

CRYOGENICS

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1 INTRODUCTION

The subject of this Accelerator School is *Superconductivity in Particle Accelerators*. Superconductors are characterised by a high degree of order in their electronic system: it is due to this high degree of order that superconducting electrons can travel as a perfectly ordered assembly through the crystal lattice without transferring energy to it. Using the terminology of thermodynamics, we say that the assembly of superconducting electrons is in a state of zero entropy.

Cryogenics is the art of creating states of low, even zero entropy. Cryoplants are *entropy pumps* that extract entropy from the system to be cooled and discharge it to an environment at higher (usually ambient) temperature, just as vacuum pumps extract gas from the system to be evacuated and discharge it to an environment at higher (usually ambient) pressure. Both cryoplants and vacuum pumps require an external supply of energy.

Cryoplant processes are closely related to heat engine processes; a heat engine can be considered as an *entropy mill*, in which entropy flows from a heat source to a heat sink (which is usually at ambient temperature). Such a process, if carefully designed, can provide external mechanical or electrical energy ('work').

Both cryoplants and heat engines are governed by the Second Law of thermodynamics, which states that the entropy output is always greater than (or — in the never reached ideal, 'reversible' case — equal to) the entropy input:

$$S_{\text{out}} \geq S_{\text{in}} ,$$

i.e. entropy always increases. There is no such thing as an entropy sink where entropy disappears without reappearing somewhere else. This is generally true, and neither a cryoplant as a whole nor any of its components is an exception.

The trick for cryoplants is to design a process that reduces *local* entropy, while allowing the *overall* entropy to increase, which is all the Second Law requires. How this package deal can be arranged will be shown in the following.

People used to purely mechanical or electrical systems tend to avoid talking about entropy. Indeed, many aspects of cryogenics can be described without reference to it. But the loss in deeper understanding is hardly justified by the momentary convenience of not having to learn how to use a professional tool, which is after all quite easily handled.

I believe there are two main reasons for the reluctance of people to deal with entropy:

- *People are not used to the terminology.* When arguing about energy, mass or temperature, we think we know what we are talking about. Only when challenged to *explain* what *is* energy, mass or temperature, do we realise how superficial our true understanding is of these (and many other) currently used physical concepts. We use them because we are used to them, not because we understand them. I am inclined to think that the roots of the entropy concept are simpler and easier to grasp than those of energy, mass and temperature, and I will try to illustrate this at the end of my talk.
- Different from energy and mass, *entropy is not a conserved quantity.* Any real thermodynamic process produces entropy. People facing the question of where the entropy comes from look in vain for a mysterious external source. In fact, entropy comes from the

lack of unlimited funds and time, from sloppy engineering, and from unreasonable operation. The task of the cryogenic engineer is to keep control of entropy proliferation.

2 UN PEU D'HISTOIRE (FIGURE 1)

Modern thermodynamics begins with a booklet of some 60 pages, entitled *Réflexions sur la puissance motrice du feu*, by Sadi Carnot, published in 1824. Carnot, born in 1796, was a young French officer and son of a hero of the French Revolution who was convinced that France's defeat in 1814/1815 was due not to military, but to industrial inferiority — particularly with respect to England. He considered that he could best serve his country by working on the emerging technology of steam engines. Carnot tried to treat heat engines as analogous with water mills. In a water mill, work is produced by a flow of water passing from a high to a low level; in a heat engine a flow of heat passes from a high to a low *temperature level*. The work produced by the water mill is proportional to the quantity of water and to the level difference. Carnot aimed at showing that in a heat engine the work produced is proportional to the quantity of heat and the temperature difference. Analysing a gas process, and using ideal gas relations (Boyle's law discovered 1662, Gay-Lussac's law discovered 1802, and Poisson's law, brand new, discovered 1822), he found, however, that the factor of proportionality itself depends on temperature. In modern terminology, we would write

$$\text{Work Output } W = \text{Heat Input } Q_{\text{in}} * f(T_{\text{in}}) * (T_{\text{in}} - T_{\text{out}}) ,$$

with

$$f(T_{\text{in}}) \leq 1/T_{\text{in}} ,$$

the equal sign referring to a reversible process. The factor $(T_{\text{in}} - T_{\text{out}})/T_{\text{in}}$ is called Carnot efficiency.

Carnot himself did not identify $f(T_{\text{in}})$ ¹. In fact, his fundamental assumption — the analogy between heat (*'le calorique'*) being the driving fluid of the heat engine as water is the driving fluid of the water mill — was not quite correct; whilst water input and output are equal, energy conservation requires a difference between heat input and output, the two being related to the work output W of the process by

$$W = Q_{\text{in}} - Q_{\text{out}} \quad (1)$$

However, in 1824 the law of conservation of energy was yet to be discovered; it took another 20 years until the *First Law of thermodynamics* was established² on the basis of systematic experiments by James Prescott Joule and William Thomson (who later became Lord Kelvin³). Little is known about Carnot's later work. He died in 1832, aged 36, from cholera and, as was the case in epidemics, was buried with all his papers and belongings. From

¹ He writes: 'Nous sommes hors d'état de déterminer rigoureusement, avec les seules données expérimentales que nous possédons, la loi suivant laquelle varie la puissance motrice de la chaleur dans les différents degrés de l'échelle thermométrique...'

² The first publication (1842) of convincing arguments and a formulation of the general principle of energy conservation, with heat included as a manifestation of energy, are due to Robert (von) Mayer, a medical doctor with a strong interest for general science who lived in a small town in Germany. This outsider's publication was, however, largely ignored by the contemporary scientific community.

³ Joule (born 1818) and Thomson (born 1824) were not only brilliant scientists, but also strongly engaged in practical and technical work. Joule, the son of a wealthy brewer in Manchester, profited greatly in his experimental work from the availability of the excellent brewery workshop. Thomson, who did most of his scientific work at the University of Glasgow, made his fortune at a young age with an invention related to transatlantic telegraphy, for which he was knighted by Queen Victoria in 1892.

remaining fragments, it appears that he worked on experiments which would have demonstrated the equivalence of heat and work and that he had quite clear ideas about the impossibility of what was later to be called a *perpetuum mobile of the second kind*.



Sadi Carnot



Robert Mayer



James Prescott Joule



William Thomson
→ Lord Kelvin

$$W_{\text{out}} = Q_{\text{in}} \cdot f(T) \Delta T. (1824)$$

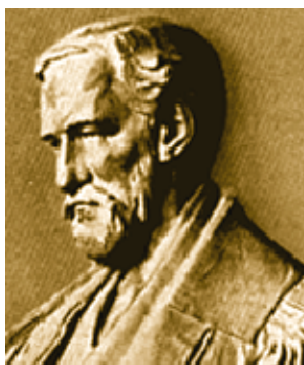
Equivalence of mechanical and thermal energy. Energy conservation. (1840s)



Rudolf Clausius

+W. Thomson/Lord Kelvin

$$\Delta S = Q_{\text{rev}}/T. (1850s)$$



J. Willard Gibbs

Statistics. Gibb's ensembles. $\Phi = \exp(S/k)$.
(End of 19th century)



Ludwig Boltzmann



Heike Kamerlingh Onnes

T_b (He) = 4.2 K. (1908)
 T_c (Hg) = 4.2 K. (1911)

Fig. 1 The pioneers of thermodynamics

The *Second Law of thermodynamics* (formulated in 1850 by Rudolf Clausius⁴) can be illustrated by the statement that, for any continuous process driven by a flow of energy and involving heat input and output,

$$\frac{Q_{\text{out}}}{T_{\text{out}}} \geq \frac{Q_{\text{in}}}{T_{\text{in}}}. \quad (2)$$

The equal sign stands for a *reversible process*, reversible meaning that input and output are interchangeable. This *reversible* process indeed matches Carnot's picture, the mill now being driven not by a flow of heat, but by a flow of a quantity Q/T , which Clausius called *entropy* S

⁴ Clausius (born 1822) is the systematic thinker sometimes referred to as the person who made thermodynamics a science. In 1850, when he published his paper with formulations of both the First and the Second Law, he was named professor of physics at the Artillery and Engineering School at Berlin. Later, he became a professor at Zürich, Würzburg and Bonn.

and which in the *reversible* case remains unchanged while passing through the engine. In the real, *irreversible* case, however, entropy increases — S_{out} is always greater than S_{in} . The process is said to have internal sources of entropy. The water mill analogy becomes somewhat artificial, but the entropy concept remains useful, the point of interest now being the nature of the entropy sources.

Clausius and Thomson proved that entropy is a *function of state*. This means that any substance in a given thermodynamic state (defined, say, by temperature and pressure) has a *measurable* content of entropy. Entropy can thus be *tabulated*, and entropy change associated with a change of thermodynamic state can be read from such tables as a difference between initial and final state. Table 1 is an example, showing data for helium.

Atomistic interpretations of the laws of thermodynamics were worked out in the last quarter of the 19th century by J. Willard Gibbs, Ludwig Boltzmann and others⁵, who developed appropriate statistical methods. The atomistic picture gives a plausible interpretation of the fact that entropy is a function of state and that it inevitably increases in all real processes. Many scientists and philosophers, however, were suspicious about any speculation concerning the atomic nature of matter, and it took quite some time until the new theories were generally accepted.

Cryogenic techniques leading successively to the liquefaction of oxygen, nitrogen and hydrogen were developed in the late 19th century. Helium was first liquefied in 1908 by Heike Kamerlingh Onnes. Superconductivity was discovered in 1911 by Kamerlingh Onnes and his assistant Gilles Holst. The first signs of superfluidity were observed immediately, but the main phenomena were discovered only in the 1930s; the term ‘superfluid’ was coined by Pjotr Kapitza in 1938.

3 ENTROPY MILLS AND ENTROPY PUMPS

The picture of thermal engines developed by the generation of Joule, Thomson and Clausius is illustrated in Fig. 2. This picture constitutes the basis for the evaluation of the performance of cryoplants (and heat engines in general), and we will refer to it in the following.

The upper row of Fig. 2 refers to *heat engines*, the lower row to *heat pumps*. The left column refers to *ideal cycles*, the right column to *real cycles* with internal entropy production.

For the purpose of the drawing (arrow widths), we measure temperatures in units of the lower temperature. At the lower temperature level, the temperature is thus ‘1 temperature unit’, and entropy (Q/T) and heat (Q) arrows have the same width. The *upper temperature is assumed to be three times higher than the lower temperature* (‘3 temperature units’). At the upper temperature level, heat arrows are therefore three times larger than entropy arrows. Work arrows (= arrows of non-thermal energy \dot{W} = arrows of energy that does not carry entropy) use, of course, the same scale as heat arrows. In all four diagrams it can be seen that energy is conserved.

⁵ Gibbs was born in 1839 in Connecticut and after five years of study in Europe became professor at Yale in 1871, where he spent the rest of his life far from philosophical quarrels about the significance of modern theories. Boltzmann, born in 1844 in Vienna, was professor at several Austrian and German universities, in particular at Vienna, centre of the positivistic school formed around Ernst Mach, who strongly criticised any attempt to introduce atomistic speculations into science. Boltzmann suffered deeply from the conflict and committed suicide in 1906. Mention must also be made of James Clerk Maxwell, born 1831, most famous for his work on electrodynamics. Maxwell, Gibbs and Boltzmann, although working without direct connection, highly respected each other's work.

Table 1

Helium

enthalpies and entropies for
saturated liquid and vapour ⇒
and for gas

or subcooled liquid or supercritical fluid



saturated...		LIQUID		VAPOUR	
p [bar]	T [K]	h [J/g]	s [J/g K]	h [J/g]	s [J/g K]
1.0	4.208	9.94	3.560	30.74	8.492
1.2	4.407	11.07	3.782	30.61	8.208
1.4	4.584	12.20	3.997	30.28	7.933
1.6	4.744	13.38	4.213	29.72	7.650
1.8	4.891	14.67	4.442	28.87	7.339
2.0	5.026	16.17	4.707	27.48	6.952
2.2	5.151	18.90	5.199	18.90	5.199

T [K]	1 bar		2 bar		5 bar		10 bar		20 bar	
	h [J/g]	s [J/g K]	h [J/g]	s [J/g K]	h [J/g]	s [J/g K]	h [J/g]	s [J/g K]	h [J/g]	s [J/g K]
4	8.95	3.32	9.30	3.22	10.66	3.02	13.21	2.81	18.51	2.56
4.2	9.90	3.55	10.14	3.42	11.35	3.18	13.81	2.95	19.01	2.68
4.4	32.38	8.87	11.07	3.64	12.09	3.35	14.43	3.10	19.54	2.81
4.6	33.92	9.22	12.16	3.88	12.88	3.53	15.09	3.25	20.09	2.93
4.8	35.36	9.52	13.53	4.17	13.73	3.71	15.78	3.39	20.67	3.05
5	36.74	9.80	15.68	4.61	14.66	3.90	16.51	3.54	21.26	3.17
6	43.05	10.96	38.84	9.06	21.42	5.12	20.75	4.31	24.61	3.78
7	48.90	11.86	45.85	10.14	33.93	7.05	26.41	5.18	28.59	4.39
8	54.54	12.61	52.11	10.98	43.78	8.37	33.93	6.18	33.29	5.02
10	65.52	13.84	63.80	12.28	58.47	10.01	50.42	8.02	44.88	6.31
12	76.29	14.82	74.99	13.30	71.09	11.17	65.06	9.36	58.35	7.53
14	86.95	15.64	85.93	14.15	82.92	12.08	78.28	10.38	72.05	8.59
16	97.54	16.35	96.72	14.87	94.34	12.84	90.68	11.21	85.34	9.48
18	108.08	16.97	107.43	15.50	105.52	13.50	102.59	11.91	98.14	10.23
20	118.60	17.52	118.07	16.06	116.53	14.08	114.18	12.52	110.52	10.88
30	170.90	19.64	170.74	18.19	170.29	16.26	169.61	14.77	168.62	13.25
40	223.01	21.14	223.03	19.70	223.09	17.78	223.23	16.32	223.66	14.83
60	327.04	23.25	327.22	21.81	327.75	19.90	328.66	18.46	330.50	17.00
80	430.97	24.75	431.22	23.31	431.96	21.40	433.21	19.96	435.70	18.51
100	534.86	25.91	535.15	24.47	536.00	22.56	537.42	21.12	540.25	19.68
120	638.74	26.85	639.05	25.41	639.96	23.51	641.48	22.07	644.50	20.63
140	742.62	27.65	742.93	26.21	743.88	24.31	745.45	22.87	748.58	21.43
160	846.48	28.35	846.81	26.91	847.77	25.01	849.37	23.57	852.57	22.13
180	950.35	28.96	950.67	27.52	951.65	25.62	953.27	24.18	956.51	22.74
200	1054.20	29.51	1054.50	28.07	1055.50	26.16	1057.10	24.72	1060.40	23.29
220	1158.10	30.00	1158.40	28.56	1159.40	26.66	1161.00	25.22	1164.30	23.78
240	1261.90	30.45	1262.30	29.01	1263.20	27.11	1264.90	25.67	1268.10	24.23
260	1365.80	30.87	1366.10	29.43	1367.10	27.53	1368.70	26.09	1372.00	24.65
280	1469.70	31.25	1470.00	29.81	1471.00	27.91	1472.60	26.47	1475.80	25.03
300	1573.50	31.61	1573.80	30.17	1574.80	28.27	1576.40	26.83	1579.70	25.39
350	1833.20	32.41	1833.50	30.97	1834.40	29.07	1836.00	27.63	1839.20	26.19
400	2092.80	33.11	2093.10	31.67	2094.10	29.76	2095.60	28.32	2098.80	26.89
450	2352.50	33.72	2352.80	32.28	2353.70	30.37	2355.30	28.94	2358.40	27.50
500	2612.10	34.26	2612.40	32.83	2613.30	30.92	2614.90	29.48	2617.90	28.04
550	2871.80	34.76	2872.10	33.32	2873.00	31.42	2874.50	29.98	2877.50	28.54
600	3131.40	35.21	3131.70	33.77	3132.60	31.87	3134.10	30.43	3137.10	28.99

An inlet/outlet temperature ratio of 3 would be respectable for a heat engine (900 K/300 K), but can be considered at best as a borderline case for a cryoplant (300 K/100 K). For a liquid-helium cryoplant this ratio would be $300/4.2 \approx 70$.

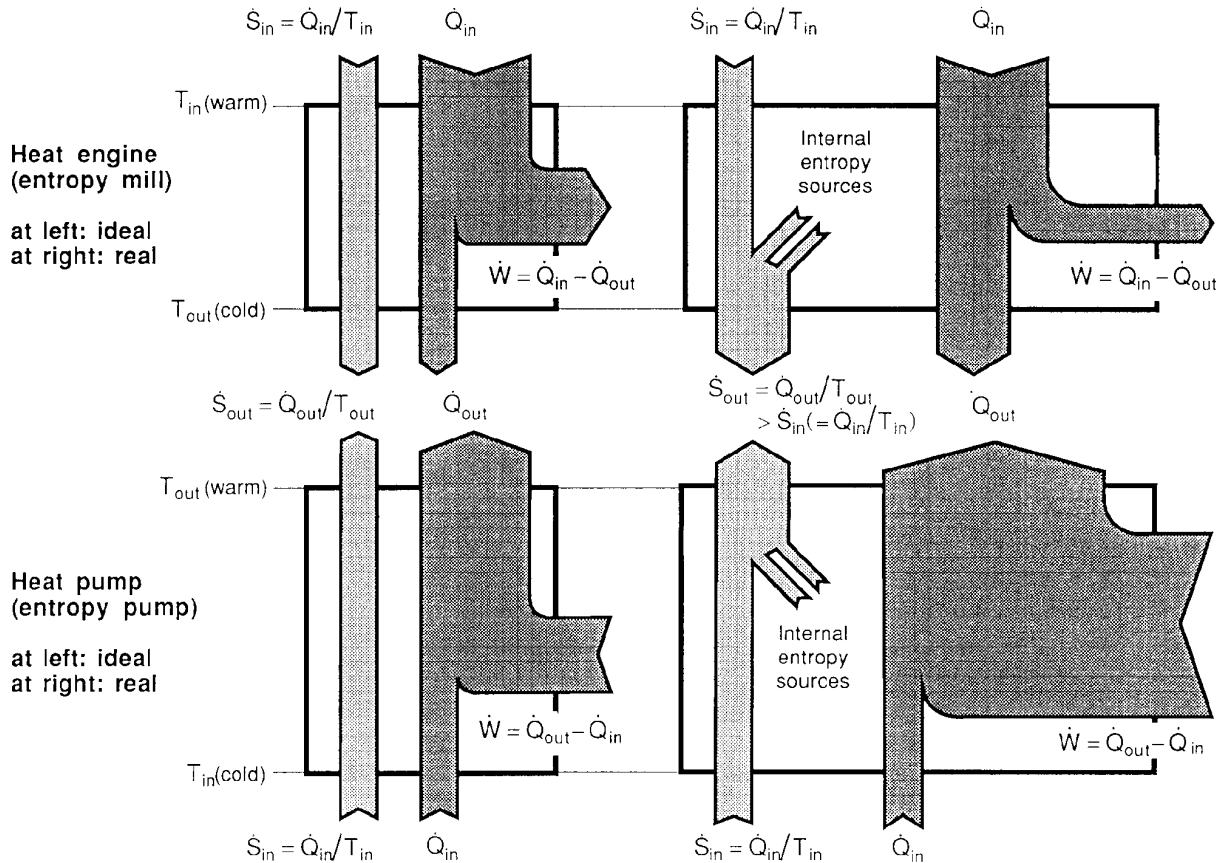


Fig. 2 Entropy flow \dot{S} and heat flow \dot{Q} in heat engines and heat pumps

For the *ideal cycles* at left in Fig. 2, input and output entropies are equal. For the heat engine, heat output is 1 unit, heat input is 3 units, and the difference (2 units) is available as work. For the heat pump, heat input is 1 unit, heat output is 3 units, whilst the difference (2 units) must be made up by work.

