Physical and Chemical Properties of Heavy Water

IN the recent joint discussion of Sections A (Mathematical and Physical Sciences) and B (Chemistry) on September 10, at the British Association meeting at Aberdeen, on heavy hydrogen, two points of some interest were referred to by those taking part. During the last two years, the experimental confirmation of the theoretical anticipations of the differences in behaviour, both physical and chemical, of the two hydrogen isotopes has proceeded at a remarkable speed. In the course of these investigations, in which both light and heavy hydrogen have been employed under similar conditions, it has been found possible to examine by isotopic labelling of the hydrogen atoms in a molecule a certain number of what may be termed exchange reactions.

The two simplest exchange reactions involve reactions between the gaseous isotopes themselves and between deuterium and water

$$H_2 + D_2 \rightleftarrows 2HD$$
$$H_2O + D_2 \rightleftarrows DHO + HD$$

In the catalytic hydrogenation of unsaturated organic compounds, such as ethylene or benzene in the presence of nickel or platinum as catalyst, the experiments on the replacement of the hydrogen by deuterium not only provide a confirmation of the view originally advanced by Sabatier that a metallic surface monohydride is the effective catalyst, but also reveal the interesting fact that exchange reactions occur and that these can proceed independently of the process of hydrogenation, namely :

$$C_2H_4 + D_2 \rightleftarrows C_2H_3D + DH$$

Whilst the energetics of these reactions have not been investigated in great detail, the qualitative evidence indicates that the energies of activation are small, suggesting that the reactions are brought about not so much by an unexpected fragility in the covalent link between carbon and hydrogen when the hydrocarbon is adsorbed, but rather by a species of atom interchange between adsorbed atoms, one being attached to the hydrocarbon, a mechanism similar in some respects to the *ortho-para* conversion in hydrogen effected by hydrogen atoms. Incidentally, our crude picture of the interactions which occur when a molecule such as ethylene is adsorbed on a nickel surface has to be modified to a very considerable extent, and also the migration of double bonds in complex organic compounds in the presence of such hydrogenating catalysts may merit thorough investigation.

Deuterium thus provides us with a tool to examine exchange reactions, some of which as we have seen are not only of a somewhat unexpected nature but also could not have been discovered by the ordinary methods of investigation. In addition, deuterium is proving of great value in assisting us to elucidate the mechanism of a number of chemical actions involving hydrogen.

Such reactions may involve participation of hydrogen atoms, hydrogen molecules or unstable intermediary compounds of hydrogen, for example, O_2H in the hydrogen-oxygen reaction or NiH in hydrogenating reactions at a nickel surface. By suitable experiments, it is possible to examine the changes both in the velocity and in energies of activation caused by the replacement of hydrogen by deuterium, and from such data to determine, sometimes uniquely, in other cases by elimination, which is the rate-governing step in the reaction mechanism and which of the three possible participants enumerated above is actually involved in this step. In this way, it has been found possible to confirm that the mercury photosensitised reduction of nitrous oxide takes place through an atomic mechanism, that the rate of the photochemical combination with chlorine is governed by the link involving a hydrogen molecule :

$$H_2 + Cl \rightarrow HCl + H ;$$

that the mercury photosensitised reduction of ethylene does not proceed through a chain mechanism; and that the chain mechanisms of the thermal combination of hydrogen with nitrous oxide and oxygen differ in that in the former a hydrogen atom is involved in the slowest link reaction and in the latter either a hydrogen molecule or a compound such as O_2H. Further information on the zero point energies of such complexes may permit of a decision between these two possibilities.

It was evident from the discussion that, quite apart from the more sensational and, at present, much more mysterious action of compounds of heavy hydrogen, especially water in biological processes, the new isotope provides an extremely effective weapon with which to extend our knowledge of the mechanism of the reaction kinetics of what are generally regarded as simple systems. E.K.R.

Hydrogenation of Coal in Germany

THE partial conversion of coal into liquid fuels by treatment with hydrogen gas under pressure at high temperatures is a technical process which is finding application in Great Britain, and a description of the method as used in Germany, given by F. Rosendahl (*Die Naturwissenschaften*, **33**, 554 ; 1934), is therefore of interest.

The development of the original process due to Bergius has been brought to a successful stage by the I. G. firm. The conditions for operation require that the reaction should be accelerated by suitable catalysts and that the sulphur, nitrogen and oxygen of the coal should be set free and united with hydrogen. The design of apparatus which could resist the action of sulphur and hydrogen under high pressure was also a difficult problem. As catalysts, the sulphides of iron, tungsten and molybdenum have been adopted, but the physical state of the contact mass is of great importance. In this way, two-thirds of the coal is converted into light liquid hydrocarbons, and it is possible to produce illuminating oil from coal.

The process occurs in two stages. In the first, the carbon compounds are decomposed and the carbon converted into hydrocarbons. This stage is practically quantitative, 15 per cent of gaseous and 85 per cent of a mixture of low and high boiling oils being formed. This stage is operated with a paste of

dried and powdered brown coal and oil under a pressure of 200 atmospheres in contact with hydrogen, the reaction chambers being tubes 18 m. long, 0·8 m. diameter, and with walls 13 cm. thick. The materials are heated to a temperature of about 500° C. The liquid product is then distilled, and heavy oil (used in mixing with the coal), petrol (benzine) and middle oil obtained.

