Commercial hydrogen, available in steel cylinders, is produced either by electrolysis or by the water shift reaction from water gas.

Electrolytic hydrogen contains 99.7-99.8% H$_2$. The only impurity is air, with the oxygen amounting to less than 0.1%. This commercial hydrogen may be treated either by passage through a combustion tube filled with reduced CuO wire at 400°C, or by passage through the "active copper tower" of Meyer and Ronge (see section on Nitrogen), followed by drying with CaCl$_2$ or P$_2$O$_5$. The gas obtained by either of these methods may be used for most laboratory applications, since its very small N$_2$ content (about 0.2%) is usually not harmful. If commercial electrolytic hydrogen is unavailable, it may be prepared in the apparatus described in the section on Nitrogen (the polarity is reversed, compared to oxygen preparation).

On the other hand, commercial hydrogen produced from water gas is contaminated with considerable amounts of CO, CO$_2$, O$_2$ and N$_2$, and sometimes also with AsH$_3$ and Fe(CO)$_5$. The CO$_2$ may be removed by absorption with KOH or soda lime; the AsH$_3$ is taken up by a fully saturated KMnO$_4$ solution (containing solid KMnO$_4$). The O$_2$ is separated out either by passage over heated copper wire or over red-hot Pt-asbestos (prepared according to the directions given in the section on Platinum Metals). The latter procedure also results in thermal decomposition of the Fe(CO)$_5$. The removal of CO is more difficult, since neither absorption in acid or ammoniacal CuCl solution nor oxidation with HgO (or HIO$_3$) is quantitative. The most reliable method of removing CO is freezing out at the temperature of liquid nitrogen. In any case, pure H$_2$ is best prepared from electrolytic hydrogen.

Very pure, completely air-free hydrogen may be prepared by any of the following methods.
I. HEATING OF PALLADIUM SPONGE

Palladium sponge, prepared by the reduction of PdCl$_2$ solution (see section on Platinum Metals), is carefully washed with hot water, dried and well calcined by heating with a burner. The hot product is charged into a preheated combustion tube (provided with a manometer sealed to one end) and allowed to cool slowly in vacuum. When the sponge reaches room temperature, a carefully prepurified and predried H$_2$ stream is admitted into the tube and is to a large extent absorbed by the Pd. The absorption produces a slight glowing of the sponge. When the sponge is then heated to about 200°C, pure H$_2$ is liberated. A steady stream of the gas may be obtained with the aid of a small pump. In this way, 100 ml. (STP) of H$_2$ may be obtained per gram of palladium.

This method is especially useful in the preparation of small quantities of very pure hydrogen. E. von Angerer (Technische Kunstgriffe bei physikalischen Untersuchungen [Industrial Techniques Applied to Physical Experiments] 6th ed., Braunschweig, p. 92) shows an apparatus capable of continuous production of 100 ml. of pure H$_2$ per hour. It operates on the principle of hydrogen diffusion through electrically heated Pd tubes.

II. DIFFUSION THROUGH NICKEL

Commercial hydrogen may also be further purified by diffusion through nickel. This may be accomplished in the apparatus shown in Fig. 87, which yields a steady stream of very pure gas at atmospheric pressure.

The basic component is a pure nickel, precision ground, seamless tube (diameter 2 mm., length 5 m., wall thickness 0.1 mm.) soldered shut at one end. Five such tubes are needed. Each is coiled into a helix, the helices are intertwined, and the open end of each tube is soldered to a brass header, as shown. The header is provided with a standard tapered male joint n. For ease of handling, the tubes are heated in a H$_2$ stream at 1000°C for two hours, after which they may easily be bent by hand. The helix assembly is inserted into a quartz reactor tube 1 m. long and 35 mm. in diameter. The front and back headers are cemented to the quartz tube with picein, as shown. The back header is provided with a needle valve v, which serves for fine control of pressure in the tube and through which the gaseous impurities, which are contained in the hydrogen and which accumulate in the reactor, may be released and subsequently burned. The front header has a connection for a mercury manometer. Only the middle part of the quartz reactor is electrically heated. Thus, the soldered points of the nickel tubes remain in the cooler sections of the apparatus.
I. HYDROGEN, DEUTERIUM, WATER

Fig. 87. Purification of hydrogen by diffusion through nickel: \( \nu \) is a needle valve for fine control of pressure in the apparatus.

Depending on the operating conditions, the apparatus is capable of delivering the following quantities of hydrogen:

<table>
<thead>
<tr>
<th>°C</th>
<th>15</th>
<th>20</th>
<th>25</th>
<th>30</th>
<th>mm. Hg</th>
</tr>
</thead>
<tbody>
<tr>
<td>750</td>
<td>20</td>
<td>27</td>
<td>34</td>
<td>41</td>
<td></td>
</tr>
<tr>
<td>815</td>
<td>27</td>
<td>36</td>
<td>43</td>
<td>52</td>
<td></td>
</tr>
<tr>
<td>860</td>
<td>34</td>
<td>45</td>
<td>55</td>
<td>68</td>
<td></td>
</tr>
<tr>
<td>900</td>
<td>41</td>
<td>54</td>
<td>68</td>
<td>84</td>
<td></td>
</tr>
</tbody>
</table>

The gas output is proportional to the pressure in the reactor but does not vary linearly with temperature. By varying the pressure, any desired gas output can be obtained almost instantaneously. Provided the feed gas cylinder has a good regulator, the reactor will give trouble-free operation for about 250 hours. However, it must be tested for leaks before each run.

III. DECOMPOSITION OF \( \text{UH}_3 \)

\[
2 \text{UH}_3 = 2 \text{U} + 3 \text{H}_2
\]

482.19  476.14  6.05

This procedure permits the production of very pure hydrogen free of noble gases. The gas may be obtained in any desired amount and at any time from previously made \( \text{UH}_3 \).

The \( \text{UH}_3 \) may be prepared in the apparatus shown in Fig. 88. Commercial electrolytic hydrogen (from a cylinder) is prepurified by passage over copper shavings in tube \( b \) at 650-700°C and drying with anhydrous \( \text{Mg(ClO}_4)_2 \) in tube \( c \). The gas may be further purified at \( d \) by passage through pulverized uranium at 700-750°C.
This prepurified hydrogen may then be converted to UH₃ in the two-neck flask \( f \), which is half filled with uranium turnings. These turnings must also be prepurified by treatment with dilute HNO₃ (to remove the oxide film), washing and drying. Flask \( f \) is heated either with a nitrate-nitrite salt bath or an electric furnace. The temperature in the flask is 250°C. Two wash bottles, one empty and one filled with concentrated H₂SO₄, are attached to flask \( f \).

