

**TECHNOLOGY AND USES OF
LIQUID HYDROGEN**

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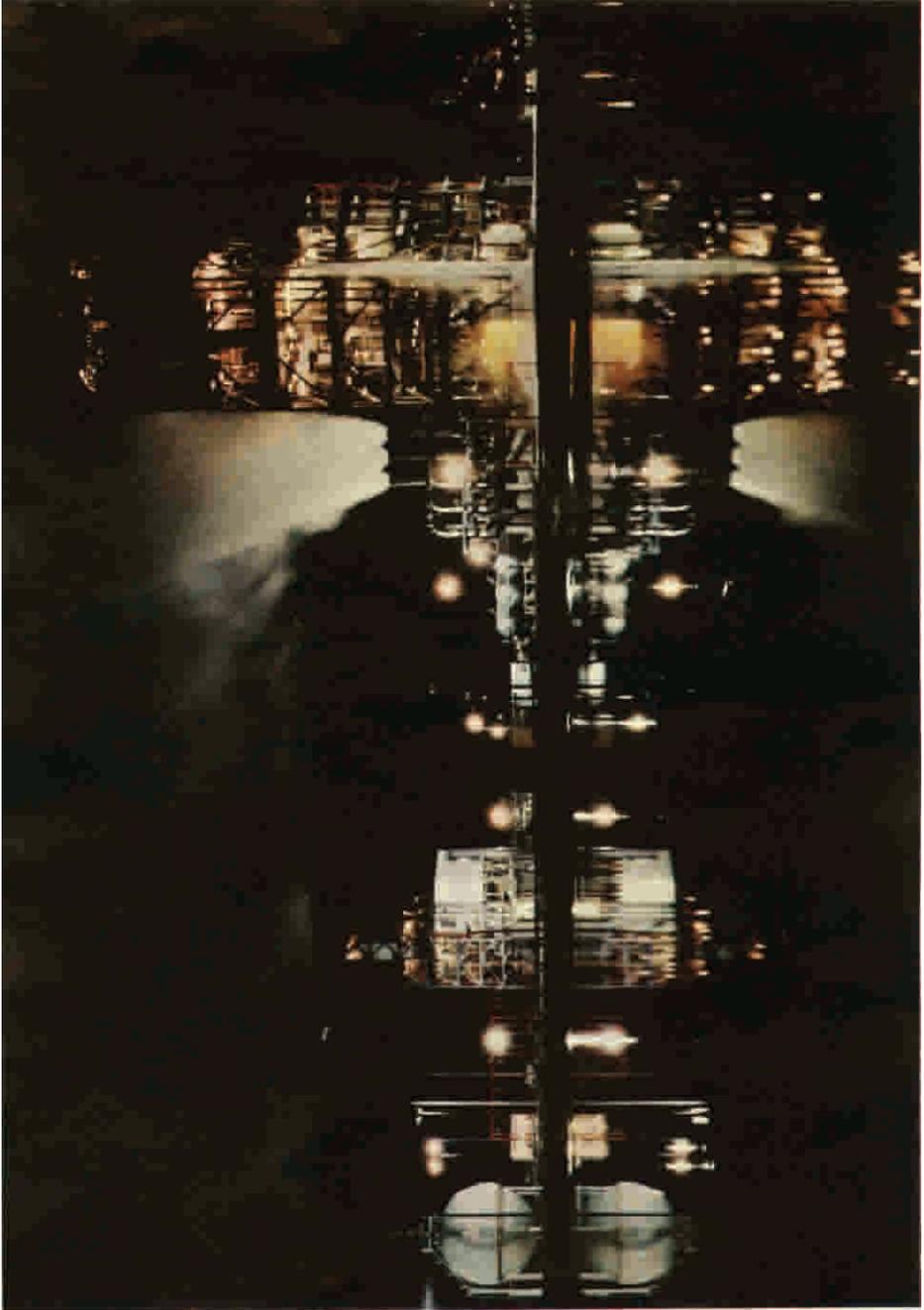


FIG. 42. Two of the test stands being used in the continued development of the RL10 engine.

TECHNOLOGY AND USES OF LIQUID HYDROGEN

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CHAPTER 1

INTRODUCTION

R. B. SCOTT

IN THE preparation of this book we, the editors, have been extremely fortunate in enlisting the help of a large number of the world's authorities in the production and utilization of liquid hydrogen. Their contributions comprise the important chapters which follow this introduction. My objective is to supply a little background, history and statistics to set the stage and present a reasonable perspective. I will select a few highlights from the book and try to discuss them in a general way so as not to spoil your enjoyment of the detailed descriptions in the technical chapters.

