

Equilibrium and temperature

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Thermodynamic variables are linked by an equation of state:

$$f(p, V, T) = 0$$

For an ideal gas we can write:

$$pV = nRT \rightarrow pV - nRT = 0$$

For a non ideal gas:

$$\left(p - \frac{n^2}{V^2}a\right)(V - nb) = nRT$$

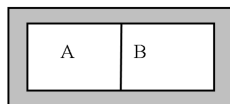
Where a and b are constants dependant on the gas.

We study thermodynamic systems, where we look at a small area (system) with the surroundings being the rest of the universe

We can combine multiple systems of interest into a composite system.

An isolated system is one with no interactions with the surroundings.

We can consider an isolated composite system



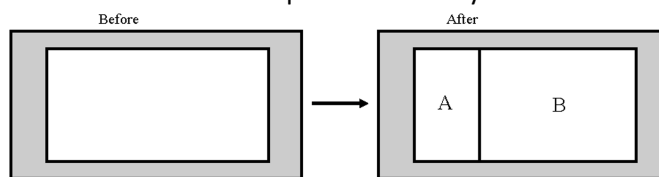
We look at several variables in this system:

Pressure, p ; Temperature, T ; Volume, V ; Moles, n ; Density, ρ

We can divide these properties:

Intensive - equal in whole system

Extensive - not equal for whole system



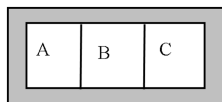
In this example, a system has a wall (with 0 volume) placed in it to separate it into 2 systems.

p, T and ρ stay the same, so are intensive properties.

V and n are not equal for each system, so are extensive.

We can allow different systems in a composite system to interact depending on the wall placed between them.

We can allow thermal contact with a diathermal wall, which allows transfer of heat. If a wall does not allow transfer of heat it is adiabatic.



0th law of thermodynamics: If A and C are both in thermal equilibrium with B ($T_A = T_B, T_C = T_B$), then they are in thermal equilibrium with each other ($T_A = T_C$)

Temperature is a property that defines if a system is in thermal equilibrium, which occurs when there is no net transfer of energy.

We can allow mechanical contact by using a moveable or flexible wall.

At equilibrium $p_A = p_B$

Moveable walls allow transfer of energy in the form of work, $W = F \times d$

We can allow mass contact using a permeable wall.

At equilibrium $\rho_1 = \rho_2$

In thermodynamics we look at what the new equilibrium will be after the removal of a constraint.

Thermodynamics predicts the result of the change in equilibrium states for composite

systems. This passage is called a process.

A quasistatic process involves a succession of equilibrium states.

A reversible process is a quasistatic process with no dissipating forces (i.e. No friction. If this is not the case, the process is irreversible.

We can define heat capacity more rigorously.

If a system has a temperature of T and we add an energy Q , the temperature will increase by an amount ΔT to a total of $T + \Delta T$. Therefore $\Delta T \propto Q$.

Heat capacity, C , is the rate at which temperature changes as energy is increased:

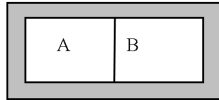
$$Q = C\Delta T \rightarrow C = \frac{Q}{\Delta T}$$

$$\lim_{\Delta T \rightarrow 0} \frac{Q}{\Delta T} = \frac{dQ}{dT}$$

Specific heat capacity, c , is the heat capacity per mass, and so:

$$Q = mc\Delta T$$

We can use heat capacity to find how the temperatures in a composite system change.



If A and B are initially separated by adiabatic wall, and have temperatures and heat capacity of T_A, T_B, C_A, C_B , what will the final temperature, T_f be if the wall is replaced with a diathermal wall?

Conservation of energy $Q_A = -Q_B$, using $Q = C\Delta T$:

$$C_A(T_f - T_A) = -C_B(T_f - T_B)$$

$$T_f(C_A + C_B) = C_B T_B + C_A T_A \rightarrow T_f = \frac{C_B T_B + C_A T_A}{C_A + C_B}$$

$$T_f = \frac{m_B c_B T_B + m_A c_A T_A}{m_A c_A + m_B c_B}$$

We can define a value:

$$\epsilon = \frac{C_B}{C_A} = \frac{m_B c_B}{m_A c_A}$$

If the heat capacity of B is much larger than A, $\epsilon \ll 1$, and so we can write our final temperature as:

$$T_f = \frac{m_B c_B T_B + m_A c_A T_A}{m_A c_A + m_B c_B} \approx \frac{m_A c_A}{m_A c_A} T_A \rightarrow T_f = \frac{T_A + \epsilon T_B}{1 + \epsilon}$$

As $\epsilon \rightarrow 0$, we find $T_f = T_A$. When this occurs, we say that A acts as a thermal reservoir (or heat bath) for B

We need a method to assign and determine temperature.

In a thermometer, the distance the liquid used increases as temperature increases, due its volume increasing. We can write:

$$X = a + cT_x$$

A gas thermometer raises a weight as the temperature increases.

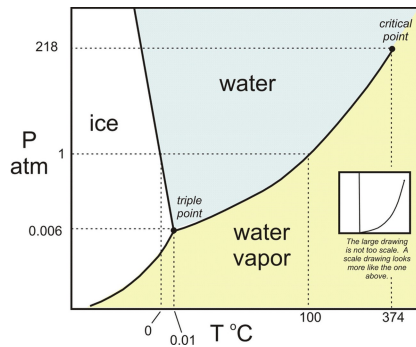
$$pV = nRT, \rightarrow p \propto T$$

When a material undergoes a phase change, energy added to it will not increase its temperature.

This occurs because added energy is used to break/form intermolecular bonds.

We define the amount of energy at a phase change as latent heat, L .

$$Q = Lm$$



$$T_x = 273.16 \left(\frac{x}{x_{TP}} \right)$$

At 1 atmosphere, the ice point, (ice and water coexist), **273.15K (0°C)**

At 1 atmosphere, the Steam point, **373.15K (100°C)**

Triple point (All 3 states can exist) **273.16K (0.01°C)**

We can look at how heat energy moves over time.