For the *real cycles* at right, internal entropy sources add an amount of entropy equal to the input entropy, with the result that the output entropy is twice the input entropy. For the heat engine, the heat output increases from 1 to 2 units; since the heat input is unchanged at 3 units, only 1 unit instead of 2 is available as work. For the heat pump, the heat output increases from 3 to 6 units, and the difference between these and the unchanged heat input of 1 unit (5 units) must be made up by work.

In Fig. 2 it is tacitly assumed that the heat input Q occurs at a well-defined temperature, T_{in} . The procedure can be generalised to heat input in a *range* of temperatures — for example, heat input between 30 K and 75 K when cooling a thermal shield, or heat input between saturated liquid conditions at 4.5 K and 300 K when cooling current leads to a superconducting magnet. In such cases, the entropy input for a given heat input must be taken from tables.

Note that the world record for efficiency of large helium cryoplants is presently held by the LEP2 cryoplants at CERN (which will be discussed in Section 7). In these plants, the incoming entropy is not only doubled, but tripled by internal entropy sources. In other, smaller or older plants (enormous progress has been made in the last ten years), the entropy increase due to

internal entropy sources may be by a factor of 5 to 10 or more. A paper size of about $1.5 \times 1.5 \text{ m}^2$ would be needed in order to show the heat and work arrows to correct scale (with the width of the entropy input arrow unchanged).

Table 2 gives a scheme for evaluating the performance of cryoplants in line with the principles of Fig. 2. The table will be referred to in the discussion of cryoplant cycles. It contains some technical terms about which details will be given in later sections.

Table 2

Scheme to evaluate cryoplant performance according to the principles of Fig. 2.

1	<p>Define the duty loads (heat load \dot{Q}_{in} and entropy load \dot{S}_{in}) of the cryoplant.</p> <p>Examples:</p> <ul style="list-style-type: none"> – A heat load of 1 W/4.5 K constitutes an entropy load of $1/4.5 \text{ W/K} \approx .222 \text{ W/K}$, – a liquefier load of 1 g/s, provided as saturated liquid at 1.4 bar and recovered as gas at 1 bar, 300 K constitutes, according to Table 1 a heat load (Δh) of $1'573.5 - 12.2 = 1571.3 \text{ W/g}$ and an entropy load (Δs) of $31.61 - 3.997 = 27.67 \text{ W/g K}$, – etc. <p>Include parasitic loads. When calculating the entropy load, decide whether you will count the entropy production during heat transfer from the load to the cycle as part of the load or as part of the cycle.</p>
2	<p>Identify internal entropy sources.</p> <p>Entropy sources regularly encountered will be discussed in Sections 5 and 6 (heat transfer from the compressor coolers to the environment in Section 5.1, entropy production associated with compression, expansion, counterflow heat exchange, internal heat and gas leaks and unsteady operation conditions in Sections 6.1 to 6.5).</p>
3	<p>Identify enthalpy extraction H_{exp} by expansion devices (enthalpy drop in piston expanders and turbines).</p> <p>Decide whether the extracted enthalpy will be fed back into the cycle as work or whether it will be dissipated as heat. In virtually any practical cryoplant, it will be dissipated at ambient temperature; if this is the case, treat the resulting entropy, obtained by dividing the extracted enthalpy by the ambient temperature, as an internal entropy source.</p>
4	<p>Adding entropies from the duty loads and from the internal entropy sources gives the output entropy \dot{S}_{out}</p>
5	<p>Dividing the output entropy by the ambient temperature gives the output heat \dot{Q}_{out}.</p>
6	<p>The required power (work) input is $\dot{W} = \dot{Q}_{out} - \dot{Q}_{in}$.</p>

4 PROPERTIES OF THE IDEAL GAS AND REAL GASES. THE TEMPERATURE-ENTROPY DIAGRAM

4.1 Terminology

The quantities of interest for us are pressure p , temperature T , volume V , internal energy U , enthalpy H (about which more will be said in Section 4.2) and entropy S . They are all functions of state, which means that their numerical value can be taken from a table or a

diagram. Many variables exist for which this is not the case, the most important ones in thermodynamics being heat and work. Both are forms of energy, and, knowing the state of something, we can say how much energy it contains, i.e. how much energy was necessary to bring it to its present state from a state of reference (say $T = 0\text{ K}$, $p = 1\text{ bar}$). However, we cannot say how much of it was provided in the form of heat and how much in the form of work.

In the following, we will generally use upper case for absolute values and lower case for specific values per unit mass, i.e. v , u , h and s for specific volume, internal energy, enthalpy and entropy per — for example — gram: $v = V/m$, ..., where m is the mass of the sample.

Exceptions to this are capitals used for C_p and C_v , the specific heats *per mole* [J/mol K] at constant pressure and volume, respectively. Using molar specific heats is justified because they are closely related to the universal gas constant $R \approx 8.31\text{ J/mol K}$, also a molar quantity. Individual specific heats and the individual gas constant of a substance are obtained by dividing the molar values by the molecular mass M [g/mol]: $c_p = C_p/M$ etc. Such quotients will often appear in a technical context.

Hybrid units within the metric system are still frequently used in cryogenics — for example, ‘Joule/g’ for specific energies (the Joule in the numerator is based upon the kg, $1\text{ J} = 1\text{ kg m}^2\text{ s}^{-2}$, rather than upon the gram used in the denominator). Consistency of units must be checked, and conversion factors (usually powers of 10) may be necessary to obtain the result in the desired unit.

4.2 Enthalpy

When describing thermodynamic processes, we have the choice of the variables best adapted to the problem. Two sets are particularly convenient:

T, V, U and S	for illustration of physical context,
T, p, H and S	for quantitative treatment of technical systems.

Internal energy is the true thermal energy of the molecules. It is *constant in a closed system* in thermal equilibrium that does not exchange energy with its environment (for example, because its volume is kept constant and it is thermally insulated), but internal energy *may vary in an open system* connected to external energy sources or sinks. In open systems it is convenient to define functions of energy that are constant under the actual conditions. For our purposes the most important function is enthalpy, introduced for dealing with compressible systems, which, when travelling in an ambience of varying pressure, change volume and therefore exchange energy (work) with their environment. Their internal energy is not constant, but the energy passed to the environment can be treated as potential energy pV of the travelling sample, and, in the absence of other external influences, the sum of the two is again constant. This sum is called

$$\text{Enthalpy } H = U + p * V. \quad (3)$$

In fact, introducing enthalpy (or other functions of energy) is a trick of bookkeeping. It depends on the situation whether I focus on the money in my pocket (when shopping), or on my bank account (when making standing orders), or on the sum of both (when paying taxes).

4.3 Entropy — more

The form in which entropy has been introduced was matched to a particularly simple example — the water mill/pump analogue for a heat engine, in which the parts of heat and work in energy transactions are clearly defined and hidden transformations of work into heat are excluded. Not all situations encountered in practice are so clear. For an unambiguous definition of entropy it is necessary to refer to internal energy rather than to heat (which, as mentioned, is

not a function of state). The following equation is suitable for comparison of entropies when *no changes of volume* are involved:

$$\Delta S = \int_{\text{reference state}}^{\text{actual state}} \frac{dU}{T} \quad \text{integration at constant volume (the formula does not account for entropy change due to volume change).}$$

Textbooks often introduce Q_{rev} as the heat that would have been necessary to reach the state in question by a reversible approach, starting from an agreed reference state. By an irreversible approach, *less* heat would be required and the difference would be made up by work W :

$$Q_{\text{rev}} = Q_{\text{irr}} + W,$$

$$Q_{\text{irr}} < Q_{\text{rev}}.$$

Heat that eventually lead to a measured increase of internal energy was not necessarily introduced as heat, but (in the case of an irreversible process) partly or totally as work. When concluding from heat input on internal energy change we must be sure that no complementary work input occurred.

The complete formulae relating entropy to traditional quantities and offering a basis for measurement (which is essentially a measurement of specific heat) are

$$s(T, v) = s(T_0, v_0) + \int_{T_0}^T \left(\frac{\partial s}{\partial T} \right)_v dT + \int_{p_0}^p \left(\frac{\partial s}{\partial v} \right)_T dp$$

with

$$\left(\frac{\partial s}{\partial T} \right)_v = \frac{m c_v}{T} \quad \left(\frac{\partial s}{\partial v} \right)_T = \left(\frac{\partial p}{\partial T} \right)_v.$$

4.4 The temperature–entropy diagram of the ideal gas

Figure 3 shows the isochors and isobars (lines of constant volume and constant pressure) of an ideal monatomic gas of molecular mass 4 g/mol (‘ideal helium’) in a logarithmic temperature-entropy diagram. The intention of this section is to illustrate the physical content of such a diagram and the quantitative relations underlying its structure.

In a T – s diagram, isotherms (lines of constant temperature) are obviously straight horizontal lines.

An ideal gas is characterised by the fact that its internal energy is proportional to temperature and independent of volume and pressure. For this reason, the isenergs (lines of constant internal energy) are parallels to the isotherms.

The equation of state of the ideal gas,

$$p * v = (R/M) * T, \tag{4}$$

states that $p * v$, the term corresponding to the potential energy of the gas, depends on temperature only, hence isenthalps (lines of constant enthalpy) are horizontal lines as well. A few isenthalps are indicated in the diagram, whilst the isenergs have been omitted to avoid graphic overloading.

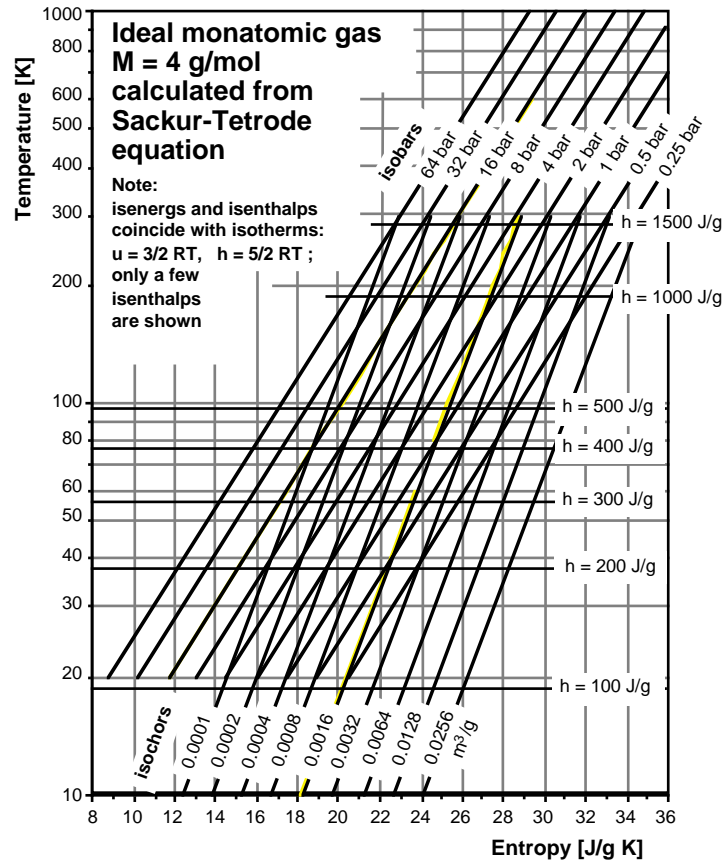


Fig. 3 Temperature-entropy diagram of 'ideal helium'

The universal gas constant in (4),

$$R \approx 8.31 \text{ J/mol K} ,$$

is related to Boltzmann's constant,

$$k \approx 1.38 * 10^{-23} \text{ J/K} ,$$

and Avogadro's number,

$$N_A \approx 6.02 * 10^{23} \text{ mol}^{-1} ,$$

by

$$R = N_A * k .$$

Specific heat at constant volume, $c_v = C_v/M$, is introduced as the proportionality factor between internal energy and temperature and, similarly, specific heat at constant pressure, $c_p = C_p/M$, as the proportionality factor between enthalpy and temperature:

$$u = c_v T = (C_v/M) * T , \quad h = c_p T = (C_p/M) * T ; \quad (5 \text{ a/b})$$

with $h = u + p*v = u + (R/M)*T$ according to (3) and (4) following

$$c_p = c_v + R/M , \quad C_p = C_v + R . \quad (6 \text{ a/b})$$

From atomistic considerations it follows that for ideal *monatomic* gases $C_v/R = 3/2$, from which in turn follows with (6) $C_p = 5/2$ and $C_p/C_v = c_p/c_v = 5/3$ for the monatomic gas.

Injection of a small amount of heat $c_v dT$ (at constant volume) or $c_p dT$ (at constant pressure) into a gas sample should lead, according to Clausius' assumption, to an increase ds of entropy:

$$\begin{aligned} \text{isochoric case: } ds &= \frac{c_v dT}{T} = c_v d \ln T \Rightarrow \left(\frac{\partial s}{\partial \ln T} \right)_v = c_v , \\ \text{isobaric case: } ds &= \frac{c_p dT}{T} = c_p d \ln T \Rightarrow \left(\frac{\partial s}{\partial \ln T} \right)_p = c_p . \end{aligned} \quad (7a/b)$$

From this follows that in a $\log T$ -versus- s diagram, isochors are straight lines with a slope of $1/c_v$ and isobars are straight lines with a slope of $1/c_p$. This is the reason for choosing a logarithmic scale for the ordinate of the temperature–entropy diagram.

Poisson's equation in its three variations [the second and third following from the first one with the ideal-gas equation (4) and the specific-heat relation (6b)] requires that *for states of equal entropy*

$$\left(\frac{p_2}{p_1} \right) = \left(\frac{v_2}{v_1} \right)^{-C_p/C_v} , \quad \left(\frac{T_2}{T_1} \right) = \left(\frac{v_2}{v_1} \right)^{-R/C_v} , \quad \left(\frac{T_2}{T_1} \right) = \left(\frac{p_2}{p_1} \right)^{R/C_p} . \quad (8a/b/c)$$

In differential form (after logarithmic differentiation) we obtain

$$C_v d \ln p + C_p d \ln v = 0, \quad C_v d \ln T + d \ln v = 0, \quad C_p d \ln T - R d \ln p = 0$$

for isentropic states, i.e. for $ds = 0$.

Generalising, i.e. inserting ds for 0 in these equations, we find the following equations, in which Poisson's equation is included:

$$ds = C_v d \ln p + C_p d \ln v, \quad ds = C_v d \ln T + R d \ln v, \quad ds = C_p d \ln T - R d \ln p .$$

By integration we obtain the following three formulae:

$$\begin{aligned} s &= C_v \ln p + C_p \ln v + \text{const} , \\ s &= C_v \ln T + R \ln v + \text{const} , \\ s &= C_p \ln T - R \ln p + \text{const} . \end{aligned} \quad (9a/b/c)$$

The second and the third of these equations represent the isochors and isobars in the T – s diagram. Obviously, exponential progression on volume and pressure (for example, steps 1, 2, 4, 8, ...) leads to equidistant isochors and isobars in our logarithmic representation.

In most cases, entropy differences rather than absolute values are required for practical calculation purposes, therefore the undefined integration constants in (9) are not a very serious shortcoming. Absolute values of entropy can, however be measured and, in certain cases, also calculated; the formula for the ideal gas, used for the calculation of the Fig. 3 diagram, was derived between 1911 and 1913 by O. Sackur and H. Tetrode on the basis of early quantum-statistical considerations.

Note that the quoted physical relations, except those of (7), were essentially known to Carnot.

4.5 The temperature–entropy diagram of real gases. Helium

Real gases show characteristic departures from ideal gas relations. Particularly important are those for isenthalpic changes of state, which occur when a compressible fluid flows, without heat input or output, in a conduit where it may undergo pressure variations.

A temperature-entropy diagram for a real gas (in this case helium) is sketched in Fig. 4. It can be seen that at ambient temperature and moderate pressure the isenthalps are in good approximation, as postulated for the ideal gas, horizontal straight lines, and that the isobars and isochors in this logarithmic representation are sloping straight lines. However, at low temperature or high pressure or both, departures from ideal gas behaviour are seen. Thus, near state A $\{p = 200 \text{ bar}, h = 1000 \text{ J/g}\}$ we notice that the 1000 J/g isenthalp rises from left to right; an isenthalpic expansion from 200 bar to 60 bar would lead to a temperature rise from 177 K to 186 K. Near state B $\{p = 10 \text{ bar}, h = 50 \text{ J/g}\}$, however, we notice that the 50 J/g isenthalp drops from left to right; an isenthalpic expansion from 10 bar to 1 bar would lead to a temperature decrease from 10 K to 7.2 K. Finally, an isenthalpic expansion from state C $\{p = 4 \text{ bar}, h = 16 \text{ J/g}\}$ to $p = 1 \text{ bar}$ would lead to a state below the bell-shaped curve ('saturation curve') that separates the one-phase from the two-phase domain of the fluid.

