Chapter 5

Consequences of the First Law

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A.1 Partial Derivatives

Consider a function of three variables, $f(x, y, z) = 0$

since only two variables are independent, we can write

$$x = x(y, z), \; y = y(x, z)$$

Then $\mathrm{d}x = (\frac{\partial x}{\partial y})_z dy + (\frac{\partial x}{\partial z})_y dz$, and

$$\mathrm{d}y = (\frac{\partial y}{\partial x})_z dx + (\frac{\partial y}{\partial z})_x dz$$

We obtain,

$$\mathrm{d}x = (\frac{\partial x}{\partial y})_z \left\{ (\frac{\partial y}{\partial x})_z dx + (\frac{\partial y}{\partial z})_x dz \right\} + (\frac{\partial x}{\partial z})_y dz$$

A.1 Partial Derivatives

$$\mathrm{d}x = (\frac{\partial x}{\partial y})_z \left\{(\frac{\partial y}{\partial x})_z dx + (\frac{\partial y}{\partial z})_x dz\right\} + (\frac{\partial x}{\partial z})_y dz$$

$$= (\frac{\partial x}{\partial y})_z(\frac{\partial y}{\partial x})_z dx + \left[(\frac{\partial x}{\partial y})_z(\frac{\partial y}{\partial z})_x + (\frac{\partial x}{\partial z})_y\right] dz$$

If $\mathrm{d}z = 0$ and $\mathrm{d}x \neq 0$,

$\left(\frac{\partial x}{\partial y}\right)_z = \frac{1}{\left(\frac{\partial y}{\partial x}\right)_z}$. This expression is known as the ***reciprocal relation***.

If $\mathrm{d}x = 0$ and $\mathrm{d}z \neq 0$,

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x = -\left(\frac{\partial x}{\partial z}\right)_y$$

A.1 Partial Derivatives

$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x = -\left(\frac{\partial x}{\partial z}\right)_y$ (previous slide)

$\left(\frac{\partial x}{\partial z}\right)_y = \frac{1}{\left(\frac{\partial z}{\partial x}\right)_y}$ (using reciprocal relation)

Substituting these equations yield,

$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1$. The ***cyclical rule***, or ***cyclical relation.***

A.1 Partial Derivatives

Consider a function u of three variables x, y, z can be written as a function of only two variables and those two variables are independent.

$$u = u(x, y\ )$$

Alternatively,

$$x = x(u, y\ )$$

Then

$$\mathrm{d}x = \left(\frac{\partial x}{\partial u}\right)_y du + \left(\frac{\partial x}{\partial y}\right)_u dy.$$

If we divide the equation by $\mathrm{d}z$ while holding u constant,

$\left(\frac{\partial x}{\partial z}\right)_u = \left(\frac{\partial x}{\partial y}\right)_u \left(\frac{\partial y}{\partial z}\right)_u$. The ***chain rule of differentiation***.

5.1 The Gay-Lussac-Joule Experiment

In general, $u = u\,(T, v)$

using the cyclical and reciprocal relations,

$$\left(\frac{\partial T}{\partial v}\right)_u = -\frac{\left(\frac{\partial u}{\partial v}\right)_T}{\left(\frac{\partial u}{\partial T}\right)_v}$$

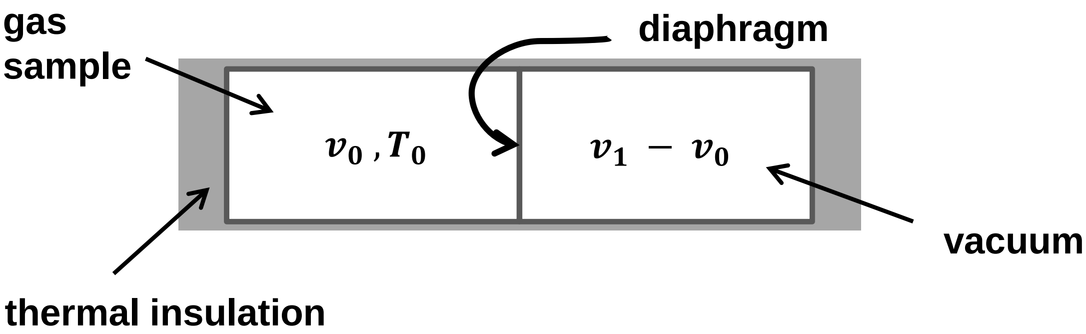
for a reversible process, $c_v = \left(\frac{\partial u}{\partial T}\right)_v$

$$\therefore\ \left(\frac{\partial u}{\partial v}\right)_T = -c_v \left(\frac{\partial T}{\partial v}\right)_u$$

Then how can we keep u constant during the expansion?