Consider a rectangular rod with cross sectional area A and length L . At one end we have a cold reservoir at a temperature of T_c . At the other is a hot object initial at T_i with heat capacity C . The rate of change of heat with respect to time is:

$$\dot{Q} = \frac{dQ}{dt} = -kA \frac{dT}{dx}$$

Where k is the thermal conductivity. \dot{Q} is called heat flux.

We now define T_h as the temperature at the other end of the rod. If we consider the heat flux of the rod we can write:

$$\dot{Q} = -kA \frac{dT}{dx} = -kA \frac{T_h - T_c}{L}$$

$$dQ = c dT \therefore \frac{dQ}{dT} = c \frac{dT_h}{dt}$$

$$\frac{dT_h}{dt} = -\frac{kA}{cL} (T_h - T_c)$$

If we define $T_0 = T_h - T_c$, as T_c is a reservoir it is constant, $\therefore dT_0 = dT_h$

$$\frac{dT_0}{dt} = -\frac{kA}{cL} T_0 \rightarrow T_0 = B e^{-\frac{kA}{cL} t}$$

To find the constant B we look at the temperatures at $t = 0$

$$t = 0, T_h = T_i, \therefore T_0 = T_i - T_c$$

$$B = T_c - T_i, \rightarrow T_0 = (T_c - T_i) e^{-\frac{kA}{cL} t}$$

$$T_h = T_c + (T_c - T_i) e^{-\frac{kA}{cL} t}$$

And so we can find the temperature of the rod at any given time.

We define the 1st law of thermodynamics:

$$\Delta U = Q + W$$

Where ΔU is the change in internal energy. U is a function of the thermodynamic variables, and is called a state function:

$$U = U(p, T, n) = n u(p, T)$$

For an ideal gas the internal energy per mole is dependant on only temperature:

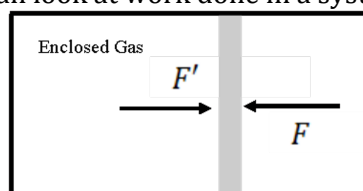
$$U = U(T)$$

We can write the first law in differential form:

$$dU = \bar{d}W + \bar{d}Q$$

Where the bar on the d represents an inexact differential.

We can look at work done in a system:



We shall assume this process is quasistatic, and so $F = F'$. If there is no friction then the process is reversible, and all work goes into the gas:

$$dW = -F dx, dW = -pA dx$$

$$F dx = p dV$$

Using the first law and our equation for work done, we can redefine heat capacity C_V and C_p , the heat capacity at a constant volume V or pressure p respectively:

$$dU = dQ + dW = dQ - p dV$$

$$pdV = 0 \text{ as constant volume } \therefore dU = dQ$$

$$C_V = \left(\frac{dU}{dT} \right)_V = \frac{dQ_V}{dT}$$

$$C_p = \left(\frac{dU}{dT} \right)_p = \frac{dQ_p}{dT}$$

We can use the 1st law in a different form:

$$dW = -p dV, dQ = CdT, dU = dQ + dW$$

$$dU = dQ_p - p dV$$

$$\rightarrow dQ_p = dU + p dV = C_p dT$$

We can now define enthalpy $H = U + pV$ (another state function - $H = nh(p, V)$), and use it to redefine C_p :

$$dH = dU + p dV + V dp$$

$$p \text{ is constant } \therefore dp = 0$$

$$dH = dU + p dV = C_p dT$$

$$\rightarrow C_p = \left(\frac{dH}{dT} \right)_p$$

We can analyse an ideal gas by using C_V , C_p , and the first law

$$\text{Ideal gas } \therefore U = nu(T)$$

$$C_V = \left(\frac{dU}{dT} \right)_V \rightarrow C_V = n \left(\frac{du}{dT} \right)_V = n \frac{du}{dT} \quad (U \propto f(T) \therefore V \text{ has no effect})$$

$$C_p = \frac{dQ_p}{dT}$$

$$C_p$$

$$dU = dQ + dW, \quad C_V dT = dU, \quad dW = -p dV$$

$$\therefore C_V dT = dQ - p dV \rightarrow dQ = C_V dT + p dV$$

$$\frac{dQ_p}{dT} = C_V + p \left(\frac{dV}{dT} \right)_p$$

$$pV = nRT \rightarrow V = \frac{nRT}{p} \rightarrow \left(\frac{dV}{dT} \right)_p = nR$$

$$\frac{dQ_p}{dT} = C_p = C_V + nR$$

$$C_p - C_V = nR$$

We can further look into state functions and what they are.

A state functions value is independent of the path taken:

$$\Delta U = U(p_B, V_B) - U(p_A, V_A)$$

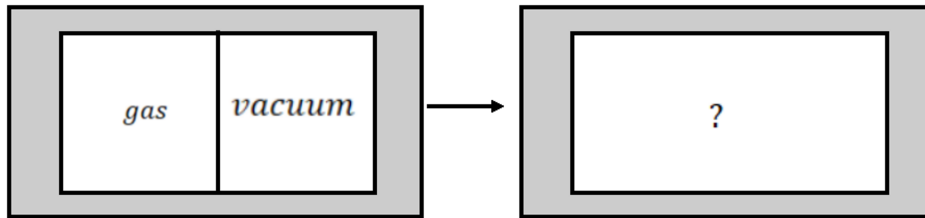
However, Q and W are not state functions and so their value is path dependent.

$$\Delta U = Q + W$$

We can talk about the energy in the system, but not the work/heat in a system, as work and heat are forms of energy transfer.

If we plot a graph with respect to pressure and volume, we use a solid line for reversible processes, and irreversible processes with a dashed line.

We can look at thermodynamics processes in an ideal gas



Removing the wall would allow the gas to fill the vacuum. This is adiabatic free expansion, and is an irreversible process.

