significant. The three sporadic examples I have named seemed to show the characteristic features of this type of structure already fully developed. The broch did not spring full-grown from the brain of some architectural genius of the prehistoric period ; it was the outcome of a slow process of evolution. The southern brochs can only have been built by intruders from the north.

We may go further. Seventeen or eighteen years ago, in surveying Sutherland and Caithness for the Royal Commission, Mr. Curle noted certain points which seemed to him to indicate a gradual improvement in the type as one moved inland from the western coast, and he saw in this—rightly, as I think—a clue to the drift of the population. His deduction has received remarkable confirmation from the Commission's recently published survey of Skye and the Outer Isles, as well as from the late Dr. Erskine Beveridge's investigations in Tiree. In the insular region we find brochs in reasonable abundance—44 are recorded there by the Royal Commission—but we also find numerous specimens of what can best be described as the broch in the making. The so-called ' semi-brochs ' of Tiree, the ' galleried duns ' of the Hebrides and Skye, all alike appear to represent experiments in the architectural form which was destined to have its fullest expression on the mainland. As the broch-builders moved farther north and then farther east, they carried with them the fruits of their ripening experience.

The facts of early Scottish history and the inferences as to the Bronze Age and the Early Iron Age are thus in complete accord. They bear out the view—in itself *a priori* probable—that for uncounted generations the trend of migration was from the direction of Ireland through the islands of the west coast to the north of Scotland. We may reasonably assume that an exhaustive examination of the chambered cairns, in continuance of the work carried out with such marked success by Prof. Bryce, would give a similar result for the Neolithic Period.

Once the set of the current has been determined, it is not difficult to understand why regions, where the sheep and the deer now wander at will, should have been thickly populated in prehistoric times. Although the causes that prompted the movements of peoples in those far-off days are obscure, one of the most potent was certainly the demand that would be created for fresh means of subsistence when the mouths to be fed were multiplied. At intervals a surplus of humanity would be spilled from Ireland. In front there stretched but one open road, and that was a *cul de sac*. For, to those who followed this route, northern Scotland was literally the end of the world.

Long afterwards, under the pressure of a similar urge, a similar stream descended from Scandinavia. But the later immigrants came in stout ships, and could at need deflect their course, as they did, to the Faroes, to Iceland, even to Greenland. With the earlier wanderers it was different. When they had reached Unst, they would scan the horizon in vain for any sign of land to tempt their frail craft further. The ocean was an insurmountable barrier. The flow from the south would be brought to a standstill on its shore, and the more nearly that limit was approached, the greater would the congestion of population tend to become. This, I think, is the real secret of the abundance of Scotland's prehistoric remains.

Active Nitrogen.

By C. N. HINSHELWOOD.

IN 1900, E. P. Lewis observed that nitrogen could be stimulated by an electric discharge to emit a bright yellow glow, which continued for some time after the discharge had ceased ; he made a number of spectroscopic observations on the glowing nitrogen. The present Lord Rayleigh investigated the phenomenon in a more general and systematic manner, discovered that the glowing gas had remarkable chemical properties, and named it ' active nitrogen.'

Certain important conditions must be observed for its production. The pressure of nitrogen should be a few millimetres of mercury : at higher pressures collisions with ordinary nitrogen molecules apparently destroy the glowing substance. The best procedure is to draw a stream of rarefied nitrogen through the discharge tube by means of a pump. The persistence and gradual decay of the glow in the gas which has left the region of the discharge can then be easily observed. When the discharge is from an induction coil, it should be a ' condensed ' discharge, the use of the condenser giving a sudden intense current. The importance of this condition can be seen from the fact that if an uncondensed discharge is passed through the gas rendered luminous by passage through a condensed discharge, the glow is actually destroyed. Finally, the presence of a small proportion of some other gas in the nitrogen is necessary for the production of the luminescence.

At first it was thought that a little oxygen must be present, but methane, hydrogen sulphide, ethylene, and various other substances are equally efficacious. It seems to be generally agreed that a trace of some ' electronegative ' gas, that is, a gas which readily takes up electrons to give negative ions, is the essential thing. A few parts per thousand of the foreign gas produce the most intense glow : larger amounts destroy it. In the presence of more than about 2 per cent oxygen, the nitrogen does not glow at all. Rayleigh thought that pure nitrogen still could be made to emit a faint glow, but Bonhoeffer and Kaminsky have shown that it emits none at all.

The glowing nitrogen was shown by Rayleigh to have great chemical reactivity, and also to excite many substances to luminescence. It reacts with acetylene to give hydrogen cyanide, and with mercury to give a nitride. Mixed with iodine vapour, it produces a brilliant blue light. Hydrogen

and the inert gases merely dilute the glow, but oxygen extinguishes it altogether. The reaction with nitric oxide is important : the gases interact with the production of a greenish flame, the evolution of heat, and the formation of nitrogen peroxide and nitrogen. Rayleigh and, later, Willey and Rideal have used this reaction as a means of estimating the concentration of the active body in a gas stream.

