12298

ANNUAL REVIEW NUMBER

23p. m. 9

VOL LXVIII

The

10 JANUARY 1953

Chemical Age

No 1748



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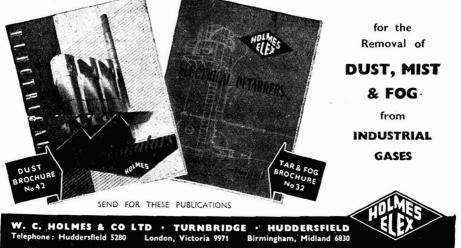
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10 January 1953



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FIRST PRIZE . . . £25 (1st, 2nd and 3rd Prizes SECOND PRIZE . . . £10 THIRD PRIZE . . . £5 In addition, One Guinea (£1 1s.) will be awarded for each photograph of sufficient interest to be retained for use by The "Drum" Engineering Co., Ltd.

The subject of the Competition will be 'DRUM' PUMPS IN USE. The basis of the awards will be good clear photography of technical interest, rather than 'artistic' presentation. It' is desired to keep the Competition as informal as possible, but the following conditions shall be considered as binding on competitors :

1. Prints submitted to be black and white, and preferably not smaller than 4 in. x 3 in.

2. Prints to be well-packed and sent marked 'Photographic Competition' to The "Drum" Engineering Co., Ltd., Bradford, Yorkshire, England.

3. On the back of each print must be pasted a label bearing the name and address of the competitor (together with a pseudonym if desired) and a description of the photograph. Any interesting data regarding the pump can also appear on this label, which should be written or typed before being attached to the print. Do not write or type on the print itself.

4. The "Drum" Engineering Co., Ltd., may wish to reproduce photographs for which an award has been made; in such cases the Company will seek from the user of the pump(s) written permission to reproduce.

5. No print submitted can in any circumstances be returned.

6. Where permission to photograph is necessary, suitable permission must be secured by the competitor before submitting any print.

7. The names (or pseudonyms) of the winners will be published in this journal; the decision of the Managing Director of The "Drum" Engineering Co., Ltd., shall be final.

8. CLOSING DATES:

'Home' Competition

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THE CHEMICAL AGE

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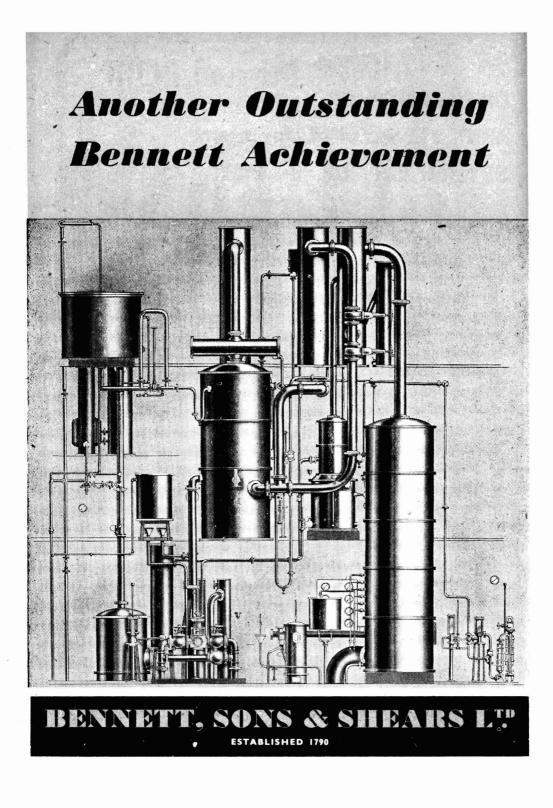
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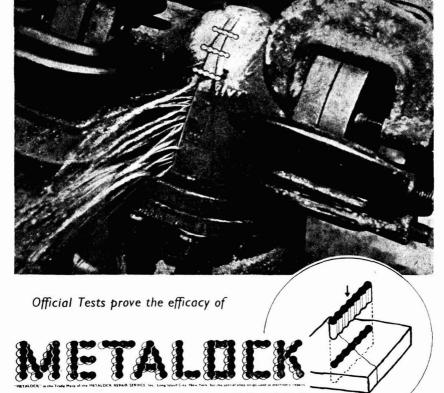


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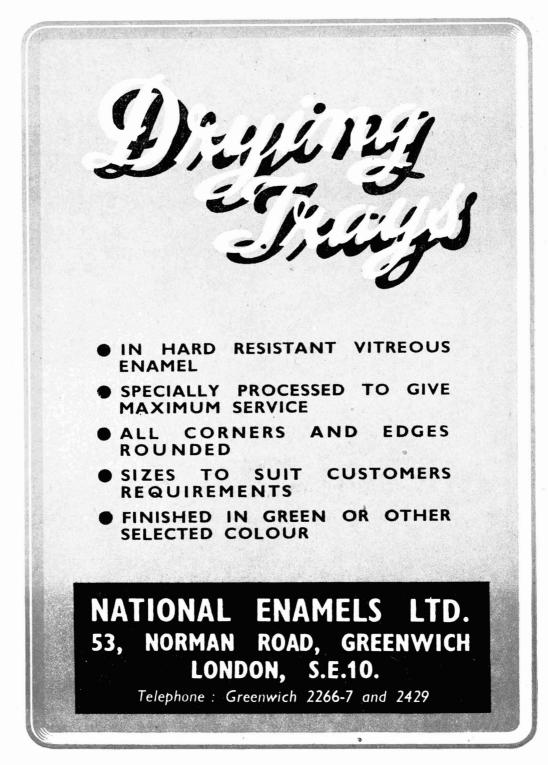
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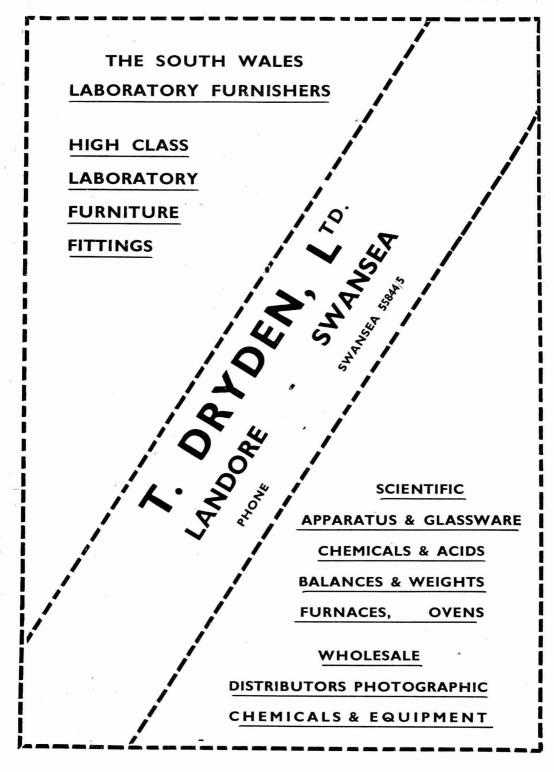
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THE CHEMICAL AGE

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10 January 1953



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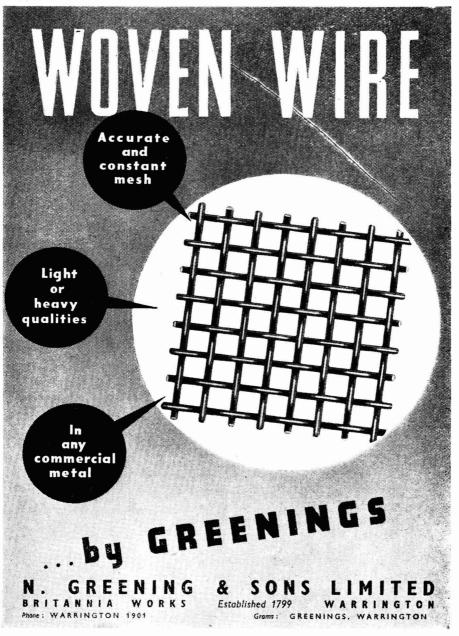
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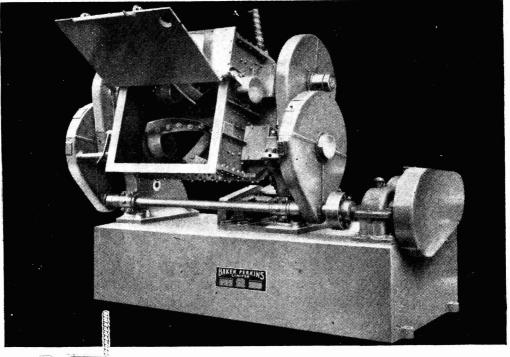
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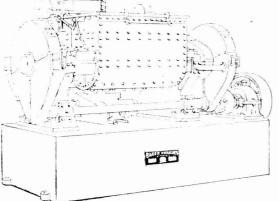
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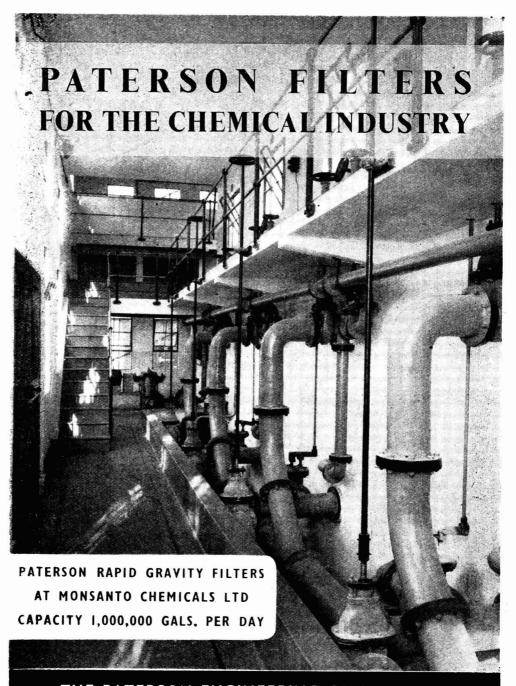


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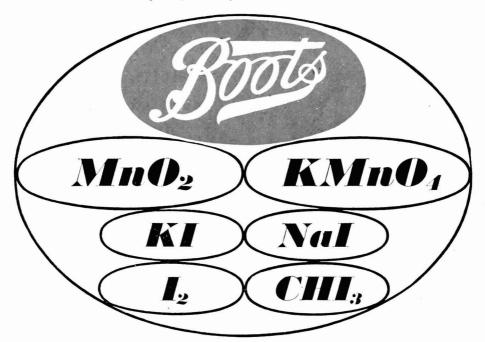
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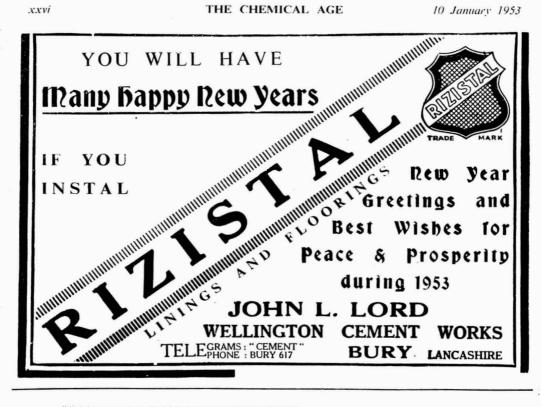
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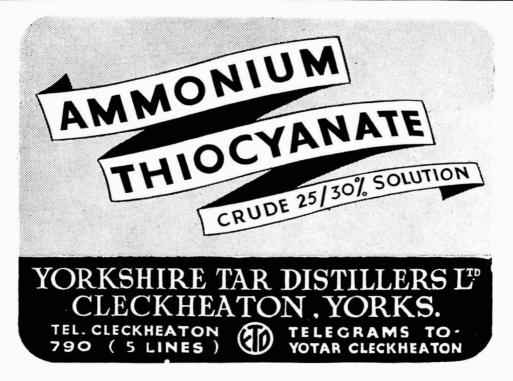
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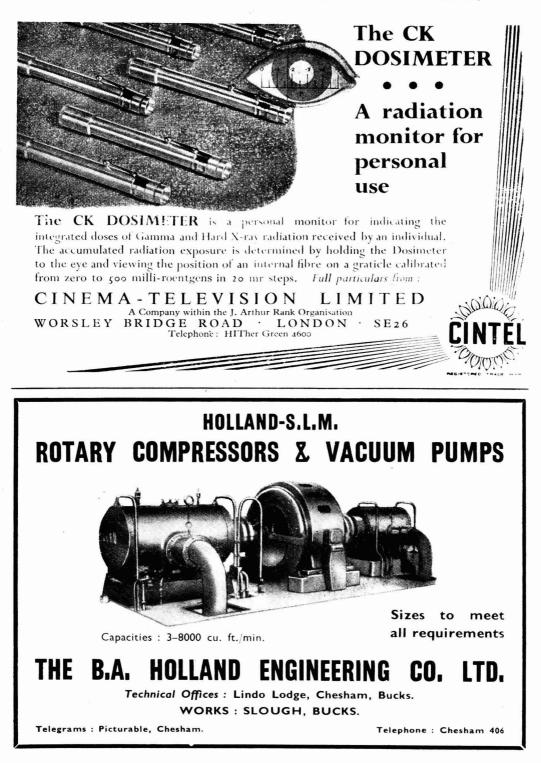
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THE CHEMICAL AGE

10 January 1953



xxviii

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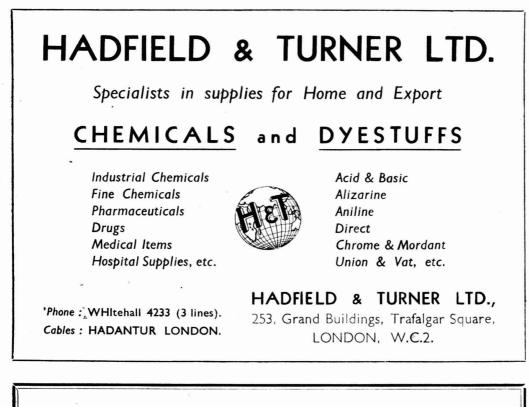
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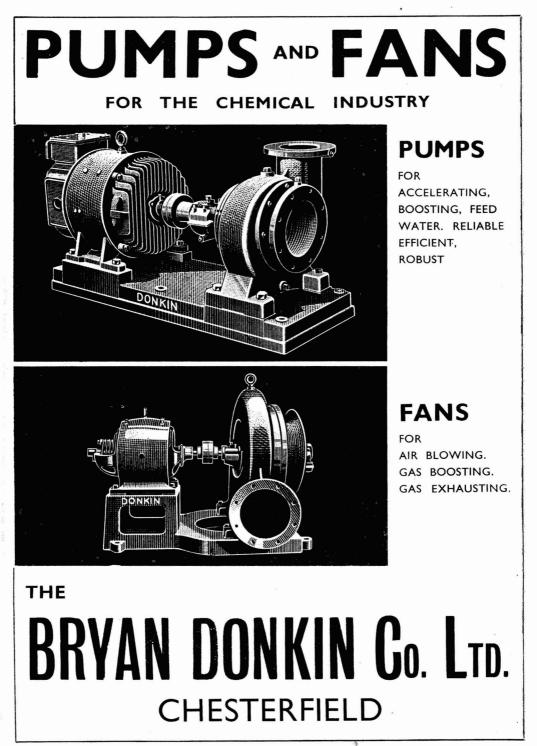


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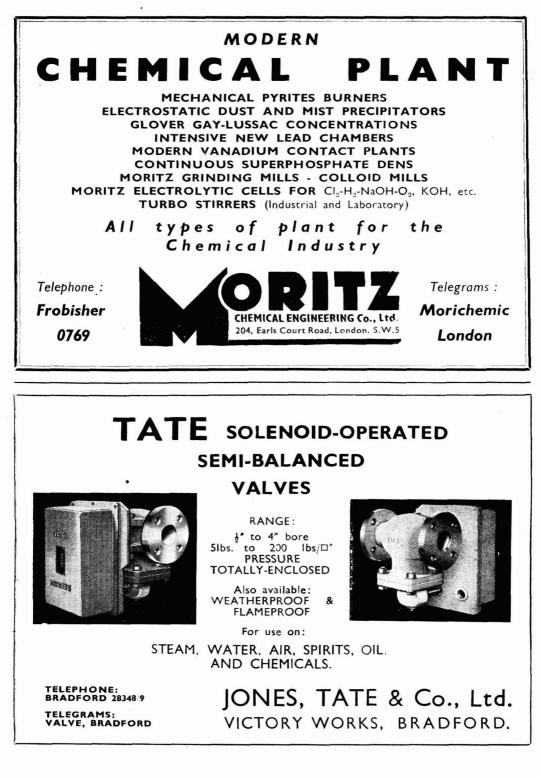
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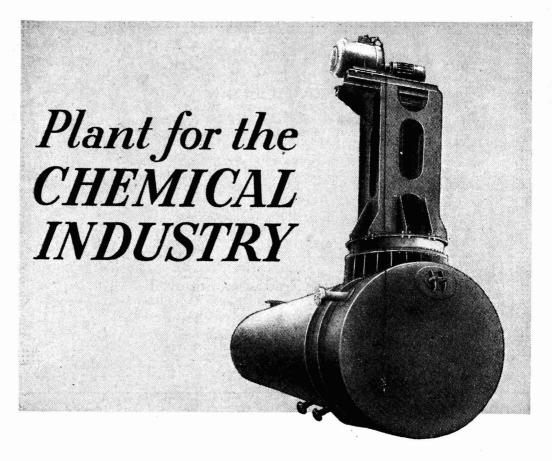
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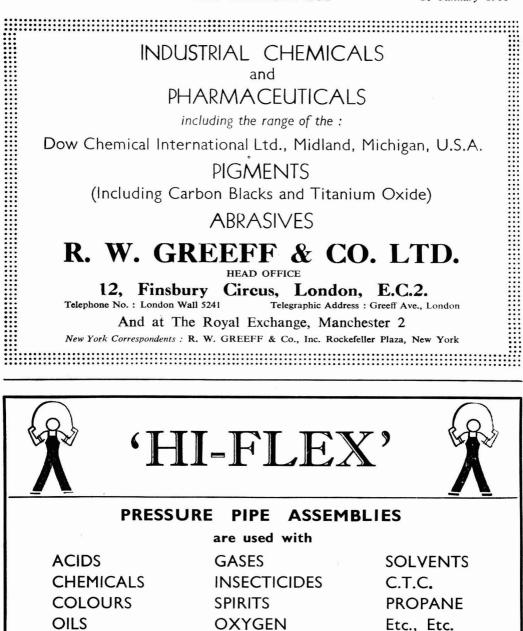
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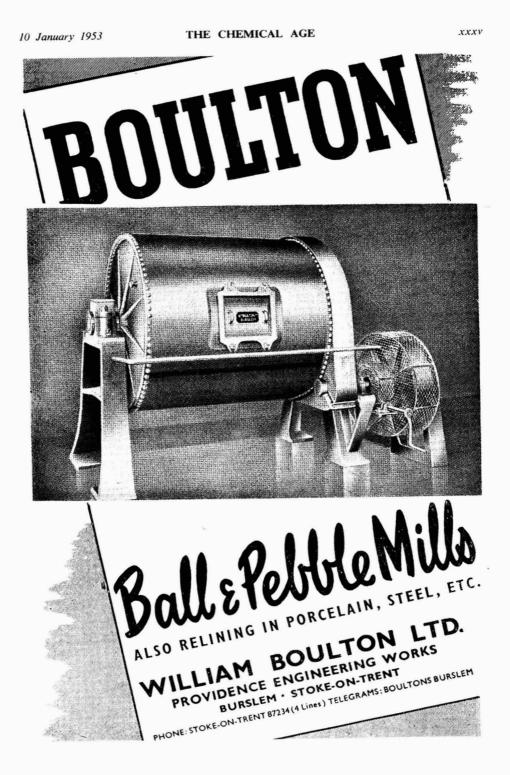


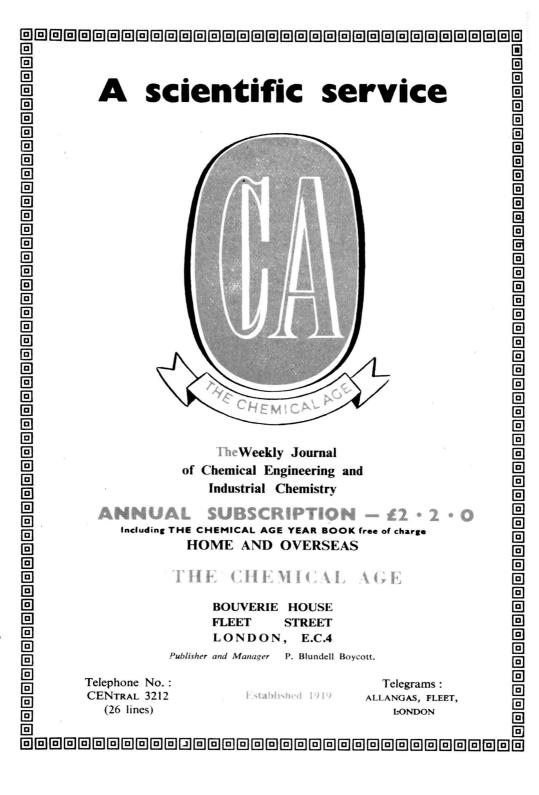
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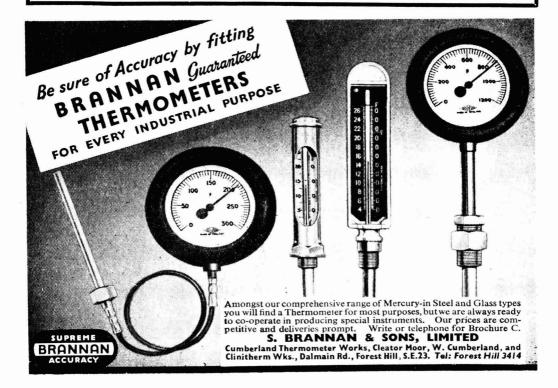
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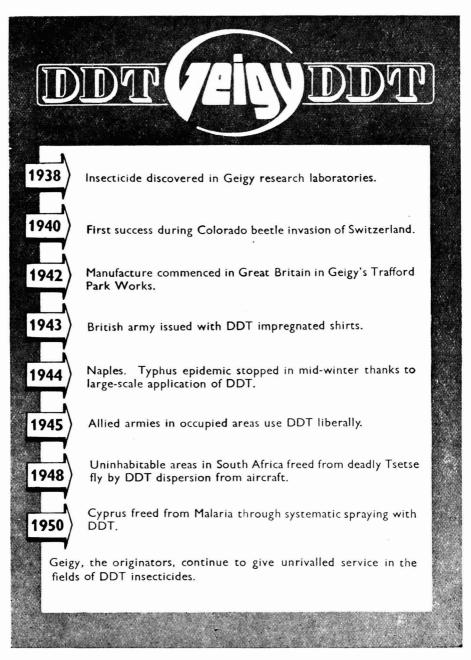
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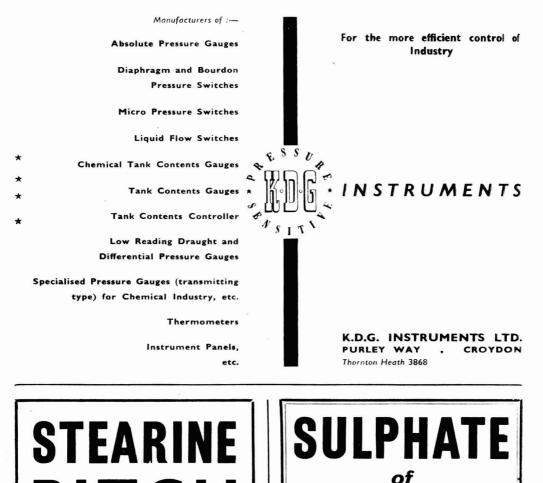
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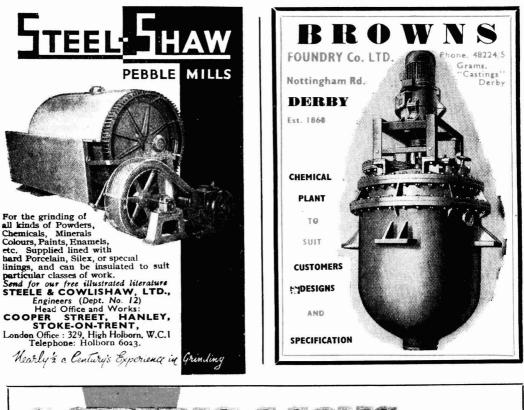


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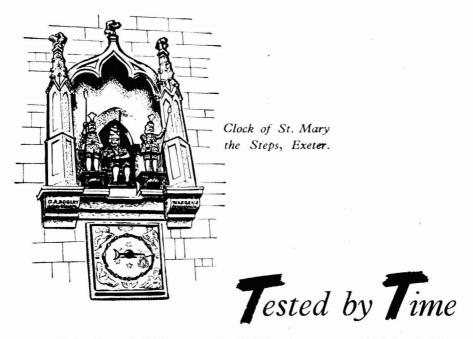




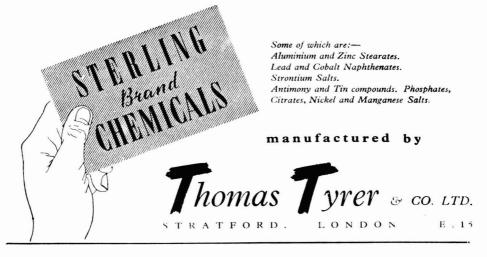








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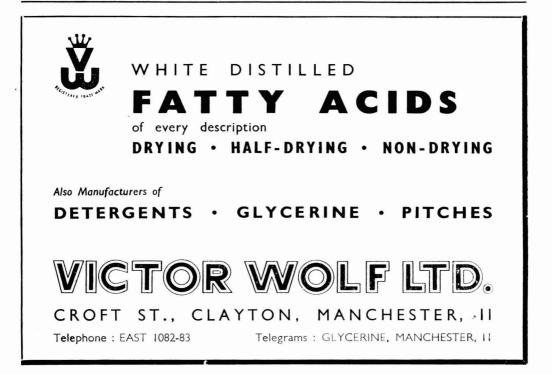
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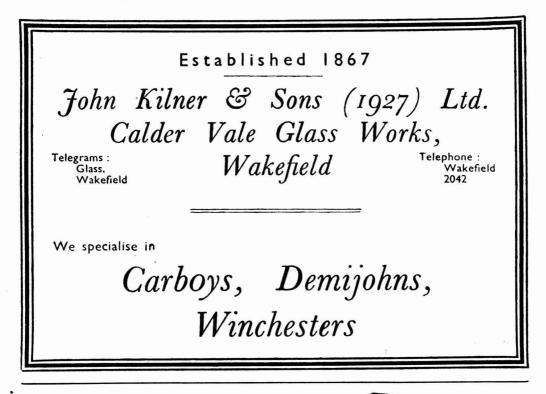
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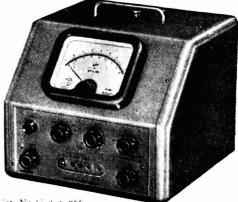
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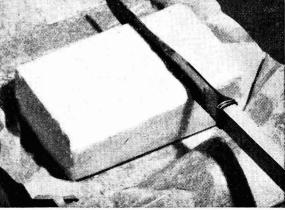
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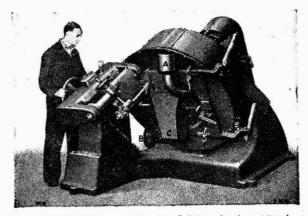
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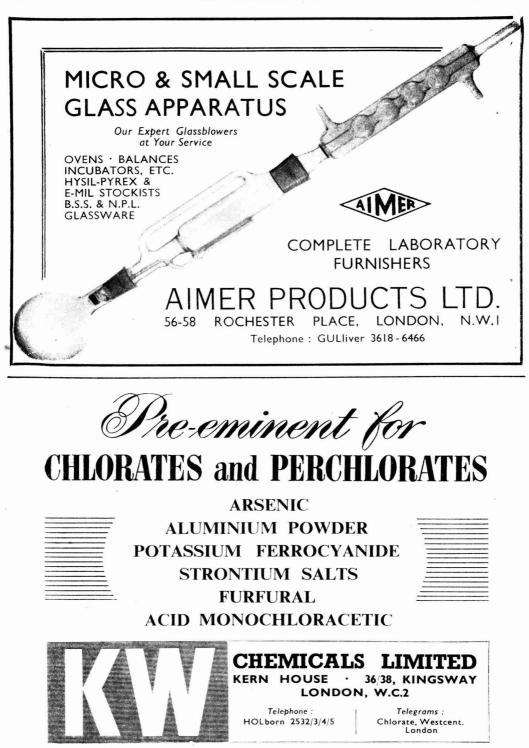
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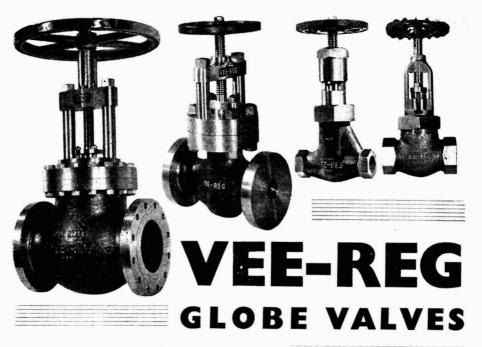




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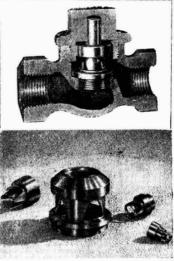
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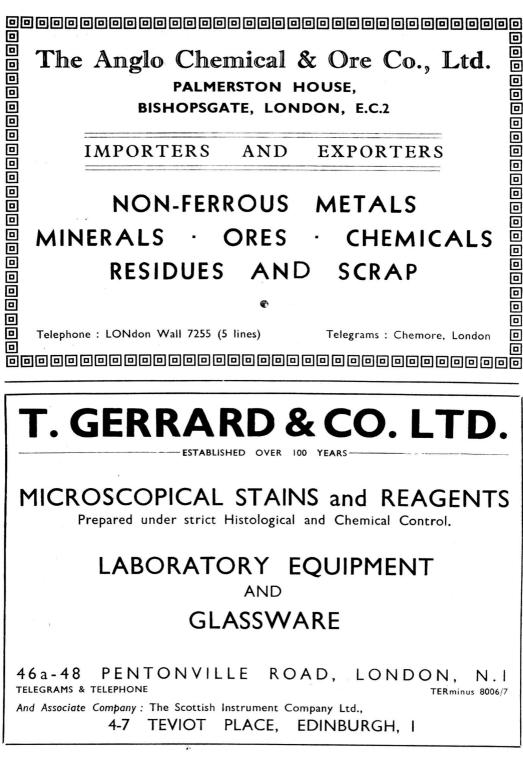
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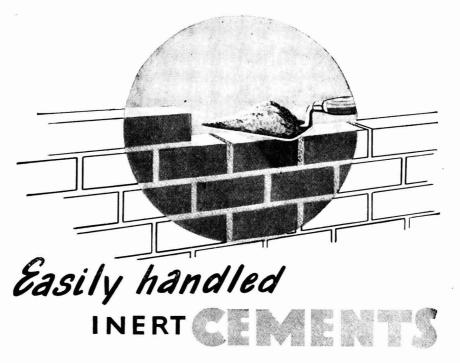
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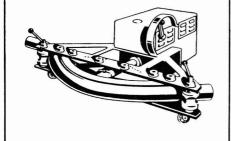
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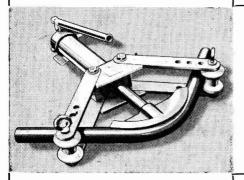
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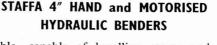
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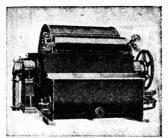
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Volume LXVIII

10 January 1953

Number 1748

The Challenge of 1953

a year when the Australian cricketers are visiting us, we may perhaps be permitted to borrow a willow-pattern phrase and remind ourselves that since the end of the war the British chemical industry has so far enjoyed a batsman's wicket. No doubt this will be hotly denied by many-but those who are concerned with production, plant expansion, and raw material supplies, must inevitably take a bowler's view of an easy-paced paradise at Lords or Leeds. Even when the wicket seemed likely to crumble, a year of Korean crisis and stock-piling brought back the seller's market. The wicket could have become very much stickier in 1952 but the expected revival of German competition did not manifest itself at all strongly. The chemical industry has become more complicated and Germany's technical rehabilitation cannot be instantaneous. The difficulties of plant expansion and re-deployment that we ourselves have had to overcome are no less formidable there, and we have had several years' start.

It may well be that 1953 will prove the first post-war year of realistic challenge.

If so, we need not meet it with self-critical apprehension or with pessimism. Without inviting charges of complacency, the chemical industry can look back with reasonable pride upon seven post-war years of prudent and striking progress. There is little or nothing that could have been done that has been neglected and much that has been achieved has been accomplished in the face of persistent difficulties. It is often said that we shall find ourselves unable to compete with the vastly expanded chemical industry of the United States; that, so far we have been protected from this risk by the 'boom' demands of the American home market. If this is true, why do so many U.S. manufacturers demand tariffs for the protection of their home market? If there are fears that British chemicals cannot compete in Chicago or California, why should their ability to compete in Canada or Brazil be doubted? We are apt to be over-awed by the American chemical colossus.

In the early period after the war there were signs that many countries were planning to develop their own industries on a large and rapid scale. As these were mostly countries we had long supplied with manufactured goods, the threat to our export trade seemed highly serious in the long run. There is good evidence predominantly now that agricultural countries cannot so readily and cheaply forge the path of industrialisation. The Peron five-year plan has produced depression and unemployment and Australia's post-war drive for industrialisation has jolted rather than increased her record of prosperity. The gloomy theory that the oldest industrial nations must eventually die on their feet because their former customers have reached high degrees of self-sufficiency is not valid in an ever more complex world. It may be that some of our former customers for nitrogen can erect plant and manufacture their own sulphate of ammonia, but there are new and more complex chemicals that we can make and sell to them insteadend-products with a much higher 'rawmaterial-conversion' value. The truth is that there is not unlimited economic room in the world for further national aspirations towards industrial production, and there is on the other hand ever more room for agricultural countries to expand their production of food, and to do so with assured prosperity.

The limitation of our chemical prospects for 1953 and thereafter is unlikely to be a limitation of opportunity. The expansion plans of 1949 have made good progress despite the series of intervening economic crises. The percentage of those plans that have been postponed or abandoned is small and probably represents no more than the expectable deflation in total plans for a complex industry. Nevertheless, the chemical industry is perpetually changing and plant re-equipment and new process development constantly require capital. The completion of most of the 1949 projects will not bring a quiet resting-time. In the ever-present capital needs of the industry we may well face the most dangerous limitation. High taxation together with capital scarcity and dearness cannot indefinitely remain the climate of enterprise; it is a climate that particularly endangers the future of the chemical industry where versatility and progress inevitably require a steady flow of capital through unhardened arteries. If this climate is not ameliorated in 1953, the longer prospects of the industry's ability to hold its own or, better still, to expand in an increasingly competitive world market will be inevitably damaged.

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Notes & Comments

The Wash-Tub War

CCORDING to a recent article in The Financial Time The Financial Times, the battle of The synthetic detergents is the greatest advertising fight since the thirties. The prize is big for 40 per cent of all domestic washing products are now synthetic and our large centres of population represent huge and compact London is said to be the markets. biggest single market for detergents in the world. Commercial history is merely repeating itself with new scientific products. The soap companies were among the first to hurl themselves into advertising battles and the principal protagonists in this new detergent phase are companies long associated with soap. Oddly enough, the expected battle between soaps and detergents has been quietly and gradually fought, though in a country of conservative habits it might well have been protracted and bitter. However, toilet soap still holds its own and seems likely to do so unless synthetic detergents can overcome the hazard of skin allergy; the limited number of people whose softer surface tissues may respond awkwardly to detergents is so far protecting soap in its best-price market. Even so, toilet soaps may steadily endure where wash-tub soaps have been forced to retreat. The modern detergent is relatively attractive when compared with the cruder bars of soap used at the kitchen-sink, but a detergent product will not so easily displace the perfumed, well-established bathroom tablets.