We can look at the first law, $\Delta U = Q + W$. As there is no opposing force, and no added heat, $Q = 0, W = 0 \therefore \Delta U = 0$

As $U = U(T)$ this result means that the temperature is constant.

$$pV = nRT \rightarrow \frac{pV}{n} = \text{constant}$$

We can study thermodynamic processes where one variable is kept constant. We name these depending on what is fixed:

Constant Pressure - Isobaric

Constant Volume - Isovolumetric

Constant Temperature - Isothermal

In a reversible process, there is no work done.

An example of a reversible isobaric process would be to add heat to a system with a piston that can move, resulting in no change in pressure.

An isovolumetric example could be a system with a fixed wall, such that adding heat won't change volumes.

An isothermal example would be adding heat to an enclosed system with a moveable piston initially at equilibrium with the surroundings. Added heat would cause the volume to increase while the pressure decreases. As $T \propto pV$ this means temperature can stay constant

For an irreversible process of this type we can find the work done.

$$W = \int dW = - \int_{V_i}^{V_f} p \, dV \quad (dW = -p \, dV)$$

$$\text{Isobaric, constant } p \rightarrow W = -p \int_{V_i}^{V_f} dV = -p[V_f - V_i]$$

$$\text{Isovolumetric, constant } V \therefore dV = 0 \rightarrow W = 0$$

$$\text{Isothermal, constant } T, p = \frac{nRT}{V} \rightarrow W = - \int_{V_i}^{V_f} \frac{nRT}{V} \, dV = -nRT \ln \left(\frac{V_f}{V_i} \right)$$

We can calculate the change in internal energy of a gas:

For an ideal monatomic gas, the internal energy is $U = \frac{3}{2}nRT = \frac{3}{2}pV$

We can use the first law to find the heat added from work:

$$\Delta U = Q + W, \quad Q = \Delta U - W$$

The change in internal energy is, ΔU can be found by:

$$\Delta U = U_f - U_i = \frac{3}{2}p_f V_f - \frac{3}{2}p_i V_i$$

$$\therefore Q = \frac{3}{2}p_f V_f - \frac{3}{2}p_i V_i - W$$

For an isobaric process:

$$W = -p(V_f - V_i) = -p\Delta V$$

$$V = \frac{nRT}{p} \quad \frac{nR}{p} \text{ is constant, } \therefore \Delta V = \frac{nR}{p} \Delta T$$

$$\rightarrow W = -nR\Delta T$$

If we equate this to our change in internal energy:

$$Q = \Delta U - W, \Delta U = C_V \Delta T, W = -nR\Delta T$$

$$Q = C_V \Delta T + nR\Delta T = (C_V + nR)\Delta T$$

$$\text{For ideal gas, } C_p - C_V = nR, C_p = \frac{5}{2}nR$$

$$Q = C_p \Delta T = \frac{5}{2} nR \Delta T$$

Another way of finding heat added for an isobaric process:

$$\Delta U = Q + W, W = -p \Delta V \rightarrow Q = \Delta U + p \Delta V$$

$$\text{From enthalpy: } H = U + pV, \Delta H = \Delta U + p \Delta V + V \Delta p$$

$$\Delta p = 0$$

$$\Delta H = \Delta U + p \Delta V = Q$$

$$\left(\frac{dH}{dT} \right)_p = C_p, \therefore \Delta H = C_p \Delta T$$

$$\rightarrow C_p \Delta T = Q, Q = \frac{5}{2} nR \Delta T$$

For an isovolumetric process:

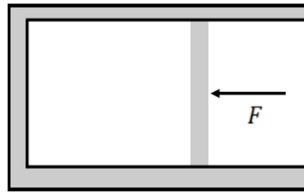
$$W = 0 (dV = 0), Q = \Delta U - W$$

$$Q = \Delta U, \quad \Delta U = C_V \Delta T, \quad C_V = \frac{3}{2} nR$$

$$\therefore Q = \frac{3}{2} nR \Delta T$$

An adiabatic process is one where no heat energy is added or taken from the system. This means $Q = 0 \therefore \Delta U = W$.

For an ideal gas we know $\Delta U = \frac{3}{2} nR \Delta T, \Delta T = T_f - T_i$ so can calculate the work done in an adiabatic process.



$$pV = nRT \rightarrow T = \frac{pV}{nR} \therefore \Delta T = \left(\frac{p_f V_f}{nR} - \frac{p_i V_i}{nR} \right)$$

$$\therefore W = \Delta U = \frac{3}{2} nR (V_f - V_i)$$

In an adiabatic process:

$$pV^\gamma = A, TV^{\gamma-1} = B$$

Where A and B are constants. We can prove this:

$$dU = dW, dU = C_V dT, dW = -p dV$$

$$C_V dT = -p dV, pV = nRT \rightarrow p = \frac{nRT}{V}$$

$$C_V dT = -\frac{nRT}{V} dV \rightarrow \int \frac{C_V}{T} dT = - \int \frac{nR}{V} dV$$

$$C_V \ln(T) = -nR \ln(V) + c_1$$

$$\text{Let } \gamma = \frac{C_p}{C_V}, C_p - C_V = nR \therefore \frac{nR}{C_V} = \frac{C_p - C_V}{C_V} = \gamma - 1$$

$$\ln(T) = -(\gamma - 1) \ln(V) + c_2 \rightarrow \ln(T) + (\gamma - 1) \ln(V) = c_2$$

$$TV^{\gamma-1} = c_2 (= B)$$

$$pV = nRT \rightarrow T = \frac{pV}{nR} \therefore \left(\frac{pV}{nR} \right) V^{\gamma-1} = c_2$$

$$pV^\gamma = c_3 (= B)$$

A polytropic process is when in the form $pV^k = \text{constant}$, where k is a constant the depends on the process:

$$k = 0 \text{ is Isobaric} \rightarrow pV^0 = c \therefore p = c$$

$$k = 1 \text{ is Isothermal} \rightarrow pV = c = nRT \therefore T \text{ is constant}$$

