

Preparation of Heavy Water by Catalytic Exchange

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The great advantages of heavy water as a moderator in nuclear reactors have been very largely offset by the difficulties of establishing a satisfactory and economical manufacturing process. This article reviews possible methods of preparation by catalytic exchange, with particular reference to a process, recently developed in Germany, for the enrichment of heavy water by high pressure exchange between hydrogen and an aqueous platinum catalyst suspension.

It has been known since 1931 that hydrogen occurs naturally in the form of two stable isotopes, with atomic masses of 1 and 2, both of which are present, in combination with oxygen, in natural water. The heavier isotope, deuterium, forms what is commonly known as "heavy water"— D_2O —which is present in nature to the extent of only 0.014 per cent. With the development of nuclear engineering, heavy water has advanced from an academic curiosity to a vital chemical product. This increase in importance is due to its exceptional power of moderating neutrons, that is, slowing down neutrons released by fission to speeds at which they can cause further fission most effectively. Heavy water is many times more efficient than graphite for this purpose, but has not been as widely exploited because as yet no fully satisfactory manufacturing process has been devised, with the result that it is available only in relatively small quantities at a cost running to many thousands of pounds per ton.

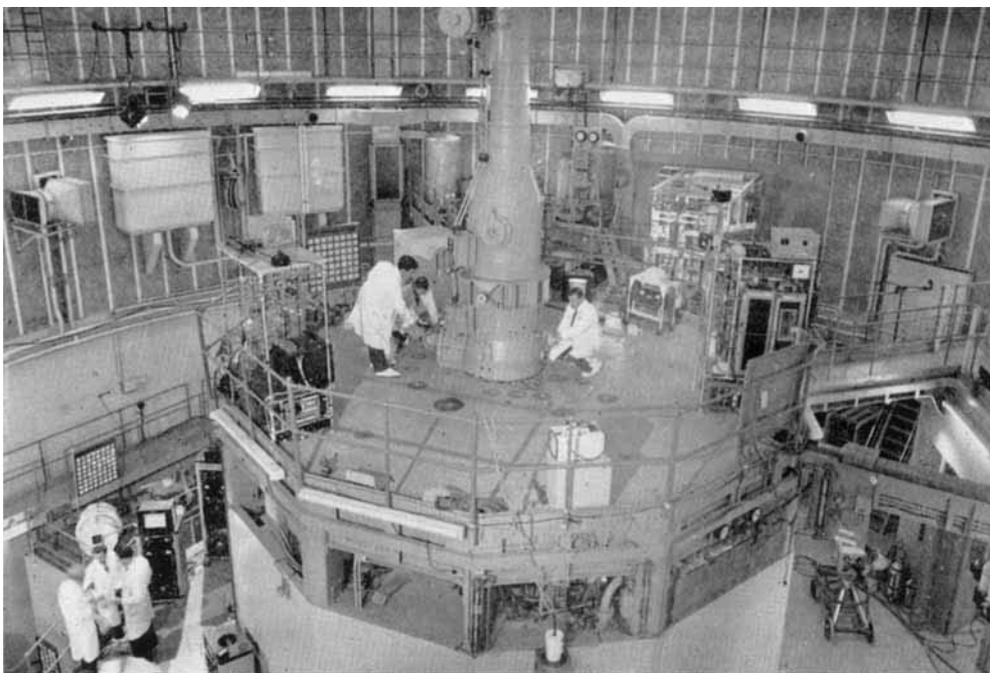
Despite this economic disadvantage, many countries have built, or have in the design stage, research reactors using heavy water as moderator, while much planning effort is being put into larger scale heavy water moderated reactors both for land use and for marine propulsion. Interest in the development of processes for the economical pro-

duction of heavy water is therefore very considerable.

