

The Design of Hydrogen Liquefiers*

CHAUNCEY STARR

Massachusetts Institute of Technology, Cambridge, Massachusetts

(Received October 19, 1940)

The general principles underlying the practical design of Joule-Thomson hydrogen liquefiers, utilizing the compressed hydrogen commercially available in cylinders, are discussed. The theory of heat interchangers is applied to these liquefiers and design formulae and data are presented. A typical design for the regenerative interchanger of a small scale liquefier is given. The liquid nitrogen requirements, expansion valve design, charcoal trap construction, and other practical aspects of these liquefiers are also discussed.

THE widespread interest in cryogenic research has recently resulted in the development of inexpensive small scale liquefiers for hydrogen. Most of these liquefiers utilize the Joule-Thomson effect and the principle of regenerative cooling. The liquefaction process involves the precooling of the pure compressed gas below the inversion point, expansion of this gas through a valve, and the use of the cooled expanded gas to lower the temperature of the compressed gas by means of a heat interchanger. The general theory of this process has been studied in detail¹ and the construction of individual liquefiers has been completely described.¹⁻⁴ Because of the need for general design formulae and data which would permit the construction of hydrogen liquefiers to meet individual requirements, this information will be presented here.

Hydrogen gas of high purity (99.5 percent) is commercially available in cylinders at a pressure of 136 atmospheres (2000 lb./in.²). Because of the relatively high cost of a compressor-gasometer system, it is sound economy to use this commercially compressed gas for small scale liquefaction and to discard the low pressure exhaust gas. The standard 200-cu. ft. capacity cylinder contains about 250 moles of H₂ at 136 atmospheres and is used down to about 25 atmospheres. With an average liquefaction effi-

ciency of 25 percent, about 50 moles or 1.4 liters of liquid H₂ is produced per cylinder. Liquid nitrogen is customarily used for precooling and for thermal shielding.

A typical liquefaction system is shown schematically in Fig. 1. The high pressure gas is led

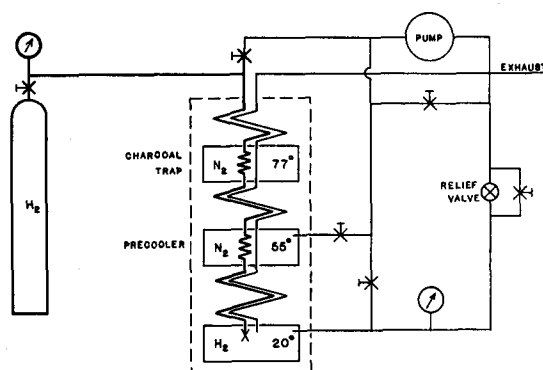


FIG. 1. Hydrogen liquefaction system.

through a charcoal trap immersed in liquid N₂ where it is purified and cooled to 77°K. It is then further cooled in a container of solid N₂ where the temperature is maintained between 63°–55°K by means of fast vacuum pumps. The gas then passes through a heat interchanger and is expanded through an adjustable valve to a pressure slightly greater than 1 atmosphere. Part of the gas is liquefied and collects in the expansion chamber. The cooled unliquefied gas returns through the heat interchanger and eventually is discharged outdoors. The low pressure outgoing gas is heat interchanged with the high pressure incoming gas between all temperature levels, until room temperature is

* Contribution No. 467 from the Research Laboratory of Physical Chemistry.

¹ F. G. Keyes, H. T. Gerry and J. F. G. Hicks, *J. Am. Chem. Soc.* **59**, 1426 (1937).

² J. E. Ahlberg, I. Estermann and W. O. Lundberg, *Rev. Sci. Inst.* **8**, 422 (1937).

³ B. V. Rollin, *Proc. Phys. Soc.* **48**, 18 (1936).

⁴ M. Ruhemann, *Zeits. f. Physik* **65**, 67 (1930).

reached. The interchanger between the solid N₂ container and the expansion valve, the regenerative interchanger, determines the regenerative cooling and thus the efficiency of the liquefaction process. The interchangers between the solid N₂, liquid N₂, and room temperatures determine the rate at which the liquid and solid N₂ are used, and therefore are not as important as the regenerative interchanger. The relation between the fraction of incoming hydrogen gas that is liquefied and the temperature and pressure of this gas before entering the regenerative interchanger has been discussed by Keyes, Gerry, and Hicks,¹ and Fig. 2 of their paper may be used as a guide to proper operating conditions. The effect of the regenerative interchanger efficiency upon the liquefaction fraction is shown in Table I. The above data is based on the Keesom-Houthoff chart.⁵