$$k = \gamma = \frac{C_p}{C_V} \text{ is Adiabatic}$$

$$k = \infty \text{ is Isovolumetric, } pV^\infty = c \therefore \Delta V = 0$$

We can calculate the work done in an adiabatic process another way, with a start point of $p_1 V_1 \rightarrow p_2 V_2$:

$$\text{Adiabatic } \therefore Q = 0 \therefore \Delta U = W$$

If expansion $\Delta V > 0 \rightarrow \Delta U = -p\Delta V < 0$

If compression, $\Delta V < 0 \rightarrow \Delta U = -p\Delta V > 0$

$$W = - \int_{V_1}^{V_2} p dV, \quad pV^\gamma = c \rightarrow p = cV^{-\gamma}$$

$$W = - \int_{V_1}^{V_2} cV^{-\gamma} dV = - \frac{c}{1-\gamma} [V_2^{1-\gamma} - V_1^{1-\gamma}] = \frac{c}{\gamma-1} \left[\frac{V_2}{V_2^\gamma} - \frac{V_1}{V_1^\gamma} \right]$$

$$p_1 V_1^\gamma = p_2 V_2^\gamma = c \rightarrow V_n^\gamma = \frac{c}{p_n} \therefore \frac{V_n}{V_n^\gamma} = \frac{p_n V_n}{c}$$

$$W = \frac{1}{\gamma-1} (p_2 V_2 - p_1 V_1), \quad \gamma = \frac{C_p}{C_v} = \frac{\frac{5}{2}nR}{\frac{3}{2}nR} = \frac{5}{3}$$

$$\rightarrow W = \frac{3}{2} (p_2 V_2 - p_1 V_1)$$

The same as our first result.

Example 1. A chamber of constant volume has a mixture of fuel and oxygen combusted inside. The chamber is surrounded by a water bath, which increases in temperature after the combustion.

Has work been done on the system?

$$W = - \int p dV$$

Constant volume, $\therefore dV = 0 \therefore W = 0$, no work done on system.

Has heat been transferred between the system and surroundings?

$$\Delta U = Q + W$$

The temperature of the water rises, so heat has been transferred from the system to the surroundings, $\therefore \Delta U < 0, Q < 0$

What is the sign of the internal change of energy of the system?

Heat has left the system, $\therefore Q < 0$ so is negative, as $W = 0, \Delta U = Q$, and so $\Delta U < 0$, so is negative.

Example 2. Show that for a reversible adiabatic expansion:

$$\frac{T}{p^{\frac{1}{1-\gamma}}} = k \text{ (constant)}$$

$$pV^\gamma = \text{const}, \quad \text{and } pV = nRT \rightarrow V = \frac{nRT}{p}$$

$$p \left(\frac{nRT}{p} \right)^\gamma = (nR)^\gamma \frac{T^\gamma}{p^{\gamma-1}} = \text{const}, \quad nR \text{ is const} \rightarrow \frac{T^\gamma}{p^{\gamma-1}} = \text{const}$$

$$\sqrt[\gamma]{\frac{T^\gamma}{p^{\gamma-1}}} = \frac{T}{p^{\frac{1}{1-\gamma}}} = k$$

Example 3. A thermonuclear explosion produces a sphere of gas with radius 15m at a temperature of 30000K. Estimate the radius when the temperature is 3000K, assuming that $\gamma = 1.4$ and the gas remains spherical

$$V_1 = \frac{4}{3}\pi(15)^3 = 1.41 * 10^4, T_1 = 30000$$

$$V_2 = ?, T_2 = 3000, \gamma = 1.4$$

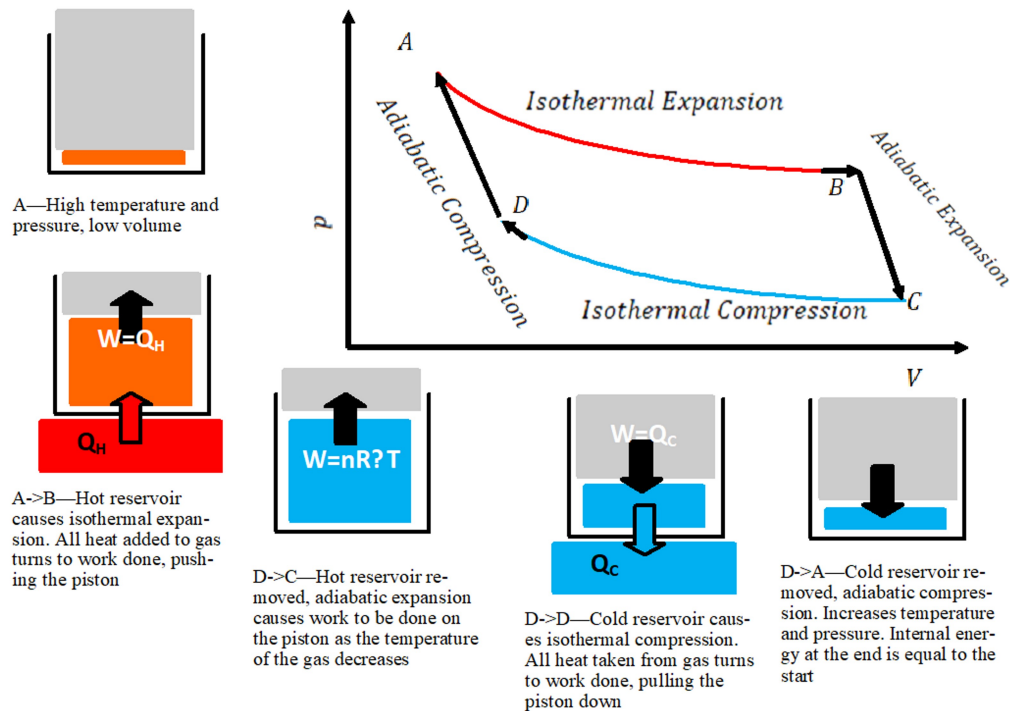
$$TV^{\gamma-1} = \text{const}$$

$$\therefore 30000 * (1.41 * 10^4)^{0.4} = 3000V_2^{0.4}$$

$$V_2 = \sqrt[0.4]{10 * (1.41 * 10^4)^{0.4}} = 4.45 * 10^6$$

$$r_2 = \sqrt[3]{\frac{3V_2}{4\pi}} = 102m$$

A Carnot engine is an engine with a theoretical maximum efficiency. It causes work to be done via a transfer of heat from a hot reservoir to a cold reservoir:

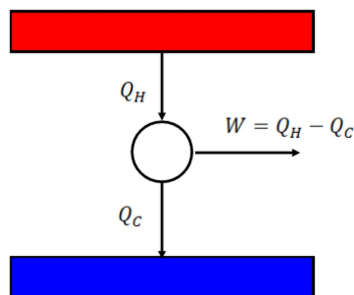


If we start at point A , an isothermal process from $A \rightarrow B$ occurs. Heat is absorbed from the hot reservoir and converted to work

The process from $B \rightarrow C$ is adiabatic. Internal heat is converted to work done.

From $C \rightarrow D$ is isothermal, with external work on gas turned into heat that goes into the cold reservoir.

$D \rightarrow A$ is adiabatic and causes work done on the gas, increasing its internal energy until it is the same as it started with, resulting in a change in internal energy for the whole cycle of $\Delta U = 0$



Over the total cycle the change in internal energy is 0. From the first law:

$$\Delta U = Q + W = 0$$

The total heat exchange for the gas is equal to the difference in heat absorbed at the hot reservoir and the heat emitted at the cold reservoir. As the gas causes work to be done to the surroundings, it is negative, and so:

$$0 = (Q_H - Q_C) - W \rightarrow W = Q_H - Q_C$$

The efficiency is the ratio of the work done and the heat absorbed from the hot reservoir:

$$\eta = \frac{W}{Q_H} = \frac{Q_H - Q_C}{Q_H} = 1 - \frac{Q_C}{Q_H}$$

The efficiency is also equal to:

$$\eta = 1 - \frac{T_C}{T_H}$$

We can prove this by finding the relative heat exchanges at the two reservoirs. The processes at each reservoir ($A \rightarrow B$ & $C \rightarrow D$) are isothermal, and so:

$$\Delta U = Q + W = 0 \therefore Q = -W$$

$$W = -p\Delta V, \quad T \text{ is constant}, \quad p = \frac{nRT}{V}$$

$$\rightarrow W = - \int_{V_i}^{V_f} \frac{nRT}{V} dV = -nRT \ln\left(\frac{V_f}{V_i}\right)$$

$$\therefore Q_H = -nRT_H \ln\left(\frac{V_B}{V_A}\right), \quad Q_C = -nRT_C \ln\left(\frac{V_D}{V_C}\right)$$

We can then find the volumes in terms of each other by looking at the adiabatic processes from $B \rightarrow C$ & $D \rightarrow A$. For an adiabatic process $TV^{\gamma-1}$ is constant.

$$T_A V_A^{\gamma-1} = T_D V_D^{\gamma-1} \rightarrow \frac{T_A}{T_D} = \left(\frac{V_D}{V_A}\right)^{\gamma-1}$$

$$T_C V_C^{\gamma-1} = T_B V_B^{\gamma-1} \rightarrow \frac{T_B}{T_C} = \left(\frac{V_C}{V_B}\right)^{\gamma-1}$$

$$T_A = T_B, T_C = T_D \therefore \frac{T_A}{T_D} = \frac{T_B}{T_C}$$

$$\frac{V_D}{V_A} = \frac{V_C}{V_B} \rightarrow \frac{V_B}{V_A} = \left(\frac{V_D}{V_C}\right)^{-1}$$

$$\therefore Q_C = -Q_H \frac{T_C}{T_H}$$

$$\eta = \frac{Q_H - Q_C}{Q_H} = 1 - \frac{T_C}{T_H}$$

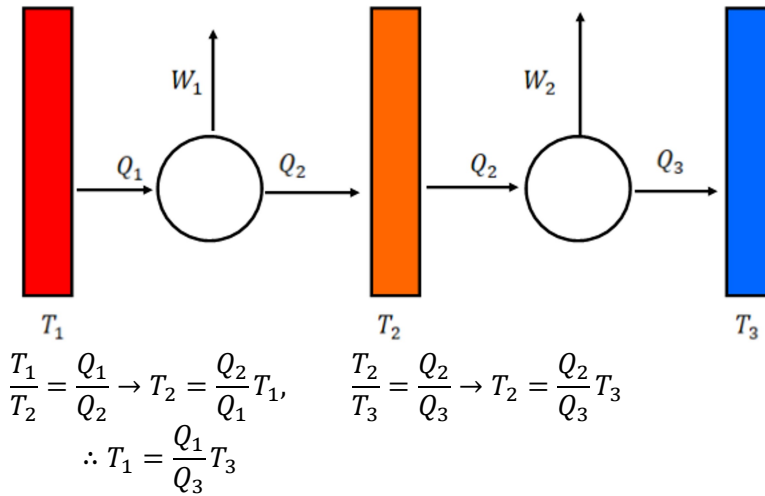
No heat engine operating between 2 reservoirs is more efficiency than a Carnot engine operating between the same reservoirs. The efficiency is independent of the substance used.

We can use the Carnot engine to define Temperature in another way.