Before the last war all the heavy water produced commercially was made by electrolysis, the largest plant being operated at Rjukan in Norway by the Norsk Hydro Co. During the war the race for the atom bomb stimulated research in the United States and in Germany into alternative methods of manufacture. In the United States H. C. Urey and his co-workers at Columbia University studied this problem and their work resulted in the erection of commercial scale units at the ammonia synthesis plant of the Consolidated Mining and Smelting Company of Canada Ltd. at Trail, B.C., and at three plants operated by E. I. Du Pont de Nemours and Co. Inc. in the U.S.A. (1).

Methods of Production

The basis of all methods of heavy water production is the separation of deuterium from a suitable hydrogen-containing raw material by utilising the slight differences in physical and chemical properties which exist between deuterium and hydrogen isotopes. In practice the raw material is almost always natural water or hydrogen. Although the mass ratio of 2 for hydrogen and deuterium is greater than for any isotopes of the heavier elements the task is made difficult by the low



DIDO, the experimental high-flux materials-testing reactor at Harwell, cooled and moderated by heavy water. A similar reactor, PLUTO, is also in operation at Harwell while a new reactor, DMTR, practically identical with PLUTO, is nearing completion at Dounreay. The Atomic Energy Authority has concluded that the best possible alternative to the gas-cooled graphite moderated reactor for small land-based power stations and for ship propulsion may well be a heavy water moderated reactor.

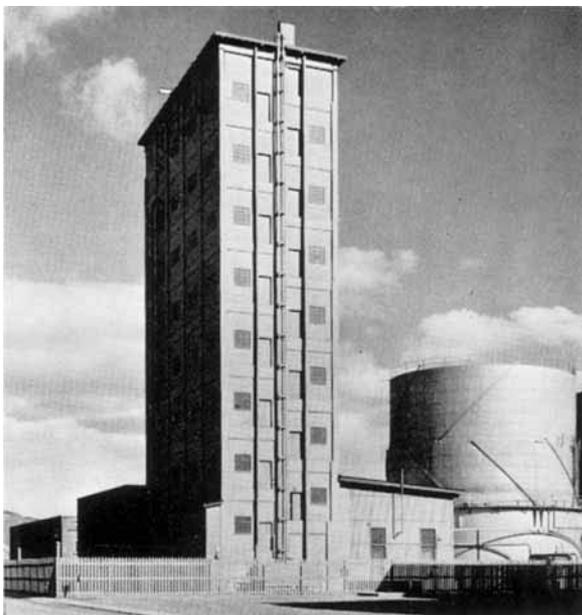
concentration of deuterium in natural water, which requires that large quantities be handled in the initial stages of the separation. An additional complication is caused by the fact that, when present in such low concentrations, deuterium is distributed in the water as HDO molecules which have properties intermediate between H_2O and D_2O . The only processes to have been operated on a large scale are the electrolysis of water—in which H_2O is decomposed more readily than D_2O ; water and hydrogen distillation; and chemical exchange, which depends on the isotopic displacement at equilibrium in certain reactions resulting in the concentration of deuterium in one component (1, 2).

In selecting suitable processes the following points must be considered: reversibility of the reaction, which is a measure of the power required, separation factor, which determines the number of reaction stages, and finally the complexity of the plant. The highest separa-

tion factor, $\alpha = 4$ to 7, is given by electrolysis, but this process is highly irreversible and the cost of power is prohibitive except in such places as Norway where very cheap hydroelectric power is available or where there is some form of natural power such as the geothermal springs in New Zealand. Electrolysis is, however, almost invariably used for the final concentration of deuterium once its level has been raised to the order of 2 to 5 per cent by other methods, since in this case smaller quantities are involved and the power consumption is much reduced.

Distillation methods are highly reversible and therefore have a low power consumption, but water distillation has a low separation factor while hydrogen distillation must be carried out near absolute zero, where knowledge of techniques is very limited.

Chemical exchange is probably one of the most promising methods for future large-scale production of heavy water. The basis of its



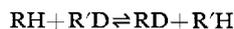
The primary heavy water plant erected at Trail, B.C., by the Consolidated Mining and Smelting Company of Canada Ltd.

in the gaseous phase, which introduced difficulties into the design of the plant, since the water had to be alternately evaporated and condensed.

