CECIL T. LANE

SUPERFLUID
PHYSICS

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PROFESSOR OF PHYSICS
YALE UNIVERSITY

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Preface

This book is based on a course of lectures which I have given to first-year graduate students in physics for the past ten years. The aim of the course is twofold: first, to provide a general survey of superfluidity for those students who do not intend to specialize in low-temperature physics; and second, to provide some sort of introduction to the subject for a smaller number of beginning students who wish to take a degree in the experimental side of this specialty.

Accordingly, the treatment throughout is elementary in nature and involves, mathematically, little more than an undergraduate knowledge of calculus. In other words, the main emphasis is upon the physical principles involved, rather than the theoretical subtleties which would have to be included in an exhaustive treatment.

Over the ten-year period the advance of the subject has been very rapid. This required reviewing the content of the course at frequent intervals, adding new material, and eliminating some of the older material when advances in research showed this to be desirable. In the present text I have tried to keep a fair balance between the old and the new, and it is in this selection that the author's personal preferences and opinions intrude most heavily.

I have, of course, profited by reading prior books and review articles. A short bibliography, which is not exhaustive, is included in an appendix, together with an attempt to evaluate these books for the benefit of the nonspecialist.

C. T. Lane

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Production and Handling of Liquefied Gases

THERMODYNAMICS OF FREE EXPANSION

Liquid helium, liquid air (or nitrogen), and, on occasion, liquid hydrogen are the indispensable tools of the low-temperature physicist. Their production involves nineteenth-century thermodynamics in a form, however, which nowadays is rather more familiar to the chemical engineer than to the average student of physics.

In principle, a gas must be cooled in order to liquefy it, and either or both of two processes are universally employed. The first of these, associated with the names of Joule and Thomson (Lord Kelvin), depends on the empirical fact that if any gas, at suitable temperature and under pressure, is permitted to expand in volume, a cooling of the gas results. This process is, thermodynamically, highly irreversible. The second process allows the compressed gas to expand and do external work in, for instance, an engine or turbine. This process is closely reversible.

Figure 1 is an Andrews diagram (familiar to all students of elementary physics) for carbon dioxide and is typical of all gases. At temperatures well removed from the critical ($\sim31°C$) the gas obeys Boyle's law tolerably well. But below the critical temperature (e.g., $t_3 = 10°C$ in Fig. 1) the gas splits into a liquid and vapor phase wherein the pressure is independent of the volume (region ab, Fig. 1) and

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depends on the temperature alone. The important point is that the CO_2 must be cooled below 31°C in order for any liquid to form at all, no matter what the pressure may be. Hence refrigeration is indispensable to any gas-liquefaction process.
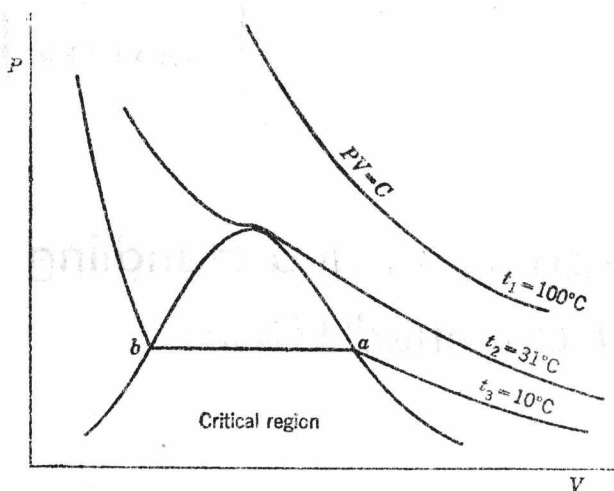
FIG. 1. Andrews diagram for carbon dioxide. The pressure P is plotted against the volume V for three temperatures.

This simple diagram would be of slight value to the designer of a liquefier, since the actual cooling process, the Joule-Thomson effect, does not appear on it. We recall that the Joule-Thomson coefficient is defined as

$$\mu = \left(\frac{\partial T}{\partial p}\right)_h \tag{1}$$

where T and p are the Kelvin temperature and pressure, respectively, and h is the enthalpy. Now it can be shown, quite generally, that

$$\mu = \frac{1}{C_p}\left[T\left(\frac{\partial V}{\partial T}\right)_p - V \right] \tag{2}$$

where V is the volume and C_p the specific heat at constant pressure. For an ideal gas whose "equation of state" is

$$PV = RT$$

expression (2) vanishes, but μ may be either positive or negative for any real gas. If an equation of state for any real gas existed, expres-

sion (2) would be of great utility to our designer, but no usable equation exists for any gas. Hence we must fall back on empirical determination of $\mu = f(p, V, T)$.