We know that the efficiency of a Carnot engine is equal to:

$$\eta = 1 - \frac{Q_C}{Q_H} = 1 - \frac{T_C}{T_H}$$

Consider a string of Carnot engines:

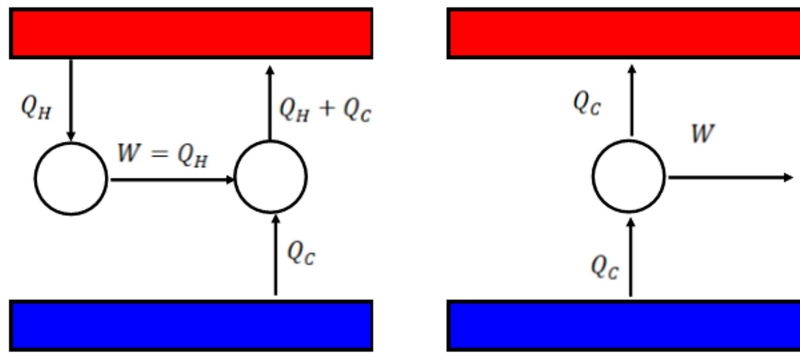


The second law of thermodynamics states *"The total entropy of an isolated system can never decrease over time"*. This can be defined in two ways:

- 1) *"It is impossible to transfer heat spontaneously from a cold reservoir to a hot reservoir in a single cycle without other changes."* - Clausius
- 2) *"A cyclic process whose only effect is the conversion of heat to work is impossible."* - Planck & Kelvin

These two statements are equivalent. We can prove this. First we look at the second statement:

Let us consider the statement to be false. Imagine a composite engine where a process drives a Carnot engine in reverse:

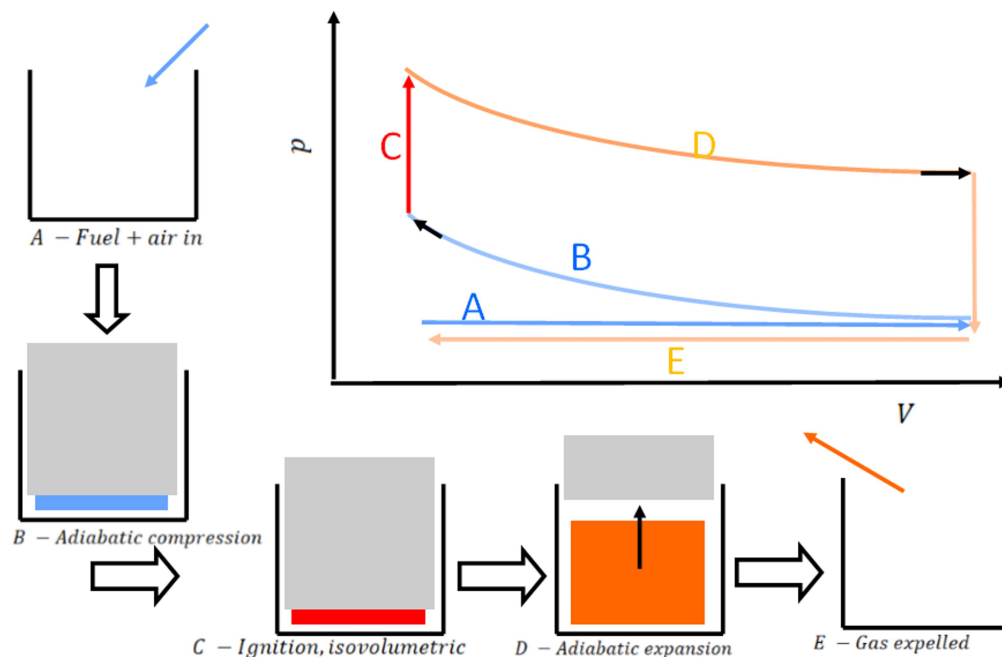


The left diagram shows a complete transfer of heat to work. This work then drives a Carnot engine in reverse. This can be represented by the composite engine on the right. The heat that leaves the system can be found:

$$Q_{out} = Q_{in} - W = Q_H + Q_C - Q_C = Q_C$$

Which defies our first statement.

The Carnot engine is an idealised situation, it is impossible to reach its efficiency. We shall look at, and find the efficiency of, the Otto cycle:



- 1) Fuel and air are drawn into a cylinder (A) and compressed (B) in an adiabatic process.
- 2) At the top of the compression the mixture is ignited, increasing the temperature and pressure.. The volume stays constant and so this is an isovolumetric process (C)
- 3) The higher temperature mixture undergoes adiabatic expansion, and pushes the cylinder. (D)
- 4) Some heat is transferred to the engine, and the burnt gas is expelled (E)

The efficiency can be found:

$$\eta = 1 - \frac{Q_C}{Q_H} = 1 - \frac{C_V(T_E - T_A)}{C_V(T_D - T_B)} = 1 - \frac{(T_E - T_A)}{(T_D - T_B)}$$

We then look at the adiabatic processes to find the temperature differences:

$$\begin{aligned} T_{CD}V_{MAX}^{\gamma-1} &= T_{DE}V_{MIN}^{\gamma-1}, & T_{AB}V_{MIN}^{\gamma-1} &= T_{BC}V_{MAX}^{\gamma-1} \\ V_{MIN}^{\gamma-1}(T_{AB} - T_{DE}) &= T_{MAX}^{\gamma-1}(T_{BC} - T_{CD}) \\ \left(\frac{V_{MIN}}{V_{MAX}}\right)^{\gamma-1} &= \frac{(T_{AB} - T_{DE})}{(T_{BC} - T_{CD})} \\ \rightarrow \eta &= 1 - \left(\frac{V_{MIN}}{V_{MAX}}\right)^{\gamma-1} \end{aligned}$$

The efficiency increases as the maximum volume gets larger than the minimum volume.

This means compressing the gas more gives a larger efficiency, up to a limit of roughly 50%. In reality the other processes decrease the efficiency to 25-30%.

