pickling bath has a remarkable effect in restraining the diffusion of hydrogen into the metal (21). Among the more important are beer yeast, sugar waste, sulphite liquor (waste from cellulose manufacture), resorcinol and compounds of the pyridine type. Sieverts and Lueg (32) regard this latter group as being the only efficient restrainers, but this is not borne out by the work of Creuzfeldt (33). The action of these additives is generally regarded as being due to the formation of an absorbed film of colloidal material on the surface of the metal which blocks the entry of hydrogen atoms.

On the question of whether hydrogen embrittlement does or does not lead to intercrystalline failure there appears to be some confusion. Zapffe and Moore (29) found that hydrogenized ferrite failed in an intercrystalline manner only when iron oxide was present at the grain boundaries; otherwise the fracture is trans-crystalline. Pfeil 28) obtained transcrystalline fracture at 25°C, but intercrystalline at slightly elevated temperatures (40°C). In tests on specimens composed of a few large crystals, trans - and intercrystalline fracture appeared to occur indiscriminately. The writer has found intercrystalline fracture in soft mild steel cathodized in ammonium nitrate solutions in the region of 100°C (p 95), while tests in sodium hydroxide solutions at room temperature resulted in transcrystalline failure with some evidence of intergranular separation (p 106). Apparently a moderate rise in temperature favours the intercrystalline type and the presence of reducible intergranular film is probably necessary, but the problem is somewhat obscure and merits further investigation.

7. INTERCRYSTALLINE ATTACK BY MOLTEN METALS.

An interesting type of intergranular failure is presented by the penetration of molten metals along the grain boundaries of several materials, and a brief notice may not be undesirable.

Perhaps the best-known example is provided by the intergranular penetration of brass by mercury. Desch (34) describes how β - brass containing aluminium disintegrates in a few seconds when moistened with mercurous nitrate and plunged into mercury, even under circumstances where the presence of internal stress is unlikely. The α - brasses fail only when a tensile load is applied. The penetration of brass, copper and steel by molten solders is also well known. A general discussion, together with a bibliography, will be found in Evans' book (35).

An interesting case in connection with the matters discussed in the previous section has been described by Bardenheuer and Ploum (36), who found that steel embrittled by hydrogen is very susceptible to the penetration of molten brass. In the absence of hydrogen the presence of tensile stress is apparently necessary.

The examples quoted above are to be regarded as particular cases (of immediate interest in that they result in intergranular failure) of the wider phenomenon of the diffusion of one phase into another [x]

[x] A general discussion is given by C. H. Desch "Metallography", London (1944) Chs. XIII and XVII.

In cases where solid solubility does not exist the diffusion process is invariably intercrystalline as is the case with tungsten in molybdenum. Even the process of self-diffusion in lead detected by von Hevesy by means of the radio-active isotope, thorium B, appears to proceed in an intercrystalline manner.

In view of the well known fact that diffusion takes place more readily in cold-worked material, it is widely held that the remarkable speed of diffusion along the grain boundaries may be attributed to the distortion of the lattice existing there. To the writer this explanation of intergranular diffusion appears incomplete. It seems improbable that the remarkable difference in diffusion rates existing between the interior and boundary of a grain can be attributed solely to an increased solubility in the distorted lattice. Accompanying the distortion however, are almost certainly a vastly increased number of discontinuities (Lockerstellen) over those existing in the body of the grain. In those regions the interatomic field of force will be extremely weak, thus permitting ready passage of the atoms of the diffusing phase. In some cases the presence of an intergranular lamellar phase may facilitate diffusion, either because the diffusing medium is readily soluble in the boundary phase, or because the number and extent of the discontinuities are greatly increased. The possibility of the latter alternative will be readily appreciated if the lattice structure of the boundary phase differs considerably from that of the bulk phase.

On this view the penetration of hydrogenized steel by brass, as found by Bardenheuer and Ploum, may be regarded as resulting from the widening of the Lockerstellen in the manner envisaged by Zapffe and Moore. In other cases tensile stress may play an equivalent role.

8. FAILURE DUE TO INHERENT INTERGRANULAR WEAKNESS.

Failures which may be attributed solely to an inherent intergranular weakness of the metal are not common, and a brief notice will suffice.

The case of mild steel containing iron sulphide has already been discussed. The trouble is overcome by the addition of manganese which combines with the sulphur to form spherical particles of manganese sulphide. The possibility of intergranular films is thus obviated.

Archbutt and Rosenhain (37) have shown that intercrystalline failure in aluminium alloys and in lead is most readily produced when the crystal boundaries are smooth, when they are serrated fracture tends to be transcrystalline.

Though surface cracks which are intercrystalline may appear in mild steel subjected to prolonged stress at 500° C, they do not exhibit any tendency to initiate intercrystalline fracture, except in the case of Armco iron (38). In tests prolonged over many years Jenkins and Mellor (39) and Rosenhain and Hanson(40) were quite unable to produce failure (either trans - or intercrystalline) in mild steel loaded above the yield point at boiler temperatures.

PART III

ON THE APPLICATION OF STATISTICAL METHODS
TO
FIELD DATA
ON
BOILER EMBRITTLEMENT.

III. On the Application of Statistical Methods to Field Data on Boiler Embrittlement.

Since the introduction of the detector unit devised by Dr. Schroeder (41) it has become possible to conduct field tests on boiler embrittlement on an extensive scale. As in most other corrosion tests of this nature the data obtained are subject to a considerable amount of experimental scatter, rendering it virtually impossible to grasp their full significance by mere inspection. Dot diagrams, or other methods of systematic tabulation, provide a useful summary of the results in that they bring any tendency towards regularity clearly to the eye. In the two extreme cases, when a definite functional relationship is obeyed by the data and when complete randomness prevails, it is possible to assess the results with some confidence. Many sets of data lie between these two extremes, however, and if they are assessed on the basis of the systematic tabulation alone, their assignment to one or other of the two classes becomes largely a matter of personal bias. Clearly this is an unsatisfactory procedure, and if erroneous conclusions are to be avoided some criterion of significance must be established. This is the task of mathematical statistics.

Within fairly recent years analytical procedures have been developed which permit the drawing of reliable conclusions from comparatively restricted sets of data. This "technique of small samples" is of particular importance in assessing the results of experiments of the type under consideration. An example of the application of such methods to embrittlement data will be found in a recent paper by the writer (42). In this case a regression line was fitted to the data and its coefficients tested for significance by "Student's" _t_-test. Such a procedure is not, however, generally applicable, and the more extensive treatment to be given in the following pages requires a more versatile method.[x]

1. CONTINGENCY TABLES.[xx]

Perhaps the most general method of analysis supplied by mathematical statistics is that embodied in in the construction of a contingency table. A contingency table may be constructed in almost every case where it is desired to test for agreement between the frequency distribution of a set of observed data and the distribution of some hypothetical infinite "population" of which the observed set is assumed to be a sample.

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[x] The subject matter of this Part will appear shortly in the Transactions of the American Society of Mechanical Engineers.

[xx] See also Appendix I.

From such a table a statistic may be computed which is characteristic of the sample as a whole, and which provides a reliable indication of the significance of the sample with regard to the assumed hypothetical distribution. The derivation of such a statistic is out-lined in the next paragraph.

Let a sample S of N members be drawn from a population I. If it is now found possible to classify the members of S in two ways, either according to a characteristic A, or according to another characteristic B, we may construct a contingency table whose columns represent the values [x] assumed by A, and whose rows represent the values [x] assumed by B. If A can assume the m values, A_1, A_2, ... A_m and B can assume the n values B_1, B_2 ... B_n then we shall have an m x n contingency table among whose cells the members of S are distributed as shown.

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[x] It is to be noted that these "values" need not be of a numerical character.

$$
\begin{array}{cccccccc}
 & A_1 & A_2 & \cdot & \cdot & \cdot & \cdot & A_m \\
B_1 & n_{11} & n_{12} & \cdot & \cdot & \cdot & \cdot & \cdot \\
B_2 & n_{21} & n_{22} & \cdot & \cdot & \cdot & \cdot & \cdot \\
\cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\
\cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\
\cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\
B_n & n_{n1} & n_{n2} & \cdot & \cdot & \cdot & \cdot & n_{nm}
\end{array}
$$

If we suppose that in the population, I, from which S is drawn no linkage exists between A and B, then the cell frequencies should be proportional to the corresponding marginal totals. That is, the expected frequency in the kth column and lth now will be

$$\vartheta_{lk} = \frac{\sum_{i=1}^{n} n_{ik} \cdot \sum_{j=1}^{m} n_{lj}}{N}$$

where, of course, $N = \sum_{i} \sum_{j} n_{ij}$

The deviations of the m_{ij} from the corresponding μ_{ij} are then given by -

$$x_{ij} = n_{ij} - \vartheta_{ij}$$

We require, however, a statistic which will provide a measure of the significance of the deviations of the sample as a whole.

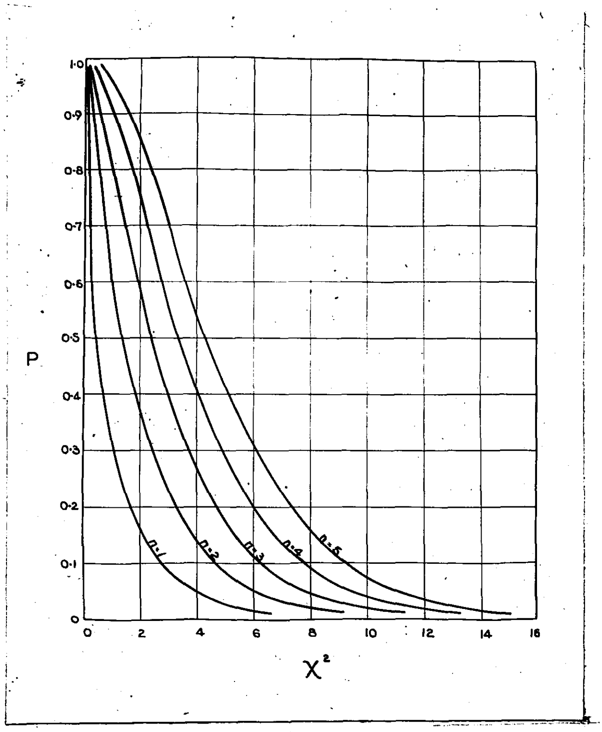

Fig. 7.

Such a statistic is given by the relationship -

$$\chi^2 = \sum_i \sum_j \frac{x_{ij}^2}{\nu_{ij}} \quad .$$

The sampling distribution of χ^2 was found by Pearson to be -

$$dP(\chi^2) = \frac{2^{\frac{1}{2}(2-\varrho)}}{\Gamma\left\{\frac{\varrho}{2}\right\}} \cdot e^{-\frac{1}{2}\chi^2} \cdot \chi^{\varrho-1} \, d\chi .$$

Where ϱ is the number of degrees of freedom of the table; that is, the number of cells which can be arbitrarily filled without altering the marginal totals. From this distribution may be computed the probability, $P(\chi^2)$, that the value χ^2 found in any particular case may be ascribed to sampling variance. A table of values of χ^2 has been constructed by Fisher (43) for $P = 0.01$ to $P = 0.99$ and $\nu = 1$ to $\nu = 30$, and some curves plotted from his table are shown in Fig 7. The selection of the value of $P(\chi^2)$, above which the deviations cannot be regarded as significant is to some extent a matter of choice. In biological and actuarial work a value of $P = 0.05$ is conventionally regarded as the limit of significance, but for the practical purposes of boiler control the somewhat more stringent value of 0.02 is probably to be preferred. The particular value chosen is not, however, of any great moment, provided it is within reasonable limits.

The conditions which the data must fulfil in order that the χ^2 - test may be applicable are not at all onerous. The assumption of continuity in deriving the sampling distribution of χ renders the method somewhat inexact when the cell frequencies are low, however, and it is advisable to arrange the data in such a way that the cell frequencies always exceed 5. Otherwise the nature and sequence of the groups are quite immaterial.

2. ORIGIN AND TABULATION OF THE DATA.

Before applying the statistical method outlined in the preceding section to a particular sample, it is convenient to insert here a brief description of the tests in which the sample originated, and of the tabulation of its data.

In a paper published in 1942 Partridge, Kaufman, and Hall (44) described a series of tests conducted by Hall Laboratories on a large number of boilers distributed widely throughout the U.S.A. and other countries. Schroeder detectors were fitted to the boilers and kept under careful observation, being adjusted whenever necessary, and the number of days required to produce cracking of the specimens noted. If failure did not occur within a certain period (usually 30 days) the test was discontinued. The result of each test, together with the analyses of the feedwaters and some supplementary data (rolling treatment, type of feedwater pretreatment and so on) were recorded in an extensive series of tables. These were made available to the writer through the courtesy of Hall Laboratories, and constitute the sample to be analysed here.

Since the tables are arranged according to an arbitrary system of serial numbers, some rearrangement is necessary before statistical tests can be conveniently applied. The data are first divided into groups according to the values assumed by the characteristic whose influence it is desired to assess, care being taken to ensure that a sufficient number of members are included in each group to ensure the validity of the χ^2-test.

The number of cracked and the number of uncracked specimens in each group are then counted and their frequencies entered in the appropriate cells of the table.

3. THE APPLICATION OF THE χ^2 - TEST TO THE DATA.

(a) The influence of the constituents of the Feedwater.

Almost every common constituent of boiler feedwater has been regarded at one time or another as having some influence on the incidence of embrittlement. Very often precisely opposite effects were attributed to the same component by different investigators.

Recent research has done much to clarify the position, but the remnants of controversy have not altogether disappeared. In the writer's submission, many cases of disagreement are due to personal bias in assessing data whose significance, were they submitted to a sufficiently critical statistical examination, could be determined with complete certainty.

Table I summarises the results obtained by applying the χ^2 - test to various constituents of the feed. Variations in the concentrations of hydroxide, chloride, oxide (R_2O_3), silica and phosphate exert no influence on the relative frequency of cracking, for the analysis shows that the value of P exceeds the stipulated limit of 0.02 by a comfertable margin in each case. We may therefore reject such variations as being of no significance with complete confidence.

TABLE I.

CONSTITUENT	χ^2	ν	P
OH	0.114	3	0.90
SO_4	6.925	3	0.02 - 0.05
Cl	0.507	3	0.90 - 0.95
R_2O_3	4.325	2	0.10 - 0.20
SiO_2	4.058	3	0.20 - 0.30
PO_4	1.167	3	0.98 - 0.99
TANNIN	11.021	1	$<$0.01

Whether the absence of any of these substances would materially alter the relative frequency of cracking is a question to which the data cannot supply an answer [x], since each is present to some extent in every member of the sample. The matter is properly the subject of an extensive and carefully controlled laboratory investigation.

Referring again to Table I, it will be observed that the foregoing remarks do not apply to the constituents sulphate and tannin.. With regard to sulphate, the value of P lies sufficiently close to 0.02 to merit a more detailed examination of the characteristics of the distribution, while the value of P corresponding to tannin places the significance of this constituent beyond all doubt.

The distribution of the data with regard to sulphate is shown on Table II.

TABLE II

see over.

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[x] These remarks do not apply to phosphate, for in numerous members of the sample the concentration of this substance is zero.

TABLE II.

SO_4 ppm.	UNCRACKED	CRACKED	TOTALS.
0 -	37 (32.52)	12 (16.48)	49
200 -	43 (48.45)	30 (24.55)	73
400 -	26 (29.87)	19 (15.13)	45
600 -	44 (39.16)	15 (19.84)	59
TOTALS	150	76	226

$$\chi^2 = 6.925$$

$$\nu = 3$$

$$0.02 < P < 0.05$$

At low concentrations some protective action is apparent, while at intermediate values (200 - 600 ppm) there appears to be a stimulation of cracking; inhibition again becomes apparent at values exceeding 600 ppm. The deviations are however sufficiently slight to engender some doubt of their reality; a doubt which finds quantitative expression in the value of P.

In the past, considerable importance has been attached to the maintenance of a high sulphate - hydroxide ratio. Lately, however, it has been suggested that this will only be effective in preventing failure when combined with a high chloride - hydroxide ratio. The support offered by the data to these two statements is examined in Tables III and IV. In neither case does the observed distribution differ significantly from the expected, so that no benefit can be derived from the fulfillment of either of these conditions.

TABLE III.

$\frac{Na_2SO_4}{NaOH}$	UNCRACKED	CRACKED	TOTALS.
0 -	43 (42.76)	23 (23.24)	66
2 -	40 (39.52)	21 (21.48)	61
4 -	29 (27.86)	14 (15.14)	43
6 -	26 (27.86)	17 (15.14)	43
TOTALS	138	75	213

$\chi^2 = 0.506$

$\nu = 3$

$0.90 < P < 0.95$

TABLE. IV.

		Na_2SO_4 / NaOH				
		0-		4-		TOTALS
		Cracked	Uncracked.	Cracked	Uncracked.	
NaCl/ NaOH.	0 -	73 (72.03)	39 (38.65)	54 (57.09)	29 (27.23)	195
	2 -	9 (9.97)	5 (5.35)	11 (7.91)	2 (3.77)	27
	Totals	82	44	65	31	222

$\chi^2 = 2.454$

$\nu = 3$

0.30 P 0.50.

Indeed as far as Table IV is concerned, the significance of the deviations has probably been over-estimated, for the expected value in the right bottom cell is rather low: a situation which tends to give a value of $P(\chi^2)$ which is less than the true one.

The analysis of the influence of tannin is shown in Table V. In the original tables this constituent is characterised as being "added" or "not added" in many cases, and a 2 x 2 contingency table has therefore been constructed on this basis. The large value of χ^2 (corresponding to a $P < 0.01$) is clearly to be adduced significant. Inspection of the table indicates that it is due to the low observed frequency in the

TABLE V

TANNIN	Uncracked,	Cracked	Totals.
Added	69 (57.46)	17 (28.54)	86
Not added	88 (99.54)	61 (49.46)	149
Totals	157	78	235

$\chi^2 = 11.021$

$\nu = 1$

$P < 0.01$

"added-cracked" cell. Tannin must therefore be regarded as a definite inhibitor of embrittlement and is, in fact, the only determined constituent of the feedwaters which can be classified as such.

Further tests, in which the tannin content is determined quantitatively, are necessary before the amount of tannin required to reduce the relative frequency of cracking to zero can be determined with precision.

(b) The Influence of the Type of Pre-treatment.

When the tests are classified according to the type of pre-treatment employed as in Table VI, some curious and highly significant deviations become apparent.

TABLE VI

Treatment	Uncracked	Cracked	Totals.
Raw	60 (48.72)	14 (25.28)	74
Lime-soda	32 (42.80)	33 (22.20)	65
Zeolite	30 (30.29)	16 (15.71)	46
Evaporated	11 (11.19)	6 (5.81)	17
Totals	133	69	202

$$\chi^2 = 15.633$$

$$\nu = 3$$

$$P < 0.01$$

Tests in which the feedwater is treated by the lime-soda process show a relative frequency of cracking greatly in excess of that expected, while tests in which raw water is employed evince a marked deficit in cracked specimens. The relative frequencies in cases where the feed is zeolite-treated or evaporated do not differ much from their expected values.

It is quite clear that these deviations cannot be ascribed to differences in feedwater composition (in so far as it is analysed) since such variations have been shown to be without effect. The only exception to this statement is tannin, and it might be just thought conceivable that some relationship exists between the amount of tannin present in the feed and the type of pre-treatment employed. That this is not the case, however, is clearly shown by the analysis of Table VII. The cause of the deviations, therefore, remains obscure. Possibly complete analyses of the feedwaters, of each group, in which particular attention was paid to organic components, would have

TABLE VII

Tannin	Raw	Lime-soda	Totals.
Added	29 (30.06)	32 (32.94)	61
Not added	39 (37.94)	38 (39.06)	77
Totals	68	70	138

$\chi^2 = 0.312$

$\nu = 1$

$0.70 < P < 0.80.$

revealed significant variations to which these results could be attributed.

(c) The Influence of Rolling Treatment.

Table VIII illustrates the distribution assumed by the data when classified according to whether the specimens are hot or cold rolled.

TABLE VIII.

	Uncracked.	Cracked	Totals.
Cold-rolled	146 (141.70)	67 (71.30)	213
Hot-rolled	13 (17.30)	13 (8.70)	26
Totals	159	80	239

$$\chi^2 = 3.584$$

$$\nu = 1$$

$$0.05 < P < 0.10.$$

The value of χ^2 can scarcely be adduced significant; but if it is accepted as being so, it represents an extremely slight preponderance of cracking in hot rolled specimens. The effect is obviously of a secondary nature, due possibly to the different surface conditions produced by the two treatments.

4. SUMMARY.

In the preceding paragraphs the methods of mathematical statistics have been applied to the results of experiments carried out with Schroeder detector units.

It has been shown that differences in composition of the feedwaters with regard to hydroxide, chloride, silica, oxide, and phosphate do not materially influence the susceptibility of the specimens to cracking.

Sulphate has been found to stimulate cracking somewhat when present at concentrations in the region 200-600 ppm. At concentrations outwith this range it offers a certain amount of protection. But the variations, though significant, are slight and no undue importance should be attached to them.

The data offer no evidence which might be adduced as sustaining the supposedly beneficial effect on a high $Na_2 SO_4 /NaOH$ ratio. Nor do they support the view that the association of a high value of this ratio with a high value of the $NaCl/NaOH$ ratio will reduce the incidence of cracking to a significant extent.

Specimens subjected to the action of water containing appreciable amounts of tannin are shown to be remarkably immune from attack.

Tests in which feedwaters pre-treated by the lime-soda process were employed show a remarkable preponderance of cracking, while tests employing raw waters exhibit an equally marked immunity. Zeolite-treated and evaporated feeds are not found to influence the frequency of cracking to a significant extent.

The influence of differences in rolling treatment is of a secondary nature. Hot-rolled specimens are found to be slightly more susceptible to cracking than cold-rolled.

PART IV.

THE ELECTROCHEMICAL BEHAVIOUR OF IRON
in
STRONGLY ALKALINE SOLUTIONS.

IV. THE ELECTROCHEMICAL BEHAVIOUR OF IRON IN STRONGLY ALKALINE SOLUTIONS.

1. Corrosion of Iron in Caustic Alkali.

The corrosion of iron in strong solutions of sodium and potassium hydroxide resembles that in strong acids in that it results in the evolution of free hydrogen and in the formation of a non-protective corrosion product, and further in that it is virtually independent of the presence of dissolved oxygen. The overall reaction, namely,

$$3\ Fe + 4\ H_2O = Fe_3O_4 + 4\ H_2$$

is similar to the diredt oxidation of red-hot iron by the reduction of steam, but the mechanism of the process in alkaline solutions is naturally quite different.

At normal temperatures and in sodium hydroxide solutions having concentrations between 0.01 mols/litre and 2 mols/litre approximately, iron (and steel) remains virtually immune from attack. The passivity of the metal within this range of alkali concentration is to be attributed to the formation of a compact, protective film of oxide on its surface. The film, on separation from the surface is found to have a composition corresponding to ferrous oxide, but "in situ" it is probable that the linkages existing between the film and the metal lattice are of a higher order. In any event the protective nature of the film is maintained by the extremely low solubility of the basic ferrous hydroxide in the alkali; according to a recent determination the solubility product $[Fe^{\cdot\cdot}] \cdot [OH^{1}]^{2}$ is of the order 10^{-15}. The inertness of the metal under these circumstances is reflected in its noble potential with respect to hydrogen of + 0.1 to + 0.2 volts (45).