Before we consider this, it is necessary to prove a general proposition concerning the enthalpy function. To do this, we make use of a trick, common in thermodynamics, illustrated in Fig. 2. Consider unit mass of any gas initially at pressure p_1, volume V_1, and thermal energy (i.e., energy due to the rms velocity of the atoms) U_1. Let this volume be forced at constant pressure p_1 through a fine opening which offers a resistance to the gas flow so that its pressure falls to p_2, its volume
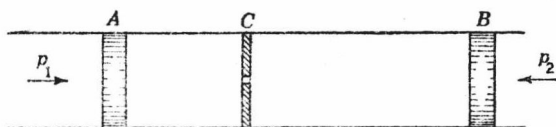
FIG. 2. Arrangement for a free-expansion process.

increases to V_2, and its thermal energy becomes U_2. We could, in principle, accomplish this by using a pair of frictionless pistons A and B (Fig. 2) with pressures p_1 and p_2 acting as shown. As the volume AC (V_1) is reduced to zero, piston B sweeps out the volume $V_2 = BC$. Applying conservation of energy, we have

$$\text{Work done in system} = p_1V_1 - p_2V_2$$
$$\text{Change in energy} = U_2 - U_1$$

Hence
$$p_1V_1 - p_2V_2 = U_2 - U_1$$

that is,
$$U_1 + p_1V_1 = U_2 + p_2V_2$$

or
$$h_1 = h_2 \tag{3}$$

In words, the enthalpy remains constant in this process of "free expansion," which is sometimes called a throttling process by engineers. We note that the process must be slow enough so that no kinetic energy is acquired by the expanded gas.

We have described what amounts to a Joule-Thomson expansion, and this suggests that an enthalpy versus temperature diagram would be more useful than Fig. 1. By way of an introduction, suppose we calculate the enthalpy of an ideal gas:

$$h = U + pV = U + RT = C_vT + RT = C_pT \tag{4}$$

where C_v is the specific heat at constant volume. Since C_p is independent of temperature for such a gas, this plots as a straight line on the diagram. Now it is true that any of the "permanent" gases at vanish-

ingly small pressure (say a few millimeters of mercury) approximate an ideal gas very well. But for real gases at elevated pressures the enthalpy turns out to be a function of pressure as well as temperature. Figure 3 shows the essentials of such a diagram for nitrogen, wherein the dotted curve marks the boundary of the liquid-vapor region; a few temperatures are shown for reference, as well as three isobars, i.e.,
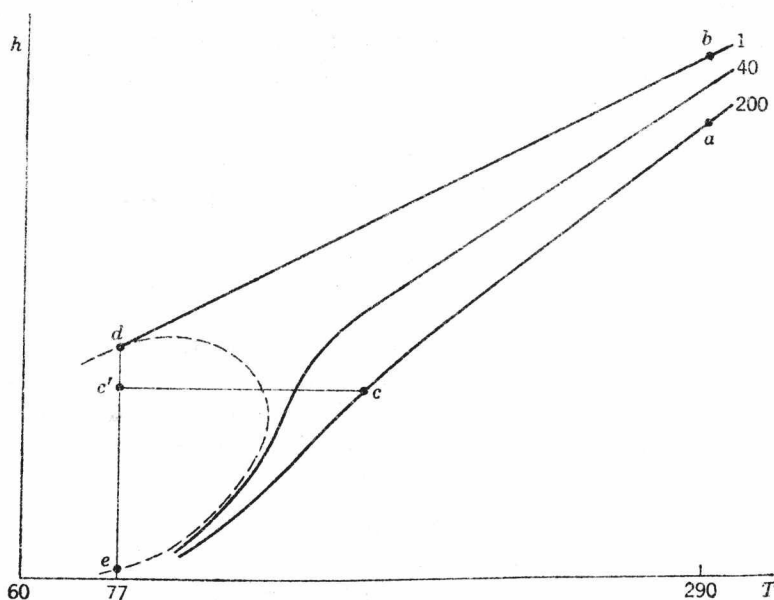
FIG. 3. Schematic diagram of enthalpy h versus temperature T for nitrogen.