We can now introduce Entropy

In a Carnot engine the processes are reversible, which means:

$$\frac{T_C}{T_H} = \frac{Q_C}{Q_H} \rightarrow \frac{Q_H}{T_H} = \frac{Q_C}{T_C}$$

For an irreversible process Clausius found:

$$\frac{Q_H}{T_H} < \frac{Q_C}{T_C}$$

And so in general for a singular reversible and irreversible processes, and for many processes:

$$\frac{Q_H}{T_H} - \frac{Q_C}{T_C} \leq 0, \quad \sum_i \frac{Q_i}{T_i} \leq 0$$

If we have a continuous process in the form of a closed loop:

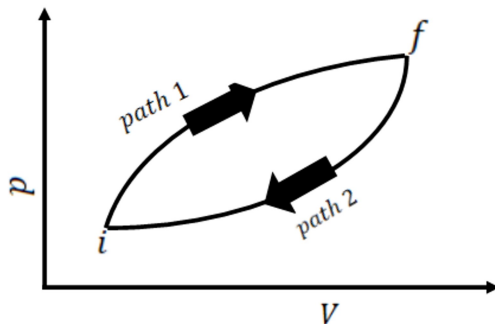
$$\text{Reversible: } \oint \frac{dQ}{T} = 0$$

$$\text{Irreversible: } \oint \frac{dQ}{T} < 0$$

Clausius called this ratio entropy:

$$\frac{dQ}{T} = ds, \quad \text{Reversible } ds = 0, \quad \text{Irreversible } ds < 0$$

Consider a reversible process with a closed path on a pV diagram:

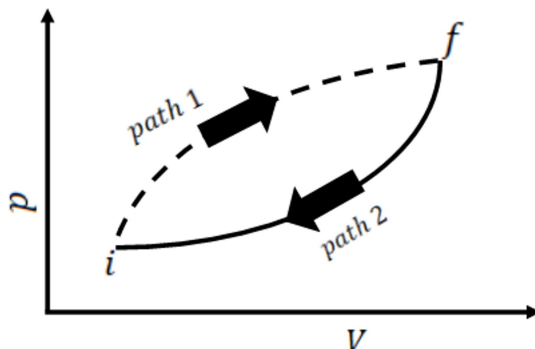


$$\begin{aligned} \int_i^f \frac{dQ_{rev 1}}{T} + \int_f^i \frac{dQ_{rev 2}}{T} &= 0 \\ \rightarrow \int_i^f \frac{dQ_{rev 1}}{T} - \int_i^f \frac{dQ_{rev 2}}{T} &= 0 \\ \therefore \int_i^f \frac{dQ_{rev 1}}{T} &= \int_i^f \frac{dQ_{rev 2}}{T} \end{aligned}$$

The integral is independent of the path, and so entropy is a state function. Entropy, s , is given by:

$$\Delta s = s_f - s_i = \int_i^f \frac{dQ}{T} \leq 0$$

If we instead consider a closed path on a pV diagram, but with one path being irreversible:



$$\begin{aligned} \oint \frac{dQ}{T} &\leq 0 \\ \int_i^f \frac{dQ_{irrev 1}}{T} + \int_f^i \frac{dQ_{rev 2}}{T} &\leq 0 \\ \int_i^f \frac{dQ_{irrev 1}}{T} &\leq \int_i^f \frac{dQ_{rev 2}}{T} = \Delta s \\ \rightarrow \Delta s &\geq \int_i^f \frac{dQ_{irrev 1}}{T} \end{aligned}$$

For an irreversible process a change in entropy must occur. This is the Clausius inequality.

$$\frac{dQ}{T} \leq ds$$

For an infinitesimal irreversible process between 2 equilibrium states a change of entropy occurs that is larger than the ratio of the heat transferred at two reservoirs.

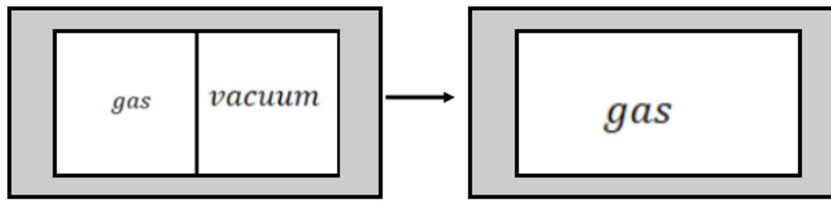
In a thermally isolated system entropy is constant for reversible processes, and increases for irreversible processes.

$$dQ = 0, \quad ds \geq 0$$

Entropy in a thermally isolated system either stays the same or increases, it cannot decrease.

We can look at a statistical interpretation of entropy.

Consider an adiabatic free expansion for 1 mole of a gas doubling in volume



In adiabatic free expansion, $\Delta T = 0$, $Q = 0$. We therefore must find entropy another way:

$$V_f = 2V_i$$

$$dU = dQ + dW \rightarrow dQ = dU - dW \rightarrow dQ = -dW$$

$$\rightarrow dQ = p dV$$

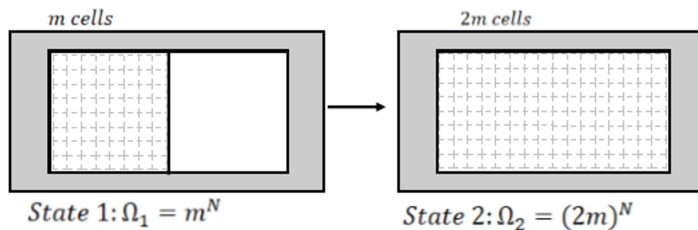
$$\Delta S = \int_{V_i}^{V_f} \frac{dQ}{T} = \int_{V_i}^{V_f} \frac{p dV}{T}$$

$$\frac{1}{T} = \frac{nR}{pV}, V_f = 2V_i \rightarrow \Delta S = \int_{V_i}^{2V_i} \frac{nR}{V} dV$$

$$\rightarrow \Delta S = nR \ln(2)$$

The entropy of the system increases, proving it to be an irreversible process. Boltzmann associated entropy as the transition from a less probable state to a more probable state.

If we divide the box into $2m$ cells, with m cells for each half of the system and let Ω be the number of ways of arranging N atoms into the cells:



Boltzmann stated: $s = k \ln(\Omega)$, where k is Boltzmann's constant.

$$\begin{aligned} \Delta S &= s_2 - s_1 = k [\ln(2m)^N - \ln(m^N)] \\ &= kN \ln(2) = nR \ln(2) \end{aligned}$$

The same result as the adiabatic calculation.

This suggests that entropy related to the number of ways a system can be arranged.

We can combine the first and second laws of thermodynamics.

The first law states:

$$dU = dQ + dW$$

We know in reversible processes:

$$dW = -p dV, \quad dQ = T ds$$

And so

$$dU = T ds - p dV$$

This is true for reversible and irreversible processes as all quantities are state functions.