At high temperatures the film loses its protective character and corrosion of the metal surface proceeds at a rate which depends on the concentration of the alkali. In experiments carried out at 310°C, and using sodium hydroxide solutions at concentrations ranging from 0.025 to 1.25 mols/litre, Berl and van Taack (46) showed that the rate of corrosion of iron filings increased with the alkali concentration, becoming very marked at concentrations above about 0.5 mols/litre. The addition of a small quantity of sodium sulphate (0.1 mols/litre) restricted the corrosion rate to a low value throughout the range; probably by virtue of its oxidising nature the sulphate maintains the oxide film in a state of repair. It does not appear to be effective at higher concentrations of the alkali (cf p.153)

When the concentration of sodium hydroxide exceeds about 2 mols/litre iron is no longer immune from attack even at room temperatures. The loss of passivity is reflected in the rapid fall in the potential of the metal as the concentration of the hydroxide is raised above this figure to a value (- 0.86 volts hydrogen in a solution of concentration 15.7 mols/litre), which permits the evolution of hydrogen to take place (45). The reason for the activity exhibited by the metal surface under these conditions is to be found in the fact that in strong alkali the oxide film becomes partially soluble and thus loses its protective character. The process of solution of the ferrous oxide (or hydroxide) is not simply physical, but is accompanied by the formation of anionic complexes. Whilst normally ferrous hydroxide behaves as a base, ionizing in such a way as to give rise to hydroxyl ion,

$$Fe(OH)_2 \rightleftharpoons Fe^{\cdot\cdot} + 2\,OH'$$

in solutions of extreme alkalinity it reveals its amphoteric character by ionizing so as to give rise to hydrion,

$$Fe(OH)_2 \rightleftharpoons 2\,H^{\cdot} + FeO_2'' ,$$

with formation of the complex salt, sodium, hypoferrite, or sodium ferr~~i~~oate, Na_2FeO_2. Under similar conditions ferric ion produced by the oxidation of ferrous ion in solution gives rise to sodium ferrite, formally, $2Fe(OH)_3 \rightleftharpoons 2H^{\cdot} + Fe_2O_4'' + 2\,H_2O$

The solid reaction product resulting from the attack of iron in alkaline solutions is invariably a ferroso-ferric oxide, which may not, however, correspond to the formula Fe_3O_4, an excess of FeO sometimes being present (47). The reaction mechanism is not certainly known, but on the basis of a careful and extensive examination of the process as it occurs in pure air-free water. Schikorr (48)(49). concluded that in the presence of iron ferrous oxide is oxidised to the intermediate compound by the reduction of water. He suggests the reaction scheme

(1) $3\,Fe = 3\,Fe^{\cdot\cdot} + 6\,E$

(2) $2\,Fe^{\cdot\cdot} = 2\,Fe^{\cdot\cdot\cdot} + 2E$

(3) $8\,H_2O = 8\,H^{\cdot} + 8\,OH^{\prime}$

(4) $8\,H^{\cdot} + 8E = 4\,H_2$

(5) $Fe^{\cdot\cdot} + 2\,Fe^{\cdot\cdot\cdot} + 8\,OH^{\prime} = Fe_3O_4 + 4\,H_2O$

giving as a total

$$3\,Fe + 4\,H_2O = Fe_3O_4 + 4\,H_2.$$

It is not immediately clear why, even in the presence of oxygen, the oxidation process

$$Fe^{\cdot\cdot} = Fe^{\cdot\cdot\cdot} + E$$

does not go to completion,[x] but an explanation is provided

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[x] The proportion of two-thirds as envisaged in the scheme of Schikorr is of course purely formal, and in no sense exact.

in the work of Krause (50). In a solution of pH greater than 5.2 colloidal ferric hydroxide carries a negative charge due to the adsorption of hydroxyl ions. Colloidal ferrous hydroxide on the other hand carries a positive charge due to adsorbed hydrions, the iso-electric point lying at a pH in excess of 11.5, the limit of Krause's measurements. Coalescence of the oppositely charged particles therefore takes place to form particles of a ferroso-ferric compound whose composition naturally depends on the charges carried by the two hydroxides. Symbolically the colloidal reaction may be written as an acid-base reaction,

$$Fe(OH)_2 + Fe_2O_3 . H_2O = Fe_3O_4 + 2H_2O.$$

The above discussion is primarily intended to apply to the reaction as it occurs in pure water saturated with ferrous hydroxide, but no particular difficulties appear to arise in applying the arguments to its occurrence in solutions of a strong alkali.

2. Anodic Current - Potential Behaviour.

When anodised in strongly alkaline solutions of sodium hydroxide, iron (or mild steel) exhibits certain peculiarities in its potential behaviour. The matter has formed the subject of a very thorough investigation by Grube and Gmelin (51). Working with 40 per cent.

solutions, they obtained evidence that anodic dissolution takes place in two distinct potential stages. At low current densities electrolysis proceeds at a potential of about - 0.85 volts on the hydrogen scale, whereas at higher values it changes suddenly to + 0.65 volts, the potential corresponding to oxygen evolution. The critical current density increases rapidly with temperature, reaching a maximum at about 70°C. Evidence was adduced by Grube and Gmelin that the lower (more negative) potential stage is associated with the ferrous complex sodium salt, sodium ferroate having the probable composition $(Na_2)^{''}(FeO_2)^{''}$ x while the higher is associated with the formation of hexavalent iron ion, giving rise to sodium ferrate of the composition $(Na_2)^{''}(FeO_4)^{''}$. The experiments not did reveal the formation of sodium ferrite, $(Na_2)^{\cdot\cdot}(Fe_2O_4)^{''}$, at a separate potential stage, but it is regarded as probable that this compound was indeed formed, though perhaps only in small quantities. At the potential stage resulting in the formation of the ferroate the electrolyte assumed the greenish hue characteristic of ferrous ion, while the electrode surface remained clear and bright.

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x Carius (Ref.(16) p. 76) suggests the alternative formulation
$(Na)^{\cdot}(FeO)(OH)^{'}$

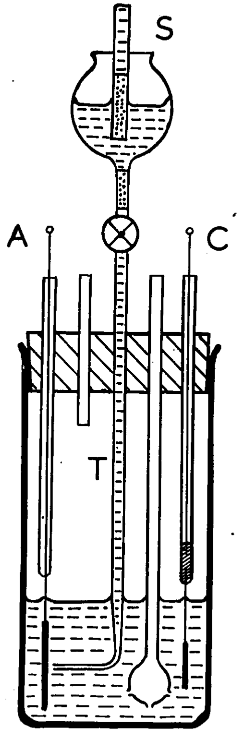

Fig. 8.

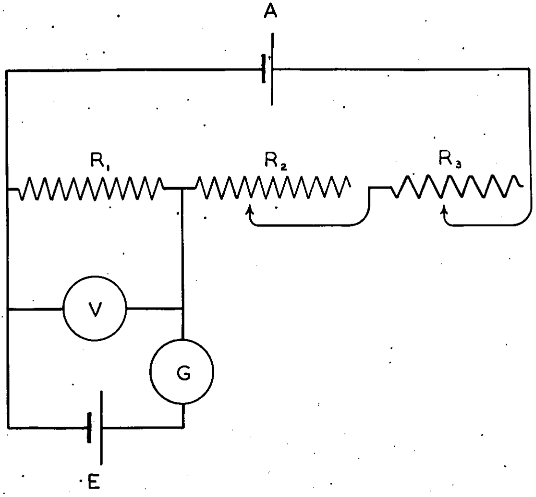

Fig. 9.

The hexavalent compound (ferrate) dissolved to form a solution of a reddish hue, and its formation was accompanied by the evolution of oxygen, and the appearance of black oxide as a coating on the anode surface and as black flecks in the solution.

A few exploratory experiments on similar lines have been carried out by the present writer (52) with special reference to the influence of the molality of the solution. The apparatus in which the experiments were carried out is illustrated in Fig. 8 . The solutions of sodium hydroxide were contained in an electrolysing cell of resistance glass, which had been previously well seasoned in strong caustic soda, and into which dipped the anode A of mild steel (0.05 per cent carbon) and the cathode C of platinum foil. A tubulus T of the form shown was pressed firmly against the surface of the anode, and made electrolytic connedtion through a salt bridge inserted at S with a saturated calomel half-cell. Before beginning an experiment the lye was swept free of dissolved oxygen by passing hydrogen into the solution through the gas stirrer shown; the gas left the cell through a mercury trap which is not shown. During the experiments, however, the solution was unstirred.

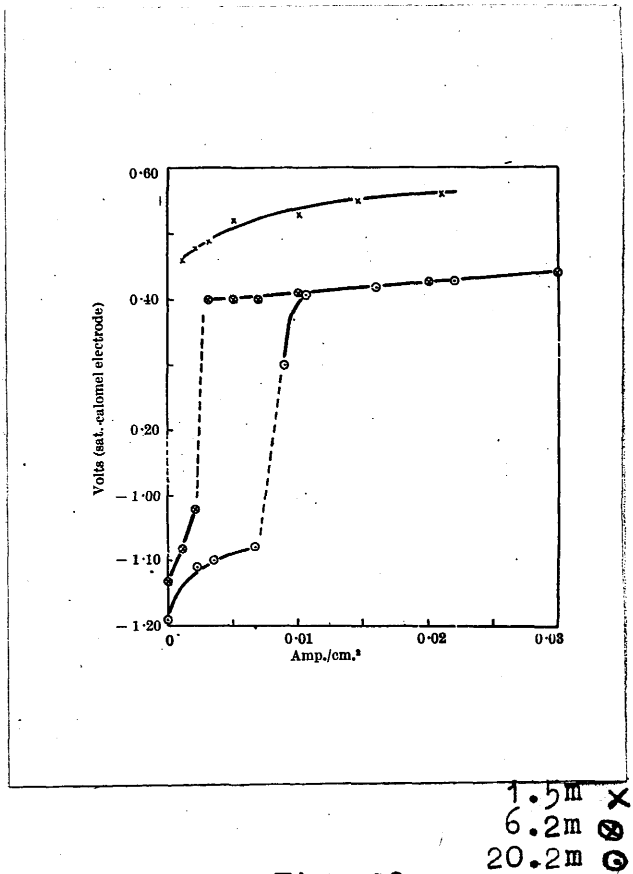
0·60
0·40
0·20
− 1·00
− 1·10
− 1·20
Volts (sat. calomel electrode)
0
0·01
0·02
0·03
Amp./cm.²
1.5m ×
6.2m ⊗
20.2m ⊙

Fig. 10.

The cell was polarised by means of a 12 volt battery, the circuit including a variable resistance and a milliammeter reading to 500 mA. The potential of the anode against the calomel electrode was measured by means of a voltmeter embodied in the modified Poggendorf - Hildebrand circuit shown in Fig. 9 . In this system the point of division of the potentiometer is altered by adjusting the coarse resistance R_2 and the fine resistance R_3 until the galvanometer G reads zero. The voltmeter V then reads the no-current voltage (e.m.f.) of the anode-calomel electrode cell E; the current to actuate the voltmeter arises, of course, from the potentiometer cell A.

The experiments were carried out with the electrolysing cell immersed in a water bath thermostatted at 80°C. Pure solutions of sodium hydroxide were used, being prepared from an analytical grade product by the methods described in Appendix II. The anode of area 9,68 cm^2 was metallographically polished and given a medium etch in a two per cent solution of nital.

Three sets of results are represented in Fig 10 , in which the anode potential is plotted to a base of apparent current density. In the case of the 1.5 molal solution the lower potential stage was non-existent; it appeared, however, with the 6.2

molal solution, and to a rather greater extent with the 20.2 molal solution. A certain amount of instability of the lower potential stage was observed near the critical current density, and more especially in experiments carried out with 6.2 molal solutions. Further work indicated that this effect was attributable to the influence of time, in that the electrode tended to become passive at a current density considerably below the supposed critical value, provided sufficient time was allowed. For example, in a 12.9 molal solution in which the apparent critical current density was about 0.003 amp/cm^2 the electrode became passive after 10 - 12 minutes at 0.002 amp/cm^2 and after 40 minutes at 0.001 amp/cm^2. In this respect the present results do not agree well with those of Grube and Gmelin, who found that the potential corresponding to a current density just less than the critical remained virtually steady over a period of hours, though it is to be remembered that in their experiments the solutions were vigorously stirred.

The existence and quasi-stability of the lower potential stage is most probably to be attributed to the slow formation of a non-conducting film of oxide on the anode surface with a consequent increase in true current density. The process is a slow one because of the appreciable solubility ~~in~~ the of oxides of iron in the strong alkali. This explanation coincides with the views of W.J. Müller, Evans and others[x], but another explanation suggested itself to the writer when the work was first published and perhaps still merits consideration.

As has already been mentioned, and like Grübe and Gmelin, the writer subjected the anode in these tests to a preliminary cathodic polarisation. Now experiments which will be described later have shown that hydrogen is occluded by iron when the latter is cathodized in strongly alkaline solutions in quantities which increase rapidly with the strength of the solution. It appears possible therefore, as has been pointed out by Carius (45) in a different connection, that the reducing action of the occluded gas will effectively prevent the formation of an adherent oxide film and consequent onset of passivity as long as it can diffuse to the surface of the metal in sufficient quantities. Some support is lent to this argument by the fact that the potentials at the lower stage differ by only a few centivolts

[x] As described, for example, in the article by R. Kremann, Handbuch der Experimentalphysik (ed. Wien-Harms), Leipzig (1933), vol. XII (II) Ch. VI.

from the reversible hydrogen potential in the same solution as estimated from activity data [x]. As an example, the potential of the anode in a 6.2 molal solution at zero current was found to be - 1.13 volts while the estimated corresponding potential of the hydrogen electrode is - 1.15 volts. As the current density increased the anode potential became rather more positive; since iron occluding hydrogen can scarcely be expected to function as an efficient hydrogen electrode under anode polarisation the observation is rather what one might expect. Another observation, apparently favouring the present point of view, was made in an experiment employing a 20.2 molal solution in which the anode, having previously undergone cathodic polarisation, was subjected to a current density of 0.03 amp/cm^2 for 30 seconds. This current density was sufficiently high to ensure passivitation by the formation of an oxide film. On reducing the

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[x] The activity data were obtained from the accurate work of Akerlöf and Kegeles (J. . Amer. Chem. Soc. v. 62(1940), p. 620) and substituted in the equation

$$E_{H_2} = E_{cal} - \frac{RT}{F} \ln \frac{Kw}{a_{OH'}},$$

where $\underline{E_{cal}}$ is the potential of the saturated calomel electrode, $\underline{Kw}$ the dissociation constant of water at the relevant temperature, and $\underline{a_{OH'}}$ the activity of hydroxyl ion, assumed in the present case to be equal to the mean activity of the electrolyte. The accuracy of the estimation is probably sufficiently good for present purposes.

current to zero the electrode assumed, within the course of a few seconds, a potential of approximately -0.66 volts. It seemed unlikely to the writer at the time that this rapid fall could be attributed solely to a solution of the oxide film by the alkali. Obviously however, the matter requires a much fuller investigation than the writer has been able to afford it.

Though perhaps of interest in their own right, the results of the above experiments do not appear to shed much light on the problem of intercrystalline failure. A careful examination of the anodes used showed no evidence of intercrystalline attack by the alkali, either at the lower potential stage associated with the formation of ferroate[x] or at the higher associated with the formation of ferrate. The results were not, therefore, regarded as sufficiently encouraging to justify the continuation of these experiments beyond the exploratory stage.

[x] It is perhaps worth noting that the formation of sodium ferroate is not necessarily associated with an oxide-free metal surface, as appears to be implied by Grube and Gmelin, nor does ferrate appear to result from the normal corrosion process.

3. CATHODIC CURRENT - POTENTIAL BEHAVIOUR.

There is considerable evidence that the overpotential of hydrogen[x] evolution at different cathodes is closely bound up with the ability of the electrode surface to adsorb hydrogen. Now it is this preliminary adsorption of the gas which largely conditions its subsequent absorption into the metal lattice; it therefore seems of interest, in view of the results to be described in Part V, to determine whether the overpotential of the same metal in different solutions bears any relationship to the degree of absorption (as indicated by mechanical tests in the present case) which occurs. Several workers have carried out investigations with this idea in mind, special attention being paid to the influence of the "poisons" mentioned in Part II, Section 6 . The work to be discussed here, however, is concerned mainly with variations

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[x] A general treatment of hydrogen overpotential can be found in almost any textbook on electrochemistry; the writer has had recourse mainly to:
S. Glasstone, "Electrochemistry of Solutions", London (1945) Ch. XVII;
N.K. Adams, "The Physics and Chemistry of Surfaces", London (1941) Ch. VIII;
J.A.V. Butler, "Electrocapillarity," London (1940), Ch. VI;
as well as to original sources.

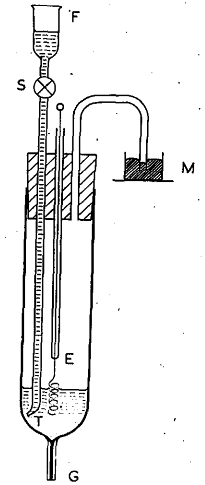
F
S
M
E
T
G

Fig. 11.

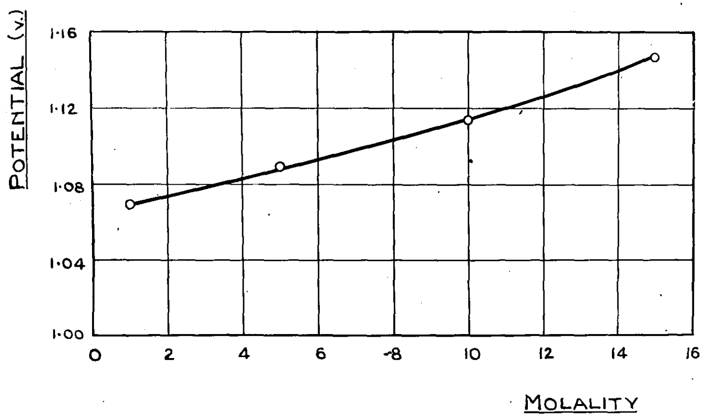
POTENTIAL (v.)
1·16
1·12
1·08
1·04
1·00
0
2
4
6
8
10
12
14
16
MOLALITY

Fig. 12.

in overpotential attributable to variations in concentration of pure solutions, but an opportunity to discuss the work of previous investigators will arise later.

(a) Potential of the Electrode. Pt(H_2) : OH^1

The hydrogen overpotential of a given cathode at a given current density is defined as its potential measured against a reversible hydrogen electrode in the same solution. In the experiments presently to be described (as in many others), it has been found more practicable to measure the potential of the cathode against a saturated calomel half-cell, and it is necessary on this account to calibrate the results by measuring the potential of the saturated calomel electrode against the hydrogen electrode in the corresponding solutions. The method of carrying out this calibration is described below.

Apparatus and Technique. The measurements were carried out in a well-seasoned gas cell of the form shown in Fig. 11 . Hydrogen entered the cell through a capillary at the bottom and passed out through a mercury trap, as shown. Connection was made to the calomel electrode through a tubulus, and a salt bridge containing a saturated solution of potassium chloride. The stopcock of the tubulus was ungreased and kept closed during the measurements, the liquid junction between the hydroxide and chloride being formed round the barrel. The hydrogen electrode consisted of a spiral of platinum wire coated with platinum black by electro deposition from a 5 per cent solution of platinum chloride and was calibrated before use in M/10 potassium hydrogen phthalate. The potential of the cell was measured to the nearest millivolt by means of a Gambrell dial - type potentiometer. The solutions were prepared from analytical grade sodium hydroxide by the methods described in Appendix II, and the titre found by means of a density method.

In carrying out the measurements the apparatus was set up with hydrogen passing through the solution in a slow but steady stream and the potential of the cell noted at regular intervals until equilibrium was attained.[x] In the

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[x] It is interesting to note that the attainment of equilibrium may be followed by the progressive decrease in potential fluctuations as the depth of immersion of the electrode is varied.

solutions of higher molality equilibrium was only reached after the lapse of several hours, and in a 19 molal solution the potential showed no evidence of settling down even after a period of 48 hours. The value of the potential at this molality used in the calibration of the overpotential measurements had therefore to be obtained by extrapolation, and must be accepted with reserve.

The results, corrected to 10°C.[x] are plotted in Fig. 12 . They appear to be quite self-consistent and in view of the care taken to ensure that equilibrium was attained may be accepted as a reasonable basis for the calibration of the overpotential data.

(b) Overpotential of Mild Steel in Sodium Hydroxide Solutions.

Successful overvoltage measurements are notoriously difficult to carry out, for the values obtained are very largely dependent on factors

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[x] The experiments were carried out in air, since the controlling system of the thermostatic bath available was found seriously to affect the measurement of cell potentials; all attempts to eliminate this trouble were quite unsuccessful. The corrections necessary (applied through the medium of the Nernst equation) were not unduly large however, and the slight errors possibly incurred may be safely ignored.

which are not readily susceptible to close control; for example, the condition of the electrode surface and the degree of concentration polarisation may both vary within wide limits despite the upmost care, and both may actually change during the course of a single experiment. If the measurements are to be carried out at low current densities the electrolyte must be rigorously freed from dissolved oxygen if consistent results are to be obtained, while at high current densities, measurements are affected by the potential drop in the electrolyte between the cathode and the tip of the tubulus, and by the possible existence of a "transfer resistance" at the metal-electrolyte interface. Provided sufficient care is exercised in ensuring the removal of dissolved oxygen, it appears to be borne out by previous work that more consistant measurements may be obtained by the use of low current densities (less than about 0.001A/cm^2) [x]. This was the method adopted by the writer.

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[x] Some workers at high current densities have employed an interrupter circuit. On account of the extremely rapid fall in overpotential when the polarising current ceases to flow, their results are of questionable significance. The introduction of a valve circuit by Hickling Salt (cf. Ref. 55), however, introduces new possibilities in this direction.

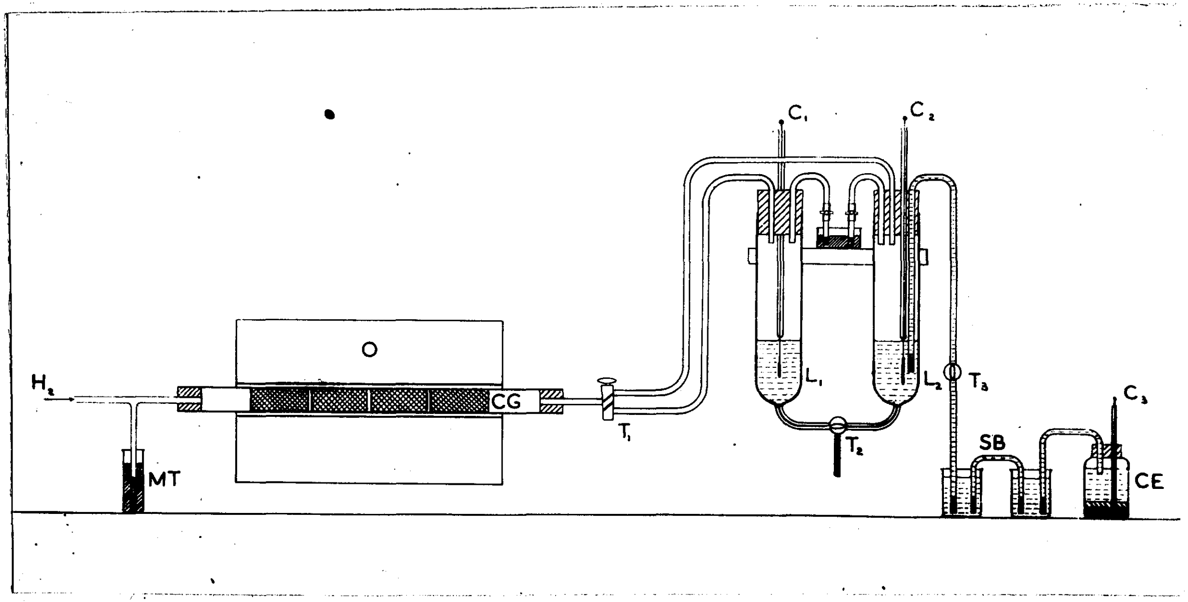

Fig. 13.