Detergent Poisoning

THE British Medical Journal (20 Dec., 1952, p. 1,348) has expressed some concern about the rapid expansion of synthetic detergents. An American case in which a woman died half an hour after mistakenly drinking a detergent solution sold for domestic cleaning purposes was referred to. 'It might be well to consider the scheduling of concentrated liquids as poisons. Alternatively, the manufacturers might add something to give a characteristic odour that would prevent their accidental administration.' Are these materials in their concentrated and, as-sold' form actually toxic? If they can kill bacteria at very dilute concentrations, a general toxic effect upon living cells is not an incompatible expectation. Their surface-active nature would make their effects on the body very speedily felt. This, certainly, is an aspect of the detergent invasion that will not appeal to the front-line pioneersunless one of them can claim that 'vou can drink ours safely." We ourselves feel that a far stronger case for domestic detergent toxicity would have to be made out before any question of poison scheduling could be considered. We find it difficult to believe that more than one person in many years could drink more than a sip of a detergent solution in mistake for whisky, lemonade, or some such totally different liquid; though there is, of course, the incalculable question of children who often do the most unlikely things in kitchens.

Teaching Bottleneck

WE have referred frequently to the increasing scarcity of science teachers in schools, and only the fact that Nature (1952, 176, 4,339) devoted its final editorial of the year to this subject makes us do so again. The hard facts presented by Nature should be studied by all who profess any interest in the future of British science. For the whole of the present school year some 250 posts for science teachers will be vacant. In girls' schools the situation is especially serious for there are 120 unfilled posts, and it has become almost impossible to get teachers for girls' school sixth-form science. '. . . the cessation of the supply of women science graduates is within sight, since girls' schools will shortly be unable to train girls up to the standard for admission to the science faculties of the universities."

Salaries Inadequate

THE leader writer in Nature supports our own view of the principal cause for this decline—that the salaries offered to science teachers are inadequate and non-competitive with other scientific Before the war the science posts. teacher's £480 per annum was not significantly different from basic salaries in Government or industrial science. Today his £766 per annum is well below university, Scientific Civil Service, or industry levels. If the advice of an economist had been sought on how best to reduce the number of entrants to the profession of science teaching, nothing more effective than the present Burnham scale arrangements could have been suggested. Nature is not hopeful for the 'The situation will get profuture. gressively worse and lead to a lowering of our standard of life unless prompt measures are taken The position warrants a survey at the highest level of the utilisation of science graduates in Britain. But a survey takes time, and unless salaries offered for teaching more reasonably reflect the value of scientific knowledge and qualification graduates will continue to prefer industry, the universities, and even the civil service.

The New Year Honours

Peerage for Sir Clive Baillieu

THE first New Year Honours to be conferred by the Queen were announced last week.

Among the three new barons was Sir Clive Latham Baillieu, K.B.E., C.M.G., chairman of the Dunlop Rubber Company. for public services.

The list of Knights Bachelor included:— Harold Roxbee Cox, chief scientist, Ministry of Fuel and Power; Lincoln Evans, general secretary, Iron and Steel Trades Confederation; Charles Kenneth Felix Hague, deputy chairman and managing director, Babcock & Wilcox, Ltd., and deputy chairman, Royal Ordnance Factories Board; William Henry Pilkington, chairman, Pilkington Brothers, Ltd., and vice-president Council of Building Material Producers. Other honours conferred included the following: —

C.B.

William Henry Glanville, director, Road Research Laboratory, Department of Scientific and Industrial Research; Robert Spence, chief chemist, Atomic Energy Research Establishment, Harwell, Ministry of Supply.

K.B.E.

Colonel Harold Charles Smith, C.B.E., chairman of the Gas Council.

C.B.E.

Donald Neil McArthur, director, Macaulay Institute for Soil Research. Aberdeen; Professor Robert Alexander McCance. M.D., F.R.C.P., director, Department of Experimental Medicine, Medical Research Council and University of Cambridge; Charles Archibald Philip Southwell, M.C., managing director, Kuwait Oil Co., Ltd.; Leonard Charles Tyte, chief scientific officer, Fort Halstead, Ministry of Supply; Samuel Arthur Henry Whetmore, lately joint managing director, Billingham Division, Imperial Chemical Industries, Ltd.

O.B.E.

John Stanley Carter, deputy chief alkali inspector, Ministry of Housing and Local Government; John Ralph Furlong, principal, Colonial Products Advisory Bureau (Plant and Animal), Colonial Office; William Kenneth Hall, works general manager, Billingham Division, Imperial Chemical Industries. Ltd.; Graham Llewellyn Hopkins, senior principal scientific officer, Ministry of Supply; leuan Maddock, principal scientific officer, Ministry of Supply; Ernest Harold Mott, senior principal scientific officer, Ministry of Supply.

M.B.E.

William Watson Dawson, experimental officer, Servicing Research and Development Branch, Ministry of Supply; Albert Elson, accident prevention officer, Samuel Fox Company branch, United Steel Companies. Ltd.; Frederick Fletcher, manager, special technical productions, General Electric Co., Ltd ; Thomas Kirkup, general manager, Palliser Magnesia Works; Charles Horace Crosby Pavne, construction designer, Billingham Division, Imperial Chemical Industries. Ltd.: Ernest Saunders, lately works manager, Silvertown Works, Imperial Chemical Industries, Ltd.; Miss Norah Sullivan, senior experimental officer. Department of Scientific and Industrial Research.

Britain's First Flash Roasting Plant

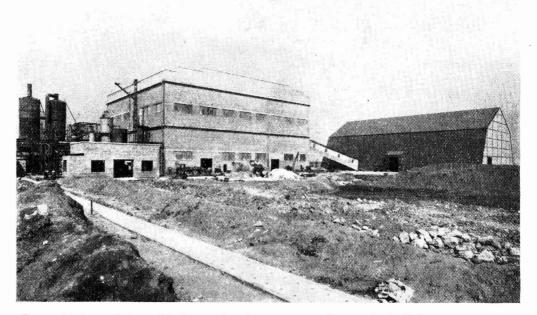
Journalists Visit British Titan Products

S INCE the onset of the sulphur shortage during the second half of 1950 some countries have made and are still making great efforts to conserve supplies and to find new sources for this extremely important metalloid. The United Kingdom has done a great deal in this direction and at present the situation with regards both sulphur and sulphuric acid is not so serious as was expected. The increased use of pyrites and anhydrite for the production of sulphuric acid has helped considerably in easing the position.

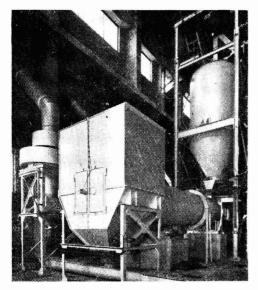
Government estimates for 1952 indicated that the United Kingdom would require 316,000 tons of 'acid sulphur' compared with 365,000 tons consumed during the previous year and 356,000 tons during 1950. It was estimated that 125,000 tons of 'regular sulphur' would be used during 1952 compared with 120,000 tons used in 1951 and 111,000 tons in 1950. In 1938, 73,000 tons of 'acid sulphur' were used but no 'regular sulphur' was consumed. From these figures it will be seen that the requirements for acid manufacture are falling whereas other demands are steadily rising. This fall in the consumption of acid sulphur is largely due to the conversion of sulphur burning plants to pyrites burning.

Some 18 conversions were in hand during 1952 and some of these have already been completed while others are nearing completion. The first pyrites roasting sulphuric acid plant to be completed was one built by British Titan Products Co., Ltd., at their Grimsby works and on 17 December a small party of editors of technical journals visited Grimsby and saw the plant in operation.

Apart from ilmenite, sulphuric acid is the major raw material of the titanium industry which is the fourth largest user of the acid in Britain. British Titan's new plant, which was started up in June, was designed and built to supply the acid requirements of the company's Grimsby extension, and has



General view of the acid plant, showing storage silo, main building and external conversion plant under construction



One of the rotary driers

aroused considerable interest in the chemical engineering field. It was the first of its kind to operate in Britain and, moreover, offers several facilities heretofore not available in this type of plant-notably the facility to operate in conjunction with an existing sulphur burning plant. The main contractors were Cyanamid Products Co., Ltd., with Simon-Carves as sub-contractors. Huntington Heberlein Co., Ltd., were the flash roaster specialists and British Titan Products did the co-ordinating. Piling was commenced on 1 March, 1951 and the time taken for construction from a bare site to full operation was just over one year, this being a great achievement when one considers that the entire plant had to be built on piles.

The pyrites burning plant at Grimsby, when completed, will supply SO₂ to a cold SO₂ oxidation plant and it will also be able to supply SO₂ in admixture with hot SO₂ from the combustion of sulphur, to the hot SO₂ oxidation chamber which is part of the original sulphur burning plant.

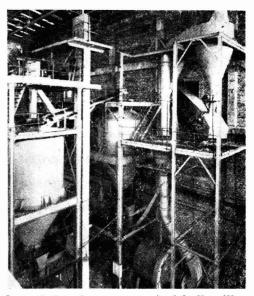
In the first part, now in operation, the sulphuric acid plant has a nominal capacity of 140 tons per day in terms of 100 per cent H_2SO_4 . The acid produced is 95 per cent. This is in addition to the 120 tons per day produced by the existing sulphur burning plant.

The pyrites, which is imported from Cyprus, is dried in a rotary drier and ground in a conical ball mill with a forced draught. The residue of approximately 20-30 per cent is retained on a 200 mesh screen.

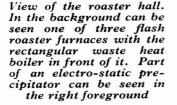
This fine material is pneumatically conveyed into the roasting room where it is injected in through the roof of one of two flash roasting furnaces where spontaneous decomposition of the pyrites occurs. The air which supports the combustion is supplied partly as primary air, in which the pyrites is suspended before being injected into the furnace, and by secondary air (of approximately equal quantity) which enters the furnace through the cinder outlet at the bottom of the cone. This secondary air is cold on entry but it removes the sensible heat from the discharging desulphurised cinder so that in normal circumstances the cinder leaves the furnace at almost room temperature.

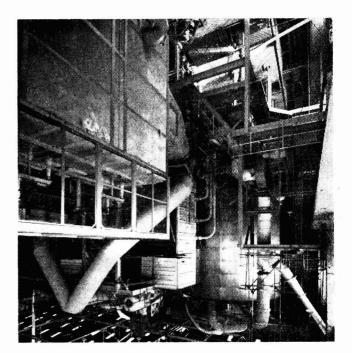
When pyrites containing 50 per cent of sulphur is burned in air to produce a gas with a strength exceeding 10 per cent SO_2 , the xothermic reaction is such that temperatures in excess of 1,000 °C. are produced. In most of the older type of furnace this heat was mainly dissipated or the gas diluted so that operations were possible.

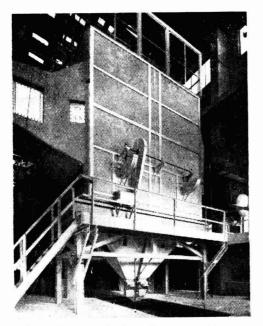
With the flash roasting units installed at



One of the air swept conical ball mills, feed hoppers and cyclone separator





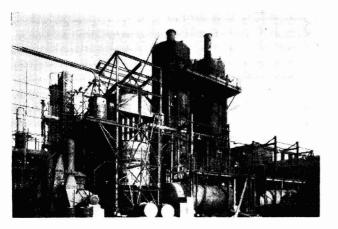


View of one of the electro-static precipitators

Grimsby all of the heat is recovered in a waste heat boiler and it is also possible to obtain a high SO₂ strength by recirculating a portion of the cooled gas leaving the waste heat boiler back to the furnace. The boiler, in fact, acts as an external cooler. In actual operation SO₂ strengths of 10-13 per cent are obtained with furnace temperatures maintained at 950° and steam equivalent to 3 lb. steam/lb. of sulphur burned is produced. The gases leave the waste heat boiler at 350° to 400° C.

By means of a series of hot Cottrell precipitators, wash towers, mist precipitators and a drying tower the gas is cleaned, washed, and cooled, acid mist is removed, and the gas dried. Centrifugal blowers, by means of a series of heat exchangers, inject the cold gas into a four-pass vanadium converter, the heat of reaction of the SO_2 being used to pre-heat the incoming gases to the ignition point. The conversion of SO_2 to SO_3 is 98 per cent complete.

The SO_3 is absorbed in 98 per cent acid in a conventional absorber and the product of 95 per cent acid is produced by mixing absorber acid with the 93 per cent acid from the drying tower. The heat of dilution is removed in water-cooled, cast iron coolers.



General view of part of the conversion and mist precipitators under construction

The cinder from the roasters, from the boiler and from the hot Cottrell precipitator is collected by means of a drag scraper and elevated to a storage hopper from which it is conveyed to rail wagons via a pug mill mixer in which the cinder is dampened to prevent dust nuisance.

Of the three roasters two have been completed and are in operation. These are both employed on the main sulphuric acid plant. The third will produce a gas in similar manner to that already described and this will be mixed after cleaning and drying with hot gas from the sulphur burner on the sulphur plant in the proportion of approximately two parts of hot gas to one part of cold gas, and then fed to the hot gas converter.

The entire plant covers an area of approximately three acres. The main building is constructed of reinforced concrete columns and beams with 9-in, thick brickwork. The building is divided into two parts with a 9-in, thick partition separating the drying and grinding sections from the flash roasting section. The flash roasting section contains a transformer house, pump house, instrument house, and compressor house-each virtually independent and having its own roof.

Dust extraction from the SO₂ gas is by means of electro-static precipitators and washing. Two precipitators are included in the gas stream, one before and one after a wash tower. In the dust precipitator the voltage is built up to 100,000 and rectified by means of synchronously-driven mechanical rectifiers. In the mist precipitator straight-forward rectification, also operating at a voltage of 100,000, is used. It is expected that the consumption of sulphur at Grimsby will be reduced to approximately 60 per cent of what it was formerly, the acid plant capacity in the meanwhile having been increased by some 125 per cent. At the present moment some acid is being sold but eventually it will all be used by British Titan Products either at Grimsby or at its other works at Billingham.

Cosmetic Chemists Dinner

THE annual dinner and social evening of the Society of Cosmetic Chemists of Great Britain will be held at the St. Ermin's Hotel, Caxton Street, Westminster, London, S.W.1, on Thursday, 22 January, 1953, at 7 for 7.30 p.m. (Dress optional).

Tickets will be 18s. 6d. each, which will include gratuities but exclude wines. Applications should be made to the hon, treasurer. Mr. E. Polan. 228 Worple Road, Wimbledon, London, S.W.20. Members are invited to bring guests with them and ladies will be welcome. Although it is believed that the accommodation will be ample for our needs, based on previous years, it is suggested that members desiring to attend should contact the hon, treasurer as early as possible. Early application will assist the committee in making full arrangements.

Members who wish to stay in London overnight may obtain accommodation at St. Ermin's Hotel. If they desire to do so, they are advised to contact the managing director of the hotel, Mr. A. Gilles, as soon as possible.

Hopeful Chemical Outlook in Germany

Petroleum Processing Capacity Meets Requirements

PERMAN chemical industry ended 1952 Gon a rather more hopeful note than the preceding year. At the beginning of the past year stocks of chemicals in consumers' hands were so plentiful that the recession of business in German consumer goods industries immediately led to a sharp contraction of the demand for chemicals. Production in the first quarter of 1952 was therefore lower than in the fourth quarter of 1951 in the case of all chemical products except fertilisers which were favoured by seasonal factors. In the second quarter of the past year production fell off further but in June a remarkable recovery occurred in chemical manufactures which by July spread to most basic chemicals. Holiday influences however delayed a further improvement, and it was not until autumn that the lower production levels of the first half of the year were finally overcome.

Considerable progress has been made during the past year in the rehabilitation and modernisation of plant and equipment. and the productive capacity in most sectors of the German chemical industry is now larger than at any time since the war. That chemical production fared worse last year than other German industries is partly due to the disappointing course of exports, especially of dyes, paints and pharmaceutical products. German chemical manufacturers believe that greater efforts will be needed in future to maintain and increase sales and anticipate further wide fluctuations in demand even though the basic trend should be upward, because of import restrictions in foreign countries and the disinclination of home consumers to hold larger stocks than absolutely necessary.

Production Targets Set

In Eastern Germany the production targets have now been set for 1953, the third year of the current Five Year Plan. The East German chemical industry is reported to have slightly exceeded the overall 1952 targets, but the plan figures were not reached for a number of chemical items. The electro-chemical industry has had to supply electric power to the public grid in order to alleviate the general shortage of electricity.

with the obvious result of a falling-off in its own production. Production in 1953 is to be raised for many chemicals, including particular such basic products as in sulphuric acid. alkalis and nitrogenous and phosphatic fertilisers. Output of the latter is to be raised by twothirds but will still be below requirements. Efforts are being made to use plastics on a larger scale as substitutes for non-ferrous metals, and the chemical fibre production continues to receive priority.

Raw Material Throughput

Raw material throughput of the West German mineral oil refining and hydrogenation industry is to be raised by 35 per cent to 7,300,000 metric tons in 1953 under a programme drawn up by the trade association concerned. The output will be large and variegated enough to meet almost the whole of the domestic consumption. With German crude oil production expected to exceed 2,000,000 tons and less than 1,000,000 tons likely to be imported from Venezuela and Mexico, the bulk of the German demand for crudes will have to be met by Middle Eastern sources.

Hydrogenation plants play an important part in converting the crude petroleum into the fractions needed by German consumers. A fourth hydrogenation plant, at Welheim, is likely to join those at Gelsenkirchen, Wesseling and Scholven this year. With a modern catalytic cracker in operation since early October, West Germany is approaching a crude oil processing capacity equal to any quantitative or qualitative demands likely to be made in the foreseeable future.

Under the existing price and supply conditions it is unlikely that the hydrogenation plants will revert to coal as a raw material. Crudes and topping residues are the most economical raw materials at present, and a combination of cracking and hydrogenation is claimed to be most suitable for providing Germany economically with the oil products she needs in the tonnages required.

Construction of plant for manufacturing petroleum chemicals, on the other hand, is making only slow progress. Chemische Werke Huels which resumed the production of buna rubber in 1951 aims at an output of 20,000-25,000 tons and is still using large quantities of coal in addition to natural gas and residual gas from hydrogenation plants. This target which would be four times the maximum production reached so far cannot however be attained on the present raw material basis and would necessitate investments estimated at more than £4,000,000.

Such a plant, it is claimed, would be able to sell synthetic rubber as cheaply as the U.S. producers; most of the finance would have to be provided by the Federal authorities and rubber consumers. Lack of finance and the heavy duties on mineral oils have hitherto prevented more rapid development of the petroleum chemicals industry in Germany.

Nitrogen Output

Period of Transition for the U.K.

WORLD production of fixed nitrogen rose by about 10 per cent to 5,500,000 tons during the season 1951-52 which ended on 30 June last. This increase was due mainly to the coming into operation of new plants. The demand for industrial forms increased by $13\frac{1}{2}$ per cent. But since about 85 per cent of nitrogen output is used for fertiliser, and as the rise in agricultural consumption was only $7\frac{1}{2}$ per cent, working stocks at the end of the year showed some increase.

These figures are taken from the 32nd annual report of the British Sulphate of Ammonia Federation Ltd.

In the United Kingdom the 1951-52 fertiliser year was a period of transition in which political events affected agricultural production.

The steadily rising curve of demand from 1947 to 1950 had resulted from the Government's agricultural expansion policy. But by July, 1951, the policy of subsidy withdrawal from fertiliser prices had just been completed. As a result stocks held by merchants and farmers were high.

It was clear by the end of 1951 that high prices of fertilisers were adversely affecting sales. In particular sales of phosphates dropped seriously because their prices had risen most. Subsequent introduction of a phosphate fertiliser subsidy, and a new programme of food production covering at least four years ahead came too late to expand fertiliser sales last season.

In the case of sulphate of ammonia sales were normal until January of last year. But a further price increase on 1 February owing to transport and other charges came as a shock to buyers just at the beginning of the spring consuming season. Soon afterwards, owing to the break in jute prices and a falling in shipping freights for phosphate rock, there were rumours of price reduction in fertilisers.

Price reductions announced on 1 April did little to improve demand. Total deliveries of sulphate of ammonia last season for home agricultural use were down by over 22 per cent.

Exports of sulphate of ammonia from the U.K. during the period under review. exceeded 348,000 tons—the highest figure since 1931/32—and showed an increase of 45 per cent on 1950/51. The allocation to overseas markets was controlled by the Government Departments concerned. When it became apparent in the early spring that ample provision had beeen made for the home market, allocations to Commonwealth markets were increased and towards the end of the season large shipments were made to the Far East.

Important Investigations

The Research Department had done considerable work on the determination of impurities in saturator liquors and tenta, we methods of analysis had been circulated to members. These analytical methods are of increasing importance because the reduction in imports of sulphur has made the production of sulphate of ammonia more dependent on acid derived from pyrites and spent oxide.

Experiments were started on the protection of metals from corrosion in acid liquors by the application of electrochemical methods. Although many teething troubles had been encountered the results so far obtained were encouraging.

Due to the shortage of special alloys such as molybdenum-bearing austenitic steel, the use of resin cements and lacquer for protective coatings had been extended. A new type of bonding primer had been developed which had given much better adhesion of the lacquer to the metal.

The DSIR in 1952

Work on Conservation of Scarce Materials Continued

THROUGHOUT 1952, the Department of Scientific and Industrial Research continued to be actively concerned with the conservation of scarce materials. A survey of the sulphur and sulphuric acid position was published for the Department by HMSO. Besides reviewing available sources of sulphur, it gives details of many methods of conserving sulphuric acid, mainly in the fertiliser industry and in iron and steel pickling. Economy of sulphuric acid in the manufacture of phosphate fertilisers is still being studied by a working party set up by the Committee for Scientific and Technical Matters under OEEC. Mr. A. L. Thorogood, of the DSIR, is Technical Secretary of this working party, which met twice during the year. A further meeting was scheduled to take place in Paris this January to consider the final report. A full account of the investigations into the production of fertilisers by the use of nitric and sulphuric acid mixtures was given to a meeting of the Fertiliser Manufacturers' Association.

Sulphur Studies Room

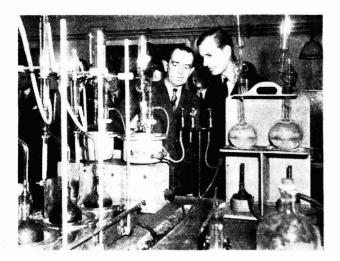
At the Chemical Research Laboratory a large staff has been provided for investigations into the microbiological production of Experiments have shown that sulphur. elemental sulphur can be produced by the combined action of pure cultures of sulphatereducing bacteria and the photo-synthetic green or purple sulphide-oxidising bacteria in a common medium. They provide strong evidence that some of the sulphur in the Cyrenaican lakes was produced from sulphate by a similar combined action. A high rate of reduction of sulphate to sulphide is one of the essentials for economic success in microbiological production. One method of obtaining a high rate is to use a continuous process in which the bacterial cells are kept in their logarithmic phase of growth. Through the courtesy of the Ministry of Supply, a team from the CRL is now employing a continuous process developed by the Experimental Station at Porton.

At the Fuel Research Station the Fulham-Simon-Carves ammonia process for the recovery of sulphur dioxide from flue gases, which was first tested on a small pilot plant treating 1,000 cu. ft. of flue gas per hour, is now being studied in a larger plant designed to treat 25,000 cu. ft. per hour. The results obtained from a series of experiments in the new plant were encouraging, but seemed to indicate that the packing depth was insufficient to allow the requisite time of contact between the flue gas and the solution. In order to increase the efficiency, an additional section of 3 ft. is being added to the tower and the depth of packing will be increased from 2 ft. 6 in. to 4 ft.

The Fuel Research Station has also been engaged on large-scale experiments directed towards further examination of the possibilities of producing metallurgical coke by carbonising blends of high-quality coking coal with other more plentiful coals. This work has shown that as much as 30 or 40 per cent of weakly-coking coal may be incorporated in the blends carbonised without seriously affecting the quality of the coke. To increase the use of fine low-grade



The Duke of Edinburgh's visit to the Chemical Research Laboratory on 22 April, 1952



The Duke of Edinburgh inspecting the analytical laboratory of the Fuel Research Station on 20 March, 1952

fuels and thus release higher-grade fuels for other purposes, experiments on the gasification of small-sized non-coking coal by the fluidised-solids technique are also in progress. A pilot plant to produce 30 to 50 gallons of oil a day by the Fischer-Tropsch synthesis, by the fluidised catalyst and by the liquid-phase techniques, is now almost completed.

One of the most important events at the Chemical Research Station was the completion of the new Radiochemical Building. which is now in occupation. In their analytical work the Radiochemical Group have sought to extend the scope of inorganic chromatography to elements other than uranium and thorium. Physical methods of analysis have also been further improved. The measurement of a large number of radioactive tracers has been carried out in connection with investigations in analytical and other work. Research into the use of ultrasonics in chemical work has been started, the aim being to explore the behaviour of ultrasonics on the solution of metal oxides and salts in acid or alkaline media and the effect of these vibrations on precipitation from solution. The Laboratory is now applying ion-exchange technique to the separation from solution of metals such as gold, nickel, iron and cobalt. An outstanding discovery in the field of ionexchange is the preparation of improved semi-permeable membranes for use in the determination of molecular weights by osmometry. These membranes, made from polyvinyl alcohol, give rapid and reliable measurements of the number-average molecular weights of polymers of relatively low degrees of polymerisation.

As a result of collaboration between DSIR and commercial laboratories, there is no longer any need to import supplies of pure germanium for electrical purposes. Improved methods of purification and analysis have been found which makes it possible to produce from British flue dusts germanium which can be used for making efficient rectifiers and transistors. The Inorganic Group at CRL have developed a radioactive tracer method for following the elimination of arsenic, the most important Radioactive arsenic was introimpurity. duced into the germanium and the efficiency of its removal by various methods checked by Geiger counter. By distillation of germanium tetrachloride in the presence of hydrogen chloride and chlorine the arsenic content of the resulting germanium dioxide was reduced to 1 part in 1 thousand million.

At the Pest Infestation Laboratory the provision of two cool air-conditioned rooms. each equipped with a fumigation chamber, has made possible a great expansion in the work on the toxicity of fumigants to insects at relatively low temperatures. Experiments with certain chlorinated hydrocarbons have shown that when insects are fumigated at 10° or 15° C. and subsequently kept at that temperature, the percentage mortality increases over a long period and the dose necessary for a final complete kill is correspondingly decreased.

A valuable addition to the equipment of

the Forest Products Research Laboratory is a tropical testing house with dry and wet rooms, in which tropical temperature and humidity cycles can be maintained for test purposes. In addition, there is a workroom in which any constant air temperature and humidity can be maintained and the effect of the sun's heat can be obtained by infrared lamps. In addition to its use for the experimental work of the Laboratory, the testing house is being used for a limited number of tropical storage tests for industry.

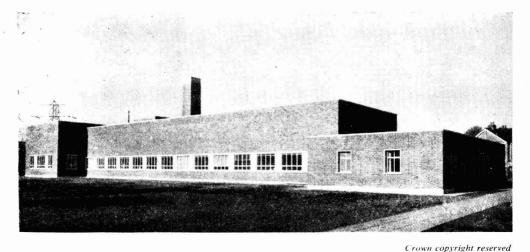
A special laboratory has been built by the Water Pollution Research Organisation for studying the effect of radio-isotopes on processes used for the treatment of sewage. Two series of experiments have been made, one at Coventry and one at Birmingham, on treatment of sewage by alternating double filtration. At Coventry, the effect of omitting a stage of sedimentation, between the primary and secondary filters, was examined. The results agreed with those previously obtained at Birmingham with larger plant. In the other series of experiments some of the filters used are fitted with electrically driven rotary distributors so that the speed of rotation can be altered. The efficiency of the process has increased as the speed of rotation has been reduced. The Laboratory has also shown that vigorous growth of some of the fungi found in percolating filters depends on the supply of a number of trace metals and of the Vitamin B complex. The rate of growth is also greatly dependent on the supply of oxygen to the fungus.

Further progress has been made towards

tringing the establishment of the Mechanical Engineering Research Organisation at East Kilbride into being, though restrictions on the Government building programme and on staff recruitment have drastically slowed down the rate of advance. Unfortunately one of the projects which has to be deferred on account of the severe Government restrictions on building is the erection of the heat transfer building, for which a very urgent need exists.

A notable event was the publication by the British Leather Manufacturers' Association of a critical survey of this association's work for its industry. The strong panel which made the survey produced a clear, readable document in which the achievements and shortcomings of the industry were frankly stated and a number of recommendations were made. This survey was instituted by DSIR as an experiment which, it was hoped, might prove beneficial to the councils of all research associations.

Good progress is being made in making the results of research more widely known, and it is reported that better use is being made of technical information. Talks have been given to chambers of commerce, regional boards, advisory committees and other regional bodies in all areas except Manchester, which is already well covered by the Manchester Joint Research Council. Public libraries and technical colleges have also been addressed, the aim being to give them an insight into the work of the Department and the importance of technical information. Arising from these activities, attention is



The new Radiochemical Building at the Chemical Research Station

being accorded in some centre to the pooling of technical literature through the aegis of public libraries or other suitable establishments.

During the year the DSIR Headquarters Technical Information Service was merged with the Technical Information and Documents Unit, which retains the name TIDU. This unit maintains a technical inquiry service and is the British centre for an international questions and answers scheme, which is organised to provide information about industrial techniques from the U.S.A., Canada, France, Germany, Ireland, Sweden and the U.K.

In collaboration with the Ministry of Materials, under whose sponsorship is the National Industrial Salvage and Recovery Advisory Council, TIDU has been able to help firms to find an outlet for their waste materials.

Industrial Drying

Among the most important publications which appeared during the year was a 'Bibliography of Industrial Drying.' which covers the period 1924-50 and has eight hundred pages carrying some 4,500 entries. The first two sections deal with principles and equipment and inc'ude a limited number of references on heat transfer and drying of gases. A further three sections cover the various drying methods that can be used in agriculture, in the food processing industry. and in the drying of industrial materials.

A welcome trend is the increasingly close liaison which is being established between DSIR research stations and the Colonies and Dominions. The Building Research and Road Research Stations both have Colonial Liaison Officers, and their example has now been followed by the Pest Infestation Laboratory. As Colonial Liaison Officer to the Laboratory, Mr. D. W. Hall made his first tour—to East Africa—early in 1952. Officials of the DSIR also attended a number of important congresses overseas and kept in close touch with research developments in other countries.

Of far-reaching importance to Commonwealth research was the third British Commonwealth Scientific Conference, which took place in Australia under the chairmanship of Dr. Clunies Ross, chairman of the Australian Commonwealth Scientific and Industrial Research Organisation. The delegation from the United Kingdom was headed by Sir Ben Lockspeiser, Secretary of DSIR, and it included Sir William Slater, Secretary of the Agricultural Research Council; Dr. F. H. K. Green, representing the Medical Research Council; Dr. Alexander King, head of the Intelligence Division of DSIR; and Dr. G. A. C. Herklots, of the Colonal Office. All self-governing countries within the Commonwealth were represented.

The Conference reviewed the existing facilities and machinery for the dissemination of information and for personal contacts between scientists. It then examined a number of subjects, which, after previous consultation between the various countries. were suggested as possible topics for collaboration. Almost all the discussions were concerned more with administration than with individual research problems, the primary objective being to determine what subjects for research were likely to be important during the next five years. The subjects selected include industrial microbiology, the utilisation of seaweed, the utilisation and beneficiation of low-grade ores and wastes, soil mechanics, and the utilisation of solar energy by physical or biological means.

Consideration was also given to joint action by Commonwealth countries in developing backward areas. Particularly serious in Far Eastern countries, populated by races which are backward according to Western ideas, is the shortage of scientists. One suggestion put forward at the Conference was that scientific organisations in Britain, such as the DSIR and the Agricultural Research Council, might be encouraged to second a small percentage of their staff to these scientist-hungry countries. Unfortunately the United Kingdom itself is now very short of scientists, due to the suspension of recruitment on grounds of economy.

Caustic Soda for Canada

Work will begin shortly at Marathon. Ontario, on a new chemical plant to produce caustic soda and sodium sulphite simultaneously. Operated by the Marathon Paper Mills of Canada, this \$3,000,000 plant will be the first of its kind in the Western hemisphere. The plant will produce chemicals needed for the manufacture of highgrade bleached sulphite pulp and will provide chlorine, caustic soda and hydrochloric acid, all of which are normally in short supply in the Dominion.

Important Developments in Spectrophotometry

by G. S. EGERTON, M.Sc., Ph.D., F.T.I.

DNE of the most characteristic properties of organic and inorganic compounds is their ability to absorb selected radiations of different wavelengths. This absorption is of considerable practical importance in the ultra-violet, visible and infra-red regions. Colour is, of course, the result of selective absorption in the visible region. Since the experimental techniques involved in the quantitative measurement of absorption are similar for ultra-violet and visible radiations, but are different for those in the infra-red. it is usual to discuss ultra-violet and visible spectrophotometry as one subject, and to treat infra-red spectroscopy separately. The basic principles involved are however, the same, and the instrumental requirements are a source of radiation, a dispersing system and a highly sensitive detecting system. Many substances are highly transparent in the ultra-violet and visible regions, but all substances absorb at some wavelength or other in the infra-red. Consequently, considerable problems arise in the selection of suitable solvents, windows and prism materials for use in infra-red spectroscopy.

ULTRA-VIOLET & VISIBLE SPECTRO-PHOTOMETRY

Instrumentation.—The development of photoelectric ultra-violet and visible spectrophotometers led to a considerable increase in technical and scientific interest in the applications of absorption spectrophotometry, and today many important commercial instruments of this type are available. In the United States considerable use has been made of the General Electric recording spectrophotometer (range 4,000-7,000 Å), the Beckman quartz spectrophotometer (nonrecording; range 2,000-10,000 Å) and the Cary recording quartz spectrophotometer (range 2,000-8,000 Å).

The automatic instruments are much more rapid than non-recording instruments in the determination of absorption (or reflection) spectra, but have a much higher initial cost. The main photoelectric instruments used in Great Britain have been the Unicam and Hilger Uvispek quartz spectrophotometers, which have a range and performance similar to the Beckman instrument. Details have recently been announced by Unicam Instruments (Cambridge), Ltd. of a new spectrophotometer suitable for absorption measurements in the region from 3,600-10,000 Å. Since this instrument incorporates a glass prism it is much cheaper than the more accurate quartz spectrophotometer, and should have a wide field of application in qualitative and quantitative chemical analysis.

Details Published

Details of two spectrophotometers for use in the far ultra-violet have been published by Astoin (J. Phys. Radium, 12, 695 (1951)). and by Piore, Harvey, Gyorgy and Kingston (Review Sci. Instr., 23, 8 (1952)). Krumholz (Review Sci. Instr. 22, 362 (1951)) has described a medium resolution replica grating spectrophotometer capable of covering the spectral region from 3,600 to 9,000 Å, and Lange and Stenius (Review Sci. Instr. 22, 865 (1951)) a spectrophotometer which is equipped with photomultiplier tubes and intended for the determination of light absorption in heterogeneous microscopic objects.