Trail Plant

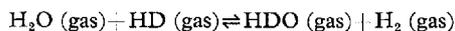
A plant using this process was installed during the last war at the synthetic ammonia plant of the Consolidated Mining and Smelting Company of Canada Ltd. at Trail, B.C. The necessity of using hydrogen as one of the raw materials restricted this process to

operation is that if in the general equation

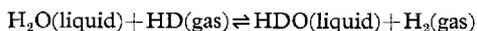


where R and R' are radicals attached to hydrogen and deuterium, the equilibrium constant K, which is equivalent to the separation factor α , is not equal to 1, some concentration of deuterium will be possible.

Many reactions are known which satisfy this condition but only those with water as one component are of practical importance. The reaction between water and hydrogen has often been suggested for this purpose—it can take place with water in the gaseous or liquid phase:



or



The two-phase reaction provides the better separation factor, $\alpha = 3.87$ at 25°C compared with 3.62 for the single-phase reaction, but it has been found in practice that the hydrogen-water system comes to equilibrium only very slowly, so that a catalyst is required, and until very recently no catalyst was known which would give efficient service in liquid water. Consequently the reaction had to be operated

sites where there was an abundant supply of the gas. In effect the hydrogen, produced by electrolysis, was borrowed for the purpose of extracting its deuterium content and then returned for the synthesis of ammonia. The deuterium was concentrated by a combination of catalytic exchange and electrolysis, carried out in the so-called primary and secondary plants.

The feed to the primary plant comprised steam and hydrogen gas from the ammonia plant. The deuterium concentrated in the steam and was raised to a proportion of about 2.3 per cent D_2O by this method in combination with electrolysis—further concentration to 99.8 per cent D_2O was effected in the secondary plant by electrolysis alone. The most effective catalysts for the exchange reaction were found to be platinum-on-charcoal and nickel-chromium, the former being used in the first three exchange towers and the latter in the fourth.

The primary heavy water plant at Trail is shown in the illustration above, and a simplified diagram of one of the exchange towers is given below. A stream of water containing H_2O and HDO flowed in at the top of the tower and a gas-vapour stream,

consisting of a mixture of H_2 , HD, H_2O and HDO flowed into the bottom. This gas stream was obtained from partial electrolysis of the water leaving the column and from stripped gases leaving the top of the subsequent tower. In the exchange tower the HD was partially absorbed in the descending water stream, the remainder of the vapour passing on to the next catalyst layer. Since the catalyst did not operate satisfactorily if wet, the scrubbing water was by-passed around each catalyst section and heaters were provided to dry the gas stream before it entered the catalyst bed. On leaving the tower the water entered an electrolysis cell where it was partially electrolysed; the hydrogen and some of the undissociated water returned to the tower as the vapour stream while the rest of the water—enriched in D_2O —entered a subsequent tower for further concentration.

