An apparatus for the production of high isotopic purity deuterium

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Abstract An apparatus for the electrolytic preparation of high purity D_2 is described. D_2 with isotopic purity exceeding 99·98% (atomic percentage) was obtained with this apparatus by electrolysing D_2O (99·8% isotopic purity) down to about 30% of its original volume.

1 Introduction

Commercial deuterium gas usually contains 0·2% or more H atoms as an isotopic impurity. However, higher isotopic purities may be necessary in some studies, such as the exchange reaction of H atoms with D_2 molecules (Kuppermann and Persky 1974). In the present paper we describe an apparatus designed to produce deuterium gas with a [HD]/[D_2] concentration ratio smaller than 4×10^{-4}. In addition, the D_2 produced by this apparatus has a high chemical purity and is not contaminated by mercury vapours, which makes it suitable for use in photochemical systems in which photosensitized reactions must be avoided.

2 Apparatus and performance

The apparatus is based on the isotope effect in the electrolysis of water (Duncan and Cook 1968), in this case D_2O containing small amounts of HDO. In this process the fraction of the light isotope, H, in the hydrogen gas formed at the cathode is higher than in the water, and therefore the liquid D_2O in the cell becomes isotopically purer as the process proceeds.

Figure 1 is a schematic diagram of the apparatus. D_2O stored in the original 100 ml syringe bottle (Bio-Rad Laboratories, Richmond, California, 99·8% stated isotopic purity) is transferred by suction into the electrolytic cell. This is done through a short piece of rubber tubing with the aid of two syringe needles soldered back to back, turning the bottle upside down around the joint J and applying vacuum suction carefully. The electrolytic cell E is made of two 30 ml Pyrex bulbs connected by a V shaped tube, 10 mm in diameter. The electrodes are made of platinum rod, 1·0 mm in diameter. The oxygen formed at the anode leaves the system through the mercury manometer M_1, overcoming a pressure of about

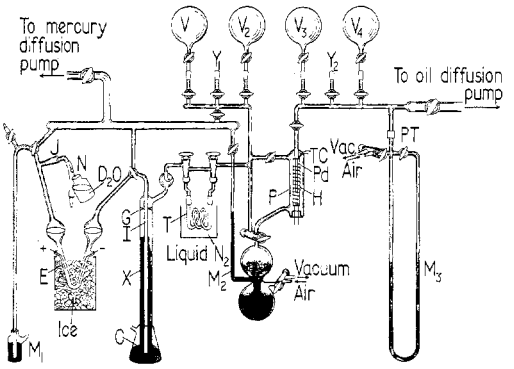

Figure 1 Diagram of apparatus for the electrolytic preparation of pure D_2. E, electrolytic cell; J, Pyrex joint; N, two syringe needles soldered back to back; M_1, M_2 and and M_3, mercury manometers; T, liquid nitrogen-cooled trap; P, hydrogen purifier (General Electric Model 22HL010) containing a 75% Pd–25% Ag membrane, heater (H) and thermocouple (TC); PT, pressure transducer; TP, Toepler pump

30 Torr above atmospheric pressure. The hydrogen formed at the cathode also overcomes a similar pressure, bubbling from the inner tube I, through the mercury column in X, into the 3 l flask V_1 (or V_2). The trap, T, cooled with liquid nitrogen, traps water vapour carried by the deuterium. The amount of mercury in flask C (volume 1·5 l) is adjusted so that when V_1 is evacuated, the level of water at the anode is about 8 cm below the level at the cathode, and the level difference is inverted when the pressure in V_1 is about 600 Torr. The operation of this part of the system is similar to that described by Dutt (1960), but in our apparatus special precautions were taken to avoid any exchange of water in the system with moisture in the atmosphere. In Dutt's apparatus the anode section is open to the atmosphere and there is no provision for introducing D_2O into the electrolytic cell without contact with the atmosphere.