Temperature dependence of entropy at fixed pressure:

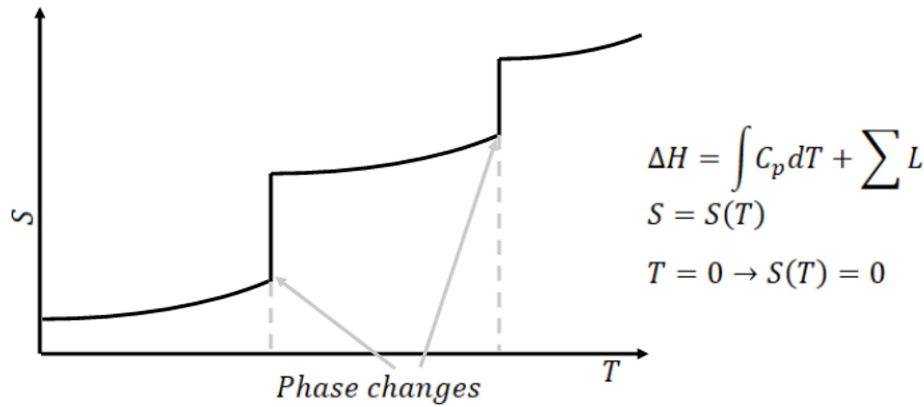
If in a single phase the entropy is:

$$dS = \frac{dQ_{rev}}{T} = C_p \frac{dT}{T}$$

Then at phase transition:

$$\Delta S = \frac{Q_{rev}}{T} = \frac{L}{T} \rightarrow \Delta S = \int_{T_i}^{T_f} \frac{C_p(T)}{T} dT + \sum \frac{L}{T}$$

And so we can find entropy as a function of temperature from measurements of C_p



We can derive ΔH for a constant pressure

$$H = U + pV \rightarrow \Delta H(T) = \Delta U(T) + (pV)(T)$$

$$pV = nRT \therefore \frac{d}{dT}(pV) = \text{const}, \quad T = \frac{\Delta U}{\Delta S} \rightarrow \Delta U = T \Delta S$$

$$\Delta H = \Delta U = T \Delta S = \int C_p dT + \sum L$$

The internal energy can be written as a function of non thermodynamic variables, and is known as the Fundamental Equation of thermodynamics.

The fundamental Equation can be written in two forms. The internal energy as a function of entropy and volume, or entropy as a function of internal energy and volume:

$$U = U(S, V) \rightarrow dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$$

$$S = S(U, V) \rightarrow dS = \left(\frac{\partial S}{\partial U}\right)_V dU + \left(\frac{\partial S}{\partial V}\right)_U dV$$

Which we can combine this with the first law to find temperature as a function of internal energy and entropy, and pressure as a function of internal energy and volume.:

$$dU = dQ + dW = T dS - p dV$$

$$\rightarrow T = \left(\frac{\partial U}{\partial S}\right)_V, \quad p = -\left(\frac{\partial U}{\partial V}\right)_S$$

The specific forms of these equations depend on the system. In practice, $dU = T dS - p dV$ is more useful.

For a monatomic ideal gas we can find the functions $U(S, V)$:

$$dU = dQ + dW \rightarrow dQ = dU + p dV$$

$$dQ = T dS \rightarrow T dS = dU + p dV$$

$$dS = \frac{1}{T} dU + \frac{p}{T} dV$$

$$U = \frac{3}{2} nRT \rightarrow \frac{1}{T} = \frac{3 nR}{2 U}, \quad pV = nRT \rightarrow p = \frac{nRT}{V}$$

$$dS = \frac{3 nR}{2 U} dU + \frac{nRT}{V} dV$$

$$\rightarrow S = \frac{3}{2} nR \ln(U) + nRT \ln(V) + c$$

The constant can be found by equating values.

If we consider a process in a system that is in thermal contact with a thermal reservoir with a temperature of T , we can use the second law to find the bounds of the total entropy changes:

$$\Delta S_{\text{system}} + \Delta S_{\text{surroundings}} \geq 0$$

In this example the surroundings are the thermal reservoir with a fixed temperature, and so the addition of heat to the surroundings is reversible:

$$\Delta S_{\text{surroundings}} = \int \frac{dQ_{\text{rev}}}{T} = \frac{Q_{\text{sur}}}{T}$$

We can define Helmholtz free energy. It is a form of the second law for a system with fixed

volume and temperature:

$$\Delta U_{sys} = Q_{sys} = -Q_{surr} \rightarrow \Delta S_{surr} = -\frac{\Delta U_{sys}}{T}$$

$$\Delta S_{sys} + \Delta S_{surr} \geq 0 \therefore \Delta S_{sys} - \frac{\Delta U_{sys}}{T} \geq 0$$

$$\Delta U_{sys} - T \Delta S_{sys} \leq 0, \quad \text{If } T \text{ is constant:}$$

$$\Delta(\Delta U_{sys} - TS_{sys}) \leq 0$$

$$\text{Helmholtz free energy } F = U - TS$$

$$\Delta F \leq 0$$

Helmholtz free energy is the energy available for thermodynamic processes after the energy transfer from the reservoir is accounted for.

We can also define Gibbs free energy, a form of the second law for a system with fixed pressure and temperature:

$$\Delta H = C_p \Delta T = Q, \quad \Delta S_{sys} = Q_{sys} = -Q_{surr}$$

$$\Delta S_{surr} = \frac{Q_{surr}}{T} = -\frac{\Delta H_{sys}}{T}$$

$$\Delta S_{sys} + \Delta S_{surr} \geq 0 \rightarrow \Delta S_{sys} - \frac{\Delta H_{sys}}{T} \geq 0$$

$$\rightarrow \Delta(\Delta U_{sys} - TS_{sys}) \leq 0$$

The Gibbs free energy is $G = H - TS$, and is the available energy in a process with fixed pressure after reservoir transfer is accounted for