1, 40, and 200 atm, respectively. Clearly, a Joule-Thomson expansion would be represented on the diagram by a horizontal line ($dh = 0$) connecting any two pressure curves. Also,

$$dh = dU + p\,dV + V\,dp$$
$$= dq + V\,dp$$

Hence
$$\left(\frac{\partial h}{\partial T}\right)_p = \left(\frac{\partial q}{\partial T}\right)_p = C_p \tag{5}$$

Thus the slopes of the lines give the specific heat at constant pressure. We wish to emphasize again, however, that these diagrams are strictly empirical, being evolved from actual measurements of $p = f(V,T)$, specific heats, latent heats, etc.

In order to illustrate the utility of these data, consider the simplest possible device which could be used to liquefy, say, air (Fig. 4). This consists of a "heat exchanger," a needle valve, and a container to receive the condensed air; the whole is thermally insulated from contact with the surroundings. We have chosen the very simplest heat exchanger extant, namely, a pipe within a pipe. No means for removing the liquid is shown, but this is irrelevant to the present discussion.

High-pressure air ($\sim$200 atm) at room temperature ($\sim$290°K) is admitted to the inner pipe at a. Upon reaching the valve J, its pressure is reduced to about 1 atm and it enters vessel W, whence it returns through the space between the two pipes and is exhausted to the atmosphere at b. If left to itself for some minutes, liquid air will begin to accumulate in W.

The heart of the process is the Joule-Thomson expansion at the valve plus the action of the heat exchanger. As the enthalpy diagram shows, a Joule-Thomson expansion between any two pressures at any temperature leads to a reduction in temperature of the gas, i.e., a cooling. Thus the air leaving the valve is always colder than that entering it. In its passage back through the exchanger, since the low- and high-pressure streams are in thermal though not in physical contact, heat is continually removed from the high-pressure stream and hence its temperature falls continuously. After a few minutes, the temperature at point c reaches a low steady value. Along the heat exchanger

FIG. 4. Diagram of a simple gas liquefier.

(typically some 20 ft) the difference in temperature between the two streams, at any point measured from a, varies approximately exponentially along the length. Thus $(\Delta T)_{ab} \cong 1$°K or less, whereas $(\Delta T)_{cd} \cong 30$°K or more.

When this steady state has been reached, we find that liquid accumulates at a steady rate in W; in other words if, say, unit mass per second enters a, a fraction ε remains as liquid, and accordingly $1 - \varepsilon$ units of mass per second are exhausted at b. The pressure, temperature, and
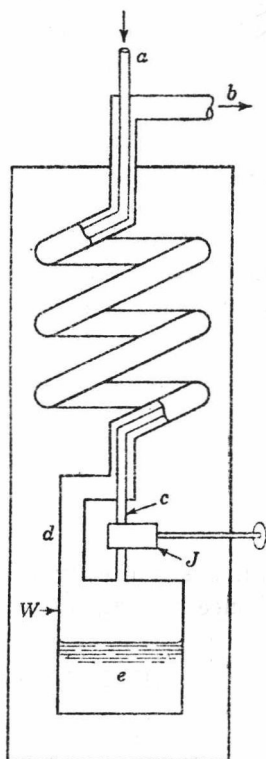
enthalpy of the gas at a, b, d, e are labeled with the same letters on the diagram in Fig. 4. Point c remains to be found.

Now the heat energy (enthalpy $\times$ mass) entering the device per second is h_a and leaving it is $(1 - \varepsilon)h_b$. Also h_d represents the enthalpy of the saturated vapor in equilibrium with liquid nitrogen under a pressure of 1 atm (temperature approximately 77°K), while h_e is the enthalpy of the liquid. This is less since heat energy must be removed from the vapor to condense it (latent heat). Thus by conservation of energy,

$$h_a - (1 - \varepsilon)h_b = \varepsilon h_e$$

or
$$\varepsilon = \frac{h_b - h_a}{h_b - h_e} \tag{6}$$

This is the "yield" of the device, i.e., the fraction of liquid produced per unit mass of processed gas; it is clearly known once the input and output pressures and temperatures are decided upon.

Now
$$\varepsilon h_e + (1 - \varepsilon)h_d = h_c$$

since the enthalpy of unit mass of gas at point c is, as we know, unchanged by the expansion in the valve. Rearranging, one obtains

$$\varepsilon = \frac{h_d - h_c}{h_d - h_e} \tag{7}$$

Since ε is already known, this determines the enthalpy of point c and hence its temperature.

YIELD OF SIMPLE LIQUEFIER

For an input pressure of about 200 atm and room temperature the above expression gives a yield $\varepsilon \cong 0.04$, and this is close to the experimentally determined value. Inspection of expression (6) plus Fig. 3 shows that by admitting the gas to the liquefier at a temperature below room temperature, the yield is enhanced, since this will increase the numerator and decrease the denominator. In actual practice, if the input air at 200 atm is precooled by a bath of dry ice and acetone (temperature about 200°K), the yield is increased approximately fourfold.

The type of liquefier we have been discussing would not, of itself, liquefy either hydrogen or helium. This is because in both gases the Joule-Thomson effect is negative (i.e., a reduction in pressure leads to an increase in temperature) unless we are well below room temperature to start with. Thus it is necessary to precool the hydrogen with a

bath of liquid nitrogen before admitting it to the present liquefier. For helium we should require a liquid-hydrogen precool. Having decided upon the precool temperature, we consider next the question of optimum input pressure. In this respect we wish [cf. Eq.
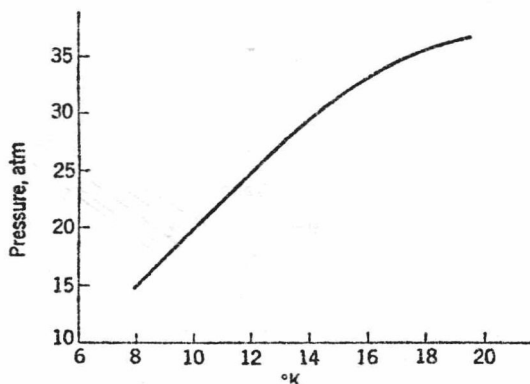

FIG. 5. The function $\mu(p,T) = 0$ for helium.

(6)] to make h_a a minimum to render ε a maximum, since h_b and h_e are not really within the operator's control, i.e., ε_{max} requires

$$\left(\frac{\partial h_a}{\partial p}\right)_T = 0$$

Now $h = f(p,T)$

hence $dh_a = \left(\frac{\partial h_a}{\partial p}\right)_T dp + \left(\frac{\partial h_a}{\partial T}\right)_p dT$

which leads to

$$\left(\frac{\partial T}{\partial p}\right)_h = -\frac{(\partial h_a/\partial p)_T}{(\partial h_a/\partial T)_p}$$

Recalling that $C_p = \left(\frac{\partial h_a}{\partial T}\right)_p$

$$\mu = \left(\frac{\partial T}{\partial p}\right)_h$$

we get $\left(\frac{\partial h_a}{\partial p}\right)_T = -\mu_a C_p$ (8)

Thus for ε_{max}, $\mu_a = 0$, since C_p can never vanish. Now μ is clearly a function of p and T, and it is an experimental fact that a series of p's and T's can be found for which μ vanishes. A plot of these pairs of p and T will therefore produce a different curve for different gases. Figure 5 is such a plot for helium. This curve is called an "inversion

curve" for the Joule-Thomson effect. Off the curve, on either side, a throttling process will produce either a heating or a cooling. It is most important to understand clearly that the condition $\mu = 0$ for maximum yield refers to the temperature condition at the input to the heat exchanger. The Joule-Thomson valve, where the desired
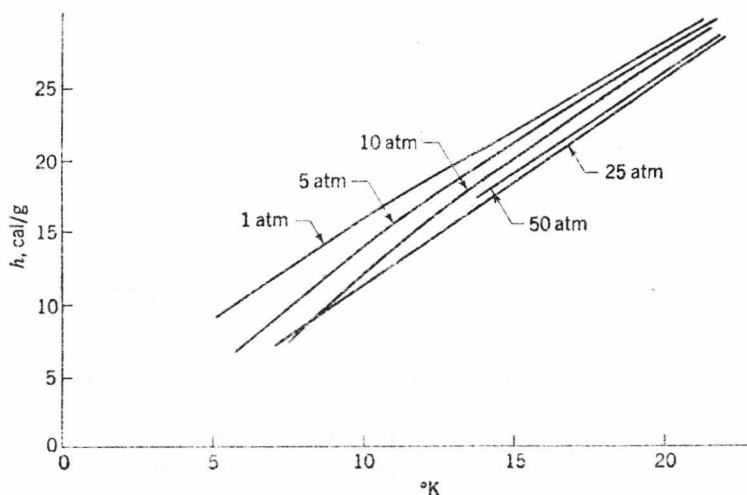

FIG. 6. A part of the enthalpy-temperature diagram for helium.

cooling takes place, is always at a lower temperature, and the cooling effect at this valve is over a wide pressure range. In other words, the cooling is due to the "integral Joule-Thomson effect," i.e.,

$$\Delta T = \int_{p_1}^{p_2} \mu(p,T)\, dp \tag{9}$$

and is represented by the horizontal line cc' in Fig. 3. The above, of course, is borne out in practice.

A rather more illuminating demonstration of the above is provided by Fig. 6, which shows a portion of the enthalpy-temperature curve for helium. Recalling expression (6) for the yield, we observe that if the input temperature to the heat exchanger were, say, 15°K (which is about that used in practice), then the yield would be greater for an input pressure of 25 atm than would be the case if we used 50 atm. Actually (Fig. 5) at this temperature the maximum yield would be at about 32 atm.

REFRIGERATION WITH EXTERNAL WORK

In the system we have been discussing, all the refrigeration was produced by the Joule-Thomson effect. There is a second method which, in principle, is quite different and which has also been successfully employed to liquefy helium and other gases. To study this, we need still another diagram, also empirically devised, wherein entropy is plotted against temperature. To introduce the diagram, consider once again the case of an ideal gas. For a reversible process the entropy S is defined via the relation

$$dS = \frac{dq}{T} = \frac{C_p \, dT}{T}$$

if the process is carried out at constant pressure. Thus, since C_p is independent of temperature,

$$S = C_p \ln T + \text{const} \tag{10}$$

Hence on the T-S diagram an isobar for an ideal gas would plot as an exponential. It is a fact that, for low enough pressures, the isobars for real gases are indeed of this form. Figure 7 shows the plot for a typical real gas, where it will be seen that an expansion at constant entropy (1 to 3) produces a much larger drop in temperature than the corresponding one at constant enthalpy (1 to 2). The best possibility for achieving the first process is to allow the gas to expand against a retarding force and thus do external work as happens, for instance, in a steam engine or a turbine. The process must be adiabatic and as nearly reversible as possible. For cooling purposes the cycle is very similar to that used in a reciprocating steam engine. A certain mass of gas is admitted at constant pressure p_1, and the piston advances a distance S_0. The supply of gas is then cut off and the gas present in the cylinder allowed to expand to a lower pressure p_2; the piston advances a further distance $(S - S_0)$, where S is the "stroke" of the engine. It is this second process which removes energy from the gas and hence cools it. On the return stroke the piston pushes (without compression) the cold gas from the cylinder into the heat-exchanger system, and the cycle repeats.

We recall that a throttle expansion of an ideal gas produces no cooling; this is not the case for an engine. Using the ideal-gas laws, we

may readily show[1] that the amount of heat extracted by a single adiabatic expansion is proportional to

$$S_0 \left[1 - \left(\frac{S_0}{S} \right)^{\gamma-1} \right] \tag{11}$$

where γ is the ratio of the specific heats and S_0 and S are defined above. Actually, the use of an engine for gas liquefaction was introduced, near the turn of the century, by the French engineer G. Claude, who used it in liquid-air production. The principal technical difficulty
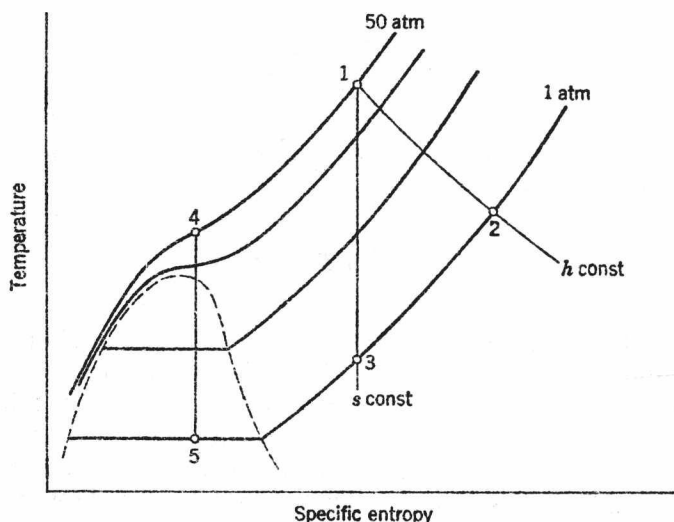

FIG. 7. Schematic of a temperature-entropy diagram for a gas such as helium.

concerns lubrication at these low temperatures—ordinary lubricants freeze solid. At liquid-air temperatures very light oils (such as gasoline) retain some lubricating properties, but at hydrogen or helium temperatures no substance known possesses any lubricating properties at all. This undoubtedly delayed the application of engines to the problem of liquid helium for many years; and it was not until 1934, more than a quarter of a century after the first liquefaction of helium by Onnes using the Joule-Thomson effect, that the first successful piston-engine helium liquefier was devised by the Russian physicist Kapitza.[2]

[1] C. T. Lane, *Rev. Sci. Instr.*, **12**:326 (1941).
[2] P. L. Kapitza, *Proc. Roy. Soc. (London)*, **A147**:189 (1934).

The lubrication dilemma was evaded in a most ingenious way. The engine was arranged so that the travel of the piston was vertical, and the piston was "loosely" fitted in the cylinder. Actually, this gap was of the order of 10^{-3} in. In addition, the piston had a series of concentric grooves cut in it, each a few thousandths of an inch deep and wide. Upon admitting high-pressure gas to this engine, some escaped in the gap between piston and cylinder, but since the motion of the piston was rapid, this loss amounted, in practice, to only a few per cent and did not materially affect the engine's efficiency. And it was this leakage gas which created, by flowing around the grooves, a radial pressure on the piston which had the effect of requiring the axes of the piston and cylinder to be coincident as the condition for equilibrium.
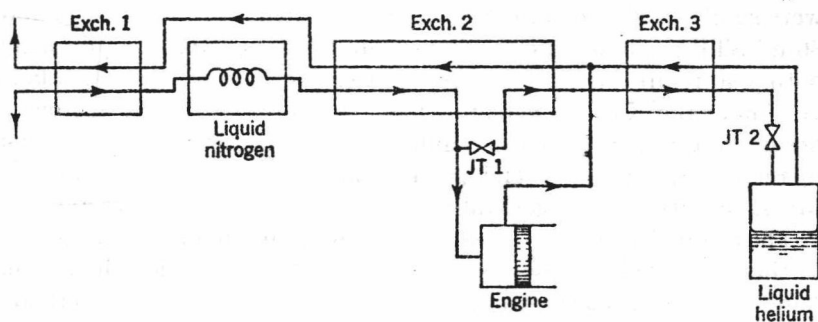

FIG. 8. Flow sheet for the Kapitza liquefier.

Thus, in a sense, the helium gas served as its own lubricant! Inspection of Fig. 7 shows that by starting the expansion at a low enough temperature (e.g., point 4), which might be produced by a heat exchanger ahead of the engine, we could, with a single expansion, proceed into the saturated region (point 5) and thus produce liquid directly in the engine, from which it could be drained.

In practice this is found to decrease sharply the efficiency of the engine, and hence a compromise is effected.[1] The engine is used strictly to refrigerate the gas, and final liquefaction is accomplished by Joule-Thomson expansion of part of the process gas.

Chemical engineers make use of "flow diagrams," which are analogous to the block diagrams used in electronics. Figure 8 is such a

[1] In Fig. 7 we have shown ideal conditions, i.e., expansion at constant entropy. In practice a certain amount of irreversibility is inevitable, and hence the entropy increases somewhat during the expansion. Nevertheless, modern helium engines have efficiencies of 70 to 80 per cent of an ideal reversible engine working between the same temperature limits.