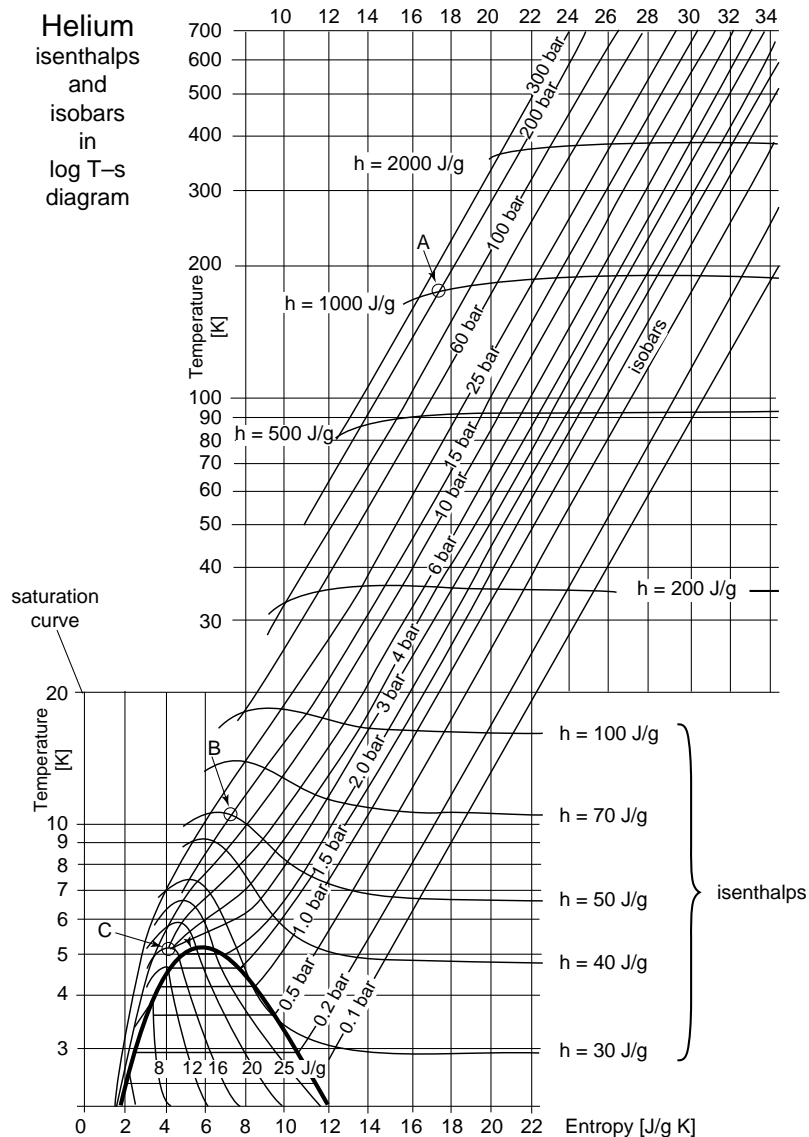


Fig. 4 Temperature-entropy diagram of real helium

Careful measurements of these phenomena have been taken since 1852 by Joule and Thomson, who studied the departure of real gases from ideal gas laws. The temperature increase or decrease after isenthalpic pressure changes is called the *Joule-Thomson effect*. The observed

phenomena were explained in 1876 by Johannes van der Waals⁶ on an atomistic basis. Van der Waals assumed that real molecules, different from ideal-gas particles, interact by small but finite attractive forces and have a small but finite volume. Both facts lead to a volume-dependence of enthalpy in states of high density. Molecular attraction lets internal energy u and enthalpy $h = u + pv$ *decrease* with decreasing distance between molecules (in the T–s diagram: when going from right to left at constant temperature); the energy reduction is independent of temperature and becomes negligible when internal energy is high at high temperature. Finite molecular volume has no effect on internal energy, but influences the term pv in enthalpy. At high temperature, it lets enthalpy *increase* with decreasing intermolecular distances. The behaviour of helium at state A in Fig. 4 is thus explained by the finite molecular volume, the behaviour at state B by the intermolecular attraction, which, in the region below state C, finally leads to liquefaction.

5 CRYOPLANTS

5.1 Evaporative refrigeration at temperatures close to ambient

As a particularly simple example, let us discuss the following cycle, suitable for refrigeration at close-to-ambient temperatures and therefore preferred in domestic appliances.

The cycle uses a refrigerant fluid which at ambient conditions is gaseous but readily liquefies when compressed. A high molar heat of evaporation is desirable. Typical examples are shown in Table 3.

Table 3

Refrigerants for evaporative cooling close to ambient temperature

	Boiling temperature at 1 bar	Saturation pressure at 0 °C	Latent heat of evaporation	Critical temperature	Critical pressure
Refrigerant R40 = CH ₃ Cl	–24 °C	5.0 bar	17.6 kJ/mol	143 °C	67 bar
Refrigerant R12 = C Cl ₂ F ₂	–30 °C	5.8 bar	20.2 kJ/mol	112 °C	41 bar
Refrigerant R22 = C H Cl F ₂	–41 °C	9.4 bar	20.2 kJ/mol	96 °C	49 bar
Propane = C ₃ H ₈	–42 °C	8.3 bar	18.8 kJ/mol	97 °C	42 bar
Isobutane = (CH ₃) ₃ CH	–11 °C	3.0 bar	21.3 kJ/mol	135 °C	37 bar
Ammonia = C H ₃	–33 °C	8.7 bar	23.3 kJ/mol	132 °C	115 bar
Sulphur dioxide = SO ₂	–10 °C	3.2 bar	24.9 kJ/mol	158 °C	79 bar

Figure 5 shows the refrigerator components (a compressor with its aftercooler-heat exchanger, a throttling device and an evaporator equipped with external fins for heat exchange with the load) and the T–s diagram of the cycle.

⁶ Van der Waals, born 1837, Nobel laureate 1910, was a self-taught scientist who for several years worked in public schools as a teacher before being nominated professor of physics at the newly created University of Amsterdam in 1877. He had already attracted great attention with his doctoral thesis, entitled ‘On the continuity of the liquid and gaseous state’, presented in 1873.

Evaporative cycle

(domestic refrigerator)

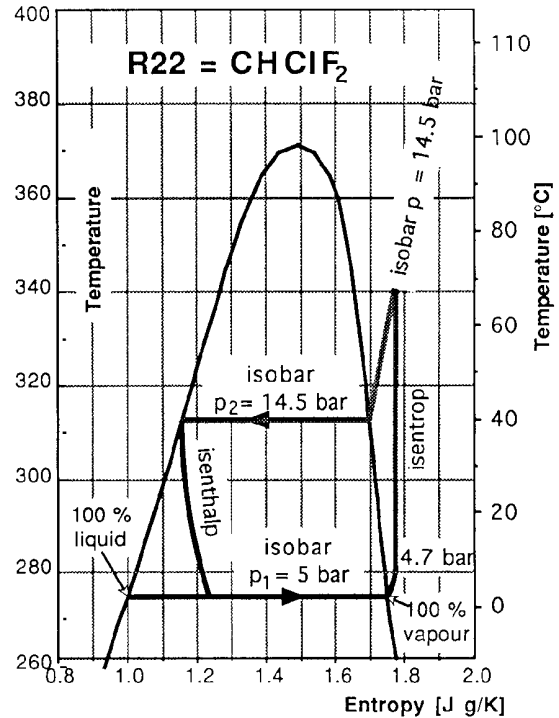
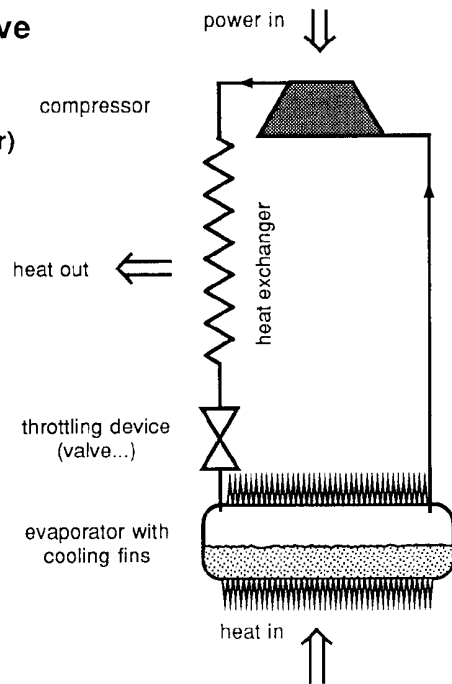


Fig. 5 Flow scheme and temperature-entropy diagram of the evaporative refrigeration cycle (reverse Hirn cycle)

The cycle operates between pressures p_1 (compressor suction) and p_2 (compressor discharge), with p_1 the vapour pressure of the refrigerant at the *desired cooling temperature* T_1 , and p_2 being chosen somewhat higher than the vapour pressure of the refrigerant at *ambient temperature* T_a . It is convenient to use a refrigerant for which p_1 is somewhat (but not much) higher than 1 bar (atmospheric pressure).

Under compressor suction conditions ($p_1, T_1 \approx T_a$) the refrigerant is gaseous. By adiabatic (approximately isentropic)⁷ compression from p_1 to p_2 , the refrigerant temperature is raised from T_1 to T_2 , well above T_a ; the refrigerant is still gaseous. After cooling in the aftercooler from T_2 to T_a at constant pressure (i.e. along the p_2 isobar), associated with heat transfer to the environment, the refrigerant is completely liquefied. The liquid passes through the throttling device (valve, pipe constriction etc.), where its pressure drops from p_2 to p_1 . The throttling, an isenthalpic process, leads to phase separation into a low-enthalpy, low-entropy liquid phase and a high-enthalpy, high-entropy vapour phase in such proportions, x_{liq} and $x_{gas} = 1 - x_{liq}$ that the initial enthalpy h is conserved:

$$x_{liq} h_{liq} + (1-x_{liq}) h_{gas} = h .$$

The available refrigeration capacity for extraction of entropy or heat is

$$\dot{S}_{in} = \dot{m}_c \cdot x_{liq} \cdot (s_{gas} - s_{liq}); \quad \dot{Q}_{in} = \dot{m}_c \cdot x_{liq} \cdot (h_{gas} - h_{liq}) = T_1 \cdot \dot{S}_{in} , \quad (10 \text{ a/b})$$

where \dot{m}_c is the compressor throughput.

⁷ *Adiabatic* means that the system neither gives nor takes *thermal* energy. *Isentropic* means that the entropy does not change during the process considered. Since thermal energy input or output always involves a change of entropy, adiabasy is a necessary condition for isentropy, but not a sufficient one: a change of entropy (always towards increasing entropy) is possible even without thermal energy transfer by internal dissipation of non-thermal energy ('work').

Note that this is the entropy *received* by the cycle; the entropy *delivered* by the load, which must be at a higher temperature than the gas in order to ensure the desired heat transfer, is smaller.

The entropy discharge to the environment is greater than S_{in} . Obviously, some entropy is produced by the isenthalpic throttling process (isenthalpic expansion left–right towards increased entropy). Also, rather than being exactly isentropic (i.e. vertical), the compression line will slope from left to right towards increased entropy. Numeric values of entropy production can be determined from tables on the basis of measured input and output data (for example, pressure and temperature).

A major entropy source (often dominant) is the aftercooler. By heat transfer to the environment, the enthalpy of the process gas (inlet and outlet temperatures T^+ and T^- , enthalpies h^+ and h^- and entropies s^+ and s^- assumed) is reduced by an amount $H = \dot{m}_c \cdot (h^+ - h^-)$. The entropy of the process gas is reduced by $S_{HX} = \dot{m}_c \cdot (s^+ - s^-)$. The entropy of the environment is, however, increased by the much larger amount $S_{env} = H / T_a$, where T_a is the ambient temperature. That $S_{env} > S_{HX}$ follows from the fact that at any longitudinal element of the heat exchanger the heat exchanger temperature T is greater than the ambient temperature T_a . The entropy production is

$$\dot{S}_{env} - \dot{S}_{HX} = \frac{\dot{H}}{T_a} - \dot{m}_c (s^+ - s^-) = \int_{T^-}^{T^+} \frac{\dot{m} c_p dT}{T_a} - \int_{T^-}^{T^+} \frac{\dot{m} c_p dT}{T} = \dot{m} c_p \int_{T^-}^{T^+} \left(\frac{1}{T_a} - \frac{1}{T} \right) dT > 0 .$$

With this information about internal entropy sources, the performance of the plant can be evaluated using Table 2 and Fig. 2.

5.2 Large-scale liquefaction of oxygen, nitrogen, air etc: The Linde Cycle

The cycle introduced by Carl von Linde⁸ in 1895 aimed at large-scale air liquefaction. Air, oxygen and nitrogen belong to what were then called ‘permanent’ gases, because they will not liquefy under any pressure at ambient temperature: their critical temperature⁹ is below ambient. The process described in the preceding section thus cannot be used. Before 1877, when Georges Cailletet in Chatillon-sur-Seine (France) and Raoul Pictet in Geneva succeeded in liquefying minute quantities of oxygen, it was doubtful whether ‘permanent’ gases could be liquefied at all.

Cailletet used a single-shot non-cyclic process. Pictet used a ‘cascade process’, precooling his oxygen cycle by a CO₂ cycle (critical temperature 32 °C), in turn pre-cooled by an SO₂ cycle (critical temperature 158 °C). By pumping on the CO₂ cycle, he reached a temperature of about –140 °C ≈ 130 K, sufficiently below the critical temperature of oxygen, 155 K, to allow a small quantity, compressed to 320 bar, to be liquefied. Cascade processes continued to be used for a long time afterwards. Historically, they were used for the first liquefaction of hydrogen by James Dewar in 1898 and of helium by Heike Kamerlingh Onnes in 1908. Kamerlingh Onnes' apparatus is shown in Fig. 9 as an example of a cryoplant made before the age of stainless steel and aluminium. Cascade cycles are, however, no longer of practical interest in large modern laboratories.

⁸ Linde belonged to a new generation of engineers who systematically used the new thermodynamics for optimised plant design on the basis of theoretical considerations. The economic production of oxygen from air by cryogenic separation (1901), an achievement of great importance for steel manufacture, had been an early target of Linde's systematically pursued work.

⁹ Critical temperature = temperature of the highest point of the saturation curve in the T–s diagram.

Linde ensured the precooling of his final expansion stage by inserting a counterflow heat exchanger (see Fig. 6) between the compressor and the expansion device. He made use of the fact that the *inversion temperature*¹⁰ for oxygen, nitrogen and air is above ambient temperature, leading to a Joule-Thomson effect that, even at ambient temperature, ensures an appreciable temperature decrease when high-pressure (200–300 bar) gas is expanded. In the counterflow heat exchanger, the low-pressure gas, cooled after expansion in the ‘Joule-Thomson valve’ and returning to the compressor suction, pre-cools the high-pressure gas prior to expansion. Because of the gradually decreasing temperature upstream of the Joule-Thomson valve, the cooling effect is enhanced until eventually the expansion leads to liquefaction.

Linde cycle: Carl Von Linde 1895. First industrial liquefaction of air

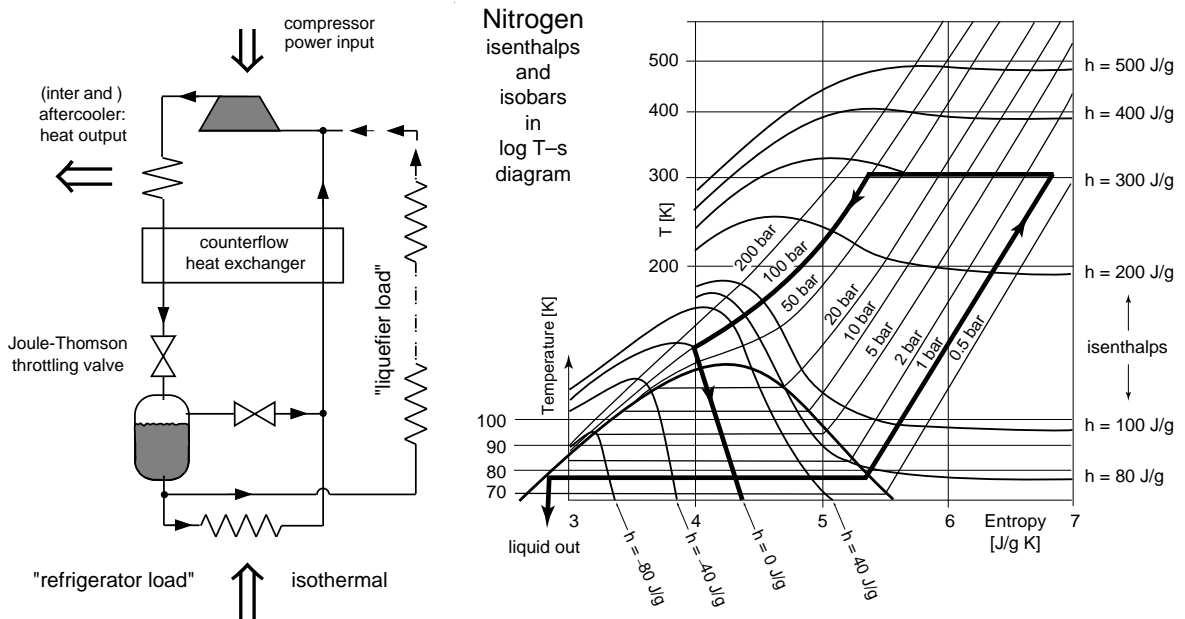


Fig. 6 Flow scheme and temperature-entropy diagram of the Linde cycle, using counterflow heat exchangers and making use of the Joule–Thomson effect

The phenomena of counterflow heat exchangers will be discussed in more detail in Section 6.3. Two typical technical designs are shown in Fig. 7.

The total entropy production of the heat exchanger follows from the specific entropy values at its terminals and from the known mass flow values \dot{m} :

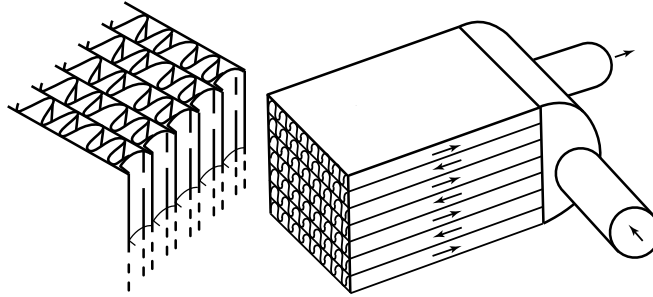
$$\dot{S}_{\text{heat exchanger}} = \sum_i \dot{m}_i s_i ,$$

the summation extending over all i terminals (2 inlets and 2 outlets in case of a two-passage heat exchanger), with inlets being counted positive and outlets negative.