INTERCHANGER DESIGN

Liquefier heat interchangers are of the counterflow type, the high pressure incoming gas flowing oppositely to the low pressure outgoing gas. It is obviously desirable that the heat interchanger efficiency be as high as possible. The efficiency is best defined as the ratio of the actual temperature rise of the outgoing gas, between the two ends of the interchanger, to the maximum possible temperature rise. This is approximately the ratio of the actual amount of heat exchanged between the two gas streams to the maximum possible. The regenerative interchanger should be at least 95 percent efficient, and all other interchangers should be at least 90 percent efficient. The fall in pressure should be low in both sides of the interchangers in order to maintain a high efficiency of liquefaction. Excessive pressure drop in the high pressure side of the regenerative interchanger results in Joule-Thomson cooling along the length of the interchanger, and this self-cooling reduces the heat interchange with the outgoing gas by reducing the temperature difference. Excessive pressure drop in the low pressure side raises the pressure in the liquid hydrogen chamber and reduces the

TABLE I. Liquefaction fractions in percent.

PRECOOLING TEMPERATURE °K	PRESSURE IN ATMOSPHERES	INTERCHANGER		EFFICIENCY 80%
		100%	90%	
77	150	18	14	9
	100	16	11	6
	50	10	5	-1
	25	4	-2	
63	150	29	26	22
	100	26	22	18
	50	19	14	10
	25	8	3	-3
55	150	40	38	35
	100	37	35	32
	50	26	24	20
	25	12	8	3

over-all efficiency of the liquefaction process by causing liquefaction at a higher temperature and pressure. Low pressure in the hydrogen chamber is also desirable for structural reasons. A pressure drop of 0.5 atmosphere from the liquid hydrogen chamber to the room temperature outlet (or inlet) is satisfactory for both sides of the interchanger system. Most of this pressure drop usually occurs in the high temperature portion of the interchanger system, the regenerative interchanger contributing a drop of only 0.1-0.2 atmosphere.

The design of counterflow heat interchangers may be divided into two parts. The first part is the determination of the heat transfer conditions required to give the desired efficiency. This is determined only by the heat capacities of the two gas streams and their rate of flow. Designate m_i the moles per second of incoming gas, m_o the moles per second of outgoing gas, C the molar specific heat at constant pressure (joules/mole °C), U the total heat transfer coefficient between the two gas streams per unit length of interchanger (joules/sec. cm °C), L the length of the interchanger, Θ the total temperature difference between the hot and cold ends of the interchanger, Δ_H and Δ_C the temperature difference between the two gas streams at the hot and cold ends, respectively. The solution to the differential equation of heat balance along the interchanger is then

$$UL = \frac{m_o C_o m_i C_i}{m_i C_i - m_o C_o} \ln \frac{\Delta_C}{\Delta_H}$$

⁵ W. H. Keesom and D. J. Houthoff, Leiden Comm. Suppl. No. 65 (1928).

Since the interchanger efficiency $E = (\Theta - \Delta_H)/\Theta$, and $m_i C_i (\Theta - \Delta_C) = m_o C_o (\Theta - \Delta_H)$, then

$$UL = \frac{m_o C_o m_i C_i}{m_i C_i - m_o C_o} \ln \frac{m_i C_i - E m_o C_o}{(1-E)m_i C_i} \quad (1)$$

Consider a Joule-Thomson process operating at an incoming gas pressure of 50 atmospheres, a precooling temperature of 55°K, and a regenerative interchanger efficiency of 98 percent. The liquefaction fraction will then be about 25 percent. The Keesom-Houthoff data⁵ give about 1.7 for the ratio of specific heats at 50 and 1 atmospheres in the temperature region involved. With C_o equal to 21 joules/mole °C, and $m_o = 0.75m_i$, Eq. (1) gives $UL = 126m_o$. It is of interest to calculate the temperature differences at the two ends of the interchangers. Since the temperature in the liquid hydrogen chamber is about 22°K, $\Theta = 33$, and with $E = 98$ percent, $\Delta_H = 0.66^\circ\text{K}$ and $\Delta_C = 18.8^\circ\text{K}$. The temperature of the high pressure gas immediately before expansion is therefore about 41°K, and this temperature is only slightly affected by the interchanger efficiency. The critical temperature of H_2 is 33.3°K, so that no liquid H_2 forms in the high pressure side of the interchanger before reaching the expansion valve. A simple calculation shows that this is true even at the lowest usable pressure of a cylinder, 25 atmospheres.