Hydrogen was first liquefied by Sir James Dewar in 1898. For more than a half-century, however, liquid hydrogen was produced only in small quantities, and its use was confined to laboratory experiments.

Not only was Dewar the first to liquefy hydrogen, but his development of the vacuum-insulated vessel with reflecting walls, which reduced heat transfer by radiation, has been indispensable for the storage and utilization of liquid hydrogen and other low-temperature materials. He first described an evacuated metallic container in 1873 and in 1893 described experiments in which evacuated glass vessels were used. It should also be stated here that Dewar invented evacuated powder insulation and used an adsorbent, charcoal, to achieve better vacua, especially in metal vessels. He recognized the fact that metals continue to give off gas and that a means of removing this gas must be provided. Moreover, one of his diagrams depicts a vessel with an intermediate shield, so he should also be given credit for multiple-shield insulation. These inventions of Sir James Dewar are mentioned here only to point out that the basic principles of some of the schemes, now considered new and modern (in fact some recently have been patented), were described by Dewar more than 60 years ago.

Among the early uses of liquid hydrogen should be listed an important series of experiments, particularly by Simon at Oxford, in which liquid hydrogen was used to provide the temperatures needed to verify the Nernst heat theorem. Measuring specific heats, from the lowest temperatures that could be reached with liquid (solid) hydrogen (about 12°K), and extrapolating to absolute zero furnished convincing experimental evidence that the entropy of a pure, perfect crystalline substance is zero at absolute zero.

Similar specific heat measurements, from temperatures obtainable with liquid hydrogen up to reasonable temperatures for chemical reactions, provided information about the free energies of elements and compounds which could be used to predict whether or not a specific chemical reaction was theoretically possible.

During the 1920's and 1930's the low-temperature laboratory of the University of California, under the direction of Nobel Laureate, Professor W. F. Giaouque, produced a large amount of very important work in the two fields mentioned above.

In later passages of this book there will be discussions of ortho-hydrogen and para-hydrogen. While the following does not necessarily involve *liquid* hydrogen, a little history concerning the prediction and discovery of these two forms may be of interest. For many years, physicists had been puzzled by the anomalous specific heat of hydrogen. Then the theoretical work of two Nobel Prize winners, Heisenberg and Schroedinger, explained the mystery. Their theoretical studies showed that hydrogen consists of two different kinds of molecules: ortho-hydrogen in which the spins of the two atomic nuclei are in the same direction, and para-hydrogen in which the spins are in opposite directions. Later, in 1929, Bonhoeffer and Harteck produced experimental evidence of the existence of these two different molecular varieties of hydrogen. They used a catalyst to promote the reaction to the low-temperature modification and obtained almost pure para-hydrogen. They demonstrated the difference between ortho- and para-hydrogen and analyzed the composition of mixtures by measuring the thermal conductivity. Since para-hydrogen, both at room temperature and moderately low temperatures, has a greater specific heat than ortho-hydrogen, its thermal conductivity is correspondingly greater because each molecule carries more energy. Nearly all the ortho-para analyzers used today exploit this difference in thermal conductivity.

Heisenberg showed that at high temperatures the ortho variety should be three times as abundant as the para variety. Although we now consider that Heisenberg's contributions which earned him the Nobel Prize were the development of quantum mechanics and the elucidation of the uncertainty principle, the employment of his theory in explaining the allotropic forms of hydrogen is included in this citation for the Nobel Prize.

To the practical user of liquid hydrogen the important characteristics of ortho- and para-hydrogen are their large differences in energy at low temperatures. When hydrogen of "normal" composition, 75 per cent ortho and 25 per cent para, is liquefied in an ordinary liquefier, the liquid product has a composition that is nearly "normal". However, the equilibrium concentration of the two varieties at the boiling point of liquid hydrogen is very nearly pure para-hydrogen (99.8 per cent para). Liquid hydrogen of "normal" composition undergoes a slow conversion, caused by self-catalysis, to the low-temperature equilibrium concentration. This conversion is accompanied by evolution of heat, because of the considerable energy difference between the two forms, and the result is evaporation of the liquid. In fact, liquid normal hydrogen in a perfectly insulated container will evaporate at an initial rate of about 1 per cent per hour because of the unavoidable conversion to para-hydrogen. For long-term storage of liquid hydrogen such a high loss cannot be tolerated, so modern liquefaction plants are usually equipped with catalysts which promote the ortho to para reaction during

the cool-down and liquefaction so that the liquid product is nearly pure para-hydrogen.