The nature of active nitrogen and the mechanism of its formation and decay have been the subjects of much research and speculation. The problem is not yet completely solved, but the range of possibilities has been very much narrowed down.

In the first place, although the production of the glow is determined by the presence of other gases, the actual emission process is one, apparently, in which nitrogen alone is concerned, for the spectrum is identical whether the impurity is oxygen, methane, or hydrogen sulphide. Moreover, the most important group of bands, the ' α-group,' which are three conspicuous bands in the red, yellow, and green, are simply part of the well-known ' first positive ' bands in the ordinary nitrogen spectrum. (The intensity relationships are, however, quite different, a few of the bands being specially prominent in the glow and the rest entirely absent.) The ' β '- and ' γ '-groups of Fowler and Rayleigh have by many been attributed to nitric oxide, but these are not so characteristic, and are of less importance.

The glow is not associated with any ionic form of nitrogen : it is unaffected by the removal of ions from the gas which has passed through the discharge. Moreover, the spectroscopic evidence goes to show that the first positive bands of nitrogen are emitted by the neutral molecule itself.

In order to be clear about the value of the spectroscopic evidence, we must consider for a moment the nature of band spectra. In a given spectrum there may be several systems of bands in regions quite far removed from one another ; each system has a number of more or less evenly spaced bands, the frequency differences between the centre of one band and the next being much smaller than those between corresponding bands of different systems. Finally, each band is composed of a number of lines which crowd together at one side or the other, producing a fluted appearance, the frequency differences here being on a still smaller scale. Now, according to the Bohr principle of energy levels, the frequency of the light emitted by an atom or molecule is equal to the difference between the energies of the initial state and the final state, divided by Planck's constant h. The energy of an atom, for this purpose, is determined by the quantum state of its electrons ; changes in this correspond to the different lines in the *line* spectrum of the atom. The same applies to a molecule, but for each electronic energy level there are various degrees of vibrational energy possible ; hence each line is multiplied into a system of lines. For each electronic and vibrational state various amounts of rotational energy may be possessed by the molecule ; hence the system of lines becomes a system of bands.

The quantitative differences between the different kinds of energy fit in exactly with what is required to account for the relative frequency differences of system, band and component lines, so that there can be very little doubt that the nature of the spectrum proves the glowing of active nitrogen to be due to a molecule. It may also be mentioned that a line spectrum due to the nitrogen atom is known, but is not shown by active nitrogen ; that Wien, by his canal-ray method, showed the emitting system of the nitrogen first positive bands to be uncharged, and that Rayleigh was unable to condense out anything which might indicate the existence of a body such as N_3. It seems fairly certain, therefore, that the characteristic luminescence is emitted by simple diatomic nitrogen in some unusual state.

The spectroscopic investigation carries us still a little further. From the frequency of the lines and from the Bohr principle, combined with measurements of the energy of the electrons necessary to stimulate the emission of various bands in the spectrum, an idea can be obtained of the actual energy levels from which any given line or band is emitted. In this way Birge, Sponer, and others arrive at the conclusion that the strongest bands in the afterglow correspond to transitions from a state where the nitrogen molecule possesses 9·3 volts of electronic energy,[1] with about 11 quanta of vibrational energy, which are equivalent to 2·1 volts. After these particular bands are emitted, the molecule still appears to have about 8·0 volts. Before emission it possesses 11·4 volts, or about 260,000 calories, which must be approaching the heat of dissociation of nitrogen. Saha and Sur conclude that the energy corresponding to the maximum frequency of the lines emitted when active nitrogen reacts with metals is $8·2 - 8·5$ volts : but this is inconclusive, since chemical reactions are involved here, and it is well known that chemical energy may appear as light (chemiluminescence).

Willey and Rideal made a direct measurement of the heat liberated when active nitrogen reacts with nitric oxide, and found that 42,500 calories were contributed by the nitrogen for each molecule of nitric oxide which reacted. They assumed that each molecule of nitrogen accounted for one molecule of nitric oxide. This gave 42,500 calories (2 volts approximately) as the energy of the active nitrogen, in conflict with the spectroscopic evidence. The doubtful part of this procedure is simply the assumption of equimolecular equivalence: Rayleigh, for example, had assumed the reaction $2NO + N = NO_2 + N_2$, which would involve four molecules of nitric oxide to one of nitrogen. But this question may be left, since the conflict is resolved in another way. It has often been pointed out that active nitrogen may be complex, and contain different products in different states of excitation. Willey

[1] An energy of 1 volt means an energy equal to the kinetic energy which an electron would acquire in falling under a potential difference of one volt. 1 volt corresponds to about 23,000 calories per gram molecule.

has recently confirmed the fact that the glow and the chemical activity are independent : the glow may be destroyed, by Rayleigh's method of passing the gas through a weak subsequent discharge, without destroying the chemical activity. Hence it is clear that the average energy of nitrogen which is chemically active may be much smaller than that of the light-emitting molecules. Indeed, the balance of evidence seems to be that the chemical activity of the nitrogen is much smaller than it would be if all the molecules which are ' active ' at all possessed energy equivalent to the spectroscopic 11·4 volts. For example, it does not excite molecules of hydrogen in any way, nor does it stimulate the combination of hydrogen and oxygen. Energy exchanges tend to be so specific that these arguments must not be pushed too far ; but the evidence at present available seems to show that the glowing nitrogen is only a fraction of the total chemically active nitrogen, and in a considerably more excited state than the average.

We now come to the question of the mechanism by which these active molecules are produced and decay. In this connexion it must be remembered that most of the quantitative work on the subject refers to the glowing nitrogen, and not to other forms which are produced simultaneously, or in the course of the decay, which may still possess chemical activity although they are non-luminous.

It has been suggested that, in the discharge, free atoms of nitrogen are produced, in a manner analogous to that in which Wood's atomic hydrogen is formed. These have to give rise to a molecular spectrum, which they can do in two ways, either by simple recombination, or by communication of the energy of recombination to a normal nitrogen molecule which collides with two atoms at the moment of their union. It must be remembered, however, that the analogy between active nitrogen and active hydrogen is a very imperfect one. There is a marked correlation between the occurrence of active hydrogen and the appearance of the Balmer series, which is known to be emitted by the hydrogen atom, whereas the active nitrogen spectrum, as we have seen, is definitely molecular.

We thus have three possible views : (a) molecules of nitrogen excited in the discharge to a high energy level are ' metastable,' that is, they have a considerable life and can continue to exist for some time after leaving the discharge, when they slowly revert with emission of light ; (b) atomic nitrogen emerges from the discharge, and then recombination takes place to give the molecules which are at a high enough energy level to emit the spectrum ; (c) nitrogen atoms emerge from the discharge and cause excitation of normal molecules in a ternary collision $(2N + N_2)$.

Of (a), all that can be said is that ordinarily an excited molecule loses its energy after about 10^{-7} seconds, but that ' metastable ' states occasionally have to be assumed in spectroscopy. With nitrogen it would be an assumption made directly for the purpose of explaining the facts, and without independent evidence. The arguments against (a) are, however, principally the arguments for (b) or (c).

The rate of decay of the glow, for a constant total pressure, shows that the process is a bimolecular one (Rayleigh, Angerer, Bonhoeffer and Kaminsky, Willey). The simplest, though not the only possible, interpretation of this is that recombination of two nitrogen atoms takes place. This interpretation is also consistent with the fact that the estimated energy of the initial state from which the α-bands are emitted approaches the heat of dissociation of the nitrogen molecule. If we now assume (b) to be the mechanism, a spectroscopic difficulty arises, in that we should expect a certain amount of continuous spectrum from the recombination of free atoms. This difficulty possibly may not be a very serious one. However that may be, there is some theoretical reason for believing that free atoms cannot combine, unless they suffer a collision with a third molecule which can remove the excess energy liberated in their union. Otherwise, according to Herzfeld, they would fall apart again immediately. Thus (c) becomes a natural hypothesis to make, the third body being a nitrogen molecule which is excited to luminescence in the process.

Rayleigh found that the active nitrogen decayed more rapidly at low temperatures than at high temperatures. If the decay depends upon a ternary collision, this is natural, since the chance of such encounters decreases with increasing speed of the molecules.

If this hypothesis is true, the rate of decay should be directly proportional to the total pressure of the ordinary nitrogen. Opinion on this point is somewhat divided. It seems to be clearly shown that the glow decays more rapidly when the pressure of nitrogen is increased (Rudy, Bonhoeffer and Kaminsky, Willey), but Bonhoeffer and Kaminsky find that if more nitrogen is added to the glowing gas, it weakens instead of brightening the glow as might be expected. They consider this to disprove the suggestion that the decay is accelerated. The fact remains, however, that the weakened glow persists for a shorter time. Further investigation therefore seems to be needed.

It remains now to consider the part played by the small proportion of foreign electronegative gases in the production of active nitrogen. It must suffice to mention the possible explanations, without, at the moment, attempting to decide between them. We have seen that the impurities play no part in the actual light emission process. Their function must therefore be in some way to catalyse the formation of the atoms on the excited molecules in the discharge,—which is very unlikely,—or to retard the spontaneous reversion of the active nitrogen, which in their absence may be very rapid indeed, or take place by some process not attended with luminescence. Birge, from the point of view of the theory that the glow is emitted by metastable nitrogen molecules, suggested that these could only remain in their metastable state in the absence of a disturbing field, and that free electrons from the discharge would therefore cause a rapid reversion : a small amount of electronegative gas would ' clean up ' these free electrons, while too

much would begin to exert a disturbing effect itself.

The alternative explanation is based upon analogy with atomic hydrogen, which can be definitely proved to recombine catalytically with great rapidity on clean glass walls of containing tubes : impurities such as water are shown to poison the walls and stabilise the atomic hydrogen. The impurities could have an exactly similar effect in preventing the destruction of the atomic nitrogen in a ' useless ' wall reaction. In this connexion it is significant that Rayleigh found the decay to be much influenced by the walls of the vessel, while Bonhoeffer and Kaminsky showed that the effect of the different foreign gases was particularly a function of the walls.

The British Association at Glasgow.

THE 1928 meeting of the British Association will linger in the memory as a delightful reunion, at which, without the announcement of any sensational discovery, much useful and important work was accomplished. Centred in the midst of one of our greatest industrial and commercial communities, it has accomplished valuable propaganda work for science, driving home into the mind of the ordinary citizen some appreciation of the fact that not merely his material prosperity and comfort, but also a large proportion of all that renders civilised existence possible, is dependent upon science and its advancement.

The formal proceedings commenced upon the evening of Sept. 5, when Sir William Bragg took over the presidential chair in succession to Sir Arthur Keith. Between seven and eight o'clock the St. Andrew's Hall began to fill with an immense audience, who whiled away the time listening to an excellent organ recital and watching the platform fill with well-known figures of the worlds of science and citizenship. At 8.30 precisely, Sir Arthur Keith appeared, followed by the president-elect, the Lord Provost, and the Principal of the University. The proceedings opened with short speeches from the two last-mentioned, who with kindly warmth and facile wit bade the Association welcome to Glasgow. Incidentally, it may be mentioned that an outstanding feature of the Glasgow arrangements was the cordial and smoothly working co-operation of all concerned in making the meeting a success. In his presidential address, so admirably conceived to fit a great centre of art and craftsmanship and applied science, Sir William Bragg held his vast audience throughout with that success to which auditors of his lectures at the Royal Institution and elsewhere are accustomed.

On Thursday, Sept. 6, the various sections settled down to work, and those members of the Association more particularly who flit from section to section, whither for the moment their fancy leads, appreciated to the full the advantage of having the various sections housed, each in its own appropriate department, within the one ring fence of the University.

The sectional proceedings themselves have proved of great and varied interest and have aroused much appreciative comment. Here and there, glints of the sunshine of humour have illuminated the sombreness of scientific exposition and debate, as for example the comment that was heard after a paper by one of our brilliant marine zoologists upon a method which he had devised for collecting and recording upon a continuous band of silk gauze the minute forms of life constituting the plankton along the track of his ship. " What a wonderful young man ! " the commentator said, "just fancy catching *whales* in a machine like that ! "

As usual, during the week the centre of organisation has been the Reception Room in the Bute Hall of the University, the normally somewhat austere and cheerless interior of which, brightened up by the presidential banners hung round the gallery, has been from morning to night a scene of cheerful activity and bustle.

On Saturday, Sept. 8, the members for the most part forsook town for country—many accompanying one or other of the numerous excursions which had been arranged beforehand, others going off by motor-car on unofficial expeditions of their own. The good fortune of the Glasgow meeting did not fail it, for the gloom and rain of preceding days cleared away entirely and a pleasant south-westerly breeze with blue sky and heavy clouds gave to the full these light and shade effects which show western Scottish scenery to its greatest advantage. On Sunday again the same conditions held, and there were many who sought their sermons not in cathedral or church, but in the stones and running brooks of the Highland glens.

As was to be expected, social activities were a conspicuous feature of the Glasgow meeting : in fact, its activities may be said to have been inaugurated by a luncheon given on the opening day by the Glasgow Chamber of Commerce—the oldest of such chambers—to a number of the chief officials of the Association, while almost at its close came the annual dinner of the Clyde Navigation Trust, to which again were invited representative members of the Association's organisation. Both the usual evening parties were well attended. The first of these, on the evening of Thursday, Sept. 6, was given by the Lord Provost and Corporation in the magnificent City Chambers, and the invited guests had a delightful time—conversing with their friends, listening to an admirable programme of music, dancing, or looking on—and listening—during the — to many — unfamiliar evolutions of the Scotch reels. The second party, still larger though less crowded, was held in the spacious galleries of Kelvingrove, where the artistic and other treasures provided an endless source of interest.

On Monday, Sept. 10, a special honorary graduation ceremonial was held, in the presence of a somewhat restricted company owing to the Bute