The second part of the design is the adjustment of length, size, and arrangement of tubing to fulfill the required heat transfer conditions with the minimum pressure drop, least material, and least construction difficulty. The general principles of this subject have been satisfactorily treated both experimentally and theoretically.^{6,7} The specific application to Joule-Thomson liquefiers will be presented here. The total heat transfer coefficient U is related to the individual coefficients according to the formula

$$\frac{1}{U} = \frac{1}{H_i} + \frac{t}{k} + \frac{1}{H_o}$$

where H_i and H_o are the individual coefficients between the gas and metal wall for the incoming

and outgoing streams, t is the thickness and k is the conductivity of the metal wall between the two gas streams. The metal wall conductivity may usually be disregarded since its effect on the interchanger efficiency is less than 0.1 percent. Only the condition of turbulent gas flow need be considered, since this is the situation that commonly exists in liquefiers.

The considerations involved in the dimension design may be found from an analysis of the relation between the heat transfer and pressure drop in a tube carrying a gas. The transfer coefficient H and the pressure drop δp (g/cm²) per unit length are related according to the theoretical formula

$$\frac{H}{\delta p} = \frac{\pi^2 g c P d^4}{16 m R T} \quad (2)$$

where d is the tube diameter (cm), g the acceleration of gravity (980 cm/sec.²), c the specific heat at constant pressure (joules/g °C), m the rate of flow (moles/sec.), P the pressure (atmospheres), R the gas constant (82), and T the absolute temperature. This formula would indicate that the optimum conditions require large diameter tubes, but, as will be shown later, the value of H decreases as the diameter increases. Therefore, large diameters require longer lengths for the same total heat transfer and the requirements of size and weight must be considered. Equation (2) also shows that the high pressure side of an interchanger has a very favorable ratio because of the large P , and that the low temperature interchangers benefit from the small T . It is apparent from these considerations that the best interchanger design is one in which every surface that contributes to the pressure drop should also contribute to the heat interchange, i.e., form a conduction path between the two gas streams. Several arrangements suggest themselves as fulfilling the above principle, such as two parallel tubes soldered together or one tube within the other and soldered together. Such arrangements have the disadvantages of small contact area between the two tubes and the poor thermal conductivity and high heat capacity of the solder. Because of the favorable conditions in the high pressure tube, the best practical design is to place the low pressure tube within the high

⁶ W. H. McAdams, *Heat Transmission* (McGraw-Hill, 1933).

⁷ R. B. Jacobs and S. C. Collins, *J. App. Phys.* **11**, 491 (1940).

pressure tube, so that all of the low pressure tube wall is utilized in the heat transfer and the outside wall of the high pressure tube contributes only to the pressure drop. The customary reversed arrangement, in which the high pressure tube is within the low pressure tube, is a poor design. The design, sometimes used,¹ in which the high pressure tube in the form of a tightly wound helix fits snugly within the low pressure tube is a compromise, since most of the low pressure stream flows through the center channel of the high pressure coil

The approximate formula for the heat transfer per unit length between the gas stream and the metal wall of the tube is

$$H = 0.15c\eta^{0.25}(Mm/d)^{0.75} \text{ joules/sec. cm } ^\circ\text{C}, \quad (3)$$

where η is the viscosity in poises (g/cm sec.), M is the molecular weight of the gas, and the other symbols are the same as above. The value of H for various tube diameters and gas temperatures are given in Table II for H_2 gas at pressures of 1 and 50 atmospheres, and with a rate of flow of 1 mole per minute ($m = 0.0167$). The pressure drop per unit length along a tube carrying a gas is given approximately by the equation

$$\delta p = 0.21 T \eta^{0.25} M^{0.75} m^{1.75} / P d^{4.75}, \quad (4)$$

where δp is the drop in g/cm² and P is the pressure in atmospheres. The more exact formula includes a correction for the change in temperature and pressure along the tube, but this correction may be disregarded for long tubes. The values of the pressure drop in g/cm² per meter length of tube are given in Table III for H_2 gas

TABLE II. The heat transfer coefficient in joules/sec. cm² for hydrogen gas with a flow of 1 mole per minute.

PRESSURE, ATMOSPHERES	TUBE DIAMETER, INCHES	GAS TEMPERATURE, ^o K			
		300	77	50	20
1	1/16	0.066	0.038	0.034	0.027
	1/8	.039	.022	.020	.016
	3/16	.029	.017	.015	.012
	1/4	.023	.013	.012	.010
50	1/16	.066	.053	.064	.038
	1/8	.039	.031	.038	.023
	3/16	.029	.023	.028	.017
	1/4	.023	.019	.023	.014

TABLE III. The pressure drop per meter length of tube for hydrogen gas at 1 atmosphere pressure with a flow of 1 mole per minute.

