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Norwegian-British-Swedish Antarctic
Expedition, 1949-52
A New Era in Microscopy
Ultra-Violet Examination of Works of Art
Mechanisms of Chemical Change
Ion Exchange
Titanium: a New Metal for Engineers
Philosophical Analysis and Scientific
Progress
Research Report



Adm. N.Y.U.
N.Y.C.

SCIENCE NEWS

26



SCIENCE NEWS

EDITED BY A. W. HASLETT

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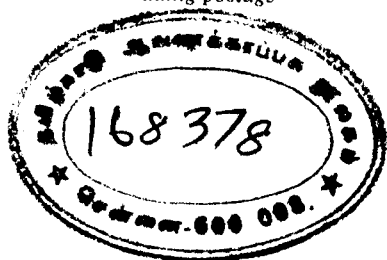
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EDITORIAL

THE bringing into operation of the Brookhaven 'cosmotron', or proton synchrotron, noted elsewhere in this issue, marks the beginning of a new era in experimental nuclear physics. Twenty years ago, J. D. Cockcroft and E. T. S. Walton achieved the first stage in a transition of techniques that is still continuing: the production of nuclear transmutations under controlled conditions by the impact of charged particles of which the energy could be varied. In round figures, this can be described as the period of one million electron-volt energies. Most experiments which before were dependent on natural radioactive sources could now be carried out with artificially accelerated particles, and additional particles became available for use as projectiles. The principle of repeated small accelerations given to particles constrained to follow a spiral path was developed by Professor E. O. Lawrence almost at the same time, and his cyclotron sufficed to pass the next two landmarks: the production of energies of one hundred million electron-volts and, at a somewhat higher energy, the creation of meson particles in the laboratory. The energies provided by natural radioactive elements having already been surpassed, attention was increasingly directed to cosmic radiation as a source of particles of still higher energies, and the photographic plate was added to the Wilson cloud-chamber as a method of observation. Of the many new particles thus discovered and suggested, those of 276 and 209 electron-masses are the only ones which have so far been produced under controlled conditions, and their masses accurately determined. One of the first uses of the 'cosmotron' will be the attempted production of more of these particles not yet artificially created. Their astonishing multiplicity has been reviewed lately by Professor A. M. Tyndall in his presidential address to the section of physics at the Belfast meeting of the British Association. All of them have been discovered in cosmic radiation, whether by the exposure of nuclear photographic plates during balloon ascents to high altitudes or by the use of the

cloud-chamber method at mountain laboratories. Credit for the discovery of these further new particles is shared between the Bristol and Manchester schools of physics, though with some possibility of overlap, owing to the use of different methods of observation. As a result there is now available for artificial creation a series of probable, short-lived charged particles with masses of the order of 530, 970, 1,070, and 1,450 electron-masses. The two lighter of these particles, and also neutral particles with masses of the order of 550 and 800 electron-masses, should be brought within the possibility of controlled creation by the 'cosmotron' and other particle-accelerators now approaching completion. There is here an ample field for research; and, as with the two lighter meson particles already created, it will be a matter of interest to see the extent to which conclusions, more laboriously obtained by other methods, are supported by high-energy experiments. However, it has been the habit of cosmic radiation workers to keep always one step ahead of those who work with laboratory accelerators. This position is still maintained; and it may not have been entirely with regret that Professor Tyndall, with his long interest in work at Bristol, should have recalled in his review that certain of the heavier of these particles appear to require bigger energies for their production than will be available from any machine, built or building. If these are some of the more spectacular rewards to be expected from the operation of new machines, progress in the study of intra-nuclear forces demands that there shall be systematic experiments on the interaction of simple nuclear particles at the highest energies. Such experiments, unexciting in themselves, are needed to provide more solid foundations for the theoretical physicist than have before been available, and should lead in the long run to a knowledge of the atomic nucleus at a level which has so far proved elusive. There is work for more than one laboratory, and it is to be hoped that the Birmingham proton synchrotron will be soon also in operation.

THE NORWEGIAN-BRITISH-SWEDISH ANTARCTIC EXPEDITION 1949-52

E. F. ROOTS

THE challenge of geographical exploration has undergone several changes as human activities have gradually spread from hospitable and accessible to more remote regions. The unvisited portions of the land surface of the earth have been reduced to places so inaccessible that there is little incentive to explore them in the hope of direct material gain; and even the satisfaction of overcoming the various physical and mental obstacles involved in being among the first in any particular part of the world is becoming more difficult to experience. Instead, exploration now offers its greatest attraction, and its most permanent rewards, not when undertaken for its own sake, but when used as a medium to meet the more indirect and much wider challenge of general scientific investigation. The Norwegian-British-Swedish Antarctic Expedition was organized and undertaken in this spirit; it was never regarded, by its planning committees or by its members, as an entity in itself, bent merely on occupying a parcel of land or journeying for the sake of viewing new scenery and seeing where one could get to. Instead it set out with a definite, though by no means rigid, plan to collect information in the fields of meteorology, glaciology, geology, geophysics, physiology, etc., and to relate that information to various scientific problems of the day. From the start, it was intended that the success of the expedition should be judged solely on what was brought back in its notebooks and specimen boxes.

The expedition has now returned, and its members are beginning to evaluate and integrate the facts gathered in the field and

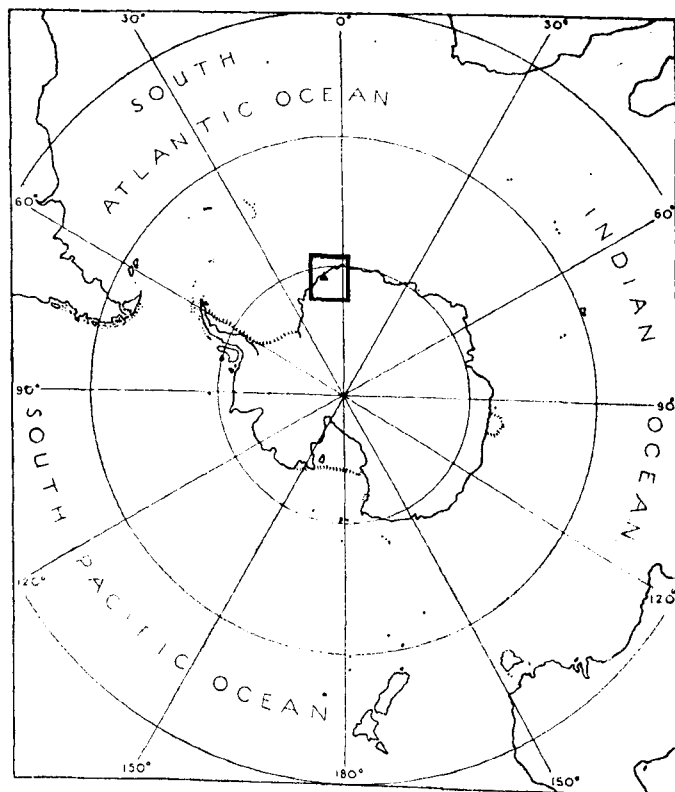


Fig. 1. Antarctic and the Southern Ocean, showing the area visited by the Norwegian-British-Swedish Antarctic Expedition, 1949-52. The position of Maudheim, the expedition base, is shown by the black triangle.

at the base. Most of the information collected is of little significance in itself, and it will be months or years before conclusions can be drawn or the 'results' of the expedition can be stated in general terms. In this sense the present note is premature; but it may be of interest to review the various scientific activities of

the expedition, in the light of the kind of problems that the members had in mind when collecting their data. The area visited by the expedition, and the position of its base, are shown in Fig. 1, opposite.

METEOROLOGY

The expedition base at Maudheim in Dronning Maud Land (Lat. $72^{\circ} 03' S.$, Long. $10^{\circ} 55' W.$) was well sited for general meteorological investigations. The whole southern portion of the southern hemisphere is an excellent proving ground for many large-scale meteorological theories; for here there is a roughly circular continent, a great flattened dome mainly devoid of large meridional topographic irregularities, surrounded by an ocean relatively free from abnormal currents or temperature gradients. Consequently the pattern of atmospheric circulation is much simpler than in the corresponding latitudes of the northern hemisphere, where a variety of irregular land masses and the existence of ocean currents generated or influenced by conditions in other latitudes produce many complications. Many related problems of heat transfer and storage in the atmosphere, and absorption by and loss of heat from the earth's surface could be studied from quite a new angle, for here measurements could be taken over a uniform snow surface whose character and reflectivity can be relatively accurately determined, under conditions ranging from continuous radiation, in the summer, to no direct solar radiation in the winter.

Upper air studies thus formed a considerable part of the meteorological programme. During the two-year stay some 650 successful radiosonde-rawin balloon ascents were made, some of them to heights of 22,000 metres (72,000 ft). The radiosonde consists of a barometer, thermometer, hygrometer, and small radio transmitter that broadcasts signals of air pressure, temperature, and (though of questionable reliability) of humidity during the flight; the 'rawin' (radio-wind) transmitter, attached to the same balloon, sends signals that can be picked up on a direction-finding receiver at the base to show the horizontal direction and angle of elevation of the balloon, and thus enable

the wind velocity and direction to be calculated. The analysis of these data is scarcely begun, but one phenomenon of interest is the apparent dependence of stratosphere-temperatures on direct incoming solar radiation. At low latitudes and in the temperate zones the stratosphere is a region of almost constant temperature throughout the year, independent of fluctuations at lower levels of the atmosphere. Above Dronning Maud Land, however, during the winter, when the sun was well below the horizon, the temperature of the stratosphere became as low as -90°C . (-130°F). In spring, when solar radiation again struck the top of the atmospheric blanket, the stratosphere gradually warmed, apparently from the top downwards.

Many of the special meteorological researches at Maudheim were connected with the problem of heat exchange. For this, Maudheim's featureless surroundings and uniform snow-cover (Inset 6) provided conditions of almost laboratory simplicity. Incoming and outgoing radiation were measured at different levels; temperatures were recorded periodically or continuously at various heights up to 10 metres (33 feet), and complemented by the glaciological temperature measurements at various depths within the snow. To the layman, one of the most remarkable features of the local climate at Maudheim was the temperature inversion that occasionally obtained; it was sometimes 10 degrees warmer at the top of the 10-metre-high meteorological mast than at the bottom. This inversion is responsible for the extraordinary mirage effects characteristic of the region, and indeed noted by most polar travellers.

Essential to the general problem of heat transfer is a knowledge of the wind gradient at various levels above the surface, and its relation to the temperature gradient. Continuously-recording anemometers were placed at intervals from $\frac{1}{2}$ metre to 10 metres, and it has been possible to work out a much improved and simplified expression of a 'wind law', dealing with the variation of wind speed with height, that may prove to have a comparatively wide application.

Aside from general meteorological investigation, it was obvious that a year-round weather station on the coast of Ant-

arctica, almost equidistant from South Africa and South America, would be of great benefit to forecasters and analysts of the weather of the Atlantic section of the Southern Ocean. This was proved to be the case. Daily contributions from Maudheim to the pool of weather information from this area* were of acknowledged value in forecasting in South Africa. Forecasts were also issued from Maudheim, particularly during periods when flying operations were carried out in inland Antarctica.

GLACIOLOGY

From its earliest stages, the expedition's scientific programme was planned largely around glaciological researches. The distribution of photographs taken by the Deutsche Antarktische Expedition 1938-9 first drew Dronning Maud Land to the attention of Ambassador H. W:son Ahlmann, then Professor at the Geographical Institute, Stockholm. Ahlmann's climatological and glaciological researches in Greenland, Iceland, Spitsbergen, and Scandinavia had established a picture of climatic fluctuations of magnitude great enough to affect profoundly all types of life in and around the North Atlantic Ocean. Phenomena, at first sight quite unrelated, such as the ease with which the early Norsemen made long voyages in open boats at high latitudes, the present transition of the Greenlanders' mode of life from seal-hunting to cod-fishing, and the fact that it seems quaint, nowadays, to read of the characters in a Dickens' novel skating on the Serpentine, were all seen to be manifestations of regional temperature changes - changes that are accurately recorded by variations in the size, movement, and structure of the glaciers. It was most important to ascertain whether or not these climatic changes were world-wide, for obviously very different causes and controlling factors would have to be considered if the fluctuations could be regarded as irregularities in the distribution and circulation of atmospheric heat, than if the planet as a whole underwent variations of surface temperature. In the

*Notably from Cape Town, Tristan da Cunha, the bases of the Falkland Islands Dependencies Survey, the Falkland Islands themselves, South America, and, in summer, various whaling ships.

Alpine land-forms of Dronning Maud Land, Ahlmann saw a chance to obtain data comparable to those he had been accumulating in the northern hemisphere. Here was a large ice-cap, pierced by mountain ranges and isolated rocky crags or *nunataks*, whose form and detailed features should bear evidence of the immediately past glacial history. The mountains themselves carried independent glaciers, ranging in size down to small snow-patches; each of these would be sensitive, in its own degree, to climatic changes.

But to study the climatic history recorded in the Antarctic glaciers and their deposits a great deal of fundamental information was necessary. To understand glacial flow, and the balance between accumulation and wastage, it was first necessary to understand the metamorphism of snow into glacier ice, and to learn something more about the physical properties of 'polar' ice. Most of the studies of the development of glacier ice have been carried out in the so-called 'temperate' glaciers of the Alps, Scandinavia, and western North America. By a common definition, compacted and recrystallized snow or *firn* becomes ice when the air spaces between or within the grains are no longer intercommunicating. In a temperate glacier this occurs at a specific gravity of about 0.82; as the process of recrystallization proceeds, air is progressively expelled until nearly pure ice, with a specific gravity of about 0.91, results. Recrystallization has been found to take place mainly at temperatures near the freezing point – as is broadly the case in the main mass of most temperate glaciers – and many researchers have concluded that during the metamorphism of snow into pure glacier ice it is necessary for each particle to pass through a liquid phase. In the Antarctic, it appeared that the body of the ice-cap never warmed to near the melting-point. How, then, was the air expelled, and how did the snow become converted into ice? Or were the Antarctic glaciers not true ice, as the term is understood in the Alps, but merely masses of compacted snow? If so, what was the nature of their motion? What erosional effect did they have on the topography? The underlying rock-surface was presumably losing heat, from radioactive disintegration, at a rate compar-

able with that of other parts of the earth's crust; what effect did this have on the temperature of the ice at depth, and on the energy required for recrystallization and flow?

These, and many others, were the glaciological questions in mind when the expedition sailed from Europe. But when, eventually, the expedition winter-quarters, Maudheim, were established on a floating ice shelf instead of a solidly grounded glacier, a whole set of new problems arose. The large floating skirts of level, compacted snow, variously known as shelf ice, barrier, and ice shelf, that fringe a great deal of the Antarctic continent, have been the subject of a considerable discussion and some controversy. Some authorities considered them to be essentially the floating overflow of a radially-moving central ice-cap, receiving relatively minor nourishment from snow that falls directly on their surfaces. Others thought them mainly the products of direct accumulation of snow upon land-fast sea ice. Still others have presented evidence that these features grow from below by the progressive freezing of sea-water on their under surfaces. Clearly some definite facts were needed.

At Maudheim, a series of aluminium stakes was planted at regular intervals over an area of about 25 square kilometres (10 square miles). The height of the stakes, and their relative positions, were accurately and periodically surveyed, so that the net snow-accumulation (precipitation *plus* incoming drift *minus* outgoing drift *minus* evaporation or sublimation) and the relative differential movement of the surface of the ice shelf itself could be determined. The movement pattern has not yet been fully calculated, but it appears that in the vicinity of Maudheim, which is located near the seaward edge of a 40-km. (24-mile) wide shelf, the shelf surface is spreading gradually; the greatest relative movement, about 1½ metres per km. (8 feet per mile) per year, is approximately parallel to the coastline. It is assumed that the outer edge of the shelf is moving seaward *en bloc*, but the absolute movement could not be determined; for the nearest 'solid' point was a *nunatak* 205 km. (126 miles) away. A line of levels was run from the sea surface to undisturbed ice shelf 2.3 km. (1.5 miles) inland. This was repeated 21 months later;

despite the accumulation of nearly 2 metres (5 ft) of snow, the surface of the shelf along most of this line, at a height of about 40 metres (130 ft) above sea level, had not changed in height by more than 2 centimetres ($\frac{1}{2}$ inch). There is obviously a very delicate equilibrium between accumulation and differential spreading controlling the thickness of the ice shelf. A plane-table map was made of the detailed irregularities of the seaward edge of the shelf; this was repeated a year later to check the relative movement of crevasses and cliff faces.

A pit was dug in the ice shelf to a depth of 14 metres (46 ft), and various bore holes drilled to depths of as much as 100 metres (325 ft). In the uppermost 10 metres or so of the shelf it was found possible to distinguish the successive annual accumulation layers by the changes in the snow texture. For the ten years 1939-49 the mean annual net accumulation was found to be equivalent to 38 cm. (14.9 inches) of water. Platinum resistance thermometers recorded the variations of temperature at different depths. The colder air of winter chilled the upper layers of snow; this snow in turn absorbed heat from the underlying snow, and so a 'cold wave' was found to travel gradually downward, followed by a 'warm wave' started at the surface during the summer. At a depth of 4 metres (13 ft) the difference in temperature between summer and winter 'waves' was about 5°C. ; at 20 metres (65 ft) the amplitude was about 0.1°C. , and the *firn* had a temperature that closely corresponded to the mean annual air-temperature, -17°C. ($+1^{\circ}\text{F.}$). At lower levels the temperature gradually increased. The curve of this increase, to meet the freezing temperature of sea-water at the bottom of the shelf, has not yet been fully worked out; its shape may give some suggestion as to whether or not the mean air-temperature has been approximately constant in the immediate past. On the other hand, the apparent slowness of the rate of increase of temperature in the lower layers of the shelf may be simply a function of the mass-movement of snow and *firn* to depth, as the cold upper layers are successively buried by surface accumulation and transported to deeper levels faster than thermal conduction can establish a uniform temperature-gradient.

Considerable information was gathered on the general problem of the transformation of snow to *firn* to shelf ice. The specific gravity of the shelf material was found to increase systematically from about 0.45 at the surface to about 0.88 at a depth of 100 metres (325 ft). From the density-depth curve, projected, and the known height of the surface above sea level, the thickness of the shelf can be calculated; the resultant figure of about 190 metres (620 ft) is in harmony with the thickness found independently by seismic methods. The grain-size likewise increases: from finely crystalline *firn* with an average sectional area of 0.18 sq. mm. at 1 metre depth, it reaches nearly 3 sq. mm. at 80 metres (262 ft), and a logarithmic plot of the average sectional area against depth is, like the density plot, a straight line; so that, if the depth were doubled at successive observations, the increases in grain-size and in density would be in equal steps. The recrystallization thus seems to be a gradual and continuous process, that neither proceeds nor stops at any critical depth. Neither do studies of grain orientation at depths down to 100 metres show any obvious two-stage development as, influenced by surface load and bodily flow, has been noted in Alpine glaciers. The air passages become sealed, and the shelf material can, by definition, be called ice, at a depth of about 60 metres (200 ft); it is interesting that although the general appearance of the material and the temperature at which the change takes place is different, the specific gravity at this depth is about 0.82, the same as that at which *firn* changes to ice in temperate glaciers. At greater depths the density increases mainly by what appears to be a simple compression of the trapped air in the grains; several experiments, too involved to be described here, have suggested the magnitude of the pressure in the air bubbles.

The floating ice shelf was found to abut the grounded ice inland, along what might be called a hinge-zone, usually about 1 kilometre ($2/3$ mile) wide. Within this zone are numerous small cracks running parallel to the 'shore line', and nearest the grounded ice, commonly a curious and persistent valley as much as 6 metres (20 ft) deep and 50 to 1,000 metres (150-3,000 ft) wide. Inset 9 shows the examination of surface features in the

hinge-zone. The width of the cracks was measured, and a theodolite profile was measured across the hinge-zone almost continuously for 24 hours. It was established that as the shelf ice rises and falls with the tide, its movement is taken up at the junction with the grounded ice partly by the opening and closing of the small surface cracks, and partly by a gentle rolling flexure across the whole hinge-zone. Stakes planted in the profiles were resurveyed a year later to obtain a measure of the movement of the grounded ice seaward to become floating shelf ice.

These researches into the nature of the ice shelf provided a basis from which to carry out the field studies inland. Stakes spaced approximately every $2\frac{1}{2}$ km. ($1\frac{1}{2}$ miles) along a line running from Maudheim 307 km. (204 miles) to the inland mountains were measured intermittently during two seasons to ascertain the magnitude and distribution of the overall snow accumulation. At selected places in and near the mountains, lines of stakes were placed in the ice streams, and surveyed from fixed points on the surrounding *nunataks* to determine the absolute ice-velocity. It is premature to state the results of this work, but profiles across the ice streams showed movement in parabolic form, similar to that of temperate glaciers, with the central part moving downstream fastest. The middle of a glacier 12 kilometres ($7\frac{1}{2}$ miles) wide, draining an effective area of about 150 square kilometres (60 square miles), taken at a point where the surface slope is about 1 in 50 and the channel is about 900 metres (3,400 ft) deep in the centre as measured by seismic sounding, moved approximately 14 metres (46 ft) between January and November 1951, giving a mean absolute surface velocity of the order of 4.5 cm. ($1\frac{1}{4}$ inches) per day.

It was not possible to obtain direct measurements of the velocity of the ice at depth, or of the velocity-depth profile. But from seismic measurements of ice-thickness and the aerial mapping it is possible to get some idea of the volume of ice in the drainage streams; and, if one assumes that there is no great change in the total amount, then from an average figure for the net yearly accumulation, recorded in the upper snow layers at any individual place, one can obtain a rough measure of the

magnitude of the yearly flow. It will be most interesting to compare this 'calculated' velocity with the observed surface velocity, for the 'average' velocities calculated in this way for some Alpine glaciers are quite out of harmony with the observed velocities on the surface and at depth, as measured in boreholes deformed by ice-flow; some of the differences are still unexplained.

Temperature measurements and observations of density and texture were made from pits and boreholes among the mountains and on the inland ice plain. It was found that the curves of seasonal temperature-variation at depth were essentially parallel to those on the ice shelf. Once a curve could be established, from a single set of readings at any particular time of the year it was possible to calculate the mean annual air temperature for that locality. In this way it was determined that the mean annual air temperature at about Lat. $74^{\circ} 15' S.$, Long. $0^{\circ} 00'$, at an altitude 2,700 metres (8,800 ft) above sea-level, is close to $-40^{\circ} C.$ ($-40^{\circ} F.$).

There is no doubt, from the smoothed and scratched summits, and the presence of ice-carried stones, far from their parent outcrops, on peaks high above the present ice level, that nearly all of the Dronning Maud Land mountains were once completely covered by ice. But several lines of evidence seem to suggest that the ice level has been relatively stable for the past century or two. Tiny, isolated *nunataks*, so small that they would quite disappear were the general ice-cover 2 metres thicker, carry lichens to the very edge of the snow. Nowhere is there a 'bare band' of vegetation-free and less-weathered rock just above the ice level, such as is almost invariably found above the present-day glaciers in the northern hemisphere. The needle-like, apparently frost-riven topography extends right to the present ice level – though this argument based on land forms has lost some weight since the recognition of the unexpected severity of the sub-ice topography as revealed by seismic sounding. One of the best geomorphological arguments for the stability of the present ice level appears to be that over an altitude range of more than 1,500 metres (5,000 ft) the cirques seem to be adjusted in size and, apparently, depth, to their present ice supply; they are

neither being abandoned, occupied by small misfit glaciers, nor swamped by excess ice.

Here and there among the mountains are patches of bare, blue ice. From the air and from a distance they look like frozen lakes (Inset 19), for which they were mistaken by the Deutsche Antarktische Expedition, with consequent discussion in the press, and among climatologists and glaciologists. They were found to occur where the topography is so shaped that violent local winds are developed; many are also close to cliffs of dark rock which can produce a local increase of surface temperature on calm days. The patches themselves are composed of coarse-grained bubbly ice, similar in every respect to that found at depth in the Maudheim ice shelf. Although – near dark cliffs – some parts of some patches may perhaps develop a thin film of water on their surface a few times each summer, there is nothing to suggest that they have ever been bodily flooded in the manner of a skating rink, and no grounds for considering them as products of melting and refreezing. It is quite clear from a study on the ground that these blue-ice patches are found where local winds have eroded the ice-cap to a lower 'stratigraphic' level, exposing ice that is covered elsewhere by several tens of metres of snow and *firn*. In a few places the patches might be regarded as 'remnant' glaciers, in that the exposed blue ice appears to be at a higher absolute level than the buried ice of similar character around it.

SEISMIC SOUNDING

Reference has already been made to determinations of the thickness of the ice shelf and the ice-cap by seismic sounding. The general seismic principle of detonating an explosive charge and measuring the time interval required for the shock wave to be reflected back by the underlying surfaces is widely used in petroleum, mining, and engineering exploration*; and various techniques for determining ice thicknesses have been worked out by previous expeditions in Antarctica, in Greenland, and on

*A general account of seismic methods was given by E. Tillotson in *Science News* 8, 63 (1948).

numerous smaller glaciers. Building on this accumulated experience, it was possible to develop at Maudheim a procedure that has given consistent and, it is felt, reasonably reliable measurements. Inset 11 and 12 show the seismic party in the field.

The seismic experiments themselves provided supplementary glaciological information regarding the character and uniformity of the snow and ice cover. The speed of propagation of longitudinal shock waves in shelf ice – about 3,780 metres per second (12,400 ft/sec.) – was nearly the same as that in much colder ice at 2,700 metres (8,800 ft) above sea-level, and of the same order of magnitude as that found in temperate glaciers. The compressibility and elasticity of ice or compacted snow seem to depend, as might be expected, mainly on the density of the grain-aggregate, and to be more or less independent of the method or degree of recrystallization. Reflected and refracted echoes have shown no physical discontinuity within the ice itself.