In 1952 the U.S. National Bureau of Standards established a laboratory at Boulder, Colorado, for the U.S. Atomic Energy Commission, to produce relatively large quantities of liquid hydrogen and perform experiments, measurements, and tests of an engineering nature. After the invention of the bubble chamber, this laboratory also assisted several high-energy physics laboratories in the design of liquid hydrogen bubble chambers using volumes of liquid hydrogen as large as 1500 liters. This laboratory has, among other duties, provided special designs, tests, measurements of physical properties, and advice and consultation on a multitude of other practical cryogenic problems, including most of those described in the technical chapters of this book.

Also the National Bureau of Standards Cryogenic Engineering Laboratory has pursued its own research on the properties of low-temperature fluids, has established the world's foremost Cryogenic Data Center, and is continuing its role in determining the properties of materials at low temperatures and disseminating these data through the Data Center.

It was not until 1959, however, that a really large-scale application of liquid hydrogen became public knowledge. In May of that year, Lieutenant-General Bernard A. Shriever, Chief of the U.S. Air Force Air Research and Development Command, announced the use of liquid hydrogen as a rocket fuel. Since that announcement, the public press has carried information about several giant plants for the production of liquid hydrogen in the U.S.A.

Most of these large installations furnish liquid hydrogen to the U.S. National Aeronautics and Space Administration because it has been determined, for reasons that will presently be explained, that liquid hydrogen is the optimum propellant now available for nuclear and chemically fueled upper stages of high-performance space vehicles. The largest of these liquid hydrogen plants will have a capacity of 62.5 tons per day. It is scheduled to be in operation in 1964. Estimates of the total amounts of liquid hydrogen that the space program of the U.S.A. will need have been projected as far ahead as 1966, at which time the expected consumption will be 4000 tons per month. This great increase in the need for liquid hydrogen stems from the plans to use it as a propellant in several of the more advanced designs of space vehicles.

The first successful launch of a liquid hydrogen-oxygen-propelled rocket stage took place at Cape Kennedy on November 27, 1963. This was the upper stage of the NASA's Centaur, which used an Atlas booster. The Centaur was powered by two of the hydrogen-oxygen rocket engines described in Chapter 5.

The use of liquid hydrogen in rocket motors is only one of many practical applications, but because the quantities involved are several orders of magnitude larger than those used for other purposes, and space flight is a subject of great interest, a large proportion of this book is devoted to

hydrogen-propelled rockets and the production and handling of the large amounts of liquid hydrogen required.

Later chapters will present technical analyses of the advantages of liquid hydrogen as a rocket propellant, but since I have chosen to emphasize this application in the introduction, it may be desirable to present here an elementary discussion of the reasons for selecting liquid hydrogen as a rocket propellant. Notice that I use the word propellant rather than fuel. This permits me to include nuclear-fueled rockets which use hydrogen as the propellant.

The basic principle of rocket action is well known—the expulsion of the exhaust gas from the rear of the rocket produces a thrust in the opposite direction which accelerates the rocket. This is a direct application of Newton's second law of motion. We can use the elementary physics formula, $E = \frac{1}{2}MV^2$, to compute the theoretical velocity of the exhaust gas. E is the average energy that each molecule has by virtue of its mass, M , and exhaust velocity, V ; M is the average molecular weight of the exhaust gas. Thus, for a given energy, it is apparent that the velocity, V , is proportional to $\sqrt{1/M}$. Now the thrust produced by ejecting the exhaust gas is (by Newton's second law) equal to the rate of change of momentum. Conservation of momentum dictates that this rate of change of momentum is exactly the same for the rocket as it is for the escaping exhaust gas. Therefore, for a given energy, the thrust is proportional to $\dot{m}V$ or to $\dot{m}\sqrt{1/M}$ where \dot{m} is the rate of consumption of propellant and M is the average molecular weight of the exhaust gas. Thus it is very advantageous to have exhaust gas of low molecular weight. This argument is greatly over-simplified because it does not take into account the other forms of energy that a molecule may have—vibrational and rotational energies which do not add to the molecular velocity. However, the inclusion of these energies would only strengthen the case for a propellant of low molecular weight, because light-weight molecules are of simpler structure and a greater fraction of their total energy is accounted for by their translational motion.