The development of modern photoelectric spectrophotometers seems likely to continue in the direction of automatic and faster recording instruments. In this respect two papers by Kaye and Devaney (J. Opt. Soc. Amer., 41, 658 (1951)); ibid., 42, 567 (1952)) are of considerable interest. These workers have described a method by which the Beckman quartz spectrophotometer can be modified to record automatically absorption spectra from 2,100 Å to 2.7 microns. The red-sensitive phototube of the original instrument is replaced with a lead sulphide cell, and the ultra-violet sensitive phototube with a photomultiplier tube. A rotating slotted drum is used to interrupt the light beam and an electronic recorder is provided. It is possible to use the null meter circuit of the spectrophotometer if necessary, and also all the standard Beckman accessories. Details of the actual performance of the modified instrument are given. The authors consider that in view of the ruggedness, resolving

power, and the relatively low cost of the modified instrument, it is likely to open a new field for analysis. The production of a still more rapid recording instrument has recently been announced by the American Optical Company. This rapid scanning spectrophotometer traces 60 separate curves per second on the face of a cathode ray tube over the visible spectrum from 4,000-7,000 Å. The curves can be photographed for record purposes.

Techniques of Calibration

Normand and Kay (J. Sci. Instr., 29, 33 (1952)) have discussed the techniques of calibration and adjustment of spectrophotometers, together with some of the general principles of their design, with particular reference to the use of the Dobson spectrophotometer for measurements in the near This instrument is primarily ultra-violet. intended to investigate atmospheric ozone, but the methods described are of general application. The degree of accuracy of analytical results carried out with the Beckman spectrophotometer, and the various sources of variability, have been discussed by Caster (Anal. Chem., 23, 1229 (1951)). A paper by Haupt (J. Opt. Soc. Amer., 42, 441 (1952)) will be found useful for testing the reliability of the photometric scale of spectrophotometers in the ultra-violet region. Measurements were made with a standard solution of potassium chromate in caustic potash, and results are given for the absorption at different wavelengths under specified conditions.

The practice of varying the cell length rather than the concentration of the compound under study in the determination of ultra-violet absorption spectra has the advantages of greater speed and the necessity for less manipulation. Hirt and King (Anal. Chem., 24, 1545 (1952)) have described how the choice of cell lengths available to the ultra-violet spectroscopist can be extended below 5 mm. to a few hundredths of a millimetre by the use of Hilger micrometer Baly cells in adapters built for their use with the Beckman and Cary instruments. Hammond and Nimeroff (J. Opt. Soc., Amer., 42, 367 (1952)) have described the use of the Beckman instrument in measurements of spectral reflection, and have shown how to minimise any errors that may arise in the measurement.

Applications.—A very useful review of

the application of spectrophotometry to the solution of problems in the dyestuff and textile industries has been made by Stearns (Amer. Dye. Rep., 40, 563 (1951)). This paper also includes a very extensive bibliography which should be of much assistance to workers in these fields. The more general aspects of the principles and applications of chemical spectroscopy, including also infra-red spectroscopy, form the basis of an important article by Brode (Proc. Amer. Soc. Testing Materials, 50, 513 (1950)). which deserves extensive study. Other contributions on the subject of absorption spectrophotometry and its applications have been provided by Hirt (J. Chem. Education, 29, 301 (1952)) and Timma (Ohio J. Sci. 52, 117, (1952)).

The ultra-violet and visible spectra of ten purified thioindigoid dyes have been measured in benzene and chloroform solution by Brode and Wyman (J. Res. Nat. Bur. Stand, 47, 170 (1951); J. Amer. Chem. Soc., 73, 1487 (1951)). From observations of the effect of light on the absorption spectra of these dyes it appears that an equilibrium exists between the cis- and trans-forms of the dye. These investigations have been extended to include aromatic azo compounds by Brode, Gould and Wyman (J. Amer. Chem. Soc., 74, 4641, (1952)).

Observation Results

Observations with these derivatives of azobenzene have shown that many of the cisisomers have only a short life, and in order to measure their absorption spectra satisfactorily a rotating shutter and a sample illuminator were specially constructed for use with the Cary recording spectrophotometer. Details of this device are given in a paper by Gould and Brode (J. Opt. Soc. Amer. 42, 380 (1952)). By the use of this device the dye solutions could be exposed to a strong light source during the dark periods of the chopping shutter of the instrument In this way solutions which show a very rapid photochange can be studied.

An interesting method for the identification of azo dyes by spectrophotometric identification of the amines or diamines produced from them on reduction has been described by Jones and Harrow (J. Assoc. Offic. Agric. Chem., 34, 831 (1951)). The quantitative analysis of mixtures of eugenol and isoeugenol can be carried out with the aid of photometric measurements in the ultra-violet



Unicam SP.500 quartz spectrophotometer

region (Vespe and Boltz (Anal. Chem., 24, 644 (1952)). Determination of the amount of unsaturated fatty acids in oils can be made similarly (Martens, Farbe u. Lack, 58, 51 (1952)). Ultra-violet absorption spectra have also been found useful for investigations of isolated double bonds in triterpenes (Halsall, Chemistry and Industry, 867 (1951)), for the study of the complexes formed between benzene and halogens (Ham, Platt and McConnell, J. Chem. Phys. 19, 1301 (1951)), and for the determination of steric hindrance in stilbene derivatives (Beale and Roe. J. Amer. Chem. Soc., 74, 2302 (1952)).

Collections of Data.—During the last year some useful collections of data on ultraviolet and visible absorption spectra have been published. One of the most useful of these publications (Ultra-violet Spectra of Aromatic Compounds, by Friedel and Orchin -published by John Wiley & Sons, Inc.), which was reviewed in this journal (THE CHEMICAL AGE, 66, 831) contains the spectra for a very large number of compounds. Another very comprehensive collection of ultra-violet and visible spectra has been provided by Schroeder, Wilcox, Trueblood and Dekker (Anal. Chem., 23, 1740 (1951)). These workers have measured the spectra in ethyl alcohol solution of some 135 nitrogen-containing compounds, which were of interest in relation to smokeless powders. The ultra-violet absorption spectra of a number of benzene carboxvlic acids (Berman, Ruof and Howard, Anal. Chem., 23, 1882 (1951)), arylphosphonic and diarylphosphinic acids (Jaffé and Freedman, J. Amer. Chem. Soc., 74. 1069 (1952)), and of phenyl sulphides, sulphoxides and sulphones (Szmant and McIntosh, J. Amer. Chem., Soc., 73, 4356 (1951)) have been recorded. Some interesting measurements by Phibbs and Giguère (Can J. Chem., 29, 490 (1951)) of the near

ultra-violet absorption spectra of hydrogen peroxide and its deuterium analogue have shown that replacement of hydrogen by deuterium shifts the absorption continuum towards shorter wavelengths. In the vacuum ultra-violet Pickett and co-workers (J. Amer. Chem. Soc., 73, 4862 and 4865 (1951)) have studied the spectra of a number of cyclic compounds, including benezene, cyclohexane and 1,4-dioxan.

INFRA-RED SPECTROSCOPY

Instrumentation and Technique.—Prior to 1939 the study of infra-red spectra was largely confined to a small number of academic research workers, who were primarily concerned with measuring the spectra of a variety of substances and of investigating the fundamental principles involved. Under the impetus of the urgent requirements of the war years the important applications of infra-red spectroscopy to the solution of industrial problems gradually began to be realised. This was particularly so in the United States in the petroleum and synthetic rubber industries. As a result various manufacturers of scientific instruments began to supply infra-red spectrometers to suit particular needs. The earlier instruments were of the automatically recording single beam type, but in the last few years the considerable advantages attached to double beam instruments recording directly in per cent transmission have been widely recog-Various attempts have also been nised. made to secure the advantages of a double beam instrument by modification of a single beam spectrometer. Modern double beam instruments are capable of recording the spectrum of a substance in the region from 2 to 15 microns in times of the order of 10 to 15 minutes. Still more rapid measurements can be made if the spectrum is recorded on a cathode-ray tube, and subsequently photographed.

Two papers by Van Zandt Williams (Review Sci. Instr., 19, 135 (1948)); Applied Spectroscopy (6, No. 1, 14 (1951)) will be found to provide very comprehensive accounts of the instruments and techniques used in infra-red spectroscopy. Another important review (Lord, McDonald and Miller, J. Opt. Soc. Amer., 42, 149 (1952)) of useful devices and techniques that can be applied in infra-red spectroscopy includes descriptions of techniques for the preparation and use of absorption cells, some useful modifications of the Perkin-Elmer single beam infra-red spectrometer and of the technique involved in spectroscopy in the far infra-red. Sheppard (Analyst, 77. 732 (1952)) has also discussed some recent advances in the design of infra-red spectrometers that seem likely to be incorporated in future new instruments designed for analytical work.

Conversion to Double Beam

In the instrumental field, new developments include further attempts to convert single beam spectrometers into double beam instruments, improvements of existing types, and new instruments with cathode-ray presentation. Martin (Ind. Chemist, 28, 243 (1952)) has described the optical layout of a recent commercial spectrometer, and has discussed the principles involved in its use, and how it is possible to convert this instrument from single to double beam operation. Cannon (J. Sci. Instr., 29, 50 (1952)) claims that many of the advantages of a double beam infra-red spectrometer can be realised by continuously varying the slit width so as to obtain a constant energy background. Except for the interference due to atmospheric absorption, which can be considerably reduced by drying the atmosphere, the record so obtained is said to give a per cent absorption curve adequate for most purposes without measuring and replotting manually. Cannon describes a simple exponential drive mechanism which can be used with any prism or grating to control the slit programme required to produce an approximately constant energy background. The same problem has been tackled in a different way by Carrington and Reynolds (J. Sci. Instr., 29, 197 (1952)). The use of single beam instruments necessitates recording two separate consecutive traces, one of the blank

and the other of the sample. From these records the per cent transmission curve of the sample can only be calculated and plotted by an arduous and time-consuming process. These authors have described an apparatus by which the results recorded by a single beam instrument can be converted into per cent transmission with considerable economy in time and labour.

Three recent papers by Walsh (J. Opt. Soc. Amer., 42, 94 and 96 (1952), and with Ham and Willis, ibid., 42, 496 (1952)) seem likely to have an important bearing on the design future monochromators for infra-red of spectrometers. Walsh has described a simple method for converting a conventional monochromator to a double or multiple monochromator with much higher resolving power and with almost complete elimination of scattered radiation, and has discussed its application in the improvement of a small prism infra-red spectrometer. The new Perkin-Elmer Model 112 infra-red spectrometer (Review Sci. Instr. 23, 141 (1952)) incorporates a double pass monochromator of a similar type, together with the source unit and recording system of the older Model 12C (single beam) instrument.

Some other new instruments include a spectrometer for measurements in the wavelength range from 1 to 1.9 microns (Tsuboi, *J. Chem. Soc., Japan*, **72**, 616 and 663 (1951)), a spectrograph for use in the spectral region from 40 to 150 microns (Oetjen, Haynie, Ward, Hansler, Schauwecker and Bell, *J. Opt. Soc. Amer*, **42**, 559 (1952)), and a far infrared grating spectrometer for use at wavelengths between 100 and 700 microns (McCubbin, Jr., and Sinton, *J. Opt. Soc. Amer.*, **42**, 113 (1952)).

Recording Spectrometer

A fast scanning infra-red recording spectrometer in which the optics are basically those of the Perkin-Elmer Model 12C spectrometer, has been described by Wheatley, Vincent, Rotenberg and Cowan (J. Opt. Soc. Amer., 41, 665 (1951)). The resolving power is low by conventional standards, but is satisfactory for broad bands such as those exhibited by gases under high pressure. The spectra are displayed on a cathode-ray oscillograph and are recorded photographically. This spectrometer was designed for the study of solid-propellant flames, but is stated to be also useful for the study of fast, but not explosive, gas reactions. Another infra-red prism spectrometer with cathode-ray presentation suitable for use in an industrial laboratory has been described by Powell (Applied Spectroscopy, 6, No. 2, 3 (1952)). This instrument is capable of scanning a region of 3 microns in 12 seconds anywhere within the range from 1 to 15 microns. It has been used for the continuous examination of liquid streams in connection with the testing of various catalysts for desulphurisation reactions in the presence of hydrogen, and for investigations on purification by distillation. The production of a commercial instrument with cathode-ray presentation has been announced by Hilger and Watts, Ltd. (J. Sci. Instr., 29, 29 (1952)). This instrument is a development of the type first described by Daly and Sutherland (Proc. Phys. Soc., 59, 97 (1947)) and King, Temple and Thompson (Nature, 158, 196 (1946)). An attempt has been made to produce a system with a performance approaching that of the slower scanning pen recording infrared spectrometer but with a much more rapid rate of scan. The instrument is suggested for the study of transitory phenomena, such as the rapid appearance or disappearance of absorption bands, and can be used to observe the changes in the absorption bands of a liquid flowing through a pipe.

Measurement of Reflection

Details of two instruments suitable for the measurement of the reflection of infra-red radiation from surfaces have been published by Oldham (J. Opt. Soc. Amer., 41, 673 (1951)) and by Derksen and Monahan (ibid., 42, 263 (1952)). A zirconium concentrated arc source of infra-red radiation suitable for use in spectrometers has been described by Hall and Nester (J. Opt. Soc. Amer., 42, 257 (1952)).Goulden (J. Sci. Instr., 29, 215 (1952)) has described a simple experimental arrangement by which a plane replica grating can be used in place of the more costly lithium fluoride prism in order to obtain high dispersion with an infra-red spectrometer in the 3 micron region. The calibration of infra-red spectrometers has been discussed by several workers (Tilton and Plyler, J. Res. Nat. Bur. Stand., 47, 25 (1951)), Ross and Little (J. Opt. Soc. Amer., 41, 1006 (1951)); Marrison (J. Sci. Instr., 29, 233 (1952)). Martin (Trans. Faraday Soc., 47, 1182 (1951)) has discussed in detail the more important errors involved in optical measurements, particularly in the infra-red region. These are considered to be (a) uncertainty of the measurements of radiation, (b) stray light, (c) error due to mismatch of absorption cells. and (d) inaccuracy due to non-linearity of the measuring system. Some useful filters for the infra-red region have been described by Plyler and Ball (J. Opt. Soc. Amer., 42, 266 (1952)). These workers have shown that deposited films of tellurium, bismuth, antimony and of magnesium oxide are opaque in the visible region and have short-wave cut-offs ranging from 1 to 3 microns.

Carbon disulphide and carbon tetrachloride are suitable transparent solvents for use in the measurement of the infra-red spectra of solid substances, but do not always dissolve substances of which spectra are required. The addition of 0.5 to 2.5 per cent triethylamine to such solvents is useful in the measurements of some solid organic acids according to Ard and Fontaine (*Anal. Chem.*, 23, 133 (1951)). A simple method for the measurement of the infra-red spectra of amino-acids and other polar compounds,



Unicam SP.600 spectrophotometer for the visible range

which are insoluble in a non-polar solvent transparent in the infra-red, has been described by Schiedt and Reinwein (Z. Naturforsch., 7b, 270 (1952)). Another method (Sands and Turner, Anal. Chem., 24, 791 (1952)) for examining the infra-red absorpton spectra of solids is claimed to be faster, more convenient and more accurate than present methods, and to possess a wide range of applicability. It consists in laminating or impregnating the substance under study between or into sheets of other materials having transparent regions in the infra-red, e.g., mica, silver chloride and polyethylene The technique is illustrated by a description of the determination of the amount of acrylonitrile in butadiene-acrylonitrile copolymers.

Applications.—The infra-red spectrum of a compound is unique for each compound and many absorption bands can be definitely attributed to specific chemical groups. For this reason measurements of infra-red spectra have been found to be extremely useful for the identification of unknown materials by spectral matching with known substances, for investigations of chemical structure and in qualitative and quantitative analysis. Martin (Ind. Chemist 28, 243 (1952) has provided a very clear illustration of how mixtures of ortho-, meta-, and para-cresol can be readily analysed by infra-red measurements using only a single drop of sample. Gauthier (Compt. Rend, 233, 617 (1951)) has described two interesting examples of the use of infrared spectra as an analytical tool in following the course of a chemical reaction. The first reaction, the hydrogenation of propiolic acid, was followed by measurements of the characteristic CH≡ absorption band of propiolic acid, the CH = band of acrylic acid, and the CH- band of propionic acid. The second reaction studied was the isomerisation of diethyl maleate and fumarate in the presence of iodine as a catalyst. Kuratani (Rept. Inst. Sci. Technol., Univ. Tokyo. 5, 25 (1951)) has studied the keto-enol equilibrium of ethyl acetoacetate in solution by measurements of the relative intensities of the infra-red absorption bands at 1650 cm.⁻¹ (enol form) and 1740 cm.⁻¹ (keto form). In non-polar solvents such as carbon disulphide, hexane, ether and benzene, it was shown that ethyl acetoacetate is more enolisable than in polar solvents such as methyl alcohol and pyridine. This optical method is considered to be superior to chemical methods for the study of keto-enol equilibrium.

General Evaluation

A general evaluation of the use of infrared spectra in quantitative analysis has appeared (Robinson, *Anal. Chem.*, **23**, 273 (1951)) and other workers (Ferguson and Levant, *Anal. Chem.*, **23**, 1510 (1951)) have discussed its application in the analysis of mixtures of bromochlorobenzenes. Some other analytical uses include the estimation of free phenol in phenol-formaldehyde resins (Smith, Rugg and Bowman, *Anal.* Chem., 24, 497 (1952)), and the determination of the amount of hydrocarbon oils and phenol present as contaminants in industrial effluent waters (Simard, Hasegawa, Bandaruk and Headington, *Anal. Chem.*, 23, 1384 (1951)).•

Measurements (Broomfield, J. Inst. Petroleum, **38**, 424 (1952)) of the infra-red spectra between 6 and 15 microns of various alkyl naphthalenes indicate that the similarities between the spectra of homologues is very marked in the series with longer chain substituents, but that the two types of substitution, α and β , can be readily distinguished by their infra-red spectra. The presence of the *cyclopropyl* group in an organic molecule is difficult to establish by chemical means, but it has been shown that characteristic infra-red bands can be used for this purpose (Wiberley and Bunce, Anal. Chem., **24**, 623 (1952)).

Exhibit Absorption Patterns

The problem of determining the type of substitution in aromatic compounds can also be greatly simplified by measurements of their infra-red spectra, since benzene derivatives exhibit absorption patterns in the region from 5 to 6 microns which are characteristic of the number and location of substituent groups in the benzene ring (Young, DuVall and Wright, Anal. Chem., 23. 709 (1951)). Tarte (Bull. Soc. Chim. Belges, 60, 227 and 240 (1951)) has measured the infra-red spectra of alkyl nitrites and has suggested that infra-red measurements can be used to distinguish between primary, secondary and tertiary nitrites.

Two interesting applications in the polymer field have been described. The isothermal crystallisation of a film of a vinylidine chloride copolymer has been studied by recording the optical density of the film at 750 cm.⁻¹ as a function of time (Burton, Cobbs Jr. and Haskell, J. Polymer Sci. 7, 569 (1951)). The chemical changes that result when films of polystyrene are exposed in air to ultraviolet radiation have been followed by measurements of the infra-red spectra of the degraded films. Achhammer, Reiney and Reinhart (J. Res. Nat. Bur. Stand., 47, 116 (1951)) were thus able to show that hydroxyl and carbonyl groups are formed as a result of irradiation.

Infra-red spectra throw important light on the chemical structure of molecules, and attention should be directed to an important review of the interpretation of the infrared spectra of acetylenic and olefinic hydrocarbons by Sheppard and Simpson (Quarterly Reviews, **6**, 1 (1952)) and to the correlation of rotation-vibration spectra and the structure of simple polyatomic molecules by Herzberg (*Nature*, **169**, 997 (1952)).

Collections of Data.-There is considerable information on the infra-red spectra of organic and inorganic compounds present in the literature, although data on any particular compound may not be readily found. In view of the great number of possible compounds in which research workers and others may be interested some simple system of classification seems eminently desirable. Martin (Ind. Chemist, 28, 243 (1952)) has suggested the use of a card index system to record the essential data of the infra-red spectra of the half million or so known organic compounds. It is not practicable to mention here all the data on infra-red spectra that has been recorded recently, and reference will only be made to results of more general interest.

Useful Correlation

McMurry and Thornton (Anal. Chem., 24, 318 (1952)) have provided in both tabular and chart form a very useful correlation of the infra-red spectra of paraffins, olefines and aromatic compounds with various structural groups. This work should improve the reliability and convenience of structural analyses of hydrocarbons by infrared spectra. Another most useful paper by Cannon and Sutherland (Spectrochim. Acta, 4, 373 (1951)) records the infra-red spectra of 104 aromatic compounds, and establishes correlations between the structures of the molecules examined and the main features of their spectra. Other important collections of new data include the spectra of a large number of pure inorganic compounds, principally salts of polyatomic ions (Miller and Wilkins, Anal. Chem., 24, 1253 (1952)), phosphorus compounds (Daasch and Smith, Anal, Chem. 23, 853 (1951)), substituted guanidines and related compounds (Lieber, Levering and Patterson, Anal. Chem., 23, 1594 (1951)), sulphur- and oxygen-containing compounds (Pozefsky and Coggeshall, Anal. Chem., 23, 1611 (1951)), compounds containing saturated 5-membered rings, such as tetrahydrofuran, tetrahydrothiophene and pyrrolidine (Tschamler and Voetter, Monats., 83, 302 (1952)), pyrophosphates (Bergman, Littauer and Pinchas, J. Chem. Soc., 847 (1952)), and ozonides (Briner, Susz and Dallwigk, *Helv. Chim. Acta*, **35**, 340, 345 and 353 (1952)). A useful paper by Bovey (*J. Opt. Soc. Amer.*, **41**, 836 (1951)) records the infra-red absorption and reflection spectra of thin solid layers of the four ammonium halides at various temperatures.

Inaugural Meeting

THE inaugural meeting of the newly formed Organic Finishing Group of the Institute of Metal Finishing will be held at the Charing Cross Hotel on Thursday, 19 March, 1953.

Programme for this first meeting includes lunch, inaugural meeting, and two technical papers followed by discussion, with a break for afternoon tea. At the meeting the committee which will be in charge of the group's activities for the following year will be elected. This committee is to consist of eight officers in addition to the president and honorary secretary of the Institute who will be *ex officio* members of the committee.

In order to extend the scope of the group's work nominations to this committee are invited from interested parties who need not, necessarily, be members of the Institute of Metal Finishing but will, of course, be expected to become members in the event of election. Each nominee must be nominated by two persons whose names, business address and status should be given on the nomination form. This form is obtainable from the head offices of the Institute, 32 Great Ormond Street, London, W.C.1, and must be returned not later than 1 March, 1953.

Anyone interested may attend the meeting, whether I.M.F. members or not, and further details of the authors and subjects of the technical papers will be published in later announcements.

Aden Refinery

The contract for building the oil port at Aden, which is complementary to the Anglo-Iranian refinery, has been given to George Wimpey & Co. Construction plant for the refinery has already been shipped to Aden where 300 British and 50 American technicians are on the site. The refinery is scheduled to be operating by the end of 1954, by which time the port must be ready to receive tankers.

Increased Nickel Output

Canadian Resources & Expansion

A CCELERATED expansion of existing production facilities and the advent of new and potential producers were the highlights of the free world's nickel industry in 1952 according to Dr. John F. Thompson, chairman of the board of directors of the International Nickel Company of Canada, Ltd., in an end-of-the-year review.

Output of nickel in the free world Dr. Thompson estimated would this year be approximately 315,000.000 lb. compared with 295,000,000 lb. in 1951. Canadian production would be 280,000,000 lb. or about 90 per cent of the total. Free world production of nickel was believed to be more than five times that of the rest of the world.

Nickel supplies for the free world were not now, however, according to reports, sufficient to meet the large Government accumulation of reserves at the same time as the unrestricted civilian consumption and the requirements of the defence programmes.

Search for New Deposits

Search for new deposits of nickel were being vigorously pushed ahead throughout the world. In Canada, particularly, the wave of prospecting which was opening up new areas was attracting considerable attention to the country's untapped mineral resources. Most of this work was being financed by private capital.

International Nickel's \$150,000,000 programme of underground mining expansion in the Sudbury district of Northern Ontario, was scheduled for expansion next year. This would give the company an annual capacity of 13,000,000 tons of ore entirely from underground operations, assuring maintenance of its current yearly rate of refined nickel.

Many civilian uses of nickel and nickel alloys had been restricted by the various governments, and manufacturers had been forced to improvise substitute materials. Industry had co-operated fully in complying with these restrictions.

The largest proportion of nickel continued to be consumed by the steel industries of the U.S.A., the United Kingdom and Canada, mainly in engineering steels, stainless steels and jet engine alloys.

Various types of corrosion-resisting

Ni-Resist had been used more extensively. Typical uses of this nickel alloy cast iron were in parts for engines for heavy duty service, pumps and valves, chemical process equipment, and in non-magnetic castings for military purposes.

In conclusion, Dr. Thompson said: 'The nickel requirements of the free world during the present emergency will continue to impose upon the industry the dual obligation of maintaining the highest possible production and promoting the most efficient use of every pound of nickel produced.'

New ' Cold Rubber ' Process

A PROCESS which makes 'cold rubber,' a hard-wearing synthetic rubber, 50 times more quickly than present methods and at less cost was announced at Akron. Ohio, U.S.A.. on 1 January, by Mr. J. L. Collyer, president of the B. F. Goodrich Company.

The new method, said Mr. Collyer, was the result of 12 years of research by the company's scientists and had been perfected under a research contract financed by the synthetic rubber division of the Governmentsponsored Reconstruction Finance Corporation.

It is claimed that the new process, which is still in the pilot factory stage, can produce high-quality cold rubber in 15 to 20 minutes compared with the 10 to 12 hours required by present production methods. The rubber is made in stainless-steel pipes instead of the expensive pressure vessels now in use.

Major technical problems, said Mr. Collyer, rendered the new process unsuitable for use in existing synthetic rubber factories, which raised the question of the possible obsolescence of present facilities.

The small size and simplicity of the new method, he added, eliminated the need for much expensive equipment, and reduced the size of the buildings required to house the rubber-producing operations. The new process, according to Mr. Collyer, was made possible by the development of extremely active catalysts which speeded up the chemical reaction.

Company engineers estimated that the cost of buildings and equipment for the process of rubber-making could be halved by the new method.

Soil Science & Plant Nutrition

by JOSEPH TINSLEY, Ph.D., F.R.I.C. (Department of Agricultural Chemistry, University of Reading)

MAN is of the earth ' wrote St. Paul and thought in material as well as in its spiritual aspects. That human life is sustained by food derived in large measure, directly or indirectly, from the soil is obvious. What is not so generally realised is that the soil resources are limited yet the demand for more and better foodstuffs increases at an alarming rate as the population of the world expands—at the present time, by about sixty thousand souls daily.

With this thought uppermost in their minds a group of prominent British scientists have presented various facets of the problem in a book edited by Professor Le Gros Clark and Dr. Pirie¹ entitled 'Four Thousand Million Mouths.' This vast number is a reasonable estimate of the world population within less than a century provided always that a major war be averted. Several other publications that have appeared in recent years bear witness to the growing concern for the future food supplies of all peoples in all countries, more particularly in Asia. Among these may be mentioned the authoritative reports of the Food and Agriculture Organisation of the United Nations² and an American symposium edited by De Turk³ entitled ' Freedom from Want' -a survey of the possibilities of meeting the world's food needs. Also there are the more colourful if less scientific writings of Vogt⁴ in 'The Road to Survival,' of de Castro⁵ in 'The Geography of Hunger' and of Hyams' in 'Soil and Civilisation.'

Soil Resources & Food Production

There can be no doubt that the provision of adequate food is a task requiring concerted action from different directions. There are those who dream or even expect that scientists and technologists will one day supplement if not supplant the farmer with his crops and livestock by the synthesis of basic food materials on a gigantic scale, but this thesis we do not propose to pursue further here. Others, among whom Pirie is the chief protagonist consider that drastic changes in conventional systems of cropping, of food processing, and of diet must be adopted. Recently⁷ he has pointed to the fact that, for the potato crop, all the energy of the sunlight is wasted on bare ground during the early part of the growing season because this crop is not frost hardy, while a wheat field wastes most of the light in the second half of the season because it ripens early. He considers the potential food supplies would be much greater if leafy crops were utilised directly without waiting for the plant or a herbivorous animal to transform them into the traditional foods. This implies the successful extraction of protein and other components from leaf tissue for human food and feeding the cellular residue to livestock. It also implies a diet mainly vegetarian in character and the acquirement of new tastes-perhaps the most formidable obstacle to the general adoption of such a scheme!

Conservative Attitude

A more conservative attitude to the problem is taken by Sir John Russell⁸ who devoted his presidential address before the British Association in 1949 to this matter of world population and world food supplies. He was more hopeful that conventional farming methods could be improved to meet the need and cited the wheat crop as an example of what might be achieved. A century ago the average yield in Great Britain was about 10 cwt. of grain per acre. Now it is about 20 cwt. and crops of double this amount are by no means rare, yet the average yield of wheat for the whole world is still below 10 cwt. per acre. Towards this aim of increased output from existing cultivated land the advances in each and every branch of agricultural science must be allied with efficient education of the practical farmer and with inspiring organisation by More intensive responsible authorities. cropping is not without its dangers especially in the exposure of the soil to the destructive agencies of erosion and calls for very careful conservation practices especially in those areas having extremes of climate ranging from torrential rain to devastating winds. Pari passu, a vigorous drive to win more land from the uncultivated regions should

lead to considerable expansion in production. Salter^a made a careful analysis of the position in 1948 and concluded that world food production could be doubled by 1960 using the present cultivated lands to better advantage and bringing new areas under cultivation. In the light of experience with the ground-nut scheme in East Africa, British opinion is most likely less optimistic at the present time. This rather abortive effort to bring a large area of virgin tropical land quickly under cropping will not have been in vain if it teaches the need for careful preliminary trial on a pilot scale to examine the factors likely to limit crop growth and to find whether these can be effectively In this particular instance the remedied. poor crop yields in the Kongwa district were due mainly to lack of water because of drought which proved more severe than was expected.

Water Supply a Critical Factor

Over vast areas the water supply more than any other single soil factor limits cropping capacity well below its potential maximum That is why large scale irrigation schemes such as in the Sudan Gezirah have shown remarkable results and why other vast projects are under way or under consideration at the present time in each of the continents of the world. Perhaps the most ambitious scheme yet is the plan to divert the waters of the Snowy river in Australia through mountain tunnels to the head of the Murray and Murrambidgee rivers on the western slopes of the Great Divide, and so extend enormously the area at present under irrigation in New South Wales and Victoria. This inspiring project was cited recently by Slater⁹ in a paper on science and an expanding agriculture.

The more arid the climate the greater the demand for water because of higher transpiration and evaporation rates. Given sufficient water the desert can be made to 'blossom as the rose,' but such schemes need careful planning and technical control otherwise the accumulation of soluble salts may soon curtail plant growth even to the point of barrenness. One of the practical lessons now fully appreciated is that soluble salts must be kept below specific levels for each crop, and different crop species show widely different tolerances to soil salinity. Investigations on this problem have developed as a major part of the U.S. Regional Salinity Laboratory's work at Riverside, California, and a review of plant growth on saline and alkaline soils has been published by Havward and Wadleigh.¹⁰ The electrical conductivity of the soil solution displaced by pressure from saturated soil is considered the most useful single measurement for assessing oil salinity in relation to crop growth. For plants with low salt tolerance, including fruit trees and many of the leafy vegetable crops, the critical level is below 4 millimhos/cm. For moderately tolerant crops such as cereals and forage plants the specific conductivity should not exceed 8 millimhos. Alfalfa. cotton and members of the beet family can stand higher concentrations once the germination stage is passed. One interesting feature of this work is the fact that different varieties within a single species often show marked differences in their salinity tolerance and this offers plenty plenty of scope to the plant breeder for extending the cropping capacity of saline soils. Incidently salt damage can arise in temperate climates where heavy manuring of soils with soluble fertilisers is practised, especially with horticultural crops under glass. Grainger11 has described the damage to lettuce following tomatoes grown in glass houses of West Scotland.

Increasing salinity is proving a serious obstacle in some irrigation areas, notably the Punjab of Pakistan. In such arid regions the irrigation water itself, whether from rivers or wells often contains a relatively high concentration of dissolved salts and much of the water must be used, not for the crop but for washing the accumulated salts from the soil either into the deeper subsoil below the root range, or, more effectively, into drains for pumping away. Irrigation technology is a rapidly developing subject of great importance and current interest is evident from the numerous publications appearing in recent years.

American References

Among these, mention should be made of the following three books by American authors—the second edition of Israelson's¹² well-known text 'Irrigation Principles and Practice, "Moisture Requirements in Agriculture,' by Roc¹³ which deals mainly with farm practice, and 'Irrigation Engineering' by Houk.¹⁴ A general account of irrigation agriculture and soil research in the United States has been given by Parks¹⁵ while Keller and Peterson¹⁶ have presented a more specialised report on irrigated pastures with particular reference to their establishment and management.

Thoughts on irrigation are naturally directed first to the parched soils of arid and semi-arid region, but it is now established that summer rainfall is often inadequate for optimum growth of crops in more temperate and humid areas. In Europe, Holland is recognised as the foremost country in developing practical control of the water supply in soils, firstly in the bulb growing fields, and now on a much wider scale for general agriculture. This is to be expected since much of her land has been won from under the water and can be retained only by ceaseless effort and care. Members attending the Congress of the International Society of Soil Science at Amsterdam in 1950 were able to see at first hand something of these magnificent achievements. For those who have not had this privilege there has appeared recently a symposium by Dutch workers on Soil Science in the Netherlands. Two of the papers by Hellinga¹⁷ and by Hooghoudt¹⁸ deal with water control and with tile drainage and subirrigation respectively Very marked increases in the yield of grass are obtained on subirrigated pastures whether by open channels or through tile or mole drains.

British Studies

Lest it should be imagined that little interest in this matter is shown in Britain mention should be made of the studies at Cambridge by Nicholson and his associates. The effect of maintaining the water table at different levels in the fens is of great practical importance in the cropping of these fertile soils, and a description of the field experiment in progress has been published by Nicholson, Alderman and Firth.¹⁹ Nicholson³⁰ has recently reviewed the control of ground water in reclaimed marsh land with special reference to Dutch and English experience on peat soils. At the same time Childs, also working at Cambridge, is continuing the more academic study of water flow in soils on the basis of Darcy's law:

$$= - \mathbf{K} \Delta \phi / \mathbf{1}$$

v

where V = effective velocity of water flow through a permeable column and $\Delta \phi / 1 =$ the hydrostatic potential gradient per unit distance. Thus K = the permeability constant characteristic of a particular soil. By analogy with electrical potential, the water flow boundaries and stream lines can be established in soils in relation to the spacing of drainage channels. Childs and Collis-George²¹ have presented an extensive review of the physical factors governing the movement and control of water in soils.

Sprinkler Irrigation

Much of the farm land in the southern and eastern counties of England would benefit from extra water during most summers, yet a high proportion of the region has an undulating terrain quite unsuited to irrigation by gravity flow through channels or drains. Nevertheless an increasing area is being watered by turning on 'artificial rain' delivered under pressure through spray pipe lines of various designs or through rotating nozzles. As yet the chief development has been for intensive horticultural cropping and the leading pioneer in this country, Secrett,^{22,23} first published a brief account of his irrigation plant and cropping system in 1946 followed later, in 1948, by a discussion on the use and abuse of artificial irrigation for horticultural crops. Secrett was quick to appreciate the potentialities of overhead irrigation not only for the supply of water at critical periods but also for the simultaneous application of nutrients dissolved in the water. In addition insecticides and fungicides may be applied in this manner when necessary and spraying with water can also be used to ward off frost from sensitive crops. Here is an instance of the practical man with progressive ideas who forged ahead in an empirical manner leaving the scientists to follow in his wake, to study and resolve the more technical details. Where economic returns allow for the capital cost, the most successful system of irrigation appears to be the automatically oscillating pipe line with jets at intervals of about 2 ft. along the pipe. High pressure mains, below or above ground, deliver water to the spray pipes arranged in parallel at intervals of 30 ft. Each spray line is constructed of short lengths of light metal tubing with easy coupling joints and supported on movable chairs for the full length of 200 or 250 ft. As each such length slowly oscillates in its bearings through an angle of about 90° the moving line of water jets covers about 15 ft. on either side of the pipe line which is usually placed from 2 to 4 ft. above ground level depending on the crop. It is important to prevent

the rate of application exceeding the capacity of the soil to absorb water and for this reason loam soils with a good crumb structure are most satisfactory.