The main object of the seismic work was to measure ice thicknesses along a profile running from the floating shelf to the relatively high interior ice plain. The ultimate length of this profile was about 616 km. (393 miles; see Fig. 2); in addition, short profiles were run across the junction between the ice shelf and the grounded ice, across glacier streams in the mountains, and up to the edges of *nunataks*. The resulting picture of the ice thickness, and of the form of the bedrock surface, is rather remarkable (see Fig. 3).

It was found that the rounded hills and promontories within and bordering the ice shelf are composed entirely of ice, much thicker than the floating shelf, that is grounded on shoals. The great increase of thickness of ice where it is grounded seems to be a function of the resistance to flow offered by the supporting rock compared with the negligible friction encountered by the floating shelf; the ice accumulates to a greater thickness to produce the forces necessary to slide over the shoals. Where crossed by the profiles, the shoals supporting the grounded ice are slightly deeper than the bottom of the shelf ice, so the lower surface of the ice curves downward to meet the ocean bed at

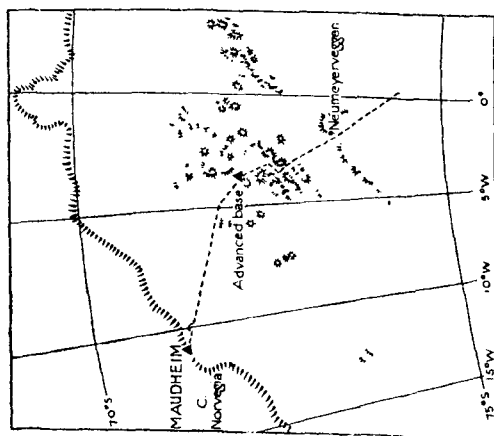
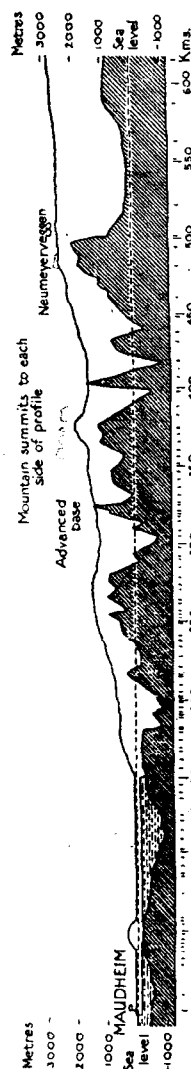


Fig. 2 (left). The part of Dronning Maud Land explored by the Norwegian-British-Swedish Antarctic Expedition 1949-52, showing the distribution of mountain ranges and groups of rock outcrops. The dotted line represents the line of the seismic sounding profile shown in Fig. 3.

Fig. 3 (below). Profile of the ice surface and of the bedrock surface as determined by seismic sounding along the line shown in Fig. 2. The vertical scale is exaggerated 20 times compared with the horizontal scale.



about the point where the top surface curves upward to form a hill. It is quite possible, however, that these profiles are not representative, and that the main parts of most ice hills surrounded by floating shelf are resting on shoals as shallow as or shallower than the lower surface of the ice shelf. Under the summit of one investigated hill the rock surface rises to within 100 metres (330 ft) of sea-level. The curious valley on the surface of the shelf along its hinge-zone may be connected with a lag between the change of velocity from grounded to floating ice and the attainment of an equilibrium-thickness by the shelf itself.

Inland, the snow surface rises in great undulations, until, near the first exposed rocks, 120 km. (75 miles) from the inner edge of the ice shelf, it reaches an altitude of about 1,450 metres (4,600 ft). The underlying rock surface also rises; its irregularities are reflected, generally in subdued but sometimes in exaggerated manner, by the snow surface. The absolute thickness of ice is considerable; broad ridges rise more than 500 metres (1,600 ft) above sea-level where the bedrock surface is below sea-level. Near and within the mountain front, the broad ice-streams flowing coastwards were found to be occupying fjord-like depressions, whose bottoms are below sea-level in places 200 km. (120 miles) upstream from their apparent mouths at the inner edge of the ice shelf. The altitude of the main inland depot, shown in Inset 10, is about 1,330 metres (4,360 ft), but the rock floor of the valley, seen partly in the foreground, descends below sea level. The depth and ruggedness of inter-montane valleys, and the depth of individual cirque-like basins and the steepness of their buried walls suggest that a deep ice cover may produce more rugged land forms, and have less smoothing action, than has heretofore been generally realized.

Dronning Maud Land is like the Ross Sea sector of Antarctica in that the traveller going towards the interior of the continent passes into a belt of mountains and then climbs an escarpment marked by rock outcrops and ice cliffs or crevassed slopes to emerge on to a high snow-covered plain. This plain has been called the interior plateau and has given rise to published state-

ments that Antarctica is the highest of the continental masses. The seismic profile shows that the final escarpment in Dronning Maud Land is not the edge of a plateau, but merely one side of a mountain range that has dammed back the seaward-moving ice until the crest has been overtopped. (See the aerial photograph reproduced as Inset 18.) Inland from this range the rock surface is rolling, and at one point is only some 200 metres (650 ft) above sea-level, buried under about 2,450 metres (7,500 ft) of ice.

GEOLOGY

The exposed mountain ranges and *nunatak* groups form large northeast-trending units (Inset 13 and 14), separated by the deep, ice-filled troughs or fjord-like valleys mentioned above. The largest of these valleys, feeding a major ice stream that debouches near the meridian of Greenwich, separates the two main areas of differing rock-types found.

To the south-east of this trough the mountains are almost entirely a mixture of metamorphic rocks, mainly light-coloured, foliated rocks, or gneisses, composed of quartz, feldspars, micas, and hornblende. Many of the gneisses are rich in garnets. Mixed with the banded gneisses are innumerable bodies up to 300 metres (1,000 ft) thick of black amphibolite, a rock consisting mainly of hornblende, or of hornblende, feldspars, and micas. The whole assemblage is cut and re-cut by a multitude of coarse-grained quartz-feldspar dykes, or pegmatites. In a few places the rocks are less coarsely crystalline, and are varieties of green slate and schist. In other places metamorphism has progressed to such an extent that small samples of the rock approach granite in appearance. But there are no large granitic bodies; although in at least two places the gneisses have been intruded by plug-like masses of coarse-grained syenite, or feldspar-hornblende rock. Inset 24 shows a metamorphic rock-face, with round holes worn by wind erosion.

The structure of this metamorphic complex is variable. The layering of the banded gneisses, on a large scale, is in places gently undulating; in other places it outlines folds that suggest

compressional deformation of large thicknesses of rock. On a small scale, the individual gneissic bands are fantastically contorted, with the long zig-zag folds and intricate convolutions typical of rocks that have, at least in part, recrystallized during their deformation.

No definite information is available regarding the age of these metamorphic rocks, but they are probably of considerable antiquity. They are similar to the basement complexes, or 'shields' forming the cores of most continental masses, and there is good reason to suppose that they represent part of the ancient stable core of Antarctica. On the opposite side of the continent, in South Victoria Land, similar metamorphic rocks underlie Cambrian sediments.

At the south-west end of their known area of outcrop, the banded gneisses are truncated by an old undulating erosion-surface and overlain by nearly flat-lying sediments. Similar sediments, and the younger igneous rocks that intrude them, make up almost all of the exposures to the north-west of the large ice stream that discharges near the Greenwich meridian.

The sediments are almost entirely of shallow-water or continental character, and are not known to contain any chemical depositions. Impure sandstones, greywackes, and siltstones are the most common types, and there are many beds of mudstone and of boulder- and pebble-conglomerate. A large proportion of the sediments is cross-bedded; that is, the larger units are built of many thin, short, more or less steeply-inclined, curving beds that possibly have been laid down in deltas or alluvial fans. Ripple-marks and polygonal cracks due to drying of exposed mud flats are very common. The whole sedimentary assemblage tells a story of relatively rapid and irregular deposition in an environment such as would be found at the edge of a shallow sea near a rocky coast, or in a desert basin, of material brought a relatively short distance by mainly small, fast-flowing streams. The metamorphic complex now exposed to the east has not, directly, supplied this material. No conglomerates that were once boulder clay, or scratched and polished cobbles, or other deposits characteristic of a glacial age have been recog-

nized in these beds, and there is nothing in the sedimentary record to suggest that the climate was anything but mainly dry and, if not necessarily warm, at least not frigid, at the time when the sands and muds were laid down. Little pits and spattering left on the surface of a sun-dried mud-cake by a passing rain-shower can be found today, well preserved on a frost-riven, ice-scoured *nunatak* in a land where rain is at present unknown.

The thickness of the sedimentary series has not as yet been worked out; the total is probably more than 1,500 metres (5,000 ft). The beds have never been folded by mountain-building forces. And no identifiable fossils could be found in them.

An area of about 800 square kilometres (290 square miles) adjoining the main region of exposed sediments is underlain by altered volcanic rocks of intermediate composition. Some of these old lava-flows may be of the same age as parts of the sedimentary section, for they overlies what appear to be relatively low beds in the stratigraphic sequence.

The sedimentary rocks have been intimately intruded by relatively basic magma, which has spread between the beds to such an extent that nearly every large exposure contains flat-lying sheets, or sills, of gabbro and diorite. Some of the sills are 200 metres (650 ft) thick and at least 150 square kilometres (55 square miles) in area. Inset 25 shows flat-lying sedimentary rocks overlain by one of these sills. The conditions of their crystallization were such that many of them contain rhythmically alternating layers rich in feldspars or in iron-magnesium minerals; others are uniformly graded from iron-and-magnesium-rich material at the base to relatively alkali-rich material near the top.

Subsequent to the consolidation of these sills, the region suffered a minor fracturing, and both the metamorphic complex and the sediment-sill assemblage were cut by small basalt dykes. These are the youngest rocks yet recognized in Dronning Maud Land.

The last recorded earth movement seems to have been a block faulting, of no very great magnitude, that relatively lifted

various portions of the area to form the masses from which the present mountain ranges have been carved.

On the basis of the somewhat scanty evidence available, it appears that normal stream-erosion had already dissected the large blocks to an advanced degree, and developed the main pattern of mountain ranges and valleys, before the area was occupied by ice. Many remnants of the rolling surface left by this earlier erosion-cycle can be seen, being slowly destroyed rather than modified by the present-day glacial attack. The glacial drainage was undoubtedly profoundly influenced by the pre-existing pattern of stream-drainage, but erosion during the period (or periods) of ice-occupation has been sufficient to greatly modify this pattern, at least at the present level of exposure. It may be that the evidence, quoted earlier, of the former presence of ice at much higher levels than found today does not indicate a time when climatic conditions favoured a deeper ice cover, but rather a time when the mountain wall was less breached, and a more effective dam, than at present. Recent theoretical calculations have suggested that there may be a relatively direct relationship between the surface-slope of an ice-cap and its thickness; and the present apparent stability of the ice-level, through a time long enough to develop the modern cirque basins, may possibly be not so much a reflexion of climatic stability as of the degree to which the mountain wall has been breached, so allowing an approach towards the theoretical equilibrium-thickness of an unimpeded ice-cap – a thickness that will not be developed until the mountain dam has been entirely removed by erosion.

CLIMATOLOGICAL IMPLICATIONS

In the foregoing paragraphs, an attempt has been made to show that some aspects of various lines of study have a direct or indirect bearing on the general question of climatic change, and in particular of recent change in mean annual temperature, in the Antarctic regions. It is rash to make, at this early stage, any definite statements about the results of these studies, except to say that there appears to be little evidence of climatic fluctua-

tions and general temperature amelioration on a scale comparable with that found around the North Atlantic Ocean. Whether or not an actual climatic stability is indicated is a question that requires much consideration. Many factors are involved; and the following points, none of which is suggested here as a conclusion, are among those that must be kept in mind by the expedition members as they compile their results:

(a) The lack of signs of fluctuation in the Antarctic glaciers might be due to the fact that the Antarctic ice-cap may be too large, with too great a reserve of ice, to be sensitive to short-term (a few centuries) climatic fluctuations; the lag between climatic change and change in form of the glacier may be longer than the period of climatic change itself. Furthermore, the Antarctic ice-cap is, in effect, one great accumulation area; but it is in the wastage zone of temperate glaciers that the effects of climatic fluctuation are most conspicuous.

(b) The temperate glaciers of Patagonia and New Zealand are, for the most part, retreating at present, and attesting to a present-day climatic change in somewhat lower latitudes of the southern hemisphere. A recent statistical analysis of the average winter and annual temperatures recorded during the past 50 years has suggested that the trend to warmer mean annual temperatures is most marked in the Arctic and subarctic, less pronounced near the equator, and, if anything, is reversed south of Lat. 30° S. The net change suggests a slight rise of average world temperature. Why does the Antarctic appear to lag? The possibility exists that the ice-cap is large enough to control its own climate to some extent, for a certain length of time.

(c) A further possibility, mentioned earlier, is that the thickness of the Antarctic ice-cap is not dependent on climatic conditions at all, provided there is sufficient snow accumulation to develop an equilibrium cross-section determined by the physical properties of ice and the resistance offered by the rock floor.

BIOLOGY

Megascopic vegetation in Dronning Maud Land is restricted to lichens and a few species of mosses. Collections were made of

these, and their range and general ecology noted. A systematic study was carried out of the rather remarkable increase in vigour and diversity of plant life with decreasing latitude. Between Long. 03° and 04° W., lichens were found to be abundant at an altitude of 200 metres (650 ft) at Lat. 71° 20' S., rare at 1,300–2,500 metres (4,000–8,000 ft) at 72° 30' S., and extremely rare at 2,000–2,700 metres (6,500–8,500 ft) at 73° 30' S. In this area higher latitudes are usually, but not in every case, combined with higher altitudes, and, as far as the observations go, with lower mean annual temperatures and a smaller proportion of stormy and cloudy (usually relatively warm) weather than at the coast. A rather obvious comparison might accordingly be drawn between rigour of climate and vigour of plant life; the interest lies mainly in the manner in which the diversification of vegetation has been accomplished. If, furthermore, the glacial history suggests that some *nunataks* have been exposed for a significantly longer time, another complication might be introduced.

Two types of *Arachnida* were found on the northernmost, relatively vegetation-rich *nunataks*. The tiny creatures (measuring 0.24×0.11 mm. and 0.5×0.25 mm.) have not yet been identified.

Observations were made of the occurrence and abundance of sea birds, which visit the inland mountains during the summer. The snow petrel and the Antarctic petrel were the most common nest birds; the former were found frequenting *nunataks* as far south as Lat. 73° 40' S., at least 200 km. (125 miles) from their nearest possible food supply. Little, however, was learned of their nesting habits. The skua gull (Inset 17), though rarely abundant, is ubiquitous; it appears to be the only scavenger in inland Antarctica.

The seas around Maudheim are inhabited by three genera of seal: the crabeater, the Weddell seal, and the relatively rare Ross seal. Measurements were made and skulls collected of the last-named. The stomach contents of several seals were collected; this material includes several fish which have not yet been identified.

OCEANOGRAPHY

Very little is known about the extent and distribution of pack-ice and icebergs in the Atlantic sector of the Southern Ocean. During each of the three voyages of the expedition ship *Norsel* to Maudheim, a relatively detailed ice-log was kept for both the incoming and outgoing passages. This information has now been plotted, and is being combined with that obtained by various whaling ships and the few previous voyages in the area; it should then be possible to make a rough analysis of the character and summer movement of the ice east of and in the approaches to the Weddell Sea.

Measurements were made of the water temperatures, salinities, and currents at depth at the front of the Maudheim ice shelf. The presence of a relatively thick upper layer of less saline water, and the existence of an active circulation under the edge of the shelf, with the returning water losing heat to the ice itself, have been established.

MAGNETIC AND AURORAL OBSERVATIONS

It was hoped that measurements of the strength and direction of the horizontal component of the earth's magnetic field would provide a useful correction to the application of the calculated harmonic analysis of magnetic forces in high southern latitudes. Periodic measurements, supplemented by two-week-duration continuous measurements, were taken with Le Cour quartz-fibre magnetometers. The results have not yet been computed, but it appears that the vector change, and the rate of change, of the field was so great that the expedition's readings, by themselves, may have relatively little general value at present. The rapid rate of change is of interest; it now remains to combine these observations with others, made earlier and still being made, around the fringe of Antarctica.

Information was also gathered on the relation between magnetic disturbances and auroral activity. Maudheim did not have the fortune to be close to the belt of maximum Aurora Australis activity, but photographs were obtained from Maudheim of

nearly all conspicuous auroral displays seen in the 1950 and 1951 winters, and the type, frequency, and positions, though not the heights, of the aurora were charted.

PHYSIOLOGY

The physiological researches were mainly extensions of those carried out by various American expeditions to the Antarctic, and by physiologists studying the effects of winter and Arctic conditions on the armed forces in northern Canada. They were designed to elucidate the reaction of the human body to the various stresses imposed by short and long periods of exposure to low temperatures, with and without bodily exertion, and to note the effects, under these conditions, of prolonged periods on restricted diets. Each member of the expedition was tested monthly, while at the base, for his basal metabolic rate, his adrenalin factor, and his blood sugar, haemoglobin, and red and white corpuscle content. The blood tests were begun before the expedition left the temperate zone on the way to Antarctica, and continued until it returned to Europe. During one season the tests were carried out in the field, on dog-sledging journeys. Almost every member of the party led a rather specialized life; the radio operators, for instance, had a sedentary, almost completely indoor job; the base meteorologists were frequently exposed to low temperatures for short periods without the opportunity of indulging in physical exertion, while some of the field men spent almost exactly 50 per cent of the entire time away from the base, leading a comparatively strenuous life. It was thus possible, allowing for individual variations, to build up a fairly comprehensive picture of bodily reactions and acclimatization to different degrees of exposure to cold and adjustment to a known and unvarying diet. For example, the rise of blood sugar content upon becoming accustomed to Antarctic conditions was relatively uniform for all members; but the white corpuscle counts varied strikingly in relation to the activities of the individual. The haemoglobin factor and the body weight showed characteristic yearly curves, while the red corpuscle count remained essentially unchanged. Much analysis and comparison

of these results with studies made elsewhere must be done before a generalized statement can be made, but the approach of considering individual long-term responses to cold in relation to different conditions of work promises to lead towards some worth-while contributions.

FURTHER READING

For the results of some earlier investigations relevant to the work of the expedition, see:

Ahlmann, H. W.:son. 'Glaciological Researches on the North Atlantic Coasts. *Royal Geographical Research Series*, 1 (1948).

Ritscher, A. *Deutsche Antarktische Expedition 1938-39*. Leipzig, 1942.

Nye, J. F. 'A Method of Calculating the Thicknesses of the Ice-sheets'. *Nature*, **169**, 529 (1952).

For general accounts of scientific investigations in Antarctica, see:

Hayes, J. G. *Antarctica: a Treatise on the Southern Continent*. London, Richards Press, 1928.

Simpson, F. A. *The Antarctic Today*. Wellington, New Zealand Antarctic Society, 1952.

Taylor, G. *Antarctic Adventure and Research*. London, Applleton, 1934.

A NEW ERA IN MICROSCOPY

J. G. THOMAS

As long ago as 1873 Ernst Abbé realized that, no matter how much he might strive to perfect the microscope, there would be a limit to the fineness of the detail which he could expect to see in an object. This limit was set by the very nature of light itself. In fact, two neighbouring points in the object could never be distinguished as separate if the wavelength of the light in which they were viewed was greater than about twice the distance between them. For yellow light, the smallest 'resolvable' distance would be about 3,000 angstrom units (0.0003 mm.), and for the shortest ultra-violet light not strongly absorbed by glass it would be about 1,500 Å.

Abbé evolved the now well-known oil-immersion technique for getting the best possible resolving power, and, for some fifty years after that, microscopy was in a sort of consolidating process. It is only in the last quarter of a century that really important advances have again been made.

Let us imagine ourselves as microscopists of twenty-five years ago, and try to think of some of the ambitions we should have had, and some of the improvements we would have liked. Afterwards we shall consider to what extent some of the more important needs have been satisfied by the developments of these intervening twenty-five years.

We would certainly have wished to find some way of overcoming the resolving power difficulty mentioned earlier, and, as we have seen, the way to do this was to find some radiation with a wavelength shorter than that of visible light. Secondly, a method of producing contrast in an image other than by staining the specimen was badly needed. We would have liked also a longer working distance between microscope-objective and

specimen, while at the same time maintaining an adequate resolving power.

Had it been suggested to us, the idea of a reflecting microscope must have had a very strong appeal. There would be no troublesome colour effects (chromatic aberrations) which one gets with lenses, and if focused in, say, yellow light, it would still be in focus on changing to ultra-violet or infra-red light. It could be used at wavelengths far below those at which glass (3,300 Å.), or even quartz (2,000 Å.), strongly absorb radiation. There would be no lens surfaces to scatter light, and the working distance could be quite large. There were, however, serious obstacles to the construction of a reflecting microscope with a resolving power as good as that of the best lens microscopes.

Finally, as applied microscopists, we might reasonably have looked forward to refinements in instruments for projection and photomicrography, etc., and to the development of various new accessories for microscope work.

It is not to be inferred from this approach that the advances in microscopy which we shall now describe have resulted from direct attempts to satisfy the needs mentioned above. Indeed, in the case of the reflecting microscope, it has been said that: 'This instrument was made largely for the sheer fun of making a microscope with mirrors instead of lenses.'

ELECTRON MICROSCOPY

We have seen that short-wave radiation means higher resolving power and, in 1912, when the wave nature of x rays was discovered, it was hoped that an x-ray microscope might be made. There were, however, no substances to bend the x-ray beams and form an image, in the way that glass bends light, and for the time being the idea was dropped.

Some 20 years later it was found that electrons have wave properties and that electron beams could be bent by suitable electric or magnetic fields. M. Knoll and E. Ruska, and E. Brüche set to work to make an 'electron' microscope. The first results were very modest, but great progress was made and higher and higher resolving powers achieved. In 1947, this was

called to a halt, when J. Hillier and E. G. Ramberg obtained a resolving power not much different from the effective theoretical limit of 7 Å. This limit arises from imperfections in the electron lenses, the electrons passing through the middle of the lens coming to a focus at a different point from those coming through the edges of the lens. To get another ten-fold increase in resolving power this 'spherical aberration' must be reduced *one ten-thousand fold*. This means that a two-fold increase of resolving power is really optimistic.

Nevertheless, a resolving power of 10 Å. is already a hundred times better than the ordinary microscope could do – a very substantial advance, which has been accompanied by a host of new discoveries. Today, electron microscopy has a tremendous number of techniques of its own – ultra-thin sectioning, electron 'staining', shadowing, replicas, and many others. For the future, perhaps the brightest prospect is the possibility of resolving detail down to 1 Å. by applying to electron microscopy a new microscope principle. We shall discuss this later, but shall now go on to consider another type of microscope.

X-RAY MICROSCOPY

In addition to having very short wavelengths, as have high-energy electrons, x rays have also a great penetrating power. They are much less readily absorbed by solids than are the charged electrons, so that an x-ray microscope offers not only the possibility of a high resolving-power, but also of revealing the internal structure of small opaque objects. There should be no need to cut the specimen up into thin sections in order to examine it, and this contrasts strongly with the case of the electron microscope, where sections of 1/10,000 mm. thickness are needed to avoid absorption of electrons.

The earliest x-ray microscope was of the kind shown in Fig. 1. A shadow of the object was thrown onto the photographic plate. As in the pinhole camera, a good image demanded a small pinhole, but the smaller the pinhole, the less radiation got through, so the exposure had to be very long. The picture had to be greatly enlarged, so an emulsion of fairly fine grain

was needed, which increased the difficulty. This was an obstacle to the development of this type of instrument. However, if an electron-beam is brought to a focus on a metal target, then x rays are generated at the point of impact, and in place of a pinhole we have the equivalent of a point-lamp (actually of less than $1/1,000$ mm. diameter), and satisfactory shadow enlargements can be obtained. (For recent developments see *Science News* 25, 117, 1952.)

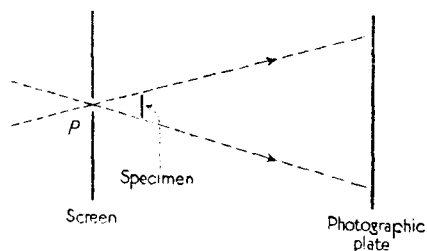


Fig. 1. The earliest x-ray microscope: a shadow microscope, using pinhole illumination. In its more recent development, the pinhole-source P is replaced by a localized source of x rays obtained by focusing an electron beam onto a metal target at P .

Fairly recently, W. Ehrenberg (1947) and P. Kirkpatrick and A. V. Baez (1948) have imaged x-ray beams by reflexion at grazing incidence from concave mirrors, as shown in Fig. 2.

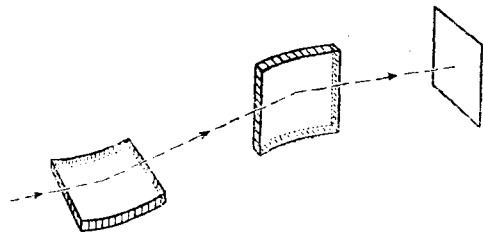


Fig. 2. Focusing of x rays by glancing reflexion at two surfaces each of elliptical section.

If the surface of the mirror were part of an elliptic cylinder, then we would expect rays from a point source at one focus to

come to a point at the other focus. This follows from the well-known proposition in geometry, illustrated in Fig. 3. For reflexion at grazing incidence, the ellipse would be much more elongated than the one shown.