5.1 The Gay-Lussac-Joule Experiment

$du = \underbrace{\delta q}_{\substack{=0 \\ \text{(adiabatic)}}} - \underbrace{\delta w}_{\substack{=0 \\ \text{(no work)}}} \Rightarrow$ free expansion



$$T_1 = T_0 + \int_{v_0}^{v_1} \left(\frac{\partial T}{\partial v}\right)_u dv, \quad \eta \equiv \left(\frac{\partial T}{\partial v}\right)_u$$: Joule's coefficient

From Joule's experimental result,

$$|\eta| = \left|\left(\frac{\partial T}{\partial v}\right)_u\right| < 0.001 \text{ K kilomole m}^{-3}$$

5.1 The Gay-Lussac-Joule Experiment

for a Van der Waals gas, (Problem 5-3)

$$\eta = -\frac{a}{v^2 c_v}$$

for an ideal gas,

by using the equation $du = Tds - Pdv$,

$$\left(\frac{\partial u}{\partial v}\right)_T = T\left(\frac{\partial s}{\partial v}\right)_T - P = T\left(\frac{\partial P}{\partial T}\right)_v - P = T\,[\frac{\partial}{\partial T}\left(\frac{RT}{v}\right)]_v - P$$

$$= \frac{RT}{v} - P = 0$$

Then $u = u(T)$

5.1 The Gay-Lussac-Joule Experiment

for a real gas,

by using the equation $dq = \left(\frac{\partial u}{\partial T}\right)_v dT + \left[\left(\frac{\partial u}{\partial v}\right)_T + P\right] dv$ divide by the temperature T,

$$\frac{dq}{T} = \frac{1}{T}\left(\frac{\partial u}{\partial T}\right)_v dT + \frac{1}{T}\left[\left(\frac{\partial u}{\partial v}\right)_T + P\right] dv$$

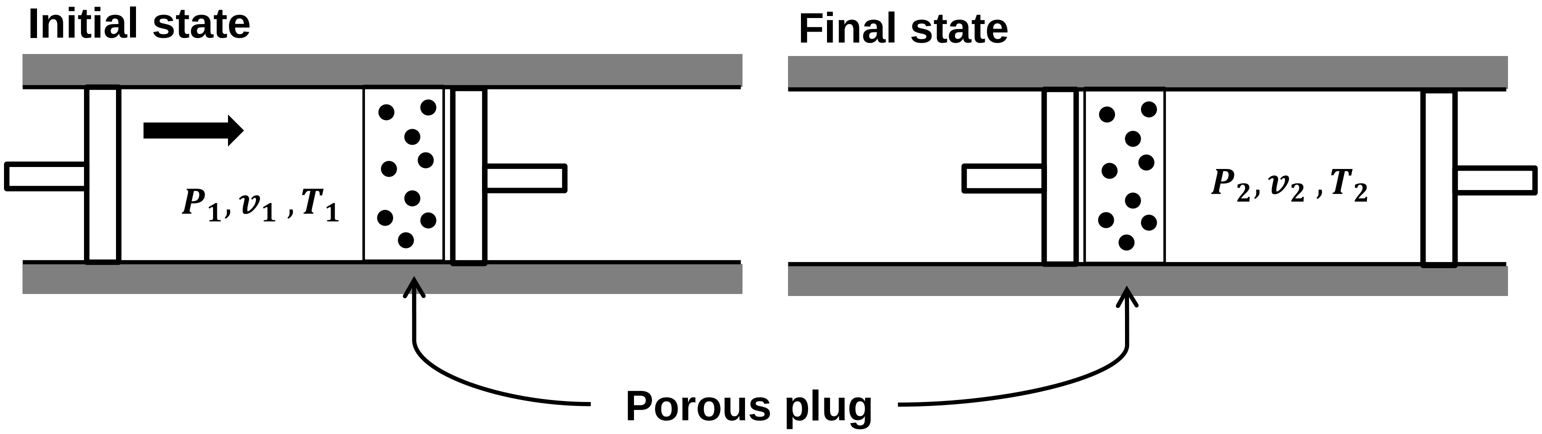
$$\frac{\partial}{\partial v}\left(\frac{1}{T}\frac{\partial u}{\partial T}\right) = \frac{\partial}{\partial T}\left[\frac{1}{T}\left(\frac{\partial u}{\partial v} + P\right)\right]$$

