

# Approach To Absolute Zero

## 1. Liquefaction Of Gases

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Absolute zero of temperature is unattainable. One may approach as close to absolute zero as technically possible. In this four part series an attempt will be made to trace developments in the approach to absolute zero. In Part I, I will explain the principles governing liquefaction of gases.

### Introduction

Temperature is a measure of the hotness or coldness of an object. It can be measured with a thermometer. The thermometer contains a working substance such as a liquid in a liquid-in-glass thermometer or a wire of some metal in a resistance thermometer. Some property of the substance varies with temperature such as the volume of a given mass of liquid or the resistance of a given piece of wire. To calibrate the thermometer one chooses two standard baths, say a bath of melting ice and a bath of water boiling at one atmosphere pressure. The thermometer is brought into good thermal contact with each bath and the value of the property measured. Arbitrary values are given to the temperatures of the two baths to define a scale of temperature. In the centigrade scale these values are zero for the ice bath and 100 for the boiling water bath. Assuming the value of the property to vary linearly with temperature, one can find the temperature of any other object by bringing the thermometer in contact with the object and measuring the value of the property. It is obvious that the temperature of an object measured using two different thermometers containing different working substances may not agree with each other. Also there is no *a priori* limit for the lowest temperature of an object. The temperature of an object can be negative without any limit. Thus the scale of temperature chosen is not an absolute one.

Temperature scale defined by a thermometer such as a resistance or liquid-in-glass thermometer is not absolute.



All gases under low pressure and high enough temperature obey Boyle's law

$$PV = f(t),$$

where  $P$  is the pressure of the gas,  $V$  the volume of  $n$  moles of the gas and  $f(t)$  is a function of temperature. A gas which obeys the above relation at all temperatures and pressures is called an ideal gas. No gas is ideal. Every gas approaches the ideal gas behavior at low pressures and high temperatures. We may define a scale of temperature, called the ideal gas scale, in which we may assume  $PV$  to vary linearly with temperature. Experiments indicate that the function  $f(t)$  in the ideal gas scale is

$$f(t) = nR(t_c + 273.16),$$

where  $t_c$  is the temperature on the centigrade scale and  $R$  is the gas constant. If one measures the pressure of a constant volume of gas the temperature values obtained with different gases as working substances will differ very little, especially if the pressure of the gas is low and the temperature is high. To this extent the gas thermometer is superior to the liquid-in-glass or resistance thermometers. However even this thermometer is not absolute as one can choose the zero of temperature at will.

### Absolute Temperature Scale

Two remarkable discoveries were made in the study of the efficiency of heat engines initiated by Sadi Carnot, a French engineer. A heat engine absorbs a quantity of heat  $Q_1$  from a high temperature heat reservoir, rejects a quantity of heat  $Q_2$  to a heat reservoir at a low temperature and performs external work  $W$ . It is found that heat absorbed at the higher temperature cannot be completely converted into work. Considering an ideal engine in which the processes take place infinitesimally slowly, so that the working substance is in thermodynamic equilibrium throughout the cycle and the cycle is reversible, it can be shown

The absolute temperature scale is defined in terms of the efficiency of a Carnot engine.

that the efficiency,  $\eta$ , of the engine defined as  $W/Q_1$ , is independent of the nature of the working substance. So a temperature scale defined in terms of  $\eta$  will not depend on the nature of the working substance in the thermometer. Assuming that a perfect gas is the working substance it is found that

$$\eta = (t_{c1} - t_{c2}) / (t_{c1} + 273.16),$$

where  $t_{c1}$  and  $t_{c2}$  are temperatures of the hot and cold reservoirs on the ideal gas centigrade scale.

One may define a new scale of temperature, the Kelvin or absolute scale, by

$$T = t_c + 273.16.$$

On this scale the efficiency of the Carnot engine will be

$$\eta = (1 - T_2 / T_1).$$

The efficiency will approach unity when  $T_2$  approaches zero. The conservation of energy tells us that  $\eta$  cannot be greater than unity. So there is a natural lower limit to the temperature of any object. This is the temperature of the cold reservoir when the efficiency of the Carnot engine will approach unity. On the absolute scale of temperature this will be called the absolute zero.

### Unattainability of Absolute Zero

Absolute zero of temperature is unattainable.

Kelvin, who introduced the absolute scale of temperature, realized that the absolute zero is a limiting temperature. One can get very close to absolute zero but one cannot reach it. To reach a low temperature one must remove heat from a system. One can use an ideal refrigerator based on the reverse Carnot cycle. This refrigerator will remove a quantity of heat  $Q_2$  at a low temperature  $T_2$  and reject a larger amount of heat  $Q_1$  at a higher temperature  $T_1$  (say room temperature). This is what any refrigerator does.



Since  $Q_1$  is larger than  $Q_2$ , work  $W$  must be done on the refrigerant in the process. This is why the domestic refrigerator consumes electrical energy. For an ideal Carnot cycle

$$Q_2/T_2 = Q_1/T_1 = W/(T_1 - T_2).$$

So the work required to remove unit quantity of heat at  $T_2$  is

$$W/Q_2 = (T_1 - T_2) / T_2.$$

As  $T_2$  approaches zero this ratio approaches infinity. It becomes more and more difficult to remove heat as one approaches absolute zero. This is the reason for the unattainability of absolute zero.

The science of production of low temperatures is called *cryogenics*. This is derived from two Greek words, *cryos* meaning cold and *genesis* meaning production. Since the middle of the last century scientists have expended enormous effort in the march towards absolute zero. Cryogenic research was started and sustained by the insatiable urge of man to approach the unattainable and the curiosity of the scientist to find out how matter behaves at low temperatures. This research has resulted in the discovery of several new phenomena occurring at low temperatures. The most well known of these are superconductivity exhibited by some metals, alloys and compounds at low temperatures, and superfluidity exhibited by liquid helium. There are many more interesting phenomena exhibited by solids at low temperatures. As it happens in every scientific endeavour, basic research in low temperatures has led to many applications in such diverse areas as space research, food preservation, medical diagnostics, surgical techniques, high energy accelerators etc. A new and active branch of engineering, called cryogenic engineering, has come into vogue.

The science of production of low temperatures is called cryogenics.

In this series of articles an attempt will be made to trace the development of cryogenics. The aim will be to explain crucial concepts which have contributed to the development of this

branch of physics. Part I of the series will deal with the liquefaction of gases.

### Liquefaction of Gases

The first major step that was taken in the march towards absolute zero was the liquefaction of the so called permanent gases. It is well known that a gas like sulphur dioxide can be liquified at room temperature, whereas a gas like nitrogen cannot be liquified at room temperature however high the pressure may be. This earned gases such as nitrogen, oxygen and hydrogen the appellation of permanent gases. The research of Andrews, Amagat and others showed that a gas can be liquified by the application of pressure only if it is cooled below a temperature characteristic of the gas. This temperature is called the *critical temperature*,  $T_c$ . For sulfur dioxide the critical temperature is 430.8 K, which is above room temperature. That is why it can be liquified under pressure at room temperature. The critical temperature of nitrogen gas is 126.20 K. It can be liquified under pressure only if it is cooled below the critical temperature. There are no permanent gases. Any gas can be liquified if it is cooled below its critical temperature. The concept of critical temperature is crucial in understanding how to liquify gases. The critical temperatures of the various permanent gases are given in *Table 1*.

A gas must be cooled below its critical temperature before it can be liquified.

The first step in the liquefaction of a gas is to cool it sufficiently so that its temperature is below the critical temperature. One way of doing this is to pass the gas through a bath of a liquid, the boiling point of which is below the critical temperature of the gas. If the critical temperature is well below room temperature it may not be possible to find a suitable liquid bath. One must seek other methods of cooling the gas.

There are two other processes which may be used to cool the gas. The first is adiabatic expansion and the second is Joule-Thomson expansion (J-T expansion) of the gas.



**Table 1 Properties of cryogenic liquids.**

(Taken from *Cryogenic Process Engineering*. Klaus D Timmer hauss and M Flynn. Plenum Press. New York, 1989).

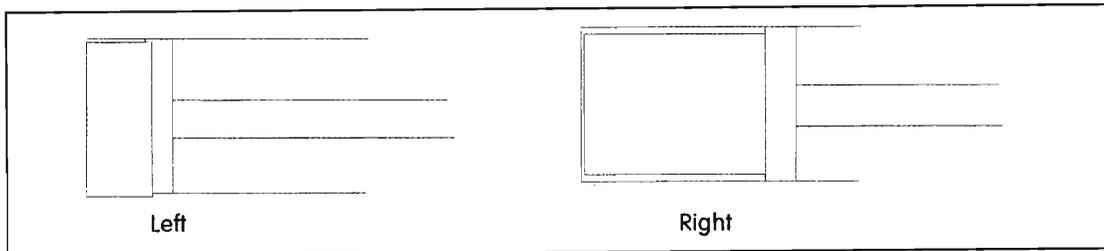
	LO <sub>2</sub>	LAr	LN <sub>2</sub>	LH <sub>2</sub>	LHe <sup>4</sup>
Critical Temp. $T_c$ (K)	154.6	150.7	126.2	32.976	5.201
Normal BP $T_B$ (K)	90.18	87.28	77.35	20.268	4.224
Triple Point $T_t$ (K)	54.35	83.8	63.148	13.803	-
Density (kg/m <sup>3</sup> )	1141	1403	808.9	70.78	124.96
Heat of vaporization (kJ/kg)	212.9	161.6	198.3	445.6	20.73
Specific heat (kJ/kgK)	1.7	1.14	2.04	9.78	4.56

If a gas is enclosed in a cylinder under pressure, it can expand to a lower pressure by pushing the piston out and doing work on the piston, *Figure 1(a)*. If the cylinder is thermally insulated so that no heat enters or leaves the system, the expansion is said to be adiabatic. Conservation of energy requires that the gas must lose an amount of internal energy equal to the work done on the piston. The internal energy of the gas is mainly made up of the kinetic energy of its molecules. Adiabatic expansion of a gas should result in a decrease in the average kinetic energy of the molecules of the gas. From the kinetic theory of gases we know that the average kinetic energy of a molecule of a gas is proportional to the absolute temperature of the gas. So adiabatic expansion of a gas always results in cooling. One uses a piston-cylinder or turbine type of an expansion engine to cool the gas.

Adiabatic expansion always cools the gas.

A second method of cooling is by expansion of the gas through an orifice, (*Figure 1b*). This process is the Joule–Thomson cooling. Here the gas does not perform external work. The total enthalpy, (see *Box 1* for a definition of enthalpy) rather than the entropy, remains constant in this process. Such a process may result in

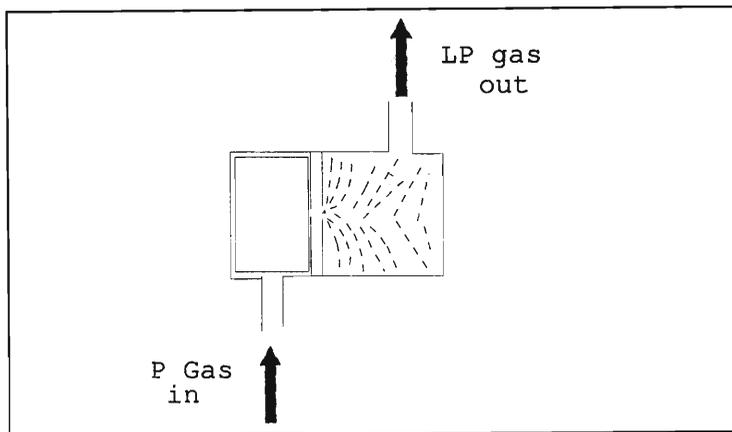




**Figure 1 (a) Adiabatic expansion in a piston-cylinder expansion engine. Compressed gas is enclosed between the cylinder and the piston (figure left). The gas pushes the piston out (figure right) with a drop in pressure and increase in volume. If the expansion engine is thermally isolated, this process always produces cooling.**

an increase or decrease of temperature depending on the temperature of the high pressure gas. If the temperature of the gas at the inlet of the orifice is more than its inversion temperature, the gas warms up on expansion (see *Box 1* for an explanation). For example helium gas at room temperature undergoing Joule-Thomson expansion at an orifice warms up. Only if the inlet temperature of the gas at the orifice is below its inversion

**Figure 1(b) Joule-Thomson expansion. Here high pressure gas expands through an orifice in the plate partitioning the chamber. In this process no external work is done. This process will produce a cooling only if the temperature of the high pressure gas is below the inversion temperature for the gas.**



**Box 1**

The enthalpy of a system is defined as

$$H = U + PV$$

where  $U$  is the internal energy and  $P$  and  $V$  are the pressure and volume of the system. Since the internal energy as well as the work done on the system can be converted to heat,  $H$  is called the total heat content of the system. In the Joule–Thomson expansion, no heat enters or leaves the system and no external work is done. So the enthalpy remains a constant in this process. The rate of fall of temperature with decrease in pressure in such a process is given by

$$(dT/dP)_H = - \{ (dU/dP)_T + [d(PV)/dP]_T \} / C_p.$$

Here  $C_p$  is the specific heat at constant pressure of the system. For a gas the internal energy is made up of the kinetic energy of the molecules, which is only a function of temperature, and the potential energy of the molecules due to intermolecular interaction. This interaction is attractive and decreases in magnitude as the molecular separation increases. An attractive energy is negative. As the pressure increases, the molecules come closer to one another and the potential energy becomes more and more negative. So  $(dU/dP)_T$  is negative. For an ideal gas which obeys Boyle's law  $PV$  is only a function of temperature and hence  $[d(PV)/dP]_T$  is zero. An actual gas is less compressible than an ideal gas at high temperatures and more compressible than an ideal gas at low temperatures. This means that at high temperatures  $[d(PV)/dP]_T$  is positive and at low temperatures it is negative. At some intermediate temperature the value of this derivative cancels the value of  $(dU/dP)_T$ . This is the temperature of inversion. Above this temperature the numerator within flower brackets above is positive. So  $(dT/dP)_H$  is negative leading to an increase in temperature with a decrease in pressure. The gas will warm up during a J–T expansion if its temperature is above the inversion temperature. On the other hand if the temperature is below the temperature of inversion, the numerator within the flower brackets in above is negative. So  $(dT/dP)_H$  is positive. The gas cools on isoenthalpic expansion.

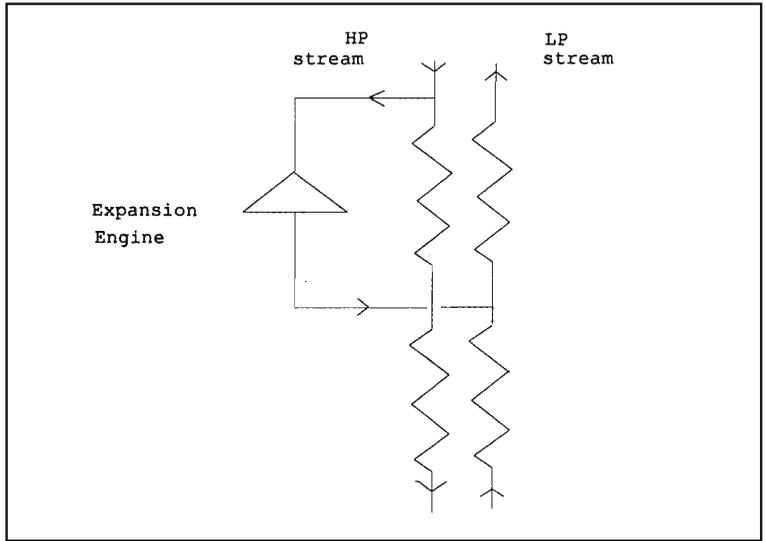
temperature will the gas cool on expansion. For helium gas the inversion temperature is below 40 K.

One can use adiabatic expansion or J–T expansion to cool the gas. Such a cooling has to be used in a regenerative way so that the expanded cold gas is used to cool the incoming high

J–T expansion cools the gas only if the temperature of the high pressure gas is below its inversion temperature.



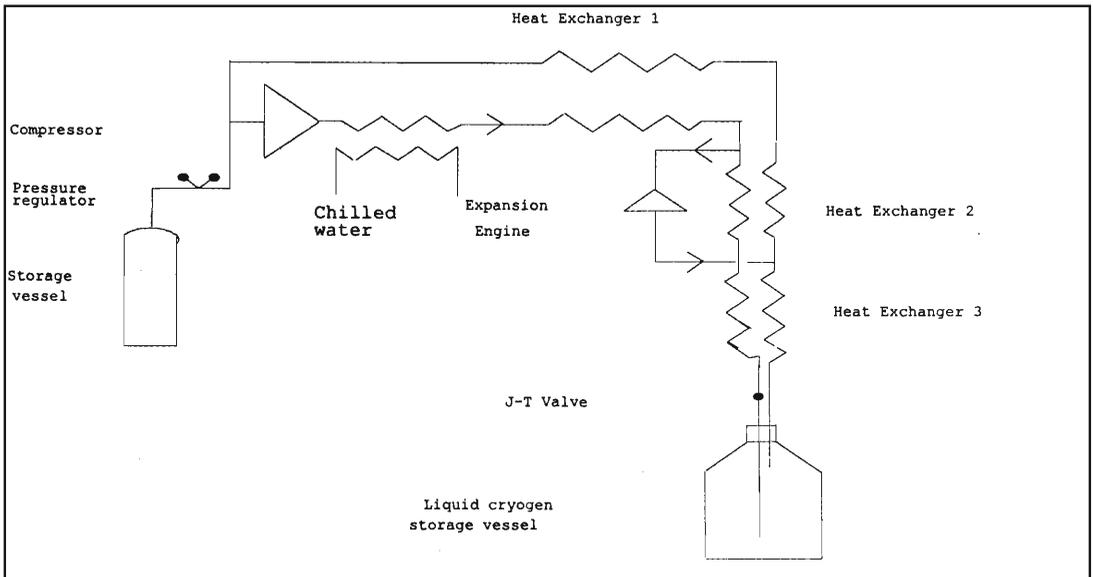
**Figure 2 Regenerative cooling produced by an expansion engine in combination with a heat exchanger train. Part of the high pressure gas entering the heat exchanger is diverted to the expander. It expands there to a low pressure and cools. The low pressure gas joins the returning low pressure stream in the heat exchanger. This cold low pressure gas cools the incoming high pressure gas in heat exchanger 1. Thus the temperature of the high pressure gas entering the expander is progressively cooled.**



pressure gas. In this way the temperature of the gas after expansion progressively falls till the gas liquifies on expansion.

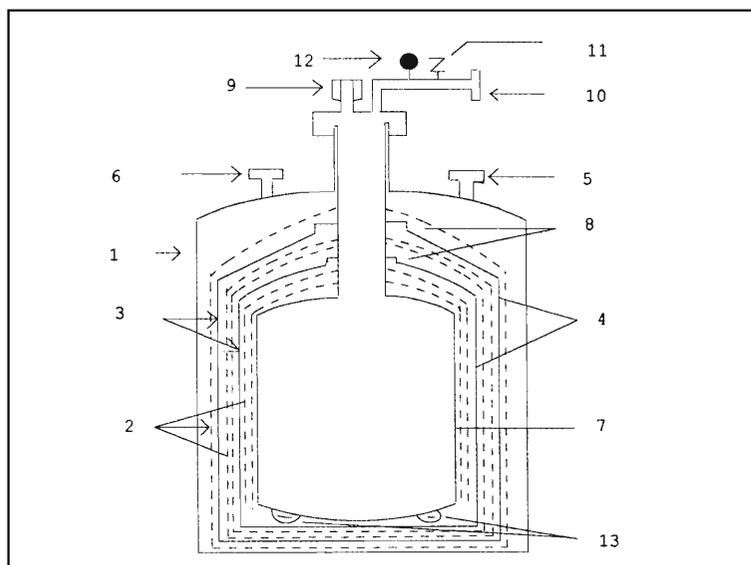
**Figure 3 Schematic diagram of a liquefier. Read text for explanation.**

This regenerative cooling is achieved by the use of a heat exchanger. A counter-flow heat exchanger with an expansion engine is shown in Figure 2. A part of the high pressure gas



stream is expanded adiabatically. The cold low pressure gas stream flows in one arm of the heat exchanger while the rest of the high pressure stream flows in the other arm. The two counterflowing streams exchange heat. High efficiency heat exchangers are essential parts of a liquefier. *Figure 3* shows a schematic diagram of a liquefier. High purity gas at atmospheric pressure from a storage tank is compressed. The heat of compression is removed by circulating chilled water in the cooler. The high pressure gas enters a train of heat exchangers. Part of the high pressure stream is diverted to pass through an expansion engine. The expanded gas in counterflow cools the rest of the high pressure stream. The final stage in a liquefier is always a J-T expansion stage. On expansion, a part of the expanded gas (about 8 to 10%) liquifies and collects in the storage vessel. The rest of the cold gas returns to the compressor via the heat exchangers. The density in the liquid state is very much higher than the density in the vapour state. So when a part of the gas liquifies the volume of the gas is reduced suddenly. If an expansion engine is used it will result in knocking of the piston on the cylinder. This will cause problems for the mechanical design of the expansion engine. This is the reason why the final expansion stage is a J-T expansion through

*Figure 4 Storage vessel for liquid cryogen. (1) Outer vacuum vessel, (2) Layers of superinsulation (these are thermally anchored at different points along the neck tube), (3,4) Copper radiation shields anchored at different points along the neck tube, (5) evacuation and seal off port, (6) bursting disc, (7) thin walled SS storage vessel, (8) copper rings soldered to the neck tube to which the radiation shields are anchored, (9) Wilson seal for transfer tube, (10) recovery connection if liquid helium is stored or vent to atmosphere if liquid nitrogen is stored, (11) pressure relief valve, (12) pressure gauge, (13) adsorbent charcoal.*



an orifice. With suitably designed liquefiers air was first liquified by Cailletet in France in 1877, hydrogen by James Dewar in U.K. in 1898, and helium by Kamerlingh-Onnes in Leiden in 1908. It appears that Kamerlingh-Onnes obtained his helium gas from the monazite sands of North Carolina, USA to produce small quantities of liquid helium. Now commercial large scale liquefiers producing hundreds of liters of liquid helium are available.

The normal boiling points of the various cryogenic liquids are given in *Table 1*. Liquid helium has a boiling point of 4.22 K.

Cryogenic liquids have to be stored in evacuated insulated storage vessels.

Cryogenic liquids have to be stored in special vessels so that the heat leaking from the ambient to the cold liquid is a minimum. These are double walled evacuated vessels as shown in *Figure 4*. Evacuation of the space between the inner and outer vessels reduces heat leak by convection. The inner vessel is surrounded by layers of aluminized mylar to reduce heat leak by radiation. The inner vessel in which the liquid is stored is suspended by a thin-walled stainless steel tube to reduce heat leak by conduction. Stainless steel storage vessels of different capacities with about 2% evaporation loss per day are commercially available. With such storage vessels 100 liters of liquid helium can be stored for about 40 to 45 days.

Today closed circuit refrigerators, with limited refrigeration capacity, operating on the Gifford-McMahon cycle, are available to reach low temperatures. With these refrigerators one can perform low temperature measurements down to 10 K in the laboratory.

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### Suggested Reading

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