Overhead irrigation is now well established in many countries and its use is rapidly extending even in arid regions which have the traditional furrow system of watering because of its greater adaptability, more economical use of water and more efficient use of dissolved nutrients. A brief review of the world situation was given by Riester.²⁴

Estimation of Water Requirements

In the more arid regions where climatic conditions may be reasonably-well predicted much information has been accumulated from practical experience and experiment on the time to apply the water and in what quantities. In some cases various instrumental devices are installed to measure the change in water status in the field. Two types of apparatus are commonly employed: the tensiometer which measures the suction force of the soil on water enclosed in a porous cup buried in the soil, and the gypblock which has two electrodes sum embedded in gypsum whereby the electrical resistance between them can be measured and correlated with the changing moisture content in equilibrium with the soil. The technical limitations of these devices will not be discussed here for while they are in extensive use for experimental field work, their use by commercial growers is greatly restricted because of the high cost of the large number of units required to give a fair picture of the water status in depth over a whole field and, because of the technical skill required for their operation. However, the practical use of gypsum blocks for irrigation control has been described in recent papers by Bouyoucos,25 the originator, and by Ewart²⁶ in Hawaian sugar plantations.

Nevertheless, as van Bavel and Wilson²⁷ have written, it seems fair to state that none of the instrumental methods has yet emerged as a satisfactory, practical and economical means for determining when to start irrigating a crop and for this reason considerable interest has been aroused in the prediction of water requirements from meteorological data.

What are known in America as 'evapotranspiration' estimates are the outcome of ideas advanced by Thornthewaite in 1946 and particularly those developed by Penman at Rothamsted. The water deficit which arises on drained land when evaporation and transpiration losses exceed the gains by rainfall can now be calculated with reasonable accuracy for a given period provided records are available of the rainfall and the mean air temperature, mean air vapour-pressure, mean wind force and duration of bright sunshine. The fundamental studies undertaken on the meteorology of evaporation from open-water surfaces and of transpiration from vegetation were presented in detail by Penman²⁸ in 1948. Subsequent reports by Schofield²⁰ and by Penman³⁰ illustrate the good agreement between estimated evaporation and that measured experimentally from rainfall and drain gauge data at several different sites.

The basic equation derived by Penman³⁰ to represent the rate of evaporation from open water can be written in the form

 $E_{\alpha} = 0.37 (e_s - e_d) B mm.$ per day where e_s is the mean-saturation vapourpressure at the water surface which is determined by the temperature.

 e_d is the mean vapour-pressure in the air measured in standard screen.

B is the mean Beaufort wind force measured 10 m. above ground level.

Practical recommendations to the farmer of irrigation water requirements are based on an appropriate factor for relating the transpiration by a crop in the vegetative phase to the evaporation from open water. For turf this factor E_T/E_0 varied from 0.6 in winter to 0.8 in summer under British conditions. American workers are now actively concerned with these practical aspects as the reports of Houston³¹ from Nevada, of Davis, Evans and Hazen³² from North Dakota, and of Blaney³³ demonstrate.

Preliminary Experiments

The results of three years of preliminary experiments on the irrigation of sugar beet have been reported by Penman.³⁴ The Rothamsted workers also began an extensive trial at Woburn in 1951 using four crops of grass cut frequently for drying; and barley. sugar beet and early potatoes in a three course rotation. It is too early to draw reliable conclusions but Schofield³⁵ has reported the yields for the first year which show remarkable increases from irrigation. In the case of potatoes 2.2 in. of water applied by overhead spray to supplement the 3.9 in. of rainfall between 1 May and 30 July doubled the yield of tubers.

Fertiliser Application in Irrigation Water

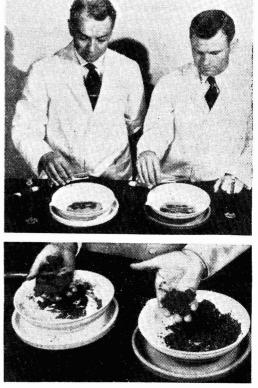
Next to water, the supply of mineral nutrients is of critical importance in obtaining optimum growth. In fact, the spectacular development in the use of fertilisers during the past century has made their production a major industry and still greater output is required to meet the potential demand from an expanding agriculture, especially in the countries of the East which, until recent years, have used very little inorganic fertilisers. The nutrient status of a soil may be quite adequate under natural rainfall but when crop growth is stimulated by irrigation the supply of nutrients from the natural soil is usually below the optimum.

The traditional method of applying fertiliser materials is broadcasting by hand on the seed bed and later as a top dressing. Where mechanised farming has developed the fertiliser is drilled either separately or with the seed. The same practice of broadcasting has been widely applied to soils under irrigation but it is obvious that much labour could be saved by dissolving nutrients at some control point in the irrigation water. Other advantages might follow from the continuous supply of nutrients in the water such as better utilisation by the crop enabling economy in the use of fertilisers. Many of the common fertilisers are not sufficiently soluble, particularly the phosphates such as superphosphate, and so development was retarded somewhat until the soluble phosphate materials such as the ammonium phosphates and phosphoric acid became avail-Nitrogen compounds employed are able. chiefly ammonium and potassium nitrate, urea and recently liquid ammonia. Supply of potassium is not often important in arid regions but when it is required the chloride is used in addition to nitrate. There has been a large increase in the use of fertliser solutions in California since the war years and a summary of developments in America was published by Jones and Rogers³⁶ in a review of new fertilisers and fertiliser practices. Under high temperature conditions the loss of ammonia by volatilisation may be very serious.

All nutrients added to water for ground application are absorbed by the roots and the fundamental reactions and mechanism are but little different from normal soil culture, but when the nutrients are applied by overhead spray irrigation the leaf tissue is able to absorb some of the dissolved material and the surplus will pass into the soil with the run-off water.

The use of dilute solutions of appropriate salts for correcting deficiencies of microelements such as manganese, iron, zinc and copper has been developed extensively in an empirical manner during the past twenty years Magnesium too is best applied as a dilute solution of the sulphate sprayed on to the leaves. Few workers have been concerned with the mechanism of this leaf absorption though it has been observed that spray damage will easily result if the solutions employed were too strong or the weather was too hot and dry.

Recently, particularly in America, experiments have been reported on the foliar application of the major nutrients, especially nitrogen. It is rather surprising that in the



Monsanto Chemists showing what happens when equal amounts of water are worked into ordinary clay soil (left) and Krilium treated soil (right)

most recent book on the subject of the 'Mineral Nutrition of Plants'³⁷ written by a group of American authors under the editorship of Professor Truog, only root absorption is considered. If plants had feelings one wonders what reactions would follow this abrupt and enforced change in their feeding habits at the hands of rude scientists!

Nutrient Sprays

Jones and Rogers³⁶ have reviewed the use of plant nutrient sprays with chief reference to the micro-elements and magnesium. Savre³⁸ in 1943 reported that nitrogen was absorbed by tomato leaves but phosphate was ineffective when applied in this manner compared with starter solutions poured around the roots. Knott and Lorenz³⁰ in a recent review of vegetable production mention a report of the American Du Pont Chemical Company that potatoes had responded to a mid season spray of 20 lb. of urea per 100 gal. of water. Mayberry and Wittwer⁴⁰ have reported trials in Michigan with urea sprays on tomatoes and celery which gave significant responses, while Benson and Bullock⁴¹ in Washington obtained good results with urea sprays on apple foliage. A 1 per cent solution caused some leaf scorch. Fisher and Cook⁴² found that spraving three times in the season produced a higher yield of apples than the same amount of nitrogen applied to the soil. There can be little doubt that considerable investigation of nutrient application by leaf spraying will be carried out in the next few years but it is hard to forecast the outcome. A few sprayings with relatively concentrated solutions is rather different from the more continuous spraying of very dilute solutions employed by Secrett, using about 50 parts of potassium nitrate per million of water. Automatic injection of the concentrated solution into the main water stream at a pre-determined rate is achieved by an ingenious mechanical device known commercially as the 'Solufeeder.'

Stabilisation of Spil Structure

A stable structure is important in cultivated soils not only to give a friable tilth and to resist erosion by wind or water action, but also to preserve a happy medium between adequate water retention and satisfactory aeration and so enable vigorous root development without which high yields cannot be obtained. In most soils structure is

the result of aggregate formation by the adhesion of primary mineral grains together, including all the size fractions from finest colloidal clay to coarse sand. This is achieved in a large proportion of soils mainly through the cementing action of its organic matter, especially the colloidal 'humus' fraction.

The Advent of 'Krilium'

In recent years soil scientists have been particularly busy investigating the chemical, physical and biological aspects of humus accumulation and decay. Many of the details of chemical composition and properties of the natural products were in process of discovery when suddenly, early in 1952. came news of the remarkable synthetic substance known by its trade name as 'Krilium' which the Monsanto Chemical Company had begun to manufacture, following six years of research and development work. Heralded with the high-powered publicity of American big business this commercial product has now captured world-wide attention by its remarkable stabilising action on soil structure. Authentic and rigorous tests with soils under laboratory and field conditions leave no doubt on this issue, but what is not so certain is the long-term effect of the material when applied to the soil and whether it can be marketed sufficiently cheaply for widespread use.

A symposium of papers on the subject of synthetic soil conditioners was presented in the June number of *Soil Science* mainly describing the results of experiments conducted by the staff of the Monsanto Chemical Company. These have been critically reviewed by Quastel⁴³ who was closely connected with the development work. Hedrick and Mowry,⁴⁴ the principal workers in the development of 'Krilium,' presented a lecture before an audience in London on 27 May and this has since been published.

As yet little information has been made public on the synthesis and detailed chemical composition of these synthetic 'polyelectrolytes' though this was promised by Hedrick and Mowry.⁴⁵ A long chain acrylonitrile polymer is hydrolysed and presumably develops numerous carboxyl groups which enable a sodium salt to be prepared. This is a deliquescent material readily soluble in water and it may be applied as a powder to dry soil or sprayed on in aqueous solution. Another product (CRD 186) is formulated as the partial calcium salt apparently intended more for use in saline soils with a high sodium content.

The important feature about their use under field conditions is that the soil must first be reduced to the desired state of tilth by normal cultivation methods and, when it is as dry as possible, the 'Krilium' powder is applied at the rate of about 1 ton per acre and mixed as thoroughly as possible to give about 0.1 per cent in the top soil. The 'Krilium' then 'fixes' the crumbs and so a stabilised structure is obtained. How long it will persist under adverse weather conditions remains to be settled by extensive field trials, but the substance is not leached or decomposed by micro-organisms to any appreciable extent. It is not toxic.

Ruchrwein and Ward⁴⁶ contributed a paper to the symposium on the mechanism of clay aggregation from which it appears that the anion groups of the molecule become attached to the surface of the clay and so the large molecules 'tie' the particles in the aggregate together.

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New Calcium Carbide Prices

THE Ministry of Materials has given notice of an increase of £3 10s. per ton in the prices of calcium carbide sold through Carbide Distributing Agency Ltd. The revised prices, per ton of 2,200 lb., packed in 200 or 220lb. drums, which came into effect on 1 January are as follows:-

A. Sales delivered in one consignment from factory direct

Grade	4 tons and over		4 cwts, but under 4 tons			Under 4 cwts.			
50/80 mm.) £	s.	d.	£	s.	d.	£	s.	d.
50/80 mm. 25/50 mm. 15/25 mm.	}35	7	9	35	13	9	35	19	9
8/15 mm.	34	7	9	34	13	9	34	19	9
'4/ 7 mm. 2/ 4 mm.	$\}^{33}$	7	9	33	13	9	33	19	9

B. Sales delivered in one consignment to user from merchant's warehouse :

Grade	4 tons and over			4 cv unde	r 4	tons	Under 4 cwts.		
50/80 mm. 25/50 mm. 15/25 mm.	$\left.\right\}_{36}^{\text{f}}$	s. 0	d. 9	£ 36	s. 6	d. 9	£ 36	s. 12	d. 9
8/15 mm.				35	6	9	35	12	9
4/ 7 mm. 2/ 4 mm.	$\}^{34}$	0	9	34	6	9	34	12	9

Calcium carbide packed in 100-lb. or 110-lb. drums will, as previously, be charged for additionally at the rate of £1 per ton on all prices.

Chemical Plant Exhibition

First Since 1936 Planned

THE Chemical Plant Exhibition, the first to be staged in the United Kingdom since the war, will be held at Olympia, London, from 3 to 17 September, 1953. It will form a section of the Engineering, Marine and Welding Exhibition, organised by F. W. Bridges & Co., Ltd., and will be sponsored by the British Chemical Plant Manufacturers' Association.

The exhibitors, all of whom are members of the Association, cover a broad chemical engineering field and include complete process plant designers and contractors; makers of plant for performing unit operations; specialist fabricators of plant in a wide range of materials of construction; and makers of ancillary equipment such as instruments. valves, pumps, packings and jointings.

In addition to those in the Chemical Plant Exhibition, many firms who are regular exhibitors at the Engineering, Marine and Welding Exhibition will be showing chemical plant on their usual stands and visitors with chemical plant interests will, in addition, have the opportunity of seeing a comprehensive range of engineering equipment, much of which is very necessary in any chemical works

The British Chemical Plant Manufacturers' Association will have its own stand in the Chemical Plant Exhibition and its staff will be available to answer queries regarding sources of supply of chemical plant in the United Kingdom and to effect introductions to any of its 200 members.

The last chemical plant exhibition held in the United Kingdom took place in London in 1936 and the industry will welcome this opportunity of demonstrating the considerable progress it has made in the post-war years.

Inquiries regarding the exhibition should be addressed to:—The Secretary, BCPMA, 14 Suffolk Street, London, S.W.1. (Telephone: WHItehall 0766).

Ester Solvents Cheaper

FURTHER substantial reductions in the prices of ester solvents came into effect on 5 January, 1953.

British Industrial Solvents, Ltd., announced the following revised prices for its 'Bisol' amyl acetate, butyl acetate and amyl alcohol (technical grade), all quotations in \pounds per ton carriage paid:—

	Packag at Sel	ges Ret ler's E	Packages Included		
	10	1	10 5		
Amyl aceiate	ton	ton	gal. drm	gal.	gal.
Technical	 235	237	240	265	275
BSS	 237	239	242	267	277
Confectionery	 264	266	269	294	304
But vl acetate	 181	183	186	211	221
	5 ton				
Amyl alcohol Technical	 244	246	249	274	284

Prices for amyl acetate and butyl acetate are spot or contract over six months.

Prices for amyl alcohol are spot.

Bulk delivery allowances are unchanged, but certain increases have been made in large quantity rebates.

A. Boake, Roberts & Co., Ltd., announced the following new prices per cwt., all net, delivered in the United Kingdom, drums charged extra but returnable for credit:—

	10 tons spot or against a composite contract	l ton spot or against a composite contract	40 gal. drum lots
Amyl acetate			
Technical	 235s.	237s.	240s.
BSS	 237s.	239s.	2425.
Butyl acetate	 181s.	183s.	1865.
Amyl alcohol Technical	 235s.	237s.	240s.

Food Group's ' Coming-of-Age'

SPECIAL arrangements have been made to mark the 21st birthday of the Food Group of the Society of Chemical Industry and the occasion will be celebrated by a dinner and dance to be held at the Dorchester Hotel, Park Lane, London, on Saturday, 7 March, 1953.

Proceedings will begin with a reception from 6.30-7 p.m., at which most of the past chairmen of the group and their ladies will be present. Following the dinner there will be dancing from approximately 8.15 until midnight to the music of Arthur Salisbury and his dance orchestra. Mr. H. J. Tinslay will be Master of Ceremonies.

Applications for tickets (32s. 6d.) should be made as soon as possible to the assistant secretary of the society.

Dress will be evening dress or dinner jacket. It is hoped that members of the group will make a special effort to be present at this important event.

Recent Developments in the Catalytic Reforming of Hydrocarbons

by FRANK MORTON, D.Sc., Ph.D., F.R.I.C., M.I.Chem.E., F.Inst.Pet.

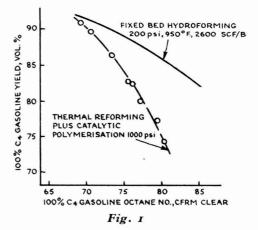
THERMAL reforming, i.e., the non-catalytic cracking of low-octane-rating naphthas, has been successfully employed in the petroleum industry for many years. Straight run distillates, usually boiling between 200°F. and 425°F., of too low an octane rating for blending with cracked gasolines for motor fuel use, are cracked in a once-through operation usually at temperatures of from 977° to 1,067°F. and at pressures from 250 to 1,000 p.s.i.g. The process is economic, since recycle operations are not usually employed. Yields of 70 per cent of the charge, with 18 per cent gas, are usually obtained, the reformed gasoline having an octane number of around 70. When higher octane rating products are required the severity of the process increases and the yields fall rapidly (see Fig. 1). The reformed gasolines are richer in low-boiling fractions than the charge, but also contain more aromatic hydrocarbons. It is doubtful if any 'cyclisation' of the paraffins is achieved in thermal reforming, but some aromatics are formed by dehydrogenation of cyclohexane derivatives.

Modifications Used

Various modifications of the reforming process have been used, the most successful being the Polyforming and Gas Reversion Processes, in which the naphtha to be reformed absorbs the C_3 and C_4 hydrocarbons formed on reforming. The rich naphtha stream then passes to the furnaces where some polymerisation of the C_3 and C_4 streams is believed to occur.

The use of molybdena-alumina catalyst combined with the recycling of the hydrogen formed in the process was developed as the Hydroforming Process by the Kellogg Company and the Standard Oil Company in 1938-40. The original process is a fixed bed regenerative process, in which the naphtha and the recycle gas are reheated to 1,050° F. and passed to one of several catalytic reactors. In passing over the catalyst, usually contact times of 15 seconds at 300 to 400 p.s.i.g., *cyclohexane derivatives are dehydro*-

genated to aromatic hydrocarbons and some normal paraffins are cyclised and dehydrogenated. Essentially the process is a dehydrogenation process, the recycle hydrogen being employed to maintain the activity of the catalyst and to suppress cracking reactions. When applied to a narrow boiling fraction (212°F.-250°F.) the process can be used for the production of toluene, and several such units were operated during the war. With wider boiling range naphthas, fixed bed hydroforming gives much higher yields for the same octane number improvement than thermal reforming. (Fig. 1.)



Thermal Reforming versus Hydroforming of East Texas Virgin Heavy Naphtha

McGrath & Hill. Taken from 'Progress in Petroleum Technology'; American Chemical Society, 1951

The process has several disadvantages, however, which are fundamental to an adiabatic fixed bed regenerative process. The regeneration of a fixed bed catalyst necessitates the use of several reactors, so that while one reactor is on stream the others are being reactivated and purged, etc. This increases the capital cost of the unit and also requires that the reactor design be such as to permit regeneration without damage to the catalyst by over-heating. In the adiabatic process the heat of the reaction is supplied by the naphtha charge which has to be heated to a temperature in excess of the reactor temperature. Temperature drops of 250°C. across such reactors are common. If two reactors are employed in series it is usual to reheat the charge between reactors. The high preheat temperatures result in some thermal cracking and this has been shown to give less favourable octane rating/yield relationships than are obtained with the same charging stock in isothermal reactors.

Improvements in the process were therefore to be expected. (a) by the development of new catalysts of non-regenerative type, and (b) by the application of moving bed catalyst techniques, by which means the reactor and regenerator would be separated and the reaction carried out isothermally.

(a) NEW CATALYSTS

(1) The Platforming Process.—The development of a new catalyst for the catalytic reforming of naphthas was announced by Universal Oil Products in 1949. The catalyst consists of small amounts (0.01 to 1.0 per cent) of platinum or palladium deposited on a halogen- or halogen-halide-treated alumina, and is active at temperatures between 450° and 800°F. for the simultaneous isomerisation and dehydrogenation of saturated hydrocarbons. The process has been developed commercially, the first unit

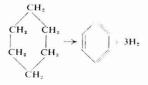
being of 1,500 b.p.d. capacity at the Old Dutch Refining Co., at Muskagon, Michigan. This unit has three identical reactors in series operating at 700 to 715 p.s.i.g. from 920°F. downwards. The process can be operated for the production of high grade motor fuel, or aviation fuels, in which case vields of 90 per cent to 94 per cent are obtained, depending upon the charge stock and octane level required (Table I). Alternatively the process can be operated for the production of aromatic concentrates. In this case a selected narrow boiling range stock is employed (according to whether benzene or toluene is the desired aromatic hydrocarbon) and a 30-50 per cent aromatic concentrate produced, from which the aromatic hydrocarbon can be recovered by solvent extraction, etc. A number of commercial units have been installed since 1949 and the economics of the process have been established. The capital cost of a 1.500 b.p.d unit is approximately \$450 per barre! and for a unit processing 10,000 b.p.d. is \$250. Although the catalyst is non-regenerative the life of the catalyst is limited by possible poisoning. When the catalyst activity has declined below a given limit it is replaced by fresh catalyst, the platinum being recovered from the spent catalyst. Experience at the Old Dutch Refinery shows that a catalyst life of 42 barrels of feed/lb. of catalyst can be expected at a catalyst cost of 9 cents/barrel of feed.

Type of Charging Stock Source of Charging Stock Properties of charging stock:			Str. Michigan	aight-run N Penn- sylvania	aphtha and Mid- Continent	Gasoline Mid- Continent	Gulf Coast	Natural Gasoline Cotton Valley
Combine I A D I			59 0	56.7	54-2	57.7	57.6	68.0
			58.0		182-402	108-392		
Boiling range, °F	N. 19.		158-387	226-350			132-399	106-359
R .V.P., Ib	C (10)		1.9	0.5	0.4	5.4	5.0	6.6
Sulphur, per cent	•0•0		0.11	0.06	0.03		0.05	0.01
Characterisation factor	10		12.09	11.95	11.95	11.99	11.95	12.30
Molecular weight			119.0	116.0	125.0	112.0	112.0	98.0
Octane Rating :								
Motor Method (F-2								
Clear	2.2	2.2	24.0	41.8	34.6	48.9	50.1	56.8
With 3 c.c. T.E.L./gal		•••	39.7	62.9	59.1	69.8	73.3	78.9
Research Method (F-1)								
Clear			24.9	39.2	34.8	49.5	54.6	57.2
With 3 c.c. T.E.L./gal			41.2	61.3	60.3	70.0	74.5	80.0
Properties of product reformat								
Yield, vol., per cent charge	8 C		93.0	94.1	91.3	93.0	93.1	90.5
Gravity, [°] A.P.I.			58.0	57.0	53.0	55.0	57.0	70.0
D 11			100-410	100-370	98-410	100 430	102-415	95-375
		• •	9.5	9.4	8.4	10.1	9.5	10.0
		2 A	0.01	0.006	0.003	10 1	0.002	0.001
	 4 		0.01	0.000	0.003		0.002	0.001
Octane rating :								
Motor method $(F-2)$					70.2			
Clear	• ((•))		77.0	75.7	78.3	77.2	78.2	7.0
With 3 c.c. T.E.L./gal			87.5	87.3	88.5	88.8	89.2	89.5
Research method (F-1)					10 A 44			
Clear			81.5	80.6	84.7	84.3	85.0	80.9
With 3 c.c. T.E.L./gal			92.5	92.2	94.5	95.1	95.0	93.5

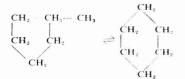
TABLE 1 Typical Results in Platforming Various Charging Stocks

The process is essentially a dehydrogenation isomerisation process in which the recycle hydrogen is employed to suppress cracking reactions and to maintain catalyst activity. The principle reactions which occur have been established by the use of pure hydrocarbons, and are claimed to be, A. Dehydrogenation of naphthene

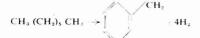
hydrocarbons to aromatic hydrocarbons:



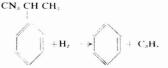
B. Isomerisation of *cyclo*pentane derivatives to *cyclo*hexane derivatives and hence by A to aromatic hydrocarbons:



C. Dehydrocyclisation of normal paraffins:



D. Hydrocracking of alkyl benzenes to benzene, etc.:

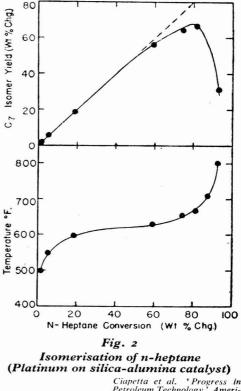


The major operating variables are temperature, space velocity, pressure and hydrogen recycle rate. By suitable choice of these variables the process is applicable to any charging stock, but the best results are obtained by use of narrow boiling range fractions of selected charging stocks.

(2) The Atlantic Refining Company Process.—The development of a suitable catalyst for simultaneous isomerisationdehydrogenation of hydrocarbons in the aboratories of the Atlantic Refining Company ias been described by Ciapetta. According b Hunter and Ciapetta, suitable isomerisaon catalysts can be prepared by combining

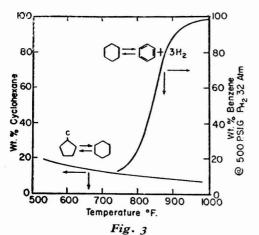
a hydrogenating catalyst such as nickel, cobalt or platinum, with a high surface area silica/alumina catalyst. Although these catalysts are active for isomerisation of hydrocarbons at temperatures between 400° F. and 800° F. they are also active cracking catalysts. Ciapetta therefore reduced the activity of the cracking catalyst by reducing the surface area of the silica/alumina base to between 10 and 65 m.²/g. by high temperature thermal or steam treatment.

The resulting catalysts are very active and selective for the simultaneous isomerisation and dehydrogenation of saturated hydrocarbons. The conversion of *n*-hexane to branched chain isomers over a nickel/silica/ alumina catalyst increases with increasing temperature between 550°F. and 800°F. (see Fig. 2), but the yield of C_a isomers reaches a maximum at 80 per cent conversion (750°F.) due to the incidence of cracking reactions at this temperature.



Petroleum Technology,' American Chemical Society, 1951

Most naphthas of boiling range 240-420°F. contain considerable quantities of alkyl cyclopentanes, usually from 35 to 50 per cent.



Methylcyclopentare Cyclohexane, etc. Ciapetta et al. 'Progress in Petroleum Technology'

of the naphtha. The conversion of these hydrocarbons to cyclohexane derivatives and thence by dehydrogenation to aromatic hydrocarbons is therefore a very desirable reaction. The calculated equilibrium concentration of cyclohexane from methylcyclopentane, and of benzenes from cyclohexane are shown in Fig. 3 plotted against the reaction temperature. In the temperature region 700-800°F., at which substantial

dehydrogenation of cyclohexane to benzene

takes place, the isomerisation equilibrium of

cyclopentane-cyclohexane naphthenes greatly

favours the cyclopentane derivative. How-

ever, the dehydrogenation reaction superim-

poses its equilibrium on the isomerisation reaction, giving an overall conversion of cyclopentane naphthenes to aromatic hydrocarbons.

Ciapetta does not claim that the catalysts developed by the Atlantic Refining Company are at all active for dealkylation of higher aromatic hydrocarbons, such as the conversion of cumene to benzene, which is an important reaction of the Platforming With this single exception the catalyst. Atlantic Refining Company process may be expected to operate in a similar manner to the Platforming process, although no details have yet been released concerning the commercial development of the process.

(3) The Houdriforming Process.—Heinemann and co-workers of the Houdry Corporation have announced the development of a metal acidic oxide catalyst which has been employed in a pilot plant for the catalytic reforming of an East Texas naphtha. According to Kirkbride, Houdriforming is a non-regenerative fixed bed catalytic process in which the metal acidic oxide catalyst has the dual function of isomerisation and dehydrogenation. The principal reactions involved are the dehydrogenation of C₈ naphthenes, dehydro-isomerisation of alkylcyclopentanes and isomerisation of *n*-paraffins. Cracking reactions are suppressed so that little hydrocracking occurs. The process is flexible in that by suitable choice of charging stocks and reaction conditions it can be applied to the production of aromatic concentrates as well as to the production of saturated aviation

TABLE II								
	Houdriforming	Naphthas fo	r Motor Gasoline	Production				
Charge Stock		.4		B	С			
C_{5} + liquid, vol. per cent ch	Ig		85.8	84.5	86.6			
C ₄ cut, vol. per cent	-		5.2	7.2	6.1			
Propane, wt. per cent			2.9	4-0	3.0			
Ethane, wt. per cent			1.7	1.8	. 1.8			
Methane, wt. per cent			0.9	1.0	0.7			
Hydrogen, wt. per cent			1.3	0.8	0.6			
Inspections of $C_5 + liquid$		Charge Stock	Cha Sto		Charge Stock			
Gravity, °A.P.I.		55.3	48.2 52.		51.6 47.1			
Distillation, A.S.T.M. (F)								
I.B.P		188	148 23	8 152	220 138			
10 per cent		215	200 26		247 208			
50 per cent		252	254 30		286 274			
90 per cent		317	326 35		354 358			
E.P		368	385 39		396 438			
Octane numbers								
F-1 clear		55.6	89.1 42.5	5 90.3	51.5 90.2			
F-1 + 3 c.c. T.E.L./gal.		76.3	97.1 65.8	3 97.4	68.8 97.4			
Reid vaour pressure, p.s.i.		0.7	2.4 0.3	2.7	- 3.0			
Chemical conposition								
Paraffins		44	41 4		34 38			
Olefines		0	1	1 2	0 2			
Naphthenes		42	3 4.		52 . 5			
Aromatics		14	55 1.	2 57	14 55			

TABLE III

Typical Pilot Plant Data (Kellogg MoO ₃ on Al ₂ O heav		catalyst,		
Experiment No. Feed Stock	1	2	3	4
Opposition and distance		208/425 °F.	Mid- Conti- nent	Naph- tha
Operating conditions: Pressure, lb/sq. inch				
gauge Temperature, °F.	500·0 911·0	500·0 920·0	500-0 927-0	500·0 938·0
Yields on feed: Gasoline (100 per cent				
C_4) wt. per cent Dry gas (C_4 — free),	86.7	83.2	82.6	79.9
wt. per cent	10.6	13.9	14.7	17.0
Carbon, wt. per cent Gasoline (100 per cent	0.05	0.38	0.31	0.30
C_4), vol. per cent Total liquid (100 per	87.3	83.5	82.5	79.9
per cent C_4), vol.	00.2	05.7	84.2	82.0
per cent	89·3 5·3	85·3 6·7	7.1	8.4
Gasoline (10 [®] lb.				
RVP), vol. per cent Total liquid (10 lb.	91.4	85.4	83.6	80.0
RVP), vol. per cent	93.4	87.2	85-3	82-1
Extra butanes for 10 lb. RVP, vol. per cent	4.1	1.9	1.1	0.1
Hydrogen produced, standard cu. ft./bbl.	415·0	315.0	360.0	40 8·0
Dry gas (C_4 — free),				
standard cu. ft./bbl.	786.0	801.0	875·0 1 41·2	1008-0 40-5
Mole per cent H_2 Mole per cent CH_4	52·9 21·8	39·3 24·7	25.5	25.4
Mole per cent C_2	13.8	19.5	18.4	19.0
Mole per cent C ₂	11.5	16.5	14.9	15.1
Mole per cent C_3 Corrected gasoline				
inspections:				
100 per cent C ₄ gasoline Gravity, °A.P.I.	53.2	51.8	51.8	51.8
Reid vapour pres-		51 0	510	
Reid vapour pres- sure, lb./sq. inch	7.2	8.7	9.2	9.9
ASTM $(D+L)$ at 158° F., vol. per				
cent	10.2	14.4	14.7	18.2
ASTM end point, °F	399.	403·0	399.0	403.0
Aromatics, vol. per				
cent (ASTM) Olefines, mole per	41.0	44 ·0	44·0	47.0
cent	1.3	1.5	1.4	1.0
Octane No CFRM clear	73.2	79.2	80.3	82.4
CFRR clear	80.3	88.0	89.5	92.2
CFRR + 3 c.c. T.E.L./gal.	93.5	98·3	99·2	101.0
10 lb. RVP gasoline				
Octane No. CFRM clear	73.9	79.5	80.4	82.4
CFRR clear	81.1	88.3	89.7	92.2
CRFF + 3 ml. T.E.L.	94.5	98.6	99.4	101.0
1.E.L	94.3	99.0	99.4	101-0

fuel components.

The process has been operated satisfactorily on a pilot-plant scale using three adiabatic reactors in series. Details of the yields for three different reaction conditions processing a 180°-370° F. 'East Texas' naphtha are given in Table II. Although the catalyst is non-regenerative, very severe conditions, such as may be employed in the production of aromatic concentrates, result in carbon deposition on the catalyst. Commercial Houdriforming units will therefore be designed to provide facilities for regeneration of the catalyst *in situ*.

(b) IMPROVEMENTS IN THE OPERA-TION OF CATALYTIC REFORMING

(1) The Fluid Hydroforming Process.—The application of the fluidised catalyst technique to hydroforming has been developed by the Kellogg Company, the Standard Oil Company of New Jersey and Standard Oil Company of Indiana. The fluidised system avoids the necessity of multiple reactors and since the regeneration is carried out in a separate regenerator the design of the reactor is simplified. Moreover, by using high catalyst-to-charge ratios the heat of the reaction can be supplied by the catalyst and recycle gas streams so that the reactor is operated isothermally, thus avoiding the thermal cracking observed in adiabatic fixed bed reactors.

Pilot plant operation indicates a substantial improvement over fixed bed hydroforming at higher octane levels. A simplified flow sheet of a fluidised hyroforming unit is shown in Fig. 4. It will be noted that the recycle gases are heated separately from the charge and used to pick up the catalyst from the regenerator and carry it to the reactor. The charge enters the reactor above the catalystrecycle gas entry. Results obtained in pilot plant operation are given in Table III and show a definite yield improvement over fixed bed operation. The capital investment and utility requirements of the fluidised process are considerably less than for the fixed bed process (Table IV) thus giving a reduction in cost per brl. of throughput as well as an increased yield for the same quality.

TABLE IV 10,000 B/SD Hydroforming Futures Interest C₄+ Product to 95 Clear Research Octane Number C₄+ Product Fluid Fixed Bed 10,000 B/SD Hydroforming Plants Mixed Base Naphtha Product \$4,350,000 \$7,370,000 Investments, on site 190,000 Utilities 390,000 Total .. \$4,540,000 \$7,760,000 Initial catalyst cost .. \$ 285,000 \$ 560,000 79.0 84.5 Yield, 10 lb. RVP, vol. per cent 84.5 79.0 Table reproduced from Murphree, Proc. 3rd World Petroleum Congress.

(2) Thermofor Catalytic Reforming.—An alternative method of moving the catalyst from reactor to regenerator is that employed in the Thermofor Catalytic process, based upon the Catalytic Cracking process of the Socony Vacuum Company. In this process (Fig. 5) the catalyst flows by gravity through the reactor and regenerator kiln into a lift pot from which it is lifted by air to the separator surge hopper above the reactor.

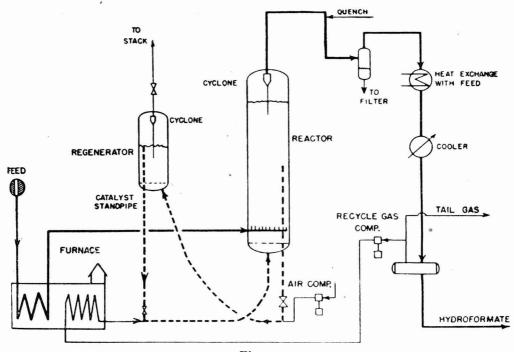


Fig. 4 Fluid Hydroformer (Courtesy Standard Oil Development Company)

Details of the application of this system to catalytic reforming have been given by S. D. Dalton and J. P. Simpson, who state that pilot plant operation (of a 50 b.p.d. unit) has shown that a 35-octane charge can be reformed to over 100 C.F.R. research octane number (with 3 c.c. lead), but do not give details of the yields obtained in such an operation. No details of the catalyst have been given except that the catalyst is durable and relatively inexpensive.