![Diagram](image)

**Fig. 88.** Preparation of uranium hydride and purification of hydrogen. b) tube filled with copper shavings; c) tube filled with Mg(ClO₄)₂; d) tube containing uranium powder supported and covered by glass wool plugs \( e \) and \( e' \); f) flask with uranium turnings; g) heating bath; \( e_1, e_2 \) ground glass joints.

The apparatus must be thoroughly purged with hydrogen prior to the run, i.e., prior to heating \( b, d \) and \( f \). The reaction is completed when the H₂SO₄ in the riser of the last wash bottle is no longer pulled upward by suction upon interruption of the H₂ stream.

The UH₃ product is a brown-black, spontaneously igniting powder. Very pure hydrogen may be liberated from it by heating, possibly at reduced pressure, to 400°C (or to a somewhat lower temperature). The uranium powder residue remaining after the decomposition reacts vigorously with H₂ at room temperature. The reaction is still quite vigorous at -80°C and ceases only at -200°C.

**IV. DECOMPOSITION OF TITANIUM HYDRIDE**

Titanium hydride is well suited for the production of larger quantities of very pure hydrogen. It has a relatively low decomposition temperature (400-900°C), a relatively high hydrogen content, and is easily regenerated. Aside from this, titanium oxide and nitride are completely stable at the required decomposition
temperatures. The decomposition is endothermic. Thus, the evolu-
tion of gas ceases whenever the flow of heat is reduced, and a con-
tinuous, well-controlled gas stream is obtained. It is advisable
to use the apparatus shown in Fig. 89, so that the very pure $\text{H}_2$
product may be immediately used in hydrogenation reactions, which
may be conducted in the space provided at $\gamma$.

Fig. 89. Preparation of very pure hydrogen from titanium
hydride. $a$) quartz reactor tube; $b$) molybdenum boat con-
taining Ti; $c$) heating winding; $d$) radiation shield; $e$) radia-
tion shields for protection of stoppers; $f$) glass wool; $g$)
apparatus for conducting reactions with the very pure
hydrogen product; the tube contains a boat for the reactants
and is surrounded by an electric furnace. This part may be
omitted if the hydrogen product is to be used elsewhere;
$m$) pressure-sensing switch; $r$) relay.

A quartz reactor tube $a$ (O.D. 34 mm., I.D. 30 mm., over-all
length 1500 mm.) is wound over a length of 650 mm. with a heating
coil $c$, which is cemented to the tube with a thin quartz-waterglass
slurry. Molybdenum boat $b$ is placed in the heated zone. The radia-
tion shield $d$ retards heat loss to the outside. Switch $m$ controls
the heat input to the winding, sensing the pressure developed by
the hydrogen product stream.

The titanium hydride is prepared as follows: commercial
titanium sponge of usual purity and medium grain size is placed
in the molybdenum boat and dried in a stream of commercial hy-
drogen at 400°C. This step may sometimes be omitted. Following
this, the temperature is raised to 700°C. The material is then heated
for 30 minutes while maintaining the gas flow. Then, after thorough
evacuation of the apparatus, the product (titanium hydride) is heated.
until a pressure of 0.1 atm. gauge is registered on switch $m$, at which point the current is shut off. The pressure decreases due to the rapid drop in temperature and consequent gas volume contraction (and/or use of the gas for hydrogenation at $g$). When the control point pressure is reached, the current is again switched on. Despite this simple "on-off" control, pressure fluctuations are small.

After the desired amount of hydrogen has been liberated, the titanium hydride may be regenerated by heating in commercial hydrogen and subsequent cooling. A charge of 500 g. of titanium sponge will liberate 100 liters of pure $H_2$ per run.

V. ELECTROLYSIS IN THE ABSENCE OF AIR

An apparatus for electrolytic preparation of $H_2$ or $O_2$ (depending on polarity) in complete absence of air is described in the section on Nitrogen. The product gas contains less than $4 \cdot 10^{-6}$% air.

PROPERTIES:

Formula weight 2.016. Colorless, odorless, tasteless gas. Its reducing action is especially apparent at high temperatures. For this reason, hot $H_2$ should not be passed through concentrated $H_2SO_4$, since it then becomes easily contaminated by $SO_2$.

M.p. $-259.2^\circ$C, b.p. $-252.8^\circ$C; $t_{cr} = 239.9^\circ$C, $p_{cr} = 12.8$ atm. gauge; $d$ (liquid) 0.070; weight of 1 liter $H_2$ at STP = 0.08987 g. Solubility in water at 760 mm.: 0.021 vol./vol. at 0°C, 0.018 vol./vol. at 20°C, 0.016 vol./vol. at 100°C. Solubility in other liquids is also very small.

REFERENCES:


I. HYDROGEN, DEUTERIUM, WATER

Pure Water

The usual laboratory distilled water contains considerable amounts of dissolved $\text{CO}_2$ and, occasionally, traces of $\text{NH}_3$ and organic substances.

This distilled water may be purified with $\text{CO}_2$- and $\text{NH}_3$-free air, which is allowed to bubble through at $90^\circ\text{C}$ for 24 hours. The air should be drawn from outside the building, since laboratory air is often quite badly contaminated. Before contacting the water, the air passes successively through a wash bottle filled with concentrated $\text{H}_2\text{SO}_4$, two bottles with NaOH, and one filled with pure water. Avoid long rubber tubing connections.

This prepurified water is then doubly distilled, first with addition of some NaOH and $\text{KMnO}_4$ and then in the presence of a small quantity of $\text{KHSO}_4$. The condenser and its connections should be of Sn, Pt or quartz. Glass condensers must be avoided. It is advisable to bend the condenser outlet at a right angle and insert the leg directly into the neck of the receiver, using no sealing materials (see Fig. 90). To avoid condensate spraying, a vapor trap is installed before the receiver, as shown in the figure (b).

![Fig. 90. Distillation of pure water. Adapters for transition from condenser to the receiver; a) simple and inexpensive; b) with a vapor trap.](image)

![Fig. 91. Distillation of "conductivity" water. ST are standard ground joints.](image)

The receivers should be of quartz, Pt or Pyrex and must be thoroughly steamed out before use. The distillation should be slow and large volumes of forerun and residue should be discarded. Contact with laboratory air should be avoided as much as possible.