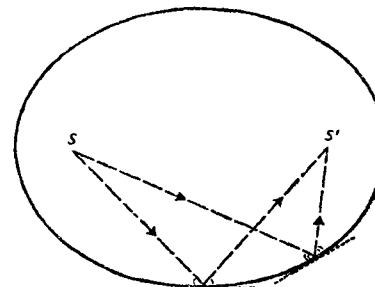


Fig. 3. The lines joining the two foci (S, S') of an ellipse to any point on the ellipse make equal angles with the tangent at that point.

Because of the difficulty of making an accurately elliptic surface, Kirkpatrick and Baez used a circularly cylindrical surface, and Ehrenberg a bent strip. These were far from ideal conditions, so a great deal could not be expected. A resolving power of about $1/1,000$ mm. (10,000 Å.) was claimed in 1948. If the technical problems of making accurately elliptic-section surfaces can be overcome and something like the theoretical limit attained (said to be about 70 Å.), then it will be a valuable instrument; it must be remembered that the early results with the electron microscope were very modest. An x-ray microscope would have the important advantage over the electron microscope that specimens need not be placed in a vacuum chamber; but let us return now to ordinary visible light microscopy.

PHASE-CONTRAST AND INTERFERENCE-CONTRAST MICROSCOPY

Phase contrast illumination was applied to the microscope by Professor F. Zernike in 1942,* and since then hundreds of papers have been written on this new type of illumination and on its

*See *Science News* 5, 63 (1947).

application to various problems. Fig. 4 shows diagrammatically the arrangement in a phase-contrast microscope. *P* is a glass plate with an annular groove. The groove is just deep enough to introduce a difference in timing amounting to one-quarter of a vibration (90° change of phase) between the light going through the grooved part and the light going through the rest of the plate. The screen *D* with an annular ring cut away allows just as much light to pass through the objective as will fill the groove in the phase-plate. Light scattered or 'diffracted' by the object will not pass through the groove, and when this light arrives at the image it is out of step with light coming direct from the source, and an interference pattern is formed. This is the image seen in the eyepiece. As the various parts of the object introduce different phase-changes into the light, according to their refractive indices, the image seen in the eyepiece is a refractive index map of the object.

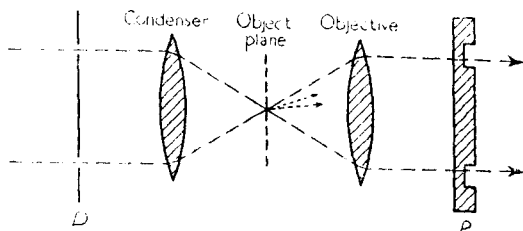


Fig. 4. Optical arrangement in a phase-contrast microscope (see text).

Of the modern developments in phase-contrast work, the most important is that for controlling the phase-retardation and amplitude of the light, for by changing these we can select at will the arrangement giving the best contrast. B. O. Payne described in 1950 a phase-contrast instrument using polarized light and a sort of polarimeter arrangement, and the same instrument has been adapted for coloured phase-contrast illumination. J. Dyson has attacked the problem in quite a different way. He has constructed an interference microscope which has advantages over the conventional phase-contrast microscope. The object is sandwiched between two half-silvered plates of glass

and examined with a special mirror system, so that some light goes straight through to the eyepiece without passing through the object (which must be small enough to allow this) while the rest of the light goes through the object. When these two components arrive at the image, interference fringes are formed. This pattern shows up the refractive index structure of the object and the best type of contrast can be selected at will, by moving the 'sandwiching' mirrors. The instrument is a full aperture, continuously variable, phase-contrast microscope.

MICROSCOPY BY WAVEFRONT RECONSTRUCTION

This is a different type of process for interference contrast, suggested by Professor D. Gabor in 1948. There are two steps in the process. The first operation is to shine a beam of coherent monochromatic light on to the object. By coherent, we mean that in a suitable experiment, the light could be made to form interference fringes. The object must be small enough to allow light to pass round it, as well as through it. The light is received on a photographic plate *P*, as shown in Fig. 5a. The arrangement is the same as the x-ray shadowing device mentioned earlier, but

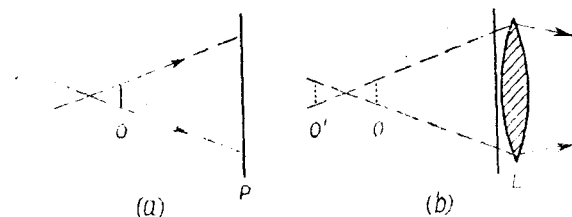


Fig. 5. Microscopy by wavefront reconstruction: (a) formation of interference pattern (hologram) by illumination of the object *O* with coherent monochromatic light; (b) reconstruction of the object, from the interference pattern, through the formation of two images at *O*, *O'*.

now the pattern does not look at all like the object because the wavelength of light is so much longer than that of x rays.

After printing, the photograph, called by Gabor a hologram, is put back and the object *O* is removed. A lens *L* is now put

behind the hologram and, on looking through this, an image of the object is seen in the old position. The hologram has given up its information about the object and an image has been reconstructed. It may puzzle us that an image can be reconstructed when the photographic plate could only record the intensity of the light falling on it, and not the phase. Sir Lawrence Bragg was once a little puzzled by this! The key to the mystery lies in the fact that two images are reconstructed, one at O and the other at O' of Fig. 5b. These can be seen on changing the focus of the eyepiece.

In the taking of the hologram, the amplitude of the wave scattered by the object is much smaller than that of the primary wave coming from the source. The amplitude at the photographic plate (which very nearly coincides with the primary wave front) is therefore very nearly the sum of the primary amplitude and the component of the secondary amplitude *in phase with it*. In Fig. 6, OR is very nearly equal to OP .

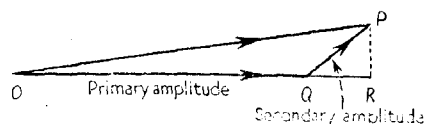


Fig. 6. Microscopy by wavefront reconstruction (see text).

In the reconstruction process, the hologram transmits an amplitude proportional to the original OP at that point and this is in phase with the primary amplitude. For this phase relationship to be right, it is necessary that *two* images should appear, so that the out-of-phase component from one 'balances out' the out-of-phase component from the other.

The application of the Gabor principle to electron microscopy is really a process of transferring one's difficulties from electron optics to the realm of ordinary light optics (where they are more easily dealt with). The idea is first to take a hologram using monochromatic electrons instead of visible light. This contains all the necessary information about the object and can be made to give up this information by reconstructing an image in visible light. This is done by using a light-optical imitation of the

original electron wave, all essential dimensions being scaled up in the ratio of the wavelengths of light and electron waves. Work has been going on for some time, at the A.E.I. laboratory at Aldermaston, to develop this new electron-optical microscope, but difficulties were encountered. Haine and Dyson, in 1950, suggested that the Gabor principle might be applied in a different way by slightly modifying an ordinary electron microscope. They put in a small stop to cut down the aperture, and to ensure coherence of the electron beam (a small aperture is essential for coherence just as coherent light must come from a small area of a source). The hologram is taken with a defocused image, and the reconstruction carried out in visible light. It has recently been reported that a resolution approaching 2 Å. has been achieved with certain objects under favourable conditions.

Quite apart from the application to electron microscopy, Professor Gabor is now making use of the fact that the hologram contains all information about the object *in three dimensions*, and is working on a new light microscope which '... takes a three-dimensional record of the object in two interference photographs which can afterwards be completely reconstructed in space.'

REFLECTING MICROSCOPES

In 1947 C. R. Burch demonstrated a high performance reflecting microscope.* A diagram of the arrangement is shown below.

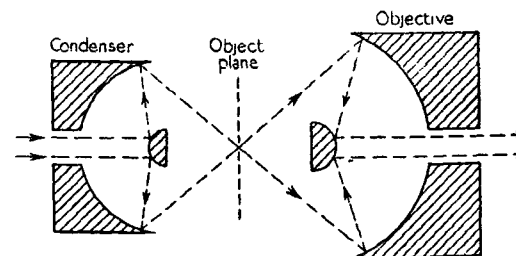


Fig. 7. Reflecting microscope: C. R. Burch's design, in which the two larger mirrors are aspherical.

*See *Science News* 5, 63 (1947).

Two of the mirrors were aspherical to cut down aberrations at high numerical aperture and these had to be accurate to a fraction of a wavelength. This was achieved by a long delicate 'figuring' process. More recently, reflecting microscopes have been made with all spherical mirrors. Apart from having a lower numerical aperture, these instruments also enjoy the advantages of achromatism, long working distance, etc.

Wynne has made solid reflecting objectives in which the space

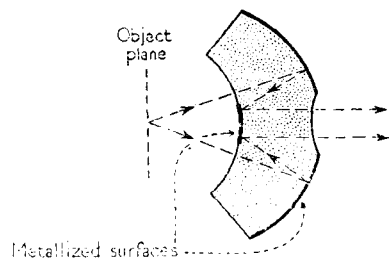


Fig. 8. Reflecting objective, made by C. G. Wynne, in which the two mirrors are formed on opposite sides of the same glass, which fills the space between them.

between the mirrors is filled with glass, as shown in Fig. 8. These are robust and cannot get out of alignment. The mirror surfaces

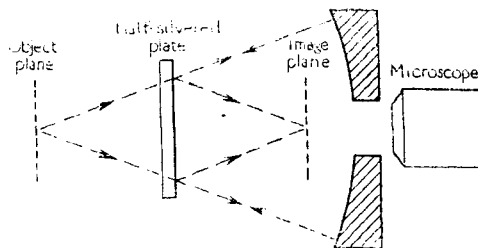


Fig. 9. Reflecting objective, of unit magnification, used by J. Dyson in conjunction with a conventional microscope, to obtain a longer working distance, for example in the viewing of a hot metal surface.

are protected, which is a big consideration in a place like London.

Finally, Dyson (1949) has used a reflecting objective of unit magnification to obtain a longer working distance with a conventional lens microscope. This is shown in Fig. 9.

MICROSCOPY TODAY AND IN THE FUTURE

Many of the aims of microscopists of twenty-five years ago have been fulfilled. A tremendously improved resolving power is available. New methods of obtaining adequate visibility in the image have been devised, principally by phase-contrast and interference-contrast methods, and by using radiation outside the visible region of the spectrum. A much greater working distance is available and has already been exploited for such diverse purposes as looking at hot metal surfaces, and looking at the surfaces of whole animals while under dissection. For the first time, we have a truly achromatic high-power microscope which, to take but one example, should prove of immense value for ultra-violet absorption measurements in single animal cells. A host of new accessories for the ordinary microscope have been produced: hot stages, optical staining devices, improved illuminators (other than the radically different *types* of illumination mentioned earlier), high resolution photographic plates for recording and many others. Specimen preparation, especially for the electron microscope, has now a tremendous literature of its own, embracing such techniques as ultra-thin sectioning, shadowing, staining, taking replicas and so on. No less marked has been the increasingly wide use to which the microscope has been put. Today we find it used not only to look at things, but to size, count, and even weigh particles of matter. We have not had space to consider all these; but see, for example, a recently published note by R. Barer on a method of mass-determination (*Nature*, 1952, 169, 366) and 'The Flying Spot Microscope' in *Science News* 22.

These have been some of the advances made in these last twenty-five years. Now let us look to the future.

Some check on the results obtained with the electron micro-

scope is badly needed. It is possible that this need may be, to some extent, met by an x-ray microscope, if anything like the theoretical resolving power can be achieved. Electron microscopy may be expected to press still further into uncharted lands and it is relevant to ask: how much longer will there continue to be new things to see? We are already approaching the sort of size which we have come to associate with single atoms of matter.

Although we have painted a rosy picture of the tremendous advantages of the reflecting microscope, we have omitted to say that very few high quality instruments are available owing to the difficulty of construction. We must hope that new methods of making aspheric mirrors will soon be developed, and work towards this goal is being carried out by C. R. Burch and his collaborators at Bristol. Other technical advances in microscopy must surely come from the use of new glasses and plastics.

Several of the important advances in the last twenty-five years may be said to have stemmed from basic considerations of the mechanism of image formation in the microscope, i.e. from treating the image as a sort of interference pattern. This approach, as we have seen, has proved very fruitful, and may well continue to do so in the future. There may, of course, be advances quite as revolutionary as those we have described, but, neglecting these, and basing our ideas only on what has already been achieved, let us imagine with Dr R. Barer (a leading practical microscopist of the day) – a 'dream microscope of the future':

'This would be a Burch microscope ... with immersion components for various spectral ranges. It would be equipped with phase-contrast illumination for the ultra-violet, visible, and infra-red regions. Interferometer microscope attachments would also be available for these regions. The image could be photographed or viewed directly on the screen of an ultra-violet or infra-red image converter. On one side of the instrument there would be an ultra-violet spectrograph, on the other an infra-red spectrograph, so that, by rotating a suitable mirror, it would be possible to record the spectral absorption of a microscopic

object over the entire region extending from, say, 2,000 Å. up to 25μ [0.025 mm.]. Provision would also be made for the direct photoelectric recording of spectra which would be projected onto the screen of a cathode-ray oscillograph. In this way, owing to the very high speed of response of electronic systems, it would be possible to observe spectral changes occurring in reactions proceeding at very high speeds, as, for example, during muscular contraction. These direct and spectrographic methods would be carried out using both polarized and unpolarized radiation, and would allow work on both dichroism and birefringence to be accomplished at any wavelength. In addition to all this, special methods of illumination would be provided for use with micro-manipulation apparatus, so that the object might be turned in any direction, cut, damaged, stimulated electrically, or substances could be injected into it, as the need arises. Where possible, means would be available to transfer the same object into other instruments, such as the electron microscope and, let us hope, the x-ray microscope. Fantastic? Perhaps, but how pleasant to contemplate!'

FURTHER READING

Electron microscopy

For an elementary account, see:

Cosslett, V. E. *The Electron Microscope*. London, Sigma Books, 1947.

X-ray microscopy

For mirror-imaging devices, see:

Ehrenberg, W. *Nature*, **160**, 330 (1947).

Kirkpatrick, P., and Baez, A. V. *Journal of the Optical Society of America*, **38**, 766 (1948).

For modern work on shadowing devices, see:

Cosslett, V. E., and Nixon, W. C. *Nature*, **168**, 24 (1951).
Science News 25, 117 (1952).

Phase-contrast microscopy

For a full but fairly elementary account, see:

Keohane, K. W. *Science Progress*, **39**, 459 (1951).

For two different methods of improving on conventional phase-contrast illumination, see:

Payne, B. O. *Journal of the Royal Microscopical Society*, **70**, 225 (1950).

Dyson, J. *Proceedings of the Royal Society 'A'*, **204**, 170 (1950).

General

For a very full account of modern practical microscopy up to October 1951, see:

Barer, R. *Journal of the Royal Microscopical Society*, **71**, 307, (1951).

ULTRA-VIOLET RADIATION IN THE EXAMINATION OF WORKS OF ART

GEORGE SAVAGE

WITHIN recent years the ultra-violet part of the spectrum has been increasingly used for the examination of works of art. Up to the present, however, little has been published on this subject in a generally accessible form, and it is not possible within the compass of one short article to do more than sketch the position as it stands today. Investigations into the potential usefulness of ultra-violet radiation are still at a comparatively early stage, and there is much to be learned about the effects observed.

The term 'ultra-violet' refers properly to radiation of all wavelengths between 100 and 4,000 angstrom units. At the latter point, ultra-violet radiation becomes visible violet light. Wavelengths from about 1,700 angstrom units (1,700 Å.) upwards can be studied in air by more or less 'optical' methods. The waveband used for the purposes later described ranges from approximately 2,300 Å. to 4,000 Å., the most useful bands being around 2,537 Å. and 3,654 Å. respectively. The source of radiation most commonly used is the high-pressure mercury vapour lamp enclosed in a quartz tube. Particular wavebands, including the two which are most useful, are obtained by interposing suitable filters between the source of radiation and the object to be examined of which those made from Woods glass are the most widely used for general purposes.

Ultra-violet radiation is commonly divided into 'near' and 'far' wavebands on the basis of transmission or absorption by glass. Wavelengths of between 1,800 Å. and 2,300 Å. are passed

by quartz, but not by glass. Glass will pass from 2,300 Å. upwards, although its efficiency of transmission increases rapidly as the wavelength approaches that of the visible spectrum. The 'near' ultra-violet region extends from approximately 3,000 Å. until visible violet is reached.

Examinations of works of art by radiation of this kind depend for their value on the phenomenon of fluorescence. When ultra-violet radiation falls upon certain substances, the wavelength is transformed into that of visible light. The colour of the visible light produced varies according to the nature of the substance, and, so far as objects are concerned which exhibit the property in a marked degree, the effect is due to the presence of trace-elements that are more than usually sensitive to radiation of this nature. In cases where the substance does not fluoresce, the small proportion of visible light passing the filter will be reflected back in an unchanged state. Phosphorescence is the persistence of fluorescence after the exciting radiation has been shut off, and is of small interest for our present purpose.

The phenomenon of fluorescence was first investigated seriously in the middle of last century by Sir George Stokes, and Stokes's law states that fluorescence is always of a longer wavelength than that of the radiation which causes it.

These differences in fluorescence between materials are extremely important, because it is usually impossible for the repairer, restorer, or faker to find substances for his purpose which will fluoresce in the same way as the material from which the object was originally made. For this reason ultra-violet radiation can sometimes be used in selected cases instead of the older method of chemical analysis, which in some degree is destructive. A method which can provide the required information without affecting the object under consideration is of the utmost value.

Ultra-violet radiation as a method of examination, however, is very much in the experimental stage at present, and results usually need to be interpreted by an experienced observer, but it has already proved its worth in the detection of restorations and, to a lesser extent, of forgeries.

REPAIRS, RESTORATIONS, AND FORGERIES

Porcelain figures of the 18th century are often extremely highly valued, several hundreds of pounds being a not uncommon price for a rare specimen. Naturally, the value fluctuates somewhat for damaged specimens according to rarity and the extent of the damage. This has led to an extensive and legitimate business in the restoration of such examples, and the restorer has attained a high degree of skill in his craft, so much so that it is often difficult in ordinary light to say where porcelain leaves off and restoration begins. Without ultra-violet radiation, therefore, the buyer is in somewhat of a quandary in estimating the desirability of particular specimens. Under ultra-violet radiation, however, there is a well-marked difference between the fluorescence of porcelain and the materials used for restoration.

As an example, if an arm be missing, a substitute is modelled in composition and attached, its surface being painted to resemble the original porcelain. If such a repair is subsequently examined by radiation of around 3,654 Å., the surrounding porcelain itself will fluoresce with varying shades of violet or blue, whereas the restorer's paint exhibits a strong whitish-yellow colour which is quite unmistakable. It is therefore a simple matter to gauge the extent of the repair.

Old marble is sometimes the subject of extensive restoration. Excavated statuary is usually found in a badly damaged condition, and the faker goes to great lengths to provide a saleable object for the art market, replacing missing parts with others made from natural or artificial stone, and, upon occasion, marrying fragments to produce a more or less complete specimen.

The fluorescence of old marble, however, differs considerably from that of new, and the use of unrelated fragments usually becomes quite obvious under this kind of examination.

It has been found by experiment on undoubted examples that, in course of centuries, a certain amount of disintegration takes place which penetrates from the surface inwards, the amount of penetration varying with age and the degree of exposure to the

disintegrative influences referred to. A surface of this sort will reveal immediately if an attempt has been made to rework it by chiselling or abrasive rubbing, since any disturbance of the original surface shows as an alteration in fluorescence.

Old bronze is often repaired with varying degrees of persuasiveness and ingenuity. There have been instances in which two fragments not belonging to each other have been soldered together to form a complete and spurious object of art.

At first sight it might appear difficult to do this in such a way as to defy detection by inspection by means of a hand-lens in ordinary light, but it must be remembered that the class of bronzes especially tempting to the faker are those which have been buried for long periods of time. Because of this burial they are often very much corroded as the consequence of chemical action between the metal and substances in the soil. Bronzes of this kind usually exhibit massive incrustations due to the formation of copper carbonates, oxychlorides, and so forth. These effects are referred to as patination, and need to be carefully preserved as evidence of age. Moreover, they are often extremely colourful, and a well-patinated specimen is much prized by the connoisseur. Imitation of this sort of corrosion is comparatively easy to the ingenious craftsman, especially over a limited area, and a variety of materials are used to obtain the effect.

Under ultra-violet radiation, however, any tampering with the products of corrosion is almost always immediately and obviously evident. As an example, one extremely corroded example had been broken into several pieces and later legitimately repaired. It was handed to a number of experienced observers with a request to point out where it had been joined. They were unable to do so. Placed under ultra-violet radiation, however, a number of dark violet lines appeared over the site of the joined edges caused by the difference in fluorescence between the original surface and the materials used to disguise the repair.

In the same way, soldered repairs are usually immediately and obviously visible, whatever pains may have been taken to conceal them.

Textiles – rugs and tapestries – are often repaired, and great

skill is usually brought to the task. Nevertheless, under ultra-violet radiation there is always a noticeable difference between the original work and the repair.

Much can be learned from the examination of old documents, prints, and drawings. It has been for many years a common police method to examine suspected documents for erasures in this way, and most tamperings, although they may be unsuspected in ordinary light, show up fairly plainly. Forgeries and repairs to old manuscripts and such things can often be detected. It is a fact, too, that shortage of materials in mediaeval times made it a fairly common practice to erase the writing on old manuscripts so that they could be used afresh. Under ultra-violet light, however, the original writing is often legible to some extent.

Holes in prints and drawings can be invisibly repaired by the skilled workman, but the difference in fluorescence between old and new paper, or paper from different sources, as well as the effect of the adhesive used, all combine to make the site of such repairs startlingly obvious.

So far as oil-paintings are concerned, both *x* rays and ultra-violet radiation have been used successfully in the detection of restorations and repairs. Repainting, because of differences in fluorescence between old paint and new, is easily detected. The original surface usually exhibits an extremely dark violet, whereas the new paint fluoresces with a much lighter shade. This is not so easily observed when the picture has been varnished subsequently to the repainting. Tears in the canvas, however, are usually much more obvious than in ordinary light, whether the picture has been revarnished or not.

Generally speaking, the appearance of oil-paintings under ultra-violet light needs rather more interpretation than most other objects, and considerable experience is sometimes necessary to be sure of the meaning of the observed effects.

The fluorescence of old woodwork exhibits some differences from that of new. The examination of old furniture in this way will often reveal repairs, replacements, and alterations which would otherwise pass unnoticed.

Old glass is an interesting subject for study. Glass resembles a supercooled liquid and has an amorphous structure. It can deteriorate to a surprising degree under the requisite conditions, and has been known, in some cases, to crumble to powder under excavation.

Deterioration of this kind is usually indicated by the formation on the surface of iridescent scales, particularly well seen in some Roman glass. The glaze of some Persian pottery of the 9th to the 13th centuries A.D., which is akin to the glass of the Romans in its composition, often shows a similar kind of deterioration.

It has been suggested that an orange-yellow fluorescence is necessarily to be associated with old glass. In my experience, however, modern laboratory glass often fluoresces with a similar colour. 'Pyrex' glass is an example. Glass containing lead, however, when it shows this colour at all, will only do so weakly, and in combination with a certain amount of violet.

Nevertheless, if a specimen fluoresces with a different colour from that of a genuine specimen of the same provenance and period, the chances are that it is spurious. Certain kinds of mediaeval Islamic glass which have been much copied could be examined in this way alongside attested specimens. Some genuine specimens have been observed to fluoresce with the orange-yellow already mentioned, whereas doubtful examples will probably exhibit a violet colour.

It should be remembered that fats and oils fluoresce strongly, usually exhibiting a luminous bluish-white, and their presence may be a little confusing. A peculiar effect may sometimes be noticed on pottery and porcelain which has a crazed glaze, inasmuch as grease, and greasy smoke, penetrates the glaze into the body beneath, obscuring the normal fluorescence, and giving an effect somewhat similar to that of restorer's paint. The true nature of fluorescence of this kind can be estimated from the appearance of the glaze, and it is not possible to remove the offending grease. On the other hand, surface grease can be removed with a little alcohol.

This brief résumé of some of the uses to which ultra-violet radiation can be put does not, by any means, exhaust the possi-

bilities, and growing experience of this instrument will make interpretation of the observed effects a simpler matter.

IDENTIFICATION OF OLD PORCELAIN

The past year or two has seen the beginning of an investigation which is far from complete, but which seems as though it may open a new field of usefulness for this kind of examination.

The inspection of old porcelain for repairs has shown that the colour of the fluorescence often varies widely between groups of specimens. The colours exhibited range from yellow to violet with a number of intermediate shades.

The history of much old English porcelain in particular is very badly documented, and for many reasons it is important to be able to assign to examples a place of origin and a date of manufacture with a considerable measure of certainty. In the past this has largely been carried out on the evidence of style, but, for a number of reasons, results have not always been entirely satisfactory, and the subject has given rise to much controversy.

For this reason chemical analysis has been resorted to in the past, because the 18th-century factories concerned were pretty largely consistent in their choice of sources from which they drew their raw materials, in the nature of the materials used, and in the manner in which they were used. Analysis, however, cannot always be carried out without damaging what may well be an extremely valuable specimen, although some useful 'spot' tests have been devised.

It has been noticed, however, that porcelain from some factories fluoresces with different colours or shades of colour from that of others, and experience shows these variations to be consistent enough to regard a particular shade as reasonably characteristic of a factory's production.

How far this method can be adapted to other things than porcelain it is difficult to say, but the possibility is one which should be borne in mind when examining articles to which similar observations could apply.