Of the five new catalytic reforming processes discussed only the Platforming process has been operated commercially for a sufficient length of time to enable process data to be studied. The first commercial unit was commissioned in October, 1949, and in the three years during which it has been operated modifications in design have resulted in greater simplicity of subsequent units. By May, 1952, ten Platforming units had been installed in various refineries, with capacities ranging from 1,500-5,000 b.p.d., whilst many additional units are projected. Of the other four processes the Fluidised Hydroforming and the Houdriforming process have been installed as commercial units, but no operating data have yet been released. It is therefore not possible at this stage to make an economic comparison of the various processes, and the choice of which process to install in any given location will depend upon many factors. A direct comparison of a process based upon the published data of laboratory and pilot plant operations may well be misleading, since the charging stocks used in the various laboratories may be of different origin.

A comparison between Houdriforming and Fluid Hydroforming is possible assuming that the East Texas naphthas used as charging stock in the Houdriforming pilot plant runs are of similar character to those used in experiments described by McGrath and Hill for fluid hydroforming. In the latter case an East Texas naphtha of 236-430°F. boiling range was used at two temperatures (902 and 921°F.). A yield (at 921°F.) of 90 per cent (by volume) total liquid, including butanes, was obtained with a clear octane rating F.1 of 87.3. The comparable Houdriforming data are that of case B in Table II in which a similar charging stock gave a yield of 91.5 per cent (volume per cent) of which the C^5 + (excluding butanes) had an octane rating F.1 clear of 90.3. The leaded value (F.1 + 3 c.c. T.E.L./gal.) is, however, identical for toth products at 97.6 and 97.4 respectively.

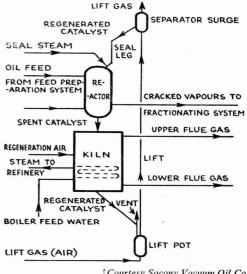
Comparison of Platforming and Fluid Hydroforming can be made on the basis of the figures for Mid-Continent naphtha given in Table I and Table III. Here, however, the naphtha described in column 4 of Table I is somewhat lower-boiling (108-392°F.) in the fluid hydrothat used than forming experiment (208-425°F.). Platforming of this naphtha gave a yield of 93 per cent (volume stabilised to 10.1 lb. R.V.P.), with an octane rating F.1 of 84.3 clear, and F1 + 3 cc. lead/gal. of 95.1. Fluid hydroforming gave yields of 89.3 per cent down to 82.0 per cent with clear octane numbers F.1 from 80.3 to 92.2. The advantage in vield/octane rating of product shown by Platforming in this instance is probably due to the lower boiling range of the charging stock.

The data available therefore suggest that differences between the yields and the qualities of the products obtained by the three processes (P'a'forming, Houdriforming, F'u'd Hydroform'ng) for s'milar charging stocks are small and that the processes by suitable adjustment of reactor conditions and so forth can produce exce'lent yie'ds of high octane fue's from similar charging stocks. The yield is reduced somewhat by increasing the severity of conditions required to produce a higher octane rating product from a given charge. This is clear from Table III and is evident in the extensive data published on the Platforming process. For the maximum yie'd of a given product quality the boiling range and naphthene content of the charging stock are probably limiting factors in all three processes.

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[Courtesy Socony Vacuum Oil Co.

Fig. 5

Flow diagram of 1951 design socony TCC

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Tar Distillation Plants

AMONG many contracts received during 1952 by Chemical Engineering Wiltons Ltd., a member company of the Simon Engineering Group, are two of considerable importance for new tar distillation plants for the National Coal Board.

The first was ordered in the early part of the year by the NC.B East Midlands Division for construction at the new Avenue coke oven site near Chesterfield, and is the first complete new tar works to be built in Britain for many years. It will comprise a Wilton continuous tar distillation plant with an initial capacity of 200 tons per day, together with ancillary plant for hard pitch, tar acid concentration, naphthalene and anthracene production, blending for road tars and pitch creosotes.

More recently the N.C.B. South Western Division placed an order for a Wilton continuous distillation plant in connection with the tar works at Caerphilly. This plant will treat 150 tons of tar per day, derived from new coke oven installations in South Wales. The plant incorporates up-to-date methods of pitch handling.

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Flour Aeration Process

May Succeed Nitrogen Trichloride

T a Press conference at the Savoy Hotel A on 2 January it was announced that the Morton Machinery Co., Ltd., of Wishaw, are now marketing a high-speed mixing machine which may be able to help the baker produce a white loaf without the use of chemical bleachers and improvers such as 'Agene' (nitrogen trichloride). It is with an 'aeration employed process ' patented by Joseph Rank Ltd., the flour millers.

Oxidisation Takes Place

With this process half the untreated, unbleached flour used in the final dough is whipped with water at very high speeds for approximately five minutes. During that period sufficient oxygen is taken from the atmosphere to produce a batter which, when discharged from the mixer, acts as an oxidising agent to bleach and improve the other half of the flour in a normal doughkneading machine.

The Morton machine prepares the batter which requires violent agitation at very high speeds to make possible the process of utilising the oxygen of the atmosphere. This agitation is achieved by two statically balanced blades, the completion of the process being determined by e'ectrical reading.

For the past eighteen months bread has been produced commercially on these machines by Beatties Bakeries of Glasgowthe largest bakers in Scotland-where a substantial proportion of their bread is made In their new by the 'aeration process.' factory at Dundee the whole of their bread production is made this way without any chemical improvers or bleachers.

In answer to a barrage of questions from baking trade paper representatives on Friday, a company spokesman admitted that the machines had not yet been tried commercially in England where the flour and baking procedure are entirely different. He also admitted that the two sample loaves he had with him to show the merits of his process were quite different, one being a pan loaf and the other a batch loaf. He could not answer questions as to whether the process 'improved' the baking qualities of the flour or whether it merely bleached. He added that the Ministry of Food were at present investigating the process but had not vet issued a report.

A Review of Biochemistry

by K. REES, M.Sc. Ph.D.

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THE intermediary metabolism of carbohydrates, fats and proteins is the subject of this article in which the author covers the period from November 1951 to November 1952

CARBOHYDRATE METABOLISM

The year has seen advances in our knowledge of the mechanism of enzymatic processes concerned with glycolysis, e.g. aldolase and the tricarboxylic acid cycle, e.g. citric acid synthesis and oxidative decarboxylation. The isolation of two crystalline enzymes associated with the tricarboxylic acid (TCA) cycle has been reported.

1. Reactions of the tricarboxylic acid cycle

(a) Synthesis of citric acid: Ochoa and his co-workers have continued studies on the reactions.

- (i) acetyl-phosphate $+ \text{CoA} \rightleftharpoons \text{Acetyl-CoA} + \text{phosphate}$ (Phosphotrans-acetylase).
- (ii) acetyle-CoA + oxaloacetate \rightleftharpoons citrate + CoA (Condensing enzyme).

Methods of isolation of the first enzyme of the TCA cycle to be obtained in a crystalline form, 'condensing enzyme,' have been described by Ochoa, Stern and Schneider. (J. Biol. Chem., 193, 703, 1952). They have detected and assayed the enzyme in a wide range of tissues, for example yeast, bacteria, and mammalian tissues. The reversibility of reaction (ii) has been demonstrated by Stern. Shapiro, Stadtman, and Ochoa (J. Biol. Chem. 193. 703, 1951), thus citrate can act as an acetyl donor to acceptors such as orthophosphate, sulphanilamide, and choline in the presence of suitable accepter namely: phosphotransacetylase enzymes, (reaction (i)), the sulphanilamide-acetylating enzyme of pigeon liver and choline acetylase.

The synthesis of citrate from acetyl-CoA and oxaloacetate in the presence of crystalline condensing enzyme is accompanied by the appearance of stoichiometric amounts of sulphydryl groups. Stern, Ochoa and Lynen (J. Biol. Chem., 198, 13, 1952) consider that this confirms the proposed acetyl mercaptide structure of acetyl-CoA. 'Condensing enzyme' has a high affinity for acetyl-CoA and calculations of the free energy change of the enzymatic synthesis of citrate indicate that the acetyl-mercaptide bond of acetyl-CoA is energy rich.

It appears that the validity of reactions (i) and (ii) is established, and that reaction (i) occurs in micro-organisms. In animal tissues acetyl-CoA is generated by the oxidative decarboxylation of pyruvate or from fatty acid oxidation.

Acetate itself may also be a source for the generation of acetyl-CoA and Lipmann, Jones, Black and Flynn (*J Am. Chem. Soc.*, 74, 2384, 1952) have investigated this process with an enzyme preparation isolated from yeast extracts. They have formulated the following two step reaction.

 $ATP + CoA \rightleftharpoons AMP + CoA \neg$ pyrophosphate CoA-pyrophosphate + acetate \rightleftharpoons acetyl \neg CoA + pyrophosphate.

The enzymes concerned with these reactions are also to be found in pigeon liver, thus the reaction may be of wide occurrence.

(b) Oxidation of a-ketoglutoric acid.

Sanadi and Littlefield (*Fed. Proc.*, **11**, 280, 1952), have obtained an α -ketoglutorate oxidase from animal tissue. It is homogenous in the ultracentrifuge and on electrophoresis. It catalyses the following reaction.

 $\begin{array}{rcl} \mbox{α-ketoglutorate} & + & \mbox{CoI} & + & \mbox{CoA} & \rightarrow \\ \mbox{Succinyl} & - & \mbox{CoA} & + & \mbox{CoI} & \mbox{2H} & + & \mbox{Co}_2. \end{array}$

The formation of succinyl - CoA has been demonstrated.

It is suggested that CoI and CoA are prosthetic groups of α-ketog'utorate oxidase.

(c) Oxidation of pyruvic acid.

A number of laboratories have turned their attention to this problem in animal tissues. Studies have been made on the oxidation of pyruvate with bacterial extracts. With preparations from Lactobacillus delbrueckii and Escherichia, flavine adenine dinucleotide, cocarboxylase, phosphate and Mg++ are required for the activity of the preparations. The nature of the primary intermediates in these oxidations is not fully understood. Jagannathan and Schweet (J. Biol. Chem., **196**, 551, 1952) and Schweet, Fuld, Cheslock and Paul (Symposium on Phosphorous Metalbolism, 1951, Editors: McElroy and Glass) report investigations on the purifications and properties of a pyruvic oxidase of pigeon liver. The enzyme requires only thiamine pyrophosphate as a cofactor and needs neither CoI or CoA. The following reactions are catalysed.

(iii) $CH_{*}CO.COOH + \frac{1}{2}O_{2} \rightarrow CH$ $COOH + CO_{3}$ (iv) $2CH_{*}CO.COOH CH_{3} + 2CO_{2}$ $CH_{3} + 2CO_{2}$

A heat stable cofactor and a soluble enzyme portion have been isolated which permit the oxidase to be coupled with CoI whereupon the pyruvate is converted to acetate and lactate together with a considerable amount of acetylmethylearbinol (Reaction (iv)). These workers postulate that an 'active acetate' group in union with the enzyme is formed from pyruvate. This 'active acetate' may then condense with another to form acetylmethylcarbinol or may be hydro'ysed to acetate, or it may be transferred to CoA to form acetyl-CoA.

The molecular weight of this pyruvic oxidase is given to be approximately 4,000,000 (Schweet, Katchman and Jagannathan, J. B'ol. Chem., **196**, 541, 1952).

Korkes, del Campillo and Ochoa (J. Biol. Chem., 195, 541, 1952) have investigated a soluble pyruvic oxidase system isolated from pig heart muscle. This preparation, in the presence of CoA and CoI catalyses the dismutation of pyruvate yielding lactate and either citrate or acetyl phosphate. Oxaloacetate and condensing enzyme are required in the former case and bacterial transacetylase in the latter. This system is similar to a system isolated by Korkes, del Campillo, Gunsalus and Ochoa (J. Biol. Chem., 193, 721, 1951) from E.coli.

Both these an mal systems described above and that of E.coli appear to have close affinities. Thus it seems likely that work on bacterial pyruvic oxidase systems might aid in the e'ucidation of the steps in mammalian preparations. Gunsalus Dolin and Struglia (J. Biol. Chem., 194, 849, 1952) have described the occurrence, isolation and partial purification of a substance a-lipoic acid which is an essential cofactor for pyruvate oxidation by certain bacteria. A-lipoic ac'd may be liberated from a large number of natural sources by acid hydrolysis. Associated with this wide distribution may be a universal rôle in pyruvic oxidation systems.

Some light on the rôle of α -lipoic acid in pyruvate oxidation has been shown by the work of Reed and de Burk (J. Am. Chem. Soc., 74. 3457, 3964, & 4728, 1952). These workers used a wild and mutant strain of *E.coli*. The mutant failed to respond to α -lipoic acid but did to thiamin and α -lipoic acid but did to thiamin and α -lipoic acid added together or to μ -lipoic acid concentrates prepared by enzyme hydrolysis. The substance present in the tissue is the amide of α -lipoic acid and thiamin (lipothiamide) and it is suggested that this moiety is part of the thiamin coenzyme required for oxidative decarboxylation.

Acid or basic hydrolysis of the tissue degrades it to α -lipoic acid whereas enzymatic hydrolysis releases the complex form required by the mutant. Soluble enzyme preparations of *E.coli* require lipothiamide pyrophosphate (the amide of α -lipoic acid and thiamin that is LTPP) for α -ketoglutate and pyruvate oxidation. It appears that the initial change in the mutant *E.coli* is the loss of a lipothiamide conjugase, present in the wild type, which will synthesise lipothiamide from its component parts. Reed and de Burk postulate the following reactions.

- (v) pyruvate (α -ketoglutarate) + LTPP + CoI \rightarrow acetyl LTPP + CO₂ + Col.2H
- (vi) Acetyl LTPP + CoA \rightarrow Acetyl CoA + LTPP

Possibly the 'active acetate' of Schweet et al. in their vertebrate oxidase system may be acetyl - LTPP.

(d) Other reactions of the cycle.

Doubts had been expressed on the intermediary formation of *cis* aconitate in the aconitase system because a study of the kinetics of the conversion of citrate into isocitrate failed to show a lag period. The problem was reinvestigated by Krebs and Holzach (*Biochem. J.*, **52**, 527, 1952) and they found Martins's earlier assumption to be correct, and that the reaction is:—

citrate \rightleftharpoons cis aconitate \rightleftharpoons isocitrate

Crystallisation of furmarase from p'g heart has been reported by Massey (*Biochem. J.*, **51**, 490, 1952). It possesses a m.wt. about 200,000 and the turnover number is over 100,000 at 20° and pH 7.3 in the presence of 0.033 M phosphate.

(e) Distribution of TCA cycle activity.

Krebs, Gunn and Eggleston (Biochem. J., 51, 614, 1952) investigated the pathway of oxidation of acetate in Baker's Yeast: isotope experiments show that acetate can be " oxidised in yeast cells through a mechanism other than the tricarboxylic acid cycle or a dicartoxylic acid cycle. The component reactions of the cycle can occur in yeast cells and evidence presented suggests that the component reactions of the cycle serve supp!y intermediates for organic to syntheses.

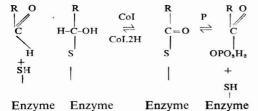
One such synthetic function in higher organisms is that of porphyrin synthesis. The TCA cycle serves to produce from acetate, an assymetrical 4C compound which is intermediate in the synthesis of porphyrin. Shemin and Kumin (J. Biol. Chem., 198, 827, 1952) considered that this 'active succinate ' may arise from two pathways (1) direct from succinate or (2) via the cycle and α -ketoglutarate. C¹⁴Me labelled succinate should produce labelled porphyrin via both routes whereas C¹⁴ carboxy labe'led succinate can only give rise to labelled porphyrin by the back reaction.

Thus malonate should affect the labelling of porphyrin in the case of C⁴⁴Me labelled succinate and have little affect in the case of C⁴⁴ carboxy labelled succinate. Incubation of these intermediates with intact and haemolysed duck erythorocytes with and without malonate gave results which confirmed that two routes for the synthesis of 'active succinate' existed. This also means that the TCA cycle is in part reversible.

2. Glvcolytic enzymes and glycolysis.

Krimsky and Racker (J. Biol. Chem., 198, 721 and 731, 1952) demonstrated that glutathione is a prosthetic group of glyceraldehyde-3 phosphate dehydrogenase. The iron inhibition of glycolysis is due to the inactivation of this prosthetic group glutathione.

They have postulated the following mechanism of aldehyde oxidation :---



They suggest that this reaction may be of widespread application, particularly as acetyl-CoA, an intermediate for keto acid and acetaldehyde is a thiol ester.

Roessler, Sanders, Dulterg and Brewer (J. Biol. Chem., 194, 207, 1952) demonstrated anaerotic glycolysis by enzyme preparations of Brucella suis. Phosphorylated hexose esters of the Emden-Meyerhot scheme are formed during the initial steps of the anaerobic dismutation of glucose and galactose. Evidence was obtained for the occurrence of glucose-1-phosphate, glucose-6-phosphate and fructose 1:6diphosphate. Ryley (Biochem. J., 52, 483, 1952) in studies on the metabolism of the protozoan cilicate Tetrahymena pyriformis showed in cell free systems, anaerobic g'ycolysis and some of the individual glycolytic reactions to occur, for example, hexok nase, phosphorylase.

STUDIES IN PARTICULATE SYSTEMS

Investigations with mitochondrial systems helps to bridge the gap of studies on isolated enzymes and on studies of whole tissues. Regulatory mechanisms are known to play an important rô'e in living organisms. Lardy and Wel'man (J. Biol. Chem., 195, 215, 1952) demonstrated regulatory mechanisms in the case of mitochondria. The availability of either inorgane phosphate or phosphate acceptors profoundly influences the rate of oxidation of a wide range of substrates by rat liver mitochondia. The regulatory phenomena are readily reversible, as they must be if they are of physiological significance. The rate of oxidation is apparently limited by the rate of transfer or hydro'ysis of high energy phosphate compounds whose synthesis is coupled with oxidative electron transport and is speeded up by phosphate acceptor systems.

Mitochondrial activity is profoundly influenced by potassium and other a'kaline cations. Pressman and Lardy (J. Biol. Chem., **197**, 547, 1952) demonstrated a specific effect of potassium maintaining optimal preparation of rat liver mitochondrial preparations especially in the presence of microsomes. The ability of microsomes to accentuate the requirement for K^+ is also possessed by an acetone extract of the cell fraction.

Studies of Siekevitz (J. Biol. Chem., 195, 549, 1952) reported an interaction between a mitochondrial extract and an enzyme system of microsomes capable of fixing free amino

homogenous cell components to their full biological significance will depend upon the elucidation of the extent and mechanisms of their interactions.

Hogeboom and Schneider (J. Biol. Chem., 197, 611, 1952) continued studies on the localisation within the cell. They demonstrated that 70-100 per cent of CoI synthesis by the Komberg reaction, that is:—

 $ATP + nicotinamide \Rightarrow$

CoI + pyrophosphate is localised in the liver nuclei and that a concentration of 5 to 6 times was achieved in this fraction. Judah (*Biochem. J.*, **49**, 271, 1951) had reported synthesis of CoI by this reaction in KCI treated liver mitochondria. Hogeboom and Schneider had used sucrose as their preparative medium and possibly synthesis by the mitochondria had in these preparations been masked.

PROTEIN METABOLISM

In recent years a renewed interest in the properties of the proteo'ytic enzymes has brought about a re-evalution of their specificities and rôle in the organism. It had been thought earlier that the endopeptidases had a relatively low order of requirement in their substrate specificities and would hydrolyse most substrates provided that they were of high molecular weight and were in the appropriate ionic state at the pH optimum of the enzyme. The work of Fruton and his school which has led to the appreciation of the high substrate specifity requirements of pepsin, trypsin and chymotrypsin has been carefully annotated and reviewed by Crook (J. Soc. Leather Trades' Chemists. 35, 27, 1951).

An important contribution to the understanding of the mechanism of the hydrolytic cleavage of proteins by chymotrypsin has appeared from the laboratory of Sprinson and Rittenberg (Nature, 167, 484, 1951). Using isotopically labelled water (H₂O¹⁸) they have shown that in the absence of the enzyme no exchanges occurred between the water and carbobenzoxyphenlylalanine, whereas in the presence of chymotrypsin such an exchange did occur. They state that the changes result from the nature of the activated structure, the formation of which precedes, and is essential for, the complete

reaction. The ensuing step, the hydrolysis of the peptide bond, would then be spontan-

The theories of Emil Smith on the mechanism of the metal activation of dipeptidase activity still excite some considerable controversy. Smith has summarised a great deal of the evidence and given his views in a very competent review in 'Enzymes and Enzyme Systems' (Ed. J. T. Edsal, Harvard University Press, Cambridge, U.S.A., 1951). Among the many papers which have appeared on this subject during the past 12 months only four will be mentioned. Lawrence and Moore (J. Amer. Chem. Soc., 73, 3973, 1951) have studied the acid hydrolysis of glycy'glycine over a range of temperatures and shown that, as could be expected from the Smith theory, the addition of Co++ speeded up the rate of hydrolysis by about 70 per cent. In a paper on similar lines Krohl (J. Amer. Chem. Soc., 74, 2036, 1952) has studied the spontaneous hydrolysis of amino acid esters over the pH range 7.5-8.5. In the absence of Co++ the rate of hydrolysis was negligible but in its presence the amino acid esters spontaneously hydrolysed to a considerable degree.

On the other hand Perkins (Biochem. J., 51, 487, 1952) has studied the stability constants of the cobalt complexes of glycine and glycylglycine. Contrary to what might have been expected from Smith's ideas he has shown that the constant for the glycylglycine-Co++ is considerably less than that for the glycine-Co++ complex. Even more damaging is the work of Gilbert, Otev and Price (J. Biol. Chem., 190, 377, 1951) in which they have investigated the nature of the red cobalt complex previously described and measured (spectrophometrically) by Smith. They have isolated this elusive complex in a crystalline form and shown it to be Co(glycylglycine)₂O and what is more they have demonstrated that this complex. which Smith has claimed to be the activated form of the substrate, is not, in fact, hydrolysed by the enzyme glycylglycine dipeptidase.

Group Transfer Reactions

During the last year, however, another aspect of the work on proteolytic enzymes has received renewed attention. It had been suggested by Bergmann and Fraenkel-Conrat as far back as 1937 that some, at least, of the familiar proteolytic enzymes could, in addition to the normal hydrolytic cleavage. catalyse group transfer reactions. Such a transpeptidation had been demonstrated by Johnston, Mycek and Fruton (J. Biol. Chem., **187**, 205, 1950) when they showed the transfer of the benzoyl-L-tyrosine group from benzoyl-L-tyrosylglycineamide on to a molecule of labelled glycineamide by chymotrypsin and there have been other reactions reported which point in the same direction.

The whole conception of proteinases acting as transpeptidases has now received a new impetus from the work of Hanes, Hird and Isherwood (Biochem. J., 51, 25, 1952) who have applied chromatographic methods for the identification of newly formed peptides. In particular they have studied a-glutamyl transpeptidase but their conclusions have wider significance and their suggestions on the mechanism of the reaction, on the possibility that such transpeptidations play an integral part in the continuous process of interchange and rearrangement which characterises the protein metabolism of the cell, and on a possible function of glutathione as a stabilised reserve of a-amino acyl peptide links available for transpeptidation, are of fundamental importance to our ideas on protein synthesis.

Rôle Investigated

At this point it should be mentioned that the rôle of a-glutamyl activation in peptide bond synthesis has also been investigated by Hendler and Greenberg. In a preliminary note to Nature (Nature, 170, 123, 1952) they report the use of C14 labelled amino acids rate in the measurement of the of incorporation of amino acids bv а variety of tissue and enzyme preparations. They were unable to show any appreciable activation of amino acid incorporation by glutamic acid, glutamine or by a-glutamyl compounds, and indeed a synthetic example of a-glutamyl glycine was considerably less efficient in this respect than free glycine. Their results in no way support the conclusions of Hanes, Hird and Isherwood (loc. cit.).

It is interesting to notice that in addition to the new ideas on a possible synthetic rôle for the classical proteolytic enzymes another group of hydrolytic enzymes have now come under investigation as possible synthetic mechanisms. Junqueira and Rothchild (*Arch. Biochem. and Biophys.*, **34**, 453, 1951) have described a possible correlation between the activity of the intracellular cathepsins and protein synthesis. Although the published material is not, in itself, convincing, it is an attractive theory to postulate that these intracellular enzymes could achieve intermolecular rearrangements without the necessity of complete hydrolysis with a subsequent resynthesis.

Receiving Attention

The in vivo synthesis of protein is also receiving renewed attention. Campbell and Work (Biochem. J. 52, 217, 1952) have studied the lactating mammary gland of the rabbit as a site of intense protein synthesis in the body. From a consideration of the rate of incorporation of labelled amino acids into the milk proteins they concluded that transpeptidation played a relatively small part in the synthesis of these proteins. They suggest that the milk proteins are built up largely from the free amino acids of the blood, but have not, so far, put forward any mechanism for this incorporation. It emerges from this study incidentally, that injected glycine is transformed into serine at a greater rate than had hitherto been supposed, so rapid, indeed, that it could be erroneous to talk of a 'glycine pool.'

There is little doubt that protein synthesis and degradation are under normal control. In the last review (THE CHEMICAL AGE, 66, 91) attention was drawn to the work of Hoberman on the size of the amino acid metabolic pool in different hormonal condi-The subject has been carefully reintions. vestigated with N¹⁵ labelled glycine by Bartlett and Gaebler (J. Biol. Chem., 196, 1, 1952) who have calculated that the normal rate of protein synthesis in the rat is about 0.62 grams of nitrogen/kilo of body weight/ day. In conditions of artificially stimulated growth (pituitary growth hormone treatment, for example) a change in the fate of amino acids occurs such that some three times as much amino acid is utilised in protein synthesis as in catabolism. Insulin is also held to promote protein synthesis.

Sinex, McMullen and Hastings (J. Biol. Chem., 198, 615, 1952) have demonstrated that an isolated diaphragm will incorporate significantly more labelled alanine in the presence of insulin than in its absence. On the other hand Forker and Chaikoff (J. Biol. Chem., 196, 829, 1952) have recently demonstrated that the serum proteins of animals deprived of insulin are turned over at the same rate as those of normal animals. This last result is difficult to understand in the face of the considerable bulk of evidence now available which points to a potentiation of growth response to various stimuli in the presence of insulin.

In our last review the present position of the Krebs ornithine cycle was reviewed in some detail. Grisolia and Cohen (J. Biol. Chem., 198, 561, 1952) have carried further their work on the enzymic synthesis of citrulline. The over-all reaction ornithine \rightarrow citrulline involves two major enzymatic steps

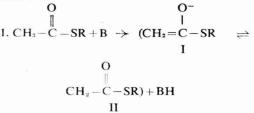
The first step is concerned with the synthesis of a derivative of carbamyl glutamate, which is formed enzymatically in the presence of A.T.P. NH₃, Mg⁺⁺ and carbamyl glutamate. The second catalyses the formation of citrulline from the carbamyl glutamate derivative plus a molecule of ornithine which leads to a regeneration of carbamyl glutamate. The nature of the carbamyl glutamate derivative is one of the few points left in the mechanism of the formation of urea which has yet to be elucidated.

FAT METABOLISM

The problem of the pathway by which the dietary fats are absorbed has attracted less attention this year. There is, however, an important paper by Reiser, Bryson, Carr and Kuiken (J. Biol. Chem., 194, 131, 1952) which provides new quantitative data on this vexed question. These authors have studied the intestinal absorption of triglycerides by using synthetic triglycerides in which the glycerol moiety has been labelled with C14 and the fatty acids marked by using fatty acids containing conjugated double bonds (linoleic). Approximately 25-45 per cent of the ingested glycerides were completely hydrolysed during absorption. The remaining 55-75 per cent were hydrolysed as far as monoglycerides. Half of the lymph phospho'ipin formed from ingested fat utilised the hydrolysed fatty acids and endogenous glycerol.

Glycerol from the ingested fat was not utilised for synthetic reactions but followed an entirely independent metabolic pathway. Once again Reiser and Bryson have been unable to confirm the view of Frazer that the particulate absorption of unhydrolysed fat is an important pathway in fat absorption.

One of the puzzling features of fat oxidation has hitherto been the finding that the degradation of fatty acids leads to the formation of more than one kind of two carbon fragment differing in their abilities to act as acetyl-donors or acetyl-acceptors. There have also been numerous experimental observations (see Novelli, in 'A Symposium on Phosphorus Metabolism,' McElroy and Glass, Baltimore, 1951, p. 414) indicating the existence of two forms of acetyl-coenzyme A. Weinhouse (Arch Biochem. & Biophys., 37, 239, 1952) suggests that acetyl-coenzyme A and its enolate anion could be the structures responsible for the respective acetylation and condensation activities of active acetyl. The two possible structures are shown in equation 1.



Where structures I and II are the resonance forms of the anion, R represents the coenzyme-A moiety and B represents a proton acceptor.

The theory is developed to explain the mechanism of the β -oxidation of fatty acids. It is suggested that the first step is an esterification of the fatty acid with coenzyme-A followed by an enclisation to provide a molecule in which the β carbon is highly activated by the adjacent double bond (equations 2 and 3).

2. $CH_3 \dots CH CH_2 \dots COOH + RSH \rightleftharpoons CH_1 \dots CH_2 COSR + H_2O$

3. $CH_3 \dots CH_2CH_2.COSR \rightleftharpoons$

 $[CH_3 \dots CH_2CH = COSR]^- + H$ A driving force is thus provided for the highly specific oxidative attack on the β -carton atom (equation 4).

 $4.[CH_3 \dots CH_2 CH = COSR]^- + \frac{1}{2}O_2 \rightleftharpoons$

 $[CH_3 \dots COCH = COSR]^- + H_2O.$

He then proposes as a final step, that the β -keto ester anion next undergoes a 'thiolytic' split by a further molecule of coenzyme-A to give an acetyl-coenzyme A molecule and the next lower homologous fatty acid ester of coenzyme A (equation 5).

5. $[CH_3 \dots COCH = COSR]^- + RSH \rightarrow$

 $CH_3 \ldots COSR + [CH_2 = COSR]^-$

This formulation leads directly to an activated lower fatty acid ready for a further β -oxidation without the necessity of postulating the intermediate formation of free fatty acids as such. The process is presumed to continue to the complete degradation of the fatty acid chain. A reversal of these steps is suggested as providing a mechanism of fatty acid synthesis from the two carbon fragments.

Another interesting contribution from the Weinhouse school (Volk, Millington and Weinhouse J. Biol. Chem. 195, 493, 1952) examines the oxidation of endogenous fatty acids by rat tissues in vitro. All tissues were found to oxidise the labelled fatty acids including brain and skeletal muscle. An analysis of their data revealed the presence of a metabolically active fatty acid fraction which was not in equilibrium with the tissue fatty acids. The active fraction did not appear to be phospholipin. The presence of this hitherto unsuspected fraction makes the earlier interpretations of short term isotopic experiments using labelled fatty acids open to severe criticism.

Further evidence for the direct utilisation of fatty acids by skeletal muscle has been provided by Wertheimer and Ben-Tor (*Biochem. J.*, **50**. 573, 1952) and by Hansen and Rutter (*J. Biol. Chem.*, **195**, 121, 1952) and it may now be taken as fairly certain that such a direct utilisation does occur in the animal body.

Factors involved in fat synthesis have been under intensive investigation during the past 12 months, the most significant contributions. coming from Chaikoff's laboratory. Baker. Chaikoff and Schusdek (J. Biol. Chem., 194, 435, 1952) have investigated the effect of fructose on the rate of lipogenesis from lactate and acetate in the livers of diabetic animals. When glucose was fed to such animals the rate of lipogenesis was as low as 10 per cent of that found in a normal animal. When fructose was fed in the place of glucose then the synthesis of fatty acids from acetate and lactate was restored almost to control levels.

Efforts Unsuccessful

In view of the fact that insulin also has a favourable action on lipogenesis from small molecules these authors also attempted to restore the diabetic's lost ability to transform glucose to fat by feeding fructose. In this they were unsuccessful and it is clear that fructose acts in a way quite different from insulin. Several possible mechanisms for the fructose effect are discussed among the more likely of which is the necessity for an active glycolysis for fat synthesis.

Fructose can provide such a pathway even in d'abetic animals by by-passing the hexokinase reaction. Such a conclusion is supported by the evidence of Lyon, Masri and Chaikoff (J. Biol. Chem., 196, 25, 1952) where the failure of lipogenesis in the livers of fasted rats is attributed to a reduction in glycolytic activity. Similarly, the results of Masri, Lyon and Chaikoff (J. Biol. Chem., 197, 621, 1952) on the effect of glucose and insulin on the rate of fatty acid synthesis in the livers of fasting rats, point in the same direction.

Addition of insulin alone to the incubation medium produced no effect on fatty acid synthesis. The addition of glucose alone caused some augmentation of lipogenesis, but the addition of both insulin and glucose caused a considerable increase in fat formation. It thus appears that an active carbohydrate breakdown is a prerequisite for the synthesis of fat.

It is interesting to notice that the synthesis of fat can occur in the extrahepatic tissues as well as in the liver although at a much slower rate (Medes, Thomas and Weinhouse, J. Biol. Chem., **197**, 181, 1952).

To Manufacture Cellulose

TWO factories, now under construction in Braz'l, will shortly be producing cellulose and making paper from bagasse of sugarcane, one at Piracicaba and the other at Monte Alegre. The Piricicaba factory has adopted the 'Celdecor South Africa' process and will have an initial output of 5,000 tons of paper annually, made from the waste of cane used in alcohol distilleries. Unlike the factories in the Philippines and India, which have separate installations for producing cellulose and paper, this plant will have one only, bagasse entering on one side and paper leaving on the other, ready for use. Particulars of the process to be used by the other factory have not been announced.

The Commission for Economic Development has received an application from *Companhia de Celulose Banex* (cf. THE CHEMICAL AGE, **67**, 297) for assistance in installing factories to extract cellulose from banana stalks. The Commission recommends consideration of the proposal.

Appointed K.B.E.

Chairman of Gas Council Honoured

Colonel Harold Charles Smith, chairman of the Gas Council, who was



Col. Smith

appointed K.B.E. in the New Year Honours of 1953, was born in 1890. He started work in the central laboratory at the Nechells Gas Works, Birmingham, 1906, and after in going through the various departments at the different gas works, was appointed assistant engineer at the Swan Village

works in 1912 and in 1919 he was appointed works superintendent. In 1920 he was appointed works superintendent at the Willoughby Lane works of the Tottenham Gas Company and in 1922 he was appointed chief engineer to the company. He was later appointed, in addition, general manager and subsequently invited to join the board as managing director and deputy chairman.

Colonel Smith became chairman of the British Gas Council in 1947, and was appointed deputy chairman of the Gas Council in 1948. He succeeded to the chairmanship on 1 January, 1952. He has been president of the Institution of Gas Engineers, president of the British Road Tar Association, and the British Tar Confederation, chairman of Prince Regent Tar Co., and was formerly a member of the Fuel Research Board and of the Scientific Advisory Council of the Ministry of Fuel and Power. He is a director of National Benzole Co., Ltd., and president of the National Benzole Association.

Japan's Chemical Fibres Plan

A FIVE-YEAR programme of development by the chemical fibres industry in Japan is being supported by the Ministry of International Trade and Industry mainly because of the contribution it will make to the country's balance of payments problem.

Of the capital outlay of £30,000,000 required to increase the production of the

chemical fibres industry to six times its present volume, about two-thirds is being supplied by loans.