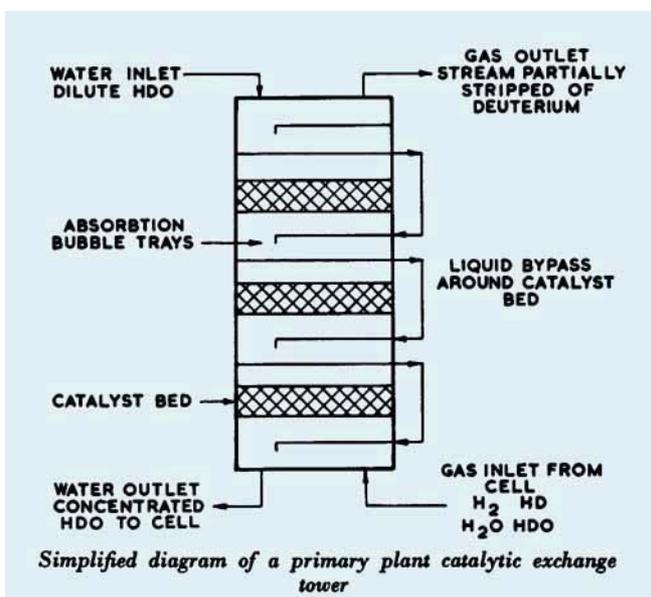
The development of the platinum-on-charcoal catalyst for the exchange reaction by G. G. Joris and his co-workers at Princeton University has been described in some detail (3). Canadian 8-mesh gas-mask charcoal and peach-nut charcoal when completely activated were found to be excellent supports. The most satisfactory combination of economy in platinum with high catalytic efficiency was attained with a catalyst containing 0.4 g platinum per 100 ml charcoal. The catalyst was easily poisoned by carbon monoxide, hydrogen sulphide, sulphur dioxide, mercury and water, even in minute traces. Regeneration was normally very simple; heating in hydrogen removed inactivation due to carbon monoxide and heating in air or oxygen removed the effects of sulphur poisons.

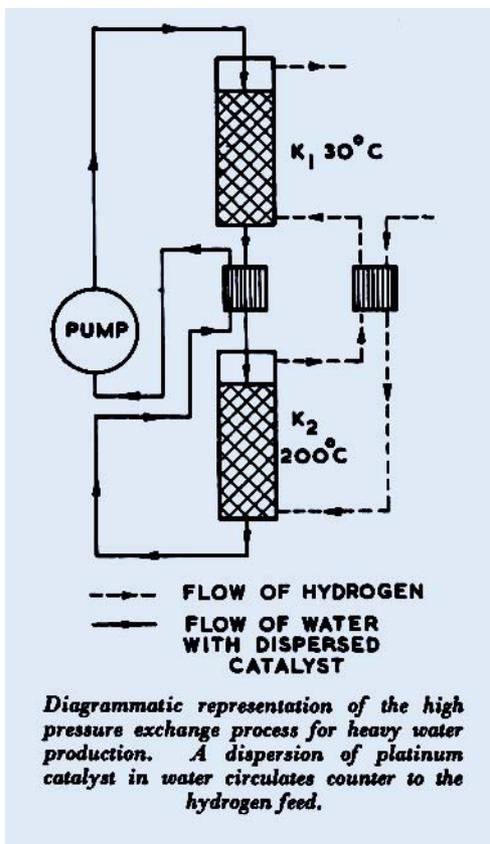
The cost of heavy water produced at Trail was more than \$60 per lb, which is comparatively high and

which led to the closing of the plant in 1955. However, it is known that by economies such as decreasing the losses of water vapour and hydrogen to a negligible value, and by cutting down the amount of catalyst, the cost of the heavy water could have been reduced to \$38 per lb. There are inherent disadvantages in this method, however, the most serious being the limitation of output imposed by the amount of hydrogen available. The Trail plant is the largest producer of hydrogen in the North American continent and yet its output of heavy water was only 6 tons per year. Since it has been estimated that in Canada alone the annual requirements of heavy water will be several hundred tons in a few years' time (4), it is evident that some further method must be sought for really large-scale production.

Dual-Temperature Processes

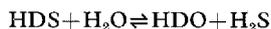
Where exchange reactions have equilibrium constants sufficiently dependent on temperature the reaction can be carried out at two temperatures in such a manner that the water is enriched at one temperature and depleted at the other. The second component carries deuterium from the depleted





to the enriched water stream and is not required as a raw material.

A dual temperature process using the system



has been developed for the plants at Dana and Savannah River in the United States (5). This system has the advantage that it requires no catalyst and can be operated in the liquid phase. Its main disadvantage, and one which held up progress for some time, is the corrosive nature of the liquids used. The plants produce about 800 tons of heavy water per year at a price of \$28 per lb.

The United Kingdom Atomic Energy Authority has studied dual-temperature chemical exchange processes between H_2S and water and between liquid ammonia and hydrogen, but no results have as yet been made available.