$$\frac{1}{T}\frac{\partial^2 u}{\partial v \partial T} = -\frac{1}{T^2}\left(\frac{\partial u}{\partial v} + P\right) + \frac{1}{T}\frac{\partial^2 u}{\partial v \partial T} + \frac{1}{T}\frac{\partial P}{\partial T}$$

$$\left(\frac{\partial u}{\partial v}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_v - P$$

5.2 The Joule-Thomson Experiment

Since the process takes place in an insulated cylinder,



$$\delta q = 0$$

specific work done in forcing the gas through the plug, $w_1 = \int_{v_1}^{0} P_1 \, dv = -P_1 v_1$

specific work done by the gas in the expansion, $w_2 = \int_{0}^{v_2} P_2 \, dv = P_2 v_2$

5.2 The Joule-Thomson experiment

The total work, $w = w_1 + w_2 = P_2 v_2 - P_1 v_1 = u_1 - u_2$

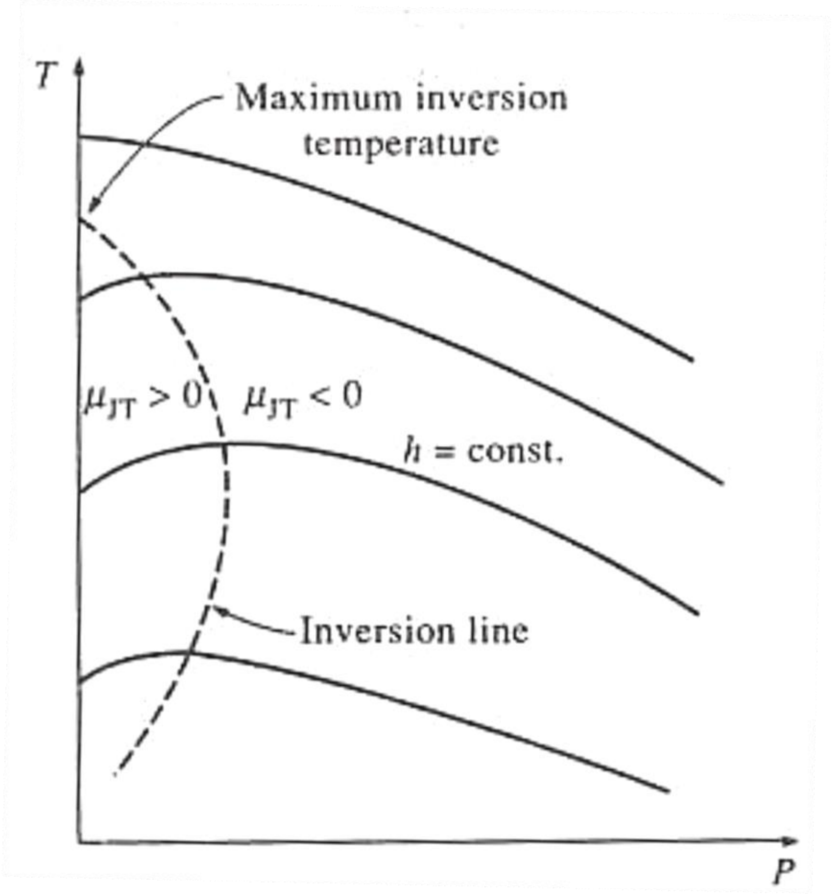
$$u_1 + P_1 v_1 = u_2 + P_2 v_2 \quad \Leftrightarrow \quad \underline{h_1 = h_2}$$

constant

Thus, a throttling process occurs at constant enthalpy.

5.2 The Joule-Thomson experiment

Joule-Thomson coefficient



$$\mu_{JT} \equiv \left(\frac{\partial T}{\partial P}\right)_h$$

the point where $\mu_{JT} = 0$ is called inversion point.

from $h = h\,(T, P)$,

$$dh = \left(\frac{\partial h}{\partial T}\right)_P dT + \left(\frac{\partial h}{\partial P}\right)_T dP$$

$$\mu_{JT} \equiv \left(\frac{\partial T}{\partial P}\right)_h = \left[\frac{T_2 - T_1}{P_2 - P_1}\right]_h$$

$$T_2 = T_1 - \mu(P_2 - P_1)$$

The gas is cooling when the μ is positive

and heating when the μ is negative

5.2 The Joule-Thomson experiment

Joule-Thomson coefficient

$$\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_h = -\left(\frac{\partial T}{\partial h}\right)_P \left(\frac{\partial h}{\partial P}\right)_T = \frac{1}{c_P}\left[T\left(\frac{\partial v}{\partial T}\right)_P - v\right]$$

for an ideal gas, $\mu_{JT} = 0,$

$$\left(\frac{\partial h}{\partial P}\right)_T = 0 \text{ and } h = h\,(\,T\,)$$

for a Van der Waals gas, $P = \frac{RT}{v-b} - \frac{a}{v^2}$

$$\mu_{JT} = \frac{1}{c_P}\left[\frac{\frac{2a}{RT}\left(1-\frac{b}{v}\right)^2 - b}{1-\frac{2a}{vRT}\left(1-\frac{b}{v}\right)^2}\right]$$

If $\mu_{JT} = 0,\ T_i = \frac{2a}{bR}\left(1-\frac{b}{v}\right)^2$

5.3 Heat engines and the Carnot cycle

Carnot cycle

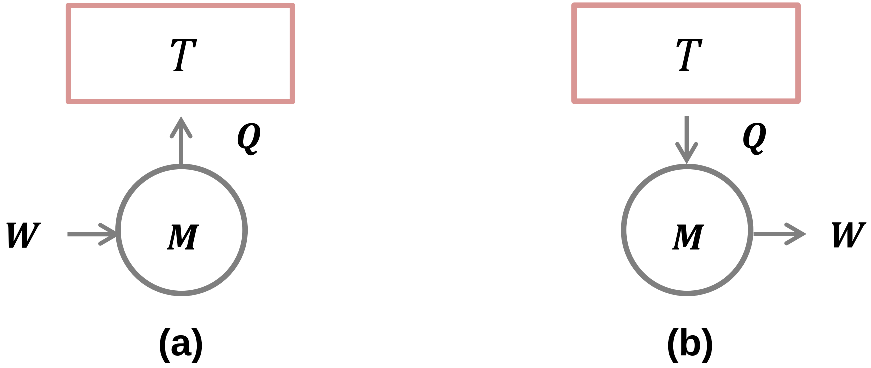


Fig. The concept of a heat engine.

In (a), work is done on the system and is converted to heat.

In (b), heat is extracted from a reservoir and is converted to mechanical work.

This configuration is not possible.

5.3 Heat engines and the Carnot cycle

Carnot cycle

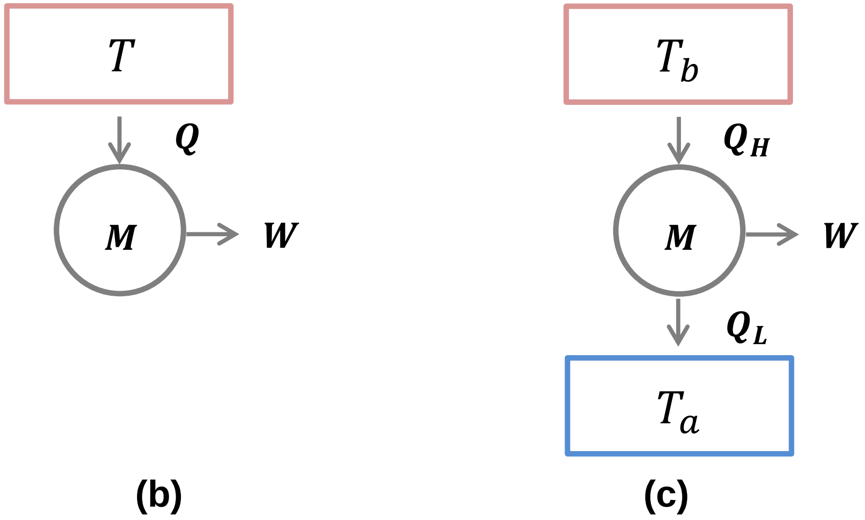


Fig. The concept of a heat engine.

Can the work done by the system be equal to the heat in?

The second law of thermodynamics states ***unequivocally*** that it is impossible to construct a perfect heat engine.

Thus case (b) must be modified as case (c)

5.3 Heat engines and the Carnot cycle

Clausius statement

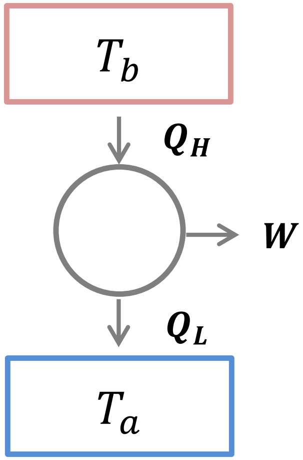
It is impossible to construct a device that operates in a cycle and whose sole effect is to transfer heat from a cooler body to a hotter body.

Kelvin-Planck statement

It is impossible to construct a device that operates in a cycle and produces no other effect than the performance of work and the exchange of heat with a single reservoir.

5.3 Heat engines and the Carnot cycle

Carnot cycle



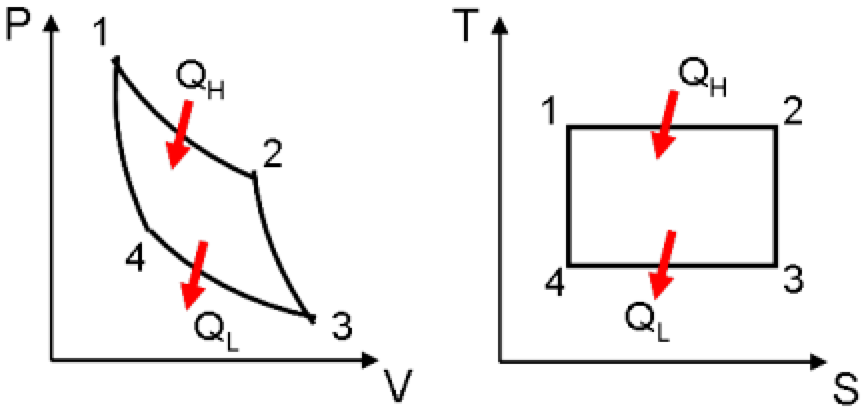


Fig. P-V and T-S diagrams of Carnot cycle.

1 – 2 : isothermal expansion

2 – 3 : adiabatic expansion

3 – 4 : isothermal compression

4 – 1 : adiabatic compression

5.3 Heat engines and the Carnot cycle

The efficiency of the engine,

$$\eta = \frac{W}{Q_H} = \frac{|W|}{|Q_H|} = \frac{\text{output}}{\text{input}}$$

Applying the first law to the system,

$$\Delta U = Q_H + Q_L - W = |Q_H| - |Q_L| - |W|$$

Since the system is in a cyclical process, $\Delta U = 0$. Then,

$W = Q_H + Q_L$ or $W = |Q_H| - |Q_L|$

Substituting the equations,

$$\eta = \frac{Q_L + Q_H}{Q_H} = 1 + \frac{Q_L}{Q_H} = 1 - \frac{|Q_L|}{|Q_H|}$$

5.3 Heat engines and the Carnot cycle

for an ideal gas, $Pv = RT\ , u = u\,(\,T\,)\ ,$

for isothermal process, $Q_H = W_{12} = n\bar{R}\,T_b\,\ln\frac{V_2}{V_1}$

$$Q_L = W_{34} = n\bar{R}\,T_a\,\ln\frac{V_4}{V_3}$$

$$\Rightarrow \quad \frac{Q_H}{Q_L} = -\frac{T_b}{T_a}$$

for adiabatic process, $PV^{\gamma} = constant\ ,$

$$T_b\,V_2{}^{\gamma-1} = T_a\,V_3{}^{\gamma-1}$$

$$T_b\,V_1{}^{\gamma-1} = T_a\,V_4{}^{\gamma-1}$$

$$\Rightarrow \quad \frac{V_2}{V_1} = \frac{V_3}{V_4}$$

$$\left(\begin{aligned} s_2 - s_1 &= c_v\ln\frac{T_2}{T_1} + R\ln\frac{v_2}{v_1} \\ &= c_p\ln\frac{T_2}{T_1} - R\ln\frac{P_2}{P_1} = 0 \\ c_v = \frac{1}{\kappa-1}R, &\qquad c_p = \frac{\kappa}{\kappa-1}R \\ \frac{P_2}{P_1} &= \left(\frac{v_2}{v_1}\right)^{\kappa} \end{aligned}\right)$$

The efficiency of the Carnot cycle, $\eta = 1 + \frac{Q_L}{Q_H} = 1 - \frac{T_a}{T_b}$

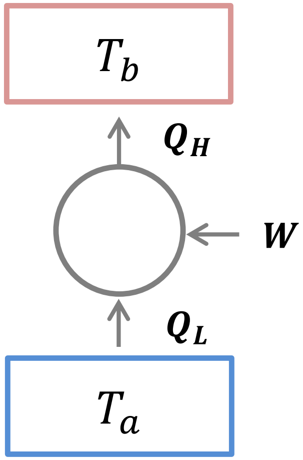
5.3 Heat engines and the Carnot cycle

Carnot engine has the maximum efficiency for any engine that one might design.

1. Carnot engine operates between two reservoirs and that it is reversible.
2. If a working substance other than an ideal gas is used, the shape of curves in the P-V diagram will be difference.
3. The efficiency would be 100 percent if we were able to obtain a low temperature reservoir at absolute zero. →However this is forbidden by the third law.

5.3 Heat engines and the Carnot cycle

Carnot refrigerator



Reverse process of Carnot engine

Coefficient of performance(COP)

$$\mathrm{COP} \equiv -\frac{Q_L}{W} = \frac{|Q_L|}{|W|} = \frac{|Q_L|}{|Q_2| - |Q_L|} = \frac{T_1}{T_2 - T_1}$$

We introduce a minus sign in order to make the COP a positive quantity :

The heat Q_L is extracted from the low temperature reservoir and W is the work done on the system. Q_L is positive (heat flow ***into*** the system) and W is negative (work done ***on*** the system)