The product may be tested for purity by the conductivity method. The freshly distilled product should have a conductivity of about $10^{-5}$ ohm$^{-1}$ cm$^{-1}$. It may be tested for $\text{CO}_2$ with $\text{Ba(OH)}_2$ solution and for $\text{NH}_3$ with Nessler's reagent.
Very pure water is stored in quartz or platinum containers. Pyrex vessels may be used, if properly steamed out and if employed only for water storage. The receiver neck should have a male ground joint and be closed by a cap with a female joint.

REFERENCES:


"CONDUCTIVITY" WATER

Extremely pure water for conductivity measurements is obtained through very careful distillation of already thoroughly purified material. This prepurified water (conductivity at 25°C: 1-2 $\times 10^{-6}$ ohm$^{-1}$) is obtained either via the method described above or through another double distillation procedure [the first distillation with KMnO$_4$ + H$_2$SO$_4$, the second with Ba(OH)$_2$, using a Pyrex apparatus with a tin condenser].

I. Single-step distillation according to the method of Kortüm is done in the apparatus shown in Fig. 91. Except for the short quartz condenser, the apparatus is made of Pyrex. All connections are made with ground joints, except where indicated. The section between the reflux condenser and the quartz condenser is wound with a 60-ohm heating coil and heated to 100°C in order to avoid creepover of liquid water. The Pyrex reflux condenser is of the internal helix type. A ground joint adapter connects the condenser and the receiver. This adapter and the receivers must be thoroughly presoaked in hot, dilute acids (several days) to remove any impurities which may increase the conductivity of the product.

The pure water charge is distilled in a stream of air. Compressed air from a cylinder flows at a slow rate of 1 bubble/second through seven wash bottles. In succession, these are filled with concentrated H$_2$SO$_4$ (1 bottle), 50% KOH (3 bottles) and "conductivity" water (3 bottles, preferably with glass frits). The same compressed pure air is used to transfer the product water from the receivers to storage vessels. The three grids heating the distillation flask consume about 300 watts. In order to improve the rate and uniformity of heat transfer, the space between the heating grid and the distillation flask is filled with ceramic beads. The center tube of the distilling flask permits charging and emptying the contents.

A conductivity cell is attached to the three-way stopcock at the outlet of the condenser. The distillate is discarded until
its conductivity matches the desired value. Only then is the system connected to the receiver.

The apparatus delivers 100 ml./hr. of water having a $\kappa (25^\circ C) = 2 \cdot 10^{-7}$ ohm$^{-1}$. At very low distillation rates, water with a $\kappa (25^\circ C) = 10^{-6}$ ohm$^{-1}$ may be obtained.

II. "Conductivity" water with $\kappa (25^\circ C) = 6-8 \cdot 10^{-8}$ ohm$^{-1}$, in volumes larger than those provided by the apparatus of method I, can be obtained with the installation of Thiessen and Herrmann. This two- or three-step distillation does not require excessively complex equipment and is capable of delivering 400 ml./hr. of product.

REFERENCES:


"pH-PURE" WATER

The method for obtaining large quantities of water with pH = 7.00 is based on addition of NaOH and KMnO$_4$ during the first distillation and H$_3$PO$_4$ (to combine the NH$_3$) in the second distillation step. A third distillation in quartz apparatus (to remove traces of alkali) follows.

REFERENCE:


Deuterium and Deuterium Compounds

Deuterium and the simpler inorganic deuterium compounds are commercially available. Nevertheless, the research chemist may occasionally be called upon to prepare some of these compounds, starting with D$_2$O—the most available of the deuterium compounds.

Heavy water is manufactured in concentrations ranging from 5 to 99.5% D$_2$O and is sold in sealed glass ampoules. Pure heavy water is very hygroscopic; i.e., it loses D$_2$O vapor while simultaneously absorbing air moisture. Therefore, certain precautions must be taken when filling or emptying D$_2$O ampoules.

If only a portion of the ampoule content is to be used, the pointed end of the ampoule is heated in a small flame and drawn out to a capillary with tongs. The capillary end is then broken off and the desired quantity of D$_2$O driven out by gentle heating,
e.g., by hand. The receiver is closed off as soon as possible and the ampoule is immediately resealed with a flame. It is best to store it in a desiccator.

The D$_2$O contents of an ampoule may be preserved from contact with air moisture and still utilized only partially in the following way: the entire contents of the ampoule are transferred by the method given below to an elongated flask, closed off by a piercable, membrane-type rubber stopper, such as used for serum vials. Then the desired amounts of D$_2$O can be withdrawn from the closed flask by means of a hypodermic syringe and injected into other vessels, which can also be closed off with the same type of stopper. The very fine capillary produced in the rubber stopper by the needle closes immediately upon withdrawal of the latter.

If the entire contents of an ampoule are to be used in a reaction, it is best to break and empty it inside the reactor itself, thus avoiding transfer operations. To accomplish this, the ampoule is placed in a snugly fitting vessel, such as shown in Fig. 92. This vessel is then melt-sealed to the reactor. The apparatus is then connected to a high-vacuum system. If avoidance of dilution of the D$_2$O content is critical, the entire apparatus is heated by fanning with an open flame to remove the film of "light" water accumulated on the internal surfaces. The vacuum is then disconnected, the apparatus is closed off, and the vessel containing the ampoule is rapidly immersed in liquid nitrogen. The sudden freezing of the D$_2$O causes the ampoule to shatter. Cooling with an acetone-Dry Ice mixture is not sufficient, because the solidification of the D$_2$O tends to be slower and its crystals begin to grow mostly in the upper, empty part of the ampoule. Alternatively, the ampoule may be broken by a sudden movement of a glass-enclosed iron bar, suspended inside the reactor and set in motion by an electromagnet.

All substances to be reacted with D$_2$O must be carefully freed of all traces of water. Hygroscopic compounds, in which the uptake of small amounts of H$_2$O during charging of the reactor is unavoidable, must be re-dehydrated in the reactor itself. This is done by heating (in high vacuum, if possible), distillation or resublimation, where applicable. Again, such hygroscopic compounds may be enclosed in sealed glass ampoules immediately after their preparation. These ampoules may then be inserted into the reactor and broken with a magnet-operated iron bar, as described above.
As far as possible, the apparatus should have fused connections and contain a minimum of stopcocks. If this is not possible, special care should be taken in sealing all possible leaks. Drying tubes should be inserted between the apparatus and its connections to the pumps (vacuum) or to the atmosphere. Better still, liquid-nitrogen-cooled gas traps should be used to prevent entrance of atmospheric moisture. Since in the presence of H$_2$O most inorganic D compounds exchange part of their D content for H, these precautions must be observed in all reactions described in later sections.