In orden to meet the growing demand in Japan for nylon and vinyl fibres it is necessary, according to a Bank of Tokyo statement, for the Government to give assistance because the cost of construction of plants for chemical fibres production is generally so high that Japanese companies could not be expected to bear the whole of the necessary expenditure.

When the programme comes fully into effect it is estimated that Japanese output of vinyl, nylon, and other synthetic fibres will reach 90,000,000 lb. a year. This would mean a saving of at least £46,000,000 a year in foreign currency which would otherwise have to be paid for imported raw cotton. wool and flax.

Reinforced Plastics Committee

FORMATION of a special technical committee consisting of representatives of firms interested in low-pressure reinforced plastics has been decided upon by the council of the British Plastics Federation.

The committee, which will be responsible to the main technical committee, is to be known as 'The Glass and Asbestos Fibre Reinforced Plastics Technical Committee.' It will hold its first meeting at the federation offices, 47-48 Piccadily, London, W.1, on Thursday, 15 January.

While membership of the committee is restricted to members of the federation, the director has written to all non-member firms represented at the informal meeting held by the federation on 14 August, 1952, informing them of the steps subsequently taken and giving firms the opportunity of applying for membership of the Federation and for the appropriate group within it.

Groups of the Federation are :---

Plastics material manufacturers (including manufacturers of synthetic resins and moulding powders); moulders; fabricators; engineers, laminated and fibrous products; raw material suppliers.

Firms eligible for representation on the committee are those carrying out experiments or production on reinforced plastics or materials for their manufacture. such as resins or fibres.

Some Current Topics in Physical Chemistry

by H. MACKLE, M.Sc., Ph.D., D.Phil. (Department of Chemistry, The Queen's University of Belfast)

THE annual output of chemical literature has steadily increased in the post-war years; it is now larger than ever before. Hence it would not be possible, even if it were desirable, to comment, however briefly, on all aspects of recent research activity. In such circumstances it would seem that the only useful procedure in a survey of the present length is to choose for discussion a few topics which appear to engage special current interest.

Recently reported developments in the fields of complex compounds, free radicals and thermo-chemistry may, with some justification, be included among such topics, and they form the subject matter of what follows. The writer does not wish thereby to imply that certain other developments are not equally important or perhaps, even more so. No selection is ever completely objective. The personal interests of the selector are a factor which it is impossible to eliminate.

(1) COMPLEX COMPOUNDS

(a) Introduction.—The elements of Group VIII of the Periodic Table have long been of special interest because of the number of valencies they display, and the ease with which they give rise to co-ordination compounds. The ammines of cobalt, platinum and rhodium are well known, but in recent years work on complexes involving metals other than these has disclosed interesting, and in some instances novel, structural and valency phenomena. Before proceeding to a survey of the latest progress in this field it may be useful to be briefly historical by way of introduction.

It is now known that the unique properties of the Group VIII elements depend essentially upon the fact that in their atoms the d orbitals are being filled. Hence, because

As Me₂

As Me,

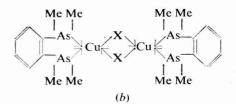
(a)

of the mutual proximity of their energy levels, d, s and p orbitals are all available for bond formation. The chief ways in which these orbitals may be 'hybridised,' and the significant energetic and stereochemical consequences of such hybridisations, were first described about 20 years ago by Pauling.' Since then a wide variety of hybridisation possibilities have been investigated, the most comprehensive treatment being that of Kimball.² Such possibilities, together with the comparatively large number of valencies which the Group VIII elements may assume, are the basis of our understanding of the stereochemistry and stabilities of the vast majority of complex compounds.

These aspects of the subject have recently been critically reviewed by Nyholm³ and by The former author discussed in Burkin.4 some detail the stereochemistry of complexes, the preparation of complexes of new types, and the nature of the forces between the metal ion and the co-ordinating atom. The latter author, on the other hand, examined the physico-chemical principals involved in complex formation, including such interesting questions as the influence of the coordinating group (or ligand) on the properties of complexes formed by a particular metal, and the variation of properties among complexes with the same ligands but different metals. Since these reviews appeared further interesting developments have been reported, and it is the latter that will be treated briefly in the remainder of the present section. They are mainly the outcome of an extended series of investigations by two independent schools, those of R. S. Nyholm⁸ and J. Chatt.⁶

(b) Salt-like and halogen-bridged structures.

Following up an earlier series of papers⁷



on the stereochemistry of complex compounds formed by the chelate group, *o*-phenylenebisd methylarsine (fig. a), with iron, rhodium, nickel and cobalt halides. Kabesh and Nyholm⁸ have studied the behaviour of this chelate group with copper.

They succeeded in isolating compounds of the empirical formulae $CuX(A_{a})$ and CuX(A), where A represents the above chelate group and X may be Cl, Br, or I. The authors conc'uded that these compounds are salts of 4-covalent copper in which the cuprous atom is co-ordinated to four arsenic atoms. Those of the first type may be written as [Cu A2] X, and those of the latter as [Cu A₂] [CuX]. Confirmation of the salt-like characters of these compounds is provided by their molecular weights and conductivities in nitrobenzene solution.

An alternative method of formulating compounds of the second type involves a halogen-bridged dimer such as (fig. t).

That such halogen bridge structures occur in the tertiary arsine and phosphine complexes of palladium, mercury, and cadmium has been shown by Mann et alii, 9 and Chatt $^{6 n}$, b (see also below) has demonstrated the presence of bridges in platinum complexes of the type (fig. c).

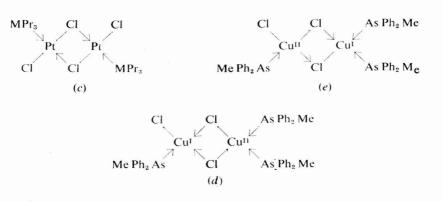
In the present instance, however, Kabesh and Nyholm reject bridge structure (b) in favour of the salt-like structure as written above. They provide what appears to be good experimental support for this conclusion, and their work emphasises the need for exercising care before assigning halogenbridged structures to co-ordination complexes of this general type.

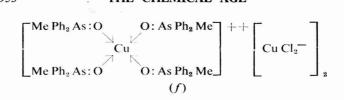
It is noteworthy in passing that Foss and Gibson ¹⁰ have also shown that certain gold complexes, for which bridge structures were originally proposed, are in fact salts. As Kabesh and Nyholm point out, solubility in organic solvents does not necessarily mean that a complex is a non-electrolyte. The solubility may simply originate from the presence of large organic groups. More recently, Nyho'm 5b has shown that the blue and brown cuprous-cupric complexes of methyl diphenyl arsine have not the bridge structures (fig. d), and (fig. e) formerly formerly proposed, but are in fact arsine oxide complexes, salt-like in character with formulae of type (fig. f).

Formula (f) underlines the potentialities of tertiary arsine oxides as ligands, and it is likely that tertiary amine and phosphine oxides behave in the same way.

These investigations raised anew the question of the existence and properties of cuprous complexes of the tertiary arsine itself and Nyholm 5c has subsequently prepared several new types of such. By suitably varying the method of preparation, complexes containing 1, 2, 3, or 4 molecules of the tertiary arsine to each cuprous atom may be isolated. The last two types had not been known previously; they have the empirical formulae Cu X. 3As Ph₂ Me and Cu X. 4As Ph₂ Me. The former are non-electrolytes containing 4-covalent copper, and the latter are salts in which X is the univalent anion.

The frequent occurrence of salt-like structures in preference to bridged structures has been emphasised in the preceding paragraphs. It will, perhaps, be useful





therefore, to discuss now in a little more detail than hitherto, some complexes to which bridged structures have been assigned. As has been noted, recent progress in this field is mainly due to Chatt and his collaborators (b).

A halogen-bridged structure was first put forward by Pfeiffer as early as 1923, but the existence of such was not confirmed until it was shown, just before the war, by complete X-ray crystal structure determinations to exist in diethylmonobromogold, (Et₂ Au Br)₂ ¹¹ and in the complex $(Me_3 As Pd Br_2)_2$. ¹² Since then, easily soluble tertiary phosphine and arsine halogen-bridged complexes containing many other metals, particularly from the second and third long series of the periodic table, have been prepared and studied. Of particular current interest are the platinous bridged complexes of type (fig c) above recently prepared and studied by Chatt.^{6a}

Since simple platinous complexes of the type L_2 Pt X_2 are the most rigid of all planar complex compounds, as shown by the existence of a large number of suitable *cis*and *trans*-isomers, it is to be expected that, if geometrical isomerism exists at all among bridged complexes, it would most probably occur in the platinous series. Actually, no evidence of such has been found; only the *trans*-symmetrical forms seem to occur. The phenomenon of the *trans*-influence of certain ligands in platinous complexes may be connected with the co-ordinating power of filled *d*-orbitals of the metal atom.

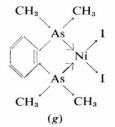
It has been found that the groups showing the highest *trans* influence are first those which Pauling ¹⁴ considered to co-ordinate by double bonds making use of filled *d*orbitals of the metal atom for π -bond formation. The question has been discussed at some length by Chatt. ¹⁵

Compounds of particular interest which have recently been prepared ^{5f} are ditertiary arsine nickel carbonyl and some of its halogen derivatives. When *o*-phenylenebisdimethylarsine (see (a) above) and nickel tetracarbonyl react together two carbonyl groups are replaced readily, and a monomeric crystalline compound of the formula Ni(CO)₂A is obtained. The remaining two carbonyl groups may not be replaced in this way. This appears to be so for several ligands; thus there are also Ni(CO)₂ Dipyridyl, Ni(CO)₂ *o*-Penanthroline¹⁶ and so on.

Oxidation of the complex Ni(CO)₂A Nil₂A, with iodine gives the first of a previously unknown class of cis-planar bivalent nickel complexes. 17 It is the nickel analogue of the palladium complex first described by Chatt and Mann in 1939 18 and the formula (fig. g) has been ascribed to it.

The corresponding bromide and chloride are much less stable. It would appear that compounds of the general formula NiX_2A became progressively less stable as X becomes more electronegative, and Nyholm has offered suggestions as to why this might be so.

(c) The nature of the metal—ligand bonds. A question of considerable interest concerns the metal-ligand bonds in some of the complexes discussed above. It is likely that the strength of such bonds is determined by two main factors: (a) the product of the effective electronegativities of the donor atom (L) of the ligand and of the metal atom (M); (b) the possibility of double bond formation between (L) and (M), involving d electrons of the metal (M) and either a p or one of the



vacant *d* orbitals of the donor atom (L).¹⁰ A recent theoretical investigation ²⁰ has shown that the use of the higher 4*d* orbitals for σ bond formation by the transition metals is feasible from the overlap viewpoint. It has further been discovered that the atoms which favour the use of the 4*d* orbitals of a transition metal are the more electronegative ones, as found in practice for so-called 'ionic' bonds.^{10b} The use of 4*s* 4*p*³ 4*a*² octahedral bond orbitals should result in bonds which are weaker than those derived from 3*d*² 4*s* 4*p*³ orbitals.

More Satisfactory

This use of higher covalent bond orbitals in the so-called 'ionic' complexes permits of a more satisfactory description than was hitherto available ^{14b} of a bond whose properties are essentially covalent in the usual sense. The suggestion that $4s 4p^8 4d^2$ bond orbitals might be used in certain transition metal complexes was first made by Huggins ²¹ in 1937. Subsequent'y other higher level covalent bond orbitals have been postulated, for example $4s 4p^3$ orbitals. ²²

A powerful experimental test for such theories of bond type in complexes involves the determination of their magnetic moments, μ . From these the number, n, of unpaired electrons may be calculated using the formula (orbital contributions being neglected)

 $u = \sqrt{n} (n + 2)$ Bohr Magnetons (1)Given n and the co-ordination number of the metal, the orbitals, used for bond formation may often be inferred if a suitable theory is accepted. In Pauling's theory 23 the bond orbitals required for a given shape are made available either by pairing electrons at lower (e.g. 3d) levels or by elevating them to orbitals above those used for bond formation. The complex, ferric triacetyl acetone, may be quoted to illustrate the application of these principles. The physical properties of this complex are such that it doubtless has some type of covalent bonds present: it dissolves in most organic solvents and volatalises readily when heated. The observed magnetic moment, however, precludes the use of $3d^2 4s 4p^3$ bond orbitals, and the higher 4d orbitals must therefore be involved in a hybridisation of the $4s 4p^3 4d^2$ type. 24

By an analogous procedure and method of reasoning Nyholm and Burstall ^{5g} have con-

cluded that $4s 4p^3 4d^2$ type bonds exist in $[M^{11}$ (Dipyridyl).] X_2 complexes when M^{11} = Mn or Co. On the other hand $3d^2 4s 4p^3$ type bonds occur when M^{11} = Fe or Cr. The nature of the bonds in the corresponding nickel compounds is also discussed in the same paper and hypotheses to account for the observed data are proposed. Finally, all ditertiary arsine complexes have been shown to contain strong covalent $3d^2 4s 4p^3$ bonds.

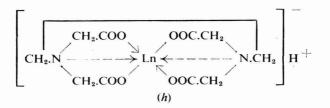
A novel method for the diagnosis of bond types in certain complexes involves the study of the exchange of metal ions between a complex molecule or ion containing the metal and free metal ions in a suitable solvent. If the bonding is predominantly ionic, exchange may be expected to occur rapidly and to decrease significantly with increase in the covalent character of the bonding.

Radioactive Cobalts

These basic ideas have been applied recently by West, 25 using radioactive cobalt, to the problem of bond type in cobaltous complexes with salicylaldehyde, salicylideneaniline and related molecules. For such complexes the exchange is rapid, indicating main'y ionic bonding. On the other hand, for cobaltous complexes with 4: 4'-dicarbethoxy-3 : 3' : 5 : 5'-tetramethyl dipyrromethine the exchange is slow, and cobaltous phthalocyanine shows no exchange whatever. The metal-ligand bonds are therefore considered to be mainly co-valent in such complexes. In all cases these conclusions are supported by independent magnetic data.

(d) Some factors influencing the stability of metal ammines and other complex ions:

As noted earlier, the conditions governing the stability of complex ions have recently been reviewed by Burkin and by Bjerrum. * Since then Fyfe ²⁶ has considered more fully in this respect the application of electronegativities and the Pauling neutrality principle.²² Pauling postulated that when a ferric ion, for example, is placed in solution six water molecules become firmly bound to the central atom by partially covalent bonds. From the difference in electronegativities of the ferric ion and the oxygen atoms of the water molecules it may be deduced that these bonds will be approximately 50 per cent covalent. This means that the ferric ion gains three electrons, its effective charge



being reduced nearly to zero, and the positive charge is relayed to the hydrogen atoms of the water molecules. The result is the formation of a large complex ion with a low charge density.

The same basic ideas have been used by Fyfe ²⁶ in a slightly different way. He points out that, since the third ionisation potential of iron is greater than the energy required to remove an electron from the oxygen of water, an oxygen-iron electron transfer process is energetically desirable. When an ammonia molecule approaches the hydrated metal ion displacement of the water should occur because nitrogen, being less electronegative than oxygen, should form a more covalent bond with the metal. This in turn means that an ammonia molecule can more effectively distribute the charge on the cation. The increasingly covalent character of the bonds which are formed when electronegative atoms are replaced by less electronegative atoms is supported by the magnetic data.

The number of ligands bound by an ion appears to depend upon two factors: (a) on the number of orbitals, hybridised or otherwise, that the metals have available for bond formation; (b) the number of linkages required to reduce the charge on the central ion to a minimum. Size is not as important controlling factor as was originally a believed: the large silver ion, for example, takes two ligands only, whereas the smaller mercuric ion takes four, and those of the transition metals six. Fyfe ²⁶ has pointed out that the magnetic data include that, for the bivalent transition metal ammines, d orbitals are not extensively used in bonding. The s and three p orbitals only appear available, and the number of ligands might therefore be expected to be four. However, for these ions, since the bond with ammonia has less than 50 per cent covalent character, six ligands are required to reduce the charge on the central ion to a minimum.

It has been suggested by Pauling ²² that these six ligands are bound by synchronised resonance of the sp^3 hybrid, and Fyfe has made the alternative suggestion that the three *p* orbitals alone are used to form six *half honds*,²⁷ and he has discussed the stability of the metal-ligand bonds, using the free energy of formation of the complex ion from the aquo-cation as an index of the bond strength. The factors which affect the stability of the complex ions of the alkaline earth metals have also been discussed recently by Williams. ²⁸

(e) Some recent miscellaneous studies.

In the post-war years ion-exchange resins have come more and more into use in the separation of both simple and complex ions from solution.²⁹ This technique has been applied recently by Salmon ³⁰ to the study of complexes involving tervalent iron and orthophosphoric acid, and it now seems that there is present in ferric phosphate solutions a complex containing three phosphate groups per iron atom. The actual composition of the complex is not yet certain: it appears to be either H_3 [Fe(HPO₄)₃] or H_6 [Fe(PO₄)₃]. Ion-exchange resins have also been employed, as one of several techniques, by Sharp and White³¹ in a comprehensive study of the cobaltic acetate complex.

Formation of complexes sometimes finds useful application in the separation of chemically similar ions. Thus March³² has recently effected a separation of Yttrium and Erbium with the aid of ethylenediaminetetra-acetic acid ('Enta Acid'). The complexes formed are of the type (Fig. h), where Ln represents the lanthanon, and their stability constants have recently been determined by Vickery.³³

(2) FREE RADICALS

The present position in this field may be assessed by a study of the papers discussed at the Faraday Society meeting in Ottawa last September. The full report of this meeting has not yet been published; the proofs issued prior to it therefore form the base of what follows.

(a) Flash Photolysis.-One of the most important experimental methods devised in recent years for the efficient production of free radicals is the so-called flash photolysis technique developed by Norrish and Porter at Cambridge. ³⁴ By its means, sufficient concentrations of free radica's in the gaseous phase may be momentarily obtained for spectrographic investigation in the visible and ultra-violet parts of the spectrum. The method depends upon the use of a powerful flash, of energy up to 10,000 J, as a photochemical source: it is, in fact, a means of 'exploding' photons into a system. The flash is obtained by discharging a bank of condensers through an inert gas such as argon or krypton.

Its spectrum is largely continuous, and it is capable of causing a very large measure of decomposition and free radical production in suitable photochemically reactive species, such as Cl₂, NO₂, CH₂CO, CH₃CO CH₃, at pressures around 10 m.m. The photographic record of the absorption spectra of the free radicals so produced is rendered possible by the use of a spectroscopic source, in principle similar to the photolysis source, capable of giving a flash with an approximately continuous spectrum in the visible and ultra-violet as far as 2,200 A°, of duration 0.05 m. sec. By means of electronically controlled triggers the time interval between the photoflash and the spectroflash may be controlled and varied with microsecond precision. In this way, by observation of the relevant absorption spectra and their change with time, short lived intermediate radicals participating in reactions may be detected, and their lifetimes determined accurately. Reaction processes complete within a few milliseconds can be readily followed.

The method has recently been applied by Norrish and his co-workers ³⁸ to a study of the intermediates involved in certain explosions, such as those of hydrogen with oxygen and acetylene with oxygen. In the former explosion reaction direct experimental evidence has been obtained for the existence of the reactions:

 $\begin{array}{rcl} H_2 &+ & O &= & OH &+ & H \\ OH &+ & H_2 &= & H_2O &+ & H \end{array}$

These had previously been postulated in 1946 by Lewis and Von Elbe.³⁶ In the ¹atter

explosion reaction between hydrogen and acetylene there are now good grounds for postulating contributory mechanisms of the following kind:

$$\begin{array}{rcl} OH &+& C_2H_2 &=& CH &+& CH_2O\\ CH &+& O_2 &=& CO &+& OH \end{array}$$

Furthermore, strong evidence for the preferential burning of carbon in equimolecular mixtures of acetylene and oxygen ³⁷ has been obtained.

These are but typical examples to illustrate the potentialities of the method, which provides the only really satisfactory way of elucidating free radical reactions in those complex explosive phases of combustion which have hitherto not been amenable to direct kinetic measurement.

(b) Free radicals and mass spectrometry.

During the past 10 years a number of studies of reaction intermediates in gaseous reactions have been made using mass spectrometers.³³ For the detection of radica's by this means use is made of the fact that the ionisation potential of a free radical is less than its appearance potential from a given compound. By a careful selection of the energy of the electrons used in the initial impact process, so that it is intermediate between the ionisation and appearance potentials of the radical, the original presence of the latter may be demonstrated. However, because of the low ionisation efficiency at such electron energies, the method in this form has been qualitative only. Recently it has been put on a more quantitative basis by Lossing, Ingold and Tickner. *5 These workers use the method outlined above for the qualitative detection and then proceed to make quantitative estimates of the radical concentration by measuring the mass spectra when a relatively high electron accelerating potential of 50V is used. Under these conditions the ionisation efficiencies are much more satisfactory and, in addition, almost independent of small changes in the electron energy. Thus a peak height may obtained which is a reasonably accurate measure of the partial pressure of the radical.

Use of this technique to determine the extent to which free radicals play a part in the thermal decompositions of ethylene oxide, propylene oxide, dimethyl ether, and dioxane has been described. With ethylene oxide it was found that each molecule decomposing gave rise to about 0.6 methyl radicals and in propylene oxide the corresponding number was about 0.36. Methyl radicals were also abundant in the decomposition of dimethyl ether, but in the decomposition of dioxane only a small number of methyl radicals were found, and these probably came from a secondary reaction. No other radicals were detected. The thermal decomposition of mercury d'methyl and di-tert-butyl peroxide have also been studied recently in this way by Lossing and Tickner.³⁹

(c) Studies based on the conventional photolysis technique.

A variety of recent contributions which may be included under this heading were reported at the Faraday Society Meeting. Majury and Steacie ³⁵ have studied the reactions of hydrogen and deuterium in the range 130-300° with CH₃ and CD₃ radicals prepared by the photolysis of the appropriate acetone. The energies of activation of the four reactions have been shown to lie in the range 9—12 k.cal. The steric factors are of the order of 10⁻⁸, and are thus considerably lower than the value of 0.1 which has frequently been assumed in the past. ⁴⁰

The activation energies for the reactions of the radicals with hydrogen are about 1.6 k.cal. less than those with deuterium, and this supports the theory ⁴¹ which predicts that at low temperatures the difference in activation energies for reactions at isotopic molecules should approach the difference in their zero-point energies, which in this case is 1.8 k.cal.

Using hydrogen (or deuterium) atoms produced by the photo-chemical decomposition of H_aS (or D₂S) Darwent and Roberts³⁵ have investigated the rates at which these atoms abstract hydrogen from ethane, propane, *n*- and *iso*-butane, ethylene, propylene and 2-butene. Their results show that the activation energy for the abstraction reaction from parafins: D + RH \rightarrow HD + R decreases in the order ethane>propane>isobutane. With the o'efines, propylene and 2-butene, the activation energy does not appear to vary significantly. The magnitude and nature of the steric factors are discussed.

Blacet and Bell³⁵ have reported some interesting preliminary observations concerning the mechanism and reaction products of the photochemical decomposition of biacetyl. The experimental results may be interpreted in terms of the following series of secondary reactions:

 $\begin{array}{rcl} \mathrm{CH}_{3}\mathrm{CO} & \rightarrow & \mathrm{CH}_{3} + \mathrm{CO} \\ \mathrm{CH}_{3} + \mathrm{CH}_{3}\mathrm{CO} & \rightarrow & \mathrm{CH}_{3}\mathrm{.CO.CH}_{3} \\ & 2 \ \mathrm{CH}_{3} & \rightarrow & \mathrm{C}_{2}\mathrm{H}_{6} \\ \mathrm{CH}_{3} + \mathrm{CH}_{3}\mathrm{CO}\mathrm{.CO.CH}_{3} & \rightarrow \\ & & \mathrm{CH}_{4} + \mathrm{.CH}_{2}\mathrm{CO}\mathrm{.COCH}_{3} \\ \mathrm{CH}_{3}\mathrm{CO}\mathrm{.CO.CH}_{2} & \rightarrow & \mathrm{CH}_{3}\mathrm{CO} + \mathrm{CH}_{2}\mathrm{CO} \\ \mathrm{CH}_{3} + \mathrm{CH}_{3} \ \mathrm{CO}\mathrm{.CO.CH}_{3} & \rightarrow \\ & & \mathrm{CH}_{3}\mathrm{COCH}_{3} + \mathrm{CH}_{3}\mathrm{CO} \\ \mathrm{CH}_{3} + \mathrm{CH}_{3}\mathrm{CO}\mathrm{.COCH}_{2} & \rightarrow \\ & & \mathrm{CH}_{3}\mathrm{.COCH}_{3} + \mathrm{CH}_{3}\mathrm{CO} \\ \mathrm{CH}_{3} + \mathrm{CH}_{3}\mathrm{CO}\mathrm{.COCH}_{3} & \rightarrow \\ & & \mathrm{CH}_{3}\mathrm{.CH}_{2}\mathrm{.CO.CO.CH}_{3} \end{array}$

Photochemical reactions of diethyl ketone with oxygen have been studied by Finkelstein and Noyes³⁵ and various possibilities for the reaction of ethyl radicals with oxygen are discussed. Dacey³⁵ has investigated the photolysis of trifluoromethyl iodide. The quantum yield of the overall process varies from 0.02 to 0.13; it is increased by the presence of both nitric oxide and silver.

It appears that the division of the molecule into a trifluoromethyl radical and an iodine atom has an efficiency of unity and that the low overall efficiency is caused by the reverse reaction. Melville, Robb, and Tutton³⁵ have measured the reactivities of unsaturated compounds toward the addition of a trichloro-methyl radical produced by the photolysis of bromo-trichloromethane.

(d) Free Radicals and Reactions in Solution.

An interesting aspect of free radical reactions in solution is the possibility of initiating such reactions by heavy metal ions. It is well known that the salts of the heavy metals catalyse a wide variety of reactions in which molecular oxygen takes part. For example, as Bawn³⁵ has pointed out, the autoxidation of saturated and unsaturated hydrocarbons, aliphatic and aromatic aldehydes, the degradation of high polymers, the drying of oils and, in biochemistry, the transformation of oxygen, all depend upon such heavy metal catalysis.

The precise formulation of mechanisms for these reactions is not only of academic interest, but also of great technical importance. For example, in the oxidation of saturated and unsaturated hydrocarbons it is common industrial practice to employ the catalyst in the form of a salt of ill-defined constitution, such as naphthenate, resinate or metallic soap, largely for practical reasons of solubility in organic media. As a consequence, the exact function of the catalyst is rarely, if ever, clearly understood.

With a view to elucidating such questions, Bawn and co-workers³⁵ have recently studied the catalysis, by the cobaltic ion, of the autoxidation of several hydrocarbons and aldehydes. It has been found that in the autoxidation processes the chain is initiated by an electron transfer reaction of the cobaltic ion either with the reactant or with a small amount of thermally formed These results have been hydroperoxide. applied to the kinetics and mechanism of the catalysed autoxidations. The related problem of the oxidation of benzene by hydrogen peroxide and iron salts has been tackled by Baxendale and Magee.35 A quantitative determination of the products of the reaction has shown that only phenol and diphenvl are formed. The variation of the amounts of these products in different conditions indicates that the phenyl radical does not react with hydrogen peroxide, but may be reduced by ferrous ion to benzene and oxidised by ferric ion to phenol. It is possible that all the phenol is produced by the latter reaction, and not by the combination of phenyl and hydroxyl radicals, as hitherto assumed.42

Two Aspects Discussed

Two aspects of the catalysis of liquid phase olefinic autoxidations have been discussed by Bateman, Hughes and Morris.³⁵ These are: (a) hydroperoxide catalysis at concentrations around 0.02M; (b) the relationship between the kinetic form of the initiating process and the mechanism of hydroperoxide decomposition in vacuo. The authors find: (1) that in the very early stages of the reaction the rate of oxidation is proportional to the square root of the hydroperoxide concentra-This implies that the initial generation tion. of free radicals is by a first-order process which is subsequently replaced by a secondorder process in the concentration region where direct proportionality to the hydroperoxide concentration prevails; (2) that the kinetics of thermal decomposition of a typical alkenyl peroxide at concentrations greater than 0.02M are consistent only with a second-order primary radical-producing This is in agreement with the reaction. of its catalytic kinetic requirements behaviour.

Other liquid phase reactions which have been studied include: (1) the photo-oxidation of anthracenes and the photochemical reaction of anthracene with carbon tetrachloride by Bowen and co-workers; (2) the kinetics of the reactions between cumene hydroperoxide and polyethylene polyamines in aqueous solution by Orr and Williams; (3) the co-polymerisation of styrene and maleic anhydride by Bamford and Barb; (4) homolytic substitution by phenyl radicals in aromatic solvents like fluorohenzene, chlorobenzene, nitrobenzene and so on, by Hey and Williams. Finally, the instability of large polymeric free radicals has been discussed by Dainton and Ivin in terms of the heat content and free energy changes involved in the breakdown processes. All these contributions are included under reference.35

(e) Some miscellaneous studies.

Herzberg and Ramsay³⁵ have shown that the so-called α -bands of ammonia which occur in emission in electric discharges through ammonia, in oxyammonia and other flames, and in the spectra of comets, are definitely due to the free NH₂ radical. This is in itself an important advance, and, in addition, it means that these α -bands may now be used as a relative measure of NH₂ concentration in chemical reactions.

An old problem, that of the mode of action of lead tetraethyl as an inhibitor of combustion processes, has been reviewed and re-examined in the light of new experiments by Chamber'ain, Hoare and Walsh.²⁵ These recent experiments indicate that: (1) lead tetraethyl, on oxidation, first forms PbO as a colloidal fog; (2) lead tetraethyl almost certainly inhibits by virtue of forming PbO; (3) PbO is an inhibitor because it causes a surface destruction of chains.

An interesting improvement of the electric discharge method for the production of hydrogen and deuterium peroxides has been described by Giguère, Secco and Eaton.³⁵ These authors have achieved a 30-fold increase in the yield of hydrogen peroxide over the highest ones previously reported.⁴³ The success of their method depends upon the use of much higher pumping speeds than previously used and a high frequency (20 Mc./sec.) electrodeless discharge.

(3) THERMOCHEMISTRY

Under this heading may be included the following: thermodynamics of surfaces and adsorbed phases; thermodynamics of polymers; thermodynamics of solutions, new thermochemical data. All of these topics have recently been surveyed by Newton," but the last one is worthy of further discussion even at this stage, for there have been reported during the past year a variety of new thermochemical data and some interesting developments in techniques. The latter are dealt with first, and a brief selection of the recent results are discussed later.

(a) New Techniques

The present position with regard to these was discussed at the seventh annual calorimetry conference held recently at the U.S.A. National Bureau of Standards Laboratory, Washington.

Among the topics included on the programme were: 'A Combustion Technique for Moderately Volatile Compounds,' by G. S. Parks and K. Manchester; 'High Temperature Drop and Adiabatic Ca'orimetry' by T. B. Doug'as; 'A Rotating Bomb for Precision Calorimetry' by W. N. Hubbard; 'A Microca'orimeter for Heat of Solution Measurements' by E. F. Westrum; 'Recent Work in Flow Calorimetry' by J. F. Masi; 'Electronic Thermoregulators' by D. C. Ginnings: 'Standard Reference Substances for Use in Calorimetry' by G. Waddington.

Unfortunately a full report of these discussions has not yet been published, and hence only those contributions which have been privately communicated to the writer can be briefly mentioned. Of these one of the most noteworthy concerns the adoption of the 'moving bomb' technique in the determination of the combustion heats of sulphur containing molecules.

Highly Successful Procedure

As is well known, highly successful procedures for obtaining accurate heat of combustion data for C, H, O, and C, H, O, N. compounds have evolved during the past twenty years. On the other hand, the position has long been unsatisfactory for compounds containing sulphur or the halogens, and this is reflected in the paucity of reliable data on such compounds. The chief problem involved is that of devising equipment and techniques capable of yielding a thermodynamically definable end state in the bomb. When compounds containing sulphur are burned in oxygen the sulphur appears in the products of combustion in both its tetra- and hexavalent states. This mixture is unstable and impossible to define. It is usual practice to direct the oxidation so that sulphuric acid alone is formed, but, even then, a problem remains, for the concentration of the acid formed varies throughout the bomb.

Since 1934 efforts have been made to burn sulphur-containing compounds in ways that would avoid such difficulties and yield accurate results. Becker and Roth 45 burned some sulphur containing compounds in a bomb to which 10 ml. of water had been added. After the combustion they made corrections for the difference in concentration of sulphuric acid in various parts of the bomb. It is probable, however, that this method does not give results of high accuracy, because equilibrium with respect to the solution of the bomb gases in the final solution is not established. In 1935 Huffman and Ellis⁴⁶ developed a method in which no liquid water is added to the bomb. They assumed that sulphuric acid was formed in the combustion process as a mist, and condensed at a uniform concentration in various parts of the bomb. Recently Sunner⁴⁷ and Hubbard et al.48 have shown that the concentration of sulphuric acid varies enough in different parts of the bomb to lead to serious errors.

Significant Attempt

The first really significant attempt to get over these difficulties by using a relatively large amount of water in a rotatable bomb is due to Sunner and co-workers.49 Immediately after the ignition, the bomb is rotated, and in this way homogeneity in the final state of the combustion process is achieved. The method has many possible applications to other combustion studies. such as those relating to halogen containing compounds, and it has been further developed recently by Hubbard, Katz and Waddington⁵⁰ at the Bureau of Mines, Oklahoma, U.S.A. These authors have determined accurate values for the heats of formation of several thiols and sulphur derivatives of Their work is within the hydrocarbons. framework of the American Petroleum Institute Research Project 48A on 'The Production, Isolation and Purification of Sulphur Compounds and Measurement of their Properties."

Another elegant development in calorimetric technique is the new twin microcalorimeter described by Evans and Richards.⁵¹ With it differential or direct heats of solution may be measured very accurately. The calorimeter is vacuumand pressure-tight, and the solutions come into contact with glass surfaces only.

(b) Some Recent Thermochemical Data.

Among the new data published during the year there are several of some industrial importance. Thus, R. B. Pepp'er and E. S. Newman⁵² have determined the heats of formation of several barium aluminates. Newman and L. S. Wells⁵³ have E. S. measuremethods for the described heat of ment of the approximate solution in acid of portland cement-pozzolan Furthermore, the authors have mixtures. shown how determinations of the amount of material undisso'ved in the calorimeter may be used, in conjunction with the heats of solution, to determine the composition of mixtures of portland cement and pozzolan. R. A. Nelson, R. S. Jessup and D. E. Roberts⁵⁴ have determined the heats of copolymerisation of butadiene and styrene from measurements of the combustion heats of polybutadiene and four co-polymers of butadiene and styrene. W. H. Evans and D. Wagman⁵⁵ have calculated several of the thermodynamic functions for gaseous sulphur, sulphur monoxide, sulphur dioxide, sulphur trioxide, and hydrogen sulphide.

Values of the heats of formation of the various atomic and molecular species have been selected from published experimental data and certain industrially important equilibria calculated.

Of more direct academic interest are the contributions which follow. R. A. Nelson and R. S. Jessup⁵⁶ have measured the heat of combustion of ethyleneimine, and, by combining the result with data on the heats of formation of gaseous carbon dioxide and liquid water, the heat of formation of liquid ethyleneimine has been obtained. P. Bender and J. Farber⁵⁷ have measured the heats of combustion of anthracene trans-annular peroxide and dianthracene. The thermodynamic properties of thiapentane and furan have been determined accurately by a team of workers at the U.S. Bureau of Mines.55 properties measured or computed The include heat capacities, heats of fusion and vaporisation, vapour pressure, entropy, heat of formation and thermodynamic functions. These investigations were carried out as part of the work of the American Petroleum Institute Research Project 48A (see above).