EQUIPMENT

An elaborate apparatus is not usually necessary. A 125-watt Osira 'black' glass lamp (which is a high-pressure mercury vapour lamp sealed in a 'black' glass envelope) is sufficient for many purposes, and, together with the necessary choke and capacitor, makes a convenient and cheap source of ultra-violet radiation. From comparison of results with more elaborate apparatus, the radiation passed appears to be especially rich in the 3,654 Å. wave-band. For experimental purposes, the more expensive Hanovia 'Detectolite' is a useful instrument, and, for important work, the big Hanovia 'Analytic' model allows filters to be rapidly and easily changed. The suppliers of these equipments will no doubt be pleased to give the requisite technical information to inquirers.

MECHANISMS
OF CHEMICAL CHANGE

K. D. WADSWORTH

CHANGE has provided inspiration for poets, philosophers, and metaphysicians for some thousands of years, and is a dominant theme both in scientific thought and in scientific experiment. Chemical change is the means by which the often unpromising materials occurring in nature are converted into products of pleasure and use to man. Integrated and inter-related chemical changes are the means by which living organisms, of all kinds, are maintained at a higher level of energy, organization, and often of temperature, than their inorganic surroundings. The mechanisms of chemical change are thus of the greatest practical, as well as of theoretical, interest. Ideas about the nature of these mechanisms have developed from an initial but delusive simplicity, through increasing difficulty and complication, to the present stage in which 'The Principle of Maximum Simplicity' is an accepted corner-stone of the science. This return to an underlying simplicity has resulted from the recognition that actual chemical changes proceed by successive steps, which individually are simple, and not, as chemists used to write them, as if prologue and conclusion were the whole story. Thus broken down and analysed, chemical change reveals a beauty of pattern which may inspire new generations of poets, just as the patterns of the structure of matter are providing new themes and inspiration to artists and designers.*

CHEMICAL COMBINATION

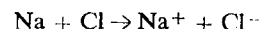
The diversity of the forms of matter is a consequence of the very large number of ways in which the atoms of some 90 different

*See *Science News* 22, Inset 20.

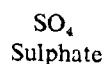
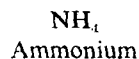
elements can be combined together in different proportions and in different ways.

The atoms are bound together in the molecules of the different compounds by chemical bonds of which three types are recognized. These differ in the disposition of the electrons which are the essential components of all three types.

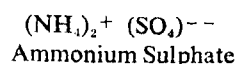
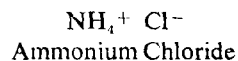
The simplest type is the *electrovalent bond* which is found in many salts, such as sodium chloride. This bond is formed by the transfer of one, or more, electrons from one atom, which becomes a positive *ion*, to another atom, which becomes a negative ion :



In the solid state, the ions are arranged in a regular array, or *lattice*, such that the electrical attractions between the oppositely charged ions, and the repulsions between the similarly charged ions, are balanced. In presence of suitable liquids, or when the solid salts are melted, the electrical forces become much weaker and the ions can separate, or *dissociate*, from one another. Consequently a solution of a salt, such as sodium chloride, contains only sodium and chlorine ions. Groups of atoms such as



can also form electrovalent bonds by losing electrons to, or gaining them from, other atoms or groups of atoms, e.g. :

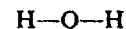


The hydrogen and nitrogen atoms in the ammonium group, or the oxygen and sulphur atoms in the sulphate group, are bound together by a different type of bond – the *covalent bond*. This bond which is present in all non-saline compounds, as well as in some salts, is the type which will concern us most here. It is formed when one, or more, electrons from each of the combining atoms is shared between these atoms. Each pair of electrons so shared is conventionally indicated by a line thus : —.

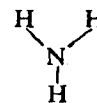
Examples are :



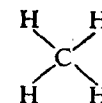
Hydrogen Chloride



Water

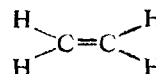


Ammonia



Methane

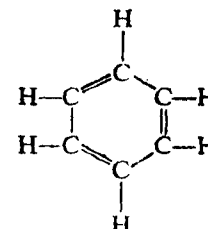
When more than one electron from each atom takes part, *double* and *triple bonds* are formed, as in :



Ethylene

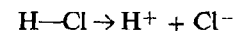


Acetylene



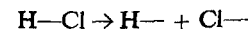
Benzene

The electrons forming a covalent bond are not always shared equally between the two atoms bound, so that the bond may be 'polarized', one atom being fractionally positively charged and the other fractionally negatively charged. In certain circumstances this polarization can go further, the pair of electrons being transferred completely to one of the atoms so that the bond dissociates giving a positive and a negative ion, e.g. :

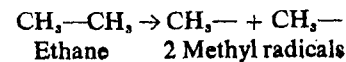


This is called *heterolytic fission* and usually occurs only in solution in certain types of solvents.

A covalent bond may in other circumstances break by *homolytic fission*, each of the electrons separating with one of the atoms, giving two *free atoms*, e.g. :



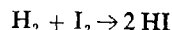
or – if the atoms concerned have other atoms bound to them – *free radicals*, e.g. :



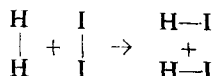
In the third type of bond, the metallic bond, found – as its name implies – in metals, a number of electrons appear to be held communally by a number of atoms, but this type of bond will not concern us here. (For a further account of these three types of bond, particularly covalent bonds, see 'The Shape of Inorganic Molecules' by R. S. Nyholm in *Science News* 20.)

THE RATES OF CHEMICAL REACTIONS

All chemical reactions consist essentially of a rearrangement of the atoms in the molecules of the substances concerned. This is self-evident – to take the simplest of examples – when the equation expressing the reaction of hydrogen gas with iodine vapour forming hydrogen iodide:



is written in a way which shows the changes in the chemical bonding which it involves:



Such a rearrangement can clearly only occur when the molecules come into close contact and collide with one another. The rate of the reaction must then depend on the frequency of such collisions which will be greater the higher the pressure, or concentration, of each reactant.

The influence of the concentrations of the reactants on the rates of chemical reactions was discovered very early in the development of chemical kinetics – which is the name given to the study of the rates of chemical reactions. Wilhelmy in 1850 showed that the rate of transformation of cane sugar into invert sugar was proportional to the amount of cane sugar remaining at each instant, i.e.:

$$\text{Rate} = k \times \text{concentration of cane sugar}$$

k being called the specific velocity constant. Berthelot and Saint-Gilles in 1862 demonstrated a similar relationship in the cases of the esterification of acetic acid with ethyl alcohol, and the reverse reaction, the hydrolysis of ethyl acetate. These observations formed the basis of the *Law of Mass Action* enunciated by

Guldberg and Waage in 1864. This stated that 'the rate at which a substance reacts is proportional to its concentration' and provided an explanation of the problem of chemical affinity and equilibrium which had long puzzled scientists.

Thus ethyl alcohol and acetic acid react together to form ethyl acetate and water. But ethyl acetate and water also react together forming ethyl alcohol and acetic acid. In such reversible reactions, it is found that after a certain time, depending on the conditions, no further change appears to occur even though each pair of reactants is still present. In fact, a 'dynamic equilibrium' is set up, the concentrations of the components being such that both reactions proceed at the same rate. Hence, using square brackets to indicate the concentration of the substance enclosed by them:

$$k_f \cdot [\text{Ethyl Alcohol}] \cdot [\text{Acetic Acid}] = k_r \cdot [\text{Ethyl Acetate}] \cdot [\text{Water}]$$

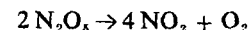
and therefore

$$\frac{[\text{Ethyl Acetate}] \cdot [\text{Water}]}{[\text{Ethyl Alcohol}] \cdot [\text{Acetic Acid}]} = \frac{k_f}{k_r} = K$$

K is termed the 'equilibrium constant'.

The Law of Mass Action led naturally to the classification of chemical reactions according to the number of components upon whose concentration the rate of the reaction depended. This number was called the (kinetic) *order* of the reaction.

Thus the decomposition of nitrogen pentoxide which takes place according to the equation

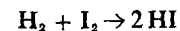


proceeds at a rate which is directly proportional to the concentration of nitrogen pentoxide:

$$\text{Rate} = k \cdot [\text{N}_2\text{O}_5]$$

This is a *first order reaction*.

The reaction between hydrogen and iodine already mentioned:



takes place at a rate dependent on the concentrations of both hydrogen and iodine—

$$\text{Rate} = k \cdot [\text{H}_2] \cdot [\text{I}_2]$$

and is therefore a reaction with *second order* kinetics.

The oxidation of nitric oxide by oxygen to nitrogen peroxide:

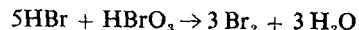


takes place at a rate which depends on the square of the concentration of nitric oxide and on the concentration of oxygen, thus:

$$\text{Rate} = k \cdot [\text{NO}]^2 \cdot [\text{O}_2]$$

This reaction therefore exhibits *third order* kinetics.

Reactions of apparently higher order are also known. For example the interaction of bromides and bromates in acid solution forming bromine and water:



can only conveniently be expressed by a kinetic equation of the type:

$$\text{Rate} = k \cdot [\text{H}^+]^2 \cdot [\text{Br}^-] \cdot [\text{BrO}_3^-]$$

and is therefore a *fourth order* reaction.

ACTIVATION

The concept of the kinetic order of a chemical reaction found a ready interpretation in the Kinetic Theory developed in the latter half of the last century principally by Clerk-Maxwell and by Boltzmann. The rate of a reaction depends on the frequency of collisions between molecules of the reactants and therefore on their concentrations. The collision-frequency Z can be calculated from considerations based on the Kinetic Theory. It might be expected, as a first approach, that the collision-frequency would agree with the reaction-frequency for the same substances. However, this cannot be correct, as can be seen readily from a simple general argument. For the purpose of calculating collision frequencies, the properties of a gas are sufficiently defined by the mass and size of its molecules, together with the pressure and temperature. But it is common knowledge that pairs of gases which are comparable as regards density react together at rates which vary from explosive to very slow. There are even bigger discrepancies when the results of calculations based on the Kinetic Theory are compared with measured reaction rates. For a 50-50 mixture of hydrogen gas and iodine

vapour, at atmospheric pressure and at a temperature of about 300° C., it is found that there are about 10^{24} collisions between hydrogen and iodine molecules per second in each cubic centimetre. But the observed rate of the reaction shows that only about 10^9 collisions per second in each c.c. result in the formation of hydrogen iodide. In general, it is found that the collision-frequency calculated from the Kinetic Theory exceeds the actual reaction-frequency by millions of millions of times. Mere collision of the molecules is therefore not enough, and only very exceptional collisions result in reaction. Arrhenius in 1889 suggested that only collisions of molecules whose energy exceeded a critical amount, E , called the energy of activation, were effective. The fraction of collisions which fulfil this condition is normally given by

$$e^{-E/RT}$$

where e is the base of Naperian logarithms, T is the temperature in degrees Absolute, and R is a constant. The velocity constant of a reaction, k , is therefore given by

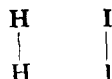
$$k = Z \cdot e^{-E/RT}$$

This theory explains the great sensitivity of the rates of chemical reactions to the temperature – a rise of 10° C. doubles the rate of many chemical reactions – and works very well, particularly for many gas-phase reactions. E can be determined by studying the variation of the reaction rate with temperature, and combination of this with the calculated value of Z according to the Arrhenius equation, above, gives values for k in good agreement with experiment.

However, there are many reactions, particularly in solution, for which the value of k calculated in this way exceeds the experimental value by a factor as large as 10^6 . This means that even in collisions involving the requisite energy E some other condition remains to be satisfied before reaction can take place. Thus, for example, in the hydrogen-iodine reaction it is to be expected that 'end-on' collisions in which the relative positions of the molecules are



will be less likely to result in reaction than 'broadside' collisions in which the mutual orientation is:



Further, it is now realized that the process of activation necessary for reaction consists largely in the acquisition by the reactant molecules of vibrational energy in excess of the average value. As the vibrational energy of a molecule increases, the atoms vibrate more and more about their normal positions. In the stretched phase of the vibration the attachment of the atoms for each other is reduced and the molecule is therefore more likely to undergo reaction by exchanging its atoms with those of another molecule. Thus, even when a hydrogen molecule collides in a suitable orientation with an iodine molecule, the energy being sufficient for activation, whether reaction occurs may depend on the timing of internal vibration of each of the molecules.

These orientation and other conditions may be expressed by including in the Arrhenius equation a further factor P , which in some cases is as small as 10^{-8} , so that now:

$$k = P \cdot Z \cdot e^{-E/RT}$$

It is convenient to separate the conditions for reaction, namely the energy-factor, depending on the activation-energy E , and the probability factor, including both P and Z , depending on the collision-frequency and the orientation and other conditions.* If the reaction is slow because P and Z are small, we may say that the reaction has a small probability of activation. This may be because the orientation or internal-timing conditions are

*The energy-factor is referred to as the energy of activation, and the probability-factor may be related to an *entropy of activation*, by analogy with the corresponding thermodynamic concepts. This analogy has led to theoretical treatments (notably 'The Transition State Method') which have found fruitful applications but are beyond the scope of the present article.

very specialized, or because reaction requires the participation of several molecules, i.e. has a high kinetic order.

DIFFICULTIES OF THE COLLISION THEORY

In spite of all modifications, the initially simple picture of the rate-concentration relationships provided by the collision theory of chemical reactions soon begins to disappoint.

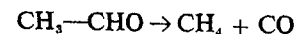
The occurrence of reactions showing first-order kinetics is an immediately obvious difficulty. If the activation necessary for reaction is acquired in collisions which clearly must involve at least two molecules, the rate of reaction should depend upon the concentrations of each participant in the collision, and first-order kinetics would be impossible.

The occurrence of reactions of third and higher order in which three or more molecules apparently collide simultaneously also appeared on closer examination to be inherently improbable. Kinetic Theory considerations show that ternary collisions are at the most one thousand times less frequent than binary collisions and simultaneous collisions of four or more molecules must be relatively even more uncommon. It is for similar reasons that, though collisions of two vehicles on the roads are all too frequent, independent collisions of three vehicles at the same time are happily rare, while those involving four or five vehicles are almost unheard of.

Again, as more reactions have been studied, many have been found to have kinetic orders which are not simple integers but involve fractional powers or complex functions of the concentrations of the reactants. Thus the reaction between hydrogen and its isotope deuterium:



— formally so similar to the simple second-order reaction between hydrogen and iodine — appears to have an order of $1\frac{1}{2}$. The thermal decomposition of acetaldehyde



and of several other carbon compounds, also appears to have an order which is neither 1 nor 2, but somewhere in between.

The reactions between hydrogen and the halogens, chlorine and bromine, forming the hydrogen halide,

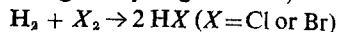


exhibit even more complex kinetics, in complete contrast to the hydrogen-iodine reaction. In the case of bromine the kinetics can only be expressed by the complicated relationship:

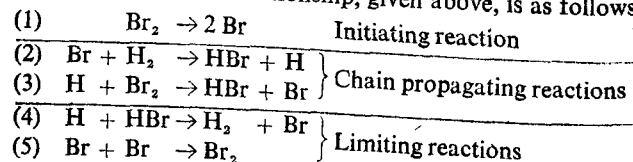
$$\text{Rate} = \frac{k' \cdot [\text{H}_2] \cdot [\text{Br}_2]^{\frac{1}{2}}}{k'' + [\text{HBr}] / [\text{Br}_2]}$$

THE PRINCIPLE OF MAXIMUM SIMPLICITY

The hydrogen-bromine reaction provides a convenient starting-point from which to show how these difficulties in the Collision Theory have been resolved, and an even greater simplicity of reaction pattern has been revealed than was at first suspected.

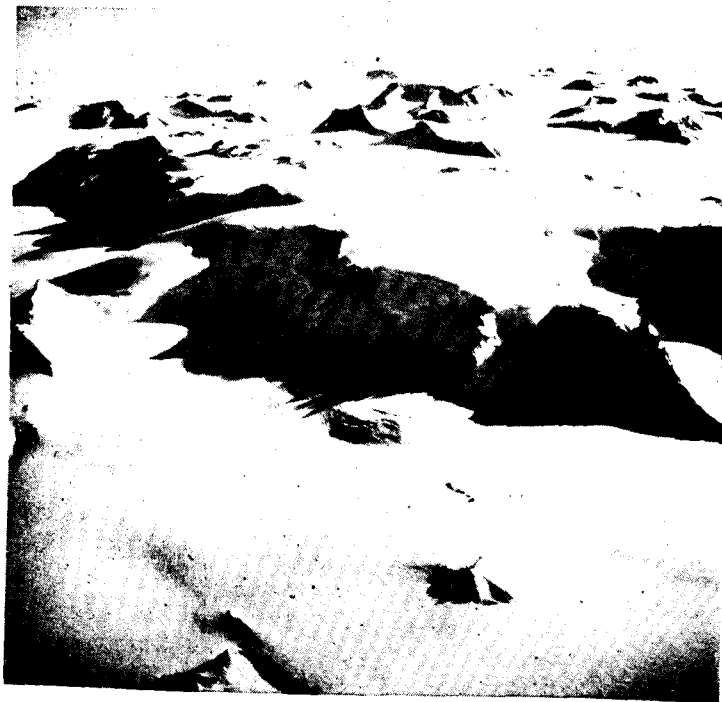
It is now recognized that reactions take place in a series of steps or stages, each of which is extremely simple, involving the reaction of only very few – rarely more than two – molecules or atoms or radicals, the breaking or formation of a single bond, or the transfer of a single atom or electron from one reacting partner to another. The reaction path adopted by a particular reaction is governed by the interplay of the energy and probability factors in activation. The often complex kinetics of the reaction as a whole result from the manner in which the simple steps in the reaction pattern are related to one another.

Taking the hydrogen-bromine reaction as an example, a scheme which explains all the features of the reaction and leads to the complex kinetic relationship, given above, is as follows:

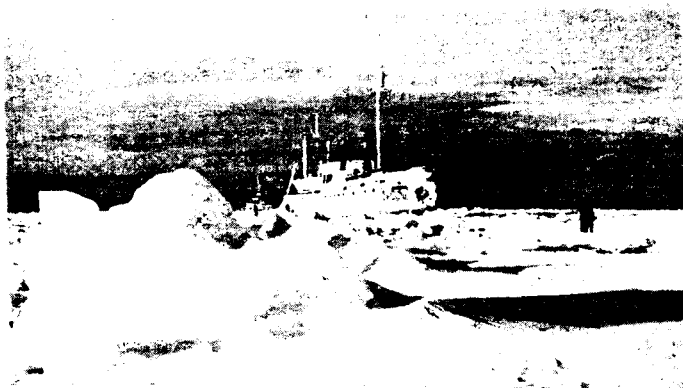


This scheme involves free bromine atoms, formed by the dissociation of bromine molecules in step (1), and regenerated after a cycle of reactions, (2) and (3), in which two HBr molecules are formed. A reaction chain is set up, which is limited only by the

NORWEGIAN-BRITISH-SWEDISH ANTARCTIC EXPEDITION 1949-52



1. Oblique air photograph looking south-west over the westernmost mountain belt of Dronning Maud Land. The southernmost escarpment (Inset 18) can be seen in the distance; and, beyond it, the horizon is formed by the high interior ice-plain. The distance across the picture, about one-quarter down from the top, is about 30 kilometres (20 miles). (This and the following 24 pictures are the copyright of the Norwegian-British-Swedish Antarctic Expedition 1949-52.)



2. The expedition ship, M.V. *Norsel*, in the pack ice about 200 kilometres (125 miles) off the coast of Dronning Maud Land.



3. General view from the air of the ice shelf fringing the coast of Dronning Maud Land, with a large piece broken free to become a tabular iceberg. About 15 kilometres (10 miles) of coastline are shown.



4. Terminal cliffs of the ice shelf, close to the expedition base. Maudheim; samples of the ice shelf, brought to the surface by a core-boring machine, were examined microscopically for grain-size and orientation in the glaciological 'cold laboratory' at Maudheim. M.V. *Norsel* can just be seen, berthed where the cliffs are lower.



5. M.V. *Norsel* berthed near the terminal cliffs of the ice shelf, close to Maudheim. Adelie penguins in foreground.



6. The expedition base at Maudheim, before its complete burial by drifted snow. Only chimneys, masts and ventilator stacks could then be seen.



7. Meteorologists prepare to launch radiosonde-rawin balloon from Maudheim. Launching in a gale, with surface-blown snow, needed all hands.



8. Inside the base hut, soon completely buried in snowdrifts, a meteorologist checks the radiation balance, and wind and temperature gradients, recorded by instruments on and above the surface.



9. Glaciologists investigate crevasses near the junction between grounded ice and floating ice shelf.



10. Main inland depot, 300 kilometres (200 miles) south-east of Maudheim. All main field journeys within the mountainous area started from here. Altitude, about 1,330 metres (4,400 ft). Depots were laid by tractor.



11. Tractors towing cargo-sledges and a caravan-sledge combining living quarters and seismic laboratory through the Dronning Maud Mountains to obtain an ice-thickness profile by seismic soundings.



12. Laying out seismometers, preparatory to sounding the thickness of the ice-cap.



13 (*top*). Panorama in the more eastern section of the Western Dronning Maud Land mountains: rocks are metamorphic, and ridges rather irregular and winding.

14 (*middle*). Panorama further to the west in the Western Dronning Maud Land mountains: here, metamorphic rocks are underlain by flat-lying igneous sills, and block-like masses are common. Heights of peaks range in both areas from about 1,000 to 1,500 metres (3,000 to 5,000 ft).

15 (*right*). Camp of the topographical and geological parties.





16. The surveying, geological, and glaciological field parties travelled by dog sledges through the mountains of Dronning Maud Land.



17. Note the skua gull, near centre. It was found, though infrequently, in all places visited; it is the only scavenger in inland Antarctica. All other birds visit the rocks only to nest.



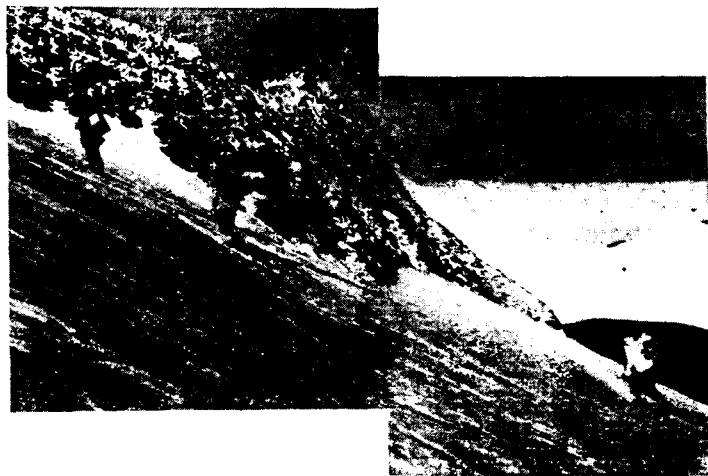
18. Air photograph of part of the southernmost escarpment in Western Dronning Maud Land, separating the high, undulating ice-plain of the interior of the continent (upper left) from the comparatively low ice-level (foreground) of the mountain belt. The darker patches close to the foot of the escarpment are exposures of bare, blue ice.



19. Looking down from a nunatak in Western Dronning Maud Land onto an area of blue ice, showing resemblance to a frozen lake.



20. Very light camp used for one-man excursions in the Dronning Maud Land Mountains.



21. Surveyors climbing with instruments: the smooth, ice-floored valleys (seen more extensively in Inset 22, *opposite*) and the blocky steep-sided mountains are typical of the western part of the area.



22. Surveyors climbing from typical ice-floored valley.



23. Camp in the Dronning Maud Land Mountains.

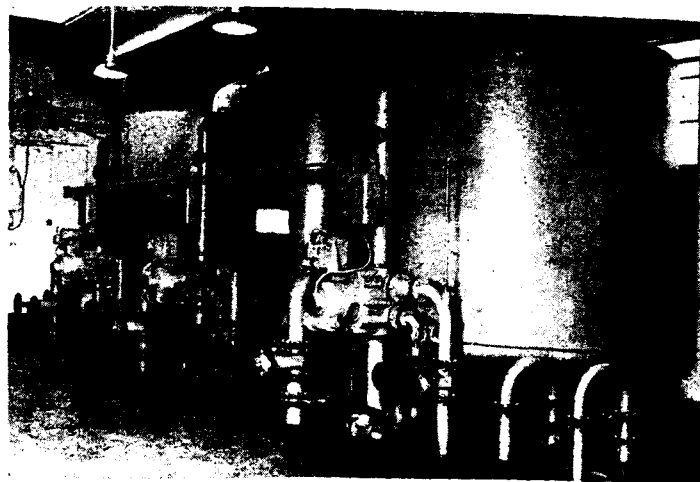


24. Cliff showing metamorphic rocks (gneiss); the great smooth slabs, and round holes worn by wind erosion, are typical of this rock.

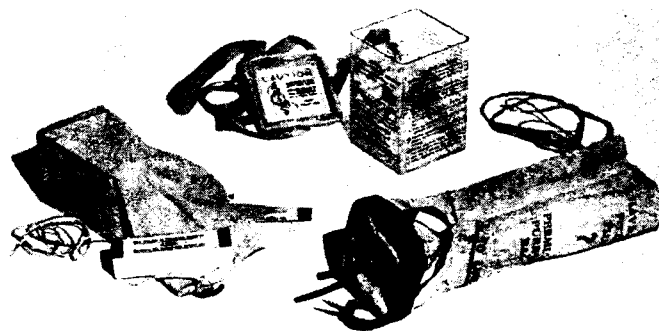


25. Nearby cliff-face showing flat-lying sedimentary rocks overlain by one of the large igneous sheets, or sills, with typical fracturing into vertical columns. (This and the preceding 24 pictures are the copyright of the Norwegian-British-Swedish Antarctic Expedition 1949-52.)