TUBE DIAMETER, INCHES	TEMPERATURE AT TUBE ENDS, ^o K		PRESSURE DROP PER METER, G/CM ²
	T ₁	T ₂	
1/16	300	77	292
	77	50	81
	50	20	39
1/8	300	77	11
	77	50	3.0
	50	20	1.4
3/16	300	77	1.6
	77	50	0.44
	50	20	0.21
1/4	300	77	0.40
	77	50	0.11
	50	20	0.05

at 1 atmosphere pressure and with a rate of flow of 1 mole per minute, the two ends of the tube being at temperatures T_1 and T_2 . The values of H and δp for other rates of flow, diameters, and pressures may be calculated from Eqs. 3 and 4. As can be seen from above, H is not very dependent upon pressure, the change being due chiefly to the change in specific heat. However, δp is inversely proportional to the pressure, so that at high pressures the drop is negligibly small for ordinary tube sizes.

The principle of the hydraulic radius permits the comparison of various unusual tube cross sections to the circular section of a simple tube. The hydraulic radius is defined as the cross section area divided by the wetted perimeter, and is equal to $d/4$ for a circle. The properties of any cross section may be considered as approximately the same as those of a circular tube of equivalent hydraulic radius. Therefore, an annulus may be considered as a tube whose diameter is equal to the difference of the two diameters forming the annulus. The effect of coiling the tubing into a helix is to multiply the heat transfer and pressure drop by the factor $(1 + 3.5d/D)$, where d is the tube diameter, and D is the diameter of curvature of the coil.

A typical calculation for the regenerative interchanger of a liquefier producing about 1 liter of liquid H_2 per hour will be presented. As before, the calculations will be based upon the assump-

tions of a 55°K precooling temperature, 50 atmospheres average high pressure, 25 percent liquefaction efficiency, and a low pressure outgoing stream of 2 moles per minute. If the desired interchanger efficiency is 98 percent, the calculation above indicates that the required $UL=4.2$. The tube arrangement in which the low pressure tube is within the high pressure tube will be used. Assume the following diameters (inches): low pressure tube 0.0625" I.D., 0.102" O.D., high pressure tube 0.130" I.D., 0.170" O.D. Since the high pressure stream passes through the outside annulus, its equivalent diameter for pressure drop calculation is 0.028". The heat transfer equivalent diameter involves only the inside of the annulus as a wetted perimeter and is equal to 0.0625". Averaging the values of H for 50°K and 20°K in Table II, and adjusting for the higher rates of flow, the heat transfer coefficients become $H_i=0.107$ and $H_o=0.0509$, resulting in $U=0.0345$ joules/sec. cm°C. This gives as the required interchanger length $L=122$ cm. Since this is a comparatively short interchanger, the design length may be arbitrarily increased to 2 meters. The pressure drop in the low pressure stream for a 2-meter length is, using Table III, 78 g/cm² or about 0.08 atmosphere. The pressure drop in the high pressure stream, using the equivalent diameter of 0.028", is 0.09 atmosphere at 50 atmospheres pressure.

The other interchangers of the liquefier are designed in a manner similar to the above. As can be seen from Table III, the largest contribution to the pressure drop in the gas stream occurs at high temperatures. Therefore these interchangers should be designed for small pressure drop even though efficiency is sacrificed. The tubing material may be any common alloy. Pure copper should not be used since its very high thermal conductivity at low temperatures causes a large longitudinal conduction loss, which may decrease the interchanger efficiency by about 5 percent. Supernickel (70 percent Cu, 30 percent Ni) has very good properties but the tubes usually require filling with a low melting substance, such as diphenylamine, before bending. The author has found ordinary low brass (80 percent Cu, 20 percent Zn) to be very satisfactory and in the annealed condition it may be bent without filling.

GENERAL DESIGN DATA

The quantity of liquid N₂ required per liter of liquid H₂ produced depends upon the over-all efficiency of the interchanger system and the quality of the thermal insulation. The minimum requirement, under the liquefaction conditions described above, is 1.66 liters of liquid N₂ per liter of liquid H₂, assuming perfect interchangers and no heat losses. If the interchangers between the solid N₂ and room temperatures have an efficiency of 90 percent, the requirement becomes about 2.0 liters N₂ per liter H₂, of which about 0.3 liter N₂ is in the solid N₂ precooler. The charcoal trap at 77°K causes a change in the normal hydrogen mixture of para- and orthohydrogen from the room temperature equilibrium of 25 percent parahydrogen to the 77° equilibrium of 50 percent parahydrogen. This transition requires about $\frac{1}{3}$ liter liquid N₂ per liter liquid H₂ produced. The amount of liquid N₂ required to maintain containers and shields at proper temperatures depends upon the radiation and conduction losses. Careful design and the use of low thermal conductivity alloys (supernickel) may cause the direct metal conduction losses to be negligible. The loss by radiation and gas conduction may be calculated from the following data for good reflecting surfaces (clean copper or brass) in a vacuum of 10⁻⁶ mm Hg. The energy per second transferred between one such surface at 300°K and another parallel to it at 77°K is 3000 microwatts/cm², and between 77°K and 20°K surfaces is 20 microwatts/cm². The rate of loss of liquid N₂ may be determined from the low temperature surface area, using 174,000 joules/liter as the heat of vaporization of liquid N₂. A liquefier with a producing rate of 1 liter liquid H₂ per hour uses approximately $\frac{1}{2}$ liter liquid N₂ per hour for these heat losses.