By the method of electron impact, Franklin and Lumpkin⁵⁹ have determined the heats of formation of the SH, CH₃S and C₂H₅S radicals. From the values obtained and known thermodynamic data several C-S.

H-S, and S-S bond strengths in alkyl sulphur compounds have been calculated. The appearance potentials of the CH₃S⁺ and C₂H₅S⁺ ions have also been measured, and the heats of combustion of t-butyl mercaptan and dimethyl- and diethyl-disulphide have been determined approximately.

Following up the work of Mackle and Ubbelohde.⁶⁰ Nichol and Ubbelohde⁶¹ have different re-evaluated $D(CH_3 - I)$ by a thermochemical cycle. Their results overlap the earlier value, which has also been supported recently by the elegant work of Carson, Carson and Wilmshurst.62 These latter authors have determined the heats of formation of mercury dimethyl, diethyl and diphenyl, and several associated bond dissociation energies. Skinner and co-workers63 have made valuable contributions to the thermochemistry of organo-arsenic and organo-boron compounds.

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Progress in Analytical Chemistry, 1952

by A. J. NUTTEN, B.Sc., Ph.D., A.R.I.C.

THE trend in recent years has been main-L tained during 1952, namely, the development of analytical methods that are both rapid and accurate. Despite the everincreasing importance of physical methods of analysis, more than half the papers published during the past year relate to titrimetric methods of analysis, although physical procedures still continue to supplant classical methods. It would be impossible in a review of this nature to survey the whole gamut of analytical chemistry. The collective reviews which appear annually in the January and February numbers of Analytical Chemistry admirably provide this service. and the Annual Reports of the Chemical Society now present a similar, but much less comprehensive survey of the numerous fields of analytical chemistry. It is the intention of the present reviewer to discuss certain discrete topics in somewhat more detail than is possible in the above reviews.

TITRIMETRIC ANALYSIS

Szabó and Sugar¹ re-examined the use of stannous chloride as a reductimetric reagent. They successfully overcame the long-standing storage problem associated with this particular reagent, and developed a general reductimetric method for the determination of various substances whose redox systems had potentials greater than 0.3V., e.g. iron (3) vanadate, dichromate, iodate, bromate, ferricyanide and iodine. The 0.1N stannous chloride solutions used in these determinations could be stored for some months with no significant change in titre. by using an automatic device for supplying carbon dioxide to the storage flask and burette.

Szabó, in collaboration with Bartha,² described a copper-catalysed alkalimetric determination of nitrate ions. In slightly alkaline solution ferrous hydroxide reduced nitrate ions to ammonia, with copper sulphate as catalyst for the reaction. The reduction was quantitative, and, by means of a steam distillation technique, a determination could be carried out in less than 10 minutes. The only interferences were from antimony (5), antimony (3) and arsenic (3).

Chloride was determined mercurimetrically with diphenylcarbazide disodium sulphonate as indicator. Parsons and Yoe³ added ferric nitrate to form the carbazone and an inert green substance to serve as a colour screen, and obtained a sharp and reversible end-point changing from green to purple via an intermediate grey.

Use of Ceric Salts

An extensive and critical survey of the use of ceric salts in titrimetric analysis was made by Miss Young.4 The steadily increasing uses for ceric solutions in analysis made such an investigation desirable. Also of importance was the related research of finding reverisble high oxidation potential indicators for use with ceric solutions, as well as the commercial production of ceric compounds from which to prepare these solutions. Both these phases of cerate oxidimetry were discussed in detail in the paper. The wide range in oxidising potential of the ceric-cerous system with variation in the ceric salt used and in the acid medium for the titration made these salts unique among oxidising agents. Their great stability in solution even at considerable dilution was also of importance.

A study of the use of trivalent manganese as an oxidimetric reagent was made by Belcher and West.³ The notoriously unstable manganic ion was stabilised with pyrophosphate and the stabilised reagent remained unchanged in titre over a 6-week period. The reagent was successfully applied to the titration of ferrous iron, even in the presence of 5N hydrochloric acid, and to the titration of arsenite vanadate and peroxide. The redox potential of the reagent is 1.22 V at 25°C. Unlike permanganate, the reagent is not sufficiently highly coloured to act as its own indicator.

Hitherto the reductimetric determination of tellurous acid involved the use of reagents unstable in air, viz., chromous and titanous salts. Johnson and Fredrickson⁶ described a direct thiosulphate method for this determination, the reaction being induced by the addition of iodide ions to form the iodotellurite complex. The most satisfactory results were obtained by adding an excess of thiosulphate and back-titrating with standard iodine solution. Szabó and Csányi⁷ have determined as little as 0.1 mg. of bromide by oxidation with chlorine at pH 6.5-7.5 to bromine pentachloride, followed by hydrolysis to bromate at pH 8.5-9 and iodometric titration of the latter. In addition to oxidising substances only mercuric and molybdate ions interfered, but these interferences could be eliminated.

Belcher, Nutten and Stephen⁸ have described the titration of small amounts of gallium with potassium ferrocyanide using 3,3'dimethyl naphthidine and its disulphonic acid as internal indicators. Accurate results were obtained on 0.74-2.94 mg. of gallium with an average error of \pm 0.25 per cent.

Sulphonic Acid Derivatives

The same workers⁹ prepared the sulphonic acid derivatives of naphthidine and 3,3'dimethylnaphthidine and used them as indicators in the titration of zinc and cadmium with ferrocyanide, vanadic acid with ferrous iron, and ferrous iron with dichromate and ceric sulphate. In the presence of oxidising agents and in acid solution the indicators were converted into intense red to red-violet The 3.3'-dimethylnaphthidine compounds. sulphonic acid was much more stable in its oxidised state than the corresponding naphthidine derivative. Belcher, Nutten and Stephen¹⁰ determined the transition potentials of these new sulphonic acid derivatives and their parent bases by comparison with the molar electrode potentials of the ferrousferrie and dichromate-chromic systems, in various concentrations of acid. The values obtained for naphthidine, 3,3'-dimethylnaphthidine, and their sulphonic acids respectively were 0.800, 0.706, 0.840 and 0.800 V in molar sulphuric acid.

Milner¹¹ used naphthidine as an indicator in the determination of zinc in various nonferrous alloys and rubber ashes, using the procedure originally described by Belcher and Nutten.¹²

Lederer and Ward¹³ studied the oxidation of the three tolyl anthranilic acids with a view to applying them as indicators in redox titrations. They found that the ortho derivative was the only one suitable as a redox indicator, its oxidation being a reversible reaction, yielding relatively stable products. The purple colour produced on oxidation was almost identical with that of oxidised phenyl anthranilic acid.

Several microtitrimetric procedures were published in 1952. Flaschka¹⁴ reduced the macro-scale complexometric methods of Schwarzenbach to the micro-scale, and in addition published indirect methods for the determination of sodium,¹⁵ phosphate,¹⁶ silver and halogens¹⁷ and thallium,¹⁸ with ethylenediamine tetra-acetic acid as titrant. These last three methods are of interest only from the academic viewpoint and are not likely to supplant the more direct and more rapid procedures available for these radicals.

The micromanganimetric titration of iron was described by Alvarex Querol.¹⁹ No new principle was involved. The iron was reduced to the ferrous state by means of a stannous chloride or metal reductor technique, and the ferrous iron titrated with potassium permanganate in hydrochloric acid in the presence of a preventative solution using o-phenanthroline as indicator.

Dunicz and Rosenquist²⁰ determined milligram amounts of sulphide ion by oxidising to sulphate at room temperature with 0.01M potassium hypochlorite followed by iodometric determination of the latter. Good results were reported over the range 0.6-3.2 mg. of sulphide. The method is applicable to the analysis of any sample from which hydrogen sulphide can be obtained and absorbed in potassium hydroxide solution.

Milligram amounts of vanadium in the presence of a 5,000-fold excess of uranium have been determined with considerable accuracy. Simonsen²¹ formed the cupferrate of vanadium, extracted with chloroform and, after evaporation with sulphuric, nitric and perchloric acids, the vanadate in the residue was reduced with ferrous ammonium sulphate. The excess ferrous was oxidised with ammonium persulphate and the tetravalent vanadium was determined with N/50 permanganate solution.

ORGANIC ANALYSIS

De Vries and van Dalen²² eliminated certain of the drawbacks caused by the incomplete combustion during the determination of carbon and hydrogen by a horizontal empty tube technique. They heated part of the tube electrically and eliminated any possibility of explosions by spark ignition of the vapours during gasification. The authors appeared to be unaware of the more recent work by Belcher and Ingram,23 who designed a special upright combustion tube in which the problem of incomplete combustion did not arise. The latter authors extended this rapid upright tube combustion process to the determination of sulphur and halogens in organic compounds.²⁴ The apparatus was similar to the original except that the preheater and scavenging systems, which were no longer necessary, were omitted, and a bead absorber was included in place of the horizontal outlet section of the combustion tube (Fig. 1).

It is generally known that the combustion organic compounds containing alkali of metals leads to the formation of stable a'kali carbonates, with the result that some of the carbon does not reach the absorption tube. The usual method of displacing the carton dioxide is to treat the sample with potassium dichromate or vanadium pent-Sirotenko²⁵ showed that potassium oxide. persulphate could be used with advantage instead of these two substances. Thus, in addition to its desirable oxidising action, potassium persulphate could supply the sulphur trioxide necessary for the displacement of carbon dioxide.

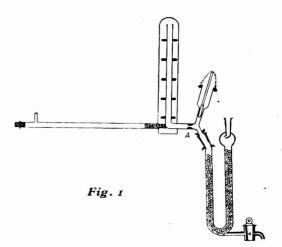
McCutchan and Roth²⁶ found that when a nitrogen-containing organic compound was preheated with thiosalicylic acid, the conversion of nitrogen to ammonia, in the Kjeldahl procedure, was facilitated, and indeed nitrogen in nitro compounds could be determined satisfactorily and rapidly.

Arsenic in organic nitrogen compounds of the guanidino type was determined by Stickler.²⁷ The compound was oxidised with concentrated sulphuric and nitric acids, followed by reduction with hydrazine sulphate and subsequent titration of the trivalent arsenic formed with standard bromate solution.

Unterzaucher²⁸ presented a historical survey of the direct micro-determination of oxygen in organic substances using the principle of reduction with carbon, and detailed the micro method developed by him in 1940, with consideration given to long years of experience in daily operation. This paper must rank as one of the most valuable contributions to the field of organic micro-analysis.

Fluorine Inorganic Compounds

The determination of fluorine in organic compounds is of particular interest in view of the growing importance of these substances. Belcher, who has already described methods for the determination of carbon and hydrogen and of fluorine itself in organic fluoro compounds, collaborated with Caldas and Clark²⁹ and extended the latter procedure to compounds containing bromine, iodine, sulphur, phosphorus and arsenic.



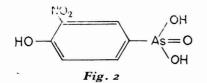
The original methods, viz., gravimetric determination of fluorine as lead chlorofluoride, could be operated without modification in the presence of bromide or iodide, but in the presence of sulphate, phosphate and arsenate, a modified procedure had to be applied, viz., precipitation with lead nitrate instead of lead chloride and titration of the halide in the lead chlorofluoride precipitate by the well-known Volhard procedure.

ORGANIC REAGENTS

Malissa and Miller³⁰ made an extensive study of the reactions of metal ions with disubstituted dithiocarbamates, including the determination of the sensitivities of the reactions and to what extent they were suited to serve as the basis of quantitative separations Excellent possibilities for many separations were offered by these reagents. which had several additional advantages. Thus, the reagents were easy to prepare and, in most instances they yielded crystalline salts. The metal dithiocarbamates also exhibited characteristic colours in some cases.

A promising new reagent for tin (4) is 3-nitio-4-hydroxybenzene arsonic acid (Fig. 2). Karsten, Kies and Walraven³¹ determined as little as 0.1-0.2 mg. of tin in the presence of 1,000 times as much antimony. The method was based on the turbidity given by tin (4) and the reagent. The reagent was found to be highly selective, only zirconium and titanium (4) interfering.

Figgis and Gibson³² examined a number of quaternary arsonium iodides as possible reagents for antimony. One, triphenymethylarsonium iodide, was found to be



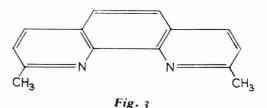
' suitable for the colorimetric microdetermination of this metal, the procedure finally adopted determining 10 to 100 μ g. of antimony per ml., with an accuracy of about 2 per cent.

The complex-forming properties of several Group II elements have been examined and as a result new organic reagents have been proposed. Smith and McCurdy³³ synthesised the compound 2,9-dimethyl-1,10-phenanthroline (Fig. 3) and found that it was sensitive to 1 part of copper in 1,660,000 and was. moreover, specific for that element. The reagent could be used with advantage instead of 2,2-diquinolyl, because it was stable for extended periods and the maximum absorption (454 m μ) occurred over the wide pH range 3-10.

Small amounts of copper in dyes and rubber chemicals were determined colorimetrically by Martin and Githins³⁴ using the zinc salt of dibenzyl dithiocarbamate as reagent. The corresponding sodium diethyl compound, generally used, was found to be unstable in acid solution.

Walter and Freiser³⁵ described the use of 2-(o-hydroxyphenyl)-benzoxazole (Fig. 4) as a reagent for the gravimetric determination of cadmium. They determined 1-80 mg. of cadmium with an accuracy of 0.3 mg. by precipitating at pH 10.5 in a tartrate buffer. Virtually all interferences were eliminated in this way.

Phenyl boric acid precipitates mercury (2) as white, sparingly soluble mercury diphenyl [(C₆H₅)₂ Hg]. Holzbecher³⁶ carried out the precipitation in a solution buffered with sodium acetate solution, dried the precipitate at 70°C, and weighed in vacuo. Nitrate. sulphate, tartrate or citrate did not interfere under the conditions of the precipitation. nor did chloride, bromide or thiocyanate when precipitation was effected in ammonia-The same worker suggested cal solution. the use of the phenylhydrazone of pyruvic acid for the detection of mercury (2). In neutral or slightly acid solution, mercury (2) gave a blue-violet precipitate soluble in organic solvents to give a reddish-brown solution. Cadmium and zinc salts appeared



to accelerate the reaction, while trivalent gold salts interfered; tetravalent elements decreased the sensitivity.

Hall^{at} critically examined existing methods for the determination of small amounts of bismuth in lead, and proposed a new method based on the separation of bismuth from lead by co-precipitating the bismuth with manganese dioxide in dilute nitric acid solution, the *p*H of which was adjusted to between 1.0 and 1.7. After dissolving the precipitate and evaporating the solution to dryness, the bismuth in the residue was determined colorimetrically with thiourea. Results were satisfactory with bismuth concentrations of 0.01-0.12 per cent, the mean error being not greater than 3 per cent.

Colorimetric reagents for zinc included o-[α -(2-hydroxy-5-sulphophenlazo) benzylidene-hydrazino] benzoic acid, proposed by Yoe and Rush.³⁸ The reagent gave a dark blue complex with zinc ions, but copper. iron, cobalt and nickel gave a similar reaction.

Jean³⁹ studied the behaviour of various barbiturates towards cobalt. Several of these compounds gave colours with divalent cobalt and isonitroso malonyl guanidine was finally proposed as a satisfactory reagent for the determination of cobalt in ferrous metals, especially in high speed steels. Another member of the phenanthroline series. 4,7-diphenyl-1,10-phenanthroline (Fig. 5) was reported by Smith, McCurdy and Diehl⁴⁰ to give a colour reaction with 1-10 µg. of iron (2) in 100 ml. of water. The reagent was ideally suited for the ultramicrospectrophotometric determination of iron in raw and treated municipal water supplies.

The now well-known colour reaction between calcium and ammonium purpureate, which was discovered many years ago by Beilstein, was applied by Osterlag and Rinck⁴¹ to the colorimetric determination of calcium. Strontium gave a similar colour.

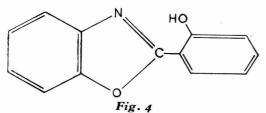
Methods were described for the detection or determination of the so-called rare metals:—molybdenum, titanium, zirconium. thorium and palladium. Yoe and Will⁴² proposed the compound Tiron (disodium-1,2dihydroxybenzene-3,5-disulphonate) for the detection of hexavalent molybdenum. The reagent gave a bright yellow colour with as little as 1 part of molybdenum in 10,000,000 parts of solution.

The yellow colour given by ascorbic acid and titanium conforms to Beer's Law over the range 0.1-25 p.p.m. of titanium, and Hines and Boltz⁴³ used this colour reaction for the spectrophotometric determination of the element. Ovenston and his co-workers⁴⁴ determined traces of titanium using chromotropic acid as reagent, and carried out a detailed investigation of the reaction. Trace amounts of the related metal zirconium were rabidly determined by Oesper, Dunleavy and Klingenberg⁴⁵ using derivatives of azomandelic acid as reagents.

A satisfactory method for the determination of thorium in magnesium base alloys was developed by Mayer and Bradshaw:⁴⁶ a 0.1 per cent solution of the disodium salt of 1 - (*o*-arseno-phenylazo)-2-naphthol-3.6-disulphonic acid gave a red colour with thorium. Zirconium interfered in the determination, but the thorium could be separated as oxalate before addition of the reagent.

Venkataramaniah, B. Rao and C. Rao⁴⁷ succeeded in separating thorium from the rare earths of monazite and from uranium by precipitation with *m*-cresoxyacetic acid and igniting the 'precipitate to thoria. 0.2 Mg. of thoria could be determined with accuracy using this procedure.

o-Phenanthroline, now one of the best available methods for the colorimetric determination of iron (2), was used by Ryan⁴⁸ as a reagent for the microgravimetric determination of palladium and for the separation of palladium from platinum. The precipitate was of constant composition and was weighed as the complex Pd.C₁₂H₈N₂Cl₂. A double precipitation was necessary to effect an uncontaminated separation of palladium from platinum and iridium, but a single precipitation permitted a complete separation from rhodium.



Freiser⁴⁰ who in the first paper of an intended series reported the results of a study of the structure and stability of chelates that are of analytical significance. He determined the acid ionisation constants, in 50 per cent dioxan solution at 50°C., of a number of well-known organic reagents. He also determined the chelate formation constants of the compounds formed with these reagents and various cations, and discussed the significance of these constants with respect to the selectivity of these reagents.

Mention must be made of the work of

MISCELLANEOUS

Calcium acid malate hexahydrate was proposed as a primary standard by Shead.⁵⁰ The substance had a comparatively high equivalent weight (207.143), always an advantage, and could be applied as a primary standard in alkalimetry, calcium chelatometry and the calibration of pH meters.

Quill and Salutzky⁵¹ quantitatively separated praseodymium from lanthanum by precipitation as carbonate from homogeneous solutions containing the trichloroacetate ion.

In a further paper describing their studies in the separation of phosphate in elementary qualitative analysis, Nutten and Stephen⁵² reported a new rapid method for the preparation of the reagent. N-Butyl titanate dissolved in nitric acid of the appropriate strength provided a reagent of accurately known titanium content, which could be readily prepared without the intermediate preparation and subsequent filtration of *ortho*titanic acid, as was necessary in the earlier method.

The reaction:-

 $Fe^{++} + Cu^{++} + 7CNS^{-} \rightleftharpoons$

$$[Fe(CNS)_6]^{---} + CuCNS$$

goes completely from left to right when sufficient thiocyanate is present to satisfy the needs of the equation. Belcher and West⁵³ used this fact, proved thermodynamically by them in an earlier paper, as the basis of a new method for the gravimetric determination of copper as cuprous thiocyanate. They used ferrous ammonium sulphate to reduce the copper to the cuprous state. When the

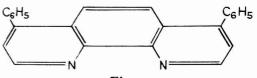
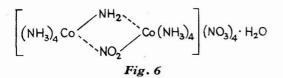


Fig. 5



amount of copper was unknown, the indicator properties of the ferrithiocyanate complex provided a useful means of estimating the correct amount of thiocyanate to add.

Several papers were published during the year dealing with various aspects of steel analysis. A valuable contribution to this subject was the work of Pemberton⁵⁴ on the separation and analysis of metallic carbides from steel. A technique for isolating the carbide phase from solutions of highly alloyed steels was first described, and then the individual methods for determining the elemental composition of separated residue were given. The steel specimen was anodically decomposed in a citric acid-potassium iodide e'ectrolyte, a residue of carbides remaining. The residue was collected and analysed by semimicro analytical methods. The author described procedures for the determination of carbon, manganese, chromium. vanadium, molybdenum, tungsten, titanium, columbium and iron in the residue. The determination of sulphate has always been one of the major problems in analytical chemistry. The classical method, precipitation as barium sulphate, is subject to coprecipitation errors. In particular, the nitrate ion interferes and must be removed. Mahr and Kraus⁵⁵ determined sulphate as the sparingly soluble complex hexa-amminocobaltic bromide sulphate, but little confirmatory information is available on this Belcher and Gibbons58 examined method. five co-ordination compounds of cobalt as precipitants for the sulphate ion, and developed a new gravimetric procedure for the determination of sulphate using one of these compounds, octa-ammino-µ-amino-µnitro-dicobaltic nitrate (Fig. 6), as reagent. The method has the advantages that interferences are few, and, in particular, the nitrate ion has no effect.

Two interesting papers appeared which added to the information available on buffer solutions. Freiser and Dessy⁵⁷ pointed out that it was of interest to those who used buffer solutions to know just how much acid or base a buffer could absorb before a given pH change occurred. They described a rapid and reliable technique for obtaining this information. Hahn⁵⁸ showed that the buffer capacity of a solution, exactly titrated to equivalence, could be calculated from the equilibrium constant of the titrating reaction. Hahn was thus able to establish a theory of 'endpoint sharpness,' applicable universally to the different classes of titrations (acidimetre, redox, precipitation, etc.). The results were formerly derived from the study of the titrated solution further off the equivalence point.

Finally, mention may be made of an invaluable critical review by Atkinson. Steigman and Hiskey⁵⁹ of the main separative reactions employed in the analysis of tantalum and columbium.

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A Year of Organic Chemistry

by J. R. MAJER, M.Sc., Ph.D., A.R.I.C., D.I.C.

CONSIDERABLE proportion of the A research in organic chemistry carried out during 1952 was devoted to the isolation. identification and synthesis of natural com-The technique of extracting antipounds. biotics from cultures of micro-organisms, which has already had such fruitful results, has continued, and is providing new systems for elaboration. In the chemotherapy of tuberculosis the situation has become rather confused; there are many types of compounds, the latest being the hydrazides of isonicotinic acid which have been found useful clinically, but there has been little in common between the diverse structures, and the most promising compounds appear to be those extracted from living material such as viomycin and terramycin.

Two Great Syntheses

There have been two great syntheses in the classical manner reported, and it is an interesting commentary upon the essential waywardness of fortune in research that while one of them is of the greatest social importance, the other will probably never again be described, except in the scientific textbooks of tomorrow. This latter is the elegant academic synthesis of morphine carried out at the University of Rochester. New York, by Dr. Gates. It involves some 30 steps and will never have more than theoretical significance because of the relatively simple and cheap method of extracting the alkaloid from the poppy. It has been calculated that the synthetic product will cost £20 per grain compared with 6d. per grain for the natural extract. In any case there are now cheaper and better painrelieving agents than morphine, and more are being discovered each year.

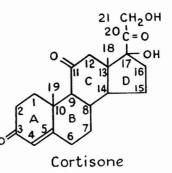
A recent series of local anaesthetics which has been described are the substituted 5alkoxy-phenyl pyrazolines. The most potent which can be administered through the mucous membrane or intradermally is 1-phenyl-5-(3'methoxy,4'-*n*-propoxy)-phenyl- $3-\beta$ -diethylaminoethyl pyrazoline. In the field of neuro-muscular blocking agents or curarising agents there has been a tendency in the past to replace the complex structure of tubocurarine by much simpler substances such as succinyl choline or polymethylene bis-quaternary ammonium salts. Now the tendency has been reversed, and the new curarising agents are becoming more complex with substances such as the deca-methylene bis-laudanosine quaternary salts. It has come to be generally realised that the structure containing two ternary or quaternary nitrogen atoms, separated by a carbon chain, has a great physiological significance, and examples of this type of structure are appearing in many chemotherapeutic substances such as N,N—bis-(4-amino-cinnamoyl) guanidine.

The synthesis which has by far the greatest importance, however, is that of cortisone. There have been many syntheses of this compound starting from natural products, but it was not until October of this year that a total synthesis was achieved.

CORTISONE

The starting material for most preparations of cortisone has been desoxycholic acid which is obtained from ox bile. The comparitive scarcity of this material, and the long and complicated series of reactions needed for conversion, has stimulated many attempts to find new starting materials or alternative routes.

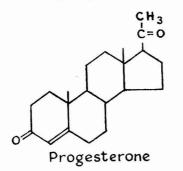
In order to assess the problem it is convenient to examine the structure of cortisone and compare it with that of the available intermediates. The first problem is the oxygen atom at position 11. There are very few natural materials with this structure. Desoxycholic acid, for instance, has the oxygen atom at position 12, and much of the

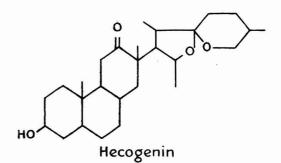




difficulty is in the transference of this atom. Usually 11 steps are needed, the route being via a Δ'' function to 12- α -bromi-24,24diphenylchol-23-ene-3- α -ol-11-one. A simpler process which uses seven steps to convert desoxycholic acid into dimethyl-12- α bromo-3- α -succinoxy-11-keto-cholanate has been used to prepare an intermediate in the Kendall synthesis, but the second problem, which is the elaboration of the dihydroxy acetone side chain, is then encountered.

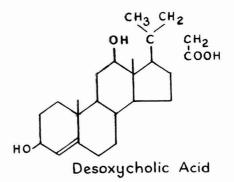
Steroid Δ^7 -9, (11)-dienes have been proposed as intermediates for the preparation of 11-oxygenated steroids. A key step which has been carried out this year is the selective hydrogenation of Δ^5 -6-sterol-dienes to the Δ° mono unsaturated compounds. Thus ergesterol and its four isomers have been catalytically hydrogenated over Raney nickel to the 5-dihydro derivatives. These, however, all require animal tissue as the raw material, and many attempts have been made to find substances of plant origin which could be used as intermediates. Such substances are the steroidal sapogenins, diosgenin and hecogenin. The latter substance has been discovered in sisal waste; the juice of the leaves after the fibre has been extracted contains about 0.1 per cent of hecogenin, and a pilot plant has been erected





in Nairobi to produce hecogenin from this source. 22-isoAllospirostan-3- β -ol-11-one has been prepared from this hecogenin and converted to cortisone. A more widely distributed sapogenin, diosgenin, has also been converted to the same intermediate by performic acid oxidation. Both these routes require about 20 stages and involve the difficult elaboration of the side chain.

A simpler method for the production of the 11-oxygen atom has been reported by chemists of the Upjohn Co. in the U.S.A.: this technique has been christened microbiological oxidation. Progesterone allowed to ferment in a medium in which a Mucorales mould is growing, and the 11oxygenated steroid is extracted after a suitable interval. The method appears to be of general application and has been used with several other steroids such as androsterodione, 11-deoxy-corticosterone. and 11deoxy-17-hydroxy-corticosterone. This new technique may make the simpler steroids such as stimasterol and cholesterol suitable raw materials for the synthesis of cortisone. As a sideline to the main stream of research in this field there is the search for simpler substances with cortisone activity. Early in the year there was a report from Spain that nitrogen mustard, dichlor-diethylamine had had successful clinical trials.



A partial synthesis of cortisone which concentrated on the simple introduction of the side chain had as its key reaction the formation of a tertiary alcohol at C/17 in the α configuration. This was accomplished by perbenzoic acid oxidation of the dienol triacetate of 3-a-hydroxy-pregnane-11,20-dione, in which only the 17-20 double bond was Mild alkaline hydrolysis of the oxidised product produced 3-x-17-x-dihydroxy-pregnane-11,20-dione, which by bromination and hydrolysis produced a hydroxy group at C 21. Oxidation with N-bromo-acetamide vielded 17.21-dihydroxy-3-11.20-pregnanetrione Acetvlation, bromination at C 4 and dehvdrobromination with semicarbazide completed the conversion to cortisone acetate.

All these routes, however, have been based upon natural compounds, and the total synthesis was not achieved until late this year by a team of chemists in the U.S.A. working in the Merck Laboratories. The route is too complex, and the nomenclature too lengthy to discuss in any great detail: but the stereochemical difficulty of establishing the transanti configuration between the three centres C 10, C 9 and C 8 was overcome by making use of the stereospecific course of the Diels-Alder reaction, and proceeding via a-cis-1methyl-2-keto-perhydronaphthalene. The oxygen atom at position 11 was built into the molecule from the beginning by the use of ethoxy-pentadiene, which when reacted with a *p*-quinone provided the structure for the central two rings of the cortison molecule (B and C).

Despite this great chemical achievement it is probable that the cortisone will continue to be produced from natural products for some time to come. The manufacture from desoxycholic acid was started in Britain in the middle of the year, and this, and the route via hecogenin may compete for some time.

ANTIBIOTICS

The number and diversity of chemical compounds extracted from cultures of microorganisms continues to grow. Among the new and unidentified compounds is Globicin, which has been isolated from an orange pigmented strain of *B. subtilis*, found to be antagonistic toward *M. phlei*. *B. subtilis* is a very versatile organism and can produce a variety of different substances depending

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upon the conditions and the substrate. Globicin is precipitated from the medium with acid, and purified by fractional precipitation from ammonium sulphate. The molecule contains loosely bound sulphur and tryptophane. It is heat-stable and irreversibly adsorbed upon charcoal, and is active against a variety of gram positive organisms.

Another such material has been named Norcardianin as it has been isolated as a crystalline red compound from an unidentified strain of Norcardia. It is extracted from the medium with ether and chromatographed upon alumina, where it forms a readily identified zone. It can be eluted from the column in a pure state, and upon examination has been shown to have a molecular weight of about 1375. The molecule contains C, H and N, but no halogen or sulphur. It is, surprisingly enough, not a polypeptide, since it forms no amino-acids upon acid hydrolysis. It is active against gram positive organisms.

Structure of Viomycin

Ot considerable interest is the work being carried out upon the structure of viomycin. a tuberculostatic agent obtained from cultures of *Actinomycetes*. It has been shown to be a strongly basic polypeptide with the empirical formula $C_{18}H_{31-33}N_0O_s$. Acid hydrolysis of the substance has yielded ammonia. carbon dioxide and urea, in addition to a mixture of amino-acids. From the hydrolysate has been isolated *l*-serine, α , β diamino-propionic acid, and an amino-acid isomeric with lysine. In addition, an unidentified guanidino compound was found.

The work upon terramycin, the other promising antibiotic with tuberculostatic properties, has proceeded farther. Alkaline hydrolysis has been the chief instrument in the identification. Upon alkaline fusion a complete breakdown of the molecule occurs to give salicyclic acid, *m*-hydroxy-benzoic acid, and succinic acid, while aqueous alkaline treatment has vielded more complicated structures such as 7-hydroxy-3-methylphthalide, and terracinoic acid, which has been shown to be 4-carbethoxy-5-hydroxy-3methyl-indanone-2-acetic acid. From these and other data chemists of the Pfizer Co. have elucidated the structure as a tricyclic. polyhydroxy phenol. Terramycin, which can be classed as a wide spectrum antibiotic. has the unique properties of having a very high oxygen-to-nitrogen content, and of being compatible with human serum. In body fluids it is said to be dipolar and to form salts which are analogous to those formed by amino-acids. The rather complex structure makes it unlikely that it will be synthesised in the near future.

Mycomycin, on the other hand, is a much simpler substance. It has been isolated from the metabolic products of *Norcardia acidophilus*. It has now been obtained in crystalline form and has been characterised as a highly unsaturated, optically active, straight chain carboxylic acid with an empirical formula $C_{13}H_{19}O_2$. The pure compound is thermally labile and sensitive to oxygen. An examination of its infra-red spectrum has indicated that the molecule may contain acetylenic and allenic groups. Its methyl ester has been prepared and its reduction product identified as *n*-tridecanoic acid.

TROPOLONES

Interest has been maintained in the tropolone structure during this past year, particularly because of the existence of this structure in the molecule of colchicine, the spinal anaesthetic. An improved synthesis of B. y-benztropolone has been reported. phthalaldehyde being found to condense with methoxy-acetone to give the methyl ether, which readily splits upon treatment with strong mineral acids. Neither compound gives the characteristic aromatisation reaction shown by colchicine, colchiceine and monocyclic tropolones. The 3-nitro derivative is, however, rapidly isomerised by alkali to 1-nitro-2-naphthoic acid. α , β -Benztropolone has been prepared by the bromination and dehydrobromination of benzcvcloheptene-4,5-dione. Colchicine and its isomers have been the subject of many papers, and simpler synthetic routes are being investigated. One such route has involved the von Pechmann coumarin condensation. Tricyclic structures having some of the features required have been prepared. but no close relatives of colchicine.

PICROTOXIN

Picrotoxin is a representative of the class of non-nitrogenous bitter principles called amaroids. It can be isolated from the fruit of the shrub *Cocculus Indicus*, and it has a very powerful physiological action. Isolated in 1812 it was found 70 years later to consist of a mixture of two constituents, picrotoxinin, $C_{15}H_{16}O_6$, and picrotin, $C_{15}H_{18}O_7$.

Infra-red absorption studies suggest that each contains a dilactone structure. Picrotoxinin contains a single double bond and a hydroxyl group, picrotin is saturated and contains two hydroxyl groups. Neither gives any carbonyl derivatives, and it has been assumed that the remaining oxygen atom in each compound forms part of an ether linkage. Picrotoxinide, a new transformation product of picrotoxinin, has now been converted by a step-wise degradation into a bicvelic hydrocarbon, picrotoxinin, which as its name suggests is doubly unsaturated. The hydrocarbon retains the important structural features of the picrotoxinin carbon skeleton.

The structure of this hydrocarbon has been proved by synthesis to be 5-isopropyl-8-methylhydrin-4,6-diene. This identification has made it possible to propose a tentative formula for picrotoxinin, and it is interesting that this proposed structure has affinities with both the terpenes and the steroids. It has been suggested, therefore, that the substance represents an intermediate in the biosynthesis of steroids, or else a degradation product. In any case it has been considered significant that picrotoxinin is the first natural product which has been found to have structural affinities with the steroid class of compounds and yet not to retain the steroidal carbon skeleton.

THE OXO PROCESS IN AMERICA

This year has seen the climax of a long period of investigation into and development of the Oxo process in the U.S.A. This process, which is particularly suitable for the production of acids, aldehydes and alcohols from petroleum hydrocarbons was invented by Otto Roelen just before the last war, and exploited in Germany. The reaction, which consists essentially of the addition of the elements of formaldehyde in the form of water gas across a double bond to form an aldehyde, has been renamed hydroformylation.

The Longview plant of Texas Eastman Co. has been designed to manufacture ethanol, n, and *iso*-butyraldehydes and butyric acid from natural gas and propane. Natural gas is mixed with carbon dioxide and steam at high temperature to give hydrogen and synthesis gas, the latter being reacted catalytically with propylene, obtained by the cracking of propane, to yield a mixture of aldehydes. This mixture is separated into the *n*- and *iso*-butyraldehydes. Part of the *n*-isomer is to be converted into butyric acid for use in the production of cellulose acetobutyrate, and part converted to 2-ethyl-hexyl alcohol for the manufacture of octyl phthalate. The *iso*-butyraldehyde is to be converted into the alcohol and acetate to replace the *n*-isomer in lacquers. Ethylene is also produced in the cracking of propane, and this is used as a source of ethyl alcohol, oxidised elsewhere to acetic acid and anhydride for cellulose treatment.

