

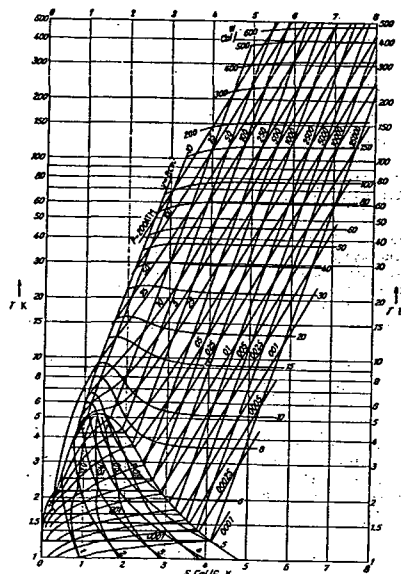


Fig. 2 Temperature-Entropy Diagram for Helium

when sufficient pressure is applied. There is a relatively large change in enthalpy and the heat released is large, being equal to the sum of the work done and the decrease in enthalpy of the refrigerant for steady-flow operation. In other refrigerants, such as air, there is a slight reduction of enthalpy on compression at room temperature and the heat released slightly exceeds the work of compression, but liquefaction does not occur because the critical temperature of air is far below room temperature. By including in the apparatus a counter-flow heat exchanger (see Fig. 4) air may, nevertheless, be liquefied. The heat which flows from the air in the warm zone is given by the equation:

$$Q_1 = h_2 - h_1 + W_1 \quad (1)$$

where

Q = heat flow.

h_1 and h_2 = enthalpy at positions 1 and 2.

W = work done.

The refrigerative effect of the air stream at position 3 in the diagram is given by the relation $Q_2 = h_1 - h_3$, there being no work done at the expansion valve. If an external work machine such as an engine, is substituted for the valve, the refrigerative effect is increased to the extent of the work done, that is:

$$Q_2 = h_1 - h_3 + W_2$$

If the cold zone is well insulated so that no heat enters, the

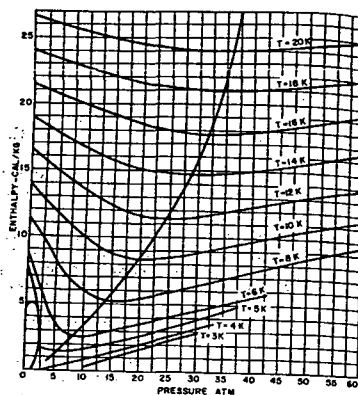


Fig. 3 Variation of Enthalpy with Pressure for Helium at Several Temperatures

refrigerative effect is applied to the gas itself and the temperature continues to fall until the liquid state is reached.

Returning to the properties of helium it is apparent that at any temperature above 30 K the enthalpy is actually increased by compression. The simple apparatus (Fig. 4) could not, therefore, liquefy helium which is initially at room temperature. The temperature would rise at the expansion valve. On the other hand, the replacement of the expansion valve by an engine makes it possible to liquefy helium by the cycle. The liquid is formed within the engine itself. In actual practice the efficiency of this cycle is always low.

Effective liquefaction procedures are illustrated in Fig. 5. In diagram A of Fig. 5 a simple expansion valve is used at the cold end of heat Exchanger A. The compressed helium is cooled to about 15 K by contact with liquid hydrogen boiling at reduced pressure. By reference to Fig. 3 the optimum pressure, the pressure of lowest enthalpy at 15 K, is found to be about 30 atm.

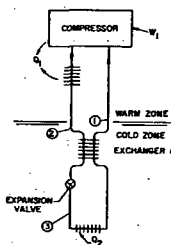


Fig. 4 Simple Refrigeration Cycle with Heat Exchanger

Cryogenics

In diagram B of Fig. 5 an expansion engine has replaced the hydrogen coolant rather than the valve. It has been found expedient to use a final heat exchanger and an expansion valve even when an engine is used for extra cooling. When an engine is used the pressure level is very flexible. If the pressure is low the temperature at the warm end of Exchanger A will be low, perhaps as low as 6 K. At higher operating pressures the temperature is higher.