It is essential in the liquefier design to provide facilities for the rapid cooling, from room temperature, of all parts of the apparatus. This is best accomplished by direct contact with liquid N₂ introduced through reasonably large sized tubing. The time required to cool the apparatus to the proper operating temperatures depends chiefly upon the heat capacity of the various parts. The amount of liquid N₂ used in cooling is about 0.4 liter per kilogram of metal. If liquid

N_2 is used to cool the liquid hydrogen chamber, care should be taken to completely remove it before liquefaction is started. Nitrogen has a transition at $35.6^\circ K$ which liberates a large amount of energy and as a result any N_2 remaining in the hydrogen chamber will boil away large quantities of liquid H_2 .

The solid N_2 precooler involves the difficult problem of a good thermal contact between the metal gas tubing and the block of solid N_2 . A gas film usually forms at the points of contact of the metal and solid N_2 and this renders the heat conduction inadequate for cooling the gas passing through the tubing. This problem is best solved by the method described by Keyes, Gerry and Hicks,¹ in which the tubing is soldered to a series of trays, each tray offering a large independent surface for contact with the solid N_2 .

The charcoal trap purifies the hydrogen gas and cools it to $77^\circ K$. Approximately 100 g (200 cc) of charcoal at liquid N_2 temperature should be used for each standard cylinder of hydrogen. The adsorbed impurities are removed from the charcoal between liquefactions by warming the trap to room temperature and removing the gas with a vacuum pump. A very suitable container for the charcoal is a coil of copper water tubing, $\frac{1}{2}$ " O.D. and $\frac{3}{8}$ " I.D., since all the gas must then pass through all the charcoal. The high pressure interchanger tube leading to the trap from room temperature should be very large in diameter ($\frac{1}{4}$ – $\frac{1}{2}$ inch) so that all water vapor, etc., may condense in this tube without closing it.

The expansion valve is the only valve that requires special construction. The requirements for this valve are that it work at $20^\circ K$, be externally adjustable, and have delicate control of a small quantity of gas with a pressure on the high side of 136 atmospheres and 1 atmosphere on the low side. Small size is also desirable. The ordinary screw valve is unsatisfactory because the friction between the valve needle and seat and in the screw mechanism renders erratic the control of the very minute opening necessary to

meet the above conditions. The author has found that the very best valve is one in which the valve needle moves toward or away from the seat without turning, so that no friction enters into its operation. With a stainless steel needle fitting into a coned brass seat, the adjustment of the pressure on the needle adjusts the flow of gas through the valve. This pressure is best controlled externally by means of a push rod operating through a tube. If the tube is attached to the valve seat, and the rod to the needle, the rod is in compression, the tube is in tension, and none of the forces is transmitted to the rest of the apparatus. Associated with the expansion valve should be a device for separating the expanded gas and the liquid H_2 droplets. A short metal cylinder, so placed that the mixture strikes the metal wall immediately after expansion, is a very effective separator. The other valves used in the liquefier are all commercially obtainable. The low pressure valves are standard refrigerator type diaphragm packless valves. The valves in the high pressure circuit are the "Hoke" diaphragm type packless high pressure valve. The pressure relief valve is a simple poppet type adjustable valve, and is used to prevent too large a pressure in the hydrogen chamber due to misadjustment of the expansion valve.

The vacuum container for the liquefier may be either a metal case or a glass Dewar. The metal case has the advantage of great flexibility in design and greater strength and safety, but has the disadvantage of requiring a high vacuum pumping system attached to the liquefier. The glass Dewar is, of course, permanently evacuated during construction, and therefore has the advantage of simplicity. In general, the metal case has been used for large liquefiers and multiple purpose apparatus, and the glass Dewar has been used for small units.

The author is indebted to the members of the low temperature staff, and especially to Professor F. G. Keyes for the many discussions and suggestions concerning liquefier design and construction.