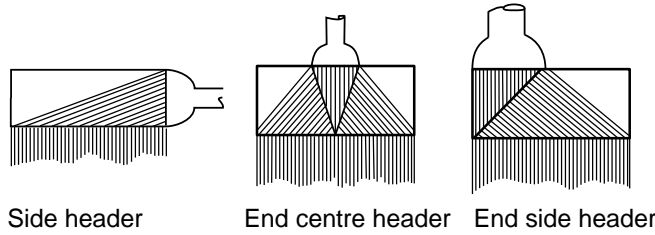
With this entropy source included, the performance of the plant can be evaluated by means of Table 2 and Fig. 2.

¹⁰ Inversion temperature = the temperature that, at a given pressure, separates the regions where the Joule-Thomson effect leads to heating and to cooling (somewhere between A and B in Fig. 4).

Plate and Fin Heat Exchanger



Headers for plate and fin heat exchangers



Tube and Shell Heat Exchanger

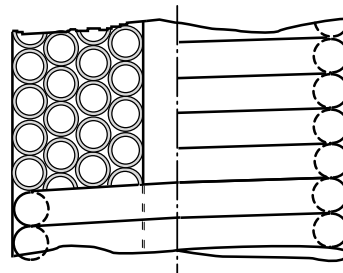


Fig. 7 Technical forms of simple counterflow heat exchangers

5.3 Work-extracting expanders: The Brayton Cycle

The cooling effect of the previously described cryoplant cycles is due to intermolecular forces within the refrigerant. If these forces are strong, they lead to direct liquefaction at ambient temperature when the gas is compressed (case C in Fig. 4). If they are weaker, they usually still lead to a perceptible cooling effect under isenthalpic expansion at ambient temperature (Joule-Thomson effect, case B in Fig. 4). In a few cases, however — namely neon, hydrogen and helium, the intermolecular forces are so weak that at ambient temperature liquefaction is not only impossible, but isenthalpic expansion leads to heating rather than cooling (case A in Fig. 4).

Cooling of such gases, and, generally, the cooling of the ideal gas, in which no intermolecular forces exist, requires an *expansion engine* to extract molecular energy to the outside. In an expansion engine the gas molecules discharge part of their kinetic energy to a receding piston or a turbine wheel, which then transmits it to the outside. The resulting cooling effect is the inverse of the heating effect in a compressor.

A particularly simple cycle consisting of a compressor, an expansion engine, a counterflow heat exchanger between the two, and the heat exchangers linking the cycle to the load and to the environment, is shown in Fig. 8. The T-s diagram shows the two adiabatic (ideally isentropic) phases of compression and expansion with input/output of external work, and the two isobaric phases of internal counterflow heat exchange. For the ideal cycle (full lines), heat is transferred from the load to the cycle at 1 bar between 70 K and about 120 K, and from the cycle to the environment at 4 bar between about 500 and 300 K. It is obvious from the drawing that the entropy transfer is equal in the two cases (horizontal distance between the 1-bar and 4-bar

isobars equal at 300 K and at 120 K). For the real cycle (dashed lines), both the expansion and compression lines are diverted from vertical towards increasing entropies, which increases the entropy output and reduces the entropy input to the cycle. To simplify the argument, we have tacitly assumed that no entropy is produced in the counterflow heat exchanger, i.e. that a temperature difference between inlet and outlet exists neither at the cold nor at the warm end of the heat exchanger.

Brayton cycle: adiabatic compression/expansion; isobaric heat exchange

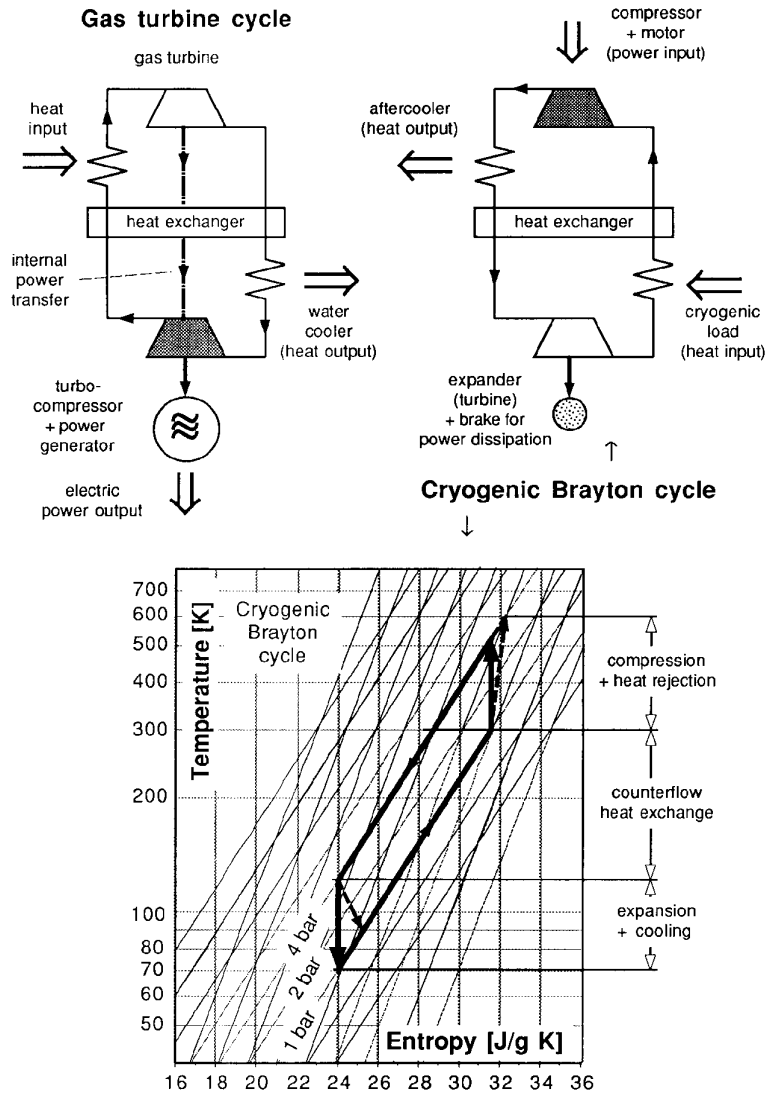


Fig. 8 Flow schemes and temperature-entropy diagram of the Brayton cycle. Top left: gas turbine cycle (Brayton cycle operating as heat engine). Top right: cryogenic Brayton cycle (Brayton cycle operating as heat pump). Bottom: Temperature-entropy diagram of Brayton cycle with ideal gas.

The principle of this cycle, generally referred to as the Brayton cycle, is widely used and by no means limited to helium, hydrogen and neon. George B. Brayton, an American engineer, worked on internal combustion engines in the late 1800s.

A few words should be said about expanders and expander cycles (in particularly turbine cycles).

A *piston expander* can be considered as an inverted reciprocating compressor. Molecules lose part of their momentum when reflected from the receding piston, thereby transferring energy to the piston, which then transmits it to the outside.

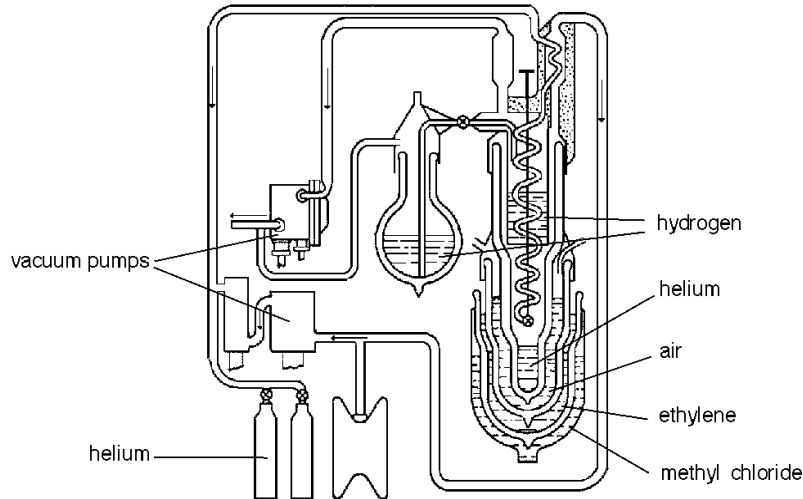


Fig. 9 Cascade liquefier used by Kamerlingh Onnes for the first helium liquefaction in 1908. From J.A. van Lammeren, *Technik der tiefen Temperaturen*, Springer, Berlin 1941, quoted by R. Plank, *Hdb.d.Kältetechnik*, Springer, Berlin, Vol. 1 (1954).

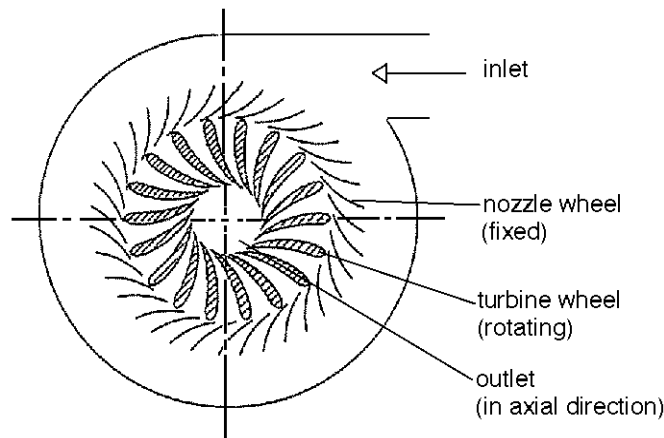


Fig. 10 Radial inflow - axial outflow gas turbine

A *turbine expander* consists of two wheels: the fixed nozzle ring and the rotating turbine wheel (see Fig. 10). In the nozzle wheel, the gas undergoes adiabatic expansion, during which its temperature is reduced according to equation (8c). The corresponding enthalpy reduction [equation (5b)] is balanced by an increase in kinetic energy of the gas¹¹, which is transferred to the turbine wheel and from there to an external device — for example, an electric generator or a device for producing useful mechanical work such as the compressor of a gas turbine cycle (see below), or both. In cryogenics, where energies involved are small and turbine design has to

¹¹ The reduction of enthalpy (temperature) of a gas and the corresponding increase of kinetic energy can be observed when the valve of a compressed-gas cylinder is opened and gas is discharged in a jet: the valve and the top of the gas cylinder cool down rapidly. The often heard, but incorrect explanation is that this is the Joule-Thomson effect — during the expansion, which is by no means isenthalpic, internal energy is transformed into kinetic energy. The effect corresponds to the expansion in the nozzle wheel of the turbine.

respect stringent requirements because of the low operating temperature (in particular excellent thermal insulation), the complication associated with energy recovery is economically not justified. The power extracted from a cryogenic turbine is therefore usually dissipated as heat in an appropriate external brake circuit at ambient temperature. Thus the expander produces the following entropies:

- on the process gas side (at low temperature) $\dot{m} * (S_{\text{expander outlet}} - S_{\text{expander inlet}})$
- on the brake side (at ambient temperature T_a) $\dot{m} * (h_{\text{expander inlet}} - h_{\text{expander outlet}}) / T_a$.

Both entropies must be treated as internal entropy sources when evaluating the performance of the plant by calculating the required power input according to Table 2.

It is plausible that the work required by the compressor is greater than the work delivered by the expander, ideally by a factor corresponding to the ratio of compressor temperature to expander temperature¹², because this gives the ratio of the gas volumina handled by the compressor and the expander. (It is volume that determines the energetic performance of a volumetric machine such as a compressor or an expander.)

If we assume that the work produced by the expander is entirely recovered, we find for the so-called Coefficient Of Performance (COP) of the ideal cycle the expression

$$\frac{\text{Work required by compressor} - \text{Work recovered from expander}}{\text{Work delivered by expander}} = \frac{T_{\text{compressor}} - T_{\text{expander}}}{T_{\text{expander}}},$$

the heat-pump analogue to the Carnot efficiency, usually given as ‘watt per watt’. (The term ‘coefficient of performance’ is misleading: a *low* COP is desirable.)

The cryogenic Brayton cycle is the reverse of a *gas turbine cycle* of the same name, sometimes plainly referred to as *the* gas turbine cycle. Here (top left of Fig. 8) a turbine is driven by hot gas; the heat is injected either by internal combustion or via a heat exchanger upstream of the turbine. We consider the second case (the first case would lead to an open circuit without parallel in cryogenics). The mentioned heat exchanger corresponds to the water cooler downstream of the cryogenic compressor. The residual heat of the expanded gas is partly used to preheat, by counterflow heat exchange, the high-pressure gas feeding the turbine. The remaining heat is transferred to the environment by an air- or water-cooled heat exchanger. The gas, now at ambient temperature, is then recompressed to the turbine inlet pressure by a turbocompressor, preheated by the low-pressure gas in counterflow heat exchange as described, exposed to the external heat source and, having reached its final high temperature, is reinjected into the turbine. An essential point about the gas turbine cycle is that the compressor can be mechanically coupled to the turbine, which thus directly provides the driving power for the compressor.

5.4 Regenerators: The Stirling Cycle

Considering that a compressor is in principle an inverse expander, and vice versa, we notice a remarkable symmetry in the Brayton cycle (Fig. 11, top left). The Stirling¹³ cycle profits from this symmetry by using the same reciprocating engine alternately (half-stroke by half-

¹² If temperatures are taken at corresponding points of the compressor and the expander — for example, inlet or outlet — it is easily shown that the argument is valid even though compression and expansion take place over a temperature range rather than at a fixed temperature.

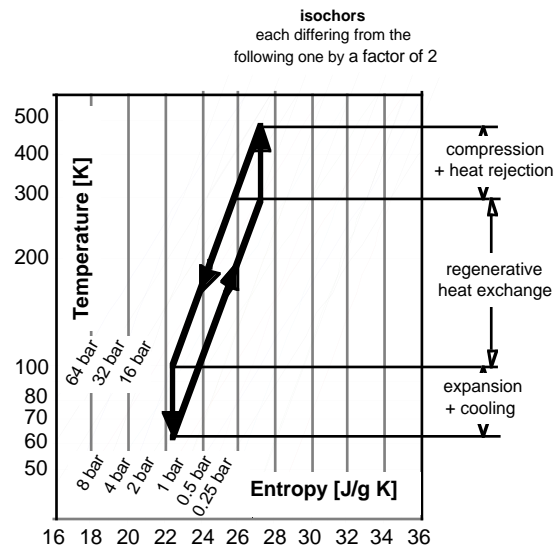
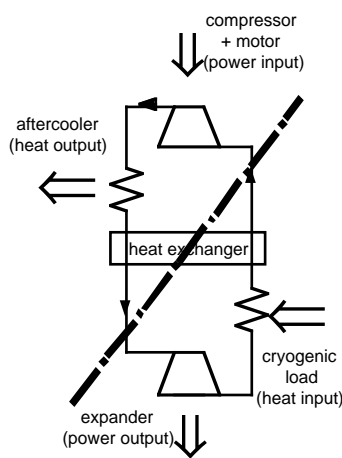
¹³ Robert Stirling, a minister of the Church of Scotland, in 1816 invented and patented a hot-air engine using this cycle. Its potential to run as a refrigerator has been known since 1834 but was not much exploited. However, small Stirling-cycle hot-air engines driving a dynamo to power mobile radio sets that were developed and built by Philips in the early 1940s, turned out to be quite efficient as heat pumps, and Philips decided to develop them for cryogenic use. Since the 1960s, powerful cryogenerators for cooling at liquid-nitrogen temperature (up to 20 kW) and, in a two-stage version, at liquid-hydrogen temperatures, were brought to the market.

stroke) as a compressor and an expander and by replacing the counterflow heat exchanger by a single-passage heat exchange/heat storage device called a *regenerator*, through which the refrigerant shuttles between a warm compression space and a cold expansion space.

The principle of the Stirling engine is illustrated, in simplified form, in the lower part of Fig. 11. An essential component is the displacer, used to move the gas back and forth between the water-cooled warm compression space (at the bottom) and the cold expansion space equipped with an external heat exchanger connected to the load (at the top). The four phases of the cycle are explained in Table 4.

Stirling cycle: adiabatic compression/expansion isochoric regenerative heat exchange

↓ **Symmetry of Brayton cycle**



↓ **Working principle of the Stirling engine**

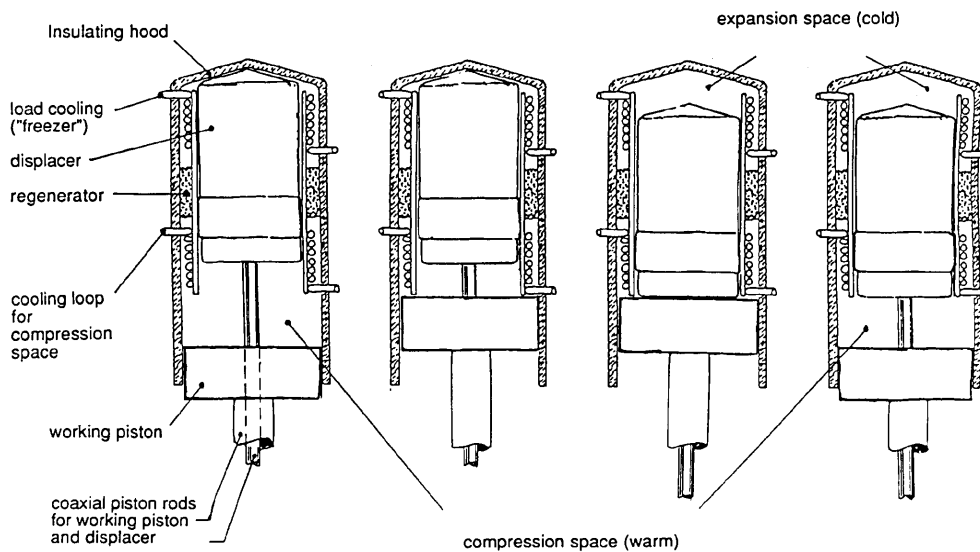


Fig. 11 The Stirling cycle. Top left: relation to the Brayton cycle. Top right: Approximation of temperature-entropy diagram of Stirling cycle. Bottom: Mechanical concept and motion of the working piston and the displacer. Note their phase difference of 90°.

Table 4
Operational phases of the Stirling cycle

Phase	Working piston position	Displacer position	Gas mainly located in
1	down	up	compression space
1→2	<i>compression</i>		
2	up	up	compression space
2→3	<i>gas displacement warm→cold</i>		
3	up	down	expansion space
2→4	<i>expansion</i>		
4	down	down	expansion space
4→1	<i>gas displacement cold→warm</i>		
1	down	up	compression space
...	...		

While moving between the warm and the cold space, the gas passes through the regenerator, a structure of large heat exchange surface and high heat capacity, consisting, for example, of stacked stampings of fine copper or phosphor bronze gauze, or of stratified lead beads. By contact with the gas, the regenerator is periodically heated at its warm end and cooled at its cold end, and a regular temperature gradient is established both in the regenerator and in the gas, exactly as in a counterflow heat exchanger. However, whilst the temperature distribution in the counterflow heat exchanger is established by continuous heat transfer from the warm to the cold gas, the regenerator is subject to alternating heat transfer gas→regenerator (when the gas moves warm→cold) and regenerator→gas (when the gas moves cold→warm).

At upper right of Fig. 11 is the T-s diagram of the ideal cycle, which is adiabatic-isochoric, since the regenerative cooling-heating takes place at constant volume. (The Brayton cycle is adiabatic-isobaric.) Equality of entropy input and output can be shown using the same arguments as for the Brayton cycle (horizontal distance of isochors equal at 300 K and at 100 K). The diagram can only give a rough idea of the process in a Stirling engine. Since there is no continuous flow, gas elements in different locations are subject to different cycles. Moreover, a real engine, rather than producing abrupt up-down motions, will run piston and displacer in a sinusoidal mode with a 90° phase shift, and the distinction between compression/expansion and displacement phases is problematic.

Since the pressure drop across the displacer is small (just the flow resistance of the gas), the displacer motion requires little energy, and the leakage between compression and expansion space bypassing the regenerator is kept small. The T-s diagram shows that the pressure amplitude everywhere in the entire gas space (on either side of the displacer) is remarkably high — in spite of the small volume change produced by the piston (a factor of two is assumed in the diagram). The reason for this large amplitude is the isochoric pressure change when the gas passes the regenerator in alternating directions. In the compression phase the piston acts under higher pressure than in the expansion phase. The work required for compression is therefore greater than the work recovered during expansion. The ratio is the ratio of the temperatures, because they determine the pressures. Our arguments used to find the Carnot efficiency of the Brayton cycle (we noticed the difference of volumetric throughput of compressor and expander) can be repeated, *mutatis mutandis*, for the Stirling cycle: we have to replace volume by pressure. Again we find the Carnot efficiency corresponding to the parallelogram-shaped cycle in the log T-s diagram.

Piston and displacer are connected to the same crank drive, which not only supplies the work for compression, but also recovers the work from expansion. This feature accounts for the remarkable efficiency of the process, in particular when used for cooling at relatively high temperature (for example, liquid nitrogen temperature).

CERN uses two-stage Stirling machines for the cooling of liquid-hydrogen targets¹⁴.

5.5 Combination of Brayton and Linde Cycle: The Claude Cycle

Most large, modern cryoplants in particle physics laboratories can be regarded as a combination of a Linde cycle, used for liquefaction, and several ‘degenerated’ Brayton cycles used for precooling the Linde cycle. Such a compound cycle for air liquefaction was first developed by Georges Claude¹⁵ in 1902; the company *L’Air Liquide* was created on the basis of his patents. The principle of the Claude cycle is shown in Fig. 12. At left, the Brayton and the Linde cycles are shown separately; at right is shown how Claude, by matching the compressor pressures and interconnecting the gas cycles, arrived at an economic integration of the two. Note that the heat exchanger parallel to the expander has unbalanced mass flow: the high-pressure mass flow warm→cold is smaller than the low-pressure mass flow cold→warm, since part of the high-pressure stream is deviated to the expander. This fact, which has important consequences for the heat exchanger operation, will be further analysed in Section 6.3.

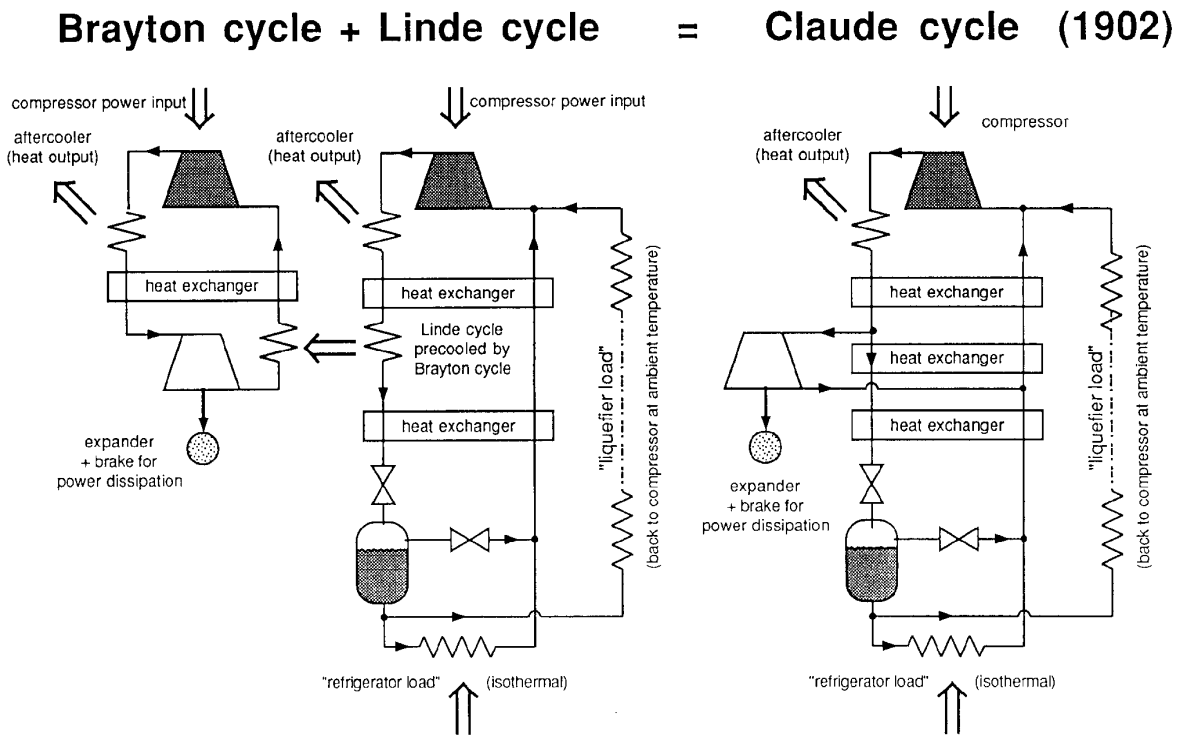


Fig. 12 The Claude cycle as a combination of Brayton cycle and Linde cycle

¹⁴ Related cycles using regenerators rather than counterflow heat exchangers, but operating between two fixed pressures provided by an external compressor rather than at variable pressure under isochoric conditions are the Solvay cycle and the Gifford–McMahon cycle. Several multistage Gifford–McMahon cryocoolers are used at CERN for cooling at $T \geq 20$ K.

¹⁵ Claude had begun his career with the development, in 1897 of the method, still used today, to dissolve acetylene in acetone for storage and transport in order to avoid the risk of autoignition and explosion of this metastable compound. Among many other inventions in various fields, the use of gas discharge tubes as light sources (1910) is particularly remarkable.

Claude used a reciprocating piston expander. Modern cryoplants of the size of interest in particle physics laboratories (cooling capacity above 100 W/4.5 K) generally use turbines¹⁶, mainly because the maintenance requirements of turbines are modest and because turbines of remarkable efficiency have been developed. Piston expanders have their advantages for small plants: they can handle high pressure differences, and their speed can be adapted to wide ranges of gas flow, allowing the plant output to be matched to load requirements without loss of efficiency. Turbines lose a good deal of their efficiency if operated at non-optimal speed, and efficient part-load operation can only be obtained at the price of a considerable sophistication of plant design.

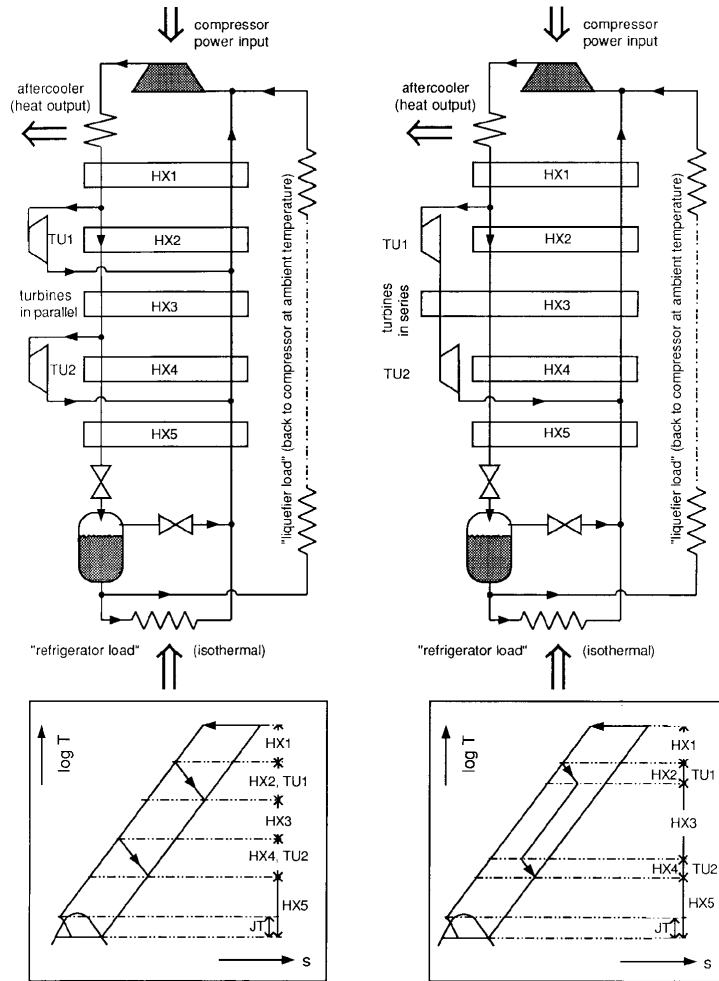


Fig. 13 Two versions of a 2-stage Claude cycle: At left: Brayton stages in parallel. At right: Brayton stages in series

It is possible (and in general necessary for plants designed for cooling below liquid-nitrogen temperatures) to have turbines at several temperatures. Figure 13 shows two two-stage cycles, the turbines being run either in parallel or in series. The T-s diagrams are given at the bottom of the page. Operating turbines in series has the advantage of resulting in smaller pressure and enthalpy differences for handling by each turbine, and, therefore, in smaller gas velocities. There are other reasons for preferring the serial scheme in many cases. On the other

¹⁶ Turbines were proposed for cryogenic use as early as 1898 by Lord Rayleigh, but tremendous technical problems, to the solution of which Pjotr Kapitza (1939) made decisive contributions, delayed their practical introduction. Turbines for hydrogen and helium became available around 1960; the refrigerator of the CERN 2 m bubble chamber was one of the first hydrogen cryoplants using turbines.

hand, the three-passage heat exchanger involves some complications. The relation of the parallel scheme to the original Claude scheme is obvious, whilst the serial scheme may require some contemplation. The essential point is that in both cases the turbines, bypassing the high-pressure passage of HX2 and HX4, interact with the heat exchange process by reducing the high-pressure flow to be cooled with respect to the cooling low-pressure flow.

I would define the characteristic features of a generalised Claude cycle as follows:

In a string of counterflow heat exchangers, part of the gas is diverted from the high-pressure stream to one or several energy-extracting expanders and then reinjected into the cycle at a lower temperature. As a consequence, the mass flow balance in the counterflow heat exchanger partly bypassed on its high-pressure side by the expander is shifted in favour of the cooling (low-pressure) stream. This results in a reduction of the cold-end temperature difference between the counterflow paths and therefore of the entropy production of the plant.

More about this will be said in Section 6.3.

5.6 Carnot's Cycle

Let us finally discuss the ideal cycle studied by Carnot in 1824 to determine general efficiency limits for thermal engines. Figure 14 illustrates a Carnot cycle in both heat engine and heat pump mode (cycle progressing clockwise and anticlockwise, respectively). Although Carnot engines have never been built for technical purposes, it is useful to discuss even this ideal process with realistic gas data; we again use those of Fig. 3. We assume ambient temperature at the beginning of the cycle and a starting pressure high enough to avoid subatmospheric pressures in all phases.

As Fig. 14 shows, both cycles use the isentropic change of state for switching between heat-sink and heat-source temperature. The required energy for switching from low to high temperature (corresponding to the distance between the horizontal isenthalps in a T-s diagram) is quantitatively recovered when switching back to low temperature in a later phase.

During the isothermal phases, the internal energy of the gas, proportional to its temperature, is constant. The energy (work) put into the system during compression at ambient temperature is therefore exactly compensated by the energy (heat) discharged to the environment. Similarly, the entire energy (work) extracted from the system during expansion at heat-source temperature is exactly compensated by the energy (heat) the system receives from the heat source. Input and output entropies are equal, provided no temperature differences occur during heat transfer load→cycle and cycle→environment.

That the entropy intake at heat source temperature is equal to the entropy output at ambient temperature is as obvious in this diagram as in the diagrams shown previously for the ideal Brayton and Stirling cycles (the parallelogram has now become a rectangle); it is not a specific feature of the Carnot cycle.

The simplicity and transparency of Carnot's fundamental *gedankenexperiment* make it an ideal tool for theoretical considerations. In particular, the assumption of heat input and output at two well-defined temperatures simplifies arguments.

For practical purposes, however, the Carnot cycle has severe drawbacks:

- The condition of isothermality requires careful control of the compression and expansion process in the isothermal phases of the cycle in order to keep temperature gradients negligible and avoid entropy production. Such control is all the more difficult to ensure as the gas pressure varies strongly during the isothermal phases.
- The beauty of avoiding heat exchangers (which are a horror for the theorist because of the complex phenomena they exploit) is stained by the fact that most so-called isentropic processes involve non-negligible residual entropy production. Such entropy production would occur in the compressor and in the expander.

Carnot cycle
Isentropic-isothermal cycle

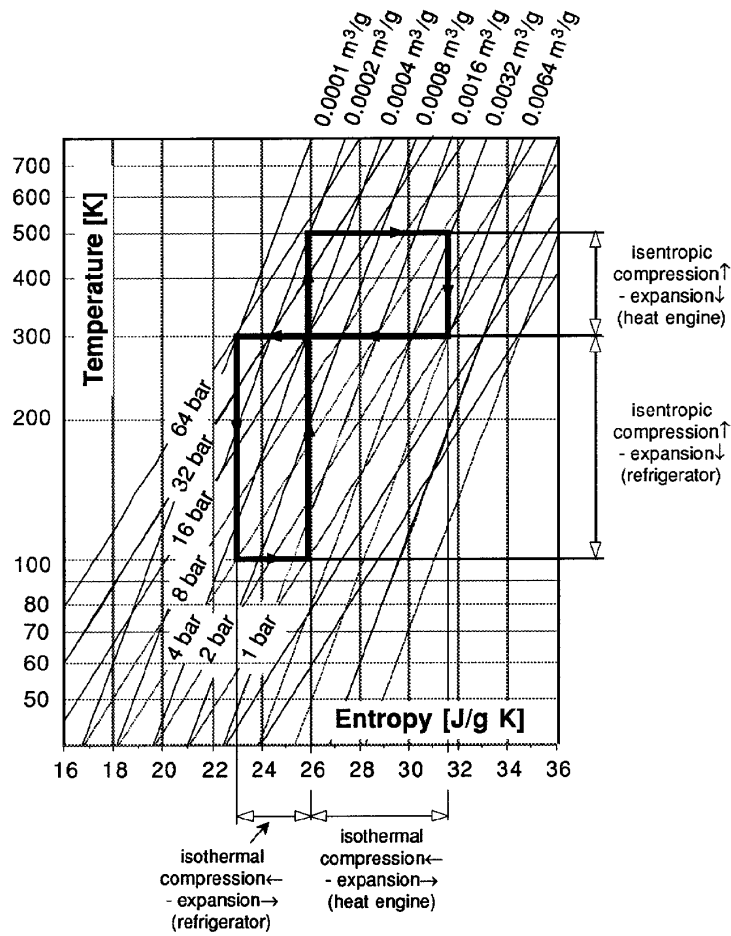


Fig. 14 Carnot cycle operating as heat engine between 500 and 300 K and as refrigerator between 100 K and 300 K

Magnetic refrigeration cycle
based upon Carnot cycle

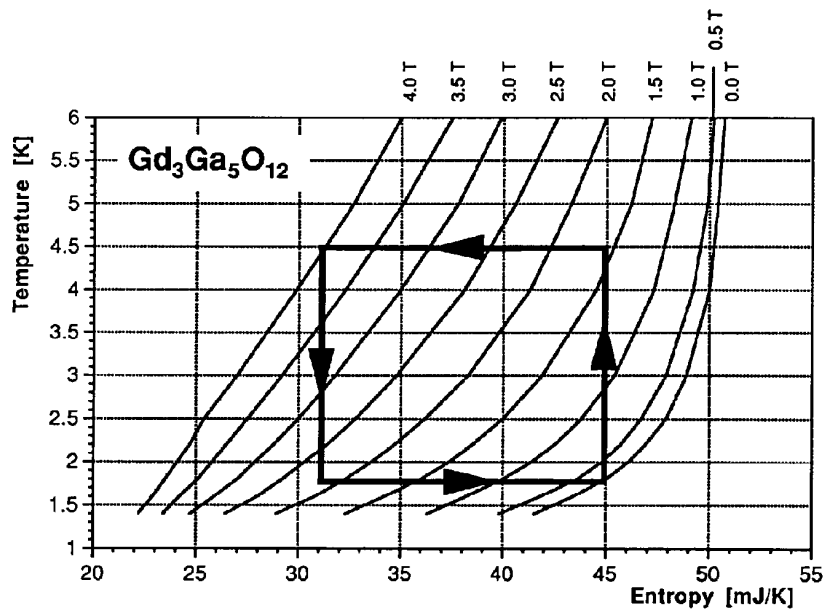


Fig. 15 Application of Carnot cycle for cooling by adiabatic demagnetisation of Gd₃Ga₅O₁₂ (GGG = Gadolinium Gallium Garnet)

- Very high pressure ratios¹⁷ would be required to span temperature differences of practical interest.
- After all, a real Carnot cycle would not even be free from internal heat exchange, since not only the gas, but also its massive containment must follow the temperature cycle, and this again leads to entropy production.

In total, it turns out that adiabatic switching between temperature levels would produce more entropy than a well-designed counterflow heat exchanger.

In spite of all this, the Carnot cycle has found practical application in refrigerators based upon adiabatic demagnetisation, which hold some promise for the pumping of heat at low temperatures and low temperature ratios, for example from 1.8 K to 4.5 K. Magnetic refrigeration cycles use the fact that in a certain temperature range¹⁸ the entropy of suitable paramagnetic crystals depends on external magnetic fields, similar to the entropy dependence on compression of a gas. A T–s diagram for the crystal gadolinium gallium garnet ($\text{Gd}_3\text{Ga}_5\text{O}_{12}$, ‘GGG’), with indication of a possible Carnot cycle, is shown in Fig. 15. The desired Carnot cycle would have the phases:

- (α) Magnetisation of the crystal in thermal contact with liquid helium at 4.5 K, accompanied by heat transfer crystal→helium under isothermal conditions (4.5 K),
- (β) Thermal isolation of the crystal; demagnetisation, accompanied by a temperature drop in the crystal from 4.5 K to 1.8 K,
- (γ) Establishment of thermal contact between the crystal and the load; continued demagnetisation accompanied by heat transfer load→crystal under isothermal conditions (1.8 K),
- (δ) Thermal isolation of the crystal; magnetisation accompanied by a temperature increase in the crystal from 1.8 K to 4.5 K.

The GGG diagram shows that the theoretical entropy throughput would be about 14 mJ/g K per magnetic cycle $0\text{ T} \rightarrow 4\text{ T} \rightarrow 0\text{ T}$. In reality, much less can be expected, since the ideal Carnot cycle is implemented in very rough approximation only. In particular, phases (β) and (δ) are not clearly separated from (α) and (γ), which results in entropy production due to undesired internal heat transfer.

5.7 Summary of cryogenic cycles. Nomenclature

The *cryogenic* cycles discussed (disregarding those cycles working close to ambient temperature) have in common:

- a compression phase,
- an expansion phase,
- between the two, a temperature-staging device (in most cases a counterflow heat exchanger) ensuring that compression and expansion take place at different temperatures levels,
- heat exchangers for heat (entropy) transfer from the load to the cycle and from the cycle to the environment.

The purpose of *compression* is to bring the refrigerant gas into a low-entropy state, preparing it for taking over entropy from the load. Compression is combined with entropy discharge to the environment via heat exchangers that are more or less closely combined with the

¹⁷ Or the availability of highly efficient *cold compressors* (suitable for gas compression at low temperature) for multistage configuration of Carnot cycles...

¹⁸ Suitable for magnetic cooling are temperatures close to the characteristic temperature for spontaneous ordering of magnetic ion dipoles. The phenomena are somewhat comparable to the behaviour of a real gas near condensation temperature. The interaction of the ion dipoles with the crystal lattice must be small.

compressor. To promote heat (entropy) transfer, a certain overtemperature with respect to ambient temperature is necessary.

The purpose of *expansion* is to bring the low-entropy refrigerant to a temperature somewhat lower than the load temperature, thus promoting heat (entropy) transfer from the load to the refrigerant. We distinguish between isenthalpic expansion in throttle valves, where cooling results from work against Van der Waal forces, and adiabatic (ideally: isentropic) expansion in a piston expander or turbine, where cooling results from energy (work) transfer to the outside. All these devices produce entropy, which can be directly read from the T–s diagram (expansion line dropping from left to right, in the sense of increasing entropy). Gas passing a Joule–Thomson throttling valve usually (but not always) enters the liquid domain under the saturation curve of the T–s diagram. Gas passing a turbine or a piston expander may also do so; a special design is then required, and we speak of *wet expanders*.

The purpose of the *temperature staging device* is to prepare the refrigerant for compression and expansion at optimum conditions. If a counterflow heat exchanger is used, this is done by internal heat and entropy transfer between the refrigerant in its low- and high-pressure (high and low entropy) states. In case of the Carnot cycle, it is done by isentropic compression/expansion. In simple, two-path counterflow heat exchangers with equal mass flow in both channels, the entropy production appears as an increased horizontal distance between the points representing the terminals at the warm end with respect to the cold end. For more complex situations (multipath heat exchangers, different mass flows in channels etc.), this simple graphic illustration is, however, not possible, and (in all cases, simple and complex) entropy production is better evaluated numerically from entropy tables.

Usually, the heat exchanger connecting the cycle to the load is fed by the refrigerant in saturated liquid form¹⁹, and heat transfer from the load leads to progressive evaporation of this liquid. This process is isothermal, characterised by a horizontal line in the T–s diagram, and efficient heat transfer to an isothermal load can be ensured by relatively simple means.

The heat exchanger connecting the cycle to the environment is usually fed by hot gas coming from the compressor, because the efficient isothermal compressor, sufficiently cooled during the entire compression process, has not yet been invented. Heat transfer to the environment thus involves high temperature differences and leads to substantial entropy production (usually the dominant component of the plant's entropy budget).

The entropy production associated with heat (entropy) transfer from the load to the cycle and from the cycle to the environment does not appear in the usual simple T–s diagram. Representation would require separate diagrams (sometimes given as inserts) for load and cooling water conditions. However, since the transferred heat as well as the temperatures of the load and the cooling water are usually known, the entropies taken from the load and received by the cooling water are readily calculated from transferred enthalpies, and compared to the corresponding values received (by the load heat exchanger) and discharged (by the compressor heat exchangers).

Many closely related cycles figure under different names. There are national preferences. Sometimes, due to technical shortcomings, a given cycle can be considered as a crude approximation of several ideal cycles. In general, it is better to give a brief description of the cycle than to rely upon the clarity of a name.

¹⁹ Refrigerators are therefore often incorrectly called liquefiers. In principle, the term *liquefier* is reserved for the operation mode of a cryoplant in which the liquid is extracted from the plant and supplied to an external user who will return the evaporated gas at ambient temperature. Contrastingly, in a *refrigerator* the refrigerant is returned to the plant at or close to saturated vapour conditions; a refrigerator is designed for essentially isothermal cooling. All intermediate cases are possible with gas recovery at a temperature well above saturation, but well below ambient; such plants are loosely called cryoplants or cryogenerators.

To the best of my knowledge:

- the Bell–Coleman cycle is identical to the Brayton cycle, which is sometimes plainly called the *gas turbine cycle*,
- the *ideal* gas turbine cycle is sometimes called the Joule cycle,
- heat engine cycles corresponding to the reverse of the evaporative refrigeration cycle described in Section 5.1, are called (Clausius–)Rankine cycle and Hirn cycle, the evaporative refrigeration cycle itself is sometimes called reverse Hirn cycle,
- the Ericson cycle, which is similar to the Brayton cycle, but differs from it by aiming at isothermal rather than isentropic compression/expansion, is sometimes also called the Ackeret–Keller cycle,
- the Linde cycle is sometimes referred to as Joule–Thomson cycle or Hampson cycle (George Hampson patented, a few days before Linde, a cycle with counterflow heat exchangers, but which was not specifically designed to work on the basis of the Joule–Thomson effect),
- the Stirling cycle is sometimes referred to as the Philips cycle.
- the Gifford–McMahon cycle and the Solvay cycle are similar to the Stirling cycle in using regenerators and displacers, but differ from it in using external compressors and operating between two constant pressure levels (isothermal-isobaric cycles comparable to the Ericson cycle).

As for the name ‘Claude cycle’, I use it in a very broad sense for the combination of one or several expander cycles with a liquefaction cycle making use of the Joule–Thomson effect, such as the Linde cycle and its variations. A definition is given at the end of Section 5.5.

6 ENTROPY PRODUCTION IN CRYOPLANTS

There are countless sources of entropy. We can only discuss the most important ones: entropy production associated with compressors, turbines and heat exchangers and entropy production due to the mixing of cold and warm fluids and to unsteady operation conditions.

6.1 Entropy production associated with compression

The largest single source of spurious entropy in cryoplants is usually associated with the compressor. Three types of compressors are currently used for helium service:

- Reciprocating (piston) compressors,
- Screw compressors, and
- (at very low temperatures only²⁰) Turbocompressors.

A *reciprocating compressor* performs compression in a close-to-isentropic process. For helium with $C_p/R = 5/2$, a pressure ratio of 3 according to equation (8 c) leads to an isentropic temperature rise from 300 K to 465 K ≈ 190 °C — close to the tolerable limits of compressor components. For this reason, compression to higher pressures is undertaken in a multi-stage process — for example, from 1 bar to 20 bar in stages 1 bar \rightarrow 3 bar \rightarrow 8 bar \rightarrow 20 bar, with recooling to ambient temperature between stages (‘intercooling’)²¹. Multistage compression may

²⁰ The requirement of circumferential velocities comparable to sound velocity is not favourable for turbocompressors for compressing light gases such as helium at ambient temperature: achievable rotational speeds are too low for good efficiency.

²¹ C_p/R and C_v/R values are particularly low for monatomic gases such as helium (3/2 and 5/2, respectively), and therefore the heating effect is particularly strong. For polyatomic gases, C_p/R and C_v/R values are higher —

greatly reduce entropy production. Whilst entropy production in a close-to-isentropic process is *a priori* low, the energy invested in the heating of the gas must somehow be discharged, either to a work-producing secondary cycle such as a gas turbine — a theoretical solution generally ruled out for many practical reasons — or by transfer to the environment (usually a water circuit) in the form of heat. Generalising equation (8c) for compression from the initial pressure p_0 to the final pressure p_n in n stages of equal compression ratio $(p_n/p_0)^{1/n}$, we find that the required heat transfer is

$$\Delta h = n C_p * \Delta T(\text{stage}) = n C_p * T_0 * \left[(p_n/p_0)^{R/nC_p} - 1 \right]$$

and the corresponding entropy transfer $\Delta S_n = \Delta h/T_0$. Compared to the entropy transfer necessary during isothermal compression,

$$\Delta s_T = R \ln(p_n/p_0),$$

following from (9c), we have the relative increase of entropy production

$$\frac{\Delta s_n}{\Delta s_T} = \frac{n C_p}{R} * \frac{(p_n/p_0)^{R/nC_p} - 1}{\ln(p_n/p_0)}.$$

For $p_n = 20$ bar, $p_0 = 1$ bar, $C_p/R = 2.5$ we find (for example)

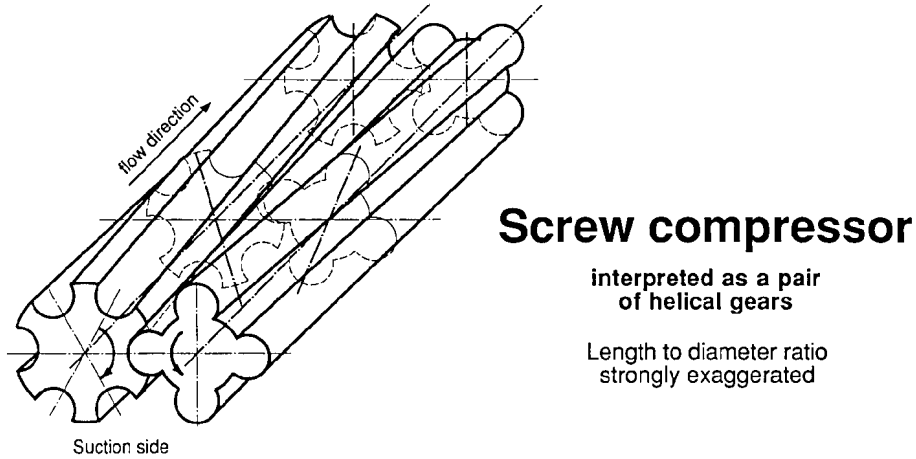
Number of stages n	1	2	3	4	–	∞
$\Delta s_n/\Delta s_T$	1.93	1.37	1.23	1.17	–	1.00

Multistage compression is thus obviously advisable for energetic reasons, but high investment costs and maintenance requirements usually limit the number of stages to two or three.

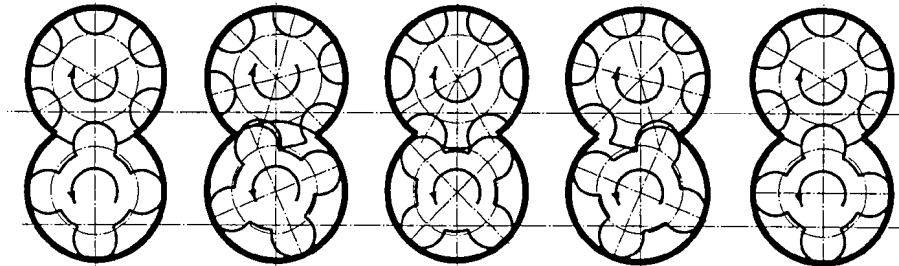
Screw compressors involve lower compression temperatures. The advent of the screw compressor in cryogenics is of recent date, since milling machines for economic rotor production became available only in the 1960s and 1970s. It may be useful to recall the working principles of a screw compressor. A screw compressor (Fig. 16) consists of a pair of helical gears ('screws', 'rotors') of a tooth profile specially designed to compress the fluid trapped between mating threads and to displace it in axial direction. The rotors are installed in a close-fitting casing with apertures for suction and discharge at opposite ends. The upper part of the figure gives an intuitive view of the progressive trapping of fluid between mating teeth. The length of the rotors is strongly exaggerated; in reality rotors are less than two diameters long and the pitch is comparable to the length. A series of cuts through the engaging pair is given in the lower part of the figure, which can be read either as a movie sequence of gear positions at a given location or as a picture of simultaneous gear positions at various axial locations. Helium is usually compressed as a mixture with (incompressible) oil; quantitative separation after compression is required in a carefully designed coalescer/purifier. The oil not only reduces the otherwise prohibitively high leakage across rotor gaps, but also improves cooling; in fact it is the high heat capacity of the oil that limits the helium temperature to less than 100 °C even at compression ratios much higher than those of reciprocating compressors. The reduced temperature and of course the reduced leakage (which, however, remains considerable) are features improving efficiency, but other mechanisms — for example, internal friction in the oil-gas mixture — result

for example, 5/2 and 7/2 for diatomic ideal gases. Hydrogen and air compressors therefore require a smaller number of stages for the same final pressure, and it is for this reason usually not possible to use a hydrogen or air compressor for helium without major modifications.

in new losses. For the time being, the efficiency of screw compressors is no better than that of reciprocating compressors. Their main advantages are low maintenance requirements, vibration-free operation and therefore modest requirements on foundations, and relatively low cost.



Below: **Cut across screw compressor** seen from suction side
 ↓ can be read either as a cinematic sequence of gear positions at a given location or as a picture of simultaneous gear positions at various axial locations of the cuts see table below



Location on gear in units of pitch of male screw	↑ Position at time ↓	↑ Position at time ↓	↑ Position at time ↓	↑ Position at time ↓	↑ Position at time ↓
0	0	1/16 rev	2/16 rev	3/16 rev	0, 4/16 rev...
1/16	1/16	2/16 rev, 6/16 rev...	3/16 rev, 7/16 rev...	0, 4/16 rev...	1/16 rev, 5/16 rev...
2/16	2/16 rev	3/16 rev, 1/16 rev...	0, 4/16 rev...	1/16 rev, 5/16 rev...	2/16 rev, 6/16 rev...
3/16	3/16 rev	0, 4/16 rev...	1/16 rev, 5/16 rev...	2/16 rev, 6/16 rev...	3/16 rev, 7/16 rev...
4/16	0, 4/16 rev...	1/16 rev, 5/16 rev...	2/16 rev, 6/16 rev...	3/16 rev, 7/16 rev...	0, 4/16 rev...
-	-	-	-	-	-

Fig. 16 Working principle of a screw compressor

In recent years cryoplants for cooling temperatures below 4.2 K have increasingly made use of *cold compressors* designed to bring helium evaporated at subatmospheric pressure to a pressure more favourable for efficient operation of heat exchangers (heat exchangers for very-low-pressure gas are bulky, expensive and may be major producers of entropy). Considerable development work is going on. Turbocompressors are generally used at very low temperatures. They benefit from the fact that the required rotor speeds are moderate, as molecular speed and sound velocity decrease with temperature. The compression process is adiabatic, leading to a

considerable temperature increase. Required compression ratios may be very high (10 mbar : 1 bar = 1 : 100), and many stages may be necessary. When cold compressors are connected in series, pressure and temperature variations at the outlet of the first compressor complicate operation of the second, since efficient operation of turbomachines depends crucially upon inlet conditions kept to the design point within narrow tolerances. A method for fixing inlet conditions is the recooling of 'compressed' low-pressure helium to a well-defined temperature in counterflow heat exchange with gas from other branches of the process. The layout of the recooling loop can strongly influence its entropy production.

Generally, it must be stressed that a compressor/aftercooler assembly is to be judged by its *entropy* production and *entropy* rejection rather than by its heat production and heat rejection, since it is the final *entropy* transfer to the environment at ambient temperature that largely determines the power requirements of the plant. The entropy eventually discharged can be traced back to the many individual entropy sources, of which it constitutes the arithmetic sum, whilst a similar procedure for heat is not possible, since most of the heat eventually discharged has its origin in non-thermal power provided by the compressor. Praising low-heat production (and corresponding low-power consumption) as a specific advantage of cold compressors is an incorrect appreciation of the situation.

6.2 Entropy production associated with expansion

Expansion takes place not only in sophisticated work-extracting expansion engines such as piston expanders and turbines, but also in simple devices such as valves, and generally in any part of the cycle where flowing compressible fluids undergo a pressure drop. In the first case, the goal is *isentropic* expansion, and entropy production means deviation from that goal. In the second case, we limit our discussion to expansion without external heat transfer; the change of state is then *isenthalpic*.

Isentropic expansion in piston expanders or turbines occurs along a vertical line in the T-s diagram (see Fig. 4). Adiabatic, but not exactly isentropic, expansion occurs along an inclined line more or less close to vertical. Suppose the inlet state is given by pressure p and temperature T ; the associated enthalpy and entropy values h and s can be found in tables. The ideal outlet state is determined by the given outlet pressure p' and the isentropy condition that the outlet entropy is $s'_{ideal} = s$. T'_{ideal} and h'_{ideal} again are easily determined. To determine the real outlet conditions, one parameter, for example, temperature T'_{real} , must be measured. h'_{real} and s'_{real} are again easily determined. If the mass flow is \dot{m} , the entropy production is $\dot{m}(s'_{real} - s)$. The work extracted is equal to the enthalpy decrease $\dot{m}(h - h'_{real})$. The value $\eta = (h - h'_{real})/(h - h'_{ideal})$ is generally referred to as the efficiency of the expansion.

Entropy production in turbines (we skip reciprocating expanders in view of their limited practical interest) may be due to turbulent dissipation of kinetic energy in the turbine wheels, but also due to heat inleak by conduction or radiation, or to inleak of warm helium from the gas bearings carrying the rotor of modern cryogenic turbines.

Entropy production during isenthalpic expansion is as easily determined as the entropy difference between outlet and inlet state: $\Delta s = s(h,p) - s(h,p')$.

For isenthalpic expansion $p \rightarrow p'$ of ideal gases, for which isenthalps and isotherms coincide, the entropy production follows, with $T' = T$ and $\Delta p = p - p'$, from (9c),

$$\Delta s_h = \Delta s_T = \frac{R}{M} \ln \frac{p}{p'} = \frac{R}{M} \ln \left(1 + \frac{p - p'}{p'} \right) = \frac{R}{M} \ln \left(1 + \frac{\Delta p}{p'} \right) \approx \frac{R}{M} \left[\frac{\Delta p}{p'} + \frac{1}{2} \left(\frac{\Delta p}{p'} \right)^2 + \dots \right].$$

At high pressures, the entropy production due to pressure drop in normal flow channels may be negligible because $\Delta p/p'$ is small. At low pressure, however, and in particular at

subatmospheric pressure, pressure drop in pipework and heat exchangers may be a major source of entropy.

6.3 Entropy production associated with counterflow heat exchange

This section is devoted to counterflow heat exchange. Simple heat exchange has already been treated in Sections 5.1 and 6.1 as a major problem in the context of compressor heat rejection.

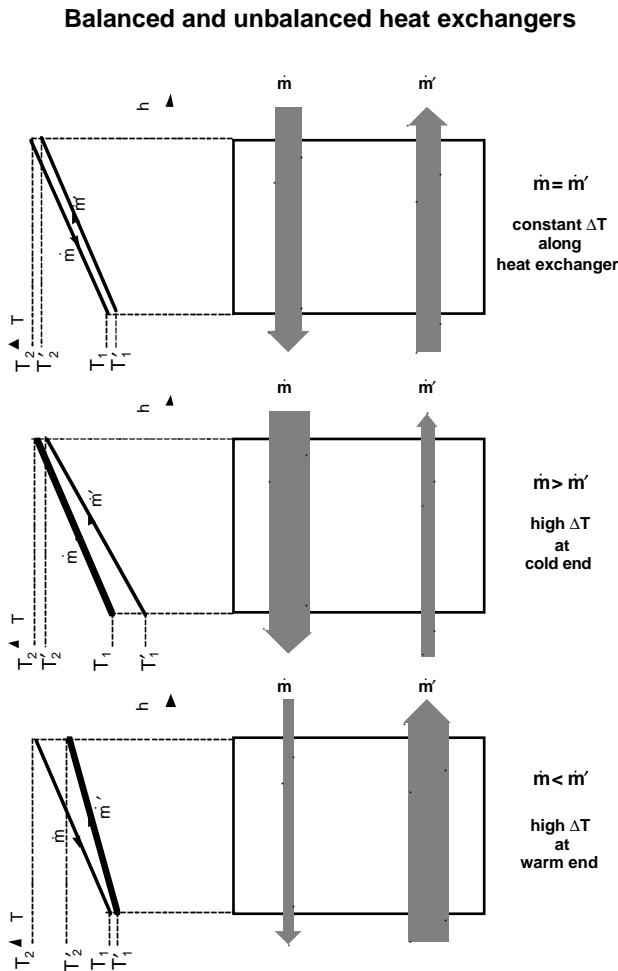


Fig. 17 Temperature distribution on balanced and unbalanced counterflow heat exchangers

We consider (top picture of Fig. 17) a two-passage counterflow heat exchanger, in which heat is transferred from a stream \dot{m} (cooled stream, flow direction $T_2 \rightarrow T_1$, i.e. warm \rightarrow cold, $T_2 > T_1$) to a stream \dot{m}' (cooling stream, flow direction $T_1' \rightarrow T_2'$, i.e. cold \rightarrow warm). We assume that there is no other heat exchange with the exterior. As a result of the internal heat exchange, the temperature of stream \dot{m}' increases in flow direction, while \dot{m} decreases in flow direction. The First Law requires that, at any longitudinal element of the heat exchanger, the heat (enthalpy dH) given by stream \dot{m} equals the enthalpy dH' received by stream \dot{m}' ; the difference of enthalpies between the two streams is therefore the same at any two corresponding locations. Applying this conclusion to the four terminals, we find $H_2 - H_2' = H_1 - H_1'$, hence $H_2 - H_1 + H_1' - H_2' = 0$, or, summing over all terminals, with the convention to count as positive the flows entering the heat exchanger (H_2, H_1') and as negative the flows leaving the heat exchanger (H_2', H_1):

$$\Sigma \dot{H} = 0 . \quad (11)$$

This equation is valid for any number of passages, i.e. also for multistream heat exchangers.

Let us consider the simplest case, namely that of two equal mass flows having the same constant specific heat: $\dot{m} = \dot{m}'$ and $c_p = c'_p$. We then have because of $H_2 - H'_2 = \dot{m} c_p (T_2 - T'_2) = \dot{H}_1 - \dot{H}'_1 = \dot{m} c_p (T_1 - T'_1)$

$$T_2 - T'_2 = T_1 - T'_1 \quad \text{if} \quad \dot{m} c_p = \dot{m}' c'_p , \quad (12a)$$

i.e. a constant temperature difference between corresponding locations at any place of the heat exchanger.

With similar reasoning we find that

$$T_2 - T'_2 < T_1 - T'_1 \quad \text{if} \quad \dot{m} c_p > \dot{m}' c'_p , \quad (12b)$$

i.e. the temperature difference increases from warm (T_2) to cold (T_1), and

$$T_2 - T'_2 > T_1 - T'_1 \quad \text{if} \quad \dot{m} c_p < \dot{m}' c'_p , \quad (12c)$$

i.e. the temperature difference decreases from warm to cold.

Summing up, we state that the *temperature difference* between corresponding locations *increases in the flow direction of the dominating stream* (the stream with the larger $\dot{m} c_p$). This is illustrated in Fig. 17.

In cryoplants we frequently encounter case (12b);. \dot{m}' may be lower than \dot{m} because some liquefied or cold gas has been withdrawn at the cold end of the plant to be returned at ambient temperature only (liquefier mode). In addition, the specific heat of real gases is somewhat pressure-dependent and often higher at high pressure than at low pressure. For this reason, temperature differences in heat exchangers in the absence of expansion engines tend to increase from warm to cold. When discussing the Claude cycle we noted the fact that the introduction of the expansion engine in parallel to a heat exchanger creates an imbalance of mass flow in the heat exchanger in favour of the low-pressure stream, as the expander takes gas from the high-pressure stream warm→cold, bypassing the heat exchanger, and eventually restitutes it to the low-pressure stream cold→warm. It thus creates a situation corresponding to (12c), leading to decreasing temperature differences in the flow direction of the high-pressure stream. This temperature decrease can be designed so as to compensate earlier temperature increases and to keep temperature differences under control. An illustration is given in Fig. 18.

The entropy production in a counterflow heat exchanger is

$$\dot{S} = \int_{h_{\text{out}}}^{h_{\text{in}}} \left(\frac{\dot{m}'}{T'} - \frac{\dot{m}}{T} \right) dh ; \quad \dot{m}' \text{ not necessarily equal to } \dot{m} ; \quad T' < T .$$

The usefulness of thermodynamic computer programs for avoiding tedious integration is demonstrated by Table 5 prepared with HEPAK. The table refers to a 'balanced' heat exchanger handling equal mass flow of helium at pressures 20 bar and 1 bar. The table was calculated for a given temperature difference of 10 K at the warm end of the heat exchanger and for finite enthalpy transfer elements $\Delta h = 100$ J/g (steps 1580, 1480, 1380... J/g in the high-pressure channel, and 1522, 1422, 1322... J/g in the low-pressure channel). It is obvious that the entropy flow cold→warm shown in the last column increases continuously from 25.78 to 31.44 J/g, due to the entropy produced during heat transfer. The total entropy production can be calculated by summation over all terminals, using the convention to count as positive the flows entering the heat exchanger and negative the flows leaving it:

$$\Delta\dot{S} = \sum \dot{S} = \sum \dot{m} s > 0 \quad (14)$$

(s from tabulated values or computer programs).

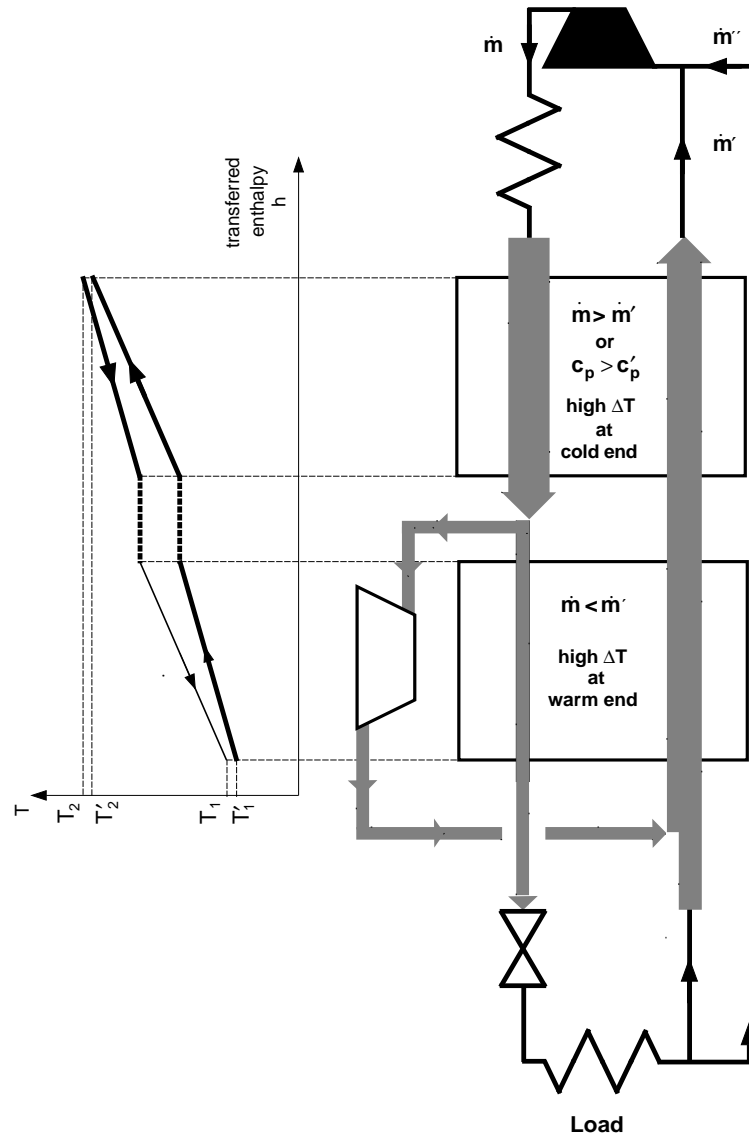


Fig. 18 Temperature distribution on the two heat exchangers of a Claude stage

This formula allows entropy production to be calculated for heat exchangers of any number of passages. It is the most important formula for the evaluation of entropy production in a cryoplant of any complexity.

The reason for keeping temperature differences small by introduction of expansion engines in Claude stages is of course the intention to minimise entropy production. As, according to (13), entropy production depends on

$$\Delta \frac{1}{T} \approx -\frac{\Delta T}{T^2},$$

it is most important to achieve small values for ΔT at the lowest temperatures of the plant.

Table 5
Entropy production on heat exchanger 300 K... 100K

pressure	temperature	enthalpy	entropy	pressure	temperature	enthalpy	entropy	entropy flow upward
p	T	h	s	p	T	h	s	$\Delta s = s(1 \text{ bar}) - s(20 \text{ bar})$
bar	K	J/g	J/g K	bar	K	J/g	J/g K	J/g K
20	300.07	1580	25.39	1	290.08	1522	31.44	6.05
20	280.81	1480	25.05	1	270.82	1422	31.08	6.03
20	261.54	1380	24.68	1	251.57	1322	30.70	6.02
20	242.29	1280	24.28	1	232.31	1222	30.28	6.00
20	223.03	1180	23.85	1	213.05	1122	29.83	5.98
20	203.77	1080	23.38	1	193.80	1022	29.34	5.96
20	184.52	980	22.87	1	174.54	922	28.80	5.93
20	165.28	880	22.30	1	155.29	822	28.19	5.90
20	146.04	780	21.65	1	136.03	722	27.50	5.85
20	126.82	680	20.92	1	116.78	622	26.71	5.79
20	107.62	580	20.06	1	97.52	522	25.78	5.71

We have tacitly assumed in the preceding that, in any cross-section, the heat exchanger is characterised by only two temperatures — one for the cooled stream (T) and one for the cooling stream (T'). That this is so is by no means granted by nature but depends on the skill of the designer and the manufacturer of the plant. In particular, flow distribution in a heat exchanger as shown in Fig. 7 can be such that, although the flow, averaged over the entire heat exchanger cross-section, is balanced, certain parts are preferred by the cooled stream and others by the cooling stream, which leads to local unbalance of flow and may result in unexpected temperature differences and major losses of cooling capacity. The reason for this may be an inadequate header design (see Fig. 7), obstructions in passages or, particularly in horizontal heat exchangers at very low temperatures, stratification due to gravity.

6.4 Entropy production due to heat leaks or gas leaks

The consequences of heat inleaks to cold parts for the performance of a cryoplant are often underestimated. Since $S = Q / T$, the entropy production due to a given heat inleak increases with $1/T$. An often encountered case of bad practice is heat introduction by cables of 'small' cross-section handling electrical signals. Such cables can constitute a heat load of quite unexpected importance because of the very high thermal conductivity of good electrical conductors at cryogenic temperatures. Bridging of large temperature differences must therefore be avoided, and incoming heat should be intercepted at the highest possible temperature level, in order to minimise entropy production.

Often overlooked are gas leaks between different temperature levels via leaking valves or faulty components. The requirements on sealing properties (geometric matching) are higher at low than at high temperatures because of the increased gas density, and they are more difficult to meet because of the lack of elasticity of cold sealing materials. Mixing of warm and cold gas is a typical example of an entropy producing process: while enthalpies are additive, resulting in a mixing enthalpy

$$h' = \frac{\dot{m}_1 h_1 + \dot{m}_2 h_2}{\dot{m}_1 + \dot{m}_2}$$

a similar relation does not hold for entropy. The mixing entropy is given by the mixing enthalpy and other boundary conditions (e.g. pressure, if mixing occurred at constant pressure) and can be determined from tables. Always,

$$s' = s(p, h') > \frac{\dot{m}_1 s_1 + \dot{m}_2 s_2}{\dot{m}_1 + \dot{m}_2}$$

Internal gas leaks, but also other heat leaks, can have further serious consequences by unbalancing critical heat exchangers, shifting working points for delicate components (for example, the Joule–Thomson valve) or creating an unexpected pressure drop at constrictions in the process piping.

6.5 Entropy production due to unsteady operating conditions

Whilst entropy production in compressors, turbines and heat exchangers falls under the responsibility of the cryoplant designer or manufacturer, who may also be responsible for some heat and gas leaks, operating conditions are usually imposed by the operator or user. It is therefore particularly important that the user be aware of the consequences of his requirements for the performance of the plant. This awareness is often missing. In particular, users often require the cryoplant to be able to cope with rapid changes of load conditions ('rapid' in cryogenics means 'within a few minutes...'), not realising that any control action on a thermodynamic system results in temporarily increased temperature differences in heat exchangers and therefore in increased entropy production, thus jeopardising efficiency.

Ensuring steady operation conditions is therefore mandatory for efficient plant operation. It turns out that primitive and apparently brutal methods are often more efficient than sophisticated controls designed by specialists of non-thermal systems. A barbaric method that is often successful consists of adding complementary heat (provided by an electric heater) to the load, to keep constant the sum of the original load and the stabilising complement. The entropy produced by the heater is then smaller than that which would have been produced by an imperfect control system.

In the worst case, unsteady operating conditions include the breakdown of utility supply (electricity or water) or off-design operation of the load (for example, quenches of superconducting magnets). Economic considerations generally exclude a cryoplant design capable of coping with such situations. Asking for increased cooling capacity for all eventualities or for maximal redundancy of components or for ultimate investments in controls is usually not economic, being less efficient than an investment in reliable conventional utilities and restricting operating requirements to those matched to the realistic potential of the cryoplant.

7 HOW TO DEAL WITH COMPLEX CRYOGENIC SYSTEMS

Figure 19 shows the flow scheme and the associated T–s diagram of a large cryoplant at CERN. The plant handles a total entropy load of about 12 kW/4.5 K and uses seven turbines. Two plants of this type were provided by Linde/Sulzer and two similar ones, designed to the same specification, by L'Air Liquide. The specification was drawn up to meet the needs of LEP2, but with the possibility of a later upgrade by about 50% for use with LHC. In view of the upgrade, two low-pressure paths are provided: one, handling the return gas from the liquid-helium vessel and passing by points ...39, ..., 31; and the other handling the return gas of the upper turbines and passing by points 29, ..., 21. At present the two paths are at identical temperature and pressure conditions; for the upgrade, however, they can be separated and the turbine path

operated at higher pressure and mass flow without affecting the pressure in the liquid-helium vessel. The upgrade will also require the installation of an additional turbine between TU3 and TU5; this turbine will bear the now missing number 4.

We call the cycle a multistage Claude cycle because its central Linde cycle is precooled by seven turbines, bypassing the cooled (high-pressure) stream of heat exchangers HX 2, 4, 6, 8, 10 and 12, and shifting the mass flow balance there in favour of the cooling stream. We introduced a corresponding definition of the generalised Claude cycle in Section 5.5.

The purpose of this section is to show how to use Table 2 and Fig. 2 to analyse a complex installation. The plant shown in Fig. 19 serves as an example; details are neglected. Since entropy considerations play an important role in what follows, numeric values of entropies at component terminals are explicitly given in the T–s diagram. Entropies are given in conventional units [J/g K or W/g K (for entropy flow)] and in units based upon the temperature level of the main heat load of the plant, 4.5 K (a practice introduced with Fig. 2), namely J/4.5 K or W/4.5 K.

Step 1: Definition of duty loads

The plant specification defines the following simultaneous loads:

Designation	Quantity	Supply conditions	Recovery conditions
Main load	10 kW	saturated or subcooled liquid at 4.5 K	saturated vapour at 4.5 K
Liquefier load	13 g/s	saturated or subcooled liquid at 4.5 K	gas at 300 K, ~ 1 bar
Heat intercept load	6.7 kW	gas, T < 75 K, any pressure	gas, T < 75 K, any pressure

The total *heat load* is

$$\dot{Q}_{in} = 10 \text{ kW} + 13 \text{ g/s} * (1'573.5 - 11.6) \text{ J/g} + 6.7 \text{ kW} = 37.0 \text{ kW} ,$$

taking the enthalpy values for helium gas at 1 bar and 300K (1'573.5 J/g) and at 4.5 K (11.6 J/g) from HEPAK.

The corresponding *entropy loads* \dot{S}_{in} follow from the data of the T–s diagram:

Designation	Entropy load
Main load	510.5 g/s * (8.250–3.741) J/g K = 2'302 W/K = 10.358 kW/4.5 K, with respect to the specified 10 kW, a slight reserve is included
Liquefier load	13 g/s * (31.477–3.781) J/g K = 360 W/K = 1.620 kW/4.5 K
Heat intercept load	28.1 g/s * (19.568–13.301) J/g K = 176.1 W/K = 0.792 kW/4.5 K
Total \dot{S}_{in} according to flow sheet	(2'302 + 360.5 + 176.1) W/K = 2.84 kW/K \approx 12.8 W/4.5 K

Parasitic radiative and conductive heat loads are neglected.

Step 2: Identification of internal entropy sources

We might individually calculate the entropy load of all components — for example, that of heat exchanger HX11:

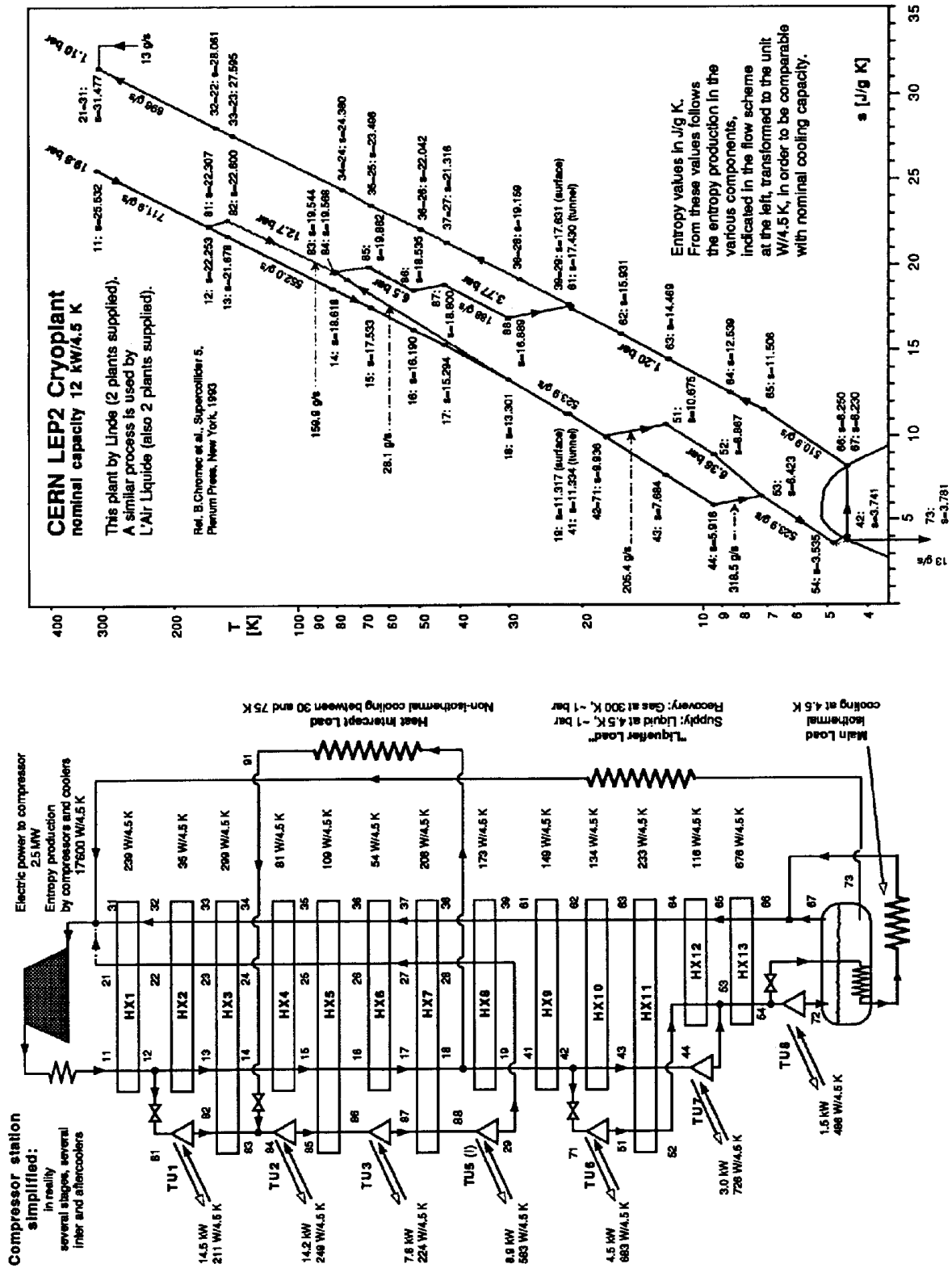


Fig. 19 Flow scheme and temperature-entropy diagram of a large cryoplant at CERN

$$\begin{aligned}
 \dot{S}_{HX11} &= \sum_i \dot{m}_i s_i \\
 &= \dot{m}_{51} s_{51} - \dot{m}_{52} s_{52} + \dot{m}_{43} s_{43} - \dot{m}_{44} s_{44} + \dot{m}_{63} s_{63} - \dot{m}_{64} s_{64} \\
 &= 205.4 \cdot (10.675 - 8.867) + 318.5 \cdot (7.684 - 5.916) + 510.9 \cdot (12.539 - 14.469) [\text{g} / \text{s} \cdot \text{W} / \text{gK}] \\
 &= -51.6 \text{ W} / \text{K} = -232 \text{ W} / 4.5 \text{ K}
 \end{aligned}$$

(negative since coming out of the heat exchanger). Such calculations are extremely useful for the individual evaluation of components. They are easily done on a spreadsheet, the usefulness of which, and of programs like HEPAK, is gratefully acknowledged, remembering the time when such calculations had to be done on slide rules and mechanical calculators with graphical data from diagrams on A0 format. The results for our present example (including *internal* entropy production by turbines, i.e. entropy production at process temperature) are given in the flowsheet of Fig. 19.

Step 3: Identification of enthalpy extraction by expansion devices

The power extracted by turbines is indicated in the flow sheet of Fig. 19; the total is

$$\sum \dot{H}_{\text{turbines}} = 14.5 + 14.2 + 7.8 + 8.9 + 4.5 + 3.0 + 1.5 = 54.4 \text{ kW} .$$

This energy will be dissipated at 300 K (entropy production $54.4/300 = 0.2 \text{ kW/K} = 0.8 \text{ kW}/4.5 \text{ K}$).

Step 4: Output entropy, not including entropy production by compressor coolers

The output entropy can be found by summing up the entropies found in the preceding steps or, more easily, directly from the T-s diagram of Fig. 19:

$$\begin{aligned}
 \dot{S}_{\text{out(excl.compressor)}} &= \dot{m}_{11} \cdot (s_{11} - s_{21}) + 0.2 \text{ kW} / \text{K} = 711.9 \cdot (25.532 - 31.477) - 200 [\text{W} / \text{K}] \\
 &= -4.43 \text{ kW} / \text{K} = -19.9 \text{ kW} / 4.5 \text{ K} .
 \end{aligned}$$

Comparing this with the result of Step 1, we notice an entropy increase by 66%.

Step 5: Output heat

The heat output corresponding to $S_{\text{out(excl.compressor)}}$ is $4.43 \text{ kW/K} \cdot 300 \text{ K} = 1.33 \text{ MW}$.
The electric power received by the compressor is 2.5 MW .

The difference is due to entropy production in the compressor and the equipment associated with it (in particular heat exchangers). Expressed in units of entropy, it corresponds to $(2.5 - 1.33) \text{ MW}/300 \text{ K} = 3.9 \text{ kW/K} = 17.6 \text{ kW}/4.5 \text{ K}$.

Conclusion:

The duty entropy load input of the cryoplant is $12 \text{ kW}/4.5 \text{ K}$. Internal entropy sources from heat exchangers, turbines etc. increase it by a factor of 1.66. Entropy production in the compressor and associated equipment increase it by another factor of 1.88. In other words: the entropy discharged to the environment is about 3.1 times that received by the load. 0.66 times the load entropy is produced by heat exchangers and turbines, 1.47 times the load entropy is produced by the compressor.

Note that this is one of the most efficient cryoplants in the world.

8 WHAT IS ENTROPY?

Entropy is *the* fundamental quantity characterising thermodynamic systems.

Let us recall the main difference between mechanics and thermodynamics:

- In mechanics we deal with strongly constrained systems. The number of components and of degrees of freedom is small. Their parameters, if not already known, can in principle be determined, and their control is the task of the mechanical engineer.
- In thermodynamics we deal with very loosely constrained systems. The number of components and of degrees of freedom is enormous; we would not dream of determining or controlling instantaneous parameters of individual components (which, for simplicity, in the following we will call particles). Nevertheless, the few constraints that are known (for example, given number of particles, given total energy, restriction to a given volume, etc.) allow some important predictions to be made about the behaviour of the system.

Rather than dealing with *the real* state of the system, as we would do in mechanics, in thermodynamics we deal with *all possible* states compatible with the constraints. We call them *microstates*. The most important thing we know about them is that their number exists and that it is finite, although very large. (That the number is finite follows from our limited measurement accuracy, which at any rate does not go beyond Heisenberg's uncertainty principle: it would not be reasonable to count two states as different if we cannot, even in principle, discriminate between them.) We call this number Φ .

To calculate the value of Φ is *not* our objective — it can be done for some ideal systems and is a task for theoreticians, far beyond the scope of this seminar. But the simple fact that this number exists has important consequences in combination with the — plausible and experimentally confirmed — Fundamental Assumption of thermodynamics:

The Fundamental Assumption of thermodynamics is that the probability of being *real* (and not only possible) is the same for all microstates.

Based upon this assumption, we may compare two macroscopic states (we will call them *macrostates*), each loosely constrained and comprising a large number of microstates — say, Φ_1 and Φ_2 . This does not mean very much as long as the two macrostates have nothing to do with each other.

Suppose, however, that they underlie the same constraints. It then follows from the Fundamental Assumption that the one of the two macrostates containing more microstates than the other has a greater probability of being real, the probability being proportional to Φ . We may go further and decompose the state of a real system into a set of macrostates differing from each other by one property that interests us — for example, the distribution of energy over the degrees of freedom of the system — described by a suitable function. We may scan the real system according to an appropriate scheme. According to the Fundamental Assumption, the macrostate containing the largest number of microstates has the highest probability of being real. We conclude that the real distribution of energy is the one that corresponds to this macrostate.

Let us discuss the behaviour of two systems that, to begin with, underlie two different constraints — for example, total energy, volume and particle number N_1, V_1, U_1 and N_2, V_2, U_2 ; the respective microstate numbers are Φ_1 and Φ_2 .

As long we keep the two systems separate, the number describing the pair is

$$\Phi_{\text{separate}}(N_1, V_1, U_1; N_2, V_2, U_2) = \Phi_1(N_1, V_1, U_1) * \Phi_2(N_2, V_2, U_2),$$

the product resulting from the fact that each possible state of system 1 can be combined with each possible state of system 2.

If we admit interaction between the two — for example, heat exchange without particle exchange and without change of individual volumes V_1 and V_2 — we get

$$\Phi_{\text{heat change}}(N_1, V_1, U_1; N_2, V_2, U_2) = \Phi_1(N_1, V_1, U_1^*) * \Phi_2(N_2, V_2, U_2 + U_1 - U_1^*),$$

which leaves us with the problem of determining the energy U_1^* of system 1 after heat transfer.

The law of conservation of energy admits for U_1^* any value between 0 and $U_1 + U_2$. The Fundamental Assumption requires U_1^* to take the value for which $\Phi = \Phi_1 * \Phi_2$ becomes a maximum. This condition is equivalent to the condition

$$(\partial \ln \Phi_1 / \partial U)_{N,V} = (\partial \ln \Phi_2 / \partial U)_{N,V}. \quad (15)$$

If this were not so — for example, if $\partial \ln \Phi_1 / \partial U$ were greater than $\partial \ln \Phi_2 / \partial U$ — energy would flow from system 2 to system 1 and the sum $\ln \Phi_1 + \ln \Phi_2$ — i.e. the product $\Phi_1 * \Phi_2$ — would increase, which would mean that the system had not yet reached equilibrium. (We introduced the logarithm in order to find the maximum of the product $\Phi_1 * \Phi_2$; differentiation of Φ_1 and Φ_2 would have led to the maximum of $\Phi_1 + \Phi_2$.)

A quantity that becomes a maximum in thermal equilibrium between two closed systems of constant volume that exchange neither heat nor work nor particles with their environment must be closely related to entropy, which has exactly this property. In fact, entropy as defined by Clausius is related to Φ by Boltzmann's law

$$\boxed{\Phi = \exp(S/k)} \quad \text{or} \quad \boxed{S = k \ln \Phi} \quad (16)$$

where k is Boltzmann's constant, introduced in Section 4.4. From experience we know that the quantity that becomes equal for two systems in thermal contact is temperature, and in fact we can identify $\partial \ln \Phi / \partial U$ with $1/T$:

$$\boxed{\left(\frac{\partial S}{\partial U}\right)_{N,V} = k \left(\frac{\partial \ln \Phi}{\partial U}\right)_{N,V} = \frac{1}{T}}. \quad (17)$$

This is one of the most important equations in thermal physics. Referring to the question of this section's headline, we might thus answer that entropy is the abscissa of the log T–s diagram, the ordinate being $-\ln(\partial s / \partial u)$.

Equation (17) leads to the procedure for measuring entropy at constant volume, introduced in Section 4.3: measuring the change of temperature for a controlled change of internal energy ΔU (produced, for example, by an electric heater), we have

$$\Delta S \approx \Delta U / T = m c_p \Delta T / T,$$

a procedure that can be repeated stepwise in order to determine the temperature dependence of entropy at constant volume over an extended range. Volume and pressure dependence can be measured by similar methods.

Also, the other essentially thermodynamic quantities can be interpreted with reference to entropy — for example, pressure:

$$p = - \left(\frac{\partial U}{\partial V}\right)_S = T \left(\frac{\partial S}{\partial V}\right)_U = - \left(\frac{\partial U}{\partial V}\right)_T + T \left(\frac{\partial S}{\partial V}\right)_T. \quad (18)$$

A numeric example for equation (16) may be instructive: 1 g of helium at 300 K, 1 bar has an entropy of 31.44 J/K. With $k = 1.38 * 10^{23}$ J/K we find

$$\Phi = \exp(S/k) = \exp(31.44 / 1.38 * 10^{-23}) \approx 10^{2.28} * 10^{24},$$

i.e. a number of $2.28 * 10^{24}$ digits. Printed at 12 characters/inch, this number has a length of $4.82 * 10^{21}$ m \approx half a million light-years, i.e. about five times the diameter of our galaxy. In comparison, the superconducting electrons in a superconductor are in a fully defined state described by a single macroscopic wave function, which contains all the information we can possibly have about the system. Its entropy is zero, Φ has 1 digit. Appreciate the difference!

'Boltzmann's constant' k , one of the fundamental constants of Nature, was introduced under that name by Planck in homage of Boltzmann, and the formulation $S = k \ln W$, engraved on Boltzmann's tomb, is due to Planck. (W stands for *Wahrscheinlichkeit*, probability, corresponding to Φ .) Boltzmann himself spoke about proportionality. In deep depression, attacked and despised by the positivistic school as a guru of unscientific atomistic metaphysics, he committed suicide in 1906. The triumph of the atom after the overwhelming discoveries at the end of the 19th and the beginning of the 20th century, however, brilliantly confirmed Boltzmann's conclusions and the power of his methods. But the positivistic warnings survived. They, too, were justified. The atom and its constituents turned out not to be the expected classical particles, and the new physics, quantum mechanics, eventually resigned from describing them in pictures taken from our familiar world, limiting itself to *statistical* statements about *probable* results of experiments.

Superconducting electrons and superfluid helium atoms are a particularly remarkable species of quantum particles. But that is another story...

9 REFERENCES

Cryogenics can be seen under many aspects, and many good books are available on the subject. This is not the place for a detailed review. Anyhow, most people confronted with cryogenics are not looking for a textbook they would read right through but for specific information providing insight into a feature that is the object of their current interest. In this respect, it is certainly good advice to scan the proceedings of recent conferences on cryogenic engineering. Two such conferences are held alternately every two years: the International Cryogenic Engineering Conference (ICEC) and the American Cryogenic Engineering Conference (CEC). The CEC Proceedings are published under the title 'Advances in Cryogenic Engineering'. The ICEC Proceedings were published in varying form and by several editors in the past; the last conferences were the object of a special edition of the journal *Cryogenics*. This journal is also a good source of information.

My personal recommendation is:

Charles Kittel and Herbert Kroemer, Thermal Physics,
Second edition 1980, Freeman, San Francisco: 473 pages,

a fascinating introduction to thermodynamics, of great originality and in a very unpretentious form. It has strongly influenced my thinking about cryogenic problems, although cryogenics is only a small part of the book.

A very helpful and time-saving tool for access to numeric data about helium properties is HEPAK, a program written by V. Arp, R.D. McCarty and B.A. Hands and published by Cryodata, P.O.Box 558, Niwot, Colorado, USA 80544.