Large amounts of deuterium compounds are expensive. It is therefore advisable to practice each reaction with "light" starting material before attempting to use the D compounds.

REFERENCES:


Deuterium

D$_2$

1. \[ 2 \text{D}_2\text{O} + 2\text{Na} = \text{D}_2 + 2\text{NaOD} \]

40.06 45.99 4.03 82.02

Flask $E$ of the glass apparatus shown in Fig. 93 contains an Al crucible with excess metallic sodium. Vessel $V$ contains the D$_2$O reagent. The latter is introduced (as described above) in the absence of atmospheric moisture. After cooling $V$ with liquid nitrogen, the apparatus is carefully evacuated, with stopcocks 1 and 2 open. Stopcock 2 is then closed and the D$_2$O is distilled slowly onto the Na by cooling $E$ with liquid nitrogen. To complete the reaction, $E$ is then heated for several hours to 350°C. After opening stopcock 2, the D$_2$ produced is transferred for purification into a receptacle filled with degassed charcoal and left there for some time at $-196°C$. If fresh Na is used, the D$_2$ product will still contain some few percent of H$_2$ after the purification (this H$_2$ was dissolved in the metal and existed as NaOH). Pure D$_2$, containing less than 0.2% H$_2$ and other foreign gases, is only obtained in the second run with the same piece of Na.
The gas is tested for purity by measurement of the thermal conductivity or vapor pressure. The yield of $D_2$ is quantitative.

The method is especially suitable for the preparation of small amounts of $D_2$ (up to one liter).

In an elongated flask of a Pyrex apparatus, pre-evacuated to $10^{-4}$ mm., 20 g. of $D_2O$ is slowly evaporated. The vapor passes through the reaction tube, set vertically on top of the flask. The tube (I.D. 2.4 cm. and 55 cm. long) contains 130 g. of Mg shavings of various sizes, with coarse particles on the bottom and loose powder on top. The column filling is supported by a perforated platinum disk which rests on glass lugs inside the tube. The Mg is heated to 480°C by a tubular furnace.

After an extended period of time, some magnesium silicide will form on the walls of the heated glass tube. To avoid this, it is suggested that the Mg be placed in a tube of unglazed hard porcelain which is then inserted into a Pyrex or Vycor tube and melt-sealed to the latter at one end. With such an arrangement the Mg may even be heated to a somewhat higher temperature and its reactivity thus enhanced.

For purification, the $D_2$ product passes through a trap filled with glass wool and kept at $-196^\circ$C. It is taken out from the generator as quickly as possible, either by condensation with liquid $H_2$ or by forcing it into an attached storage container. An in-line flowmeter and a manometer allow constant checking of pressure. The rate of evolution can be controlled by varying the supply of heat to the $D_2O$ flask. A maximum flow of 0.5 mole of $D_2$/hour may be obtained. Since the first $D_2$ fraction may be
I. HYDROGEN, DEUTERIUM, WATER

contaminated with some H\textsubscript{2} from the Mg and from the apparatus walls, it is advisable to collect some of the first D\textsubscript{2} fraction in a separate vessel. The D\textsubscript{2} formed later is very pure. The yield is quantitative.

This method allows rapid production of large amounts of D\textsubscript{2} and utilizes the entire D content of the heavy water.

III.

a) \[2\text{D}_2\text{O} + \text{U} = \text{UO}_2 + 2\text{D}_2\]

\[
\begin{array}{cccc}
40.06 & 238.07 & 270.07 & 8.06 \\
\end{array}
\]

b) \[3\text{D}_2 + 2\text{U} = 2\text{UD}_3\]

\[
\begin{array}{cccc}
12.09 & 476.14 & 488.23 \\
\end{array}
\]

This method is especially useful in that it makes possible both the preparation (Eq. a) and the storage (as UD\textsubscript{3}—Eq. b) of D\textsubscript{2}. High-purity D\textsubscript{2} can then be liberated by thermal decomposition of the UD\textsubscript{3}. Any desired quantity of very pure D\textsubscript{2} can thus be obtained when needed.

The highly endothermic reaction of D\textsubscript{2}O vapor with U may be carried out slowly and safely in the apparatus of Fig. 94. The 50-ml. flask \(\alpha\) is connected by stopcock \(\h_1\) with manometer \(b\) and quartz reaction tube \(d\). Reactor \(d\) is heated with an electric furnace to 600-700°C and is connected to a liquid-nitrogen-cooled trap \(f\). The latter is, in turn, connected to a high-vacuum pump and a flask \(g\) which may be heated to 250°C.

Flask \(\alpha\) is about half filled with D\textsubscript{2}O and \(d\) and \(g\) with uranium shavings (the uranium is pretreated with dilute HNO\textsubscript{3} to remove all oxide, then washed and dried). The shavings in reactor \(d\) are supported on and covered with glass wool plugs \(c_1\) and \(c_2\). The D\textsubscript{2}O in \(\alpha\) is then frozen with a Dry Ice-methanol bath; this must be done slowly to avoid cracking the flask. The entire apparatus is then evacuated, while \(g\) and \(d\) are heated. The D\textsubscript{2}O is then carefully melted and the reaction is slowly started by allowing the vapor to penetrate to the uranium in \(d\). The first D\textsubscript{2} evolved is used to flush the apparatus, with stopcock \(\h_3\) closed. Only then is \(\h_4\) closed and \(\h_3\) opened. During the reaction, \(\alpha\) is kept at about 30°C. The D\textsubscript{2} product passes through trap \(f\), in which any entrained traces of D\textsubscript{2}O are frozen out, and is absorbed by the uranium shavings in \(\gamma\), forming UD\textsubscript{3}. When all of the U is finally converted to UD\textsubscript{3}, the excess D\textsubscript{2} causes an increase in pressure which suppresses the evaporation of D\textsubscript{2}O and thereby prevents any further D\textsubscript{2} formation. Thus, once started, the process is self-regulating and requires no special attention. Several grams of D\textsubscript{2}O can be converted into UD\textsubscript{3} in one hour.