A process based upon the latter reaction,

using a potassamide catalyst, has recently been announced by Constructors John Brown Ltd.; the enriched ammonia is distilled and exchanged with water, and it is envisaged that this process could be operated in conjunction with ammonia synthesis plants to produce small quantities of heavy water at a price of about \$21 per lb. In a recent patent (6) supported platinum or palladium catalysts are suggested as alternatives in the above process.

The main disadvantage in the past of a dual-temperature process utilising the hydrogen-water exchange reaction has been that only catalysts active in the vapour phase had been developed. It was widely thought that if an efficient catalyst could be developed for the exchange reaction between liquid water and hydrogen, the dual-temperature hydrogen-water exchange process might well provide the most attractive method of producing large quantities of heavy water (4).

High Pressure Exchange with Aqueous Catalyst Suspension

In the past few years a group of German workers under the leadership of Professor E. W. Becker, of the Department of Physics, University of Marburg, has been developing a process for the enrichment of heavy water through high pressure exchange between hydrogen and an aqueous platinum catalyst suspension (7). By using the catalyst as a suspension the exchange can be carried out in the liquid phase. The process, which is said to have distinct economic advantages over others being operated, is to be developed by the firms Degussa and F. Uhde GmbH.

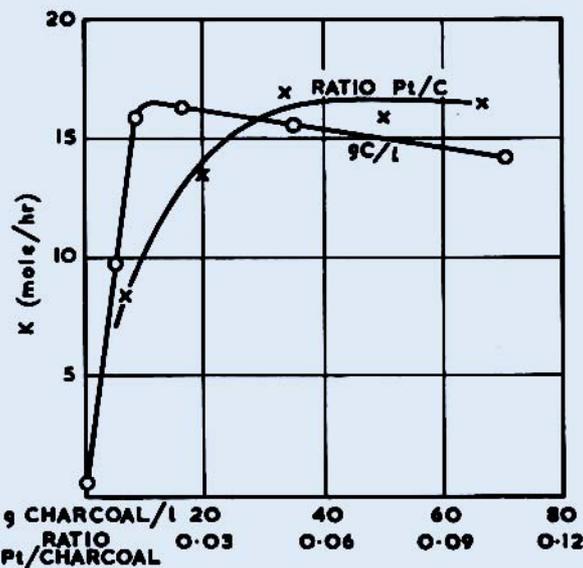
The process utilises a dual temperature cycle with hydrogen or a nitrogen-hydrogen mixture as the feed material. The suggested arrangement is shown in the diagram above.

The dispersion of water and catalyst circulates through columns K_1 and K_2 , which are held at about 30 and 200°C respectively. The feed material is introduced at the lower end of the hot column at a pressure of about 200 atm. The enriched product is drawn off between

the columns and the deuterium-poor gas is removed from the top of the cold column and returned to the supplier—probably a hydrogenation or ammonia synthesis plant. The heat carried by the materials is recovered as far as possible by means of heat exchangers. The main energy consumption is due to the incomplete heat recovery and the mechanical energy required to mix the phases. The latter is less for this process than for the hydrogen sulphide-water process because the material flow required for a given production rate is lower.

A pilot-plant has been designed in order to obtain the necessary data for the construction of a large-scale plant for D_2O production. It was calculated that the volume of the cold-column in a three-stage process should be 23 cu.m/metric ton D_2O /year. The hot column can be considerably smaller since the velocity of isotopic exchange increases rapidly with increasing temperature. In a plant of this size 10 per cent platinum-on-charcoal catalyst containing 7.7 kg of platinum is required to produce a concentration of 10 per cent deuterium. It was found experimentally that a greater concentration of catalyst reduces the efficiency of mixing between the phases and thus renders the process less efficient. Any further increase in the ratio of platinum to charcoal in the catalyst does not cause an increase in the rate of the process. The effects of catalyst concentration and platinum-charcoal ratio on the exchange constant, K , which is a measure of the rate of the reaction, are shown in the graph above.