The use of hydrogen in the nuclear rocket offers unique advantages. The energy given to the hydrogen is limited only by the power of the rocket reactor and the temperatures that can be tolerated by the materials used in the reactor and the rocket nozzle. Hydrogen is the substance which has the smallest molecular weight; therefore, when used as the propellant, it will be discharged with the highest velocity and accordingly yield the greatest thrust for a given rate of consumption. Of course, the hydrogen must initially be in the liquid state so that it can be carried in light-weight tanks that need not withstand the pressure of a compressed gas.

For chemical rockets which burn hydrogen with oxygen, or fluorine, the picture is not quite so simple, although the argument is essentially the same. Rockets in common use, which utilize petroleum distillates as fuel and oxygen as the oxidizer, discharge an exhaust product with a mean molecular weight of about 35. If hydrogen were burned with oxygen in stoichiometric proportions, the molecular weight of the exhaust gas (H_2O) would be 18,

so if the chemical reaction energies are comparable (which they are), the latter mixture would have considerably higher exhaust velocity and yield correspondingly greater thrust. As a matter of fact, hydrogen-oxygen engines are supplied with a mixture considerably richer in hydrogen than the stoichiometric ratio, thus reducing the average density of the exhaust gas still more and providing still greater thrust for a given rate of consumption of propellant. That is to say, the excess hydrogen, which does not enter into the reaction but seems to go along just for the ride, causes a large increase in thrust; or as the rocket engineers say, the specific impulse, usually designated I_{sp} , is increased. I_{sp} is defined as the pounds of thrust produced by the expulsion of one pound of propellant per second. The units of I_{sp} are frequently given as seconds because $I_{sp} = \text{lb/lb sec}^{-1} = \text{sec}$. This is erroneous and misleading because the pounds in the numerator of the fraction are pounds of force, while the pounds in the denominator are pounds of mass. The proper units are:

$$I_{sp} = \text{force/mass time}^{-1}, \text{ or}$$

$$I_{sp} = \text{mlt}^{-2}/\text{mt}^{-1} = \text{lt}^{-1}, \text{ or feet per second in British units.}$$

Should astronauts land and live on other bodies in the solar system, I feel sure that they will be thoroughly familiar with the true significance of the specific impulse of their vehicles, because *seconds* will not bring them back home, while feet per second will.

Having mentioned the use of liquid fluorine as the oxidizer in a liquid hydrogen rocket, I should explain that the H-F combination does indeed offer a somewhat greater specific impulse than the H-O mixture, and it is quite likely that some chemical rockets in the future will utilize the former combination. However, it may not be inappropriate to invite attention to the violent chemical activity of fluorine which creates serious problems in its storage and handling and also point out that the exhaust gas from an H-F rocket is exactly that, HF (hydrofluoric acid), usually considered to be the most corrosive acid available. It would be reasonable to expect that an H-F rocket would only be launched from high in the atmosphere or at sea.

It may be appropriate to mention here another oxidant which is being considered for a hydrogen-fueled rocket. This is a mixture of liquid oxygen and liquid fluorine. These two diatomic molecules are rather similar; their normal boiling points are not far apart (F_2 , 85.2° ; O_2 , 90.18°K), so it is not surprising that they can be mixed without difficulty. The mixture is somewhat more tractable than pure liquid fluorine, as well as being cheaper, so it may well serve as the compromise between the oxidants O_2 and F_2 .

Having discussed the most publicized, largest scale application of liquid hydrogen, I would like next to mention the liquid-hydrogen bubble chamber. The bubble chamber was invented by Donald Glaser, and this won him the Nobel Prize. He recognized the principal limitation of the Wilson cloud

chamber—the low density of particles in the supercooled water vapor suspended in a gas could not intercept, and present for analysis, an appropriate fraction of the high-energy particles that were speeding through it in the beams of very powerful accelerators such as the University of California Bevatron. Glaser's first bubble chamber operated near room temperature and used liquid diethyl ether. When the pressure over the liquid was suddenly reduced to a value below the vapor pressure corresponding to the existing temperature, boiling did not immediately and spontaneously ensue because vapor bubbles need nuclei as their starting points. Charged particles shot through such a superheated liquid ionize the molecules that they encounter and provide the nuclei upon which boiling starts. The immediate result is the appearance of tracks of bubbles, resulting from incipient boiling. This is the principle of the bubble chamber. By employing a magnetic field to bend the path of the charged particle, stereoscopic photographs of the tracks provide the information required to deduce the charge, energy, and other characteristics of the particles.

Nuclear physicists were quick to recognize the value of Glaser's invention. They also realized that bubble chambers charged with complex substances such as diethyl ether would produce many "stars"—atomic explosions in which many particles with different energies and charges would emerge from the collision of a high-energy particle with a heavy atom such as carbon or oxygen. These "stars" could be expected to obscure the phenomena that were being studied.

To avoid these difficulties, Professor Luis Alvarez of the University of California devised a bubble chamber charged with liquid hydrogen. Since hydrogen is the simplest atom, consisting only of a proton and an electron, it is unlikely that it will interfere much with the high-energy processes being studied with the giant accelerators, although it is readily ionized so that it serves well as the detector in a bubble chamber analyzer.

The first really large liquid hydrogen bubble chamber was installed at the Lawrence Radiation Laboratory of the University of California and first operated in March 1959. This is described in a later chapter devoted to this topic. I once heard the remark that this 72-inch liquid hydrogen bubble chamber would be the equivalent of a Wilson cloud chamber one-half mile long. I am sure that they would not really be equal because the cloud chamber does not have the great advantage of utilizing the simplest molecule as the detector.

Thus far this introduction has not included any discussion of techniques of hydrogen liquefaction, even though a large chapter is devoted to this subject. This is a deliberate omission because I believe that the material presented in Chapter 3 needs no additions. The techniques of Olzewski and Wroblewski, Dewar, and later those of Claude, have been brought to bear on the problem of liquefying a recalcitrant gas and have been successful. Engineers recently engaged in this work have profited by the work of physicists and chemists, who have provided more and more accurate data on the thermodynamic and transport properties of hydrogen, and of engineers,

who have supplied information about heat and mass transfer in practical systems. Today the design of a hydrogen liquefaction system is a problem with an optimum solution derived from the available information. Of course, more accurate data and innovations in machinery will continually increase efficiency, but no break-through is now in sight.

It will be noted that the separation of deuterium from ordinary hydrogen by distillation of liquid hydrogen and the subsequent conversion to heavy water, D_2O , is treated rather extensively. Two questions about this are likely to occur to the reader. The first is: "If this is a good way to make heavy water, why have we not been using it all along?" The second: "Why is there more interest in this low-temperature process in other parts of the world than in the U.S.A.?"

I will try to supply some answers to these questions, but I want to start by disclaiming any pretense to authoritative, privileged information on the subject. I base my comments on a rather long association with the field in which I have engaged in several conversations and have had access to reports, analyses and economic studies which made estimates of the costs of heavy water production.

In the first place, I wish to point out that the liquid hydrogen distillation process was considered and studied in some depth in the U.S.A. during the planning of the D_2O production facilities. It is my private opinion that a major factor contributing to its rejection was the primitive state-of-the-art in the practical production and handling of large quantities of liquid hydrogen at that time. Recent economic studies have resulted in claims that the cheapest way to produce D_2O is by distilling liquid hydrogen. This leads naturally to the second question: "Why is the U.S.A. less interested in a process that promises to lower costs than are other countries?" The answer depends on local economic and technical factors. Outside the U.S.A. some factors may weigh the balance in favor of this method, e.g. the availability of an adequate, cheap supply of pure hydrogen—this is a necessary prerequisite for the hydrogen distillation process. Also, under appropriate conditions the hydrogen distillation process enables one to exploit the existence of an electrolytic hydrogen plant by using the electrolytic stages for pre-enrichment of the hydrogen feed. In the U.S.A. it seems that the plants already in existence can supply present needs, and until they need replacement or augmentation, it would not be economical to replace them with plants using another process. Another factor is that highly enriched U^{235} can be economically used in a commercial nuclear power reactor with graphite or ordinary water as the moderator. Where such concentrated U^{235} is not available, a practical power-producing reactor is still possible if D_2O is used as the moderator.

Liquid deuterium also is sometimes used in bubble chambers for experiments in which deuterons (deuterium nuclei) are desirable targets. Since the deuterium nucleus consists only of a neutron and a proton, liquid deuterium is the nearest available approach to a collection of pure neutrons, so that studies of collisions of high-energy particles with neutrons can be conducted

in a liquid deuterium bubble chamber with minimum extraneous complications. Also some of the current designs of neutron moderators for producing low-energy neutrons in experimental reactors consist of masses of solid D_2O cooled to about $20^\circ K$. Heavy water and deuterium have been used in a multitude of basic experiments in pure physics and chemistry as well as in biological experiments in which the behaviors of atoms, with almost identical chemical properties but differing in mass by a factor of 2, can be compared.

Finally, one should not neglect to mention the proposed use of deuterium in nuclear fusion, the process which, if economically realized, will provide the world with almost unlimited power. Accordingly, the technological advances described in this book may also be considered as investments in the future, and it is fervently hoped that they will contribute substantially to the "taming of the hydrogen bomb" or the use of nuclear fusion for peaceful purposes to benefit all mankind.

There is another chapter in this book, "Safety in the Use of Liquid Hydrogen", which deserves some discussion in this introduction. During the long period in which liquid hydrogen was used only in small quantities for laboratory experiments, there were many accidental explosions. Although some of these were quite violent, as far as I know, no fatalities resulted. Accurate statistics are not available, but I believe that a reasonably good estimate is that approximately half of the laboratories which utilized liquid hydrogen over a long period of time experienced one or more explosions. Several of these occurred in hydrogen liquefiers and were attributed to an accumulation of solid oxygen or solid air near the bottom of the final Joule-Thomson heat exchanger. If large quantities of hydrogen had been present in many of these minor accidents, it is reasonable to suppose that the explosions would have been disastrous.

When it became necessary to produce, store and utilize larger quantities of liquid hydrogen, extra precautions were taken because it was recognized that the consequences of an accident would be much more serious. In spite of these precautions, there have been two fatal accidents, although it should be pointed out that in one case the victim was violating a safety regulation when the accident occurred. He would not have suffered injury if he had been behind the protective wall that was provided.

Although the material presented in the chapter on safety is oriented toward the use of large quantities of liquid hydrogen, the basic principles are universally applicable so that it is recommended as a guide for establishing safety regulations to be followed by all users of liquid hydrogen. Since operations in various installations using liquid hydrogen differ greatly, a universal safety manual cannot be prepared. The specific regulations will depend upon the nature of the operation, the quantities of liquid hydrogen being handled, and other factors which cannot be anticipated without detailed knowledge of the installation.

I would like to conclude these general remarks on safety with the statement that no installation using liquid hydrogen can be made "idiot-proof". There is no substitute for intelligence.

CHAPTER 2

PRODUCTION OF HYDROGEN GAS FOR LIQUEFACTION

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1. INTRODUCTION

GASEOUS hydrogen for the production of liquid hydrogen can be obtained from among several commercially feasible processes. By-product hydrogen resulting from other primary chemical production processes is also frequently available. Basic hydrogen production processes include: thermal-catalytic dissociation of ammonia or methanol; electrolytic dissociation of water; steam-iron conversion of reducing gas; catalytic steam-reforming of hydrocarbons; partial oxidation of hydrocarbons or carbonaceous fuels; and the familiar water gas process, a combustion-reduction reaction of coal or coke with steam. Common sources of by-product hydrogen are caustic-chlorine manufacture, coke-oven gas, chemical process by-product and petroleum refinery off-gas from catalytic or thermal cracking and reforming processes.

The major liquid hydrogen plants built or under construction in the United States have as respective feed sources: chlorine-cell by-product hydrogen; chemical plant off-gas; refinery off-gas; partial oxidation of oil or natural gas; and steam-catalytic reforming of natural gas or other light hydrocarbons.

The choice of hydrogen source will usually be guided by economics, determined in turn by use-point location, availability of basic raw materials or off-gas hydrogen, capacity or volume requirements, duration of need and many other factors. In most cases, the hydrogen gas stream will require some degree of further purification to be suitable as raw material for liquefaction.

This chapter discusses the more important hydrogen gas producing methods and off-gas sources applicable to most areas of the world. Gas purification requirements and methods are also discussed. Unit capital and utility requirements, together with typical economic limits for several of the producing methods, are presented in tabular form (Table 1).

2. HYDROGEN PRODUCTION PROCESSES

2.1. *Thermal-catalytic Dissociation of Chemicals*

Hydrogen compounds suitable for commercial production of hydrogen by thermal-catalytic dissociation include ammonia and methanol. These

TABLE I. UNIT INVESTMENT AND OPERATING REQUIREMENTS FOR SEVERAL HYDROGEN PRODUCTION METHODS

Process	Plant capacity range (1000 scf/d)	Unit investment range (\$ per 1000 scf/d)	Utilities			Chems. and Lubes. (cents per 1000 scf)	Labor (man hours per 1000 scf)	Maintenance material (cents per 1000 scf)
			Electric power (kWh/1000 scf)	Raw material and fuel per 1000 scf	Steam (lb/1000 scf)			
NH ₃ dissociation	50-100	1600	50	(NH ₃) 31 lb	—	—	0.4 -0.2	4
Electrolysis	50-100	3000-2200	120-125	—	—	0.2	0.4 -0.2	0.6
	300-600	1700-1600	120-125	—	—	0.2	0.1 -0.05	0.6
	1,000-5,000	1500-1300	120-125	—	—	0.2	0.03-0.02	0.6
Steam catalytic reforming of nat. gas	100-200	2000-1300	4	(nat. gas) 600-460 scf	—	2	0.24-0.12	3
	300-600	1100-750	4	—	—	2	0.12-0.06	2
	1,000-5,000	600-250	4	—	—	2	0.03	1.5
	10,000-25,000	190-145	4	—	—	2	0.01	1.0
Partial oxidation of fuel oil	1,000-5,000	760-430	7-8	(oil) 20-23 lb	—	1	0.03	2.0
	10,000-25,000	350-260	7-8	—	—	1	0.01-0.006	1.5
Steam-iron	100-200	2000-1650	8-10	(nat. gas) 1000 ft ³ (coke) 65 lb	400	5	0.24-0.12	5
	300-600	1550-1200	8-10	(off-gas) 1100 ft ³ CO + H ₂	400	5	0.12-0.06	5
Water-gas: Standard	300-600	1600-1250	8-10	(coke) 50 lb	60	6	0.12	4
	1,000-5,000	1150-850	8-10	—	60	6	0.03	4
	10,000-25,000	800-680	8-10	—	60	6	0.01	4

NOTES:

- (a) Investment and utilities included for producing oxygen for partial oxidation.
 (b) Investment and utilities included for producing reducing gas for steam-iron process.
 (c) Purification equipment included for all processes to yield final product purity of 98 per cent or higher with carbon oxides at 20 ppm or less.
 (d) Compression and electric power included to deliver hydrogen at 600 psig.
 (e) Investment based on U.S. costs.

materials are readily available in many areas of the world, capital cost of plant is low and operation is simple. Since each of these feed-stocks is originally produced from hydrogen gas, the material cost is high. For this reason, this general process will usually be practical only for small hydrogen volumes, for projects of short duration, or perhaps for situations where logistics of feed-stock supply warrant its use.

The ammonia dissociation unit employs a ferric or nickel oxide catalyst contained in a closed circuit or chamber into which the feed ammonia is admitted. The catalyst chamber is heated from an external source to the temperature required for the cracking reaction. The ammonia must be vaporized before entry to the catalyst chamber. The reaction ($2\text{NH}_3 \rightarrow 3\text{H}_2 + \text{N}_2$) occurs at an operating pressure of 1-2 atm (0-20 psig) and requires a temperature of 1700-1800°F (925-980°C).

The heat may be supplied from electrical heating elements, gas burners or other sources with suitable temperature levels. Major equipment items required for the dissociation unit include ammonia storage, gas to liquid heat exchanger and vaporizer, catalyst chamber, heat source, air blowers and product compressors. Instruments and controls to indicate and/or control operating pressures, temperatures and flows are required. Materials of construction must be suitable for ammonia service at the respective temperatures of operation. Since the product gas is at low pressure, compression will be required prior to purification and liquefaction.

The 25 mol % N_2 content in the effluent gas presents a purification problem. Primary purification can be accomplished by adsorption of nitrogen on charcoal. Removal of remaining nitrogen and final purification by condensation and low-temperature adsorption will normally be a part of the liquefaction cycle. The precious-metal-membrane diffusion process can be used to separate the hydrogen from the nitrogen and trace contaminants. Hydrogen effluent from the diffusion process is ultra-pure, and will require no further purification before liquefaction. Additional description of these purification processes is presented in section 4—Purification.

Thermal-catalytic dissociation of methanol according to the reaction $\text{CH}_3\text{OH} \rightarrow \text{CO} + 2\text{H}_2$ can be carried out in the presence of a zinc or nickel oxide catalyst. The CO content of the dissociated feed can be converted with steam in the usual manner to CO_2 and hydrogen.

The methanol reaction is endothermic and is most efficient within a temperature range of 1200-1400°F (640-760°C). A reaction pressure of 300 psig can be used.

In operation, the catalyst oxide is continuously reduced by the methanol and reoxidized by decomposition of water formed in the initial sub-reaction. Carbon deposition on the catalyst can be controlled or minimized by introduction of steam to present an excess of water in the overall reactions.⁽¹⁵⁾

Equipment requirements and arrangement for the methanol dissociation process will be much the same as for ammonia cracking. A steam source and CO conversion unit will be additional requirements.

Conversion of methanol in the reaction is high; in a properly designed and operated unit, product purity should be 97 per cent or higher. Unconverted methanol can be condensed. Residual CO and CO₂ after conversion can be methanated to low concentrations. Final CO₂ removal can be done by caustic scrub, and final CO and hydrocarbon removal can be by adsorption in the low-temperature plant.

2.2. *Electrolytic Dissociation of Water*

Electrolytic dissociation of water has long been an economic source of hydrogen in areas of the world where low-cost electric power is readily available. Where electric power is produced from coal or hydrocarbon fuel, the price of power makes electrolytic hydrogen generally economic only in relatively small volumes.

Conventional electrolytic cells operate at near atmospheric pressure. In operation, the cells are filled with a water-electrolyte mixture, normally 10–20 per cent NaOH. Direct current electric potential is applied across the cell from cathode to anode. Hydrogen and oxygen ions of the electrolyte solution are impelled by current flow to be attracted to the electrodes of the cell.⁽¹²⁾

The positively charged hydrogen ions are neutralized by electrons at the cathode and evolve as stable hydrogen gas. The negatively charged oxygen ions lose electrons at the anode to evolve as stable oxygen gas.

A common operating voltage for the low-pressure cells is 2 V. Current capacity at a given voltage is a function of the number of electrodes. Consequently the operation of a large cell is identical to operation of a number of smaller cells with an equivalent number of electrodes. Production of hydrogen per ampere hour is constant.

Cell capacities range from 500 to 12,000 A or more. Modern low-pressure cells will yield 8 scf (20°C and 760 mm) of hydrogen per kWh of power, at 2 V and 1000 A. Unit power consumption varies with cell voltage, rising with increased voltage. To control corrosive action and conductivity of the electrolyte to the optimum point for cell life, the cell temperature is controlled between 140 and 150°F (60 and 65°C).

These cells are of tank-type construction, fabricated of iron or steel. The anode is nickel plated to reduce oxygen over-voltage; other internal parts are often nickel coated to reduce corrosion. Auxiliary equipment required for a complete facility includes an a.c. to d.c. rectifier or d.c. generator, transformer, electrolyte preparation unit, water-treating unit, hydrogen and oxygen compressors, electrolyte cooling and heating system, raw material storage and product gas storage.

Relatively recent developments in Germany of high-pressure, stacked-cell construction permit commercial production of electrolytic hydrogen at operating pressures as high as 30 atm. The higher pressure results in operational advantages to some degree. These may be reduced cell corrosion, reduced over-voltage of the cathode, reduced specific power consumption

and lower compression requirements for the product gases. The higher cell pressure results in lower specific volume of the gases, allowing a more compact cell design and reduced floor-space requirements. As in the low-pressure cell, internal metal components are nickel coated. Cell diaphragms are of pressed asbestos. The cells and partition diaphragms are circular in form and are assembled by stacking and clamping many cells together in the same manner as filter press assembly. The assembled cell unit is mounted horizontally; gas collection ducts and separation chambers are mounted above the cell unit.

Electrolyte cooling, power supply and other auxiliary systems will be basically the same as for the low-pressure cell.

Operating characteristics of the two types of cells are shown in Table 2.

TABLE 2. ELECTROLYTIC CELLS FOR HYDROGEN PRODUCTION—
OPERATING CHARACTERISTICS OF LOW- AND HIGH-PRESSURE CELLS

	Low pressure	High pressure
Electrolyte	NaOH	NaOH
Operating pressure	1 + atm	to 30 atm
Temperature	140–150°F (60–65°C)	195–210°F (90–99°C)
Voltage range	1.8–2.3	1.65–1.95
Specific power consumption kWh/1000 scf (20°C at 760 mm Hg) Voltage	kWh/1000 scf	kWh/1000 scf
1.7	—	108
1.9	118	117
2.0	124	—
2.25	140	—

Purity of hydrogen product from electrolysis is high, usually 99.5 mol % or higher, dry basis. The main impurity is oxygen, which can be removed by catalytic reduction to water. Total water can then be removed by conventional drying methods.

Overall economics of electrolytic hydrogen production can be improved by making effective use of the oxygen evolved by the process. The oxygen is of high purity and, after drying and catalytic hydrogen removal, may be used for any usual oxygen requirement or sale.

2.3. Steam-Iron Reaction

The steam-iron process for producing hydrogen for liquefaction has definite economic commercial feasibility. This method has been used to