The UD\textsubscript{3} is a brown-black, spontaneously igniting powder. To prepare very pure D\textsubscript{2}, it is thermally decomposed either at atmospheric or reduced pressure (see also H\textsubscript{2} above: III). The U
IV. ELECTROLYSIS OF D₂O

An electrolytic cell, holding 60 ml. of liquid and made from a standard ground glass joint, is shown in Fig. 95. The male part of the ground joint continues into a cylindrical water jacket (only partly shown in the diagram) which surrounds the cathode. The Pt electrodes are also cylindrical and are prepared by fusing together a Pt wire with a Pt foil. The D₂O electrolyte is acidified with 25% D₂SO₄. (If no D₂SO₄ is available, carefully dehydrated K₂SO₄ or Na₂CO₃ can also be used.) After evacuation of the cell at A and B, electrolysis is begun at a low current to prevent foaming at low pressures. After a short time, however, the current can be increased to 5 amp. The temperature of the electrolyte must not be allowed to rise. If the D₂ product gas is to overcome the pressure drop due to narrow tubes and a liquid head in the attached purification apparatus or reactor, the pressure in the cell must be maintained at a higher level by means of a throttling
valve in the O\textsubscript{2} outlet. The D\textsubscript{2} product still contains small amounts of O\textsubscript{2} and D\textsubscript{2}O vapor. Very pure gas may be obtained by heating the electrolysis product over platinized asbestos, followed by drying with liquid nitrogen. At 5 amp., two liters of D\textsubscript{2} per hour is obtained.

Small quantities of D\textsubscript{2} are stored in sealed glass flasks or over mercury. Distilled water can also be used as a sealing liquid. Larger amounts may be condensed in a metal flask cooled with liquid H\textsubscript{2}. The liquid is then heated and thus forced through metal tubing into small steel cylinders.


V. Other preparative methods: Reduction of D\textsubscript{2}O with Fe or W at high temperatures.
SYNONYM:

Heavy hydrogen.

PROPERTIES:

Colorless, odorless gas. Chemical properties analogous to $H_2$, but somewhat less reactive. In the absence of catalysts, mixtures of $D_2$ and $H_2$ are stable to about $500^\circ C$. In addition, no exchange with $H_2O$ occurs at room temperature. M.p. $-254.6^\circ C$, b.p. $-249.7^\circ C$; d (liq., $-253.1^\circ C$) 0.171. Very slightly soluble in water and other liquids.

REFERENCES:


**Hydrogen Deuteride**

\[
\text{LiAlH}_4 + 4 \text{D}_2\text{O} = \text{LiOD} + \text{Al(OD)}_3 + 4 \text{HD}
\]

This reaction is conducted in a 250-ml. two-neck flask provided with a reflux condenser and a magnetic stirrer. The other neck of the flask is closed with a rubber cap. The reflux condenser is connected to a receiver and a diffusion pump via cold traps, where the entrained liquid is condensed. Gas inlet lines with stopcocks allow each part of the apparatus to be evacuated separately or, if desired, to be filled with air or $N_2$.

About 150 ml. of n-butyl ether, dried over Na, is distilled into the reaction flask and 5.75 g. of LiAlH$_4$ (40% excess) is then added under a nitrogen blanket. The mixture is frozen with liquid $N_2$. The apparatus is then evacuated, and the flask contents are brought to boiling by careful heating. After 1.5 hours, it is again
cooled with liquid N\textsubscript{2}, the evacuation is repeated, and 5 ml. of 99.5\% D\textsubscript{2}O (see above, D\textsubscript{2}O) is added to the solidified mixture, using a hypodermic syringe to pierce the rubber cap. The gas evolution is started by melting the mixture and agitating with the magnetic stirrer. Because of the low reaction temperature, the flask becomes coated with ice on the outside. By repeated immersion in liquid N\textsubscript{2}, the temperature is controlled so that the ice on the outer wall of the flask does not melt. As soon as the reaction subsides somewhat, two additional portions of 6.5 ml. of D\textsubscript{2}O each are added (for a total of 18 ml. or 150\% excess). The yield is 10 liters of HD. The purity is 97-99\%.

**PROPERTIES:**

Colorless, odorless gas. B.p. \(-251.02^\circ\text{C};\) triple point \(-256.55^\circ\text{C} (92.8 \text{ mm.})\).

**REFERENCES:**


**Deuterium Fluoride**

\[
\text{DF}\\
D_2 + 2 \text{AgF} = 2 \text{DF} + 2 \text{Ag}
\]

4.03 253.76 42.03 215.76

Some dry AgF is charged into a silver reaction flask provided with a manometer and an inlet tube that can be closed off. The AgF can also be produced by the action of F\textsubscript{2} on the inner walls of the flask itself. After evacuation, pure, carefully dried D\textsubscript{2} (see above, D\textsubscript{2}) is admitted into the flask. The latter is then closed and heated to 110\(^\circ\text{C}\) until the pressure ceases to change. The DF formed is frozen out of the reaction mixture by cooling with liquid nitrogen, and excess D\textsubscript{2} is drawn off by suction after opening the flask. The product is purified by high-vacuum distillation in which all connections and receivers must be of Ag or Cu.

To date, this method has been used only for producing small amounts of DF. Deuterium fluoride may be stored in vessels made of platinum, silver or copper.
II. \[2\text{C}_6\text{H}_5\text{COF} + \text{D}_2\text{O} = (\text{C}_6\text{H}_5\text{CO})_2\text{O} + 2\text{DF}\]

The reaction is carried out in the apparatus shown in Fig. 96. The latter is flushed out with dry \(\text{N}_2\), and atmospheric moisture is strictly excluded.

Silver flask \(a\) is charged with 168 g. (1.5 moles) of benzoyl fluoride and chilled with Dry Ice-acetone freezing mixture. Then 5 g. (0.25 mole) of 99.5% \(\text{D}_2\text{O}\) is added all at once under \(\text{N}_2\). The flask is then attached to the silver distillation apparatus. Brine at \(-15^\circ\text{C}\) is circulated through the condenser \(c\), and the quartz receiver is cooled with Dry Ice-acetone to \(-80^\circ\text{C}\). Cooling of

![Fig. 96. Preparation of deuterium fluoride.](image)

- \(a\) Silver flask;
- \(b\) thermometer well;
- \(c\) jacketed glass condenser;
- \(d\) paraffin-coated stopper;
- \(e\) calcium chloride tube;
- \(f\) quartz receiver.

flask \(a\) is then ceased and the latter is slowly heated to room temperature; the evolving DF is then distilled on a water bath at 80-90°C. To achieve analytical purity and separate entrained benzoyl fluoride, the distillation is repeated twice. The yield is 9.7 g. of DF (92% of theoretical).

III. Larger quantities of DF can be prepared by synthesis from the elements according to a method described by H. von Wartenberg for the production of HF; however, this requires extensive equipment.