The middle oil then undergoes the second stage of the treatment. It is again brought in contact with hydrogen under 200 atm. pressure, the whole mass being heated so that it becomes gaseous, and the reaction is allowed to proceed in a furnace, no details of which are given. The gaseous and liquid parts of the cooled product are separated, the excess of hydrogen being previously taken off under pressure. The liquid is distilled and the middle oil obtained again undergoes treatment.

The process is said to be capable of producing lubricating oils as well as petrol. About 20 per cent of the carbon of the coal is recovered as gaseous hydrocarbons (methane to butane), which may be used as such or converted into chemical compounds. Propane and butane are fairly easily liquefied, and can be used for lighting and heating. Such gases are used in the motors of 'zeppelins'. The gases may also be converted into hydrogen by reaction with steam.

In the hydrogenation process, which is strongly exothermic, the control of the temperature is very important, and the whole process must proceed within a narrow zone of temperature. If this is allowed to be exceeded, the temperature rises very rapidly and the reaction vessel may burst. To prevent attack of the steel vessels by sulphur, they are treated with zinc vapour, which produces a diffusion layer of iron-zinc mixed crystals. The vessels themselves are of chromium-nickel steel, containing vanadium, molybdenum and tungsten.

The whole process is one of considerable interest and importance, and possesses obvious advantages—apart from costs, which are not dealt with—over petroleum cracking, since the latter process does not produce lubricating oils of any value from the crude oil and also leaves a considerable proportion of coke.

University and Educational Intelligence

CAMBRIDGE.—The Frank Smart studentship in botany is vacant. Any graduate of the University is eligible provided that not more than fourteen complete terms have elapsed after the first term of residence. The value of the studentship is £200, and candidates' names should be sent to Prof. A. C. Seward at the Botany School before October 2. Candidates should submit a statement of the course of research it is proposed to undertake and such evidence of qualifications as they think fit.

ST. ANDREWS.—The date of the installation of General the Right Hon. J. C. Smuts as rector of the University has now been definitely fixed as October 17. The Senatus Academicus has resolved, on the occasion of the installation, to confer the honorary degree of LL.D. upon the following, among others: Sir Thomas Holland, principal of the University of Edinburgh; Mr. John Hutchinson, of Kew Herbarium; General the Right Hon. J. C. Smuts.

A COURSE of evening lectures on television will be given on Thursdays, commencing October 4, by Mr. J. J. Denton, at the Borough Polytechnic, Borough Road, London, S.E.1. The syllabus and further information can be obtained from the Principal of the Borough Polytechnic.

ACCORDING to the Berlin correspondent of the American Medical Association (*School and Society*, Feb. 17), German universities should be fortified against the debilitating influences of departmentalism and high specialisation by reforms recently decreed by the Prussian Minister of Public Instruction. A candidate for appointment to an instructional post will in future be required to have served several months in a field station or work camp in which conditions are such as to test his virility. Only after undergoing this test with credit will he be admitted to the *Dozentakademie*. Here, participating in a strictly organised community life while pursuing courses of a general scientific character, he will have to prove his worth in fields outside his specialty and will be expected to develop the general impulses requisite for the instruction of youth in the Germany of to-day. Lastly, he will be examined as a specialist. All this involves a radical breach with the tradition according to which the appointment of instructors used to be left to the unfettered discretion of the department, if not to a single member of it, with the result that candidates were selected for their scholastic attainments within their chosen special field without regard to their general qualifications. The *Dozenten* have, moreover, been organised as a society with bureaux which will deal, *inter alia*, with questions pertaining to reforms in curricula and the privileges of Germans who have emigrated to foreign countries.

Science News a Century Ago

A Lecture on Animal Physiology

Lecturers who dealt with the more popular aspects of natural science had, in early times, to consider the moods and composition of their audiences. Although no actual censorship existed, it was not deemed desirable to invest a discourse in physiology or in botany with too full details respecting the processes of function, for there was a risk of offending current established and entrenched habits of thought. The *Analyst*, in reporting a lecture on "Animal Physiology", delivered on September 29, 1834, by George Sheward, before the Worcestershire Literary and Scientific Institution, made the following comments:—"Mr. Sheward made choice of 'Animal Physiology' as the ground work of his lecture, and it becomes our duty to speak of it as a composition written for oral delivery. We wish it to be clearly understood that we do not entirely object to the peculiar matter chosen for the lecture. . . . The great difficulty however, suggested to our mind, was, how to steer clear of those technical explanations which are necessary to unfold the history of the animal economy, without trenching on the delicacy and fastidiousness of the auditors, one half of which possibly were females—but we are bound to say Mr. Sheward very dexterously contrived to throw becoming drapery over this department of his scientific research, and adapted it to the ears of the sensitive and the scrupulous. There can be no doubt