It is estimated that the total heat consumption for the plant designed will be 0.94×10^6 kcal per kg D_2O . The total power consumption is estimated to be not more than



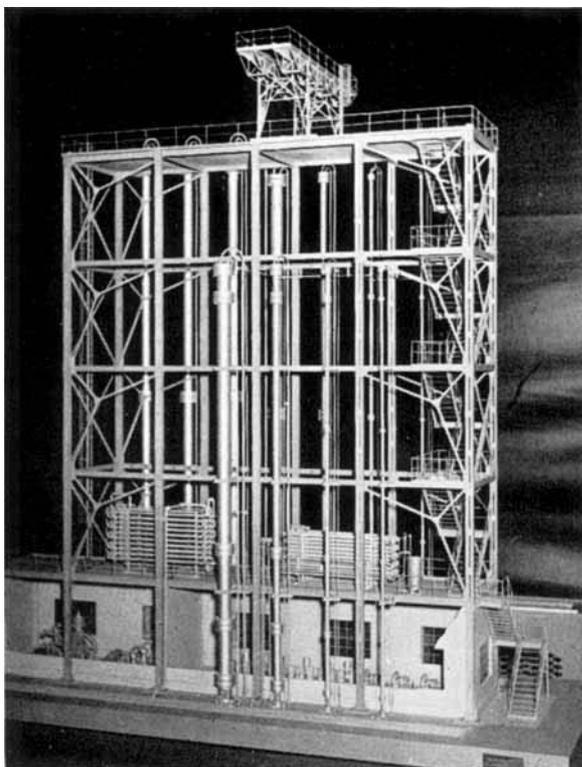
Effects of catalyst concentration and platinum-charcoal ratio on the exchange constant K in the high pressure exchange process

200 kWh per kg D_2O , which is only about a quarter of the power required for the American hydrogen sulphide process. The investment in platinum, including the necessary reserves, will be 16 kg for an annual production of 1000 kg D_2O .

These economic calculations are based on the assumption that the enrichment of deuterium is carried out exclusively in dual-temperature columns. The cost can, however, be considerably reduced by combining the dual-temperature process with some form of phase-conversion, which can be achieved by carbon monoxide conversion, water gas formation or electrolysis of water. Such phase-conversion depends on the possibility of completely separating the water from the catalyst suspension, and this has been found possible.

Future Outlook

Although this process has very favourable economic characteristics, it suffers from the same disadvantage as the Trail plant in that it uses hydrogen as feed material and therefore depends on large-scale sources of this gas.



Model of a plant to produce 10 tons a year of heavy water, using the high pressure exchange process developed by Degussa and F. Uhde GmbH. It is designed to operate in combination with an ammonia synthesis plant.

Fortunately it is possible to adapt this process for use with water as feed material. Such a modification would, however, considerably increase both the plant and operating costs due to the increased material flow required for a given D₂O production. A further modification (8) which does not require the use of hydrogen as feed material is obtained by causing the hydrogen to flow in a closed

circuit and incorporating a further exchange column in this circuit. This auxiliary column contains a catalyst such as platinum on aluminium silicate or porcelain. Water having normal deuterium content is passed through the column from the top downwards, enriches the circulating hydrogen and is removed as an impoverished product. The enriched material is drawn off between the two dual-temperature columns, as in the arrangement described earlier in this article.

If this process can be operated economically using only natural water as feed material it should prove of great value in future large-scale production of heavy water. With hydrogen as feed material the process should be of particular advantage for relatively small-scale production of about 50 tons per year.

It is probable that a number of processes for heavy water manufacture will be brought into use, adapted to suit the energy and material resources of different countries. Many of them are likely to depend on chemical exchange as the primary mechanism of separation; where the quantity needed is relatively small, hydrogen may be the favoured source of deuterium, but natural water is the only possible basis for large-scale extraction.

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