IV. Aqueous solutions of deuterated hydrofluoric acid can be prepared by the condensation of DF in \(\text{D}_2\text{O}\) or by the reaction of very pure \(\text{CaF}_2\) with \(\text{D}_2\text{SO}_4\) (see also preparation of pure hydrofluoric acid, p. 145 ff.).
PROPERTIES:

Formula weight 21.01. Colorless, waterlike liquid; pungent odor; fumes in moist air. The vapors are very toxic. Chemical properties analogous to HF. The deuterium is exchanged for hydrogen in the presence of $H^+$. B.p. +18.6°C. Very readily soluble in water.

REFERENCES:


Deuterium Chloride

$\text{DCl}$

\[ 2\text{C}_6\text{H}_5\text{COCl} + \text{D}_2\text{O} = (\text{C}_6\text{H}_5\text{CO})_2\text{O} + 2\text{DCl} \]

The apparatus shown in Fig. 97 may be enlarged if larger amounts of DCl are desired. The long capillary tube from dropping funnel $t$, which reaches into the reaction flask $r$ through the condenser $k$, ensures uniform addition of D$_2$O to the benzoyl chloride in the flask in spite of small fluctuations of pressure during the reaction. In order to trap any benzoyl chloride entrained through the condenser by the DCl gas, trap $f$ is cooled in an ice bath. Manometer $m$ (with one arm open to the air) serves both as a safety valve and as a means for following the course of the reaction (if the outlet tube is closed off, the manometer will show whether the gas continues to evolve).

As an example of DCl preparation, 5 ml. of 99.6% D$_2$O is allowed to react with 210 g. of benzoyl chloride (2-3 molar excess) containing some porous boiling chips. At first, only a few drops of D$_2$O are added, while the mixture is carefully heated. This is continued until a moderate gas stream is developed. This temperature is maintained until all of the D$_2$O is added. By varying the heat input, gas formation can easily be regulated. As the flow decreases, the temperature is slowly increased to the boiling point of benzoyl chloride (197°C) and kept there until no further gas is evolved. At the end of the reaction, a stream of dry air is slowly introduced into the apparatus through the dropping funnel, without interrupting the refluxing, to expel all the DCl. The product is analytically pure and the yield is almost quantitative.
II. \[ \text{SiCl}_4 + 2 \text{D}_2\text{O} = 4 \text{DCl} + \text{SiO}_2 \]
\[ \begin{array}{ccc}
169.89 & 40.06 & 149.88
\end{array} \]

Two thin-wall, vacuum-sealed ampoules containing 18 g. of carefully purified \text{SiCl}_4 and 1.8 g. of \text{D}_2\text{O} are shattered by shaking in an evacuated five-liter flask provided with a glass stopper with a stopcock sealed in. After 24 hours the flask is sealed to a high-vacuum system and the crude gas condensed in a liquid-nitrogen-cooled trap. The product may be further purified as in I or, even better, with a low-temperature distillation column (see original literature for details).

Liquid deuterium chloride can be stored at low temperature. The gas may be stored in a sealed glass flask or over mercury.

Other preparative methods:

III. Reaction of anhydrous \text{MgCl}_2 with \text{D}_2\text{O} at 600°C:
\[ \text{MgCl}_2 + \text{D}_2\text{O} = 2 \text{DCl} + \text{MgO}. \]

Yields very pure \text{DCl} on distillation.

IV. Reaction of very pure \text{NaCl} with \text{D}_2\text{SO}_4.

V. Aqueous solutions of heavy hydrochloric acid are prepared by condensation of \text{DCl} in \text{D}_2\text{O}.

SYNONYM:
Heavy hydrogen chloride.

PROPERTIES:

Formula weight 37.47. Chemical properties analogous to \text{HCl.} In the absence of moisture and catalysts, no deuterium exchange occurs in gaseous mixtures of \text{HCl} and \text{DCl. However, an exchange reaction occurs instantaneously in solvents containing H\textsuperscript{+}. M.p. \textit{—}114.8°C, b.p. \textit{—}81.6°C, \textit{t}_{cr} \textit{+}50.3°C.}

REFERENCES:

I. HYDROGEN, DEUTERIUM, WATER


Deuterium Bromide

DBr

\[ \text{D}_2 + \text{Br}_2 = 2 \text{DBr} \]

4.03 159.83 163.86

The glass apparatus shown in Fig. 98 is used. Prior to the run, it is evacuated for a considerable time via \( P \). Flask \( C \) is charged with carefully purified \( \text{Br}_2 \) from \( D \) (see section on \( \text{Br}_2 \)) by moving the plug \( S \) of the dropping funnel (which has no stopcock). The flask is then heated to 48°C. Dry \( \text{D}_2 \) (see p. 121) enters at \( \mathcal{A} \) at a rate of about two liters/hour and passes through stopcock \( B \) (lubricated with phosphoric acid-graphite and sealed with mercury) into \( C \), where it mixes with the bromine vapor which is replenished during the reaction from the dropping funnel. The \( \text{D}_2-\text{Br}_2 \) mixture flows into the Vycor combustion tube \( \mathcal{R} \), which is filled with

![Fig. 98. Preparation of DBr. B) Hg seal stopcock, lubricated with graphite-phosphoric acid; D) bromine storage vessel; C) reaction flask; R) Vycor tube filled with porcelain chips; E, F) condensation traps; K) column with Cu turnings.](image-url)
small pieces of porcelain and wound with heating wire so that the front part is heated to 80°C and the back to 700°C. Here, 99% of the D₂ is converted to DBr. Excess Br₂ is separated in trap G, kept at —40°C, and in column K filled with clean copper turnings. The DBr, condensed in the liquid nitrogen-cooled receiver F, can be purified several times by repeated fractional distillation in high vacuum (see purification of DI, p. 133, as well as method II). The yield is almost quantitative.

\[ \text{PBr}_3 + 3\text{D}_2\text{O} = 3\text{DBr} + \text{D}_3\text{PO}_4 \]

270.73 60.09 245.79 85.02

The vacuum-sealed ampoules with the starting materials are broken by vigorous shaking in an evacuated 5-liter flask closed by a ground glass stopper with a stopcock. To complete the deuterolysis, the mixture is left standing in the dark for two days, with occasional shaking. The reaction should not be accelerated by heating or disproportionation (4 D₃PO₃ = 3 D₃PO₄ + PD₂) will occur, and the DBr will be contaminated with PD₃. After sealing the flask to a high vacuum system, the impure gas is condensed in a receiver cooled with liquid nitrogen and purified by fractional distillation, using a low-temperature distillation flask (see Part I, p. 69).

Unlike method I, only half of the deuterium feed is converted to desired products.