5.3 Heat engines and the Carnot cycle

Typical refrigerator

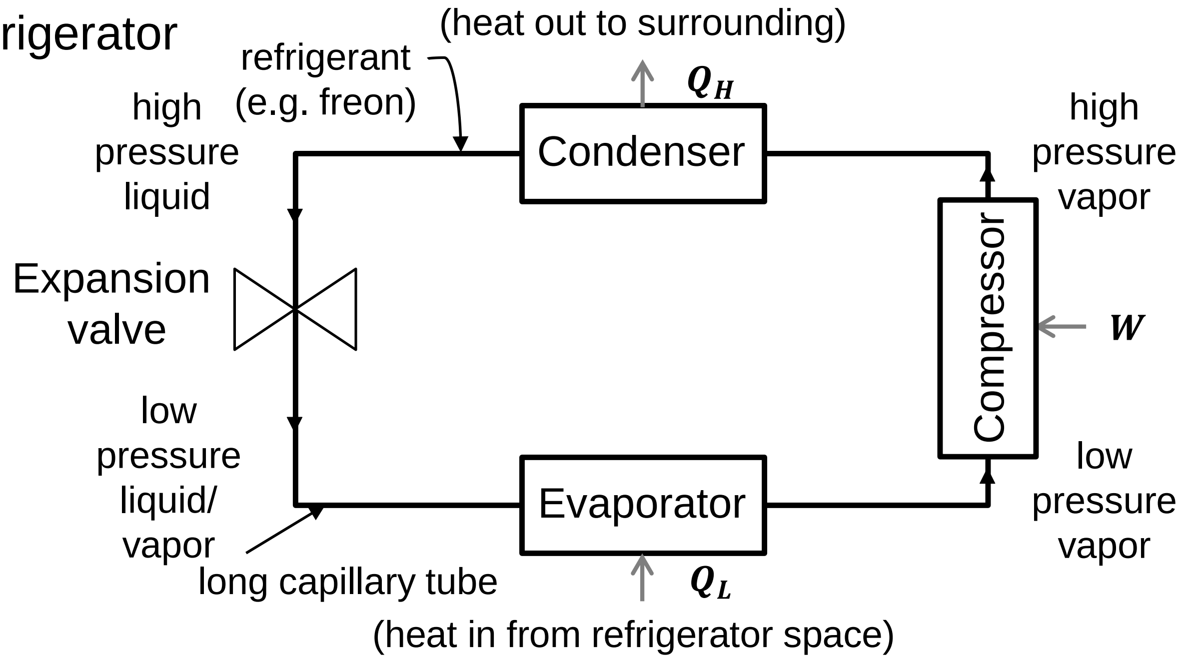


Fig. Schematic diagram of a typical refrigerator

1. The refrigerant is a substance chosen to be a saturated liquid at the pressure and temperature of condenser.
2. The liquid undergoes a throttling process in which it is cooled and is partially vaporized.

5.3 Heat engines and the Carnot cycle

Typical refrigerator

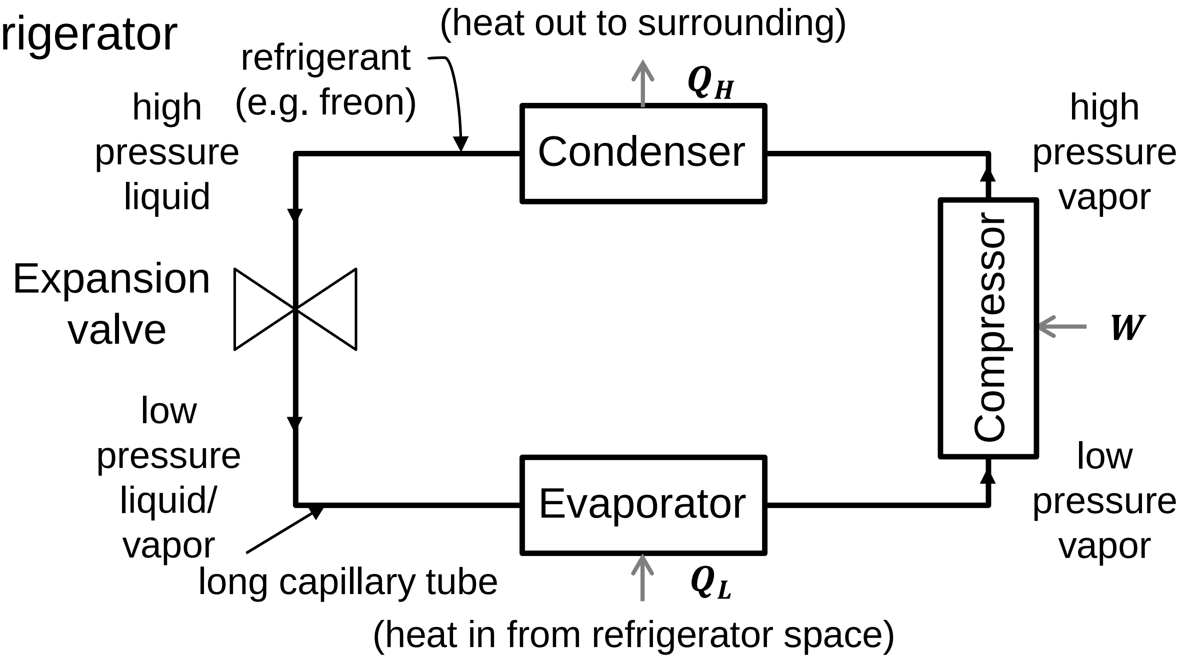


Fig. Schematic diagram of a typical refrigerator

3. The vaporization is completed in the evaporator: the heat is absorbed by the refrigerant from the low temperature reservoir (the interior refrigerator space).
4. The low pressure vapor is then adiabatically compressed and isobarically cooled until it becomes a liquid once again.

5.3 Heat engines and the Carnot cycle

Typical refrigerator

Refrigerator are designed to extract as much heat as possible from a cold reservoir with small expenditure of work.

The coefficient of performance of a household refrigerator is in the range of 5 to 10.