APPARATUS AND METHOD.

The apparatus employed in the experiments to be described here is shown diagrammatically in Fig. 13 . The well-seasoned electrolysing cell consisted of two branches L_1 and L_2, containing the anode and cathode respectively, and connected by a capillary tube. This arrangement minimised the possibility of the oxygen formed at the anode diffusing into the cathode compartment. Each limb of the cell was provided with a mercury gas trap and, in addition, the stopper of the cathode compartment carried a tubulus leading through a salt bridge S to a calomel electrode CE.

The cathode was cut from mild steel sheet (0.05 per cent carbon) and previous to each experiment was abraded on emery paper of grade 2/0; the anode was of smooth platinum foil.

Oxygen - free hydrogen was supplied to the apparatus by passing gas from a cylinder over copper gauze CG heated to redness in the Oven O. The gas line also included a safety trap MT and a two-way tap T_1.

The cell was polarised by means of a 24 volt battery, the circuit including a microammeter of four ranges (0 - 50 μA, 0 - 250 μA, 0 - 1 mA and 0 - 10 mA) and a bank of resistors varying from 3000 to 500,000 ohms approximately. The use of a high applied potential in conjunction with a heavy resistance ensures that current flowing will remain virtually constant, independent of any changes in the internal resistance or back e.m.f. of cell which may occur during the course of the experiment. The potential of the cell cathode - calomel electrode was measured to the nearest millivolt by means of a Gambrell dial-type potentiometer embodying a spot-projection galvanometer.

The solutions of analytical grade sodium hydroxide were prepared and standardised by the methods outlined in Appendix II.

The experiments were carried out at a room temperature of 10° C.

The procedure adopted in carrying out an experiment was as follows. Oxygen- free hydrogen was first admitted into the cathode compartment L_2 by properly adjusting the tap T_1 ; the mercury trap of this compartment was closed, and hence a stream of gas flowed through the capillary into the anode compartment, The solution was then poured into this compartment, where it was maintained by the pressure of the gas bubbling through it, and the stopper of the compartment replaced with the mercury trap open. The solution and cell were continuously swept with hydrogen for a period of 24 hours, to ensure complete removal of oxygen. When this period of time had elapsed the external polarising circuit was closed, and the external resistance adjusted so that a current of the order of 1 mA / cm^2 would flow on completion on the internal circuit. The solution was then allowed to enter the compartment L_2. This operation was carried out by first closing the mercury trap of the anode compartment and opening that of the cathode compartment. Tap T_1 was then adjusted so that gas flowed into L_1 thus forcing the solution through the connecting capillary into L_2. When the height of the solution in each compartment was approximately equal, the flow of gas was interrupted and the mercury trap of L_1 opened. Since the external circuit had been previously closed, current flowed immediately contact was made between the solution and the cathode, thus preventing any contamination of the solution with iron ion.

Electrolytic connection was then made to the calomel electrode by applying gentle suction to the tubulus through a safety trap and opening the tap T_3. When the tubulus was completely filled with solution the tap was closed and the end of the tubulus plugged with tightly rolled filter paper.

Polarisation of the cathode was continued at a current density of about 1 mA/cm^2 for an hour in an effort to clear up any residual traces of oxygen by a process of electrochemical reduction.

In carrying out the measurements the current was first reduced to its initial value, and potential readings taken at gradually increasing current densities. Despite the rigorous attempts which were made to remove dissolved oxygen, potential readings at extremely low current densities (less than 1 $\mu A/cm^2$) showed evidence of traces still being present. The current density at which the gas no longer influenced the potential was easily recognized, however, being accompanied by an abrupt rise in potential. Once equilibrium had been attained at this current density upward readings were continued, allowing the electrode time (a few minutes) to come to equilibrium at each stage.

Results. Experiments were carried out in 1, 5, 10, 15 and 19 molal solutions, the precise titre in each case being given in Table IX, and in 10 molal solutions containing 5 per cent tannin and

TABLE IX.

Titre of Sodium Hydroxide Solutions.

Nominal.	Actual.
1 m	0.997 m.
5 m	5.00 m.
10 m	10.00 m.
15 m	15.00 m.
19 m	18.97 m.

0.38 per cent silica respectively. The precise amount of tannin was readily determined by direct weighing ; the silica content was obtained by dissolving as much as possible of a pure sodium silicate powder (apparently the only form of high grade product available) and determining the silica content of the solution by the usual gravimetric method.

The reproducibility of the results in the worst case was about 0.01 volts, as is indicated in Table X.

TABLE X

Reproducibility of Overpotential Measurements.

19 molal, 10°C.

Measured Current. (μA)	Potential (Volts).		
	1st run.	2nd run.	Difference.
12.7	1.222	1.217	0.005
37.3.	1.242	1.243	0.001
182	1.280	1.288	0.008
402	1.302	1.311	0.009
1400	1.345	1.356	0.011
2900	1.381	1.392	0.011
		Average.	0.007

15 molal, 10°C.

Measured Current. (μA)	1st run.	2nd run.	Difference.
11.8	1.191	1.195	0.004
34.1	1.224	1.222	0.002
167	1.272	1.268	0.004
368	1.295	1.290	0.005
1340	1.337	1.335	0.002
3000	1.368	1.370	0.002
		Average.	0.003

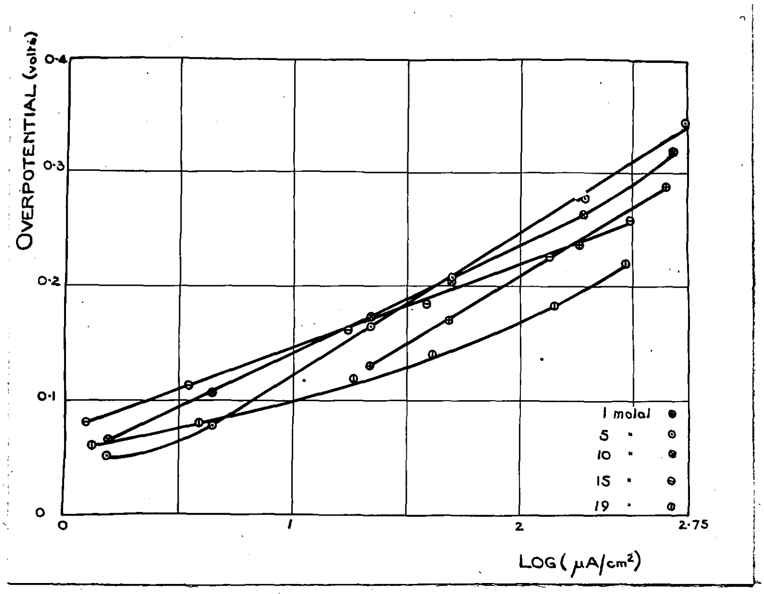
OVERPOTENTIAL (volts)
0·4
0·3
0·2
0·1
0
0
1
2
2·75
LOG (μA/cm²)
1 molal ●
5 " ⊙
10 " ⊗
15 " ⊖
19 " ⊕

Fig. 14.

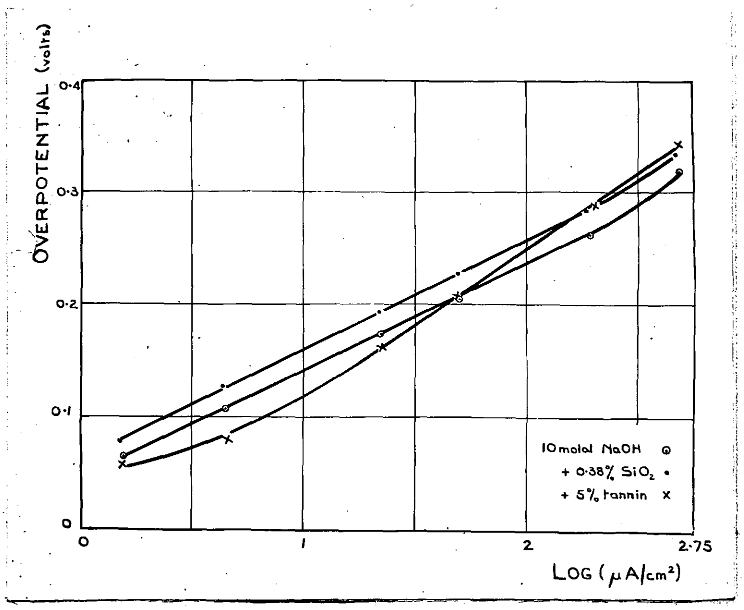
OVERPOTENTIAL (volts)
0·4
0·3
0·2
0·1
0
0
1
2
2·75
LOG (μA/cm²)
10 molal NaOH ⊙
+ 0·38% SiO₂ •
+ 5% tannin ×

Fig. 15.

When the rather extreme conditions under which the tests quoted were carried out are taken into consideration the agreement would appear to be reasonably good.

The results accruing from the measurements, as calibrated against the curve of Fig. 12., are plotted in Figs. 14 and 15. Considering the results obtained in the pure solutions first, it will be observed that they follow the theoretical linear law (pp.80ff.) fairly well, though there is some slight curvature, especially in the case of the 19 molal solution. Though as far as the absolute value of the overpotential is concerned, there is no obvious consistent variation from solution to solution, the *slopes* of the lines do appear to exhibit a definite trend, the theoretical significance of which will be discussed later. Turning to the results quoted in Fig. 15 it will be observed that the presence of silica increases the overpotential by an amount (about 0.02 volts) which remains sensibly constant over the whole range of current densities measured, and in consequence does not materially alter the slop of the line. The addition of tannin, on the other hand, results in a quite marked increase in slope. The significance of these results is best discussed in relation to previous measurements of this type and will be postponed to p.89.

Theories of Hydrogen Overpotential Measurements.

Before entering upon a discussion of the results described above in the light of the theoretical interpretation to be placed upon hydrogen overpotential measurements, it is convenient to insert here a brief discussion of the relative merits (from the present point of view) of the various theories which have been from time to time advanced.

The electrode process occurring at a cathode at which hydrogen is being evolved, namely

$$2H^{\cdot} + 2e = H_2$$

is generally regarded as taking place in two distinct stages according to the scheme.[x]

(1) $2H^{\cdot} + 2e = 2H.$

(2) $2H = H_2$

In his pioneer work on the subject, Tafel regarded stage (2), the combination of hydrogen atoms to form molecules, as controlling the reaction, and deduced a relationship of the form,

$$E_{ov} = a + b . \ln i \qquad (1)$$

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[x] Alternative Mechanisms are suggested by Gatty and Spooner, "Electrode Potential Behaviour of Corroding Metals in Aqueous Solutions," Oxford (1938), App. III.

where E_{ov} is the overpotential, a and b constants and i the current density. The factor b was deduced to have the value $\frac{RT}{2\mathcal{F}}$, where $\mathcal{F}$ is the faraday, and on this basis is therefore a parameter dependent only on the temperature. Almost all overpotential measurements do in fact follow a law of type (1) and many show a value of b approximating closely to the theoretical. There are cases however where variations are found in the value of b, and for those the theory in its unmodified form is unable to account.

Many workers regard the first stage of the above reaction as being the controlling one. Theories based on this view lead to an expression identical with the Tafel relationship (1), and, in common with Tafel's theory, cannot be made easily to account for values of b differing from the theoretical. Gurney and Fowler (53) adopted a quantum-mechanical approach, and found a value of b equal to $\frac{RT}{\alpha\mathcal{F}}$ where α is an inderminate constant arbitrarily put equal to 2 to give the Tafel relationship. These workers regard the discharge of hydrion as taking place through the transference of an electron from a high energy level in the metal to a vacant energy level of the same height in the hydrated hydrion molecule. Erdey-Grúz and Volmer (54) on the other hand, while still regarding the first stage as controlling the reaction, suppose $H_3O^{\cdot}$ ions to be adsorbed on to the metal lattice and thence discharged. An indeterminate factor is again obtained in the expression for b. These theories, and others of similar type appear to offer little help towards the interpretation of the present results, and they will not therefore be discussed further here.

Recently a modified version of Tafel's theory has been proposed by Hickling and Salt (55) in which a semi-theoretical basis is given to b, and which supplies a quite reasonable explanation of the variations which are found to occur in it. As has already been pointed out on p.69 , the present investigation is largely concerned with the possibility of establishing a relationship between the absorption of hydrogen into the metal and the overpotential existing at its surface, and since Hickling and Salt's theory offers explicit guidance on this point it will be discussed here in some detail.

These workers assume initially the first stage of the reaction $2H^{\cdot} + 2\varepsilon = H_2$ namely

$$2H^{\cdot} + 2\varepsilon = 2H$$

occurs rapidly to give adsorbed hydrogen atoms on the electrode surface, which in turn, in order that the conditions of inter-phase equilibrium may be fulfilled, give rise to free hydrogen atoms;

$$M - H \rightleftharpoons M + H .$$

Removal of the adsorbed hydrogen atoms is supposed to be possible in three ways;

(a) By the reaction symbolised above progressing to the right.

(b) By combination of the adsorbed hydrogen atoms to form a molecule,

$$\begin{array}{l} M - H \\ M - H \end{array} = \begin{array}{l} M \\ M \end{array} + \begin{array}{c} H \\ | \\ H \end{array}$$

the metal then acting as a catalyst.

(c) At high current densities when the surface approaches saturation by discharge of hydrion on adsorbed atoms,

$$M - H + H^{\bullet} + e = M + H_2$$

The potential of the electrode is regarded as being determined by the pressure of free atomic hydrogen at the electrode, which by the Nernst equation is

$$E_1 = E_1^{\circ} + \frac{RT}{\mathcal{F}} \ln \frac{a_{H^{\bullet}}}{P_H} \qquad (1)$$

where $\underline{E_1^{\circ}}$ is the standard potential of the atomic hydrogen electrode, $\underline{a_{H^{\bullet}}}$ the hydrion activity, and $\underline{P_H}$ the pressure of atomic hydrogen. Now the potential of a reversible hydrogen electrode in the same solution will be, at a pressure of 1 atmosphere of molecular hydrogen,

$$E_2 = E_2^{\circ} + \frac{RT}{\mathcal{F}} \ln a_{H^{\bullet}}$$

$$\doteq \frac{RT}{\mathcal{F}} \ln a_{H^{\bullet}} , \qquad (2)$$

the standard potential of the electrode being zero by definition. The overpotential $\underline{E_{ov}}$ of the first electrode is defined as the difference $E_2 - E_1$ and hence is given by

$$E_{ov} = -E_1 + \frac{RT}{\mathfrak{F}} \ln P_H \qquad (3)$$

At the low current densities with which the present work is concerned the reaction mechanism (b) is relevant. Thus let $\underline{x}$ gram atoms be adsorbed on each square centimetre of the electrode surface, and let $\underline{i}$ be the current density in amps/cm^2. The rate at which hydrogen atoms are adsorbed is equal to the rate of discharge hydrion, namely $i/\mathfrak{F}$ gm. atoms/cm^2/sec., and the rate at which hydrogen atoms are desorbed to form molecules is assumed to be given by the bimolecular law, i.e. k_1x^2 gm. atoms/cm^2/sec. When a stationary state is attained these rates are equal, and so

$$i/\mathfrak{F} = k_1x^2 \qquad (4)$$

Now let it be supposed that the surface concentration, $\underline{x}$, of hydrogen atoms is related to the pressure, $\underline{P_H}$ of the free atomic hydrogen in the vicinity of the electrode by the relationship

$$x = k_2 P_H^{1/n} \qquad (5)$$

This is the so-called "Freundlich" adsorption isotherm and is virtually an empirical law, though it may be given some semblance of a theoretical basis [x]

[x] See, for example, E.K. Rideal "Surface Chemistry," Cambridge, 1930. p. 184.

Substitution of (5) in (4) gives

$$P_H = \left\{ \frac{i}{\mathfrak{F} k_1 k_2^2} \right\}^{n/2} \qquad (6)$$

and substitution of this expression in the Nernst equation (3) results in the expression

$$E_{ov} = \left(-E_1^o - \frac{nRT}{2\mathfrak{F}} \ln \quad - \frac{nRT}{2\mathfrak{F}} \ln k_1 - \frac{nRT}{\mathfrak{F}} \ln k_2 \right) + \frac{nRT}{2\mathfrak{F}} \ln i \qquad (7)$$

or

$$E_{ov} = a + b \ln i . \qquad (7a)$$

This relationship is similar to that obtained on other premises, but has the advantage for present purposes that it introduces a factor <u>n</u> which is dependent on the adsorbing power of the electrode. It must not be assumed, however, that it is necessarily superior in every respect, and therefore a closer approximation to the truth than the others. Indeed, as has been pointed out by Butler (56), it is probable that no single mechanism can satisfactorily account for all overpotential phenomena. Butler considers that in the case of metals showing an affinity for hydrogen the process may well be controlled by the adsorption mechanism, while in the case of others (notably, of mercury) exhibiting no such affinity, the discharge of hydrion is the controlling factor. These remarks offer support to the outlook adopted here since iron (and mild steel) may be numbered among those metals which adsorb and dissolve hydrogen readily.

Discussion of Overpotential Results.

The values of a and b of equation (7a) as calculated from the curves of Figs 14 and 15 are quoted in Table XI . The values of a were computed on the basis of amps./cm.^{2} as the unit of current density. The variations in a do not readily admit of a theoretical interpretation on the basis of Hickling and Salt's theory (or, indeed on the basis of any other) in consequence of the indeterminancy of k_1 and k_2 ,and attention will be immediately turned to the constant b of the equation, merely noting that in view of the complication of the expression for a in equation (7) the apparently random distribution of the curves in Fig. 14 is not, perhaps, a matter for surprise.

TABLE XI.

Solution	a	b[x]	n
1 m NaOH	0.642	0.0508	4.17
5 m "	0.725	0.0564	4.62
10 m "	0.593	0.0416	3.42
15 m "	0.490	0.0316	2.60
19 m "	(0.390)[xx]	(0.0260)[xx]	(2.14)[xx]
10m NaOH + 0.38% SiO_2	0.749	0.0443	3.63
10m " + 5% tannin	0.632	0.0585	4.80

[x] Note that the logarithmic scales of the plotted curves are to the base 10; the b values given here correspond to the natural logarithms of the equation.

[xx] Mean slope of curve used as basis for these values.

It will be observed that the values of b, and the corresponding values of n, tend to decrease as the molality of the solution increases. The slightly higher value of b obtained in the case of the 5 m solution is not readily accounted for, but may perhaps be attributed to experimental variations. In terms of the overpotential theory of Hickling and Salt the interpretation to be placed upon the decrease in n will be clear : it is to be attributed to an increase in the adsorbing power of the surface as the molality of the sodium hydroxide solutions increases. This follows from the fact that, for a particular adsorbate, the exponent $\frac{1}{n}$ of the Freundlich isotherm characterises the adsorbing power of the adsorbent, in that the smaller the value of n the greater is its adsorbing power. It is worth noting, in this connexion, that the values of n to which the present measurements have given rise are in good agreement with those obtained (n equal to 2 - 5) for moderate adsorbents, into which group iron falls, by direct methods (55).

It is not easy to account, in general terms, for the improvement in the adsorbing properties of the surface accompanying an increase in the molality of the solutions; but the following remarks may be suggestive. It is widely held that the adsorbing properties of a surface are to be attributed to sub-microscopic irregularities, which impart to it a true area many times its apparent area. A detailed account of the way in which these irregularities give rise to the phenomenon of adsorption belongs to adsorption theory and need not concern us here.[x] It is sufficient to note that a surface possessing the necessary properties to function as an adsorbent may be produced by the reduction of certain metallic oxides, among which may be numbered the oxides of iron. Presumably the activity of the surface is due in such cases to the complicated "open" structure remaining after the removal of oxygen atoms from the lattice of the oxide. A structure of this type might be reasonably expected to result in the present from the reduction of the air-formed oxide film present on the electrode. The difficulty is, however, to account for the influence of increased electrolyte concentration. Possibly it may be due to an accompanying increase in the concentration of impurities, though this seems unlikely in view of the purity of the product used in preparing the solutions,

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[x] The writer has had recourse to the discussions given by:
N.K. Adam, "The Physics and Chemistry of Surfaces", London (1941) Chs. VII and VIII;
E.K. Rideal, "Surface Chemistry," Cambridge (1930) Ch. V.

and because, in any case, nearly all impurities which exert any effect at all, do so in such a way as to lower the adsorbing power of the surface. Another possible explanation is that because of its remarkable powers of seepage the strong caustic soda solutions are able to penetrate into minute cavities in the surface of the metal, reducing any oxide which exists there, and so further increasing the specific surface of the electrode; or it may be that because of the solubility of the oxides of iron in strong caustic lye the film of reduced oxide possesses a porous character which increases its efficiency as an adsorbent. The writer prefers this last explanation, but it must be admitted that the matter is rather obscure.

Attention must now be turned to the influence of tannin and silica. These two substances were selected for examination because of their apparent importance in relation to caustic cracking; there is considerable and convincing evidence that tannin may definitely inhibit the occurrence of cracking, and there is some, though less strong, evidence that silica tends to promote it. Here, however, discussion will be confined to their significance in relation to the adsorption and absorption of hydrogen. Silica increases the absolute value of the overpotential, without however, materially altering the value of $\underline{n}$. On the basis of the ideas adopted in this discussion, this presumably means that the discharge of hydrion to form molecular hydrogen is slowed down in some way other than by a decrease in the catalytic activity of the electrode surface, possibly by a blocking of the reaction stage

$$H^{\bullet} + e = H$$

In terms of the adsorption of hydrogen it appears that, at a given current density, the amount existing on the surface will be greater than in the pure solution, in virtue of the increase in the pressure of atomic hydrogen (equation (3)) which is unaccompanied by a decrease in the adsorbing power of the surface. As far as is revealed by mechanical tests, however, it does not appear that the presence of silica makes any material difference in the degree of adsorption and resultant absorption of the gas. Tannin, on the other hand, definitely decreases the adsorptive powers of the surface, as is indicated by the increase of <u>n</u>, and at higher current densities might be expected to give rise to a much increased overpotential. The explanation usually given in such cases, that the blocking of discharge is due to a preferential adsorption process which diminishes the area of the electrode available, is probably correct. Mechanical tests do show some evidence that the absorption of hydrogen is decreased by the presence of tannin.

Though perhaps somewhat irrelevant, it is convenient to note here some points concerning previous work on the relationship between hydrogen overpotential and hydrogen embrittlement. A short, but extremely careful investigation of the influence of arsenic and of hydrogen sulphide on the overpotential of steel wires in sulphuric acid has been made by Perminov (57). He finds that arsenic increases the overpotential, while hydrogen sulphide decreases it, and concludes that, since both substances are known to stimulate embrittlement, there is no relationship between the two phenomena. This statement would appear to be incorrect. The work of Bablik (p.27) indicates that, under conditions where no external potential is applied, hydrogen sulphide stimulates diffusion, whereas arsenic inhibits it. These facts are obviously in line with Perminov's results, for a decrease in overpotential implies an increase in adsorptive power [x] and vice versa. When an external potential is applied, which is sufficient to maintain a given current density despite potential changes occurring within the cell, the conditions affecting

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[x] The rate of production of hydrogen will also be increased in view of the larger effective potential differences of the local action cells.

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hydrogen adsorption are materially altered. Because [illegible] the enhanced adsorptive power of the surface is still maintained, hydrogen sulphide will continue to increase the rate of diffusion into the metal. Similarly the presence of arsenic may stimulate diffusion, but for different reasons. As is indicated by the adsorption equation (5)

$$x = k\, P_H^{1/n} ,$$

an increase in surface concentration may arise in two ways; by an increase in the adsorptive power of the surface reflected in a decrease in n, or by an increase in pressure of the free atomic hydrogen at the electrode surface. Under conditions of external polarisation, and in the presence of arsenic, it appears that a sufficiently high value of P_H is maintained (as indicated by the increased overpotential) to more than overcome the accompanying decrease in the adsorptive properties of the electrode surface. It may be emphasised, however, that the ideas advanced above undoubtedly represent a much simplified concept of potential in its relationship to hydrogen absorption, and that they do not always fit well with the results of other workers (58) (59) (32). But in the absence of a complete theory the writer feels that they present a useful basis for further research.

PART V.

HYDROGEN EMBRITTLEMENT OF MILD STEEL
IN SODIUM HYDROXIDE AND
AMMONIUM NITRATE SOLUTIONS.

V. HYDROGEN EMBRITTLEMENT OF MILD STEEL IN SODIUM HYDROXIDE AND AMMONIUM NITRATE SOLUTIONS.

The experiments of which an account is given in this part are perhaps best described as being of an exploratory nature. They arose through an attempt on the part of the writer to obtain definite evidence for or against the view that caustic cracking may be attributed to the influence of hydrogen dissolved in the metal - a matter over which there is much controversy. It may be said immediately that this aim has not been fully realised, but it is nevertheless felt that the results are of sufficient interest to justify a fairly full account of the manner in which they arose. A general discussion of their significance in relation to caustic cracking will be postponed to the concluding part of the work (p.159).

1. TESTS ON U-BEND SPECIMENS IN SODIUM HYDROXIDE SOLUTIONS.

In these tests 1 in. x $\frac{1}{8}$ in. mild steel strip was bent in the form of a U, using a 1 in. diameter rod as former, and stress applied by bolting the two arms together. The specimens, usually two or three at a time, were immersed in hot, concentrated sodium hydroxide solutions contained in a beaker of resistance glass. The concentration of the solutions was usually in the range 300 - 400 gm / litre and the temperature was maintained in the region of 100°C. The duration of the tests was up to 50 hours. In some cases an external potential was applied to the specimens (and in this, particularly, the present investigation differs from previous ones of this type), the polarising current being 200 mA on each specimen. It was not possible to prepare a microsection of each specimen tested, and in order to detect the presence of cracks, the remainder were slowly bent further by compressing the arms in a vice.

As regards failure, the investigation yielded no positive results for tests carries out under the following conditions.

(i) In concentrated solutions of commercial and pure sodium hydroxide, even though the concentration of some of the solutions neared saturation.

(ii) As in (i), but the specimens being polarised so as to be either cathodic or anodic.

(iii) As in (i) and (ii), with the addition of small quantities (ca. 1 - 5 per cent)of sodium silicate (p 150), ammonium nitrate (p 149) or of mercuric nitrate (p 28) to the hydroxide solutions.

Alternative forms of specimen were also tried, but without success; it may be noted that other investigators, e.g. Schroeder (60), have experienced similar difficulties.

In connexion with these tests there is, however, one rather curious point which is worth noting. In tests on unpolarised specimens it was observed that the solution assumed a greenish tinge, indicating the presence of the complex ion FeO_2'' (p. 59) and that the surface of the specimen became coated with a rather loose deposit of black oxide except in the region of the bend. Moreover, it was from this area that the evolution of hydrogen [x] mostly took place. Since the area of highest stress is normally anodic towards the remainder of the surface of a corroding metal, this distribution of attack by the alkali is rather surprising. It may possibly be due to the formation in the initial stages of the attack of an extremely compact and resistant oxide film.

2. U-BEND TESTS IN AMMONIUM NITRATE SOLUTIONS.

It has long been known that ammonium nitrate solutions (and to a lesser extent potassium, sodium and calcium nitrate solutions) are capable of producing intercrystalline cracking of stressed mild steel, which appears to be identical in every respect with that occurring in caustic soda. Smialowski (61) has shown

[x] Identified by the addition of sodium dichromate.

that hot 50% ammonium nitrate solutions will cause failure of steel wire at only 30% of the ultimate stress. Cracking of U-bend specimens in hot ammonium nitrate has been produced by Jones (62), who attributes the attack to the penetration of the metal by nitrogen or one of its oxides. Rosenhain and Hanson (63) have described the cracking of cold-drawn mild-steel tubing in a nitre bath at 300°C after 6 month's intermittent service. They regard failure as being due to temperature and stress effects alone. In all the above cases the cracks were typically intergranular.

Several experiments in ammonium nitrate solutions were carried out by the present writer, using U-bend specimens of the type described in the preceding section. The solutions were near-saturated at room temperature, and were maintained during the tests at a temperature of about 90°C.

(i) <u>Experiments on unpolarised specimens.</u>

After a few hours immersion in the hot solution the specimens were found to be severely and extensively cracked, the cracks extending in some cases almost right through the specimen. The surfaces of the specimens were covered with a thick coating of black oxide, while the solution was discoloured by particles of hydrated ferric oxide.

(ii) Anodically polarised specimens.

The specimens were immersed in the hot solutions as before, but rendered anodic by passing a current of about 50mA on each specimen. After several hours' polarisation they were removed and examined. They were found to be covered with a thick coating of oxide, and to have developed a number of shallow troughs at right angles to the direction of stress, but in no case were the specimens cracked. One interesting case arose, however, and merits consideration. An experiment was carried out overnight in which the specimen was polarised anodically in a cold solution of the nitrate. In the morning the current was found to have sunk to a value undetectable on the instrument, (less than 1 mA) due, probably, to polarisation. On removal the specimen was found to be covered with a slimy green coating of hydrated magnetite, and to be cracked, though not extensively. This observation is somewhat at variance with the unpublished results of Thornhill and of Wooster and Nockolds (64) who found cracking in ammonium nitrate solutions to be associated only with the black oxide formed at higher temperatures.

(iii) Cathodically polarised specimens.

In this group the same conditions obtained as in (ii), except that the specimens were cathodically

100x. Unetched.

Fig. 16.

500x. Unetched.

Fig. 17.

550x. Etched.

Fig. 18.

polarised. The current was again 50 mA on each specimen. After periods ranging from 1½ to 3 hours the specimens were invariably found to be cracked. The cracks appeared to be more numerous than was the case with unpolarised specimens, but were finer and did not penetrate so deeply into the metal. Since a slight coating of oxide was still formed on the metal, another series of experiments was carried out at a current (200 mA) sufficiently high to afford complete cathodic protection. Extensive cracking still occurred, but the cracks in this case were extremely fine and shallow, the deepest only penetrating to a depth of about 0.03 in. There was no evidence of corrosion at the surface of the specimens.

Typical micrographs of cracks produced in ammonium nitrate solutions are shown in Figs., 16, 17 and 18. Fig. 16 shows an unetched microsection, and it will be noticed that at least one branch crack of extreme fineness is associated with the large main crack. Such a structure is strongly reminiscent of caustic cracking as exemplified by the micrograph of Fig. 2 on p.5 . The fine crack in Fig. 16 is shown at a higher magnification in Fig. 17, and appears to be entirely free from corrosion products. The remarkable manner in which it surrounds an entire grain is noteworthy, and there is some suggestion that it is largely associated with the inclusion occupying the centre of the field. This micrograph may be compared with Fig. 4 on p 5 . The consistent intercrystalline nature of the attack will be clear from Fig. 18. This is a micrograph of one of the finer cracks, which is seen to have two branches. The main portion, extending from the top centre of the photograph to the bottom right corner, shows some evidence of containing corrosion products, but the secondary branch, which commences where the main crack first turns sharply right and runs about $1\frac{1}{4}$ in. on the photograph towards the bottom left corner [x] appears to be quite clear. Some other incipient branches from the main branch may also be observed, some of them of exceeding fineness, but it is noteworthy that there is little or no evidence of intergranular <u>pitting</u> such as one might expect were the corroding medium inherently intergranular in type. The micrograph also shows quite clearly the general structure of the steel. In view of its low

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[x] The course of this crack will appear more clearly if the micrograph is held some little distance from the eye.

carbon content (0.05 per cent) it is not surprising to find a considerable amount of intergranular pearlite separating the ferrite grains. The cracking does not appear to show any preference for these regions.

The evidence that hydrogen plays an essential part in the mechanism of cracking in ammonium nitrate solutions is quite convincing. Not only does cracking occur under circumstances in which the formation of hydrogen is possible [x] but the type of cracking is strongly reminiscent of that resulting, under certain circumstances, from the absorption of hydrogen by the metal. The type of crack formed under non-polarised conditions cannot be attributed solely to hydrogen attack, however. It appears, on comparison of this type with that formed when the specimens are cathodized that the absorbed hydrogen induces surface cracks into which the corroding medium penetrates. In this way the original cracks are widened and extended by the combined action of stress and corrosion. On account of the intergranular weakness which results from the presence of hydrogen in the metal the propagated

[x] In view of the strongly oxidising nature of the solution hydrogen is probably not evolved as a gas, but its formation in the atomic form as an intermediate stage is not excluded.

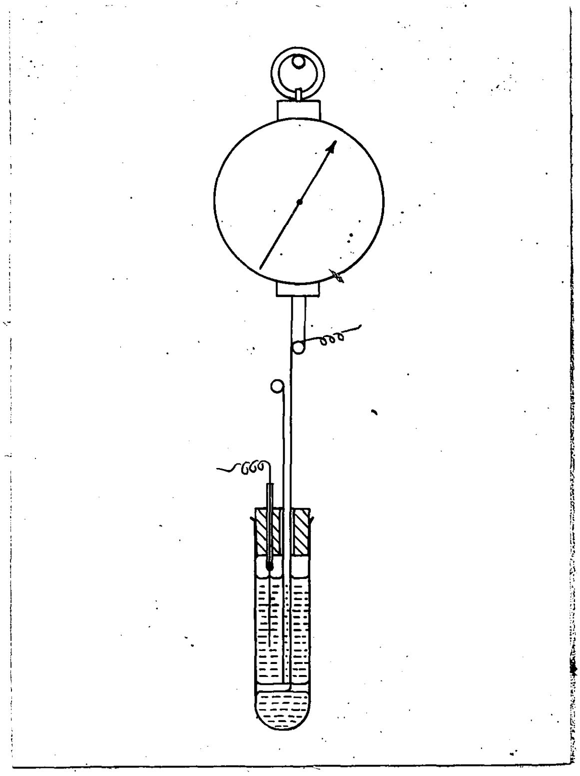

Fig. 19.

cracks will naturally follow an intergranular course.[x] A further occasion to discuss the significance of these results will arise in the final part of the work.

3. TESTS ON WIRE CATHODIZED IN CAUSTIC SODA SOLUTIONS.

In view of the results obtained by Alekseew and his co-workers, as described on p 27 , it was considered that results of some interest might be obtained by carrying out tests in which stressed wire was subjected to cathodic polarisation in various sodium hydroxide solutions.

The apparatus used in the experiments is shown in Fig. 19. The solutions were contained in a boiling tube of resistance glass to which a glass cross-piece was welded. The wire under test was attached to one end to the hook of a spring balance and passed round the cross-piece to a rigid support. The tension on the wire was adjusted by raising and lowering the spring balance by means of an adapted retort clamp. Polarisation was effected by means of the platinum electrode shown. The wire employed in the tests was of hard drawn steel, 0.008 in. in

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[x] The views of Jones (p 96) are that failure results from the diffusion of nitrogen or one of its oxides into the metal. There is no evidence that these gases are formed at the temperatures involved in the present experiments. Nor does nitrogen in steel lead to intergranular brittleness, though it may contribute to precipitation hardening.

diameter, and had a breaking load of 10.3 lb., corresponding to 2.05×10^5 lb/in^2. In the experiments carried out at 80°C the tube was immersed in a thermostatted water bath.

The results of the tests may be summarized briefly as follows:-

(a) Wire broken in air. Examination of the fracture under the microscope using a low-power objective showed it to be quite ductile and accompanied by definite necking.

(b) Wire polarised in a 33 per cent solution of pure sodium hydroxide at 80°C and at a current density of 0.35 A/in^2 ; load 9 lb. No break occurred after 3 hours, but the wire showed slight brittleness on bending between the fingers.

(c) Wire polarised in same solution as in (b) at room temperature at a current density of 0.18 A/in^2 ; load 9 lb. No break occurred overnight, though the wire was very definitely brittle.

(d) Wire polarised in 50 per cent solution of commercial grade sodium hydroxide at room temperature; current density 0.18 A/in^2 ; load 9.5 lb. Failure occurred after 30 minutes. Repeats of this experiment gave one other break (after 90 minutes), but in general spontaneous failure did not occur. The wire was, however, extremely brittle. Examination of the fractures showed them to be of a brittle character, being accompanied by no necking; the wires also showed a considerable amount of surface cracking.

(e) Wire polarised in 50 per cent pure sodium hydroxide with the addition of various "poisons"; current density 0.18 A/in^2 ; load 9.5 lb.

(i) Solution saturated with hydrogen sulphide. No spontaneous failure occurred though the wire was extremely brittle.

(ii) Solution saturated with sulphur dioxide. Results as in (i) above.

(iii) Solution saturated with mercuric nitrate. No results, but wire brittle.

(iv) Solution saturated with arsenious trioxide. No results, but wire brittle.

The results outlined above indicate that, while brittleness results from the cathodic polarisation of steel in sodium hydroxide solutions, it is not accompanied as a general rule by any lowering of the tensile strength. Especially with regard to the results of Group (e) the results are at variance with those of Alekseew, (p 27), for while there is some qualitative indication of increased brittleness resulting from the presence of poisons the experiments showed no reduction in the breaking stress. It is very possible that the contradiction is due to differences in the surface conditions of the wires employed in the two investigations. It is interesting to note that both spontaneous failures which were obtained in these experiments, and also the greater number of those induced by raising the load, were located where the wire bent round the cross-piece of the tube, while failures induced in air occurred on the straight portion. This behaviour suggests some sensitivity of the embrittled wire to asymmetric stress.

4. BEND TESTS.

The sensitivity towards bending shown by wires embrittled in the tests described above, led the writer to carry out some extremely simple experiments in which the ability of the metal to withstand bending was adopted as a criterion of brittleness.

Mild steel rods, 5 in. long and $\frac{1}{4}$ in in diameter, were immersed in the solutions at room temperature and polarised by means of a battery. Three specimens were examined in each experiment.

A definite correspondence was found to exist between the amount of bending which a rod could undergo without cracking and its previous treatment. Preliminary experiments showed that the time of polarisation beyond two or three hours did not substantially alter the results, nor did variation of the current in the range 12 - 250 mA/in^2. Specimens polarised anodically did not evince any evidence of preferential attack in pure or commercial grade sodium hydroxide solutions in the range 1 to 20 molal; it was possible to bend specimens so treated through 180° without cracking. On the other hand, cathodically polarised specimens showed striking evidence of brittleness, which increased markedly with the strength of solution employed. Specimens treated in 1 molal pure sodium hydroxide could be bent through 180° without cracking, those treated in 5 and 10 molal solutions cracked on bending through approximately 150°, while treatment in 15 and 20 molal solutions rendered the specimens incapable of standing much more than a right angle bend. An even greater loss of ductility resulted from polarisation in 15 and 20 molal solutions of commercial grade sodium hydroxide solutions, the specimens snapping off on bending through 45° - 80°. In view of this last result, and since silica is present in fair quantities in the commercial product, a solution of 15 molal pure sodium hydroxide to which was added sodium silicate in an amount corresponding to 1.2 gms silica per litre was made up. The embrittling capacity

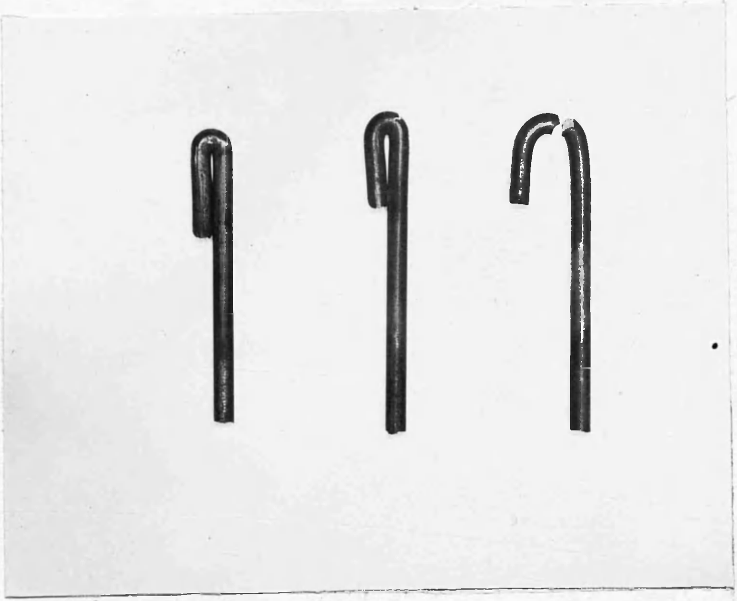


Fig. 20.

280x. Etched.

Fig. 21.

of this solution did not appear to differ greatly from that of the pure solution.

Typical examples of the behaviour of specimens in these tests are illustrated in Fig. 20. A micrograph of a typical crack is shown in Fig. 21 ; because of the distortion of the metal and the presence of numerous slag lines the course of the crack is doubtful, but it is probably transcrystalline.

5. TENSILE TESTS ON LARGE SPECIMENS.

In view of the qualitative results which have been described in preceding sections, it was considered that an attempt to obtain reliable quantitative data on hydrogen embrittlement in caustic soda solutions would be well worth while. The ordinary tensile test was employed, as being probably the least equivocal method of obtaining data in investigations of this type. Other workers, and notably Pfeil (28), have adopted a similar procedure.

Apparatus and Technique.

The tests were carried out in a 10 ton Avery tensile testing machine. The specimens, of annealed bright bar, were of conventional form, having a gauge length of 2 in. and a diameter over the test length of 0.550 in. The test lengths were emery finished. The solutions of caustic soda were contained in a glass tube, 2 in. in diameter, fitting over a rubber stopper through which the specimen passed, as shown in

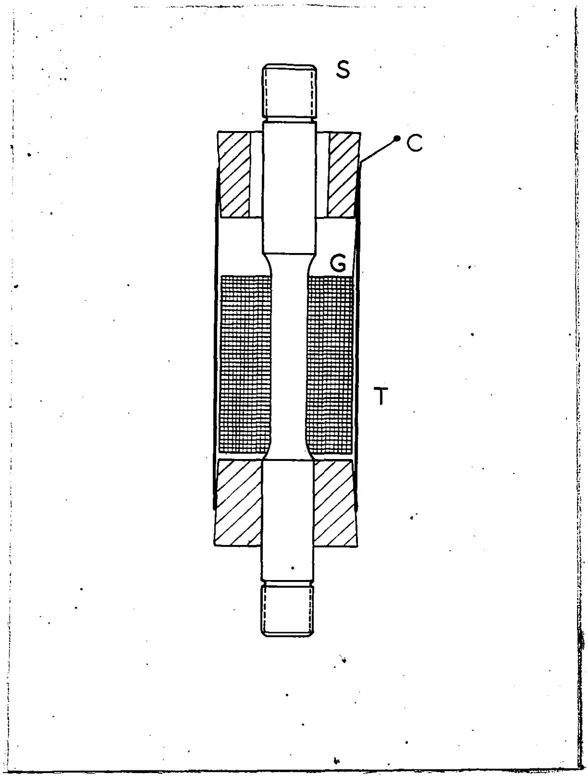


Fig. 22.

Fig. 22. A rubber stopper, having a hole rather larger than the outer diameter of the specimen, was inserted into the top of the tube and served to protect it from breakage when the specimen fractured. The anode consisted of a sheet of nickel gauze surrounding the specimen, and polarisation was effected by means of a 12 volt battery, the circuit including a 30 ohm variable resistance and an ammeter reading to 1.5 A.

In carrying out the tests, the assembly of Fig. 22. was mounted in the testing machine and the external circuit closed. The solution was then poured into the tube and the current adjusted to 1A. After 2½ hours' polarisation the specimen was loaded and broken in the usual way, polarisation being continued during this time. The tests were carried out at a room temperature of 18°C.

Results.

Details of the various tests carried out, together with their results are given in the accompanying Table XII. It will be noticed that the tests carry either the code letter A or B. This distinction is necessary because the specimens were machined from two different batches of material which, though they had ostensibly the same composition and received identical treatment throughout, unfortunately showed quite considerable differences in their

TABLE XII.

EMBRITTLEMENT TESTS ON TENSILE TEST SPECIMENS.

Gauge Length. 2 in.
Test Diameter. 0.550 in. Temperature 18° C.

Test No.	Test Conditions.	Ultimate Load lb.	Elong'n. %	Fraction of elong'n in air. %	Red'n in area %	Fraction of red'n in air. %
A.0.1.	In air	16000	35.5	100 (mean)	50.5	100 (mean)
A;0.2		16000	35.5		53.5	
A.1.1	40% Commercial NaOH. Pre-strained 10%	15900	30.0	84.5	26.4	50.8
A.1.2		15200	30.0	84.5	40.5	77.8
A.2.1	40% Commercial NaOH	-	-	-	-	- [x]
A.2.2.		-	31.5	88.7	40.5	77.8
A.2.3.		16000	33.5	94.4	43.5	83.6
A.2.4		15300	35.0	98.6	50.5	96.2
A.2.5		-	33.5	94.4	45.2	87.0
A.3.1	40% pure NaOH	15600	35	98.6	50.5	96.2
A.3.2.		15300	36	101.3	57.4	110.2
A.4.1	40% pure NaOH + 5% SiO_2	-	35.5	100	51.2	98.5
A.4.2		-	35.5	100	47.8	79.4

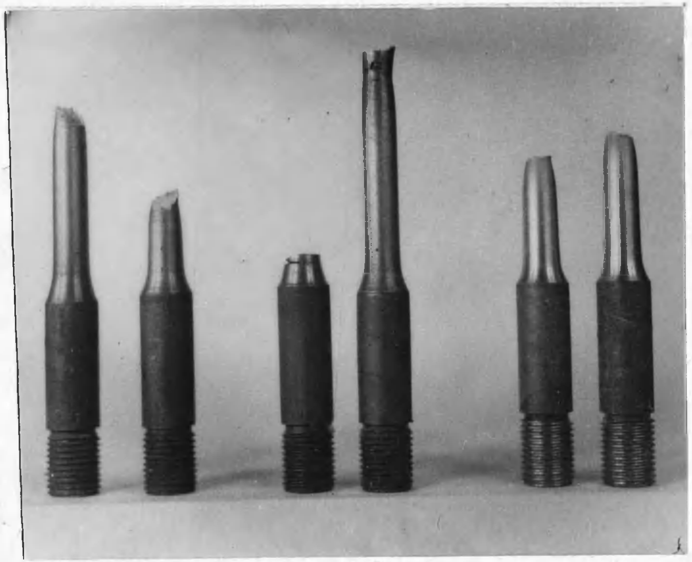
[x] Fractured at fillet.

TABLE XII (CONTINUED)

Test No.	Test Conditions.	Ultimate Load lb.	Elong'n %	Fraction of elong'n in air. %	Red'n in area %	Fraction of red'n in air. %
B.0.1	In air	14700	37.0	100 (mean)	59.7	100 (mean).
B.0.2		14700	37.0		61.4	
B.1.1.	20% Commercial NaOH	14300	38.0	102.7	55.8	92.0
B.1.2		14700	34.5	93.3	40.5	66.8
B.2.1.	10% Commercial NaOH	14800	39.0	105.2	56.1	92.5
B.2.2		14700	38.5	104.0	53.1	87.6
B.3.1	40% Commercial NaOH + 0.2% Tannin	14200	36.0	98.2	42.5	70.0
B.4.1	40% Commercial NaOH + 2.5% tannin	14500	39.0	105.3	56.7	93.5
B.4.2		14500	35.0	94.6	50.1	82.6
B.5.1	40% Commercial NaOH + 2.5% resorcinol	14800	35.0	94.5	51.1	84.4
B.5.2		14800	37.0	100.0	53.8	88.8

500x. Etched.

Fig. 24.



(a) (b) (c)

Fig. 23.

mechanical properties. The differences have been overcome to some extent by expressing the results in terms of the behaviour of the specimens in air, and may probably be safely ignored.

GROUP A1. The two specimens of this group were pre-strained by 10 per cent on the gauge length. After fracturing they were found to be covered with a large number of shallow circumferential cracks, which appeared to be associated with residual machining strains. The fracture itself was irregular, as may be seen from the photograph, Fig. 23 (a) in which a normal fracture (c) is included for comparison, and bore no relationship to the normal "cup-and-cone" fracture of ductile materials. The reduction in area and elongation were in both cases less than the corresponding values in air, but the reduction in area figures did not agree well with each other.

GROUPS A2 ., B1., and B.2. In these groups, and those following, the specimens were not pre-strained. The fractures obtained in Group A2 had characteristics similar to those of Group A1; those of Groups B1 and B2 were of the normal cup-and-cone type though somewhat ragged. In all cases surface cracks were present. The reduction in area and elongation values showed little consistency, but only in the case of specimens broken in the 40 per cent caustic soda solutions are they sensibly less than the corresponding values in air.[x]

GROUPS A3 and A4. In Group A (40 per cent pure sodium hydroxide) there was little evidence of brittleness beyond slight surface cracking. The normal type of fracture bore no resemblance to the fractures obtained in Groups A1 and A2. The addition of silica (Group A4) appeared to occasion a slightly more brittle type of fracture, as is reflected in the figures. In view, however, of the considerable variations within each group too much store should not be set upon these results.

GROUPS B3, B4 amd B5. In these groups the influence of resorcinol and tannin were examined. These substances are regarded as being inhibitors of pickling brittleness, and the former also as an inhibitor of caustic cracking. When present in small quantities (Group B.4) tannin did not materially alter the type of fracture (that of Group A.2); in larger quantities, however, both tannin and resorcinol resulted in a decrease in the amount of surface cracking, accompanied by normal fracture.

[x] The variations in the quoted figures noticeable in all the tests may be partly attributed to the difficulty of fitting together and measuring accurately the somewhat ragged fractured surfaces.

In all groups the ultimate load showed some variation from specimen to specimen, but in general the values were close to those obtained in air, and appeared to be independent of the degree of brittleness of the specimen.

The sequence of events leading to fracture in the tests described above appears to be somewhat as follows. At the commencement of plastic deformation the metal is charged with hydrogen, at least in the vicinity of the surface. The brittleness induced by the dissolved gas leads to the formation of the surface cracks which are typical of every specimen. Due, however, to the temperature rise in the interior of the metal which accompanies this initial distortion, the hydrogen is partly desorbed and the occurrence is accompanied by some restoration of the ductility of the metal. The amount of desorption which takes place is dependent, finally, on the surface pressure of the hydrogen adsorbed on the surface of the specimen (pp. 80, ff.). The higher the surface pressure (or concentration), the greater the amount of absorption which takes place during the period of polarisation, and the less the amount which is ejected on deformation, since the continuation of polarisation during deformation ensures the maintenance of the surface pressure. When the specimens are loaded to failure the type of fracture obtained will thus depend finally on the amount of hydrogen retained by the metal at the end of deformation. If the amount is small, and ductility is thus almost completely restored, separation will commence in the usual way at a point on the axis of the specimen and spread outwards along the surface of a cone, giving rise to the normal cup-and-cone fracture on which the presence of surface cracks will have but little effect. If the residual gas content of the metal is sufficient to render it sensibly brittle, however, the specimen will be extremely sensitive to the presence of surface cracks; separation will be initiated at the roots of these cracks and propagated inwards to give rise to a brittle type of fracture. Obviously this will occur when sufficient deformation of the (partly) brittle metal has taken place to raise the stress at the roots of the cracks above the separation value. The reason why brittleness should occur in concentrated solutions of sodium hydroxide solutions has already been discussed elsewhere (p.p. 86 ff.). The ideas advanced above are lent some support by the fact that pre-straining tends to increase the brittleness of the specimens at fracture. In this case the hydrogen has less chance to escape because there is, in effect, less deformation to fracture; and moreover, surface cracks appear at a later stage of the total deformation when the metal is more susceptible to their presence; the increased solubility of the gas in the already deformed metal may also play some part. The theory is also helpful in explaining the rather curious behaviour of the specimen shown in Fig. **23** (b). Although this specimen had undergone considerable local deformation and was obviously on the point of fracture at the neck, it preferred in the last resort to break in a completely brittle manner at the fillet. It appeared that the fracture was initiated by a particularly bad region of residual machining strain. Since little or no permanent deformation occurred in this region it is probable that its hydrogen content remained high, rendering it extremely sensitive to the notch effect of the tool-deformed metal. This result, and those of Group A 1/**1**., incidentally serve to illustrate that, under certain circumstances, caustic soda solutions are capable of producing extreme embrittlement of mild steel.

A micrograph, typical of the type of crack obtained in brittle specimens, is shown in Fig. **24**. It will be observed that the original surface crack, rendered blunt by subsequent deformation, is accompanied by a number of finer cracks, obviously formed at a much later stage.[x]

[x] Incidentally, the results obtained in the tensile test serve to explain why the **bend** test generally gives a more sensitive indication of brittleness, for since in the latter fracture is in any event initiated at the surface of the specimen, it will naturally be more sensitive to the presence of surface cracks.

The fine cracks are apparently mainly trans-crystalline, though there is some evidence of intergranular separation.

Turning to the chemical aspects of the tests the following facts emerge.

(a) Really serious embrittlement appears to result only in concentrated solutions of sodium hydroxide.

(b) The influence of commercial caustic soda is much more marked than that of the pure product.[x] It has not been proved that silica (present in fair quantities in the commercial product) contributes to the embrittling capacity of the solution. In any event, there are very probably other substances, such as compounds of arsenic and of sulphur, present in the impure product in sufficient quantity to enhance its effect; further investigation along these lines is obviously required.

(c) Tannin and resorcinol, if present in sufficient quantities, definitely inhibit the embrittlement in caustic soda solutions.

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[x] Though not obvious in the present tests, the bend tests described previously showed that strong solutions of pure caustic soda are capable of producing quite serious embrittlement.

A general discussion of these results in terms of their relationship to caustic cracking will, as usual, be postponed to the relevant section (p155), but it is convenient to insert here a brief discussion of the present results in relation to those obtained by Pfeil, in sulphuric acid, and to note the writer's own views on the manner whereby embrittlement of mild steel is induced by absorbed hydrogen.

In general terms the present results agree well with those obtained by Pfeil on his fine-grained specimens of iron, as described on p.29 . The degree of embrittlement noted by the writer at 18°C corresponds rather to Pfeil's results at 40°C, than to the much more severe reduction in ductility he noted at 25°C. Possibly the differences are due to the different solutions used, but in view of the one extremely brittle fracture obtained in the present tests, it seems quite possible that the differences are to variations in the experimental techniques. The type of cracking obtained agrees well with that noted by Pfeil at the lower temperatures.

With regard to the writer's views on the manner in which hydrogen embrittlement is induced, it may be said that they are on the lines of the theory of Zapffe and Sims as modified by Smith (30) (P.30). It seems probable that accumulation of hydrogen will occur in the imperfections of the lattice and result in the setting up of a triaxial stress, but the writer prefers to regard the accumulation as corresponding to the nuclei associated with precipitation hardening, rather than as a "compressed molecular fluid", since hydrogen embrittlement possesses at least a superficial resemblance to this phenomenon. For the reasons advanced on p.34 , it might be expected that a greater number of these "nuclei" of hydrogen would occur in the region of the grain boundary and thus tend to promote, to some extent, the intergranular failure of the metal under stress. In alloys or in metals containing impurities the presence of reducible films at the grain boundaries may play an essential role, as has been already noted on p.32 .

PART VI

STRESS - CORROSION TESTS
IN
SODIUM HYDROXIDE SOLUTIONS
AT
ELEVATED TEMPERATURES.

VI. STRESS-CORROSION TESTS IN SODIUM HYDROXIDE SOLUTIONS AT ELEVATED TEMPERATURES.

The various tests and experiments which have so far been described have had a rather indirect bearing on the problem of caustic cracking as it occurs in practice in that in carrying them out no effort was made to simulate boiler conditions. In the tests to be described in the present part an attempt has been made to reproduce practical conditions as far as possible. The tests were carried out at boiler temperatures, using specimens of materials typical of those employed in boiler practice and of such a form as to give rise to an asymmetrical stress distribution corresponding approximately to that found in practice. It was not, of course, possible to simulate boiler conditions precisely while still retaining some measure of control over the tests; care must therefore be exercised in assessing the practical significance of the results.

The work is still in its initial stages, and the sequence of tests will be found to be far from complete. It is felt, however, that the results so far obtained are sufficiently encouraging to justify their insertion here, though the account given must be regarded as being in the nature of a progress report.

1. Apparatus.

(a) Basic Design.

Before proceeding to a detailed description of the test assembly employed in the present work, it is convenient to insert here a very brief account of the types of apparatus employed by previous workers, and to indicate those factors which guided the writer in his choice of a basic design.

In the apparatus employed by Parr and Straub (7) the specimen was immersed in the test solution contained in an autoclave, and stressed by means of an external spring. The tension rod passed into the autoclave through a packing gland. A similar form was employed by Ulrich (65) in Germany. The main criticism which may be levelled against this system is that it is very difficult, in fact almost impossible, to make the gland really pressure tight without setting up undue friction on the tension rod. Of course, one may introduce means whereby the evaporated water is replaced at frequent intervals, or alternatively the apparatus may be dismantled and refilled when necessary, but obviously neither of these schemes is entirely satisfactory.

Later, an apparatus was developed by Straub and Bradbury (66) in which the use of a packing gland was obviated. In this design the corroding solution was contained within the hollow, cylindrical specimen. A spring-loading system was employed. Among others, Colbeck, Smith and Powell (67) and Schroeder (68) have employed similar schemes. In view of the known susceptibility of steel stressed in hot caustic soda solutions to the influence of surface irregularities a particularly high standard of reproducibility of surface finish is required, and there is considerable difficulty in ensuring this with specimens of this type. Moreover, deliberate and controlled surface variations (such as notches) cannot easily be produced.

In the apparatus employed by Jenkins and Adcock (69) at the N.P.L., the entire loading system, consisting of a dead-weight lever arrangement, was enclosed in the autoclave. By this means, gland friction was avoided, while the use of a convenient form of specimen was still permitted. Unfortunately if the dimensions of the autoclave are to be kept within reasonable limits, the load which can be applied to the specimen is somewhat small, and to attain a high stress extremely small specimens must be used. As a result, the behaviour of the specimens may be considerably influenced by general surface attack.

The Schroeder Detector has also been employed in laboratory tests (70), but has the disadvantage that the stress is indeterminate. In view of the encouraging results obtained with this apparatus in the field, it merits further consideration and development.

An arrangement in which the specimen underwent repeated torsion was developed by Schroeder and Partridge (71) in which the strain on the specimen was measured rather than the stress, thus circumventing the difficulties occasioned by friction at the packing gland. Probably, however, the type of distortion produced in the specimen resembles less closely that occurring in practice than that produced by tension or bending.

Finally, a particularly ingenious scheme has been described by Schroeder and Berk (72), in which the specimen is loaded by means of a push rod passing up its centre, and is screwed into an autoclave containing the corroding medium. In many ways this is the ideal system; a packing gland is dispensed with, so that tight joints may be ensured; the surface of the specimen in contact with the corroding medium is external, and may thus be readily machined to any desired form and given a consistently good finish; by the use of a push-rod of high tensile steel considerable loads may be applied to the specimen, which may then be given sufficient bulk to minimise the influence of surface attack. This type of apparatus is mainly open to criticism on economic grounds, since the specimens must be made with some precision to ensure truly central loading, which naturally adds to their cost; the

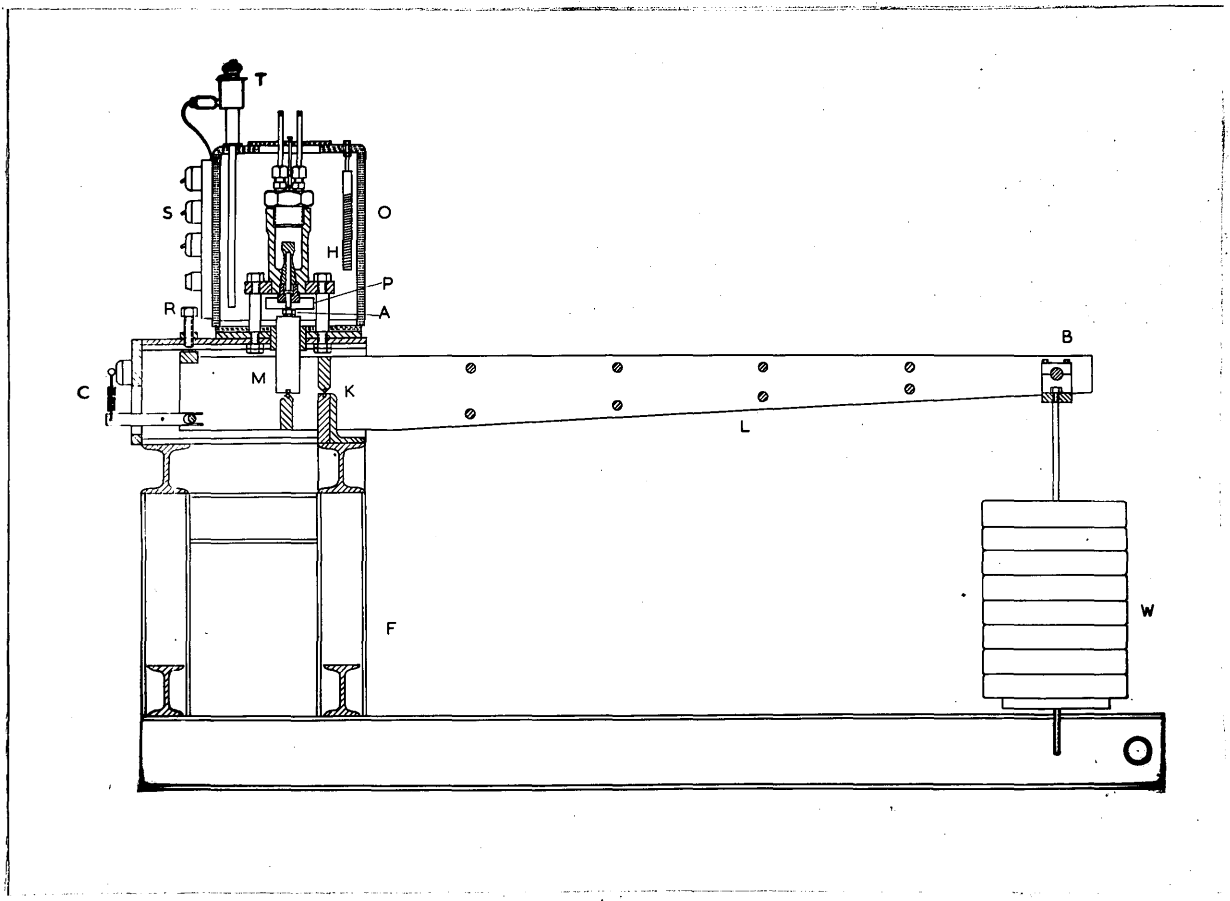

Fig. 25.

apparatus, too, is somewhat expensive to construct.

Despite its economic drawbacks the writer, when considering the selection of a design for his apparatus, decided that the last-mentioned scheme was the most likely to combine ease of operation with reliable and consistent results, and his design was therefore based on these principles. In operation the apparatus proved to be quite satisfactory. Although initial troubles were (and still are being) encountered, they do not reflect upon the fundamental design, but merely suggest some minor modifications. Three units were constructed.

(b) Framework and Lever System.

As may be seen from the assembly drawing of Fig. 25 , the load was applied by means of a dead-weight lever system. This arrangement was adopted in preference to a spring-loading arrangement, chiefly because suitable facilities were lacking for the calibration of heavy springs. The lever assembly was carried on a framework of I-beams, F, and consisted of a lever, L, bearing on a knife-edge, K. The lever actuated the main push rod, M, which was located by means of a longitudinal key sliding in a keyway cut in the framework. An adjusting screw, A, at the head of the push rod carried a pan P to protect the apparatus as far as possible from the corrosive liquid set free when the specimen broke. The dead load and pan, W, were carried by a pin-joint, B. A stop, R, at the other extremity of the lever permitted the load on the specimen to be relieved. The autoclave assembly was carried on a flange mounted on four short columns, and was surrounded by an oven, O, resting on the top-plate of the framework. The entire assembly was constructed so as to be as rigid as possible. Leading dimensions are given in Table XIII.

TABLE XIII.

LEADING DIMENSIONS OF FRAMEWORK AND LEVER SYSTEM.

Framework.	ft.	in.
Overall length	7	0
" breadth...	1	6
" height (less autoclave and oven).. ...	3	6
Lever		
Overall length	6	3
" breadth...	0	4½
Knife edge to push rod..	0	3
" " " loading point.. ...	5	0

Lever ratio ... ... 20 : 1

Capacity at loading point.. 500 lb.

Equivalent weight of lever. 44 lb.

(c) Autoclave. On the recommendation of the steelmakers a stainless steel containing 18 per cent chromium and 8 per cent nickel was first used in the making of the autoclaves, but later this material had to be

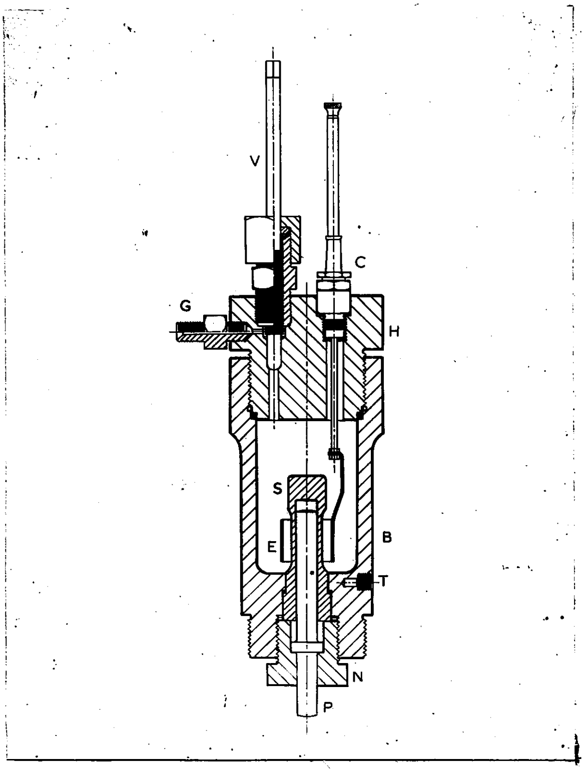

Fig..26.

discarded. Finally a straight iron-nickel alloy containing 36 per cent nickel was employed. The events leading the rejection of the 18 - 8 alloy are of considerable interest in connection with the subject matter of this report, and are discussed in detail in Appendix III.

Two half-sections of an autoclave at right angles to one another are shown in Fig. 26. The specimen, S, fitted into the body, B, the joint being made by means of a soft copper washer. The specimen and the push rod, P, of high tensile steel, were held in position by the nut N. A thermocouple insert was provided in the body of the autoclave at T. The head, H, carried two ball-ended valves, (of which one, V, is shown) which were provided with couplings, G. It was intended that these valves should be employed for withdrawing the gaseous contents of the autoclave for analysis, or for de-aerating the test solution, and filling the vapour space with gas at high pressure. Tests of this type have not so far been carried out. Two insulated connections were also provided in the head, as at C. That shown carried a nickel electrode, E, by means of which the specimen could be polarised, while the other carried a nickel needle dipping a short distance into the solution and functioned as a liquid level indicator.

Considerable difficulty was experienced in discovering an insulating material for use in these connections, which would withstand the corrosive fluid in the autoclave. Porcelain cement, mica, and fired soapstone were tried with little success. Porcelain automobile sparking plugs also lost their insulating properties in the presence of the hot caustic soda, but the new type, embodying an insulator of sintered aluminium oxide (Sinterkorund), was found to be quite satisfactory.

Concentrated sodium hydroxide solutions possess a remarkable ability to seep through joints which would be perfectly tight under other circumstances, in which respect they greatly resemble mercury. In consequence of this the setting-up of truly tight joints presented a serious problem. In designing the apparatus it was considered that simple soft washer joints on the Amagat principle should be tried first, in preference to ground-in metal-to-metal joints, which are somewhat difficult to machine. Soft steel washers were not successful, but soft copper washers on a narrow jointing face gave moderately good service. Tightness could not be guaranteed in every case, however, and in future work it is proposed to adopt proper ground-in joints, which are without question the most reliable.

(d) Heating System.

The autoclave of each machine was heated by means of a cylindrical, asbestos-lagged oven, O, (Fig.25)

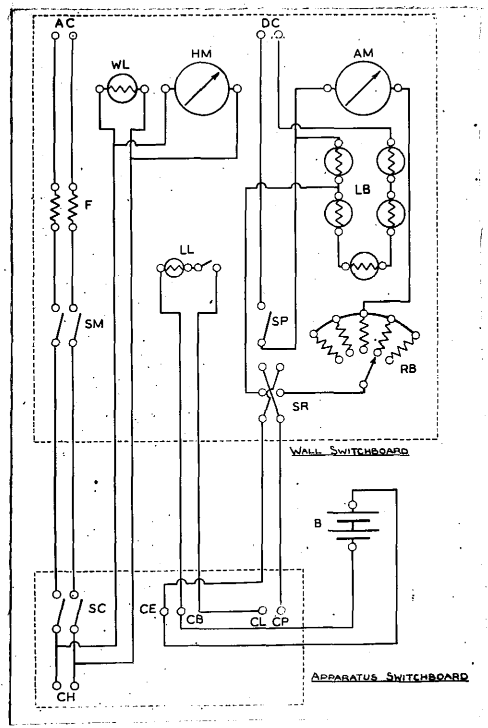
AC
WL
HM
DC
AM
LB
F
LL
SM
SP
RB
SR
Wall Switchboard
B
SC
CE
CB
CL
CP
CH
Apparatus Switchboard

Fig. 27.

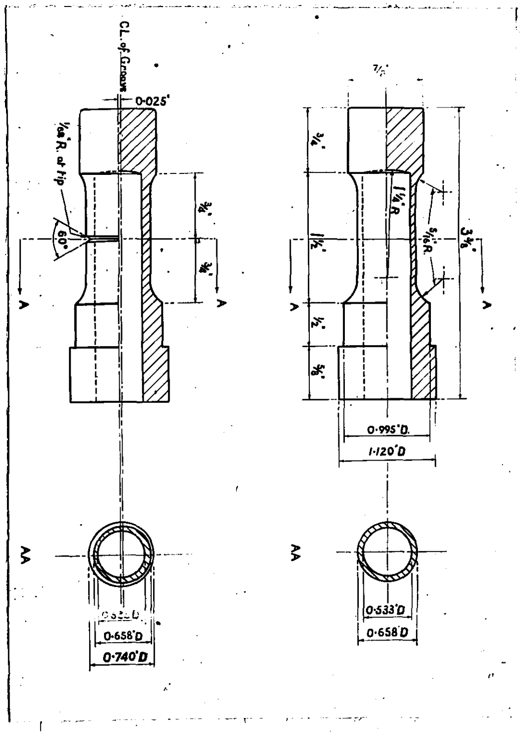
CL. of Groove
0·025"
1/64"R. at tip
60°
3/4"
3/4"
A
A
AA
0·533"D
0·658"D
0·740"D
7/8"
3/4"
1 1/2"
1/2"
5/8"
1 1/4"R
5/16"R.
3 3/8"
A
A
0·995"D.
1·120"D
AA
0·533"D
0·658"D

Fig. 29.

carrying three 250 watt tubular heaters,[x] controlled by the switches S. The temperature of the autoclave, as determined by a thermocouple inserted at T (Fig 26) was calibrated against, and controlled by, a MacLaren adjustable thermostat operating over a temperature difference of ± 3° C. An automatic cut-out switch, C (Fig 25), actuated by the dropping of the main lever when the specimen broke, was provided. By this means the heater current was interrupted, and simultaneously an hourmeter and warning lamp were switched off.

(e) Electrical Circuits.

The circuit diagram for the apparatus is shown in Fig 27 . Alternating current was used in the heater circuit, and passed through the fuses F and the main switch SM to the cut-out switch CS and heater connections CH. In parallel with this circuit and between SC and CH were connected a warning lamp WL and an hourmeter HM, both of which were thus switched off on the opening of the automatic cut-out. The polarising circuit was tapped from a lamp bank LB across the direct current mains, a switch SB being placed on the live (negative) line. The tapped circuit

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[x] Later a single 1000 watt heater was substituted.

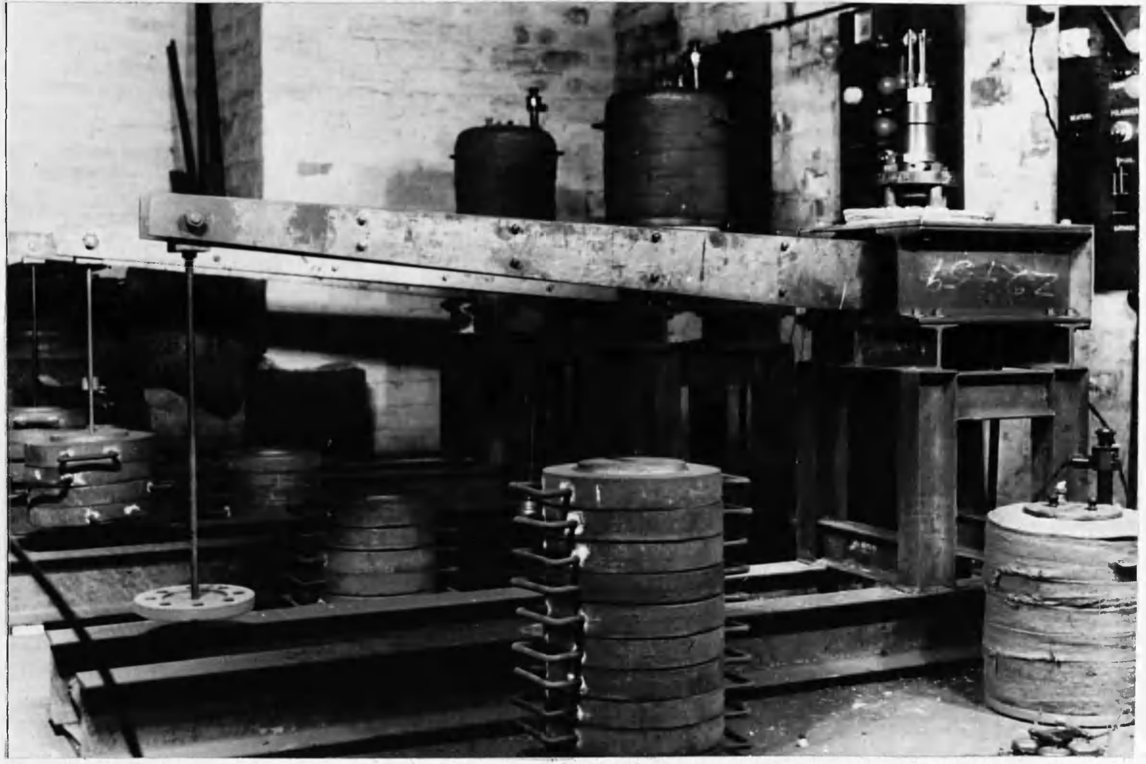

Fig. 28.

included an ammeter AM (reading to 0.1A) a resistance bank RB, and a reversing switch SR. Connection was made to the electrode of the autoclave through CP and to the framework of the apparatus through CE. The liquid level indicator, LL, consisted of a pea lamp and button switch connected to the needle of the autoclave through CL. Current was supplied by a 4 volt battery, B, connected across CE and CB. As long as the liquid in the autoclave remained in contact with the needle the pea lamp was illuminated on depression of the switch.

(f) Lay-out.

The layout of the testing machines is shown in the photograph of Fig 28. They were arranged parallel to each other in a room having a cement floor, with their heads towards the wall carrying their respective switch-boards. In order that the polarising circuits could function properly it was necessary that the machines should be insulated from earth. This was accomplished by mounting them on wooden boards covered with hard rubber sheets.

2. Specimens.

Practically all of the tests described here were carried out using notched specimens. Some tests were also made using plain specimens, but, because of leakage, had, with one exception, to be discontinued before the stipulated time. The dimensions of both types, which differ only in the diameter of the

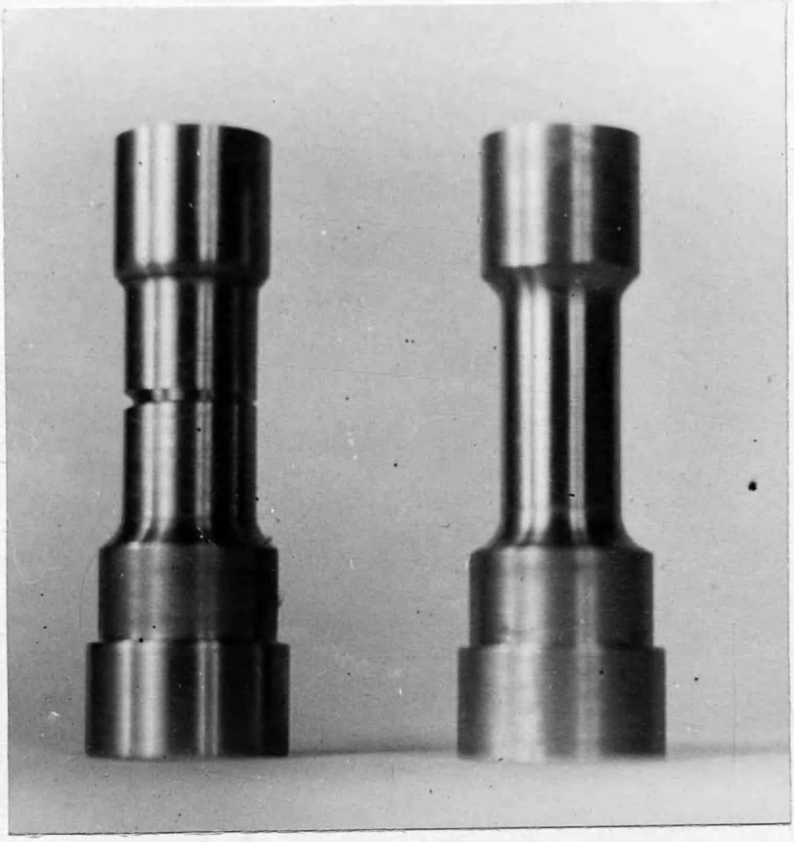

Fig..30.

test length, are given in Fig29, and a photograph of both types is reproduced in Fig 30 .

The use of notched specimens in the bulk of the tests was decided upon for three reasons which it may be well to discuss here. Firstly, it is a matter of practical experience that caustic cracking is associated only with those areas of the boiler subject to a high asymmetrical stress, and it seems reasonable to attempt to reproduce these conditions in a controlled fashion. Secondly, many previous workers, but especially Colbeck and his colleagues (67) and Schroeder and Berk (72), have found that failure can be produced only with difficulty, or not at all, in symmetrically stressed specimens, And thirdly, it appears (69) that the failure of unnotched specimens is not always typical of caustic cracking.

Great care was taken to ensure uniformity and accuracy in the machining of the notches, since it is clear that any slight variations may considerably influence the results. It is not suggested that the form of notch which was adopted in these tests was necessarily the most suitable, and when an opportunity arises to continue the work it is proposed to investigate this aspect thoroughly. However, the specimens behaved quite well in practice, though it is possible that the stressing conditions were a trifle severe.

The chemical analyses of the specimen steels,


120x. Etched.

Fig. 31.

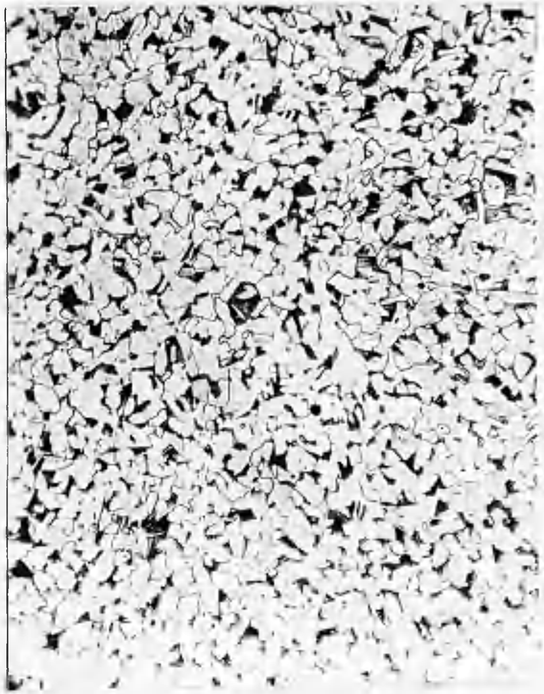
120x. Etched.

Fig. 32.

as supplied by the manufacturers, are given in Table XIV.

TABLE XIV.

ANALYSES OF STEELS USED IN TESTS.

%	A	B	C[x]	D	E[x]
C	0.10	0.135	0.105	0.13	0.165
Si	0.06	0.05	0.07	0.05	0.18
S	0.030	0.033	0.029	0.043	0.028
P	0.013	0.015	0.019	0.040	0.014
Mn	0.53	0.60	0.52	0.45	0.78
Ni	0.13	0.11	0.15	neg.	neg.
Cr	0.035	0.020	0.08	neg.	neg.
Mo	0.015	0.020	0.03	neg.	neg.

[x] Fine-grained steels. McQuaid-Ehn grain size 6/8

Steels A, B and C were used mainly in a few preliminary tests. The mechanical properties of steels D and E are given in Table XV, and their microstructures are shown in Figs. 31 and 32 respectively.

TABLE XV

MECHANICAL PROPERTIES.

Steel	Y.P. lb/in^2	U.S. lb/in^2	El. % 4 x dia	Red. of area %
D	40,100	59,200	41	63.6
E	43,700	67,600	37	60.1

The materials were used in the "as rolled" condition.

Calibration tests were carried out at 250°C on specimens of steels D and E in order to determine the breaking stresses of the notched specimens. The results are quoted in Table XVI.

TABLE XVI

AVERAGE BREAKING STRESS OF NOTCHED SPECIMENS IN AIR AT 250° C.[x]

Steel	Av. b.s. lb/in^2	
D	66,000	63,000
	61,000	
E	68,000	66,000
	64,000	

[x] It is not unusual for specimens of this type to exhibit an exceptionally high breaking stress (Schroeder & Berk, Ref.(72))

3. TESTING PROCEDURE.

In carrying out a test, the specimen was first well washed with paraffin, dried, and inserted into the base of the autoclave, with the copper jointing-ring in position. The push rod P (Fig 26) was then placed in position and the joint made by tightening down the nut N. Following this, the test solution was poured into the autoclave, and the head tightened down. In those tests in which it was not intended to polarise the specimen, it was surrounded by a short length of mild steel tube, which served to minimise the effect of any potential difference existing between the specimen and the wall of the autoclave. This precaution is very necessary, for the writer's tests have shown that polarisation of the specimen may influence the results quite considerably: a point which appears to have been ignored by many previous workers.

After assembly, the autoclave was screwed into position, and the screw A (Fig 25) adjusted so that the lever would be level on application of the load. The weight of the lever was then taken off the specimen by screwing down the stop R. The oven was placed in position and the heaters switched on, the thermostat being adjusted to give the desired temperature. After the autoclave had attained equilibrium with the oven (in one and a half to two hours) the load was applied to the specimen, by placing weights on the loading pan and slowly slackening back the stop screw R, and the hourmeter started.

4. TEST RESULTS.

As has already been mentioned, the tests to be described here cannot be regarded as forming a complete series. Nevertheless, it is felt that a sufficient number of results have been accumulated to justify the belief that the apparatus and experimental technique are capable of producing reliable data, as well as permitting a few tentative conclusions to be drawn. In the initial stages a considerable number of tests were lost, mainly through leakage or heater failure and, in general, these have not been recorded here.

The results are quoted in Table XVII which will be found to be largely self-explanatory; the following points should, however, be noted.

(i) In tests on plain specimens the duration was fixed at about 200 hours if no break occurred; using notched specimens 50 - 100 hours was regarded as sufficient, when considered in relation to the time in which failure normally took place.

(ii) In some tests the specimen was not completely severed, but merely cracked. The automatic cut-out did not then function and the time of failure was thus indeterminate, as is indicated by an interrogation mark in the appropriate column.

(iii) It was not, of course, possible to determine the true current density on the relevant area of the specimen in those tests in which a polarising current was applied. Since the tests were carried out under similar conditions, however, the results permit comparison amongst themselves.

(iv) For purposes of comparison the conditions of test of Group 7 (Table XVII) were regarded as being standard.

TABLE XVII

TABLE

STRESS - COR-

Test No.	Steel & Specimen	Test Solution	Nominal stress lb/in^2	Temp. °C.
1.1	B/N (1)	50% Commercial NaOH	58,700	280
2.1	B/N (1)	50% Commercial NaOH	52,600	280
2.2	B/N (1)	50% " "	"	"
2.3	B/N (1)	50% " "	"	"
3.1	B/P (2)	50% Commercial NaOH	35,400	280
3.2	B/P (2)	50% " "	42,200	"
4.1	A/N (1)	42.6% Commercial NaOH	43,700	250
5.1	C/N (1)	42.6% Commercial NaOH	43,700	250
5.2	C/N (1)	42.6% " "	"	"
6.1	B/P	42.6% Commercial NaOH	52,700	250
7.1	D/N	41.6% Commercial NaOH	43,700	250
7.2	D/N	41.6% " "	"	"
7.3	D/N	41.6% " "	"	"
8.1	D/N	41.6% Commercial NaOH	43,700	350
8.2	D/N	41.6% " "	"	"
9.1	D/N	41.6% Commercial NaOH	43,700	300
9.2	D/N	41.6% " "	"	"
10.1	E/N	41.6% Commercial NaOH	43,700	250
10.2	E/N	41.6% " "	"	"
11.1	C/N	41.6% Commercial NaOH	43,700	250
11.2	C/N	41.6% Commercial NaOH	"	"
12.1	D/N	30.7% Commercial NaOH	43,700	250
12.2	D/N	30.7% " "	"	"
12.3	D/N	30.7% " "	"	"
13.1	D/N	20% Commercial NaOH	43,700	250
14.1	D/N	7.6% Commercial NaOH	43,700	250
14.2	D/N	10.0% Commercial NaOH	43,700	250

XVII.

ROSION TESTS.

Polarising Current. mA	Results.		NOTES.
	Break hr.min.	No break hr. min.	
-	30-40hr.	-	Preliminary test.
66(a)(3)	13.00	-	" "
10(a)	23.30	-	" "
60(c)(3)	67.00	-	" "
-	-	91.00(4)	" " See text.
-	-	94.00(4)	" test. Spec. did not break on raising stress to 47,000lb/in^2
-	13.31	-	Preliminary test.
-	15.29	-	" "
-	16.13	-	" "
-	-	228.00	
-	1.30	-	
-	3.35	-	
-	2.15	-	
-	5.50	-	Specimen cracked.
-	-	89.07	
-	2.45	-	
-	2.30	-	
-	36.30	-	
-	70.00	-	
-	12.00	-	
-	1.02	-	
-	?	-	Specimen cracked
-	?	-	
-	2.50	-	
-	2.00	-	3 other tests lost through leakage discovered after about 70 hours.
-	9.43	-	2 other tests lost through leakage discovered after 45 and 95 hrs respectively.
-	-	120.00	

TABLE

Test No.	Steel & Specimen	Test Solution	Nominal Stress lb/in^2	Temp. °C.
15.1	D/N	40% Pure NaOH	43,700	250
15.2	D/N	40% " "	"	"
16.1	D/N	40% Pure NaOH + 5% SiO$_2$	43,700	250
16.2	D/N	40% " " " "	"	"
17.1	D/N	41.6% Comm. NaOH + 2.5% tannin	43,700	250
17.2	D/N	41.6% " " " "	"	"
18.1	D/N	41.6% Comm. NaOH + 5% tannin	43,700	250
18.2	D/N	41.6% " " " "	"	"
19.1	D/N	41.6% Commercial NaOH	43,700	250
19.2	D/N	41.6% " "	"	"
20.1	D/N	41.6% Commercial NaOH	43,700	250
21.1	D/N	41.6% Commercial NaOH	43,700	250
22.1	D/N	41.6% Commercial NaOH	43,700	250

(1) Notch 0.0125 in. eccentric.
(2) Specimen wall 0.125 in. thick.
(3)(a) Anode.
   (c) Cathode.
(4) Some leakage - test abandoned.

XVII (Continued)

Polarising Current mA	Results.		NOTES.
	Break hr. min.	No break hr. min	
-	1.00	-	
-	0.48	-	
-	1.04	-	
-	?	-	Specimen cracked.
-	4.50	-	
-	-	94.00	
-	3.45	-	
-	-	120.00	
60(a)(3)	2.13	-	
60(a)	6.44	-	
22(a)	2.29	-	
64(c)(3)	-	42.32	Anode thickly coated with black oxide
64(c)	-	72.43	Anode thickly coated with black oxide.

THE INFLUENCE OF TEMPERATURE (GROUPS 7, 8 and 9).

Tests have been quoted by Straub (7) in which the time to failure was found to depend quite definitely on the temperature, decreasing as the temperature was raised. On the other hand, the embrittlement detector results analysed by the writer (42) showed no such trend, nor is there any evidence of an increased number of failures in practice at high operational temperatures.

In the present tests, the results obtained at 300°C were similar to those at 250°C, At 350°C failure appeared to be less certain, but it is possible that the results are attributable to experimental variations.

VARIATION IN SOLUTION STRENGTH (GROUPS 7, 12, 13 and 14).

Failures were found to persist in solutions of reduced strength, one even being obtained in a 7.6 per cent solution - though there is good evidence that failure is much less likely at the lower concentrations. In general, the results appear to be in fair agreement with those of Schroeder and Berk (72), though these workers' results indicate a rather higher concentration than 10 per cent as being necessary for the occurrence of failure. The differences between their results and those presented here may probably be attributed to the different degrees of stressing of the specimens.

PURE SODIUM HYDROXIDE, AND THE INFLUENCE OF ADDED SILICA (GROUPS 15 and 16.)

Tests by Jenkins and Adcock (69) and , more especially, by Schroeder (72) have indicated that solutions prepared from an analytical grade of sodium hydroxide are much less effective in producing failure than those prepared from the commercial product. Their results further indicated that the difference is attributable to the presence of silica (as sodium silicate) in the latter.

The writer has been unable to confirm these results, for, under the conditions of the present tests, pure sodium hydroxide was found to be extremely effective in producing failure, and the addition of silica did not appear materially to influence the results.

THE INFLUENCE OF ADDED TANNIN (GROUPS 17 and 18).

The results of these groups are of particular interest in view of the undoubted ability of tannin to reduce the incidence of cracking in embrittlement detector tests (p 50). It appears from the results that, under the conditions of test, tannin will not entirely inhibit cracking, though failure is less likely. In view of the practical importance of this aspect of the work, a very much more extensive investigation is obviously desirable.

POLARISATION OF THE SPECIMENS (GROUPS 2, 19, 20 and 21.)

The results obtained by applying a polarising current to the specimens are of some interest, in view of the controversy as to whether caustic cracking is attributable to anodic attack, or to production of transient brittleness by cathodic hydrogen. As distinct from the results obtained in ammonium nitrate solutions with U - bend specimens, failure was not inhibited by anodising, and indeed Tests 2.1 and 2.2 (0.0125 in. eccentric notch) indicate a decrease in the time to failure with with increasing anodic current (c.f. Test 1.1). Cathodising, on the other hand was definitely protective though one failure was obtained after 67 hours (Test 2.3).

INFLUENCE OF THE COMPOSITION AND STRUCTURE OF THE STEEL. (GROUPS 7, 10 and 11).

It was reported by Ulrich (65) in 1930, that a fine-grained, non-ageing steel (73) (Izett Steel) developed by Krupps, had been found to be remarkably resistant to caustic cracking. American workers were, however, unable fully to confirm these claims.

The writer's test show no particular improvement in performance of the fine-grained steel C as compared with the normal steels, but the steel E of slightly higher carbon content was definitely more resistant. As no normal steel of a similar content was available it is not possible to say whether the increased resistance is due to its structure, though in view of the other results this seems unlikely.

BEHAVIOUR OF PLAIN SPECIMENS (GROUPS 3 and 6).

In agreement with the results of Schroeder and Berk (72), the writer's tests have shown that symmetrically stressed specimens are very much more resistant to attack by caustic soda than are notched specimens. The most successful test was 6.1, which indicated an ability to withstand attack considerably greater than that shown in Schroeder's tests. Other tests of this type had to be abandoned after 70 - 90 hours because of leakage.

5. NATURE OF THE FRACTURE.

The fractures which occurred spontaneously in these tests were quite similar and characteristic, with one exception. They were found to be "ragged" and had associated with them a number of small blunt cracks. Fractures produced in similar specimens in air were smooth and were not accompanied by cracks. The exception among the spontaneous fractures, that of the cathodically polarised specimen in Test 2.3, was also smooth, as were induced fractures in the other cathodically polarised specimens.

Despite the presence of the notch the fractures showed some evidence of necking on the internal surface, and an attempt was made to measure the reduction in area of the fractured surface. The results are quoted in Table XVII. It will be noted there that the percentage reduction in area of the unpolarised and anodically polarised specimens is considerably less than that of specimens broken in air, or which had undergone cathodic

100x. Etched.

Fig, 33.

550x. Etched

Fig. 34.

500x. Unetched.

Fig. 35.

polarisation.

TABLE XVIII.

REDUCTION IN AREA OF NOTCHED SPECIMENS.

Steel.	Test Conditions	Red. in area. %
D	In air	22.3
D	" "	21.0
E	In air.	17.2
E	" "	10.7
D	Standard	11.3
D	"	5.8
E	Standard	13.3
E	"	7.0
D	Anode 60mA	8.9
D	" "	neg
D	Cathode, 64 mA	16.7
D	" "	18.2

A fracture induced in a plain specimen which had undergone treatment in caustic soda (Test 3.1) occurred at the fillet and was brittle in character.

A micrograph of a crack associated with this last-mentioned fracture is shown in Fig. 33. It is probably intercrystalline, and certainly has intercrystalline branches associated with it. Figs.34 and 35 illustrate the intercrystalline nature of the fracture obtained in specimens which had undergone the standard test (Groups 1 and 7); the fractured surface shown in Fig.34 was iron plated by the standard method to permit the examination of detail at the edge

500x. Etched.

Fig..36.

500x. Etched.

Fig. 37.

100x. Etched.

Fig. 38.

of the fracture. The crack shown in Fig. 35, which is also clearly intercrystalline, occurred on the side of the notch of the specimen at a site comparatively remote from the fracture. The fine-grained steel E also gave rise to intercrystalline failure, as is shown in Fig 36. Anodically polarised specimens cracked in an intercrystalline manner (Fig. 37), but those polarised cathodically were free from this type of failure. The behaviour of a plain specimen which had undergone prolonged stressing in caustic soda is illustrated by the micrograph of Fig. 38. There is a certain amount of pitting of the surface, some of which is apparently intergranular but there is no evidence of intensive attack.

6. GENERAL SUMMARY.

Despite the exploratory nature of the tests outlined above, and the fact that several were marred through leakage, it is possible to draw from the results some quite reliable conclusions.

(i) Failures closely comparable with those occurring in practice may be produced under controlled laboratory conditions with considerable consistency. Failure is confined to asymmetrically stressed specimens.

(ii) Concentrated sodium hydroxide solutions are more effective than dilute solutions, though failure has been obtained at a concentration of less than 10 per cent.

(iii) According to the present tests analytically pure sodium hydroxide solutions are equally as effective as solutions prepared from the commercial product. Silica is not therefore necessary to produce failure nor, apparently, does its presence stimulate it.

(iv) Tannin does not entirely inhibit cracking in these tests, though it definitely does so to some extent in practice.

(v) Anodic polarisation does not prevent, and may stimulate, intercrystalline failure. Cathodic polarisation is protective; in the only case where spontaneous failure occurred it was not accompanied by intercrystalline cracks.

(vi) Fine-grained steel is no more resistant to attack than a normal steel of approximately the same carbon content (0.10 per cent).

PART VII.

GENERAL DISCUSSION.

VII. GENERAL DISCUSSION.

In this, the concluding part of the report, it is proposed to discuss some matters of general interest in connection with caustic cracking, especially in their relation to the investigations described in the preceding parts and to the published work of other investigators. Its inclusion also presents an opportunity to discuss some points which have been omitted, either intentionally or inadvertently, in previous discussions.

It is not proposed to summarise in detail the published work on the subject, since several excellent synopses have appeared (74) (75) (18), but rather to indicate those factors which appear to influence the occurrence of caustic cracking, and to discuss the theories which have been advanced from time to time to account for the phenomenon.

1. FACTORS TENDING TO STIMULATE CAUSTIC CRACKING.

(i) Chemical. The property of stimulating caustic cracking has been attributed to a number of substances.

Schroeder, Berk, and O'Brien (76) regard potassium permanganate, sodium nitrate and lead oxide (litharge) as being necessary additions to sodium hydroxide solutions to produce failure of

U-bend specimens in the region of 120°C, though they found the first two substances to be protective at high temperatures. They also submit evidence that antimony, titanium and germanium salts stimulate attack. No support for these results has been forthcoming from other quarters, and, in particular, the writer has been unable to confirm the deleterious effect of the addition of nitrate in U-bend tests.

Silica is widely regarded as enhancing the selective attack of sodium hydroxide, and indeed many American workers appear to regard its presence as being necessary. Jenkins and Adcock (69) have shown, however, that failure may be produced in sodium hydroxide solutions of the highest purity, and the present writer's tests indicate that the pure product is equally as effective as the commercial, its properties in this respect being in no way influenced by the addition of silica.

The statistical analysis of Part III indicates that no particular significance is to be attached to the amount of silica present in Schroeder Detector tests, nor is there any evidence that failures in practice are in any way connected with the silica content of the feedwater.

In view of the results obtained by Schroeder and Berk (72) it seems probable that the presence of silica does hasten failure in certain laboratory tests, but the writer is inclined to attribute this to an increased rate of surface attack, as is indeed indicated by the work of Jenkins and Adcock.

(ii) *Conditions of stress.* There is general agreement that asymmetrical stressing greatly increases the susceptibility of steel to caustic cracking. Some workers, including the writer, have been unable to produce intercrystalline failure of symmetrically stressed specimens, but others have been successful in this respect (66) (72). In some cases (67) (69) the failure of symmetrically stressed specimens appears to be predominantly transcrystalline, and cannot be regarded as true caustic cracking, which, despite statements sometimes made to the contrary, is invariably almost purely intercrystalline.

Some controversy exists as to whether stresses must necessarily exceed the yielding stress of the steel in order that cracking may occur. Straub (7) has produced failure in a spheroidized steel at a stress just below the yielding stress, though he regards a stress in excess of this as being generally necessary. Jenkins and Adcock (69) found cracks in the enlarged portions of their specimens, and a somewhat similar occurrence has been noted in connection with Fig 35. of the present work. Definite evidence is lacking, but as far as practice is concerned, both in boilers and in caustic evaporators, cracking appears to set in invariably at areas in which plastic deformation has occurred.

The type of stress applied, (tension, bending or torsion) does not appear to be of material importance, provided tension stresses exist in the surface presented to the fluid.

(iii) The condition of the steel. Leaving aside questions of composition and structure, which will be considered later, it appears that all normal steels used in boiler practice are susceptible to failure by caustic cracking to more or less the same extent, though Colbeck, Smith and Powell (67) have indicated that low grade steel is rather more susceptible.

2 . FACTORS TENDING TO INHIBIT CAUSTIC CRACKING.

(i) Chemical. In laboratory tests carried out at 250°C, Schroeder, Berk and O'Brien (76) have produced results which indicate that the addition of nitrates or other oxidising agents to sodium hydroxide solutions renders them incapable of causing intercrystalline attack. As far as nitrates are concerned it is of great interest to note that these results have obtained some confirmation (77) in locomotive practice in the U.S.A., though the writer has been unable to obtain any confirmation from his statistical analysis.

Straub and Bradbury (66) consider that by simultaneously maintaining high $Na_2SO_4/NaOH$ and $NaCl/NaOH$ ratios embrittlement may be avoided.

They also regard a high R_2O_3/NaOH, where R represents iron or aluminium, as being effective. The statistical analysis of Part III offers no support to these claims nor, apparently, have they been substantiated by other workers.

Schroeder, Berk and O'Brien (68) have indicated that in laboratory tests phosphates, carbonates and sulphates offer some protection. As inhibitors, however, these substances did not appear to be particularly effective, though sodium sulphate was found to prevent cracking completely provided the sodium hydroxide concentration did not exceed about 25 gms/100 gms water. The situation as regards sodium sulphate is particularly interesting, since Straub in his early work attached great importance to the maintainance of a high SO_4/OH ratio. Recommendations embodying Straub's results were issued by the American Society of Mechanical Engineers. Later work (including that of Straub himself) has tended to discount the protective action of sulphate, but actually there is more support for these early claims than for many of those advanced later. Ulrich (65), in Germany, obtained similar results, and the confirmatory experiments of Schroeder and his colleagues have been mentioned above. Berl and van Taack (46) have shown that the presence of fairly small quantities of sodium sulphate in sodium hydroxide solutions is capable of reducing the corrosion rate of iron filings to a remarkable extent. Some qualified support is also offered by the statistical analysis of Part III, and in this connection it is of interest to note (Tables II and III) that it is the absolute sulphate content of the feedwater which is of significance, rather than the sulphate-hydroxide ratio.

Quite recently, a great deal of importance has been attached to certain organic compounds as inhibitors. Schroeder, Berk and O'Brien have found that sulphite waste liquor, lignin sulphonate and quebracho, among other substances are extremely effective in laboratory tests. Tannin was not entirely effective in preventing embrittlement - a result which has been confirmed by the writer. This observation is somewhat at variance with the results of Schroeder Detector tests. Lignin sulphonate has been used with some success on an American railway system (77). A point which is perhaps worth mentioning in this connection, is that among marine engineers it is generally held that waters containing a large amount of decayed vegetable matter (such as is found in the Panama Canal) are among the most suitable of feedwaters. Perhaps the remarkable immunity of boilers fed with raw water towards caustic cracking (Part III) is attributable to the same origin.

(ii) Polarisation. The tests described in Part VI of this report indicate that cathodic polarisation is definitely protective. This result is confirmed to some extent by the work of Jenkins and Adcock and of

Schroeder (78), though the work of these investigators differed in the essential aspect, that symmetrically stressed specimens were used. The matter is discussed below in relation to the theory that dissolved hydrogen is a contributory factor to caustic cracking.

(iii) Structure and Composition of the steel. The claims of German workers regarding the resistant properties of the fine-grained, non-ageing steel, Izett, have not been confirmed by other workers. The improvement in performance noted by the writer of the fine-grained steel E (Table XVII , Part VI) nevertheless appears to be considerably greater than one would expect from a comparison of its mechanical properties with those of steel C, and he feels that more attention should be devoted to this matter.

In a large number of tests, Straub (7) has shown that certain steels possess a high resistance towards caustic cracking, especially those of high chromium content (stainless steels). A steel containing 18 per cent chromium and 8 per cent nickel was also found to be highly resistant, but the writer's experiences in this connection should be noted (Appendix III)

3. THEORIES OF CAUSTIC CRACKING.

On the basis of his pioneer work on the subject of caustic cracking, Parr (6) arrived at the conclusion that failure could be attributed to the embrittling action of hydrogen occluded by the metal in the course of the corrosion process. Similar views were expressed by Jones (62) and Schroeder and his colleagues (79), among others, though Schroeder now holds a different opinion. Desch (80) (81) has long argued that caustic cracking is attributable in the first place to intergranular weakness induced in the metal by occluded hydrogen, thus rendering the grain boundaries susceptible to oxidising (anodic) attack. In this connection, it is interesting to note that Desch raises objections to the term "caustic embrittlement" since, as he quite correctly states, subsequent examination shows the metal to be quite ductile. This fact does not necessarily preclude the possibility that the metal is brittle at the time of attack, however, since in the absence of a maintained surface pressure of the dissolved gas hydrogen brittleness is a transient state. White and Schneidewind (82) have demonstrated the return of ductility to a cracked mild steel tube from a caustic evaporator on exposure to the air. A number of interesting experiments have been carried out by Adcock (83), who has succeeded in showing that hydrogen penetration, accompanied by intercrystalline cracks and decarburisation, may result from the action of sodium hydroxide solutions on cold-worked mild steel at 300°C and 410°C. In these tests, oxidising attack appeared to play a secondary part, being confined to within a short distance from the surface. In a lengthy summary of the literature, Zapffe (18) has vigorously argued the case for the hydrogen theory. He considers that failure may be totally attributed to cracks resulting from hydrogen brittleness and that the corrosion products found in many of the cracks result from the penetration of the alkali after they have been formed. Some support is offered to this contention by the fact that many caustic cracks are apparently free from corrosion products at points remote from the surface - as was also the case in Adcock's experiments.

Recently the view that hydrogen embrittlement is a major factor in causing caustic cracking has fallen somewhat into disrepute. Straub (7) considers that failure by intercrystalline cracking is largely to be attributed to the strain energy residing at the crystal boundaries of the distorted metal rendering them anodic towards the remainder of the metal. If the difference in potential is not too great, selective intergranular attack will occur. Straub also supposes that the hydrogen produced in the iron-alkali reaction reduces the oxide in the intergranular crevices to form water; the resulting increase in volume further increases the stress, thus tending both to facilitate attack and to produce failure directly. Schroeder, Berk and O'Brien

(76) consider that the coating of oxide formed on the metal surface will generally be discontinuous at the points overlying the boundaries of the surface crystals. The uncovered grain boundaries will then be anodic towards the oxide coating and selective attack will occur. They attribute the differing behaviours of the various solutions employed in their tests to variations in their film-forming characteristics. McAdam (84) considers that caustic cracking (and, indeed, intercrystalline stress-corrosion cracking in general) may be attributed to a particular form of corrosion-fatigue. Intercrystalline failure will be favoured by (a) high stress, (b) low cycle frequency, (c) slight general corrosion, and (d) very little accumulation of corrosion products. His views have not met with general support. U.R. Evans has expressed his views on this subject in some detail (85) (86). He suggests that the physical nature of the oxide produced on iron immersed in sodium hydroxide solutions at high temperatures is such as to enable it to act as a cathode towards the iron exposed at the network of cracks. This combination of large cathode area and small anode area tends to induce intense localised corrosion. The corrosion products resulting at lower temperatures are unsuited to act in this way. No stifling will occur since the presence of stress will prevent the formation of a continuous film at the bottom of the fissures. Under these circumstances the attack will tend to follow the grain boundaries since the energy change involved in removing an atom from this region will be considerably less than that involved in removing it from the undistorted lattice. He considers that intergranular attack will be especially favoured if the grain boundary layers are naturally anodic towards the bulk metal, or if circumstances permit the removal of the metal ions as complexes. Due to the "creeping power" of sodium hydroxide solutions, concentration cells of the type

Fe	/	NaOH (conc.)	/	NaOH (dil.)	/	Fe,
	crevice		liquid junction		metal surface	

are set up between the concentrated solutions in the crevices and the dilute solutions outwith them. Stifling and polarisation in the crevices will be prevented by the solution of the oxide film to form complex ions (p. 57).

A considerable proportion of the work carried out by the writer, and described in this report, has been devoted to an attempt to elucidate the question of the relationship of hydrogen embrittlement to caustic cracking. In this connection the following points may be noted.

(i) Embrittlement tests carried out at room temperature indicate that a quite serious loss in ductility may result from the electrolytic production of hydrogen at the surface of mild steel immersed in sodium hydroxide solutions. The fact that the cracks produced were mainly transgranular is not of material importance since, as has been already pointed out, slightly different conditions may result in their following an intergranular path. Cold-worked specimens proved themselves to be more susceptible, in agreement with Adcock's work at higher temperatures. Commercial sodium hydroxide was found to be more effective in producing embrittlement than the pure product, a fact which is suggestive, in view of the results of several investigators of caustic cracking in relation to this point. It has not been definitely determined whether the silica content of the solutions is the significant factor. One is also led to correlate the inhibiting action of tannin in these tests with the results described in Part III, though it is obvious that the film-forming characteristics of this substance may play the dual role of stifling anodic attack and preventing the penetration of hydrogen into the metal. The possibility of a relationship between the embrittling capacity of a solution and its overpotential characteristics has already been discussed.

(ii) Despite these results, it does not appear that hydrogen penetration alone will result in failure under conditions of symmetrical stress, since the tensile strength of mild steel is not materially reduced by its presence. Even a considerable amount of asymmetrical stressing may not result in failure, as has been indicated by the polarisation tests described in Part VI, though it must be remembered that in these tests the load was applied immediately before the commencement of polarisation. The plastic deformation of the still ductile metal would therefore tend to smooth out the stress gradients to some extent. The production of intercrystalline cracks in anodic tests in the same connection, does not necessarily disprove the theory that hydrogen plays an essential role, since under conditions of low anodic current density a certain amount of hydrogen may be formed at the cathodes of local action cells. To be more precise, provided the applied anodic potential does not render the potential of the cathodic areas of the metal surface more positive than that corresponding to the relevant reversible potential of the hydrogen electrode, the formation of hydrogen is still possible.

(iii) Both in practice and in laboratory tests caustic cracking is intergranular throughout. This would appear to indicate a general intergranular weakness, for, if failure were due solely to the fissures initially formed by intergranular corrosion, one might expect the cracks to be propagated in a normal transgranular fashion under the influence of the applied stress.

(iv) In connection with the evolution of hydrogen from the stressed areas of a U-bend specimen noted in Part IV, an interesting observation of Colbeck's (87) has just come to the writer's notice. In experiments on concentration cells of the type

Fe / NaOH (conc.) / NaOH (dil.) / Fe

this worker has found that, though the electrode immersed in the concentrated solution was initially anodic, it later became cathodic towards the electrode in the dilute solution. The opinion expressed by the writer in connection with his observation that an initially anodic area may eventually become cathodic towards the remainder of the surface is thus confirmed to some extent.

(v) The striking similarity between caustic cracks and those produced by ammonium nitrate and other nitrate solutions leads one immediately to suspect that they have a common origin. The wide divergence in chemical and physical properties of the caustic alkalis and the nitrates renders the view that cracking is due to specific and selective anodic attack somewhat improbable. In particular, the role attributed by Evans to complex formation in sodium hydroxide solutions does not hold in ammonium nitrate solutions. The writer's experiments on polarised U-bend specimens immersed in ammonium nitrate solutions, which indicated that conditions permitting hydrogen evolution are essential for the production of intergranular failure, indicate that if the similarity between the two cases is real, then hydrogen penetration is the common denominator. The precise conditions under which intergranular failure will result, might reasonably be expected to differ as between hydroxide and nitrate solutions, and an investigation correlating the two groups seems highly desirable.

On the basis of the points ennumerated above and of previous discussions throughout the report, the writer's view of the mechanism of caustic cracking may be summarised briefly in these terms:- In the initial stages of the attack of concentrated alkali on stressed steel, a non-protective oxide film is formed, the process being accompanied by the formation and partial occlusion of hydrogen. As corrosion proceeds, surface pitting takes place (by virtue of the stress present in the metal) which may or may not be intergranular (cf., Fig. 38). Stress concentrations are set up at the bottoms of the pits, which result in intergranular cracking of the metal now rendered brittle by the occluded hydrogen. The subsequent penetration of these cracks by the alkali results in the formation of a voluminous oxide. They are thus widened, giving rise to the typical intergranular fissures. The local stresses set up by the oxide formed in the cracks in company with the applied stress facilitates their propagation, always in an intergranular manner, until finally rupture occurs. This conception of caustic cracking conforms largely with that advanced by Desch, and also by Zapffe, though it implies to some extent the views of Evans with regard to the possibility of a corrosion process taking place in the cracks without stifling itself through film formation or polarisation.

APPENDIX I.

APPENDIX I

CONTINGENCY METHODS.

1. Preliminary Theorems.

Though a discussion of the mathematical basis of the χ^2 - test is scarcely necessary for our purposes, a brief account is given here for the sake of completeness.[x]

A few preliminary theorems on gamma variates may first be established. The frequency distribution of such a variate of parameter $\underline{l}$ is given by

$$dF = \frac{e^{-x} \,.\, x^{l-1} \,.\, dx}{\Gamma(l)} \qquad (x \geqslant 0)$$

The factor $\Gamma(l)$ normalising the function so that $\int_0^\infty dF = 1$.

Now consider a normally distributed variate $\underline{x}$ with mean zero and standard deviation $\underline{\sigma}$. The distribution function is

$$dP_x = \frac{e^{-x^2/2\sigma^2}}{\sigma\sqrt{2\pi}} \,.\, dx.$$

---

[x] A good account is given by Weatherburn, "Mathematical Statistics", Cambridge (1947).

Making the substitution

$$u = \frac{x^2}{2\sigma^2}$$

we get

$$dP_x = \frac{e^{-u}}{\sigma\sqrt{2\pi}} \cdot \frac{du}{\sqrt{2u}}$$

Now as x varies from $-\infty$ through 0 to $+\infty$, u varies from $+\infty$ to 0 and again to $+\infty$; hence the probability distribution P_u, of u is twice as dense as that of x. Thus

$$\begin{aligned} dP_u = 2dP_x &= \frac{1}{\sqrt{\pi}} \cdot \frac{e^{-u}}{\sqrt{u}} \cdot du \\ &= \frac{e^{-u} \,.\, u^{1-\frac{1}{2}}}{\sqrt{\pi}} \cdot du \\ &= \frac{e^{-u} \,.\, u^{1-\frac{1}{2}}}{\Gamma(\frac{1}{2})} \cdot du \end{aligned}$$

since $\sqrt{\pi} = \Gamma(\frac{1}{2})$.

That is the distribution of u or $\frac{1}{2}\cdot\frac{x^2}{\sigma^2}$ is a gamma variate of parameter $\frac{1}{2}$.[x]

Now let x and y be independent gamma variates of parameters l and m respectively and let $z = x + y$; we require the distribution of z.

---

[x] This is true also if the normal distribution has a mean differing from zero.

First of all, let y have a fixed value in the interval dy then $dz = d\,(x+y) = dx$. The probability that z lies in the interval dz is then

$$dp_x = dp'_z = \frac{e^{-(z-y)}}{\Gamma(l)} \cdot (z-y)\,dz$$

But the probability that y should have a given value in the interval dy is

$$dp_y = \frac{e^{-y} \cdot y^{m-1}}{\Gamma(m)}\,dy$$

Hence the probability of the combined event that y should have a value in dy and z a value in dz is

$$dp_y \cdot dp'_z = \frac{e^{-z} \cdot dz}{\Gamma(l)\,\Gamma(m)} \cdot (z-y)^{l-1}\, y^{m-1} \cdot dy$$

Now x and y are +ve variates (otherwise the gamma integral does not converge), and hence y may assume any value in the range 0 to z. Hence the probability that z should have a value in the interval dz is

$$dp_z = \frac{e^{-z} \cdot dz}{\Gamma(l)\,\Gamma(m)} \int_0^z (z-y)^{l-1} \cdot y^{m-1}\,dy.$$

To evaluate this integral we make the substitution $y = zt$. Thus, for a given value of z, $dy = z\,dt$, and the integral becomes

$$dp_z = \frac{e^{-z} \cdot dz}{\Gamma(l)\,\Gamma(m)} \cdot \int_0^1 z^{l-1}\, (1-t)^{l-1} \cdot (zt)^{m-1} \cdot z\,dt.$$

$$dp_z = \frac{e^{-z} . z^{m+l-1} . dz}{\Gamma(l) . \Gamma(m)} . \times \int_0^1 (1-t)^{l-1} . t^{m-1} . dt .$$

$$= \frac{B(m, m)}{\Gamma(l) . \Gamma(m)} . e^{-z} . z^{m+l-1} . dz$$

$$= \frac{e^{-z} . z^{m+l-1} . dz}{\Gamma(m+l)}$$

Hence z is a gamma variate of parameter $(l+m)$. By extension of this reasoning it may simply be shown that the sum of any number of gamma variates x, y, z .... of parameters l, m, n ..... respectively is a gamma variate of parameter $(l + m + n + \ldots\ldots\ldots)$.

It follows from the above result and the previous one that if m_i $(i = 1, 2, \ldots\ldots n)$ are n independent variables with standard deviation σ_i and common mean zero, then $\sum \left(\frac{1}{2} \frac{m_i^2}{\sigma_i^2}\right) = \frac{1}{2}\chi^2$ is a gamma variate with parameter $(\frac{1}{2}n)$.

Contingency Methods.

Let a sample of N members of a population be grouped according to the h characteristics ω_1, ω_2, ..., and let the probability that any member of N have the characteristic ω_i be p_i. Then according to a well known generalisation of Bernoulli's Theorem, the probability[x] that there are n_1 members of ω_1, n_2 members of

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[x] cf. Levy & Roth, "Elements of Probability", Oxford (1936)

$\underline{w_2}$, ... is

$$P_m = p_1^{m_1} \cdot p_2^{m_2} \cdots\cdots p_r^{m_r} \cdot \frac{N!}{m_1!\, m_2! \ldots m_r!} \qquad (1)$$

Now if the $\underline{m_i}$ are not small we may write Stirling's formula for the factorial, viz:-

$$m! \simeq \surd(2\pi)\, m^{m+\frac{1}{2}} e^{-m} \quad \text{in (1):}$$

$$P_m = p_1^{m_1} \cdot p_2^{m_2} \cdots p_n^{m_n} \frac{N^{N+\frac{1}{2}} \cdot e^{-N} \sqrt{2\pi}}{m_1^{m_1+\frac{1}{2}} e^{-m_1} \sqrt{2\pi} \cdots m_n^{m_r+\frac{1}{2}} e^{-m_r} \sqrt{2\pi}}$$

That is

$$P_m = k \left(\frac{Np_1}{m_1}\right)^{m_1+\frac{1}{2}} \cdots\cdots \left(\frac{Np_r}{m_r}\right)^{m_n+\frac{1}{2}} \qquad (2)$$

where $\underline{k}$ is a constant, since $N = \sum_1^r m_i$.

Now write

$$\nu_i = Np_i$$

and

$$\xi_i = \frac{m_i - Np_i}{\surd(Np_i)} = \frac{m_i - \nu_i}{\nu_i^{1/2}}$$

hence $m_i = \nu_i + \nu_i^{1/2} \xi_i$

Substituting these transformations in (2) gives

$$\log P_m - \log k = \sum_i \left[(m_i + \tfrac{1}{2}) \cdot \log \frac{\nu_i}{m_i} \right]$$

$$= \sum_i (m_i + \tfrac{1}{2}) \log \frac{\nu_i}{\nu_i + \nu_i^{1/2} \xi_i}$$

$$= -\sum_i (\nu_i + \tfrac{1}{2} + \nu_i^{1/2} \xi_i) \log \left(1 + \frac{\xi_i}{\nu_i^{1/2}}\right)$$

Now if ν_i is large ξ_i will be small in comparison, hence we may write

$$\log P_m - \log k = -\sum_i \left(\nu_i + \tfrac{1}{2} + \nu_i^{\frac{1}{2}}\xi_i\right) \times \left(\frac{\xi_i}{\nu_i^{1/2}} + \frac{1}{2}\frac{\xi_i^2}{\nu_i}\right)$$

$$= -\sum_i \left[\tfrac{1}{2}\xi_i^2 + \xi_i\nu_i^{\frac{1}{2}} + O(\nu_i^{-\frac{1}{2}})\right]$$

where $O(\nu_i^{-\frac{1}{2}})$ denotes terms of order $-\frac{1}{2}$ or less in ν_i .

Now $\sum_i (\xi_i \nu_i^{\frac{1}{2}}) = \sum_i (m_i - \nu_i) = N - N = 0$

since $\sum_i p_i = 1$.

and hence, to order $\nu_i^{1/2}$,

$$\log P_m - \log k = -\tfrac{1}{2}\sum_i \xi_i^2$$

$$\therefore \quad P_m = k e^{-\frac{1}{2}\sum_i \xi_i^2}$$

That is, the frequency P_m varies as the sum of the squares of r normal variates of zero mean and standard deviation unity, hence from the preceding section $\frac{1}{2}\chi^2 = \frac{1}{2}\sum\xi_i^2$, is a gamma variate. But the variates ξ_i are subject to the linear restriction

$$\sum \xi_i \nu_i^{\frac{1}{2}} = 0 \qquad (3)$$

Hence there are in effect only $r-1$ independent normal variates, and the distribution of χ^2 (or rather $\frac{1}{2}\chi^2$) becomes (see below)

$$dP_\chi = \frac{1}{2^{\frac{n-1}{n}}\,\Gamma\left(\frac{n-1}{2}\right)} \cdot e^{-\frac{1}{2}\chi^2} (\chi^2)^{\frac{1}{2}(n-3)} \cdot d(\chi^2)$$

or

$$dP_\chi = \frac{1}{2^{\frac{n-1}{n}}\,\Gamma\left(\frac{n-1}{2}\right)} \cdot e^{-\frac{1}{2}\chi^2} \cdot \chi^{n-2} \cdot d\chi$$

Now let us examine the effect of linear restraints on the variates $\underline{\xi_i}$ [x] of which (3) above is an example.

Let the variates $\underline{\xi_i}$ be represented by a point in $\underline{N}$ -fold space. Then the density of distribution at this point is given by

$$k \cdot e^{-\frac{1}{2}\Sigma\xi_i^2} = k\, e^{-\frac{1}{2}OP^2}$$

where OP is the distance of the point P from the origin. Now, for any given value of $-\frac{1}{2}\Sigma\xi_i^2$ the density of distribution is constant over the hypersphere of radius OP. If now the variates are subject to $\underline{s}$ linear restraints of the type

$$a_1\xi_1 + a_2\xi_2 + \dots + a_n\xi_n = b \qquad (4)$$

This is equivalent to restricting the assumable values of $\underline{\xi_i}$ to the surface of intersection of the

[x] The constraints are usually linear with respect to the m_i , but it may then be shown that they are also linear with respect to the $\underline{\xi_i}$.

hypersphere of r dimensions and the s hyperplanes of which (4) is a type, that is to a sphere of $(r - s)$ dimensions. Hence the distribution of $\sum \xi_i^2$ will be as before with $\rho = (r - s)$ substituted for r. The variate ρ is then called the degree of freedom of the sample N.

The distribution of χ^2 then becomes

$$dP_{\chi^2} = \frac{1}{2^{\frac{1}{2}(\rho - 2)}\Gamma(\frac{\rho}{2})} \cdot e^{-\frac{1}{2}\chi^2} \cdot \chi^{\rho-1} \cdot d\chi .$$

The probability $P(\chi^2)$ that a given value χ_0^2 will be exceeded in random sampling is then given by the integral

$$P(\chi_0^2) = \int_{\chi_0^2}^{\infty} dP_{\chi^2}$$

and values of χ_0^2 for values of $\rho = 1$ to 30 and for fixed values of P have been tabulated by Fisher (cf p.42, and Fig. 7)

APPENDIX II.

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APPENDIX II.

THE PREPARATION AND DETERMINATION OF CONCENTRATED SOLUTIONS OF SODIUM HYDROXIDE.

A concentrated (approximately 45 per cent) solution is first prepared, by dissolving A.R. sodium hydroxide in a resistance-glass boiling flask which has been well seasoned with caustic alkali over a period of several weeks. Distilled water is used, and it is preferable, though not essential, that this should previously have been freed from dissolved carbon dioxide, Sodium carbonate, which is insoluble in the lye, is allowed to settle out; sedimentation may be hastened considerably by immersing the flask in a water bath at 40°C. The lye is then allowed to rest for a few days until it is perfectly clear, when it may be carefully decanted through a sintered-glass Büchner funnel into a seasoned flask of resistance glass or into a waxed bottle.

The molality of the solution thus prepared may be estimated by neutralising a known weight with hydrochloric acid, and weighing the evaporated residue as sodium chloride (88), or, since highly reliable data are available (89) (90), by a density method.

Solutions of lower molality may be prepared by weighing into a known weight of the lye the

the requisite quantity of carbon dioxide-free distilled water. This is determined from the equation

$$y = \frac{1000\ x}{1000 + m_1 M_w} \left\{ \frac{m_1}{m} - 1 \right\} \quad \text{gm.},$$

where $\underline{x}$ is the weight of lye taken, $\underline{m_1}$ its molality, $\underline{M_w}$ the molecular weight of sodium hydroxide, and $\underline{m}$ the molality of the solution desired. Solutions of low molality may be checked by titration, and if the two-indicator method is used the residual carbonate content may be estimated. By these methods it is possible to set up solutions of known molality with an accuracy of 0.2 per cent or better, and of negligible carbonate content.

Where a more approximate method will suffice, as in the preparation of solutions of the commercial product, the same preparative methods may be used, substituting tap water,[x] for distilled water. In view of the impurities in the commercial solution it is best to determine its molality by titration of a known weight.

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[x] The water supplied to the University contains a negligible quantity of dissolved salts, and in particular its silica content is extremely low.

APPENDIX III.

100x. Etched.

Fig. 39.

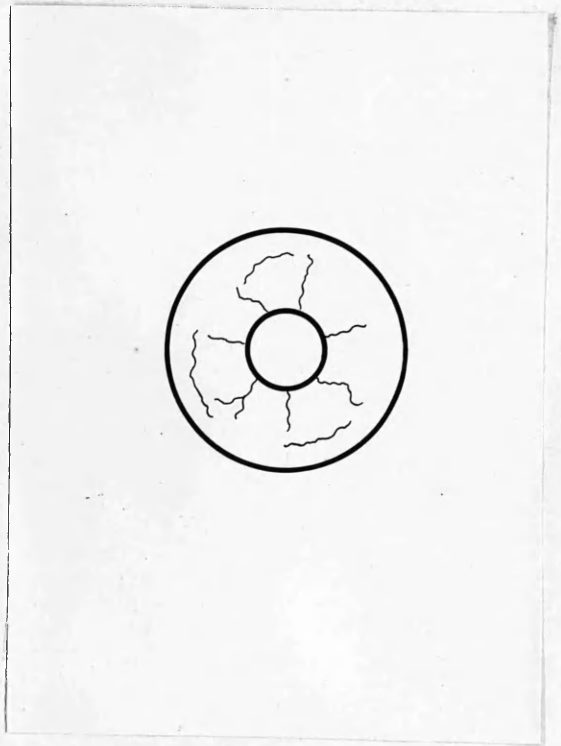

Fig. 40.

APPENDIX III.

FAILURE OF THE AUTOCLAVES OF "18 - 8" STEEL.

It has already been mentioned that the original autoclaves used in the stress-corrosion tests (Part VI) had to be discarded, because they proved to be unsatisfactory in service. The reasons leading to their rejection are of some interest, and are recounted briefly below.

According to published data (91), and in the experience of the steelmakers, the austenitic 18 per cent chromium, 8 per cent nickel stainless steel used in the making of these autoclaves shows a good resistance towards caustic alkali, and, as far as the writer is aware, there are no records of failure of this material due to the action of caustic alkali.

The first of the autoclaves was placed in service in November, 1946, and showed a quite satisfactory resistance towards surface attack. After the apparatus had been in service for an aggregate of about 200 hours, however, it was found that a large number of extremely fine cracks had developed on the inside surface of the autoclave. Cracking appeared to have set in first at the base, and to have spread later over the entire internal surface. A micrograph of a typical crack is shown in Fig.39 . It will be observed that it is quite straight, paying no attention to grain boundaries or to twinning planes, and free from corrosion products. There is no evidence of distortion in the surrounding metal.

Tests were immediately stopped on the discovery of the cracks, and the material returned to the makers for examination. In their report they made the following observations;

(i) The metal showed no abnormal properties, either with regard to mechanical properties or corrosion resistance.

(ii) It had been suggested that the cracking might be attributed to hydrogen embrittlement, but an attempt to induce embrittlement had, however, yielded negative results.

(iii) They were unable to recommend any suitable alternative material.

At the writer's request he was furnished with a number of short bars of different materials. In these, central holes were drilled to a depth of about 4 in. Into the cavities thus formed a little 40 per cent commercial caustic soda lye,was poured and the cavities sealed by welding over a plug inserted at the open end. The bars (or, rather capsules) were then placed in an oven and maintained at a temperature of approximately 200°C for 14 days. At the end of this period the capsules were removed, sectioned and polished, and carefully examined.

TABLE XIX

ANALYSES AND CORROSION RESISTANCE OF VARIOUS STEELS.

Specification.	C.	Mn.	Ni.	Cr.	Test Results.
18/8 (1)	0.12	0.57	8.4	17.9	Oxide coating. No cracks.
18/14 (1)	0.15	0.55	13.5	18.1	Light oxide coating. Extensive cracks.
Stainless iron (2)	0.08	0.48	0.44	13.1	Heavy oxide coating. No cracks.
18/2 (2)	0.17	0.86	0.198	17.0	-- ditto --
36 Ni (3)	0.12	0.41	36.1	0.19	Very light oxide coating. No cracks.

(1) Water quenched from 1050°C. (Free from intergranular corrosion as supplied)

(2) Oil quenched 950°C. Tempered 650°C.

(3) As forged.

The results of this little investigation, together with the analyses of the materials tested, are given in Table XIX. The results were confirmed by magnetic crack-detection tests, except in the cases of the non-magnetic 18 - 14 and 18 - 8 chromium-nickel steels. The cracks observed in the 18 - 14 material were similar in appearance to those shown in Fig 39 , being extremely fine and completely free from corrosion products. Their distribution is indicated in the sketch of Fig 40 .

The only probable explanation which the writer can suggest for the occurrence of these cracks, and of those in the autoclave, is that they are due to hydrogen embrittlement, for, in view of the mechanical properties of the materials, and of the position and nature of the cracks, factors such as overstressing, intergranular weakness (σ - phase), and selective corrosion may be safely discounted. If this view is accepted, then the capsule experiments offer some support to the views expressed by the writer in connection with caustic cracking. It is, moreover, particularly interesting to note that despite the fact that only slight corrosion of the 18 - 14 alloy occurred, sufficient hydrogen apparently diffused into the metal to cause very serious embrittlement.

It will be obvious from the results of Table XIX that the only definitely resistant material tested was that containing 36% nickel, and this was finally adopted in the manufacture of the autoclaves. As far as may be judged from the limited service which they have undergone, the behaviour of the new autoclaves is entirely satisfactory.

BIBLIOGRAPHY.

Note: The abreviations employed here conform as far as possible to those adopted by U. R. Evans, "Metallic Corrosion, Passivity and Protection." In cases where the original reference was not available the writer has included also the source of his information.

(1) S. A. Houghton, J. West Scotland Iron Steel Inst., v.25 (1917-18), p.153.

(2) E. B. Wolff, J. Iron Steel Inst., v.96 (1917), p.137.

(3) E. Pfleiderer, "Dampfkesselschäden," Berlin (1934) p.185.

(4) C. E. Stromeyer, discussion of paper by S. A. Houghton, J. Iron Steel Inst., v.89 (1914), p.266.

(5) C. E. Stromeyer, Engineering, v.104 (1917), p.645.

(6) S. W. Parr, Univ. Illinois Bull., No.94 (1917), 55 p.p.

(7) F. G. Straub, Univ. Illinois Bull., No.216 (1930), 125 p.p.

(8) E. Berl and F. van Taack, Archiv Wärmewirtschaft Dampfkesselwesen, v.9 (1928), p.165; see E.P. Partridge and W. C. Schroeder, Met. Alloys, v.6 (1935), p.145.

(9) W. P. Rees, Ref. (67) (communication); also A. H. Goodger, Ref. (67) (communication).

(10) A. H. Goodger, Ref. (67) (communication).

(11) (Sir) H. Carpenter and J. M. Robertson, "Metals", London (1939), v. II, p.872.

(12) W. Rosenhain and D. Ewen, J. Inst. Metals, v.8 (1912), p.149.

(13) W. Rosenhain, Trans. Faraday Soc., v.17 (1921-22), p.2.

(14) H. C. J. Czochralski and H. Schreiber, Korr, Met., v.13 (1937), p.181; see Ref. (26) p.468.

(15) C. S. Barrett, "Structure of Metals," New York (1943, Ch. XXII.

(16) C. Carius and E. H. Schulz, in "Korrosion metallischer Werkstoffe" (ed. Bauer - Kröhnke - Masing), Leipzig, v. I (1936), p.356.

(17) C. A. Zapffe and C. E. Sims, Trans. Amer. Inst. Min. Met. Eng., v.145 (1941), p.225.

(18) C. A. Zapffe, Trans. Amer. Soc. Mech. Eng., v.66 (1944), p.81.

(19) T. N. Morris, J. Soc. Chem. Ind., v.54 (1945), p.7 T.

(20) C. H. Edwards, J. Iron Steel Inst., v.110 (1924), p.9.

(21) P. Bardenheuer and G. Thanheiser, Mitt. Kaiser Wilhelm Inst. Eisenforsch., v.10 (1928), p.323.

(22) A. H. W. Aten (et al.), Rec. Trav. Chim., v.49 (1930) p.641; v.50 (1931), p.943.

(23) H. Bablik, Korr. Met., v.11 (1935), p.169; see Ref. (26), p.218.

(24) D. Alekseev and M. Polukarov, Zeit. Elektrochem., v.32 (1926), p.248.

(25) D. Alekseev, P. Afanasiev, and W. Ostroumov, Zeit. Elektrochem., v.40 (1934), p.92.

(26) U. R. Evans, "Metallic Corrosion, Passivity and Protection," London (1946),p.218.

(27) P. Bardenheuer and H. Ploum, Mitt. Kaiser Wilhelm Inst. Eisenforsch., v.16 (1934), p.129; see G. Thanheiser in "Korrosion metallischer Werkstoffe," (ed. Bauer - Kröhnke - Masing), Leipzig, v. III (1940), p.51.

(28) L. B. Pfeil, Proc. Roy. Soc., v.112, Series A (1926), p.182.

(29) C. A. Zapffe and G. A. Moore, Trans. Amer. Inst. Min. Met. Eng., v.154 (1943), p.335.

(30) G. V. Smith, Ref.(17) (discussion).

(31) C. S. Barrett and G. Derge, Ref. (29) (discussion)

(32) A. Sieverts and P. Lueg, Zeit. anorg. allg. Chem., v.126 (1923), p.193.

(33) W. H. Creuzfeldt, Zeit. anorg. allg. Chem., v.154 (1926), p.213.

(34) C. H. Desch, Trans. Faraday Soc., v.17 (1921-22), p.17.

(35) Ref. (26), p.521.

(36) P. Bardenheuer and H. Ploum, Mitt. Kaiser Wilhelm Inst. Eisenforsch., v.16 (1934), p.137; see C. H. Desch, "Metallography", London (1944), p.297.

(37) W. Rosenhain and S. L. Archbutt, Proc. Roy. Soc., v.95, Series A (1919-20), p.55.

(38) C. H. M. Jenkins and G. A. Mellor, J. Iron Steel Inst., v.132 (1935), p.179; see Ref. (II) v. I, p.184.

(39) See Ref. (38).

(40) W. Rosenhain and D. Hanson, J. Iron Steel Inst., v.116 (1927), p.117.

(41) W. C. Schroeder, A. A. Berk and R. A. O'Brien, Combustion, v.12 (1940), p.19.

(42) C. D. Weir, Mech. Eng., v.67 (1945) p.834.

(43) (Sir) R. A. Fisher, "Statistical Methods for Research Workers", Edinburgh (1944), p.112-113.

(44) E. P. Partridge, C. E. Kaufman, and R. E. Hall, Trans. Amer. Soc. Mech. Eng., v.64 (1942), p.417.

(45) E. Heyn and O. Bauer, Mitt. Mat. Prüf. Amt (Anstalten), v.26 (1908); see Ref. (16), p.151.

(46) E. Berl and F. van Taack, Forschungsarb Geb. . Ingenieurw., v.330 (1930); see Ref. (16), p.252.

(47) See Ref. (8).

(48) G. Schikorr, Zeit. Elektrochem., v.35 (1929), p.62.

(49) G. Schikorr, Zeit. Elektrochem., v.35 (1929), p.65.

(50) A. Krause, Zeit. anorg. allg. Chem., v.174 (1928), p.145.

(51) G. Grube and H. Gmelin, Zeit. Elektrochem., v.26 (1920), p.459.

(52) C. D. Weir, Nature, v.160 (1947), p.259.

(53) R. H. Fowler, Trans. Faraday Soc., v.28 (1932), p.368.

(54) T. Erdey-Grúz and M. Volmer, Zeit. phys. Chem., v.150 (1930), p.203.

(55) A. Hickling and F. W. Salt, Trans. Faraday Soc., v.38 (1942), p.474; see also ibid. v.36 (1940), p.1226; v.37 (1941), pp.224, 319, 333, 450.

(56) J. A. V. Butler, "Electrocapillarity," London (1940), p.146.

(57) D. Alekseev and P. Perminov, Zeit. Elektrochem., v.40 (1934), p.823.

(58) T. Krassó, Zeit. Elektrochem., v.40 (1934), p.826.

(59) N. Kobosev and N.I. Nekrassov, Zeit. Elektrochem., v.36 (1930), p.529.

(60) W. C. Schroeder, A. A. Berk, and R. A. O'Brien, Met. Alloys, v.8 (1937), p.320.

(61) M. Smialowski, Korr. Met., v.14 (1938), p.111; see Metallurgist, v.11 (1937-38). p.160.

(62) J. A. Jones, Trans. Faraday Soc., v.17 (1921-22), p.102.

(63) W. Rosenhain and D. Hanson, J. Iron Steel Inst., v.102 (1920), p.23.

(64) See Ref. (26), p.437. (Unpublished results).

(65) M. Ulrich, "Werkstofffragen des heutigen Dampfkesselbaues," Berlin (1930); see Ref. (3), p.185 ff.; Ref. (16) p.391 ff.

(66) F. G. Straub and T. A. Bradbury, Mech. Eng. v.60 (1938), p.371.

(67) E. W. Colbeck, S. H. Smith, and L. Powell, Proc. Inst. Mech. Eng. v.149 (1943), p.63.

(68) W. C. Schroeder, A. A. Berk and R. A. O'Brien, Trans. Amer. Soc. Mech. Eng., v.60 (1938) p.35.

(69) C. H. M. Jenkins and F. Adcock, J. Iron Steel Inst., v.143 (1941) p.102P.

(70) P. G. Bird and E. G. Johnson, Trans. Amer. Soc. Mech. Eng. v.64 (1942), p.409.

(71) W. C. Schroeder and E. P. Partridge, Trans. Amer. Soc. Mech. Eng., v.58 (1936), p.387.

(72) W. C. Schroeder and A. A. Berk, Trans. Amer. Inst. Min. Met. Eng., v.120 (1936), p.387.

(73) O. Bauer, Mitt. Mat. Pruf. Anst., Sondh. V (1929), p.12.

(74) E. P. Partridge and W. C. Schroeder, Met. Alloys, v.6 (1935), pp.145, 187, 253, 311, 355.

(75) C. H. Desch, Trans. N.E. Coast Inst. Eng., v.55 (1938-39), p.111.

(76) W. C. Schroeder, A. A. Berk and R. A. O'Brien, Met. Alloys, v.8 (1937), p.320.

(77) R. C. Bardwell and H. M. Laudemann, Trans. Amer. Soc. Mech. Eng. v.64 (1942), p.403.

(78) W. C. Schroeder, Ref. (18), (discussion).

(79) E. P. Partridge and W. C. Schroeder, Met. Alloys, v.6 (1935), p.187.

(80) C. H. Desch, J. Iron Steel Inst., v.143 (1941), p.93P.

(81) C. H. Desch, Ref. (67) (discussion).

(82) A. E. White and R. Schneidewind, Trans. Amer. Soc. Mech. Eng., v.53 (1930), p.193.

(83) F. Adcock, J. Iron Steel Inst., v.143 (1941), p.117 P.

(84) D. J. McAdam, Proc. Amer. Soc. Test. Mat., v.31 (II) (1931), p.259.

(85) U. R. Evans, Ref. (80) (etc.), (discussion).

(86) U. R. Evans, Ref. (67), (discussion).

(87) E. W. Colbeck, see Ref. (26), p.579.

(88) G. Akerlöf and G. Kegeles, J. Amer. Chem. Soc., v.62 (1940), p.620.

(89) G. Akerlöf and G. Kegeles, J. Amer. Chem. Soc., v.61 (1939), p.1027.

(90) Int. Crit. Tab., New York, v.III (1928), p.79.

(91) E. Houdremont and H. Schottky, in "Korrosion metallischer Werkstoffe," (ed. Bauer - Kröknke - Masing), Leipzig, v. I (1936), p.474.