In order to obtain higher efficiencies multiple expansion machines are sometimes used. The net requirement of a liquefier is to cool gaseous helium from room temperature to

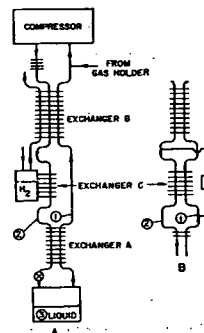


Fig. 5 Flow Diagram of Helium Liquefier

its condensing point and then condense it. The heat to be removed from the gas to change its temperature is large compared to the latent heat of condensation—the ratio being about 75:1. Additional expansion machines along the temperature scale serve to remove heat at higher temperature levels so that not all of the heat must be pumped from the lowest level. In order to extract one calorie of heat from boiling helium and discard it at room temperature, almost 75 calories of work would have to be expended on a perfect machine and still more on an actual machine of superior design. At the liquid nitrogen level only about three calories of work are required per calorie extracted.

Helium is also liquefied by the Simon free expansion method. A strong chamber is filled with gaseous helium at about 100 atmospheres and cooled to the lowest possible temperature by contact with pumped solid hydrogen. A temperature of 11 K is possible. When cold and thermally isolated, a valve is opened and a part of the charge of helium flows out. The temperature falls and partial liquefaction of the helium occurs. At the end of the expansion the bomb may be two-thirds full of helium.

The work expended in liquefying helium is generally in the range of 3 to 10 kilowatt hours per liter of liquid.

LIQUEFACTION OF HYDROGEN

Historically, hydrogen has been liquefied in small quantities for the purposes of determining its properties at low temperatures and for measurement of physical properties of

other materials. In recent years research with liquid hydrogen has promoted increased efforts to obtain engineering data on cryogenic construction materials, equipment, and processes. Hydrogen liquefiers currently are being operated by universities, industries, and government agencies, in sizes ranging from one or two liters per hour to approximately 300 liters per hour.

Problems and Properties

Consideration of hydrogen liquefaction should be preceded by mention of some of the properties of hydrogen which influence the liquefaction process. Most important of these properties are the inversion temperature (the temperature at which the Joule-Thomson effect changes sign) of hydrogen, its high and variable specific heat, its ortho-para forms and its purification requirements.

Hydrogen Inversion Temperature. The inversion temperature for hydrogen is -92°F and Joule-Thomson cooling is small for temperatures above -280°F . Thus, hydrogen cannot be liquefied by Joule-Thomson expansion unless it is pre-cooled to a temperature lower than -92°F . Efficient liquefaction by Joule-Thomson expansion is realized by precooling with subatmospheric liquid nitrogen or liquid air in the temperature range from -333°F to -352°F .

Specific Heat. The constant pressure specific heat of hydrogen gas is higher than that of any other gas. Also, in common with other gases near their critical point, the specific heat of hydrogen rises sharply with moderate pressure in the temperature range of -333°F to -415°F . These factors result in high heat exchange requirements per pound of gas circulated and considerable difficulty in balancing low temperature heat exchangers.

Ortho-Para. Hydrogen exists in both high energy ortho and low energy para forms. The equilibrium mixture of normal hydrogen at room temperature is 75 percent ortho and 25 percent para. With decreasing temperatures the ortho fraction decreases to the equilibrium value of approximately 0.2 percent at the saturation temperature of -423°F . Since the large energy release in converting from the normal to the para form results in prohibitive liquid losses, catalytic conversion in the liquefier has become a standard practice. Ortho-para conversion in the liquefier imposes an additional heat load and the catalyst beds add some structural complexity.

Purification. Purification of hydrogen is important because of its low liquefaction temperature and broad combustion limits with air and oxygen. The first problem requires removal of nitrogen and other high boiling point materials to a concentration of a few parts per million prior to liquefaction to prevent freeze-up of the system. The hazardous nature of the hydrogen-oxygen mixture requires removal of essentially all traces of oxygen before feed gas is admitted to the liquefaction system. This is accomplished by commercial palladium catalyst Deazo units which react the oxygen impurity with hydrogen to form water vapor at room temperature.

Liquefaction Cycles

With one exception, conventional liquefaction systems can be used to liquefy hydrogen. The exception is that hydrogen cannot be liquefied by a cascade process since there is no gas to bridge the gap between the triple point of oxygen and the critical point of hydrogen. Neon has been used to condense hydrogen but neon cannot be cascaded either since its critical point is 18°F below the triple point of oxygen. Use of oxygen is hypothetical at best due to the potential danger of mixing it with hydrogen.