Deuterium bromide is stored either as a liquid at a low temperature or as a gas in a sealed glass flask. Pure DBr reacts with Hg only on long exposure.

III. Aqueous solutions of heavy hydrobromic acid can be obtained by condensation of DBr in D₂O.

**SYNONYM:**

Heavy hydrogen bromide.

**PROPERTIES:**

Formula weight 81.93. Chemical properties analogous to those of HBr. In the presence of H⁺, exchange occurs. M.p. —87.5°C, b.p. —67°C; t₁ₐ₉ +88.8°C.

**REFERENCES:**


I. HYDROGEN, DEUTERIUM, WATER

Deuterium Iodide

DI

$$\text{D}_2 + \text{I}_2 = 2\text{DI}$$

4.03 253.84 257.87

The glass apparatus of Fig. 99, in which all the joints are fused, is used. The 5-liter flask $A$ contains some platinum sponge or platinized asbestos (see section on Platinum Metals) which is initially calcined for a few hours in high vacuum (evacuate through $C$) at 450°C. Dry, H$_2$-free air (in order to prevent adsorption of light hydrogen on the platinum) is allowed to flow in and 35 g. of carefully purified iodine (see that section) is added to the flask through $C$. Evacuation is then resumed until all of the air is displaced by I$_2$ vapor. Pure D$_2$ (see above) is then introduced by means of a Toepler pump, until a pressure of 120 mm. is reached. The system is then melt-sealed at $C$. The flask is heated in an air bath for six hours at 370°C; over 90% of the D$_2$ is converted to DI. The impure gas is separated from the unconverted starting materials by fractional distillation. For this purpose, the right part of the apparatus, separated from the reactor by the seal $B$, is evacuated with stopcocks $H$ and $D$ open. Then $D$ is closed and the tip at $B$ is broken by moving the glass-covered iron slug $K$ with an electromagnet. Trap $E$ is chilled with liquid nitrogen and $D$ can then be opened. With stopcock $H$ closed, the contents of $A$ are distilled into $E$. Next, the system is melt-sealed at 1 and evacuated briefly through $H$, and distillation from $E$ to $F$ is repeated, whereupon $E$ is warmed to $-79°C$ with a Dry Ice bath and $F$ is cooled with liquid nitrogen. Finally, the tube is sealed off at 2. The DI contained in $F$ is pure white, i.e., completely free from elemental iodine.
Deuterium iodide can only be stored in condensed form at low temperature.

**Other preparative methods:**

II. $\text{P} + 5\text{I} + 4\text{D}_2\text{O} = 5\text{DI} + \text{D}_2\text{PO}_4$. The readily formed side products $\text{PD}_3$ and $\text{PD}_4\text{I}$ contaminate the DI. The method utilizes only about half of the deuterium introduced.

III. Solutions of heavy hydriodic acid are obtained by reaction of $\text{D}_2\text{S}$ with iodine in the presence of $\text{D}_2\text{O}$: $\text{D}_2\text{S} + \text{I}_2 = 2\text{DI} + \text{S}$.

Deuterium sulfide is introduced with shaking into an ice-cooled suspension of $\text{I}_2$ in $\text{D}_2\text{O}$ placed in a closed recirculating glass apparatus with all joints melt-sealed. Unconverted $\text{D}_2\text{S}$ is reintroduced into the reaction mixture. The heavy hydriodic acid formed is separated from the precipitated sulfur by filtration (in the absence of air) and separated from the dissolved $\text{D}_2\text{S}$ by prolonged evacuation.

**PROPERTIES:**

Formula weight 128.93. Chemical properties analogous to HI. Deuterium is replaced by hydrogen in the presence of $\text{H}^+$. M.p. $-52.0^\circ\text{C}$, b.p. $-36.2^\circ\text{C}$; $t_{\text{cr}} +148.6^\circ\text{C}$.

**REFERENCES:**


**Deuterium Sulfide**

$\text{D}_2\text{S}$

To prepare $\text{Al}_2\text{S}_3$ (see the section on Aluminum), a stoichiometric mixture of C.P. Al powder and C.P. S is placed in a sulfur-lined Hessian clay crucible. The commercial Al powder used must be washed several times with pure benzene to remove all oils; it is then heated for some time to 150°C in high vacuum. The reaction mixture is ignited with the help of a Mg strip (caution—very violent reaction!) and the crucible is covered. The $\text{Al}_2\text{S}_3$ product is crushed while still hot, placed in ampoules, and degassed for several hours in high vacuum at 150 to 180°C. The
ampoules are sealed in vacuum. The D$_2$O reagent is also placed in small ampoules and carefully degassed in vacuum, and the ampoules are sealed.

To make D$_2$S, 20 g. of Al$_2$S$_3$ and 7 g. of D$_2$O in sealed ampoules (the excess Al$_2$S$_3$ is an excellent drying agent for the product gas) are placed in a 5-liter flask with a ground glass stopper provided with a stopcock. After evacuation to about 10$^{-4}$ mm., the stopcock is closed and the connection to the vacuum source is sealed off. The ampoules are broken by shaking the flask, starting evolution of the gas. Heavy water vapor, which may condense in the upper part of the flask, is made to react by warming the walls or by coating them with unreacted Al$_2$S$_3$. The flask is left standing in the dark, with occasional shaking, for about one week. After this, it is sealed to a vacuum system provided with several traps for fractional condensation (see Part I, p. 67 f.). Small amounts of D$_2$ are separated from the impure gas by condensing with liquid nitrogen and fractionating by repeated slow distillation (bath liquids: Dry Ice mixture and liquid nitrogen). The D$_2$S is then pure enough not to attack metallic Hg even after several weeks of contact. The yield is somewhat lower than stoichiometric.

The product may be stored in condensed form at low temperature or as a gas over dry paraffin oil.

II. Other preparative methods: Decomposition of CaS with D$_2$O in the presence of MgCl$_2$.

PROPERTIES:

Formula weight 36.10. Chemical properties analogous to H$_2$S. In solvents containing H$^+$, deuterium is replaced with hydrogen. M.p. $-86^\circ$C, t$_{cr}$ $+99.1^\circ$C.