Another plant to utilise the Oxo reaction is to be operated by the Gulf Oil Co. at Port Arthur. Here, iso-octyl alcohol is to be made from heptene by the action of carbon monoxide and hydrogen in the presence of cobalt carbonyls. The product of this stage is then hydrogenated to the alcohol. Du Pont use the same process to manufacture trimethyl hexanol, and, more recently, Shell Chemicals have marketed two new alcohols synthesised by the Oxo reaction. Nonanol is essentially 3.5.5-trimethyl cyclohexanol and has a M.W. of 144. Alphanol is a mixture of primary and *z*-methyl-substituted aliphatic alcohols with a small percentage of cyclic constituents, the average M.W. being 127.

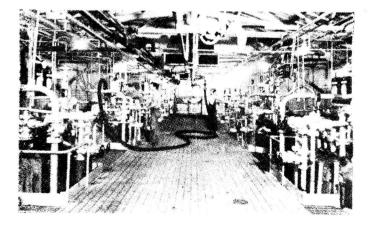
In this country a plant has been crected by Geigy and Hardesty to manufacture sebacic acid by the alkaline fission of ricinoleic acid. Castor oil is heated with caustic soda to give this highest commercially available member of the aliphatic dicarboxylic acids The product will be used as an intermediate in the manufacture of plasticisers. perfumes, resins and fibres.

PROGRESS IN PLASTICS

Despite the ever-growing flood of litera-

ture upon plastics, some idea of the volume of which may be estimated by the size of the manuals upon small sections of the field, there have been few radical advances. One of these has been the production of a highly important fundamental new class of polymers, the polyketones, which were discovered by the free radicle polymerisation of gaseous mixtures of ethylene and carbon monoxide. The reaction takes place at high pressures in the presence of free radicles, a suitable initiator being di-tert-butyl peroxide. The products are polyketones ranging from liquids to microcrystalline polymers of high molecular weight. Infra-red spectra suggest the presence of $-CH_2CH_2$ and >COgroups, and this is confirmed by the chemical properties of the substances. The materials behave very much as simpler ketones, giving polvalcohols upon reduction without cleavage of the chain, and cvanohydrins and oximes with hydrogen cyanide and hydroxylamine. Nitric acid oxidation of the polymers gives a series of saturated dicarboxylic acids ranging from glutaric to sebacic acid.

The most significant general trend has been the interest shown in glass-reinforced plastics, in particular the low pressure coldsetting polyester resins. These usually consist of an unsaturated ester such as diallyl phthalate or the polyester from a dihydric alcohol and a dibasic acid such as polyethylene phthalate or maleate and styrene. When the mixture is treated with a polymerising agent such as benzoyl peroxide, it sets to a hard, tough material, the process suffering no air inhibition. Reinforcement of the product with glass cloth or fibre has made possible the mass-production of many complicated shapes, such as boat hulls, sleds, etc.



Steps in the purification of terramycin are carried on in these tanks

Courtesy, Chas. Pfezer & Co.

Another class of resins which is finding increased application in industry, both here and in the U.S.A., is the epoxide resins. Resins of this type were developed independently by Shell Chemicals Ltd. under the name of Epikote, and by The Aero Research Co. under the name of Araldite.

Diphenylol Propane

These polyaryl epoxyethanes are prepared from diphenvlol propane and epichlorhydrin by heating at 100°C. in the presence of caustic soda. The products, whose molecular weights may range from 470 to 3,750, are polyhydric alcohols and are not filmforming, so they are modified by forming the esters with fatty acids. At elevated temperatures both the hydroxy groups and the end epoxy groups are esterified, but by cold-setting in the presence of amine, cross-linking occurs between the epoxy groups. They may also be used phenol-formaldehvde urea- and with resins, the latter combination being very strong and resistant to chemical attack.

The best acids to use are those from drying oils such as dehydrated castor oil and linseed oil. The films dry overnight and may be stoved at 250 to 300°F., or they may . be cold set in the presence of amines, the latter method having the disadvantage of a two-can pack and a short pot life. A doublefeed spray gun has been designed to overcome this difficulty, and the epoxides are now used for joining light alloys, coating chemical plant and painting aircraft.

Furfural Properties

The polymerising properties of a mixture of furfural and a strong acid have been known for many years; but it is only recently that attention has been focused upon the possibilities of furfural as a raw material for resins (here, of course, we accept its use as a nylon intermediate). As might be expected, the use of furane cements was first exploited in the U.S.A. and is now arousing interest here. The most used is polyfurfuryl alcohol, and cements prepared from it are said to be acid- and alkali-resistant and stable at temperatures up to 375°C. The cements are prepared on the sites by mixing the partially polymerised material, usually a svrupy liquid, with the filler, such as silica. carbon/asbestos, and an acid accelerator. In addition to the alcohol, resins have been made with furfural lignin sulphonic acids and furfurin, furfuryl alcohol and phenol, furfuraldehyde and phenol, furfuryl alcohol and formaldehyde. The cements have been used mainly for jointing acid-resistant bricks, but a recent innovation has been glass fabric reinforcement to form membrane liners and chemically-resistant plant.

There has been the good news that 'Terylene' fabrics will soon be generally available. and also that the material will be manufactured in the U.S.A. under the name of 'Dacron.' The makers, Du Pont de Nemours. have also developed a new form of polyethylene terephthalate which is called 'Nylar.' This film has great strength and may be used as an alternative to cellulose esters. The tensile strength of 35.000 p.s.i. is better than any known film and enables foils as thin as 0.00025 in. to be used.

Fluorine Atoms Placed

The intractable nature of polytetrafluoroethylene has led manufacturers to consider replacing some of the fluorine atoms in the molecule by chlorine. Such a material is Hostaflon, shown at the German Plastics Exhibition at Dusseldorf last year. Like the Kel-F of the Kellogg Co. and the Fluorolubes of the Hooker Electrochemical Co., it is polytrifluorochloroethylene, but it is prepared by splitting out chlorine from trifluoro-trichloro-ethane with alkaline sludges of zinc origin. The polymer is obtained as a fine white powder by the action of a peroxide in a diluent under pressure. The advantage of this material is that it may be hot moulded like a normal thermoplastic, but retains many of the resistant properties of polytetrafluoroethylene. Further, the polymerisation can be controlled to give waxy or oily products of low molecular weight.

Binding Sand Cores

A new use for urea- and phenol-formaldehyde plastics is in the binding of sand cores in foundry practice. This is usually accomplished with the aid of expensive pure linseed oil, but its replacement can provide shorter hardening time, better casting and complete breakdown in the most suitable temperature range. Thus, urea-formaldehyde, which breaks down between 220 and 270°C., is suitable for non-ferrous castings. while phenol-formaldehyde, breaking down between 400 and 500°C., a little less than linseed oil, is suitable for iron castings, and may have a future in steel.

The introduction of ion exchange resins

made possible whole sections of research, not the least being the preparation of rare earth metals in a pure form upon the pilotplant scale. Now a new principle has been discovered by the chemists of the Dow Chemical Co. which has at least as great potentialities. The principle, which they have named Ion Exclusion, is based upon the phenomenon that ion exchange particles repel ions in aqueous solution. The effect is most marked with the strongly ionised resins and has the result that the concentration of a strong electrolyte in aqueous solution is greater in the water surrounding the particles than in the water within the particles themselves, the differential sometimes reaching the high value of 10:1. Most un-ionised substances, and some that are only slightly ionised such as acetic acid or ammonia, either fail to exhibit this concentration difference or else show the reverse effect. All that is needed to regenerate the ion exchanger and elute the non-electrolyte is washing with water. This, however, can be disadvantage if it is the non-electrolyte а which is being investigated, since it inevitably produces a dilution of the original solution of the non-electrolyte.

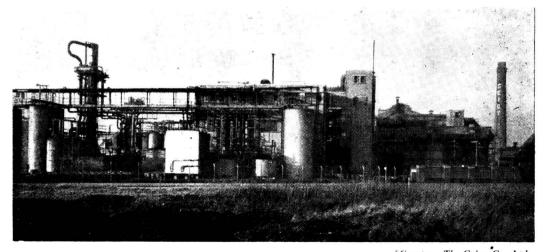
Few Limitations

Apart from this there are few limitations to the procedure; in theory the exchanger should be in the ionic form as the ionic portion of the solution; but in practice it is found that any resin not in the appropriate form suffers a

change by the normal process of ion exchange upon exposure to the electrolyte. While the best results are obtained by the use of a strongly ionised resin, with a large difference in the ionisation constants of the constituents. some separation can he achieved if there is any appreciable difference in the ionisation constant. In solutions containing strongly ionised electrolytes, such as hydrochloric acid, and weak electrolytes such as acetic acid, separation is sharp and complete; but separations can be made with hydrochloric acid and the stronger chlorand dichloracetic acids. Salt has been separated from ethyl alcohol, formaldehyde and boric acid.

Minimising the Effect

The dilution effect may be minimised by using a moving bed and the capacity of the bed is determined by the free space within the particles. Thus the volume of feed with Dowex 50, a sulphonated polystyrene crosslinked with divinyl benzene of particle size 50 to 100 mesh, is 42 per cent of the total volume for sharp separation. There is. however, no limit to the size of the bed and Dow has operated a 30 cu. ft. unit. The time taken for the operation of an ion exclusion unit depends upon the time taken to reach equilibrium and the pressure drop across the bed. The finer particles favour a more rapid establishment of equilibrium, but cause a greater pressure drop. The most successful compromise is with particles of 50 to 100 mesh size.



Courtesy, The Geigy Co., Ltd. Sebasic acid and plasticiser plant showing main building and ancillary units

Physical Chemistry

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continued from page 96]

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Useful Book of Reference

A wealth of information, arranged in a manner which makes it simple to locate, is contained in THE CHEMICAL AGE YEAR BOOK for 1953 which is now being despatched to subscribers to THE CHEMICAL AGE. Full details regarding all important chemical and allied organisations; research associations; prominent figures in academic, official or appointments; British industrial recent patents likely to interest the industrial chemist, etc., are contained in this handy book of reference. No one who buys, sells or manufactures chemicals can afford to be without THE CHEMICAL AGE YEAR BOOK. Copies can be obtained from the publisher (21s.).

Bradford Lecturers

MR. H. MIDDLETON, senior lecturer in chemistry at Bradford Technical College. reaches the retiring age of 65 on 4 May this year, but has intimated his willingness to continue until the end of the summer term. as recommended by the Bradford Further Education Committee, which has placed on record its appreciation of his 41 years' service. A native of Staffordshire and a keen gymnastic in his youth, Mr. Middleton is a Master of Science and an associate of the Roya¹ Institute of Chemistry. He served with a Royal Navy experimental unit during the first World War doing work in poison gases and smoke screens.

MR. K. L. BUTCHER has resigned from his post as Senior Lecturer in Chemical Engineering at the Bradford College in order to take up an appointment as Brotherton Lecturer in Chemical Engineering at Leeds University. Mr. Butcher, who is 37 and a native of Essex, went to Bradford six years ago to start at the college a chemical engineering course specially designed for ex-Service students. The course has proved extremely successful and has gained the recognition of London University and the Institution of Chemical Engineers.

Chemical Merger Proposed

Negotiations for the merger of the Eaglescliffe Chemical Group Ltd., and John and James White Ltd., two companies both engaged in the heavy chemical industry, are reported to be well advanced and it is hoped to circulate full details to shareholders next month. Application for the necessary consent has been made to the Capital Issues Financial details have been Committee. provisionally settled. The terms are:-White shareholders will be offered four Eaglescliffe ordinary 5s. stock units for every five White ordinary 5s. shares held, and one Eaglescliffe 6 per cent preference share for each White $5\frac{1}{2}$ per cent preference Eaglescliffe shareholders will share held. receive by way of capitalisation of reserves one additional ordinary stock unit for every 10 held and one preference share for every 10 held. As the Eaglescliffe Chemical Group is already a holding company the merger will be effected through the medium of that company. An appropriate change of name will be made.

· HOME ·

Annual General Meeting

The Midlands Society for Analytical Chemistry will hold its annual general meeting in the Mason Theatre of Birmingham University on Thursday, 5 February. At the conclusion of business G. F. Hodsman head of the research department, L. Oertling Ltd.) will give a talk on 'The Historical Development of the Chemical Balance.'

'The Magic Rinse'

A new product 'Nylo' is being marketed nationally by Nylo Laboratories Ltd., of Glasgow. The company has perfected a special rinse designed to lengthen the life of nylon stockings. A five minute rinse and squeeze is said to make the stockings safe from snags for six weeks. The product has been taken up nationally by leading departmental stores.

The Fertiliser Society

A general meeting of The Fertiliser Society will be held on Thursday, 22 January, 1953, at 2.30 p.m. in the lecture hall of the Royal Society of Tropical Medicine and Hygiene, Manson House, 26 Portland Place, London, W.1, when Mr. J. J. Porter and Mr. J. Frisken, B.Sc., M.I.Chem.E., will present a paper entitled 'The Manufacture of Triple Superphosphate.' The paper will be followed by a discussion.

Change of Address

Since 5 January all departments of Monsanto Chemicals Ltd., Sales Division, have been housed at Victoria Station House, Victoria Street, London, S.W.1. The telephone number is VICtoria 2255.

Research on Coke

A large-scale testing plant is to be built in Britain for carrying out experiments on a wide range for the production of coke for blast furnaces and for industrial and domestic purposes. One of the main purposes will be to obtain wide information in the use in coke ovens of coals not previously classified as true coking coals. Details and siting have not yet been arranged, but it is expected that the plant, which will be designed and operated by the British Coke Research Association, will be completed in about three years.

Mackinnon Research Studentship

The Council of the Royal Society has awarded one of the two Mackinnon Research Studentships to Dr. F. K. Duxbury, of King's College, University of Durham, to work on organic chemistry at Liverpool University.

Importance of Science in U.K. Recovery

Britain's scientific and technical abilities were the firm foundation for the restoration of her national prosperity, declared Sir Ben Lockspeiser, secretary of the Department of Scientific and Industrial Research. in a New Year's message for 1953. As examples of British achievement Sir Ben cited her aircraft and gas turbines as supreme in the world and said that Britain had just evolved a new power automatic loom, which could be used for all kinds of yarn, natural or artificial and was cheaper than the American and Swiss looms. In the important field of waste-saving, the coal industry had worked out a method of utilising the 'slurry' which would vield another 5,000,000 tons of fuel in a year.

Prospecting Near Widnes

A London firm, Steel Brothers & Co., Ltd., have applied for permission to prospect for oil in the Widnes area and at Croxteth For some months a specialist (Lancs.). team of three have been trying to trace the rich, oil-bearing source which they believe exists somewhere within a six-miles' strip between Liverpool and Rossendale. In the last 12 years millions of gallons of crude oil have been produced at Formby and neither the yield nor the gravity has changed very much, which leads the experts to believe that the oil is seeping through from a big oilfield in the vicinity. The firm plan to survey 400 square miles of Lancashire.

British Association's New President

Sir Edward Appleton, vice-chancellor of Edinburgh University, was installed at Burlington House, London on 2 January, as president for 1953 of the British Association for the Advancement of Science. Sir Edward will preside at the annual meeting which will be held in Liverpool in the first week of September.



Belgian Congo Tin Resources

At the annual meeting of the Geomines Congo Company it was reported that tin reserves were practically unlimited. Last vear Geomines produced some 4.000 metric tons of cassiterite. The new programme to begin in 1956 estimates production at 7.000 to 8,000 tons. The company also produced tantalo columbite concentrates weighing about 2.5 per cent of the cassiterite output. The slag from the cassiterite smelting contained as well small percentages of tantalite and columbite. Since its tin ores are associted with lithium. Geomines will build a pilot plant in the Congo to produce lithium carbonate.

New Chlorophyll Plant in U.S.A.

Work has begun at Lamar, Colorado, U.S.A., on the construction of what is claimed to be the world's largest plant for the continuous production of chlorophyll. The plant, which is being built by the National Chlorophyll Company of America, will have an annual capacity of over 100,000 lb. It is hoped to begin full operation by April this year.

Iron Ore in Mianwali

German experts working in co-operation with the Office of Industrial Development in the Mianwali area of the Punjab, have reported that large iron ore deposits have been found in the Mianwali area. Deposits were believed to be adequate to cover Pakistan's needs. It is understood that a company will soon be created to develop deposits, with half of the capital coming from private sources and half from the Pakistan Government.

Unilever in Turkey

A new factory, comprising an oil mill, refinery, hardening plant, and margarine and edible fats manufacturing section was officially opened on behalf of Unilever in Turkey on 5 January. The ceremony was attended by Dr. Paul Rykens, chairman of Unilever N.V., and Mr. Sidney J. van den Bergh, a member of the board of Unilever. The main raw material will be locally grown sunflower seed and the oil mill capacity is approximately 12,000 tons of seed a year.

Sulphur Plant for Mexico

A \$5,000,000 sulphur plant is to be built at Jaltipan. in Vera Cruz, Mexico, by the Pan American Sulphur Company, of Houston, Texas. It is scheduled for completion by August, 1954, and will have an annual capacity of between 300,000 and 600,000 tons. The company has already spent more than \$1,000,000 on exploring the Jaltipan Dome and it is considered that the extent of the reserves is adequate to justify the plant.

Canadian Safety Record

A work record of $3\frac{1}{2}$ years without a losttime accident has been achieved by employees of the Beloeil (Quebec) agricultural chemicals works of Canadian Industries. Ltd. For this record, which represents 1,236 accident-free days or about 510,000man hours, employees will receive the president's prize, one of several awards under C.I.L.'s non-accident record plan. According to the National Safety Council, the accident frequency rates in the entire fertiliser industry in Canada and the U.S. in 1951 was 14.39 per 1,000,000 man-hours of work.

Radon Plant Installed

The Institute of Nuclear Physics at Calcutta has installed in its new premises. a radon plant to produce the radioactive gas for the treatment of cancer and other diseases. The plant will go into production as early as possible. Once the plant is started it will work non-stop and produce radon at a cheap rate within the means of poor patients. The institute had procured till recently radioactive iodine and radioisotopes from Harwell. A permanent isotope service for medical treatment is also being organised. While the necessary equipment will be housed in the institute, portable units will also be provided for hospitals. It was recently stated by the Deputy Minister of Natural Resources and Scientific Research in the Indian Parliament that two persons had been deputed to the nuclear physics section of the University of Melbourne and one to the high altitude Research Laboratory in Switzerland to have training on the technique of using radioactive isotopes.

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TOTAL DISSOLVED SOLIDS	less than 1.0 p.p.m.				
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The Council of the Institution of Metallurgists has announced that HIS ROYAL HIGHNESS, THE DUKE OF EDINBURGH, has graciously accepted election to Honorary Membership of the Institution.

The North Thames Gas Board has announced the appointment of MR. L. W. ANDREW, B.A., B.Sc., as Senior Technical



Mr. L. W. Andrew

Officer at Watson House, Fulham. Mr. Andrew was educated at King Edward VI Grammar School. Nuneaton, and Oriel College, Oxford. where he took a First Class Honours degree chemistry. He in joined the research staff of The Gas Light and Coke Company in 1929 and was in charge of the La-Space Heating boratory until 1948.

since when he has been the officer in charge of the Hot Water Laboratory. His work in the laboratories has included research on refrigeration, and during the war this research was extended to include some industrial applications of gas. The author of several papers, Mr. Andrew is a Gold Medallist of the Institution of Gas Engineers for a paper of which he was a joint author. In 1946 he was president of the London and Southern Junior Gas Association.

DR. C. J. T. CRONSHAW retired from the board of Imperial Chemical Industries, Ltd., on 31 December, 1952, after 37 years' service with the company and its predecessors. He joined Levinstein, Ltd., in 1915, and in 1924 became manager of British Dyestuffs Corporation, Ltd., at Blackley. On the formation of I.C.I. in 1926 he became deputy chairman of the Dyestuffs Group Delegate Board, and from 1939 until his appointment to the I.C.I. board in 1943 was chairman of that delegate board. From January, 1944, to September, 1952, Dr. Cronshaw was the Dyestuffs & Pharmaceuticals Group director, and in 1948 he was also appointed (jointly with the late Mr. H. O. Smith) to be personnel director of I.C.I.

Dr. Cronshaw will be succeeded as personnel director by MR. R. A. BANKS, who was appointed to the I.C.I. board on 13 November, 1952. Mr. Banks was previously a managing director of the company's Alkali Division.

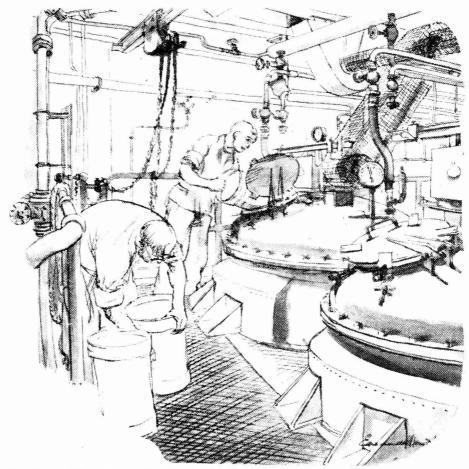
DR. T. HOWARD BUTLER has resigned from the board of the Midland Tar Distillers. He is chairman of William Butler & Co. (Bristol), coal tar distillers.

The United Steel Companies, Ltd., has announced that ENGINEER REAR-ADMIRAL C. W. LAMBERT, C.B., who is now general works manager of their Appleby-Frodingham Branch, Scunthorpe, will retire at his own request on 30 June, 1953. It is intended that he shall be succeeded by MR. ALBERT JACKSON, who is at present works manager (steel) and deputy general works manager.

As from 1 January, 1953, MR. T. P. LLOYD, B.Sc., A.I.M., T.D., will be appointed assistant works manager (steel) in which capacity he will assist Mr. Jackson. On 1 July, 1953, consequent upon the appointment of Mr. Jackson as general works manager, Mr. Lloyd will be appointed works manager (steel).

Mr. Jackson was born in Scunthorpe and joined the Appleby-Frodingham Steel Company as a chemist in 1920. He holds the Associateship in Metallurgy of Sheffield University and in 1935 he was responsible for the formation and operation of the works metallurgists department.

He has been prominent in the field of technical education and for many years has been a member of the Metallurgy Advisory Committee of City and Guilds of London Institute and serves, in a similar capacity. the Scunthorpe Technical College. He is a member of the council of the Lincolnshire Iron & Steel Institute, and was elected president in 1950. He was awarded a Fellowship of the Institution of Metallurgists in 1946 and in 1952 was awarded a City and Guilds of London Institute Insignia.



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Next Week's Events

MONDAY 12 JANUARY

Society of Chemical Industry

Leeds: University, 7 p.m. G. W. Rowe: 'Recent Experiments on the Friction and Adhesion of Solids,' illustrated by film.

Pharmaceutical Society

London: 17 Bloomsbury Square, W.C.1, 7.30 p.m. D. Train: 'Pharmaceutical Engineering Science.'

TUESDAY 13 JANUARY

Institution of Chemical Engineers

London: Caxton Hall, Westminster, S.W.1, Symposium on 'Bursting Discs.' Two sessions, 3-5.30 p.m. and 6-8.30 p.m.

Hull Chemical & Engineering Society

Hull: Church Institute, Albion Street, 7.30 p.m. Presidential address. G. E. Gray: 'Oil Additives.'

Midland Society for Analytical Chemistry

Birmingham: University, Edmund Street, 7 p.m. Discussion: 'The Rôle of the Analyst in the Electro-plating Industry,' introduced by K. E. Langford (chief chemist, Evered & Co., Smethwick; and Lecturer in Electro-deposition at the College of Technology, Birmingham).

Institute of Metals

Swansea: University College, Singleton Park, 6.30 p.m. Major L. P. Teed: 'The Metallurgical Problems Arising from Stratospheric Flight.'

Incorporated Plant Engineers

Manchester: Engineers' Club, Albert Square, 7.15 p.m. R. Wilbourne: 'Oxy-Acetylene Processes Applied to Industry.'

WEDNESDAY 14 JANUARY

Society of Chemical Industry

London: Institution of Civil Engineers, Great George Street, W.C.2, 2.15 p.m. Joint meeting of the Microbiology Group with the Society for Applied Bacteriology. Symposium on: 'Recent Advances in Microbiological Methods.' Papers by Professor M. Stacey, Dr. E. Windle Taylor, Dr. L. A. Allen, Dr. S. T. Cowan and J. Tramer, followed by discussion.

Newcastle: King's College. 6.30 p.m. Address by M. P. Appleby.

The Chemical Society

Dublin: University College, Merrion Street, 7.45 p.m. Joint meeting with the Institute of Chemistry of Ireland. Dr. Dermot Twomey: 'The Use of Lithium Aluminium Hydride in Organic Chemistry.'

British Association of Chemists

London: Wellcome Research Institute. 183 Euston Road. N.W.1, 7 p.m. N. F. Baker: 'Patents and the Chemical Manufacturer.'

THURSDAY 15 JANUARY

Society of Chemical Industry

Edinburgh: Heriot Watt College, Chambers Street, 7.30 p.m. E. Lester Smith: 'Vitamin B₁₂ and Related Factors.'

London: The Building Centre, Store Street, Tottenham Court Road, W.C.1. 6 p.m. Road and Building Materials Group. A. R. Smee and L. Mullins: 'The Use of Rubber in Bituminous Road Surfaces.'

Widnes: College of Further Education. 7 p.m. Liverpool Section. H. G. Dickenson: 'The Fine Chemicals Industry.'

Textile Institute

Macclesfield: W. Frost & Sons Ltd., Elizabeth Street Mills, 8 p.m. Film: 'The Du Pont Story.' Chairman: V. Castle.

FRIDAY 16 JANUARY

The Chemical Society

Glasgow: Royal Technical College, 7.15 p.m. Reading of original papers.

Society of Dyers & Colourists

Manchester: 10 Blackfriars Street, 6.30 p.m. G. G. Taylor (Clayton Aniline Co. Ltd.): 'The Measurement of Colour.'

Antimony Oxide Prices

Associated Lead Manufacturers has announced that its prices for antimony oxide have been reduced by £15 per ton as from 31 December. The new prices compared with those which came into force on 18 June, 1952, are as follows:—

		Old price per ton			New price per ton		
' Timonox ' (Cookson's y	chite	£	s.	d.	£	s.	d.
oxide of antimony) : Red Star in 5-ton lots	, inte	220	0	0	205	0	υ
'O' quality in 1-ton lots		217	10	0	202	10	0

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Solubilising Native Starch

A New Continuous Splitting Process

A NEW continuous electrolytic process for the splitting up of starch was shown by means of diagrams and photographs at the Achema X at Frankfurt. recently, by Aktiengesellschaft A. Hering, of Nürnberg. In this process, for which German and foreign patents have been taken out, starch milk is fed to an electrolyser, where the starch molecule is rapidly split up under controlled conditions. The splitting can be achieved over the whole range from soluble starch to starch with the lowest viscosity.

The process has been described as follows:

The starch milk of 12°-18° Bé is agitated in the churn with a small charge of NaCl and then pressed through a preheater to the electrolyser (Die Stärke, 4, 3, 54). The reaction temperatures best suited to the corresponding process stage are controlled automatically not only in the preheater, but also in the cellular electrolyser, which is equipped with a central agitator, watercooled electrodes and a cooling jacket. Besides this, acid may be added in controlled quantities to the electrolyser from an acid tank for pH adjustment. The reaction time in the electrolyser is determined by the degree of splitting required and ranges from 10 to 60 minutes. From the electrolyser the starch solution flows to a waterneutralisation tank. which is cooled equipped with an agitator.

Control of Neutralisation

The neutralisation itself is controlled by means of a pH measuring and controlling device. The electrolytic solution is separated from the starch by a centrifugal process or by decantation and flows back to the churns for further use.

In this way, only the chemical compounds actually consumed have to be recharged. The backflowing electrolytic solution is free of starch.

The preheater is generally heated by water steam or exhaust steam. Overheating of the heat sensible starch milk is avoided by automatic temperature control with an accuracy of $\pm 1^{\circ}$ C.

The power consumption is determined by the degree of splitting. For potato starch, for example, the maximum consumption is 0.1 kw. per hour per kg. for starch with a water content of 20 per cent. For soluble starch of the lowest viscosity the figures are, maximum 0.3 kW per hour per kg. dry starch, with a consumption of cooling water of approx. 0.5-1.0 m.³ per hour.

The consumption of chemical compounds such as NaCl or KCl is stated to be 1-2 per cent of the weight of dry starch. This data is based on experience gained during lengthy working tests at the starch factory at Schrobenhausen, in Germany.

This new continuous process can be automatic or semi-automatic, and no skilled personnel are necessary to operate it. The process conditions for the finished product are easily fixed and can be adapted to the different properties of the many kinds of native starch, it is claimed. The starch electrolyser guarantees an equal and homogeneous degree of the splitting and the time required is a fraction of that needed for other processes. It may be of major interest to the paper and textile industries.

Poisons Act Changes

ATTENTION is drawn to the Poisons List Order 1952 (S.I. 1952 No. 2085) and the Poisons Rules 1952 (S.I. 1952 No. 2086) which were made by the Secretary of State on 2 December 1952 and came into operation on 1 January 1953. The Poisons List Order 1952 amends the Poisons List. The changes made are set out in the First and Second Schedules to the new Order, and the current Poisons List is set out in full in the Third Schedule. The Poisons Rules 1952 consolidate with amendments the Poisons Rules 1949, 1950 and 1951.

Full details of the changes and amendments made by these Statutory Instruments are given in the Poisons List Order, 1952 (price 4d. net) and the Poisons Rules, 1952 (price 1s, 3d. net).

Copies may be obtained from Her Majesty's Stationery Office at the following addresses:—

York House, Kingsway, London, W.C.2; 13a Castle Street, Edinburgh, 2; 39 King Street, Manchester, 2; 2 Edmund Street, Birmingham, 3; 1 St. Andrew's Crescent. Cardiff; Tower Lane, Bristol; and 80 Chichester Street. Belfast; or through any bookseller.

Market Report

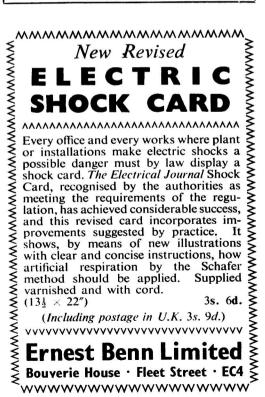
LONDON.—There has been no pronounced activity on the chemical markets during the first week of the new year but there is certainly more inquiry in circulation, and the outlook is more promising than for some time past. Contract replacements are occupying the attention of the larger consuming industries but few announcements have yet been made concerning the quotations which will operate during the first half of the year.

Substantial reductions in the prices for Bisol amyl acetate, butyl acetate, and amyl alcohol have been announced with effect from 5 January, and lower prices are now ruling for diethyl phthalate and dimethyl The latest quotation for dry phthalate. white lead is £149 15s. per ton and the basis price for dry red lead and litharge is now £134 5s. per ton.

Export trade in chemicals has been of moderate dimensions and overseas buyers are asking for competitive quotations.







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10 January 1953

CLASSIFIED ADVERTISEMENTS

SITUATIONS VACANT

The engagement of persons answering these advertisements must be made through a Local Office of the Ministry of Labour or a Scheduled Employment Agency if the applicant is a man aged 18-64 inclusive, or a woman aged 18-59 inclusive, unless he or she, or the employment, is excepted from the provisions of the Notifications of Vacancies Order, 1952.

A NALYTICAL CHEMIST with not less than three years' industrial experience of inorganic analysis are required by the Nelson Research Laboratories of the English Electric Co., Ltd., at Stafford, for work of an interesting nature. Please write giving full details of age, qualifications and experience, quoting Ref. 997A, to CENTRAL PERSONNEL SERVICES, THE ENGLISH ELECTRIC CO., LTD., 386/7, STRAND, LONDON, W.C.2.

A pPLICATIONS are invited from qualified CHEMISTS or CHEMICAL ENGINEERS by VACUUM OIL COMPANY LIMITED, now undergoing rapid expansion for a most responsible position in its Technical Depart-ment. Candidates must possess Hons. Class I or II, and good experience in, or closely related to, the Petroleum Industry. The work will be directed largely towards the supervision of a wide range of product development work, but personality, proved administra-tive experience, and the ability to lead groups of the experience, and the ability to lead gloups of technical personnel are of equal importance. There are excellent prospects of promotion and salary will reflect the qualifications and experience of the successful candidate. Pension and Life Assurance. Generous cantidate. relision and the Assurance. Generous sickness benefits. Applicants should write, giving full details of experience to INDUSTRIAL RELATIONS DEPARTMENT, VACUUM OLL COMPANY LIMITED, CAXTON HOUSE EAST, WESTMINSTER, LONDON, S.W.1, quoting reference L.S.D. 699.

E XPERIENCED CHEMIST required for Factory Laboratory, middle aged man preferred. Write stating age, qualifications, experience and salary required to BOX No. C.A. 3189, THE CHEMICAL AGE, 154, FLEET STREET, LONDON, E.C.4.

OPPORTUNITIES IN U.S.A. FOR CHEMISTS AND ENGINEERS; Large American chemical process company offers permanent positions for Chemists with Doctors' degrees (Plastics, Cellulose and Textile Chemicals also Chemical and Mechanical Engineers with degrees ; ages 25 to 35 and eligible to migrate to U.S.A.; standard American salaries; write details of personal history, education, experienc eand references to KARL S, CATE (AVIS), 26, AVENUE GEORGE V, PARIS 8, FRANCE.

South WALES LABORATORY FURNISHERS re-quire MANAGER to take control Warehouse. Know-~qure **MANAGER** to take control warehouse. Know-ledge Trade advantage, must possess organising ability, able to control personnel. Salary according to age and experience. Good prospects. Applications stating age, present position and salary (in confidence), qualifications and experience and giving three references to **BOX No. C.A. 3190, THE CHEMICAL AGE, 154, FLEET STREET, LONDON, E.C.4.**

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For fuller details apply to : ALLAN R. DAVIES, 47a, ZETLAND ROAD, BRISTOL, 6. Tel.: 41205/6.

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30 in.

Jac. Cyl. MIXERS, 30, 40, 100, 300 and 1,200 galls.
 "U" trough Powder MIXERS, 6 ft. by 2 ft. by 2 ft. deep, 400/3/50.
 Ditto, B.D., 5 ft. by 19 in. by 20 in., with sifting attach-

ment.

Stainless Cyl. Enc. Jac. MIXER, 36 in. by 221 in. diam., 400/3/50. TANKS, BOILERS, AUTOCLAVES, CONDENSERS, REFINERS, DRYERS, OVENS, STILLS, FANS, BALL MILLS, CONVEYORS, MIXERS, ETC. Lists on request

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- 4-Recessed Plate FILTER PRESSES, 30 in. square, 70 plates in each, centre fed.
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- 1-Johnson FILTER PRESS, 36 in. square, plate and frame type, double inlet and enclosed delivery ports.
- Johnson Oil FILTER PRESS, Premier type: plates 2 ft. 8 in. by 2 ft. 8 in., of which there are 45, with angle lever closing gear.
- 1-Johnson FILTER PRESS, 42 C.I. plates, 32 in.
- square, centre feed. Steam-heated FILTER PRESS, Premier type, 32 in. square, with 30 recessed plates.
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- ribbed C.I. plates.
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- 26 in. by 26 in. deep. Blending chamber feeds material to positive action brush sifter in trough screen. Broken seroll agitator. Pulley drive.
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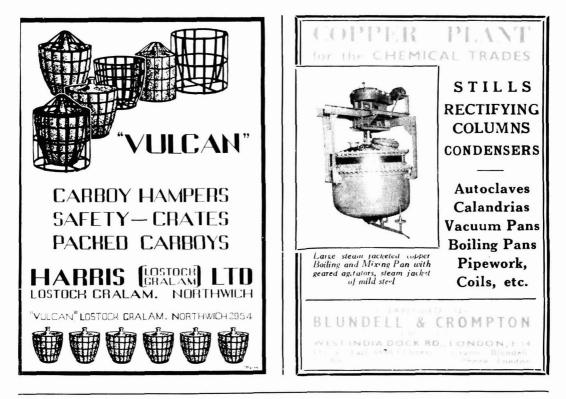


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