ION EXCHANGE



26. Base-exchange water-softeners for treating an industrial water supply.

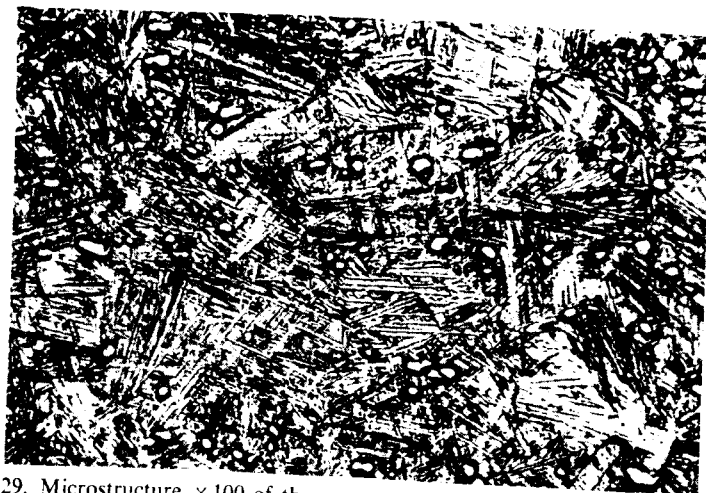


27. Desalting kit for the production of drinking water from sea water in emergency; drinking box, filter bag, and ion-exchange briquettes are here shown unpacked. (This and the preceding picture are copyright by The Permutit Company Limited.)

TITANIUM



28. Microstructure $\times 100$ of titanium, showing the alpha grain formation (see text). The particles are due to the presence of titanium carbide. Carbon content, 0.57 per cent.



29. Microstructure $\times 100$ of the same materials as in Inset 28, but after water-quenching from 1,000° C. Titanium carbide particles are still visible; background structure altered by the influence of the beta-to-alpha transformation. (This and the preceding picture are by courtesy of the British Non-Ferrous Metals Research Association.)

Mechanisms of Chemical Change

65

removal of hydrogen and bromine atoms in steps (4) and (5). These are the reverse of steps (2) and (1) respectively. Thus each single dissociation of a bromine molecule in step (1) brings about the formation of many molecules of HBr. The reaction is represented diagrammatically in Fig. 1.

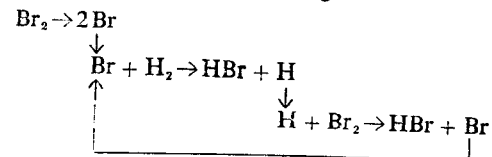


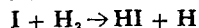
Fig. 1. Reaction between hydrogen and bromine: diagrammatic representation showing the initiating reaction (at left), and the chain propagating reactions. The limiting reactions are not shown.

The rates of each of the steps (1) to (5) are individually governed by the Law of Mass Action, and, if it is assumed that the concentrations of hydrogen and of bromine atoms attain steady concentrations such that their rate of formation is balanced by their rate of destruction, it can be shown that the overall rate of reaction is given by a relationship of precisely the form given above.

But the most significant feature of the scheme is that all the steps are extremely simple. Each consists of the reaction of two particles at a time, an atom being transferred from one partner to another. No highly specialized orientation or precise timing is required. Moreover, all the steps, apart from the first, require little or no energy of activation, because they are all reactions of highly reactive atoms with molecules. The initial split of the bromine molecule into atoms requires an activation energy of about 55,000 calories per gramme molecule (55,000 cal.), while the rearrangement mechanism, like that which prevails for the hydrogen-iodine reaction, would have an activation energy of only about 45,000 cal. The dissociation step will therefore be a comparatively rare event, but because its consequences, whenever it does occur, are so far-reaching the chain mechanism predominates and dictates the kinetics of the hydrogen-bromine reaction. This is a case where the path of high energy but high

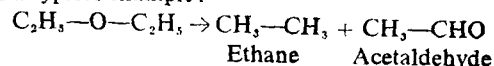
probability of activation predominates over that of low energy but low probability of activation.

The reason for the reversal of this situation in the hydrogen-iodine reaction may be stated as follows. Iodine atoms are considerably less reactive than bromine atoms and the step

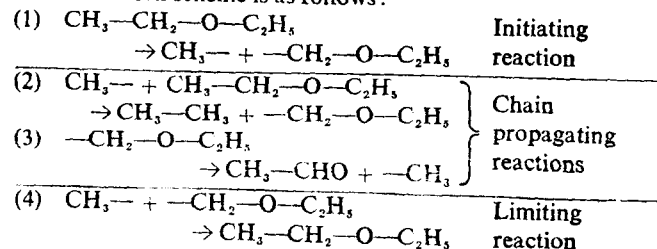


would require an appreciable activation-energy, for which the high activation-probability of the chain mechanism is not sufficient to compensate. This particular step would be slow and the iodine atoms would be removed by recombination before they could propagate the chain.

A similar type of chain mechanism, involving free radicals instead of free atoms, occurs in the thermal decompositions of many organic compounds, of which diethyl ether, $C_2H_5-O-C_2H_5$, is a typical example:



The reaction scheme is as follows:



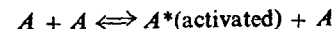
It is assumed that step (1) is first-order – a point to which we will return later – and that the concentrations of the free radicals CH_3- and $-CH_2-O-C_2H_5$ attain steady values. Application of the Law of Mass Action to each of the steps leads to first-order overall kinetics.

Examination of these steps shows that (1), (2), and (4) are very simple: (1) the breaking of a C—C bond; (2) the transfer of a single atomic group (CH_3) from one reactant (ether) to another (CH_3- radical); and (4) the formation of a bond by combination of two free radicals. There remains (3), the most complex

step, which probably itself takes place in a series of simpler stages.

The initial step of breaking the C—C bond will require a large activation energy, at least 80,000 cal., but each of the subsequent steps will require little or no activation energy. Hence the free-radical split when it occurs will bring about the decomposition of large numbers of ether molecules before the free radicals are removed by step (4). The free-radical mechanism therefore competes with the alternative non-radical mechanism, in which the whole of the necessary rearrangement is effected in a single step, that is, in accordance with the overall equation for the reaction. This requires a lower activation energy (67,000 cal.), but the probability factor is less since it requires rather specialized internal timing, amounting to a triple coincidence. In this case the balance between the two mechanisms is quite even, and the thermal decomposition of ether proceeds by both. Each mechanism shows first-order kinetics.

F. A. Lindemann (now Lord Cherwell) showed in 1922 how first-order kinetics could arise even when activation occurs in second-order collision processes. In brief, if there is a delay between activation of a molecule by collision it may be deactivated by further collisions. Provided that the delay is long enough, only a small proportion of the activated molecules will react, and an equilibrium



will be set up. The concentration of activated molecules, and therefore the rate of reaction will be given by

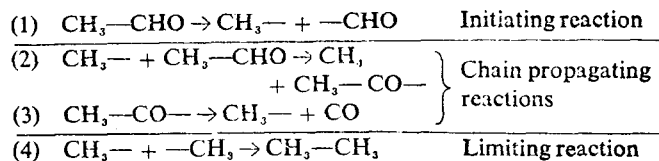
$$[A^*] \cdot [A] / [A]^2 = \text{Equilibrium constant, } K$$

or

$$[A^*] = K \cdot [A]$$

and the reaction will therefore have first-order kinetics.

Kinetics of order $1\frac{1}{2}$ can arise from chain mechanisms which differ from that outlined above for diethyl ether only in the manner in which the free radicals are removed. An example is provided by acetaldehyde which decomposes according to the following scheme:



Again the steps are simple, and the scheme differs from that for diethyl ether only in that the radicals are removed by combination with themselves instead of with radicals of a different type.

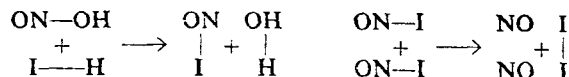
REACTIONS OF HIGH KINETIC ORDER

More refined analysis of the kinetics of the reactions of apparently high order has shown that these also take place in a series of simple steps rarely involving more than two molecules or ions at a time.

A typical example is the reaction between a nitrite and an iodide in acid solution which proceeds at a rate best represented by a fourth-order kinetic equation:

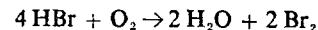
$$\text{Rate} = k \cdot [\text{NO}_2^-] \cdot [\text{I}^-] \cdot [\text{H}^+]^2$$

The reaction mechanism probably involves four steps. The first two of these consist in the formation of molecules of nitrous acid and hydrogen iodide from ions present in solution. The remaining two steps are simple partner-exchanges of two molecules at a time, as in the hydrogen-iodine reaction:

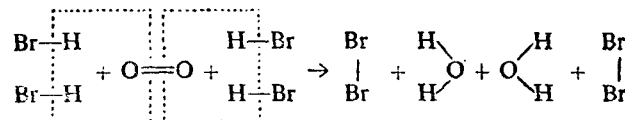


The rate of the reaction as a whole is controlled by that of the slowest step, which is the partner exchange between nitrous acid and hydrogen iodide. It is therefore proportional to the concentrations of these substances, each of which is in equilibrium with its ions so that the rate equation involves the concentrations of nitrous and iodide ions and the square of the hydrogen ion concentration.

A striking example of the application of the Principle of Maximum Simplicity is the gaseous oxidation of hydrogen bromide according to the equation:



The obvious mechanism which might have been suggested at one time

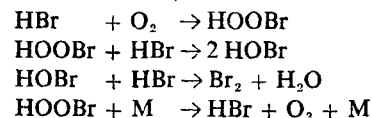


is clearly ruled out because the simultaneous collision of 4 HBr molecules with an oxygen molecule in such specialized orientation is fantastically improbable.

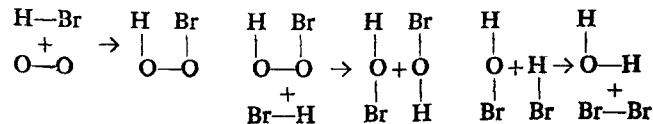
Recent kinetic studies show that the rate of this reaction is best represented by the equation:

$$\text{Rate} = \frac{3 \cdot k' \cdot [\text{HBr}] \cdot [\text{O}_2]}{k'' + [\text{M}] / [\text{HBr}]}$$

where $[\text{M}]$ represents the total concentration of all substances present. The kinetics are perfectly accounted for by the following scheme:



Examination of these steps shows that each involves simple partner exchanges:

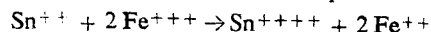


The term $[\text{M}]$ in the denominator of the rate expression takes

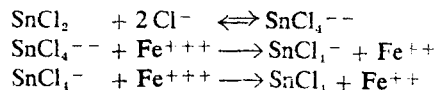
account of collisions of HOBr with HBr in unsuitable orientation, or with oxygen, bromine, and other molecules present which lead to reversal of the first step.

It is remarkable that of the few known third-order gaseous reactions, four are reactions of nitric oxide – those with oxygen, with chlorine and bromine, and with hydrogen. All these involve two molecules of nitric oxide both in the usual chemical equations and in the kinetic equations in which the rate varies as the square of the concentration of nitric oxide and directly as the other reactant. This suggests that two molecules of nitric oxide form a 'dimeric' molecule, N_2O_2 , probably only transiently, and that reaction occurs when this collides with a molecule of the other reactant.

Another third-order reaction is the oxidation of stannous salts (in which tin is 2-valent) by ferric salts to form stannic salts (in which tin is 4-valent). This follows the equation:



That this equation also represents the mechanism of the reaction is most unlikely: not only would it involve simultaneous collisions between three particles, but also these collisions would be opposed by repulsive forces between highly and similarly charged ions. The kinetics may be equally well explained by a scheme in which the steps consist of reactions either between pairs of oppositely charged ions or between an ion and a neutral molecule, e.g. in the case of the chlorides, as follows:



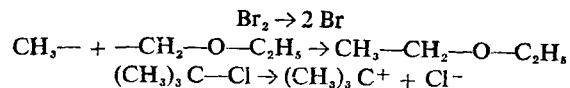
Perhaps enough examples have now been given to demonstrate the application of the Principle of Maximum Simplicity of individual reaction steps and to show how these can lead to complex overall kinetic relationships.

TYPES OF INDIVIDUAL REACTION STEPS

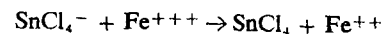
The individual steps of a reaction, to which the Law of Mass Action is strictly applicable, may be of four types:

Mechanisms of Chemical Change

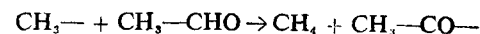
(1) Internal electron-redistribution resulting in the breaking of a bond giving free atoms, radicals or ions, or, in reverse, the formation of a bond from two such particles, e.g.:



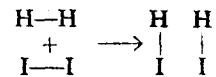
(2) Transfer of a charge from one atom or molecule to another, e.g.:



(3) Transfer of an atom or group from one molecule or radical to another, e.g.:



(4) Exchange of partners, e.g.:



This is about the most complex reaction step which is generally encountered.

The probability of activation diminishes in the order (1) to (4) as the number of particles increases and the requirements of orientation and internal timing become more stringent. Correspondingly, the activation energy of the more primitive steps is greater.

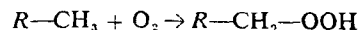
THE OXIDATION OF HYDROCARBONS

The rules which form the Principle of Maximum Simplicity have already made substantial contributions to the formulation of mechanisms which account for the kinetics and other features of many apparently complicated and puzzling reactions. Two outstanding examples of this are the oxidation reactions of the hydrocarbons and the reactions of carbon with steam and with carbon dioxide. Both are of great technological importance, the former in connexion with internal combustion engine fuels, and the latter in connexion with the gaseous fuels, water-gas and

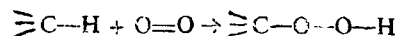
producer-gas, and have consequently occupied many research workers and whole teams for a long time. Only in recent years, with the aid of the ideas expressed by the Principle of Maximum Simplicity, has any considerable progress towards a full understanding of the mechanisms of the reactions been made.

The oxidation of propane (C_3H_8) and the higher hydrocarbons can proceed by two different mechanisms according to the temperature, the features of the low-temperature reaction being different in many ways from those of the high-temperature reaction. Hydrocarbon peroxides, such as C_3H_7OOH , can be detected during the low temperature oxidations and play an important part in the reactions. Peroxides of this type cannot be found during the oxidations at higher temperatures.

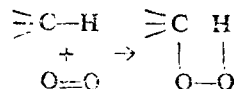
The initial formation of such peroxides involves the change:



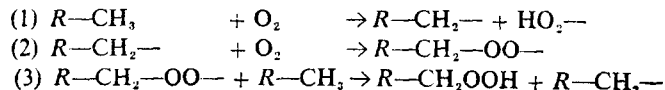
i.e. essentially:



This might occur by a partner exchange, similar to that of HBr and oxygen (see page 69) thus:



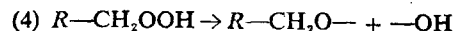
but this has rather specialized orientation and internal-timing requirements. It is probable that an alternative path of high energy but high probability of activation is followed:



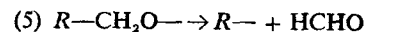
In this sequence of steps the formation of a radical in step (1) would lead to the production of many molecules of peroxide, since steps (2) and (3) form a chain reaction.

But this is unlikely to be the whole story. The primary oxidation products in such reactions are found in practice to have

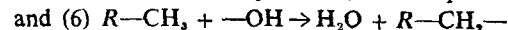
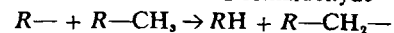
only one oxygen atom per molecule, whereas oxygen itself is diatomic. The separation of the oxygen atoms in the peroxide is, therefore, probably the key to these reactions. The O—O bond is, in fact, the weakest in the peroxide, which is therefore likely to split into two radicals $R-CH_2O-$ and $-OH$:



Each of these radicals is capable of forming fresh peroxide by the following steps:



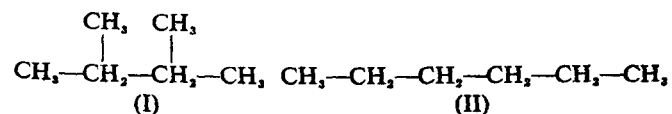
Formaldehyde



followed by (2) and (3). These steps explain the early appearance of formaldehyde in the reaction products.

However, the most important feature of the scheme is that in step (4) a peroxide molecule produces two radicals, each of which forms two further peroxide molecules and so on. A 'branching chain' is therefore set up and the concentration of radicals, and hence the rate of oxidation, will mount very rapidly, flame and explosion resulting. This is, of course, the most well-known characteristic of the oxidation of hydrocarbons.

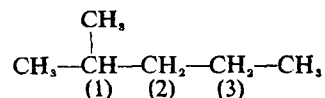
The rate of oxidation of the hydrocarbons is very sensitive to the number of carbon atoms and to their arrangement in the hydrocarbon. Thus octane (C_8H_{18}) oxidizes at about 2,000 times the rate for propane under similar conditions, while the C_4 hydrocarbon with the highly branched arrangement of its carbon atoms shown in (I) oxidizes at only 1/1600th of the rate for the straight arrangement in (II):



Both these effects can be accounted for by the supposition that

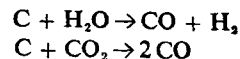
the methyl group, CH_3 , has an adverse effect on the rate of oxidation and that this effect is 'damped' by intervening CH_2 groups. This is believed to be connected with the tendency of the methyl group to repel the electrons of its bond to another atom towards this atom, the tendency being transmitted to a less and less extent along a chain of atoms. Such an access of electrons is thought to increase the stability of the $\text{O}-\text{O}$ bond and so decrease the rate of the branching step in the oxidation. This is supported by the fact that the introduction of a chlorine atom, which tends to attract electrons, into the hydrocarbon molecule produces an additional but opposite effect on the rate of oxidation.

The effect can be treated quantitatively and a 'stability factor' calculated for each carbon atom of a hydrocarbon. Thus, in the case of the hydrocarbon



the stability factors for the atoms marked (1), (2), and (3) are respectively 2.11, 1.00, and 1.22. Reaction is therefore most likely to occur at carbon atom (2). The lowest stability factors for each of a number of hydrocarbons, and chlorine-substituted hydrocarbons, have been plotted against the rate of oxidation of the compound in Fig. 2. The fact that the points for all types of hydrocarbons, and chlorine-substituted compounds, fall very near to one smooth line is very strong evidence for the explanation suggested.

Space does not permit a detailed consideration of the carbon-steam and carbon-carbon dioxide reactions:



in which a single carbon atom is abstracted (as a molecule of carbon monoxide) from the lattice of solid carbon in which thousands of carbon atoms are bound, each to two or three other

carbon atoms. The interested reader is referred to the papers by Long, Sykes, and others, quoted under *Further Reading*.

CONCLUSION

In this brief survey of the wide and still-growing subject of chemical kinetics, it has been possible only to indicate the general pattern of development and to point out some of the high-lights. The rules which form the 'Principle of Maximum Simplicity' not only assist in interpreting the kinetics of known reactions and in formulating a mechanism to explain them, but

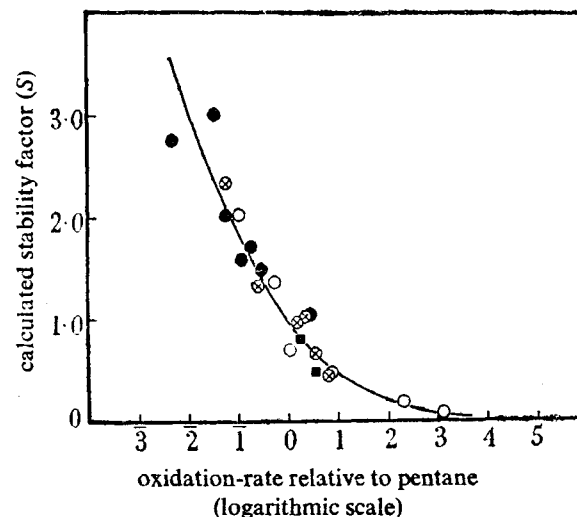
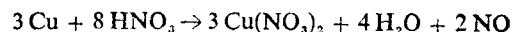


Fig. 2. Relationship between the calculated stability factor (S) and the measured oxidation-rate for a number of hydrocarbons: $\circ$ straight-chain hydrocarbons; $\otimes$ primary chloro-hydrocarbons; $\bullet$ branched-chain hydrocarbons; $\blacksquare$ secondary chloro-hydrocarbons. The range of oxidation-rates covered is about 100,000 to 1. Note that the points for all types of hydrocarbon represented fall nearly on the same curve. (C. F. Cullis, Sir Cyril Hinshelwood, M. F. R. Mulcahy; by courtesy of the Royal Society.)

also enable us in many cases to predict the most likely course of a reaction even before its kinetics have been disentangled.

Sir Cyril Hinshelwood has shown, for example, how 'the manifold and mysterious phenomena exhibited by the hydrogen-oxygen reaction are, in the light of modern ideas, almost if not quite predictable from first principles'.

U. R. Evans has likewise discussed from first principles the action of nitric acid on metals, and in particular on copper, expressed in the latter case by the equation:



— one of the horrors of school chemistry. It will be appreciated that this equation, however well it describes the results of this reaction, can have little relationship to its mechanism. Evans has shown how this equation may arise as a result of the interrelation of a series of simple reaction-steps, which also accord with the known features of the reaction.

Progress has also been made, notably by Sir Cyril Hinshelwood and his school, in the application of the principles and ideas of chemical kinetics to the study of the living cell. He has suggested how it may be that living organisms are able to synthesize complex materials and systems of a high degree of structure and organization. The improbability of such synthetic reactions may be compensated by simultaneous highly-probable degradative reactions, the compensation being possible because of an inter-relation between the two types of reactions similar to the inter-relation between the individual steps of a reaction mechanism. One of the other fascinating aspects of this work has been the re-interpretation, in the light of chemical kinetics, of the facts of bacterial adaptation. Though the conclusions of the kinetic approach to biological systems are still under discussion, the significance and scope of this approach can hardly be over-estimated.

FURTHER READING

The reader who may wish to delve more deeply is referred to the final part of Sir Cyril Hinshelwood's recent book *The Structure of*

Physical Chemistry (Oxford University Press, 1951), and to his earlier *The Kinetics of Chemical Change* (Oxford University Press, 1940). The latter contains many references to work on particular reactions. Sir Cyril's Presidential Addresses to the Chemical Society in 1947 and 1948, published in the *Journal of the Chemical Society*, are also most helpful.

The following three references are to work on reactions which have here been mentioned only in passing:

Carbon-steam and carbon-carbon dioxide reactions: Long, F. J., and Sykes, K. W. *Proceedings of the Royal Society 'A'*, **193**, 377 (1948); Gadsby, J., Long, F. J., Sleightholm, P., and Sykes, K. W. *Proceedings of the Royal Society 'A'*, **193**, 357 (1948).

Hydrogen-oxygen reaction: Hinshelwood, Sir Cyril. *Proceedings of the Royal Society 'A'*, **188**, 1 (1946).

Action of nitric acid on copper: Evans, U. R. *Transactions of the Faraday Society*, **40**, 120 (1944).

The application of chemical kinetics to the study of the cell is discussed briefly by Sir Cyril Hinshelwood in the Presidential Address for 1947 and in *The Structure of Physical Chemistry*, already mentioned, and is fully presented in his book *The Chemical Kinetics of the Bacterial Cell* (Oxford University Press, 1946).

ION-EXCHANGE

K. S. SPIEGLER

ION-EXCHANGE is an outstanding example of an old process whose manifold applications have developed only recently. It was discovered by two British soil scientists, J. T. Way and H. S. Thompson, just one hundred years ago. Their work dealt with water-soluble fertilizer salts, and they found that such salts are held by the soil and are not easily leached out by rain-water. Subsequent experiments showed that the type of absorption which occurs when soil is treated with solutions of salts is characterized by an exchange phenomenon. When the soil adsorbs a certain quantity of a component of the solution, it releases a definite quantity of a soil-component into the solution. For instance, if a solution of Epsom salts percolates through a layer of soil which contains sodium, then magnesium – which is one of the components of Epsom salts – is exchanged for sodium from the soil. The solution which has percolated through the soil contains then a sodium salt instead of a magnesium salt, while the soil is left with a higher magnesium content.

The practical use of this phenomenon is of major importance for imparting desirable properties to both soils and solutions. Sodium-rich soils are dense and the crops grown in them are poor because the roots do not obtain enough air and water. Magnesium-rich or calcium-rich soils are of granular structure, providing better drainage and access of air to the roots. If normal soil is irrigated for long periods with water containing a high concentration of sodium salts, calcium and magnesium are gradually leached from the soil, sodium takes their place, and the soil aggregates and deteriorates. On the other hand, if the irrigation-water contains a sufficient proportion of calcium or magnesium, the soil retains or even improves its desirable porous structure.

ION-EXCHANGE WATER-SOFTENING

Some minerals, such as natural greensand,* are so well suited for exchange that their exchange ability can be used on an industrial scale, for instance to make hard water soft. Hardness of water is its soap-destroying power. It is due to the presence of salts of calcium and magnesium which combine with soap and inactivate it. Calcium and magnesium salts are therefore called hardness-formers or sometimes simply hardness. Removal of hardness from water, or softening, is possible by passing the hard water through a bed of greensand, resting on a porous support. These beds are designed like the regular sand-filters in use in most municipal water works. Sodium from the greensand replaces the calcium and magnesium, and the water flowing out of the bed contains only sodium salts. As the latter do not inactivate soap, the treated water is soft. When the exchangeable sodium of the greensand bed is exhausted, the water flow is interrupted, and a concentrated solution of common salt is passed through the bed. The sodium in the common salt now displaces calcium and magnesium from the greensand and thus reactivates it for water-softening. This stage of the process is called regeneration. After a suitable excess of salt solution has been passed through the greensand bed, it is rinsed and is now ready for softening again. Such exchange-softening units are widely used in industry (Inset 26), especially for the complete softening of boiler water to prevent the scale which is formed in the boiler if hard water is used. Domestic hot-water installations also often use exchange-softeners and several large municipal softening plants operate on this principle. While this softening method is not always the most economical on a large scale, it is extremely convenient

*Greensands are natural silicate minerals which are subjected to processing for industrial use. These materials as well as other natural products such as different clays and zeolites were extensively used in the earlier water-softening installations. They have now been largely replaced by synthetic gels prepared from sodium silicate and aluminium salts and by organic materials, namely sulphonated coal derivatives and synthetic ion-exchange resins.

and removes the hardness more completely than any other known method. In most installations natural greensand has been replaced by synthetic products of similar chemical nature but of greater capacity and stability.

At first sight it might seem paradoxical that in the softening step of the process, sodium from the greensand replaces calcium in the water, while in the regeneration step, exactly the opposite occurs. One reason for this is the fact that the relative preference of the greensand for calcium and magnesium decreases with increasing concentration. When in contact with natural water or some other very dilute solution, the greensand prefers the hardness-formers over sodium; yet it releases most of the calcium and magnesium when in contact with a concentrated solution. But even if this were not so, it would eventually be possible to remove calcium or magnesium from the greensand columns by continuous passage of sodium chloride solution through them for a sufficiently long time.

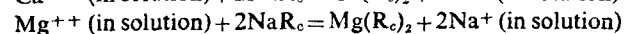
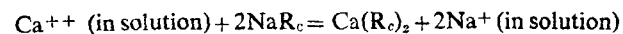
Before discussing this question in further detail, it is convenient to consider the exchange-process proper.

NATURE OF THE ION-EXCHANGE PROCESS

It was found that the solutions which are able to undergo exchange with greensand are conductors of the electric current. It was therefore natural to look for a connexion between these two phenomena; and, as will later appear, the comparison can usefully be extended to include the exchange-material as well as the solutions which undergo exchange with it.

A solution which conducts the electric current behaves as if the molecules of the dissolved material were split into positively and negatively charged particles, ions. (See preceding article by K. D. Wadsworth on 'Mechanisms of Chemical Change'.) It may be useful here to include a reminder that positively charged ions are known as cations, being the metallic component in salts, and in acids the hydrogen ion (H^+). The negatively charged ions, known as anions, are the acid radicals in salts and in acids; in a base the anion is always the hydroxyl ion (OH^-).

The exchange that takes place between greensand and a salt solution is an exchange of cations only, and the anions in the solution do not participate in it. Hence the greensand is called a cation-exchanger. The removal of hardness from water is an exchange of calcium ions (Ca^{++}) and magnesium ions (Mg^{++}), each bearing double positive unit charge, for sodium ions (Na^+) present in the greensand (NaR_c):



(R_c represents the non-exchangeable body of the cation-exchanger, greensand in this case.)

If we simply take a solution of calcium chloride and shake it with greensand, ion-exchange occurs to a limited extent. After some time a state of equilibrium is reached at which the greensand has taken up a portion of the calcium in the solution in exchange for a portion of its own sodium. But both solution and greensand still contain calcium and sodium and the exchange is incomplete. Such a process is called a batch process. If the partially softened solution is now treated with a portion of regenerated greensand, a further portion of its hardness is exchanged for sodium, and if this process is repeated many times practically complete removal of hardness from water is possible by such a succession of batch processes. A similar result could be achieved in a simple manner in a counter-current softening apparatus into whose opposite ends hard water and freshly regenerated greensand respectively are fed and move along in opposite directions, the water becoming gradually softer and the greensand more exhausted. The principle of such an apparatus is analogous to the familiar counter-current industrial heat-exchanger which consists of two concentric tubes. A hot liquid flows in one tube from one end to the other, while a cold liquid flows in the other tube in the opposite direction, and in this manner heat is transferred from one solution to the other.

Counter-current ion-exchange equipment, however, is not yet used on a large scale. Most installations in practice consist

of stationary columns of solid ion-exchange materials through which the solutions flow. This method may be considered a compromise between the continuous counterflow principle in which both solid and liquid move, and the batch equilibrium-process in which both are at rest.

At first sight it seems quite amazing that practically complete exchange takes place when a solution is passed through a column of solid exchange-material, although the exchange would take place to a much lesser extent if solid and solution were mixed in a beaker for an equal period of time and subsequently separated. Thus if water is passed through a given greensand layer only 3 ft high at moderate flow rates, more than 99 per cent of the initial hardness is removed from the water until the greensand is almost completely exhausted and no longer contains any exchangeable sodium. The process taking place in the column may then be envisaged as a succession of batch-processes which lead finally to almost complete exchange.*

SYNTHETIC ION-EXCHANGE RESINS

So far, only the water-softening process has been used as an illustration of ion-exchange, because of its great importance and because until about ten years ago it was the only ion-exchange process used on a large scale in industry. However, ion-exchange is by no means restricted to the calcium-sodium or magnesium-sodium exchange. In fact, greensand or similar inorganic synthetic materials are capable of exchanging a large number of cations, though not all.

The most significant advance in this field took place during the last two decades when organic synthetic ion-exchange materials known as ion-exchange resins became available which are able to exchange almost all known ions. Most of them have a higher capacity and greater physical stability than the natural materials. Perhaps most significant is the fact that it proved possible to synthesize anion-exchange materials,

*See 'Chromatography' by E. Lester Smith, *Science News* 13, 9 (1949).

while no mineral anion-exchange materials of practical importance are known.

The development of synthetic ion-exchange resins, in 1935, occurred at a time when chemists became aware of the great importance of synthetic materials composed of very large molecules, usually called polymers. Many natural materials such as rosin, silk, and rubber had been studied, and corresponding synthetic products such as numerous household plastics, nylon, and synthetic rubber were being developed. Two British scientists, B. A. Adams and E. L. Holmes, succeeded in preparing resinous materials which contained ion-exchange groups. Their method of synthesis* was similar to that used in the preparation of an established phenolic resin ('Bakelite'), of which many types of household articles have been manufactured. The ion-exchange resins produced by Adams and Holmes are, however, of quite different appearance and properties from Bakelite. They swell considerably when placed into water or into a solution, and in the wet, swollen state they can exchange ions with a solution at a fast rate. Subsequent improvements have led to resins of very high capacity and stability.

Ion-exchange resins are usually marketed in the form of coarse or spherical granules, about 1-2 millimetres in diameter, similar to greensand in softening columns, but they can also be prepared in the shape of rods, sheets or thin membranes. The major use of these resins is in the complete removal of salts from water by ion-exchange, a process which has also been called 'preparation of distilled water without distillation'.

COMPLETE REMOVAL OF SALTS FROM WATER BY ION-EXCHANGE

Natural water contains only comparatively small amounts of salts (usually less than one part of solid matter in one thousand parts of water). But even these small amounts of salt may cause serious trouble where a process calls for water of high purity, for instance water for high-pressure boilers, for the manufac-

*Condensation, with formaldehyde, of phenol or its derivatives.

ture of many medicines, television tubes, and for automobile batteries, and, of course, for laboratory work. Before resins were invented, salt-free water was almost exclusively prepared

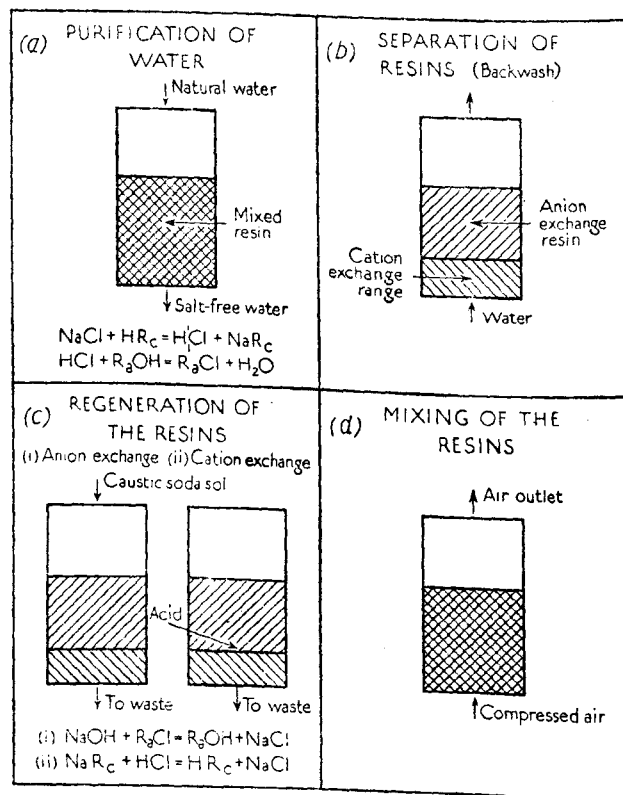
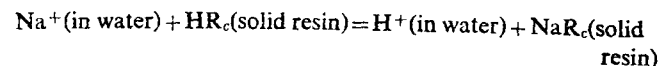


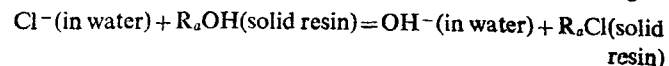
Fig. 1. Schematic representation of salt removal from water by ion-exchange (single-bed method).

by distillation, which is a comparatively expensive process. To prepare water of high purity by ion-exchange, natural water is passed through a column containing a mixture of cation- and

anion-exchange resins (Fig. 1). The cation exchanger in the 'acid' form (i.e. containing exchangeable hydrogen ions) removes all the cations from the water, exchanging them for hydrogen ions. For sodium ions, the exchange-process is:



The anion-exchange resin, on the other hand, removes all anions, exchanging them for hydroxyl ions, as shown for chloride ions (Cl^-) in the following equation in which R_a designates the non-exchangeable body of the anion exchanger.

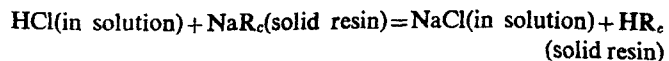


The hydrogen and hydroxyl ions produced by the exchange reactions combine and yield water (H_2O):



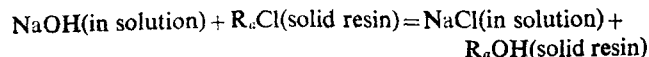
As a net result the original salt molecules, NaCl , are transformed by the exchange process into molecules of water. The other electrolytes originally in the water react in an analogous manner and hence the water emerging at the bottom of the demineralization column is completely free of salts.

When the resins are exhausted, a fast stream of water is passed through the bed in the reverse direction, i.e. from bottom to top, for a short while. This separates the two types of resin, the lighter anion-exchanger floating on top, while the heavier cation-exchanger remains at the bottom. They can now be separately regenerated. The cation exchanger is regenerated by passing through it a solution of an acid, such as sulphuric or hydrochloric. Hydrogen ions from the acid replace the metal ions adsorbed from the water and return the resin to its original form, HR_c :



The anion exchanger is regenerated by a solution of a hydroxide, usually caustic soda (sodium hydroxide, NaOH),

containing OH^- ions which replace the anions of the exhausted exchanger:



Both resins are now in their original form. They are washed, mixed by injection of compressed air into the column, and the bed is ready for salt removal again.

In many installations, separate columns for cation and anion exchanger are used and the water is first passed through the cation exchanger and then through the anion-exchanger column. Mixed beds, as described above, produce water of still higher purity and have been developed only during recent years when suitable resins became available. The resins are very stable and can be used for many years and thousands of purification-regeneration cycles.

The cost of this process is largely determined by the acid and alkali used for the regeneration of the columns. For most natural waters the cost of ion-exchange salt removal is only a fraction of the cost of distillation. The higher the original salt concentration in the water, the more expensive is this process. On the other hand, the cost of distillation does not increase appreciably with the salt concentration. Thus it is not economical to remove the salt from sea water by ion-exchange on a large scale because the concentration of salt in sea water is so high that it would exhaust the bed rapidly and the cost of acid and alkali needed for regeneration would prove excessive, in fact much higher than the cost of distillation.

DRINKING WATER FROM SEA WATER BY ION-EXCHANGE

Another ion-exchange method proved very helpful during the last war in providing Allied airmen in life-rafts on the ocean with drinking water. The 'desalting kit', developed simultaneously in the United States and Great Britain (Inset 27), contained mainly a synthetic ion-exchanger of the greensand type, but of much higher capacity. The exchanger was pre-

pared in the silver form. The main salt in sea water is sodium chloride, and when the exchanger is brought into contact with sea water, the sodium ions in sea water replace the silver ions of the exchanger. The silver ions combine with the chloride ions yielding an insoluble precipitate. In this manner sufficient amounts of salt were removed from sea water to make it drinkable. It is interesting that even a small-scale emergency application of this kind consumed considerable amounts of ion-exchange material. At peak production, the silver-exchanger plant was utilizing 4,000–5,000 pounds of silver nitrate daily to produce 7,000–8,000 pounds of silver zeolite.

While this method proved very useful in emergencies, it is much too expensive for large-scale, regular water treatment.

ION-EXCHANGE IN THE SUGAR INDUSTRY

The largest single field of application of ion-exchange resins outside water-conditioning is in the sugar industry. In sugar manufacture from both cane and beet, the sugar is extracted from the plants by leaching with water. The resulting juice contains, in addition to sugar, considerable amounts of mineral and organic impurities whose presence reduces the possible yield and the quality of the sugar crystals obtained in the subsequent evaporation process. To remove these impurities, the juice can be treated in a similar fashion to water. In this manner a number of useful by-products can also be recovered. However, in the demineralization of sugar juice, the advantages of the ion-exchange method do not always outweigh its cost, and it has not been as widely adopted as water demineralization.

In the ion-exchange treatment of water and of sugar juice, almost the whole exchange-capacity of the resin column is utilized before the undesirable ions such as hardness in water appear to any appreciable extent in the liquid leaving the column. The exchange-capacity of the resins is considerable; for instance, a regular cation-exchange resin can absorb calcium to the extent of one-tenth of its own dry weight, and a column of this resin can soften a quantity of water about 500 times its own volume before it is exhausted.

ION-EXCHANGE SEPARATION PROCESSES

Ion-exchange columns have also been used extensively for the separation of ions. In this case only a small fraction of the exchange-capacity of the column is being used, and therefore only comparatively small amounts of ions can be treated by an average column. The possibilities of large-scale separations are, therefore, limited. On the other hand, these separation-techniques have brought about spectacular advances in many fields of chemical and biological research.

The technique used in these separations is the chromatographic procedure (see *Science News* 13), the principle of which has been known for almost fifty years.

Consider a solution containing salts of two metals which are to be separated. A small amount of the solution is passed into a column containing the cation exchanger saturated with hydrogen ions. Both metals will then replace the hydrogen ions at the top of the column and be adsorbed in a thin layer there. A solution of an acid is now passed through the bed. This step of the process is called elution. The hydrogen ions in this solution tend to replace the metals from the top of the column and bring them back into solution. As this happens, and the solution moves down the column, the metals are readsorbed and brought back into solution many times. The net result that can be observed is that the band of metal ions moves down the column. The rate of this movement depends on the strength of adsorption. If one metal is less strongly adsorbed than the other, it will move down the column faster. The bands usually spread as they move downwards, but if the column is long enough, the two bands can be completely separated and solutions of each of the two components collected separately as they leave the column. The remarkable feature of this method is that even if there is only a very small difference in the strength of adsorption of the two ions, they can eventually be separated.

Separation of the rare earth and transuranic elements

In this manner it proved possible to solve some separation

problems which had puzzled chemists for many years. One of these was the separation of the rare-earth elements. This is a group of fifteen elements which are neighbours in the periodic table of the elements. They occur together in natural minerals, and their properties are so similar that all attempts to separate them and produce even small amounts of the pure elements necessitated extremely tedious procedures. This problem was of particular importance in the study of the fission of uranium which produces atomic energy. It was found that relatively large proportions of the rare-earth elements are formed in fission and their separation was the subject of intense study as a part of the 'Manhattan Project' for the development of atomic energy. When this project started, only fourteen of these fifteen elements were known. The element of atomic number 61 had never been found in any appreciable quantity in natural minerals, while its neighbours in the periodic table, neodymium (atomic number 60), and samarium (atomic number 62) had been isolated.

By skilful choice of solutions for elution it proved possible to resolve mixtures of the rare earths into their pure components and thus to reduce to a matter of hours an operation which had previously taken months to achieve. As the rare earths from the atomic pile are radioactive and reveal their presence by their radiation, it proved very simple to locate the bands on the ion-exchange columns and in the effluent from the column. Proceeding in this manner, J. A. Marinsky, L. E. Glendenin, and C. D. Coryell observed a radioactive band between the bands of neodymium (atomic number 60) and samarium (atomic number 62). This proved to contain the missing element 61 to which the name of promethium was given.

Ion-exchange separations have played a major part in the discovery and purification of synthetic elements. The most important of these are the transuranic elements, one of which is plutonium, the fuel of the atomic bomb. These elements, which are of greater atomic weight than uranium, are all unstable and decay by radioactive disintegration. They are therefore not

found in any appreciable quantity in nature. They were first produced by G. T. Seaborg, E. M. McMillan, and co-workers in small quantities in the Berkeley cyclotron, which is a machine for the acceleration of charged particles to high energies.* Their chemical properties are similar to those of the rare earths and they can be separated by ion-exchange chromatography in a completely analogous manner. Perhaps the ultimate refinement of this separation method was achieved in the discovery of the synthetic element californium (atomic number, 98) when an amount of only a few thousand atoms of this element produced by cyclotron bombardment of a few millionths of a grain of curium (atomic number, 96) was isolated from its sister elements. Its position on the ion-exchange column, revealed by its strong radioactivity, was found exactly where predicted from analogy with the rare earths.

Separation of amino-acids and sugars

A counterpart to these separations of materials from the mineral world is the separation of biological materials which are very similar to each other. Here again very small differences in the properties of materials can be multiplied by chromatographic elution to such an extent that the materials can be separated. One of the spectacular successes of this method is the separation of individual amino-acids on a preparative scale. Amino-acids are the building stones of proteins and the first question that is asked in the study of a protein is what amino-acids it contains and what is their relative proportion in the protein. It is comparatively easy to break a protein down into its component amino-acids, for instance by controlled heating with an acid. In this manner a solution is obtained which contains the individual amino-acids which must now be isolated. This can be achieved by chromatographic elution on ion-exchange columns. Because of their high exchange capacity, it is possible not only to carry out analyses, but to separate appreciable amounts of

*See 'The Acceleration of Charged Particles to High Energies' by L. L. Green, *Science News* 22, especially pp. 58-62.

amino-acids in pure form by this comparatively simple procedure.*

Ion-exchange separations are actually more widely applicable than their name implies. Non-ionic materials can often be transformed into ions and then separated. Thus the separation of different kinds of sugars, which by classical separation methods presents a laborious problem, can be carried out by ion-exchange chromatography. The solution of the sugars is treated with boric acid, which reacts with the sugars to form anions which can then be separated on an anion-exchange column.

For the separation of very complex molecules such as nucleic acids or certain constituents of snake venom, ion-exchange chromatography is the only practical separation method that is known.

ION-EXCHANGE IN MEDICINE

The preparation of synthetic ion-exchange resins made it possible to carry out ion-exchange reactions in the living body. This proves of importance in the treatment of oedema, a disease which causes abnormal swelling of the body tissues. It had been known that this swelling is related to an abnormally high sodium content of the body fluids and consequently patients were usually put on a salt-free diet because common salt contains sodium.

It was recently found that considerable amounts of excess sodium can be removed from the body, or at least most of the sodium contained in ordinary food could be prevented from entering the blood stream, if patients were fed a suitable cation-exchange resin in the potassium form. The potassium of the resin replaces the sodium in the intestinal fluid and the symptoms of oedema disappear. Originally it was feared that the resin would also remove other vital materials such as vitamins and calcium in addition to sodium, but at proper dosage these effects do not seem to be very serious.

*Separations of amino-acids had also been achieved on other adsorbents such as charcoal or paper. But the resins are superior to these materials, particularly in their reproducibility.

The ion-exchange softening process has recently also been applied to blood. When blood is removed from the blood vessels of the body, it coagulates within a few minutes, that is, it forms clots. Coagulated blood cannot be used for transfusions and is useless for blood banks. Preventing blood coagulation is therefore of major importance in the storage of blood.

It had been known for many years that the calcium ions which are normally found in blood are essential for the coagulating process. When they are removed from the blood or inactivated, coagulation does not take place. The common practice in blood banks has been the addition to the blood of small amounts of reagents such as citrates, which can bind chemically and inactivate calcium ions. This procedure prevents coagulation quite effectively and makes it possible to store blood for limited periods. However, the addition of even small amounts of these reagents causes chemical changes and hence blood preserved in this manner is not ideal for accurate studies of the properties of blood in its natural state.

It was found that ion-exchange resins can 'soften' blood just as they soften water, namely remove the calcium ions from it and replace them by sodium ions. This exchange prevents coagulation and yet it causes practically no alterations of the complex constituents of the blood so that blood preserved in this manner can not only be stored and used for transfusion like citrate-treated blood, but also provides the scientist with blood in as natural a state as possible.

The human stomach has also derived benefits from the latest developments in the ion-exchange field. Weakly basic anion-exchange resins are used to inactivate excess acid and thus relieve indigestion in a reaction similar to the anion-exchange step of water demineralization. For this purpose the resin is superior to the familiar remedy, sodium bicarbonate, because it leaves no excess alkalinity in the stomach.

TREATMENT OF INDUSTRIAL WASTES

Many industrial waste solutions contain relatively valuable materials in very low concentration whose recovery by conven-

tional methods is not economic. If these materials are present as ions, they can be concentrated by passing the waste solutions through columns of ion-exchange resins which take up these ions and replace them in the solution by comparatively cheap ions such as hydrogen, sodium or chloride. The ion-exchange recovery of copper from dilute waste liquids of acetate rayon plants is an example for this type of process. Two large plants have recovered over seventeen tons of copper per day in this manner.

Several other industries are using ion-exchange columns for waste treatment. This question is not only important for the industries which are trying to prevent the loss of valuable materials, but also from the point of view of public health, which benefits, in general, from all steps taken to purify industrial wastes before their discharge into rivers. This is particularly true of radioactive wastes, small amounts of which could cause great harm if they ever found their way into a public water supply. Many waste products at atomic energy installations are of ionic character and so are many fission products of atomic explosions. They can be taken up by ion-exchange resins and therefore much research is now being carried out on the use of ion-exchange resins for the removal of radioactive materials from waste liquids and from water.

In general, the resins offer unique advantages for the concentration of traces of metals and other ionic materials from dilute solutions. Ion-exchange treatment is usually much more economical than the recovery of the solids by evaporation of the water. Thus, in the study of a particular waste problem it was found that the use of one pound of sulphuric acid for regeneration of the resin in the ion-exchange recovery process could replace the large amount of fuel and the equipment needed for the evaporation of 4,000 pounds of water in the evaporation process.

In short, evaporation processes remove the water from the impurities, whereas ion-exchange and other adsorption processes remove the impurities from the water and are therefore often more economical.

On the other hand, the use of ion-exchangers for the manufacture of relatively cheap materials on a tonnage basis is usually not economical because the amounts of materials that the resins can adsorb are limited, and therefore, in addition to the desired adsorbed product, a relatively large amount of resin must be handled in the manufacturing process.

CONDUCTION OF ELECTRICITY BY ION-EXCHANGE RESINS

A remarkable similarity between ion-exchange resins and solutions of electrolytes (i.e. acids, bases, and salts) is their ability to conduct the electric current. The conductance is due to transport of electricity by the exchangeable ions which can apparently move comparatively freely within the resin. This movement of ions can be observed easily if the ions are coloured or radioactive, and it was found that in a cation-exchange resin the current is carried exclusively by the cations while in an anion-exchange resin only the anions can move and carry the current. In this respect a resin differs from a solution of an electrolyte; in the latter both cations and anions move and transport electricity from one electrode to the other.

It is interesting to compare metals to cation-exchange resins in the acid form (that is saturated with adsorbed hydrogen ions). In metals the electric current is carried by electrons, whereas in the resin it is carried by the hydrogen ions or protons, the units of positive electricity. This analogy is not to be taken too strictly, particularly in view of the fact that the protons in the resin are attached to water molecules, but it serves well to illustrate the process for current transport in these media. It also provides some explanation for the fact that conduction in resins is much lower than it is in metals, for the hydrogen ions are much larger than electrons, and therefore they move much more slowly.

It is seen that ion-exchange resins combine the physical properties of solids with the electrical properties of solutions of electrolytes. This combination is of particular importance in membranes consisting of ion-exchange materials.

ION-EXCHANGE MEMBRANES

Living cells are enclosed in membranes through which they obtain their food from the surrounding medium and through which they excrete unwanted materials. The concentration of components inside the cells is often quite different from the concentration in the surrounding medium. For instance, the concentration of potassium in the red blood corpuscles is sixteen times larger than in the surrounding blood plasma. Cell membranes are able to differentiate between particles in solution and transfer some kinds of them, while excluding others.*

In general, very large molecules or ions are not readily transferred through the membranes. This has been explained by comparing the membranes to sieves with holes that are so narrow that only very small particles can pass through them. However, this explanation alone is not sufficient because many biological membranes differentiate between small ions which carry different kinds of electric charge, even if these ions are of about the same size.

This property of the membranes is easily understood if one considers that cell membranes consist of materials capable of ion-exchange. The presence of ion-exchange materials in living tissues has been known for a long time, and the ion-exchange properties of such natural materials as wool or cellulose have even been utilized for practical purposes. It is not easy to demonstrate directly the ion-exchange properties of cell membranes, but the fact that some of them, under a given set of conditions, transfer only cations suggests that they can be considered as cation-exchangers, while the anion-transferring membranes act as anion-exchangers. This is in agreement with the known electrical properties of ion-exchangers and provides a satisfactory explanation for the ability of certain membranes to differentiate between cations and anions of equal size.

*For a discussion of this problem in relation to plants, see 'The Mechanism of Mineral Salts Absorption by Plants' by J. F. Sutcliffe, *Science News* 25, 52 (1952). Examples of differential concentrations effected by seaweeds are quoted in 'Research Report' in this issue.

It is outside the scope of this article to discuss the physiological consequences of this property of the membranes which is related to the electrical 'membrane potentials' or to describe its great importance for the activity of nerves and muscles.

One practical application is, however, briefly mentioned in conclusion. Recently, synthetic cation- and anion-exchange membranes of satisfactory mechanical strength have been produced and their use as 'ionic sieves' holds great promise for industrial applications such as an electrical method for the removal of salts from sea water. By passing an electric current through a series of compartments containing sea water, which are separated by cation- and anion-exchange membranes alternating with each other, one can virtually filter the ions out of a portion of the sea water and produce fresh water and concentrated brine. In this process the ion-exchange resins act merely as ionic sieves and need not be regenerated. This process is still in its development stage. It may prove more economical than any other known method for the removal of salt from sea water or other solutions.

SUMMARY AND CONCLUSION

The story of the first hundred years of man's scientific interest in ion-exchange has followed roughly a circular path starting from the observation of a natural phenomenon and returning now to the study of nature. Ion-exchange was discovered in the soil and in minerals, and these minerals as well as similar synthetic materials were put to practical use for the purpose of water softening. The search for more suitable ion-exchange materials led to the invention of synthetic ion-exchange resins. The availability of these materials created important new industrial processes such as economic removal of salts from water, and remarkable improvements in research techniques such as the rapid separation of amino-acids and nucleic acids. These new techniques and the insight gained into ion-exchange phenomena are now being applied by the scientist in research in many directions.

FURTHER READING

Monographs:

Ion-Exchange, Theory and Application, edited by Frederick C. Nachod (New York, Academic Press, Inc., 1949) covers practically all aspects of the subject up to 1949 and is recommended as a reference text.

Ion-Exchange Resins by R. Kunin and R. J. Myers (New York, John Wiley and Sons, Inc., 1950) stresses practical aspects.

Two recent short reviews, readable and highly recommended, are:

Boyd, G. E. 'Ion Exchange'. *Annual Reviews of Physical Chemistry*, Vol. II, 1951 (Stanford, California, Annual Reviews, Inc., 1951), pp. 309-342.

Glueckauf, E. 'The Nature of Ion Exchangers'. *Endeavour*, 10, 40 (1951).

Specialized aspects of ion-exchange are discussed in:

'The Separation of Rare Earth, Fission Product and Other Metal Ions and Anions by Adsorption on Ion-Exchange Resins'. A series of 15 papers in the *Journal of the American Chemical Society*, 69, 2769-2881 (1947).

A series of papers on Ion Exchange in *Chromatographic Analysis*; Discussions of the Faraday Society, No. 7, 1949 (London, Gurney and Jackson, 1949).

TITANIUM : A NEW METAL FOR ENGINEERS

F. A. FOX

THE properties of engineering materials often play a decisive part in determining what technological advances can be made. The performance of available metals and alloys is, therefore, critical not only for present success but also for future possibilities in all kinds of engineering endeavour.

Those metals and alloys which are the large-scale raw materials of the engineer may be classified not only according to the traditional division into 'ferrous' and 'non-ferrous', but also according to that very important property, density. This is not a property of a metal which can be modified; it must be taken as it is. In this classification we are accustomed already to speak of the light alloys, putting the alloys of aluminium and magnesium in one class, and all other metals in another. The chief interest of this classification lies in the important engineering advantages conferred by low density in practically all circumstances in which movement is involved. One can scarcely imagine the aircraft industry without aluminium.

Another important fixed property of pure metals is melting point. One can easily see that if in use a metal has to resist high temperatures, one is not likely to get good results from a metal of low melting point; even if the temperature of use did not actually melt the metal, the approach to the melting point would be expected to soften and weaken it. However, melting point is also a very rough pointer to the potentiality of a metal in respect of mechanical strength. The application of heat increases the amplitude of atomic vibrations on the space-lattice of the metal, till at a certain temperature the binding forces in the crystal structure give way and the metal melts. Therefore the higher the

melting point, the stronger the binding forces in the metallic space-lattice must be, and hence, probably, the greater potentiality of the metal for mechanical strength.

If one considers the common engineering metals on a density scale, it is noticeable that there is a distinct gap between, on the one hand, the specific gravity of aluminium at about 2.7 and, on the other, that of zinc at about 7.1 and of iron at about 7.8. One notices also that the light engineering metals aluminium and magnesium have comparatively low melting points near 650° C.

The metal titanium has a specific gravity of 4.5, and combined with this a remarkably high melting point for so light a metal – 1730° C. Its specific gravity, although 60 per cent higher than that of aluminium, is thus only about 55 per cent of alloy steel. To metallurgists and engineers these properties have long looked attractive: however the questions which immediately arose – can the metal be commercially extracted, and at what price? – are beginning only now to be answered in an encouraging way.

Titanium is by no means a rare metal. It occurs in many places as ilmenite (FeTiO_3) and as rutile (TiO_2): these ores are already well known as the sources of titanium dioxide (titania) for the enamel, paint, and welding-electrode industries. Ilmenite is found in massive deposits which can often be worked by open-cast methods, and rutile occurs in beach deposits. However, titanium shares with aluminium and magnesium the characteristic that it is a highly reactive metal and consequently the oxide must be supplied with a large amount of energy to liberate the metal. Furthermore, direct reduction of the purified oxide by such reducing agents as aluminium, carbon, or silicon, gives a very impure metal which is valueless.

EXTRACTION OF THE METAL

The methods of extraction which have succeeded have been indirect, through the halogen compounds of titanium. The older but non-commercial one was to convert the oxide into titanium iodide: this iodide could then be decomposed under the right conditions and the metal deposited from the vapour onto a hot wire maintained at about 1,400° C. The other method, which is

the basic one for all the metallic titanium produced today for engineering purposes, was originated by W. J. Kroll at the U.S. Bureau of Mines and was persistently developed in spite of much early indifference. Here the titania is chlorinated to produce titanium tetrachloride; this liquid, after purification, is made to react with magnesium in a heat-resistant steel vessel at red-heat under an inert atmosphere. The reaction products are spongy titanium and anhydrous magnesium chloride. This magnesium chloride is removed by being drained away in the fused state. The recovered magnesium chloride can then be treated by a known electrolytic process to give metallic magnesium and chlorine which can be used again in the process, the first for further reduction and the second for chlorination. The crude titanium sponge is purified by leaching with cold hydrochloric acid; alternatively, vacuum distillation is used. The product is titanium metal in the form of a powder or sponge having a purity of about 99.5 per cent.

This process was gradually accepted by a few who were anxious to try the virtues of titanium alloys and who thought they might supply the answers to many design problems. Interest, once established, increased with great rapidity, and the technology of the metal has been advancing at enormous speed, especially in the United States: in the last three or four years the metal has changed from one which was seen in pieces weighing grammes and pounds, to one being produced in pieces weighing many hundredweights or even a ton or so.

This development has been in the face of very great difficulties, almost wittily complicated, imposed by nature, but has also been encouraged by the emergence of remarkable properties in the metal and its alloys.

Troubles are by no means over when sponge-titanium has been produced. The liquid metal has been described as a 'universal solvent'; it either dissolves or is contaminated by all ordinary furnace-lining materials. The metal must be produced in a purity greater than a certain high level, otherwise its properties are ruined; the molten metal picks up oxygen and nitrogen from the atmosphere with great rapidity, and consequently

all melting must be done *in vacuo* or under an inert atmosphere. Finally, traces of contaminants, once picked up by the metal, cannot be removed. These are very formidable difficulties, far more severe than those besetting the path of workers with existing engineering metals.

The sponge produced by the Kroll process, or that sponge ground to powder, can be converted into solid ingot metal by melting or by a mechanical compacting method, such as placing the powder in a mild steel sheath or container, completely sealing this by welding, and then rolling or forging the whole assembly at a temperature around 800° C. However, melting, in spite of its difficulties, is receiving the most attention, since it is difficult to imagine a mechanical method being successful in producing large ingots at a reasonable price.

MELTING

The design of furnaces suitable for melting sponge-titanium is still the subject of a great deal of investigation. The two best-known types are arc and induction melting-units.*

In arc-melting, the powder is placed in a water-cooled copper crucible, and is melted in an argon atmosphere by an arc struck between the powder and an electrode, which is either tungsten or carbon. The crucible itself, being continuously cooled, does not get hot enough to contaminate the titanium, the heating of which is intensely local. However, there may be contamination from the electrode, and precautions have to be taken to keep this to a minimum. Furnaces of this kind have been designed so as to permit the building up of an ingot by the continuous addition of powder and the continuous extraction of the ingot through the bottom of the crucible.

Very recently, furnaces of proprietary design, which are said to permit the ready handling of large batches of sponge and to

*Induction melting is a process whereby metal to be melted is placed in a crucible surrounded by a copper coil through which high-frequency alternating current is passed. Corresponding alternating currents are induced in the metal; the resistance to the passage of these currents heats the metal sufficiently to melt it.

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be capable of producing slab ingots of several tons in weight, have been evolved in the United States.

The induction furnace is potentially simpler. The charge is melted in argon or *in vacuo*; however, the crucible material remains a problem, since the carbon crucibles which have been used cause such carbon pick-up as has recently been decided to be harmful. Thoria or zirconia may be usable as a crucible material, though this is not yet proved. An attractive method has been proposed for side-stepping the crucible problem: electromagnetic conditions are so arranged that the metal during heating is held floating in space, both while solid and later when liquid. Such a method is said to have been already successful as applied to small quantities of aluminium; if it could, in fact, be applied on a sufficient scale to titanium, it would provide an elegant solution to the problem of crucible contamination, although an inert atmosphere during melting would still be needed.

PROPERTIES

Titanium can be forged, rolled and wire-drawn without great difficulty. Extrusion of the metal is difficult because of its strength when hot, but a new extrusion process is now being applied to it; this is a French method whereby molten glass is used as an extrusion-die lubricant.

Titanium sold as commercially pure necessarily contains some impurities, the chief of which are carbon, oxygen, nitrogen, and possibly tungsten; these are quite distinct from those elements intentionally added to increase the strength, such as iron, chromium, aluminium, and manganese. However, the impurities if kept within certain limits may themselves contribute to the strength of a metal or alloy, and titanium of commercial purity has a strength between two and three times that of the purest titanium so far available. This enhanced strength can be an embarrassment as well as an advantage, since different batches of metal, containing slightly different amounts of impurities, may differ also in strength-characteristics. Improvements in furnace-design may be expected to remove this source of variation.

Crystal Structure

Titanium has a hexagonal close-packed crystal-structure (α) at room temperature, but changes to a body-centred cubic* (β) structure above about 885° C. This change, somewhat analogous to a change which occurs in iron, which in that metal is the cause of the hardening effects in steel, may well offer opportunities for improving the strengths of titanium alloys by heat-treatment. It has been found that additions of iron, chromium, and manganese tend to stabilize the high temperature β phase so that it persists, unchanged down to room temperatures. All high-strength titanium-base alloys, which so far have been offered commercially, are mixtures of α and β titanium. The presence of the β phase appears to be distinctly advantageous, not only from the point of view of strength and ductility at room temperatures, but of hot strength (temperatures up to about 450° C.), and of easier hot-working and hot-forming characteristics.

Alloy Prospects

By analogy with iron and aluminium it may reasonably be expected that titanium alloys will be developed with strengths many times that of the pure metal. For iron alloys, the highest strengths are about ten times that of the pure metal, while for aluminium alloys, the corresponding figure is about eight. If one applied this lower figure to a value of 19 tons per square inch (which is perhaps reasonable for the tensile strength of pure titanium), one arrives at a figure of about 150 tons per square inch as the order of tensile strength one might hope to achieve with the strongest titanium alloys. If such strengths were in fact reached, the alloys possessing them would be very greatly stronger than any other engineering material when the density is taken into account, and stronger than most other engineering materials even without taking density into account.

However, such a development takes time, as the history of the iron alloys and of the aluminium alloys shows. Meanwhile, the

*For diagrams illustrating these structures, see *Science News* 8, 138.

results even so far are very encouraging. Alloys are now commercially available with strengths of about 70 to 75 tons per square inch, combined with quite good ductility (i.e. they are not brittle), and alloys are under development with strengths of about 90 tons per square inch. One must compare these figures with about 40 tons per square inch for a strong aluminium alloy in routine production, and 90 tons per square inch for a high-strength alloy steel of aircraft quality.

APPLICATIONS

Although the high melting point of titanium was one of its early attractions, it has turned out that the metal and its alloys so far known are a disappointment at really high temperatures. If heated in air for long times above about $1,000^{\circ}\text{C}$., it is embrittled by absorption of oxygen and nitrogen. It is therefore at present useless in these ranges of temperature.

However, the tensile, creep, and fatigue strengths of titanium and its alloys are superior to those of aluminium not only at room temperatures but also at temperatures up to 450°C . This suggests that the chief field of application of titanium and its alloys will, in the immediate future, lie in the temperature range $200\text{--}450^{\circ}\text{C}$. In this range the alloys of aluminium suffer a serious loss of strength, and the heat-resisting steels may not be suitable because of their high density.

One example of such a use might be for the structure of supersonic aircraft or missiles, in which air-friction causes very considerable rises in skin-temperature, even in the stratosphere. At a speed, for example, of three times the speed of sound in the stratosphere, the skin temperature of an aircraft has been estimated to be in the region of 350°C . At such a high speed and skin temperature, aluminium alloys could not be used, and titanium alloys, even at lower speeds, would possess considerable advantages.

Even at temperatures up to 500°C . the properties of titanium alloys remain good. Although, therefore, it is not likely that they could be used for turbine blades in jet aircraft, which operate at temperatures nearer to $1,000^{\circ}\text{C}$. than 500°C ., the titanium

alloys may well be very valuable as a compressor-blading material. At present, jet-engine compressors run at only about 250°C ., but future designs may well demand running temperatures up to 500°C . The properties required are likely to be such that it is difficult to see any alternative to titanium for this use.

Although titanium has been a disappointment in its properties at very high temperatures, a very respectable consolation prize has come along in the shape of remarkable corrosion-resistance. Titanium is almost unattacked by sea water or marine atmospheres and under marine conditions generally titanium is as resistant to attack as, say, platinum.

FUTURE OUTLOOK

It is clear that titanium is a very useful metal. Even at the present price of from about \$5 to \$25 per lb. (depending on the form, whether sheet, bar, etc.), it is already an engineering metal in the United States. Great Britain is less well placed, both for production capacity and for the availability of cheap electric power (on which the cost of both magnesium and chlorine for the Kroll process depend). The future of titanium in Great Britain, therefore, depends very much on the result of researches at present in progress to devise improved methods of extraction of the metal from its ores, so as to lead to a drastic fall in price and increased availability.

PHILOSOPHICAL ANALYSIS AND SCIENTIFIC PROGRESS

JOHN E. OWEN

SCIENTISTS are analytical to the extent that the scientific quest is grounded in reason and logical inference from known facts. By experimentation and analysis the knowledge found in the past becomes a basis for knowledge that will be found in the future. The space-time relations of the observable can be analysed and the future predicted in terms of probability. Most scientists certainly would subscribe to the validity of logical inference, analysis, and induction as fundamental elements of investigation. But few scientists are sufficiently penetrating in their logical analyses; or to speak more fairly, the great scientists are philosophical in that they carry analysis several steps further than their *confrères*. Just as science involves a refinement and elongation of the judgements of common sense, so the great scientist pursues reasoned analysis to a much greater extent than the less philosophical investigators. He engages in critical reflexion to a high degree and accordingly brings ever greater advances in his realm of inquiry.

Perhaps one can distinguish between the great scientist and the researcher who is a mere technician largely on the basis of the penetrative logic of the former. Science is an intellectual endeavour, but there are differentiations in the levels of mental demand that it makes and in the degree of rational inquiry and analysis that various scientists bring to their research. The technicians in science, and they are many, are content merely to measure and calculate, to make orthodox or formal experiments within the framework of the rationale, that is the dominant assumptions and conceptions which their particular science has incorporated in its contemporary growth and development.

They seldom go beyond this. They follow the scientific formulae bequeathed to them from the past. It is true that they use a disciplined imagination in creating occasional new experiments, but for the most part their scientific thinking follows orthodox lines in accordance with the general principles, methods, and presuppositions of their field of knowledge. Their calculations are accurate, their experiments well organized under controlled conditions, and their conclusions generally valid. These investigators are useful members of the scientific fraternity, but they are essentially technicians.

The great scientist is by contrast a philosopher, and the thesis of this article is that more persistent logical reflexion and analysis could greatly advance the development of the sciences. The outstanding scientists have been philosophical in that they saw within and around their inquiries, they were philosophers of science in their wider recognition of the place of science in human experience, and in their attempt to relate it to the larger issues of contemporary thought. They could see beyond their immediate specialty. But their achievements in specifically scientific advance arose from their critical attitude towards science itself. For they questioned the main principles, the dominating concepts and postulates, the working rules, the elements of science which were normally taken for granted. And by calling in question the universally accepted axioms of science they showed their greater devotion to philosophical procedure.

Science in the past has advanced as much through the critical analysis of its first principles as through the discovery of new facts and techniques. The widespread failure to recognize that all science is based upon philosophical assumptions has probably been at least one of the responsible factors in those historical eras when scientific knowledge appeared to be stationary. It is a common view even among scientific workers that they are simply concerned with ascertaining the 'facts' of their particular field, unhindered by any preconceived notions or biases. The claim of scientific inquiry to be impartial and open-minded is erroneously associated with a defini-

tion of 'open-mindedness' as a freedom from assumptions and presuppositions. But this concept of science, needless to say, is false, for scientists make assumptions at all stages of their research, albeit often unconsciously. These assumptions may arise from personal bias, from past training, or more significantly, from the scientific and philosophical temper of the age. It is the work of analytical logic to criticize and test these assumptions, for every assertion of fact or system of facts rests on assumptions, avowed or implied. Logic seeks to analyse the first type, expose the second, and to test both.* It leaves no assumption unexpressed, or, if at all possible, untested.

It is in the light of prior assumptions that scientific facts are selected and their meaning interpreted. Philosophical assumptions and postulates are literally basic to science in that its validity is inseparably related to *their* validity. But although this is apparent to any scientist who is more than a technician, axioms and presuppositions are seldom held up to criticism in the same way in which the scientist demands that other theories be examined and analysed. These doctrines or axioms are philosophical and not just scientific. They are wider than science, as some of the more philosophically sophisticated scientists have shown.† And for this reason they require philosophical treatment, namely, rigorous, comprehensive, critical analysis. The growth of science consists not merely in extending its range of valid data, but in the revision and reconstruction of its theoretical foundations. If these are false or inadequate they can deprive an experiment of meaning. More important, they can hinder the entire development of science until revised and corrected.

The most prominent substantiation of this claim, with its

* See Hobhouse, L. T. *The Theory of Knowledge, a Contribution to Some Problems of Logic and Metaphysics*, p. 3. London, Methuen and Co., 1896.

† See, for example: Whitehead, A. N. *Science and the Modern World*. Cambridge University Press, 1926.

Northrop, F. S. C. *Science and First Principles*. New York, The Macmillan Company, 1931.

implied greater need for more rational analysis of the first principles of science, is seen in Einstein's theory of relativity. It is more than possible that the revision of Newtonian physics might have taken place much earlier than Einstein if physicists had been conversant with the analyses of the nature of space and time which were being commonly discussed among the philosophers. But the physicists of the later nineteenth and early twentieth centuries were apt to dismiss philosophic space-time analyses as empty and useless theorizing. Einstein, however, was preparing the way and laying the foundations for his epoch-making theories by reading the philosophers, notably Kant, Mach, and Hume, and his great achievement was based upon a *philosophical* criticism of the first principles of physics. But for most physicists of the pre-relativity era the first axioms of their science were sacrosanct. Analysis was permissible provided it assumed the Newtonian principles; it was not to be applied to the principles themselves, and consequently the foundations of physics remained Newtonian until very recently.* More awareness of these theoretical foundations, together with analytical criticism of them, would have greatly accelerated the development of modern physical science. The historical divorce between empirical research and philosophical analysis has in some important respects been very unfortunate for both. It was a critical and philosophical cast of mind that resulted in Einstein's becoming 'the Copernicus of the twentieth century'. Relativity theory exemplifies the advance that accrues from a philosophical analysis of the basic principles of science, as distinct from the mere extension of its empirical frontiers.

Similarly, Max Planck, German physicist and Nobel prize-

* See Nash, Arnold S. *The University and the Modern World, An Essay in the Philosophy of University Education*, ch. 3. New York, The Macmillan Company, 1944.

It is interesting to note that it is much easier to teach relativity theory to students of philosophy than to students whose mental categories have become set in the traditional framework of Newtonian physics.

winner, cites spectrum analysis, quantum mechanics, and nuclear physics as fields in which 'a reciprocal supplementation of experiment and theory' has represented a fruitful collaboration.* Experimenters are the shock troops of science; they experiment and measure empirically. But experiments have to be suggested and measurements have to be interpreted. These two tasks are for the theorist, without whose efforts empirical inquiry would run a blind and slow course. Between experimental investigation and theoretical analysis there is no quarrel. Ideally they are partners in a scientific division of labour.

But it is the theorist, the rational critic, who is the more likely to see the dangers of a scientific orthodoxy which can be just as fatal to the growth of thought in science as in other realms of human experience. It is this more philosophically mature scientist who forces lesser researchers out of their conventionally-acquired patterns of thought by analysing the basic postulates on which those patterns are founded. The more analytical mind also examines the *methods* of inquiry, aware that the way a problem is set, or a question posed, will determine the nature of the solution or the answer reached.† It recasts the hypothesis upon which scientific knowledge is organized. At the same time it is less apt to transpose to all areas of human experience methods and techniques which manifestly apply only to one realm of investigation. A critical analysis of the range of meaning within which the particular methods and postulates of the sciences possess validity might well repay inquiry. Thus the more mature development of the social sciences, to take but one example, may reveal that their early attempt to found themselves upon the techniques and thought-ways of the natural sciences was not unfraught with danger. It is the uncritical mind in science that takes undue advantage of the very natural tendency to use a new key to unlock all

*Planck, M. *Scientific Autobiography and Other Papers*, p. 112. New York, Philosophical Library, 1949.

†See Northrop, F. S. C. *The Logic of the Sciences and the Humanities*, ch. 1. New York, The Macmillan Company, 1947.

doors and to compress a complex subject-matter within the preconceived moulds of an inadequate methodology.

But the fact that certain methods have yielded good results in one particular area of investigation does not constitute logical ground for their applicability in other realms of endeavour. Rather than assuming the relevancy of methods and postulates at the outset of research, would not a more penetrating examination of these methods and postulates be in order? The increasing recognition of the philosophical and procedural inadequacies of behaviourism, for example, is but one case of how the thought-moulds which may be suitable for one realm of experience may be quite inapplicable and unsuitable when dealing with a more complex order of phenomena.

It may be noted in this connexion that there is no warrant for the view that the purpose of science is to reduce everything to matter, and the scientist, regardless of his field, has no valid justification for assuming the metaphysical theory of materialism at the start of his research. Science simply seeks to penetrate the mysteries of the universe, yet many scientists entertain the erroneous view that science naturally presupposes materialism. This leads to a dogmatism which is as unscientific as it is unphilosophical. In the social sciences it has led to the mechanistic standpoint that the world of mind and thought, being unreal, is powerless to affect the course of historical and sociological events, and to the naïve but fashionable methodological principle that the range of the measurable is identical with the range of the knowable.*

The influence of mechanism and materialism in science provides one indication of the way that many scientists who look condescendingly upon philosophy have nevertheless been profoundly influenced by the philosophical currents of their day and age. The contemporary ethos or *Weltanschauung* is apt to be uncritically absorbed by many scientific research workers. The student of the history of ideas can render a service to science by showing the great influence exerted upon modern scientific

*For a criticism of this outlook, see MacIver, R. M., *The Elements of Social Science*, pp. 15, 16. London, Methuen & Co., 1921.

thought by Newtonian physics, by the empiricism of Locke and Bacon, and by the optimistic rationalism of the eighteenth century. The consequences of these and many other patterns of thought have been mentally acquired by thousands of twentieth-century scientists. It would be revealing to inquire how many of them possess any real understanding of how their thinking has been moulded by past trends in the history of philosophy. Although scientists are quick to pride themselves on their 'objectivity' and impartiality, it is not easy to acquire a scientific detachment from the basic postulates and ideas incorporated in a scientific orthodoxy to which they have become accustomed.

The philosophical mind, on the contrary, with its awareness of the knowledge-problem, can assume towards science that same objectivity which science itself demands in empirical research. By virtue of an acquaintance with the historical growth of science and the social forces which have shaped the scientific movement, this broader type of investigator is able to regard contemporary achievements more impartially and can evaluate the current climate of opinion in the light of those historical trends of thought which have helped to produce it. From this perspective there can arise towards science and its methods an experimental attitude which is fundamental to the scientific spirit itself and to the progress of research. The present stage will then no more be seen as ultimate than earlier epochs are now regarded as sacrosanct. The structural principles of thought will be conceived not as rigid moulds into which all truth must fit, but rather as plastic elements of a growing structure in which the contemporary thought-system and ethos of science are to be regarded as merely a stage. Its certainty is that of being on the right road rather than at the end of the journey.

A more persistent logical analysis supplementing empirical research may be looked to as the source of scientific advances of the Einsteinian calibre. Plato's famous wish that philosophers be kings might appropriately be made to include a modern plea that scientists be philosophers.

RESEARCH REPORT

A. W. HASLETT

RADIO-ASTRONOMY

IF radio-telescopes could be made as discriminating of direction as is the unaided eye in the case of light waves, there would be no difficulty in 'viewing' at any time the area of the sun's disk and surrounding atmosphere from which radio waves of particular wavelengths are emitted. The general character of the pictures that would be obtained is implicit in the account given by A. J. Higgs in *Science News* 21. Observation and theory agree broadly that the longer radio-wavelengths come from greater altitudes in the sun's atmosphere. The radio-sun would thus appear larger at all wavelengths than the visible sun, and its size would increase progressively with wavelength, reaching far out into the corona at metre wavelengths. It could happen also that the radio-sun would appear brighter at the edge than near the centre. Whereas, near the centre of the sun's disk an observer on the earth is looking directly downwards on a single emitting region, the view near the edge of the radio-sun is tangential, through a considerable length of atmosphere much of it at nearly the same height above the sun. Such pictures cannot be obtained directly; and, to measure the size of the radio-sun at different wavelengths, use is made of observations during eclipse when the whole or part of the sun's disk, and part of the sun's atmosphere, are blotted out and uncovered.

Measurements on a wavelength of 3.2 centimetres (frequency, 9350 Mc./s.) were made by J. P. Hagen, F. T. Haddock, and G. Reber during the total eclipse of 1950. The area covered by the moon was then 1.8 per cent greater than that of the sun's visible disk. But at mid-eclipse 5.6 per cent of the sun's total radiation on 3.2 centimetres wavelength was still received. If the radio-sun were of uniform brightness, its radius ('viewed' on this wave-

length) would be greater than that of the visible sun by some 5 per cent, or about 4,000 miles. But in its general course, the curve of radio-intensity during the eclipse suggested limb-brightening, so that the real excess radius would be somewhat less.

Further measurements, lately reported, have been made during the annular eclipse of 1 February 1951 and the partial eclipse of 25 February 1952 by J.-F. Denisse, of the Institut des Hautes Études, Dakar, and E. J. Blum and J.-L. Steinberg, of the École Normale Supérieure, Paris. The 1951 eclipse was observed from near the Markala Dam on the upper Niger, French West Africa, and the 1952 eclipse at Dakar with the same equipment. Measurements on two wavelengths were made.

The shorter wavelength, 3.2 centimetres, was the same as had been used in the 1950 measurements already quoted – the comparison between results in an annular and total eclipse being of obvious interest in relation to limb-brightening. The area of the sun's disk which was covered at maximum eclipse in 1950, but not in 1951, was 8.6 per cent; and this area contributed between 10 and 12 per cent of the total radiation, the theoretical proportion on the basis of limb-brightening being 12 per cent. There was also evidence in support of limb-brightening from the general form of the curve relating received energy to phase of eclipse.

On metre wavelengths, particularly, it is a first requirement that the sun should be free, around the time of eclipse, from the rapid, apparently sporadic, type of variation illustrated in Fig. 2 of the article by Higgs already quoted. Conditions during the 1951 eclipse were unusually favourable, and the curve of received radio-energy at 1.78 metres wavelength (frequency, 160 Mc./s.) is believed to show changes during eclipse to an accuracy of about 1 part in 300. The decrease in received energy began 16 minutes before optical first contact, and by that time had reached 8.5 per cent. From these two figures it is possible to calculate the radius of the radio-sun, on the assumptions of circular shape (section) and uniform brightness. This calculated radius leads in turn to a figure for the expected reduction in

received energy at maximum eclipse. The observed reduction was 52 per cent; and neither with uniform brightness, nor with any reasonable assumptions about limb-effects, could this proportion be matched if the radio-sun were effectively of circular section, and so of spherical shape. Instead, the figures pointed to a markedly oval section, with its greatest extension about the equator, and the smallest over the poles. This conclusion was confirmed from measurements on the same wavelength during the 1952 partial eclipse. From the combined results, a tentative model is now proposed for the radio-sun at 1.78 metres wavelength, with the equatorial diameter about 1.8 times that of the visible disk and the extension above the poles no more than about 10 per cent.

Only a preliminary report on this work has so far been published, and questions of further interpretation are not discussed. One of them is whether there is a connexion between the shape of the radio-sun at metre wavelengths and that of the visible corona, which varies with the (approximately) 11-year sunspot cycle. Whereas at maximum activity the general outline of the corona appears roughly symmetrical, though with individual streamers irregular, at times of minimum activity there are relatively short streamers above the poles and longer ones which stretch outwards more or less at right angles to the sun's axis. The last sunspot minimum was in 1944, and the last maximum in 1947–8, the period 1951–2 being one of declining if erratic activity. The shape found for the radio-sun on metre wavelengths in 1951–2 is broadly consistent with that of the visible corona at the same stage of the sunspot cycle. It will be of interest to compare the shape now found with that around sunspot minimum, when the visible corona is more elongated. Radio measurements at a time of maximum activity would unfortunately be more difficult to interpret.

Although the region of the sun's atmosphere from which metre wavelengths are emitted has been thus shown to extend to a distance at least 700,000 miles from the sun's equator, photographs during total eclipses of the sun show that the visible corona extends commonly to about 1,000,000 miles, and indivi-

dual streamers have been traced on occasion to distances of 6,000,000 miles, or 7 solar diameters. For the study of these more remote regions of the corona, there is available a further method, results with which have lately been reported by K. E. Machin and F. G. Smith of the Cavendish Laboratory, Cambridge. When the direct path from a known radio star to the earth passes through the sun's corona, it would be expected that reception of radio waves from the star would be affected. Two different effects are possible: either radiation from the star could be cut off from the earth by refraction in the corona, or there could be an increase in the apparent size of the star caused by irregularities in the corona. With the interference method of observation used at Cambridge,* a reduction in the apparent intensity of the star could result from either of these effects. Observations on an intense radio source in Taurus were made from 5 June to 20 June 1952 on wavelengths of 3.68 and 7.9 metres (frequencies, 81.5 and 38 Mc./s. respectively). On both wavelengths there was a reduction in the apparent intensity of the star, beginning at an angular separation equal to about 5 solar diameters, and the greatest reduction amounting to three-quarters or more of the star's initial intensity. The results favour the second of the two explanations suggested, and the method offers a new means for the study of the outer structure of the sun's corona.

The radio source in Taurus which was used in these experiments corresponds closely in position with the Crab Nebula, a still expanding shell of gas which is believed to have originated in a supernova explosion observed by Chinese astronomers in A.D. 1054. This is an exceptional case, the great majority of radio-stars being not identifiable with corresponding visual objects. It is therefore of interest that R. Hanbury Brown and C. Hazard, of the Jodrell Bank Experimental Station, Cheshire, should lately have found a source of radio-emission which corresponds in position with another historic supernova – that seen by Tycho Brahe in 1572 – of which there is no visible remnant, possibly because of the greater distance of the star. The discovery resulted

**Science News* 20, 108 (1951).

from a detailed survey of that part of the sky which lies within range of the 218-ft. fixed radio-telescope at the Jodrell Bank Station. The intensity of radio-emission is less by a factor of 10 than that of the Crab Nebula source; and, in view of this low intensity, it is suggested that a further search be undertaken for the remains of a third supernova, that of 1604.

These three contributions to radio-astronomy, each using a different method, have been published within less than a month.

Denisse, J. F., Blum, E. J., and Steinberg, J.-L., *Nature*, **170**, 191 (1952).

Machin, K. E., and Smith, F. G. *Nature*, **170**, 319 (1952).

Brown, R. Hanbury, and Hazard, H. *Nature*, **170**, 364 (1952).

RADIO-PROPAGATION

In a note on atmospheric turbulence, published in *Science News* 20, the results were summarized of experiments on the reception of metre- and centimetre-wave radio, under normal atmospheric conditions, at distances further below the horizon than would be expected from simple theory. Tests by E. C. S. Megaw of the Royal Naval Scientific Service on a wavelength of 10 centimetres were extended to a distance of more than 300 sea miles (550 kilometres) from the transmitter during six passages across the northern North Sea. Continued and apparently regular reception was attributed by Megaw to scattering in the atmosphere caused by its 'permanently turbulent state'. Earlier experiments, by American workers in the Caribbean in 1945, were given a similar explanation; and the results of both series of experiments were related to a statistical theory of air-eddies developed by a Russian mathematician, A. N. Kolmogoroff. An independent theory of scattering by atmospheric turbulence was developed at about the same time by Professor H. G. Booker, of the School of Electrical Engineering, Cornell University. This has lately been extended by him to include the effects of scattering by turbulent eddies in the ionosphere. Arising out of this theory, tests on 6.02 metres wavelength (frequency, 49.8 Mc./s.) have now been carried out over a distance of 1,245 kilometres and regular, if faint, reception confirmed, although normal 're-

flexion' in the ionosphere was impossible at the wavelength used. Transmissions were from a commercial short-wave radio-station at Cedar Rapids, Iowa, using a directional aerial system. Reception, also with directional aeriels, was at the National Bureau of Standards station at Sterling, Virginia. Measurements, which extended over several months, were made in conjunction with workers at Cornell and Harvard Universities and the Carnegie Institution.

The geometry of the aerial systems supports the supposed connexion between the received signals and scattering in the ionosphere. Both transmitting and receiving aeriels were directed at 7° elevation. Allowing for the beam-width of the system used (about 5° total width in a vertical plane) and for the curvature of the earth, this would provide reasonably efficient means for the reception of radiation scattered at any height between about 60 and 150 kilometres, and particularly for radiation scattered in the *E* region of the ionosphere at about 100 kilometres height. Secondly, the curve of received energy showed daily and seasonal changes consistent with the effects on the ionosphere of ultra-violet radiation and ionization by meteors. On the other hand reception was immune from interruption at times of 'fade-out' at rather longer wavelengths, which points to scattering at somewhere below the main *E* region. Quantitatively, it had been predicted that the received energy would be one ten-millionth of that for direct, uninterrupted reception at the same distance. The actual received energy varied from one-tenth to a few thousandths of that calculated. The discrepancy could be partly explained, if scattering took place at a lower level than that for which the aerial system was designed.

Booker, H. G., and Gordon, W. E. *Proceedings of the Institution of Radio Engineers*, 38, 401 (1950).

Bailey, D. K., and others. *Physical Review*, 86, 141 (1952).

FLUORESCENCE OF TEETH

Research on the fluorescence of teeth has been reported lately by R. L. Hartles and A. G. Leaver of the Biochemical Department, the School of Dental Surgery, Liverpool University, and by the

National Bureau of Standards, Washington. The object of the Liverpool work is to identify the substances in teeth that fluoresce when exposed to ultra-violet light. That at the Bureau of Standards is on the use of fluorescence to show the fine structure of teeth. There are indications from the latter work that one of the fluorescent substances in teeth may be connected with the bonding of the surface enamel to the underlying dentine.

It has been known since 1911 that teeth fluoresce with an intense blue radiation, said by its discoverer to be second only in intensity to that shown by the lens of the eye. More lately, it has been found that dentine fluoresces more intensely and with a more vivid blue than does enamel, and also that the white spots of decay show no fluorescence. For the examination of tooth-structure in detail, G. Dickson and I. C. Schoonover of the Bureau of Standards, and A. F. Forziati, who holds an American Dental Association Research Fellowship, have prepared sections of thickness from 0.025 to 0.075 mm. Fluorescence micrographs are stated to give information on the distribution of the organic content of enamel and dentine, and to show developmental or growth lines very clearly. The most intense fluorescence comes from near the enamel-dentine junction, along lamellae, and to a shallow depth below the exposed surfaces of the enamel. Records are also being made of the fluorescence-spectra of small areas – work which will be of more value when the fluorescent substances have been identified.

Research at Liverpool has gone far enough to suggest that identifications should be possible. Strongly fluorescent extracts from powdered dentine have been obtained with ethylene glycol containing 3 per cent potassium hydroxide; concentrated by adsorption on charcoal; and partly separated by paper chromatography. The evidence at this stage is that there is more than one substance which shows fluorescence; that the activity is greater than can be accounted for by amino-acids; and, therefore, that the fluorescent substances consist, at least in part, of organic substances other than amino-acids.

Hartles, R. L., and Leaver, A. G. *Biochemical Journal*, 51, xxxvi. (1952).

CONCENTRATION OF TRACE-ELEMENTS BY SEAWEEDS

The concentration of trace-elements by seaweeds, compared with the amounts in sea-water from which they are derived, is a good illustration of the problem of selective absorption of mineral salts by plants, discussed by J. F. Sutcliffe in *Science News* 25. Figures for six species of common brown seaweeds and for fifteen trace elements have lately been published by W. A. P. Black of the Institute of Seaweed Research, Musselburgh, and R. L. Mitchell of the Macaulay Institute for Soil Research, Aberdeen. The necessary analyses were done at the latter institute, using spectrochemical methods slightly adapted from those already in use for work on land-living plants. Some remarkable contrasts were found, both in the degree of concentration of different elements, and in the range of differences between species in the case of particular elements. Titanium provided the most extreme example in both respects. Whereas it was found to be concentrated 10,000-fold by flat wrack, *Fucus spiralis*, on a wet-weight basis, the greatest concentration of molybdenum was only 15-fold. Again, titanium, although concentrated by each of three other species to the extent of 1,000-fold or more, is concentrated by ribbon weed, *Laminaria digitata*, by only 120-fold on the average, giving a range between species of about 80 to 1. In the case of zinc, although concentrations were generally high in the species examined, there were relatively slight differences between species. The greatest concentration – by knotted wrack, *Ascophyllum nodosum* – was 1,400-fold; the least – by notched wrack, *Fucus serratus* – was 600-fold. Most of the seaweed samples were collected from Atlantic Bridge, which joins the Isle of Seil with the mainland of Scotland. Samples of sea-water were collected from a depth of 20 metres off Plymouth and from a depth of 0.5 metres in positions near to those from which the seaweed-samples were taken. There was some evidence of variation in the distribution of trace-elements between different parts of seaweeds, and also seasonally.

Black, W. A. P., and Mitchell, R. L. *Journal of the Marine Biological Association*, 30, 575 (1952).

SANDHOPPERS' COMPASS

The following note has been received on some experiments which suggest that *Talitrus saltator* (a small crustacean like a sandhopper) is guided in the direction of the sea by its ability to respond to the direction of polarization of scattered light:

Science News 18 reported the experiments of Professor von Frisch on bees, and his conclusion that they are able to keep a sense of direction by using available landmarks, the smell of nearby nectar or syrup, or, as a last resort, the direction of the sun or of the plane of polarization of the light reflected from a patch of blue sky. Now two zoological workers at Pisa, L. Pardi and F. Papi, have found that *Talitrus saltator* can gauge the direction across the beach to the moist sand at the water's edge by reference either to the direction of the prevailing wind or, more accurately, to the sun's position or the polarization of its scattered light.

In one of their experiments the sandhoppers were put into an inverted bell jar, where they congregated on the side facing the sea. The jar was then taken out to sea, and the sandhoppers continued to look seawards. Again, if direct sunlight was obscured, but the sun reflected on to them from the opposite direction, they turned right round. A sheet of 'Polaroid' between them and the blue sky was used to alter the direction of the plane of polarization, and as this was slowly rotated the sandhoppers moved round inside the bell jar. It follows from these experiments that each population of *Talitrus* along the coastline learns to set itself at a different angle to the sun's direction in order to get to the sea by the quickest route. The authors convincingly demonstrated this by taking specimens from a beach on the Tyrrhenian Sea, with the seaward direction to the west, to an Adriatic beach on which the sea was to the east. The transported sandhoppers headed inland, to the west. A second corollary is that *Talitrus* (like the bee and the ant) must have developed a time-sense to allow for the change in the sun's position or the plane of polarization during the day. Anatomical studies of the eyes of insects and crustaceans have shown how they can judge the

direction of the plane of polarization, but it is not yet known how they correlate this with the passage of time – nor what they use as a clock.

Pardi, L., and Papi, F. *Die Naturwissenschaften*, 39, 262 (1952).

VIRUS DISEASES OF FRUIT TREES

Although 'apple mosaic' is one of the oldest known virus diseases of plants, virus diseases of fruit trees have received comparatively little attention until lately in Great Britain. They are less convenient to work with than are virus diseases of smaller plants, and they have not been thought important. There has been recent research on viruses affecting apple, cherry, and plum trees, and it now seems that some at least of them cause significant losses. One of the first reasons for interest was the recognition, in 1944, of abnormalities in the apple variety, Lord Lambourne, one of which, 'rubbery wood', is shown by drooping branches and leads to a marked reduction both in annual growth and in fruit-yield. Research on this virus has led as a general precaution to a decision that the well-known clonal rootstocks distributed by the East Malling Research Station, and onto which the more familiar named varieties are grafted, shall be propagated again from single plants that have been tested and found free from all known viruses. Interest in virus diseases of cherries and plums was stimulated in 1949 by a summer visit to the Long Ashton Agricultural and Horticultural Research Station of the University of Bristol by R. S. Willison, of the Dominion Laboratory of Plant Pathology, Canada; and, in the same year, A. F. Posnette, a specialist in tropical tree viruses, was appointed to the East Malling Research Station.

Research on 'rubbery wood' and other virus infections found in Lord Lambourne apple trees was begun by T. Swarbrick, and continued by L. C. Luckwill and S. H. Crowdy, at Long Ashton. By 1949, it had been shown that 'rubbery wood' could be transmitted by grafting (including transmission through varieties which did not themselves show symptoms), and that it was carried by several of the Malling rootstocks used at Long Ashton. The latter conclusion has now been confirmed at East Mall-

ing in respect of some, but not all, stools of these rootstocks. Other experiments at East Malling have established the existence of three different strains of the original apple mosaic virus, one of which is described as severe.

In the case of stone-fruit viruses, Dr Willison made a rapid survey of representative cherry and plum orchards in Kent, Somerset, Herefordshire, and Worcestershire in 1949. A preliminary survey by the East Malling Station 'showed conclusively that several important virus diseases . . . are of wide occurrence', and in 1950 six virus types found in cherries were tentatively named. Further progress was made in 1951 on the identification of cherry viruses from the symptoms caused in test species, of which a small black cherry (F12/1 mazzard) has been the most useful. Three pear viruses were distinguished by the use of quince seedlings as indicator plants, and a start was made on the study of virus diseases of plum trees, which are expected to present a more complicated problem.

Annual Report of the Long Ashton Research Station for 1949, pp. 64 and 68 (1950).

Annual Reports of the East Malling Research Station: for 1949, p. 41 (1950); *for 1950*, p. 39 (1951); *for 1951*, pp. 41, 128, and 131 (1952).

BILLION VOLT PROTONS

An article by L. L. Green in *Science News* 22 described the three machines – at Brookhaven and at Berkeley in the United States, and at Birmingham University in Great Britain – which were then under construction for the acceleration of protons to energies of one thousand million electron-volts (1,000 MeV) or over. The Brookhaven 'cosmotron' (proton synchrotron) was brought into operation in June, 1952, first at 1,300 MeV, and soon after at 2,200 MeV, the final design-output being 3,000 MeV. The Brookhaven laboratory thus becomes the first to be able to experiment with particles in the 1,000 MeV, otherwise BeV, range of energies. The principle of the proton synchrotron was first tested in a quarter-scale model of the University of California's 'bevatron', now under construction at Berkeley.

SOME BOOKS RECEIVED

THE INITIATION AND GROWTH OF EXPLOSIONS IN LIQUIDS AND SOLIDS by F. P. Bowden and A. D. Yoffe (Cambridge University Press, 1952), pp. 104, 22s 6d.

In the hands of Dr Bowden and his colleagues, the study of the birth and growth of explosions has provided an almost classical example of experimental methods and approach, well worth recording in monograph form. The statement that explosions in solids and liquids are commonly initiated in 'hot spots' formed by the compression of air bubbles trapped on impact, or else by friction, is here justified by experiments of great ingenuity, but essential simplicity, in which the significant variables are separated and identified. An example is the use of grits formed from materials of different melting points to determine the minimum temperature needed for initiation by friction. The study of propagation-rates during early growth is of theoretical as well as experimental interest, and is well illustrated.

DEMONSTRATIONS IN MODERN PHYSICS by M. C. Nokes (Heinemann, 1952), pp. 134, 10s 6d.

The author's object is to show the comparative ease with which many of the key experiments of modern physics can be adapted for school demonstration and individual work; among them are the determination of the mass and charge of the electron, the transmutation of lithium, and some experiments on radioactivity. The book may be a help also to those lacking physical experience for the sense of reality that it conveys.

ELEMENTS OF WAVE MECHANICS by N. F. Mott (Cambridge University Press, 1952), pp. 156, 21s.

Professor Mott's book is for the final year student of experimental physics. Its characteristics are the building up of the elementary theory of wave mechanics from experimental facts, the omission of some mathematical developments that can be otherwise found, a relatively extensive treatment of the hydrogen atom, and a series of compact approaches to such subjects as chemical bonding, the treatment of semi-conductors and of metals, and theories of radioactive breakdown, which together are of widely spread interest.

BELFAST IN ITS REGIONAL SETTING: A SCIENTIFIC SURVEY (British Association, Local Executive Committee, Belfast), pp. 211, 34 maps and diagrams, 8 plates, 21s.

One of the peculiarities of the British Association is that the scientific surveys prepared annually by the place of meeting have not before compelled some wider circulation. The 1952 survey, compiled under the chairmanship of Professor E. Estyn Evans, who holds the Chair of Geography at Queen's University, Belfast, and edited by Dr Emrys Jones, is a distinguished publication covering the natural science, history, ethnography, and present-day life and conditions of an area corresponding approximately with Northern Ireland. It should remain for a long time to come as the best general introduction to the region.

TOWNSMAN'S FOOD by Magnus Pyke (Turnstile Press, 1952), pp. 212, 15s.

Dr Pyke is a chemist and nutritionist who was formerly a principal scientific officer in the Ministry of Food. His book is intended to 'describe for the intelligent non-scientific reader some of the technical problems of the modern food industry', including the difficulties of large-scale supply. Pleasantly written, it is likely to be unpopular with food manufacturers for many of the facts given, and with eaters of food for an ignoring of favourite dislikes. Dr Pyke has been widely quoted, and should be widely read.

HEALTH EDUCATION by Cyril Bibby (Heinemann, 1952), pp. 222, 17s 6d.

Primarily, this is for educators. Media are critically examined, and the phases of home, school, college, and general adult education are separately discussed. Appendices include an outline scheme; films, film-strips, and bibliography; a directory of health education organizations; and selected statistics. It is the book of an enthusiast, but practical throughout.

MIND LIFE AND BODY by Reginald O. Kapp (Constable, 1952), pp. 196, 12s 6d.

The arguments developed by question and answer through the greater part of this book must stand or fall by the ability of the author to surmount a well-known difficulty: that of providing a

means by which a non-material entity, mind, can influence matter. Professor Kapp's suggested solution is a variant of the appeal to the Principle of Uncertainty: in this case, that the distribution of energy in a large organic molecule may be indeterminate in time, and that, through the timing of energy-availability, some such influence may be exerted. But to this reviewer it is not obvious why the distribution of energy in a large organic molecule should be more amenable to non-material influence than is the distribution of energy in any other collection of objects.

THE ALCHEMISTS by F. Sherwood Taylor (Heinemann, 1952), pp. 246, 12s 6d.

This seemingly slight addition to the literature of alchemy is justified by two circumstances: first, that the author has a long record of work on the subject; and, second, that his 'short and clear account' is neither overburdened with discussion nor seeks popularity through anecdote. He is particularly successful in distinguishing between the operations of alchemy and their meaning to alchemists.

PROCEEDINGS OF THE FIRST PAN-AFRICAN CONGRESS ON PREHISTORY 1947 edited by L. S. B. Leakey assisted by Sonia Cole (Blackwell, 1952), pp. 239, 35s.

Delay in publication, which is explained, is made the more evident by recent work in East and in South Africa. However, as the most important problems are those of correlation, and the Congress was of a pioneer character, there is still a value in its proceedings.

ABOUT OUR CONTRIBUTORS

F. A. FOX graduated in metallurgy at Birmingham and took his first job on a goldmine in West Africa. Since returning to England, he has been engaged in metallurgical research, and is best known for his publications on magnesium alloys for which he was awarded his D.Sc.

JOHN E. OWEN was born in Manchester, but has lived for many years in the United States. He is a graduate of Duke University, holds a Ph.D. from the University of Southern California, and has lately been Visiting Professor of Sociology in the University of Helsinki.

E. F. ROOTS studied geological engineering at the University of British Columbia (M.A.Sc.) and geology at Princeton University (Ph.D.). He worked for the Dominion Meteorological Service (Canada), the Department of Geology and Geography at the University of British Columbia, and the Geological Survey of Canada (in the north-west) before joining the Norwegian-British-Swedish Antarctic Expedition, 1949-52, as senior geologist. Now lecturing in the Department of Geology, Princeton University.

GEORGE SAVAGE studied art in European and American galleries, and is a partner in a firm of fine art dealers. Author of *Ceramics for the Collector* and of *18th-Century English Porcelain* (London, Rockliff; New York, Macmillan).

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