After about 600 Torr of D_2 is accumulated in V_1 (or V_2), the stopcock attached to it is closed and a sample of the gas being formed by the electrolysis at that time is admitted to a sample bulb of about 20 cm^3 attached to Y_1. This sample is then analysed with a mass spectrometer (CEC model 21-103C). When its protium content becomes sufficiently low, the rest of the apparatus is activated. The D_2 accumulated in V_1 is then transferred, with the aid of the toepler pump TP, through a 75% Pd–25% Ag membrane (General Electric model 22HL010 hydrogen purifier). The purifier is degassed and deuterated before being used. By heating the membrane to 400°C the average rate of deuterium transfer is about 1·5 litres $hour^{-1}$ at 500 Torr. This transfer rate is about 10 times faster than the D_2 production rate. The Pd–Ag membrane is very selective, allowing only the hydrogen isotopes to diffuse through it (Dushman and Lafferty 1962). Therefore the deuterium collected in V_3 is chemically pure. This principle was used also by Winn (1951) for purifying hydrogen chemically. The system beyond the Pd–Ag membrane is evacuated with an oil diffusion pump. The pressure in V_3 is measured with a pressure transducer (PT) (Pace model P7D) and a mercury manometer (M_3) as a reference. In this way, the purified D_2 does not come in contact with mercury.

The electrolyte used in the electrolytic cell was a 40% solution of NaOD in D_2O, with a stated isotopic purity of 99% (Bio-Rad Laboratories). In the first stage of the electrolysis 8 ml of this solution were introduced into the electrolytic

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cell, an equal amount of the 99·8% isotopic purity D_2O was added, and electrolysis was conducted until about 7 ml liquid remained. This was done in order to enrich the NaOD solution with the D isotope. An additional 35 ml of D_2O were then added to the cell and the electrolysis continued. A voltage of about 30 V was applied between the electrodes of the cell, producing a current which varied between about 200 mA and 400 mA during the electrolysis. During operation the V-shaped part of the cell was cooled with ice to avoid excessive evaporation of the solution and to maintain the electrolysis temperature approximately constant. The electrolysis is continued until about 7 ml is left in the cell, at which time the enrichment process is considered terminated. If more isotopically purified D_2 is desired, 35 ml of D_2O are added to the residual liquid from the previous purification, and the rest of the procedure is repeated.

The isotopic purity of the D_2 formed during electrolysis was regularly checked by mass spectrometric analysis. Before doing an analysis the mass spectrometer was deuterated by running isotopically purified deuterium through it for several hours. This was found to be necessary, especially for samples containing low amounts of HD, in order to reduce the amount of HD formed by exchange of D_2 in the mass spectrometer. A typical dependence of the measured $[HD]/[D_2]$ ratio of the D_2 produced on the fraction f of the D_2O removed from the cell by the electrolysis since the addition of the 35 ml of D_2O is shown in figure 2. It can be seen that as the enrichment process proceeded, the fraction of HD in the D_2 gas decreased to 4×10^{-4} when f was about 0·7, and no improvement in the isotopic purity was observed beyond this stage. It seems reasonable to assume that a large part of this residual HD is formed in the mass spectrometer, no matter how well it is deuterated, and that the actual purity of the D_2 at this stage is much higher.

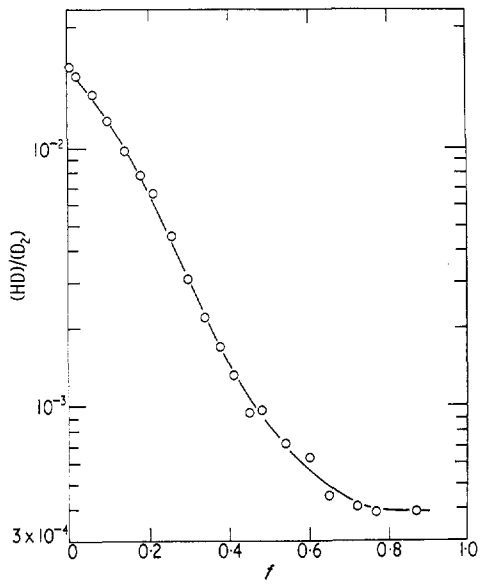

Figure 2 $[HD]/[D_2]$ ratio in the gas formed at the cathode of the electrolytic cell, as a function of the fraction of heavy water electrolysed from the cell

3 Conclusion

The apparatus described in the present paper permits the preparation of chemically pure D_2 containing less than one H atom per 5000 D atoms.

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