REFERENCES:


Deuterosulfuric Acid

\[
\text{D}_2\text{SO}_4
\]

\[
\text{D}_2\text{O} + \text{SO}_3 = \text{D}_2\text{SO}_4
\]

20.03 80.06 100.09

All joints of the glass apparatus, shown schematically in Fig. 100, are fused. Two ampoules, $F_1$ and $F_2$, contain SO$_3$, carefully pre-
purified by sublimation. The ampoules are placed in glass vessels $A_1$ and $A_2$ on top of sealed-in test tubes $S_1$ and $S_2$ so that their tips are directly below the glass-covered slugs $K_2$ or $K_3$. This placement of ampoules on "stems" eases the job of the glass blower who must fuse the joints of the apparatus. After evacuation

![Diagram of the apparatus](https://example.com/diagram.png)

**Fig. 100.** Preparation of $D_2S$. $F_1$, $F_2$) ampoules containing $SO_3$; $A_1$, $A_2$) containers for $SO_3$ ampoules; $K_1$, $K_2$, $K_3$) seal breakers; $M_1$, $M_2$, $M_3$) electromagnets; $H$) break-seal valve; $G$, $D$, $E$) receivers (can be cooled); $G$, $L$) sealing points.

and sealing off at $P_1$, ampoules $F_1$ and $F_2$ are broken by manipulation of $K_2$ and $K_3$ with the electromagnets $M_2$ and $M_3$. The $SO_3$ passes through two U tubes filled with $D_2O$-glass wool and is condensed in $C$ by means of a Dry Ice bath. During this sublimation the left part of the apparatus, which is separated by the glass barrier $H$, is filled with $D_2O$ through $G$ and that inlet sealed, and the $D_2O$ is frozen in $E$ by means of a Dry Ice bath. The system is then evacuated at $P_2$ and sealed off by fusion. After the sublimation of the $SO_3$, the tubing is also fused at $L$. The barrier $H$ is now broken with the glass-encased iron slug $K_1$ moved by electromagnet $M_1$, with the glass splinters falling into receiver $D$. The $SO_3$ is then condensed on the $D_2O$ in $E$ by slow heating of $C$. After careful melting of the reaction mixture, deutosulfuric acid of any desired concentration is obtained in $E$. The concentration is regulated by the proportion of $D_2O$ and $SO_3$. The yield is quantitative, based on $D_2O$.

The product is stored in glass vessels.
I. HYDROGEN, DEUTERIUM, WATER

PROPERTIES:

Colorless liquid, with an oily consistency. Chemical properties analogous to \( \text{H}_2\text{SO}_4 \); the deuterium is ionic and exchangeable with light hydrogen. This should be kept in mind when mixing with solvents containing \( \text{H}^+ \). Miscible with water in all proportions.

REFERENCE:


Deuteroammonia

ND\(_3\)

\[
\text{Mg}_3\text{N} + 6 \text{D}_2\text{O} = 2 \text{ND}_3 + 3 \text{Mg(OD)}_2
\]

100.98 120.18 40.11 181.05

The one-piece glass apparatus shown in Fig. 101 is used. The three U tubes are filled with 30 g. of \( \text{Mg}_3\text{N}_2 \) (see section on Magnesium for preparation), sealed to each other, and degassed at 400°C for some time in high vacuum. Meanwhile, flask \( P \), separated from the rest of the apparatus by the glass wall \( D \), is filled with 7 g. of \( \text{D}_2\text{O} \) which is freed of air by repeated freezing and melting in high vacuum. An excess of \( \text{Mg}_3\text{N}_2 \) will thoroughly dry the product gas. After both vacuum connections are fused, \( Q \) is cooled with liquid nitrogen and barrier \( D \) is broken by moving the glass-encased iron slug \( K \) with the electromagnet. Reaction between \( \text{D}_2\text{O} \) and \( \text{Mg}_3\text{N}_2 \) starts immediately, and the \( \text{ND}_3 \) formed condenses in \( Q \). When the \( \text{D}_2\text{O} \) from \( P \) is completely evaporated, the U tubes are heated for some time by fanning with a flame. The product collected in \( Q \) is sublimed twice in high vacuum to free it from \( \text{D}_2\text{O} \). To accomplish this, \( R \) is cooled.

![Fig. 101. Preparation of ND\(_3\). P, Q, R, T) receivers (can be cooled); D) break-seal valve; K) seal breaker; M) electromagnet.](image-url)
with liquid nitrogen and $Q$ is warmed in a Dry Ice bath to $-78^\circ$C. Then the connection between $Q$ and $R$ is sealed off, $R$ is warmed to $-78^\circ$C, and $T$ is cooled with liquid nitrogen. The yield is almost quantitative, based on $D_2O$.

The product may be stored in condensed form at low temperatures or as a gas over Hg.

II. Aqueous solutions of heavy ammonia are prepared by condensing $ND_3$ in $D_2O$ in high vacuum.

**PROPERTIES:**

Formula weight 20.05. Chemical properties analogous to $NH_3$. In the presence of solvents containing $H^+$, deuterium is replaced by hydrogen. M.p. $-73.6^\circ$C, b.p. $-31.1^\circ$C, $t_{cr}$ $+132.3^\circ$C.

**REFERENCES:**


**Deuterophosphoric Acid**

$$D_3PO_4$$

$$P_2O_5 + 3D_2O = 2D_3PO_4$$

141.95 60.09 202.04

In the Simon and Schulze method, heavy phosphoric acid is prepared via the gas-phase reaction of pure $D_2O$ and $P_2O_5$ in vacuum, using an apparatus consisting of flasks connected with

![Fig. 102. Preparation of deuterophosphoric acid solution.](image)
ground joints. The approximately 53% D$_3$PO$_4$ solution formed in the process is refluxed for 6.5 hours to produce orthophosphoric acid. Atmospheric moisture is blocked by a P$_2$O$_5$ tube on the condenser. The escaping D$_2$O is recovered by freezing it out in a trap cooled with a Dry Ice-ether bath, which is inserted between the condenser and the P$_2$O$_5$ tube.

The condenser is then replaced with an adapter provided with an inlet and an outlet tube (see Fig. 102) and O$_3$ is passed through the acid solution for one hour. During this treatment, the flask is kept in warm, 70°C water. Most of the D$_2$O vapor produced is retained in the flask by chilling the neck with a condenser coil. Small amounts of vapor which escape are condensed in a trap. Two tubes filled with P$_2$O$_5$ shield against atmospheric moisture.

The purified 53% D$_3$PO$_4$ solution is concentrated to 83% at 45°C in the apparatus shown in Fig. 195 (p. 543). No pyro acid should be produced at this temperature. The course of the concentration is observed by weighing the cooling trap. Further concentration by evaporation is impossible because partial conversion to the pyro acid occurs.

The purity of the acid thus prepared may be ascertained from a pure yellow precipitate of silver phosphate, which does not discolor even upon boiling.

REFERENCE: