Chapter 20

Entropy and second law of thermodynamics

1　　Content

In this chapter we will introduce the second law of the thermodynamics. The following topics will be covered.

> Second law of thermodynamics
> Reversible processes
> Entropy
> The Carnot engine
> Refrigerator
> Real engines

2　　Second law of thermodynamics

　　If a closed system is in a configuration that is not the equilibrium configuration, the most probable consequence will be that the entropy of the system will increase monotonically.

　　If an irreversible process occurs in a closed system, the entropy of the system always increases; it never decreases.

　　In a process that occurs in a closed system the entropy of the system increases for irreducible processes and remains constant for reversible process. The entropy never decreases. The second law of thermodynamics can be written as

$$\Delta S \geq 0$$

3　　Third law of thermodynamics

　　Nernst proposed what he calls the heat theorem (third law of thermodynamics). The entropy of any object at 0 K is zero.

$$\lim_{T \to 0} S = 0$$

4　　Non perfect, but realizable heat engine

　　An engine is a device for converting heat energy into work. The way a typical engine operates is to absorb heat from some substance or reservoir at high temperature, to permit the working substance to do work and thereby be cooled, and then reject some heat to a reservoir at a lower temperature.
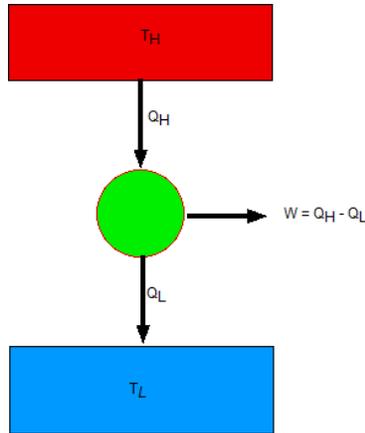
It not only absorbs heat Q_H from a reservoir at temperature T_H, but also rejects heat Q_L to some second reservoir at some lower temperature T_L. The engine does some work

$$W = Q_H - Q_L.$$

where W is the work done by the system (gas).

## 5   Non perfect, but realizable refrigerator

A refrigerator is an engine runs backward. Work is done on the refrigerator, and the net effect is to cool reservoir and heat a hotter reservoir.
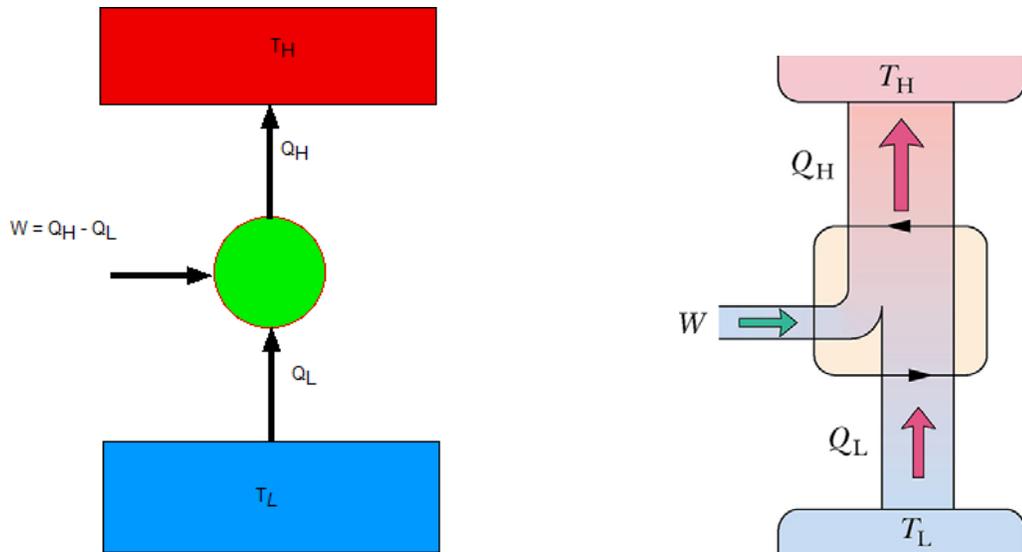
It removes heat Q_L from a reservoir at lower temperature T_L and rejects heat Q_H to a reservoir at higher temperature T_H. The work W (= $Q_H - Q_L$) is done on the refrigerator to make it function.

6   Traditional thermodynamic statements of the second law of thermodynamics

6.1   Lord Kelvin (William Thomson, 1st Baron Kelvin)
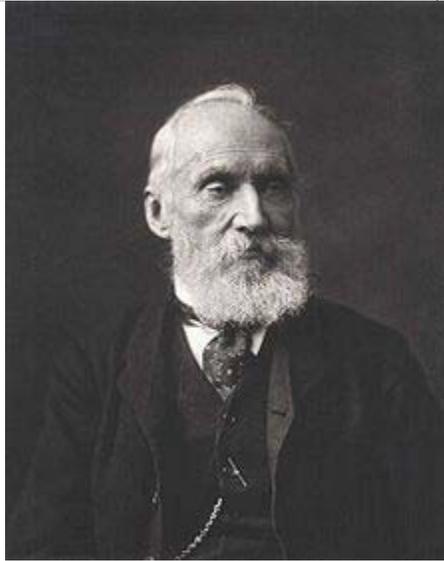
(26 June 1824 – 17 December 1907) was an Irish mathematical physicist and engineer. At Glasgow University he did important work in the mathematical analysis of electricity and thermodynamics, and did much to unify the emerging discipline of physics in its modern form. He is widely known for developing the Kelvin scale of absolute temperature measurement. He was given the title Baron Kelvin in honor of his achievements and is therefore often described as Lord Kelvin. The title refers to the River Kelvin, which flows past his university in Glasgow, Scotland.

He also had a later career as an electric telegraph engineer and inventor, a career that propelled him into the public eye and ensured his wealth, fame and honor.

6.2   Rudolf Clausius

Rudolf Julius Emanuel Clausius (January 2, 1822 – August 24, 1888), was a German physicist and mathematician and is considered one of the central founders of the science of thermodynamics By his restatement of Sadi Carnot's principle known as the Carnot cycle, he put the theory of heat on a truer and sounder basis. His most important paper,

On the mechanical theory of heat, published in 1850, first stated the basic ideas of the second law of thermodynamics. In 1865 he introduced the concept of entropy.

6.3 Kelvin's formulation of the second law of thermodynamics ((Kelvin's impossible engine))

Any device that converts heat into work by mean of a cyclic process is called a *heat engine*. Perfect heat engine: It extracts heat from a reservoir and performs an equivalent amount of work without producing any other effect on the environment.

(a)   It is impossible for any cyclic process to occur whose sole effect is the extraction of heat from a reservoir and the performance of an equivalent amount of work.

(b)   It is impossible by means of any inanimate agency to derive mechanical work from any portion of matter by cooling it below the lowest temperature of its surroundings.

Kelvin impossible engine   Kelvin impossible engine
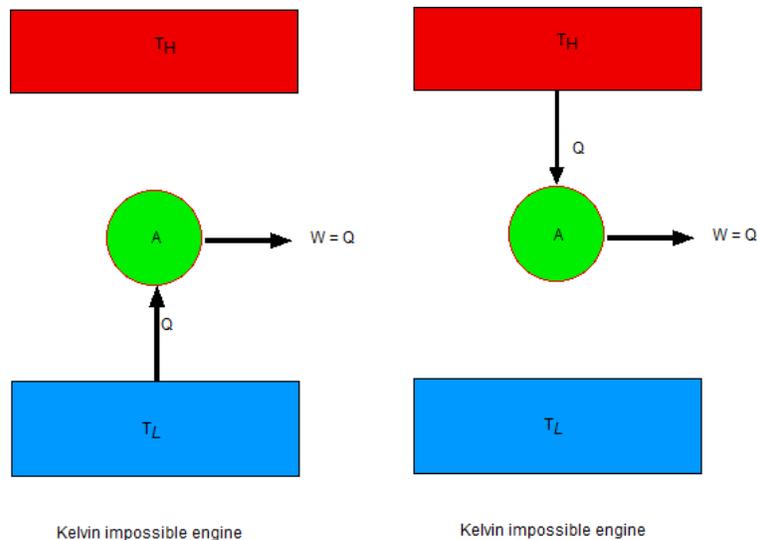
### 6.4 Perfect refrigerator ((Clausius impossible engine))

It removes heat Q from the reservoir at low temperature and transfer it to the reservoir at high temperature without affecting the environment in any other way.

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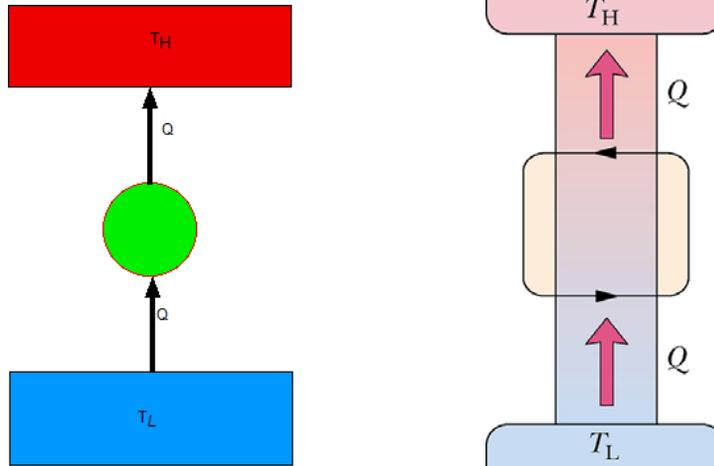
Perfect refrigerator

(a)   It is impossible to construct a perfect refrigerator. Heat cannot be taken in a certain temperature and converted into work with no other change in the system or the surrounding. In other words, heat cannot flow by itself from a cold to a hot place.

(b)   It is impossible for a self-acting machine to convoy heat continuously from one body to another which is at a high temperature.

## 6.5   Derivation of from Kelvin's impossible engine to the Clausius impossible engine
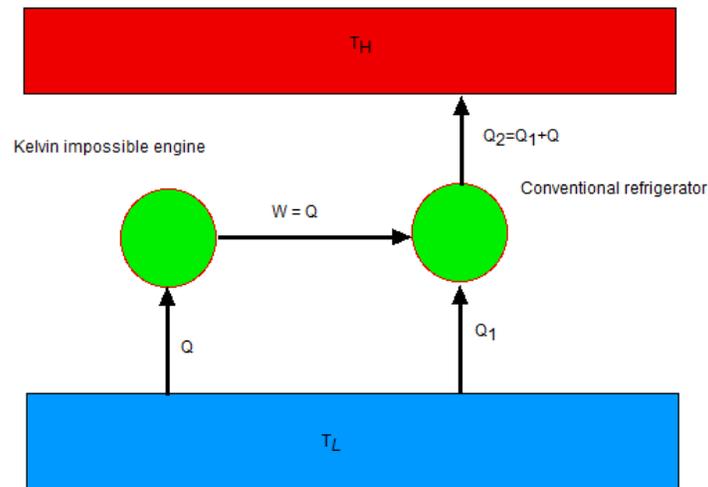
or equivalently
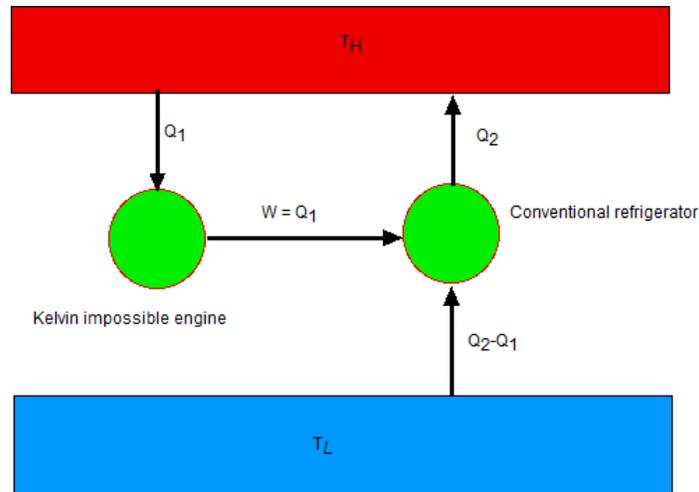
One can show that the Kelvin and the Clausius statements are equivalent to one another by proving that if the Kelvin statement is not true, neither is the Clausius statement. Then we show that if the Clausius statement is not true, neither is the Kelvin statement.

Suppose that the Kelvin's statement is false and that we have an engine which removes heat from a reservoir and does work. We now permit the impossible Kelvin engine to run a conventional engine backboard as a refrigerator, removing heat Q_1 from the cold reservoir and delivering Q_2 to the hot reservoir. Since the internal energy of these engine remains the same, $W = Q$ and $W = Q_2 - Q_1$. Therefore $Q_2 = Q_1 + Q$. The combination of the two devices is a self-acting device which removes a quantity of heat Q_2 from a cold reservoir and delivers it to the hot one in violation of the Clausius statement.

6.6   Derivation of Clausius impossible engine to the Kelvin's impossible engine
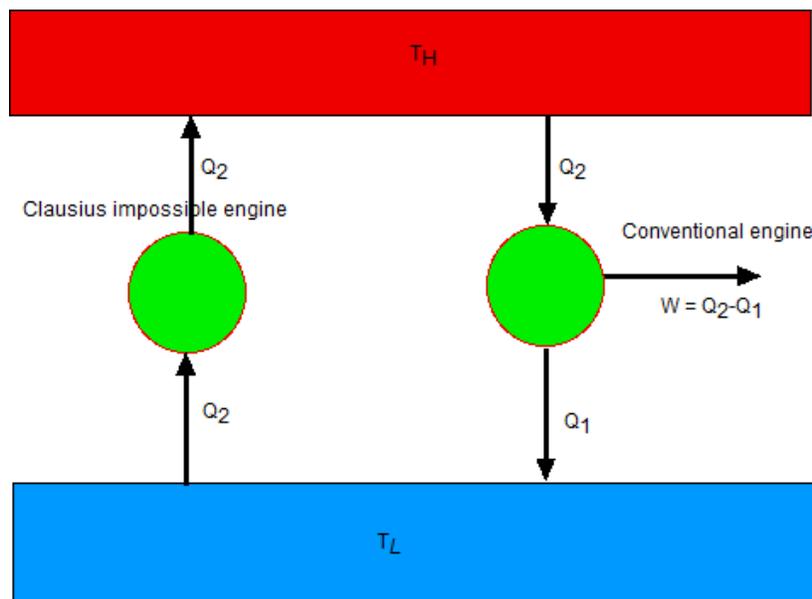
Assuming that the Clausius statement is false, we construct an engine which takes Q_2 from a cold reservoir and delivers it to a hot one, and we operate it simultaneously with a conventional engine which removes Q_2 from a hot reservoir, does work W, and delivers Q_1 to the cold reservoir. The combination of these devices removes heat $Q_2 - Q_1$ from a cold reservoir and does work W. The two devices working together therefore violate the Kelvin's statement.

7 Carnot engines for an ideal gas

A theoretical engine developed by Sadi Carnot. A heat engine operating in an ideal reversible cycle (now called a Carnot Cycle) between two reservoirs is the most efficient engine possible. This sets an upper limit on the efficiencies of all other engines. It is of interest to exhibit explicitly how such an engine operating quasi-statically between heat reservoirs can be constructed.

Such an engine is the simplest conceivable engine and is called a "Carnot engine." The Carnot engine goes through a cycle consisting of four steps, all performed in a quasi-static fashion. After four steps, the engine is back in its initial state and the cycle is completed.

All real engines are less efficient than the Carnot engine because they all operate irreversibly so as to complete a cycle in a brief time interval.

((Nicolas Léonard Sadi Carnot (1796–1832)))

His famous work on the motive power of heat (Réflexions sur la puissance motrice du feu, 1824) is concerned with the relation between heat and mechanical energy. Carnot devised an ideal engine in which a gas is allowed to expand to do work, absorbing heat in the process, and is expanded again without transfer of heat but with a temperature drop. The gas is then compressed, heat being given off, and finally it is returned to its original condition by another compression, accompanied by a rise in temperature. This series of operations, known as Carnot's cycle, shows that even under ideal conditions a heat engine cannot convert into mechanical energy all the heat energy supplied to it; some of the heat energy must be rejected. This is an illustration of the second law of thermodynamics. Carnot's work anticipated that of Joule, Kelvin, and others.

((**Note**)) How Kelvin and Clausius discovered Carnot's ideas?
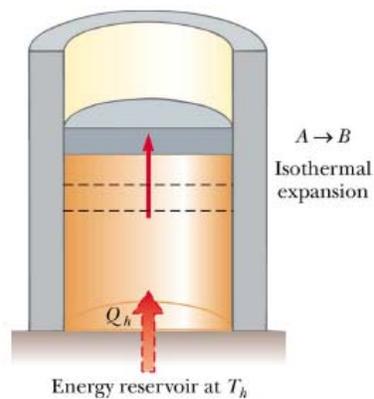
Carnotcycle the classical blog on thermodynamics

7.1   Overview of the processes in a Carnot Cycle.
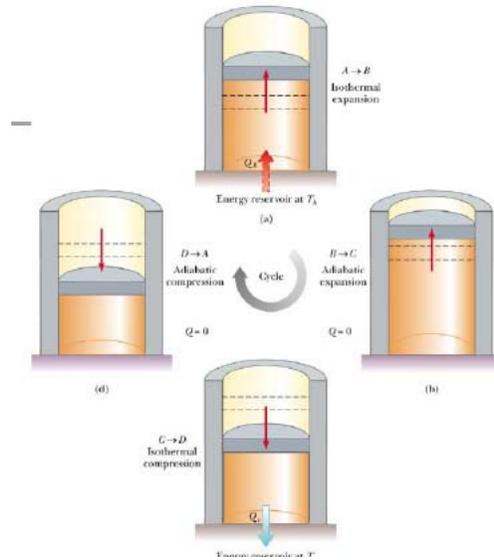
7.2   Isothermal process
A(a, 1) to B (b, 2) is an isothermal expansion. The gas is placed in contact with the high temperature reservoir T_H. The gas absorbs heat Q_H. The gas does work W_{AB} in raising the piston.

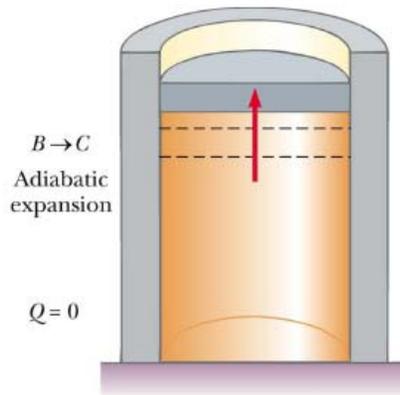$$W_{12} = -\int PdV = -RT_H \int_{V_1}^{V_2} \frac{dV}{V} = -RT_H \ln(\frac{V_2}{V_1})$$

$$E_{12} = 0 = Q_{12} + W_{12}$$

$$Q_H = Q_{12} = -W_{12} = RT_H \ln(\frac{V_2}{V_1})$$

where W_{12} is the work done on the system (gas).

7.3   Adiabatic process

B (b, 2) to C (c, 3) is an adiabatic expansion. The base of the cylinder is replaced by a thermally nonconducting wall. No heat enters or leaves the system. The temperature falls from T_H to T_L. The gas does work W_{BC}.

$B \rightarrow C$
Adiabatic
expansion

$Q = 0$

$$W_{23} = -\int PdV = -\int_{V_2}^{V_3} P_2 V_2{}^{\gamma} \frac{dV}{V^{\gamma}} = -P_2 V_2{}^{\gamma}(\frac{V^{1-\gamma}}{1-\gamma})\,|_{V_2}^{V_3} = -\frac{R}{\gamma-1}(T_H - T_L)$$

$$= -C_V(T_H - T_L)$$

$$Q_{23} = 0$$

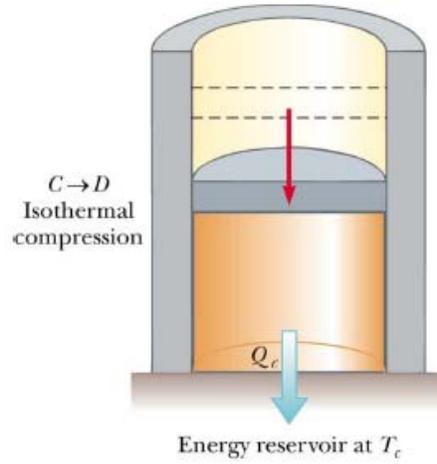$$E_{23} = W_{23} = -C_V(T_H - T_L)$$

where

$$\frac{R}{C_V} = \gamma - 1$$

W_{23} is the work done on the system during this process.

7.4   Isothermal process

The gas is placed in contact with the cold temperature reservoir. C (c, 3) to D (d, 4) is an isothermal compression. The gas expels energy Q_L. W_{34} is work done on the system (gas).

$C \rightarrow D$
Isothermal
compression

Q_c

Energy reservoir at T_c

$$W_{34} = -\int PdV = -RT_L \int_{V_3}^{V_4} \frac{dV}{V} = -RT_L \ln(\frac{V_4}{V_3}) = RT_L \ln(\frac{V_3}{V_4}) = RT_L \ln(\frac{V_2}{V_1})$$

$$E_{34} = 0 = Q_{34} + W_{34}$$

$$Q_{34} = -Q_L = -W_{34} = -RT_L \ln(\frac{V_2}{V_1})$$

((**Note-2**))

In the following way, we show that

$$\frac{V_3}{V_4} = \frac{V_2}{V_1}.$$

From the relations,

$$T_H V_2^{\gamma-1} = T_L V_3^{\gamma-1}$$
$$T_H V_1^{\gamma-1} = T_L V_4^{\gamma-1}$$

we have

$$\boxed{\frac{V_3}{V_4} = \frac{V_2}{V_1}.}$$

((**Note-2**))   Another proof

From the relations

$$P_1V_1 = P_2V_2$$
$$P_2V_2^{\gamma} = P_3V_3^{\gamma}$$
$$P_3V_3 = P_4V_4$$
$$P_4V_4^{\gamma} = P_1V_1^{\gamma}$$

In multiplying on both sides, we have

$$(P_1V_1)(P_2V_2^{\gamma})(P_3V_3)(P_4V_4^{\gamma}) = (P_2V_2)(P_3V_3^{\gamma})(P_4V_4)(P_1V_1^{\gamma})$$

or

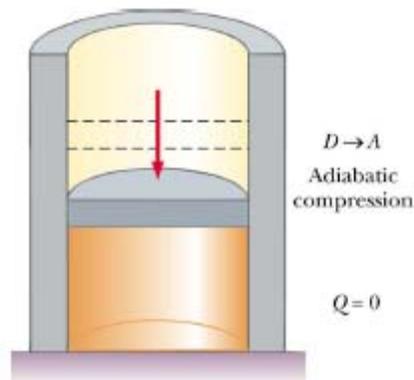$$V_1V_2^{\gamma}V_3V_4^{\gamma} = V_2V_3^{\gamma}V_4V_1^{\gamma}$$

or

$$V_1^{1-\lambda}V_3^{1-\lambda} = V_2^{1-\gamma}V_4^{1-\gamma}$$

or

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

7.5   Adiabatic process

D (d, 4) to A (a, 1) is an adiabatic compression. The gas is again placed against a thermally nonconducting wall. So no heat is exchanged with the surroundings. The temperature of the gas increases from T_L to T_H. W_{41} is the work done on the system (gas).
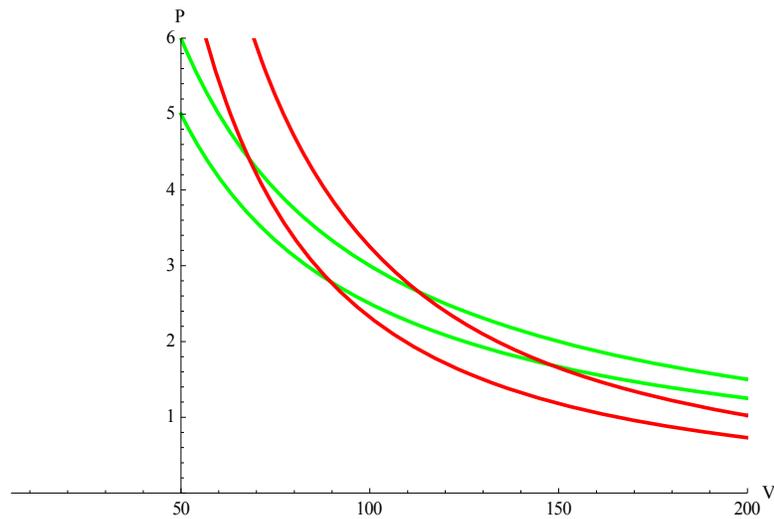

$D \rightarrow A$
Adiabatic compression

$Q = 0$

$$W_{41} = -\int PdV = -\int_{V_4}^{V_1} P_4 V_4^{\gamma} \frac{dV}{V^{\gamma}}$$

$$= C_V (T_H - T_L)$$

$$Q_{41} = 0$$

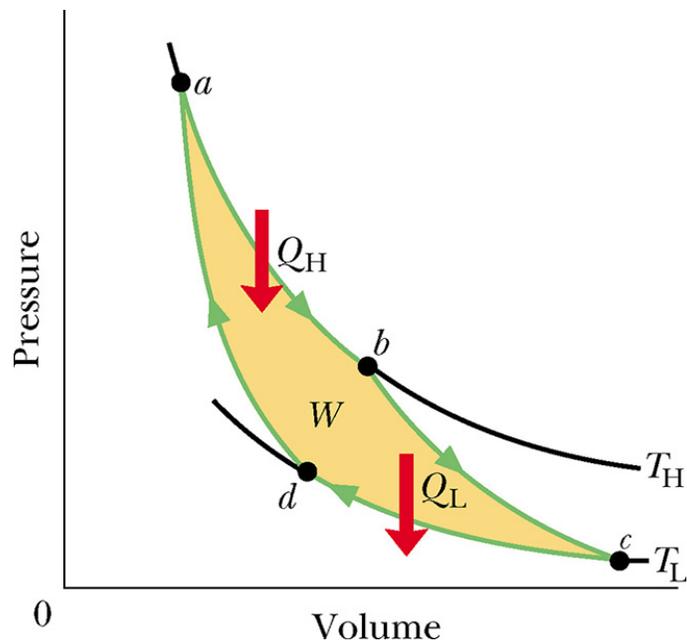$$E_{41} = W_{41} = C_V (T_H - T_L)$$

((**Mathematica**))

Green lines: isothermal process

Red lines: adiabatic process ($\gamma = 5/3$ here)

8. **Carnot cycle. *PV* diagram**

12

$$Q_H = RT_H \ln(\frac{V_2}{V_1})$$
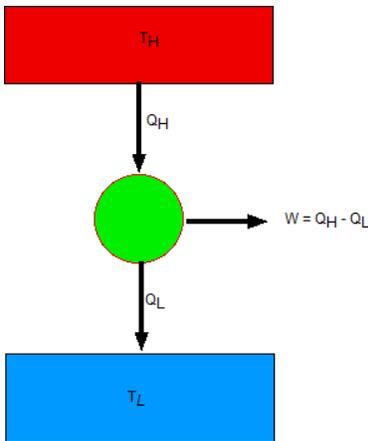
$$Q_L = -RT_L \ln(\frac{V_3}{V_4}) = RT_L \ln(\frac{V_2}{V_1})$$

$$W = W_{12} + W_{23} + W_{34} + W_{41}$$

$$= -RT_H \ln(\frac{V_2}{V_1}) - C_V(T_H - T_L) + RT_L \ln(\frac{V_2}{V_1}) + C_V(T_H - T_L)$$

$$= -R(T_H - T_L) \ln(\frac{V_2}{V_1}) = Q_L - Q_H$$

W is the total work done on the system during the process. <u>For convenience we redefine W by $-W$. The new definition of W is the work done by the system.</u>

$$W = Q_H - Q_L$$

$$\frac{Q_L}{T_L} = \frac{Q_H}{T_H} \qquad \text{(Carnot cycle)}$$

The efficiency ε_R is defined as
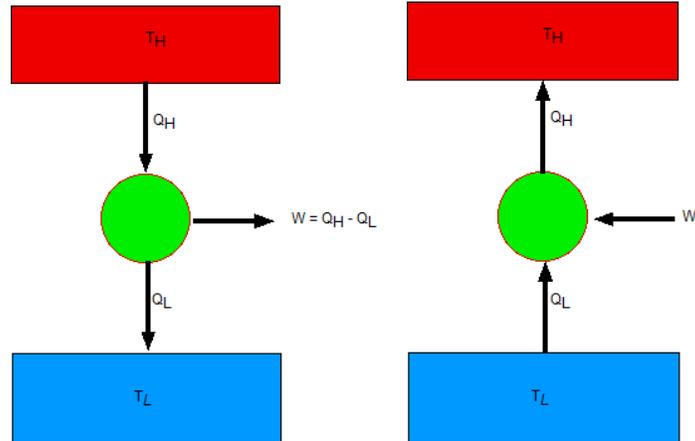
$$\varepsilon_R = \frac{W}{Q_H} = \frac{Q_H - Q_L}{Q_H} = 1 - \frac{T_L}{T_H}$$

It is dependent only on the temperatures T_H and T_L. Although proved for a perfect gas engine, it must be true for reversible engines. We mean that for a reversible engine the following two processes are possible.

((**Reversible engine**))

What is the definition of the reversible engine?

In reversible engine, all the processes are reversible.

9   Reversible cycle for an ideal gas

An arbitrary reversible cycle, plotted on a *PV* diagram consists of a family of isotherm lines and adiabatic lines. We can approximate an arbitrary cycle as closely as we wish by connecting the isotherms by short, suitably chosen, adiabatic lines. In this way, we form an assembly of long; thin Carnot cycles.

The traversing the individual Carnot cycles in sequence is exactly equivalent to traversing the jagged series of isotherms and adiabatics that approximate the actual cycle.

In Carnot cycle,

we put

$$Q_1 = Q_H, \qquad Q_2 = -Q_L$$

T1 = TH

$Q_1 (= Q_H)$

B

$W_I = Q_1 + Q_2$

$Q_2 (= -Q_L)$

T2 (= TL)

Reversible engine
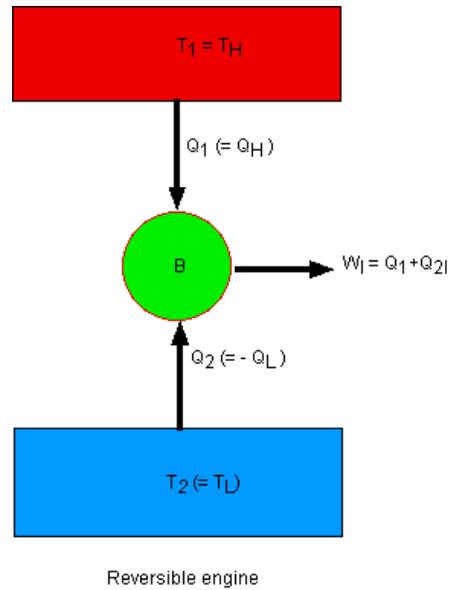
We extend the Eq. given by
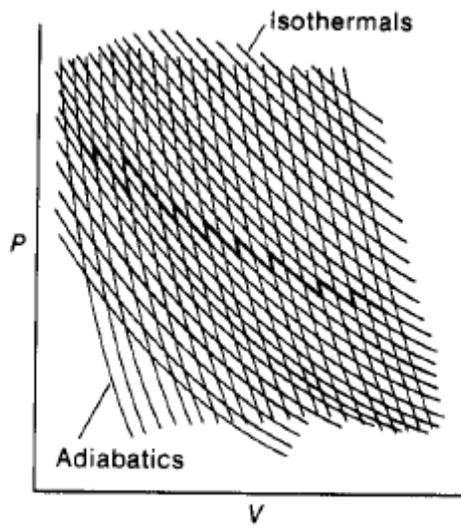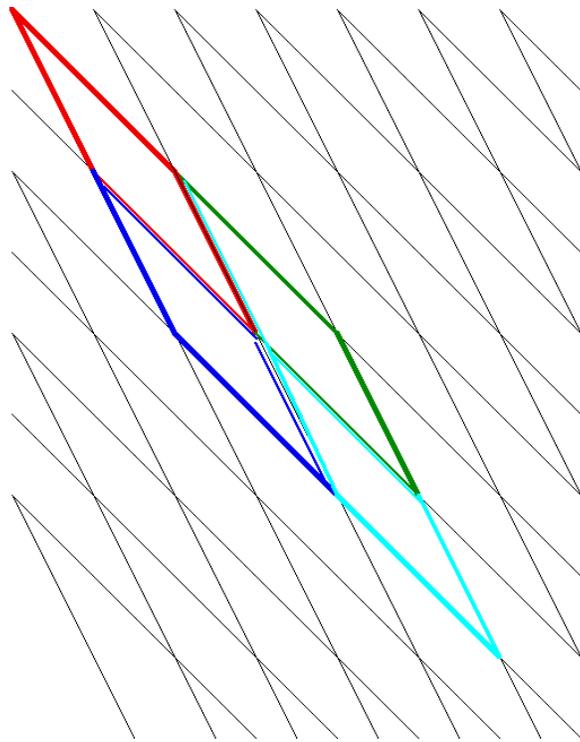
$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0$$

by writing the isotherm-adiabatic sequence of lines

$$\sum_i \frac{Q_i}{T_i} = 0$$

In the limit of infinitesimal temperature differences between the isotherms, we have

$$\oint \frac{dQ_r}{T} = 0 \qquad \text{(reversible cycle).}$$

16
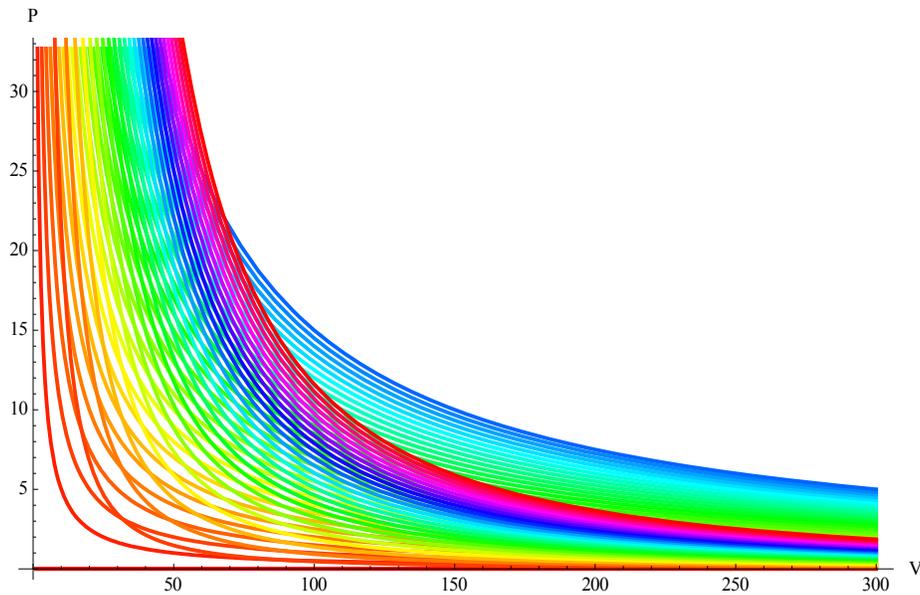
Fig.   Combination of the isothermals and adiabatics.

10   Entropy in the reversible process

Entropy is a measure of disorder of a state. Entropy can be defined using macroscopic concepts of heat and temperature

$$dS = \frac{dQ_r}{T} \qquad \text{(reversible process)}$$

Entropy can also be defined in terms of the number of microstates, W, in a macrostate whose entropy is S,

$$S = k_B \ln W$$

where W is the number of micro-states. This will be discussed in the next chapter (Chapter 20S).

The entropy of the universe increases in all real processes. This is another statement of the second law of thermodynamics. The change in entropy in an arbitrary reversible process is

$$\Delta S = \int_i^f \frac{dQ_r}{T}$$

For any reversible cycle, in general,

$$\oint \frac{dQ_r}{T} = 0$$

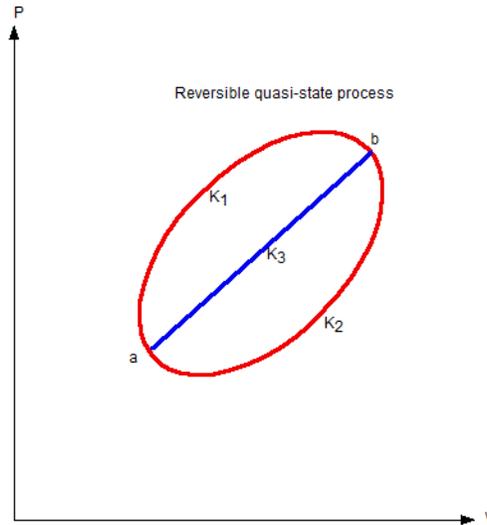This is called **Clausius' theorem**. The importance of Clausius' theorem is that it permits us to define a new physical quantity called the entropy, or more precisely, the entropy difference.

The integral symbol indicates the integral is over a closed path.

Reversible quasi-state process

We can move around on a *PV* diagram all over the plane, and go from one condition to another. In other words, we could say that the gas is in a certain condition *a*, and then it goes over to some other condition *b*.

We will require that the transition, made from *a* to *b* reversible. Now we go around the path 1 (a→K₁→b→K₃ →a). Then we have

$$\int_{aK_1b} \frac{dQ_r}{T} + \int_{bK_3a} \frac{dQ_r}{T} = 0 \qquad (1)$$

Next we go around the path 2 (a→K₂→b→K₃ →a),

$$\int_{aK_2b} \frac{dQ_r}{T} + \int_{bK_3a} \frac{dQ_r}{T} = 0 \qquad (2)$$

Subtracting Eq.(1) from Eq.(2),

$$\int_{aK_1b} \frac{dQ_r}{T} = \int_{aK_2b} \frac{dQ_r}{T}$$

which does not depend on the path taken.

We define the entropy to go from *a* to *b* by a reversible process

$$S_b - S_a = \int_a^b \frac{dQ_r}{T}$$

The entropy of a system is a function of the thermodynamic co-ordinates whose change is equal to the integral of dQ_r/T between the terminal states, integrated along reversible path connecting two states.

11   *T-S* diagram for the Carnot cycle

For each infinitesimal amount of heat that enters a system during an infinitesimal portion of a reversible process,

$$dQ_r = TdS \ .$$

In the case of a reversible adiabatic process, we have

$$dS = \frac{dQ_r}{T} = 0$$

If T is not zero, $dS = 0$ and S is constant. Therefore, during a reversible adiabatic process, the entropy of a system remains constant. In other words, the system undergoes an isentropic process.

If two equilibrium states are infinitesimally near, then we have

$$dQ = TdS$$
$$\frac{dQ}{dT} = T\frac{dS}{dT}$$

At constant volume,

$$\left(\frac{dQ}{dT}\right)_V = C_V = T\left(\frac{dS}{dT}\right)_V$$

and at constant pressure,

$$\left(\frac{dQ}{dT}\right)_P = C_P = T\left(\frac{dS}{dT}\right)_P$$

The work done by the system is the area of the rectangle:

$$dE = TdS - PdV$$
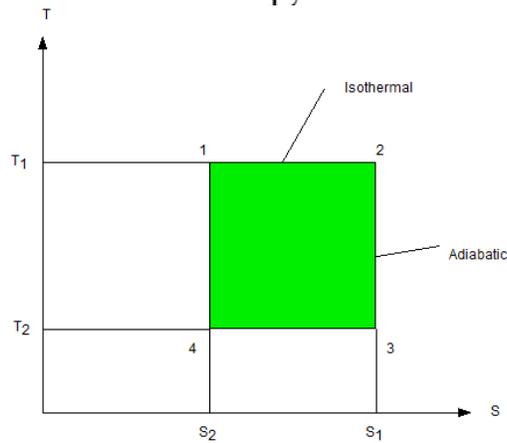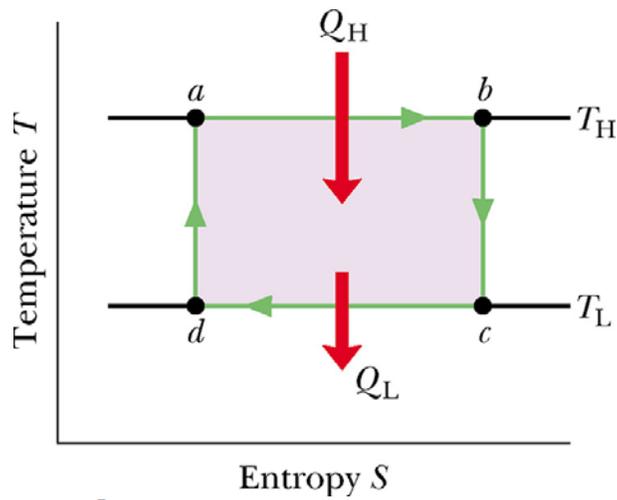$$\oint dE = 0 = \oint TdS - \oint PdV$$

19

Then we have

$$\oint T dS = \oint P dV = -W$$

where W is the work done on the system and $-W$ is the work done by the system.

((**Note**))

In a Carnot cycle,

$$\frac{Q_1}{T_1} = \frac{Q_2}{T_2} = \Delta S$$

Then the work done by the system (-W) is given by

$$\text{Area} = \Delta S(T_1 - T_2) = \frac{Q_1}{T_1}(T_1 - T_2) = Q_1(1 - \frac{T_2}{T_1})$$

The efficiency $\varepsilon_R = \dfrac{Area}{Q_1} = 1 - \dfrac{T_2}{T_1}$

12   Reversible Engine

We show that no engine can do more work than a reversible one. Suppose that A is a reversible engine (a Carnot cycle), and that B is also a reversible engine.
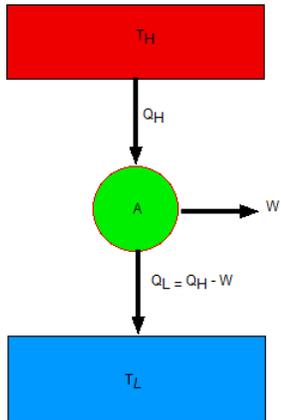
A: reversible engine (Carnot cycle)   B: reversible engine
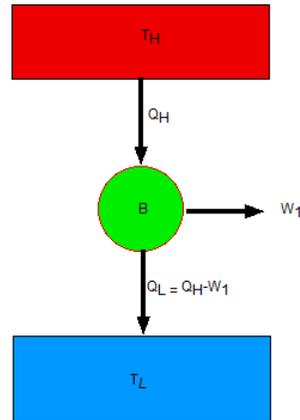
We consider the combined engine of A and B. Since A (Carnot cycle) is the reversible engine, we have
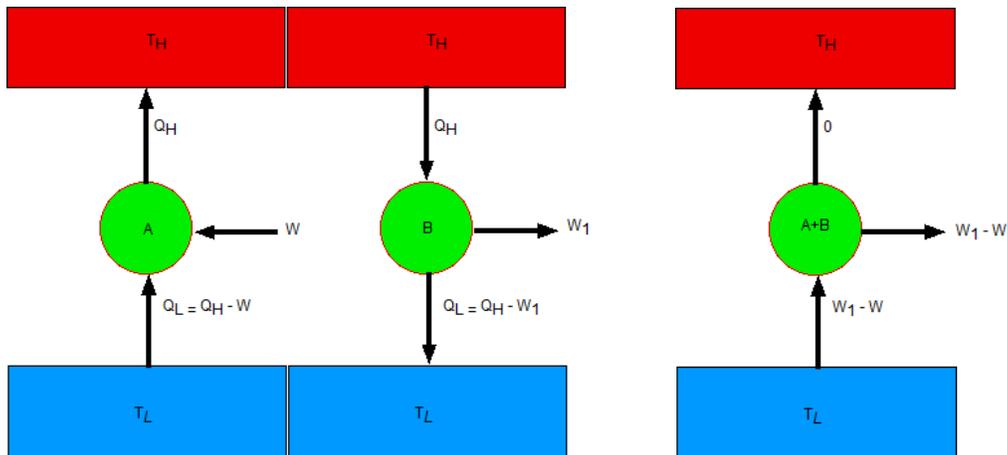
Note that A is a reversible engine. This system is equivalent to the engine of A+B. Net effect is to extract a net heat W_1-W from the reservoir at T_L and convert it into work. This process is prohibited because of Kelvin's impossible engine: it is impossible for any cyclic process to occur whose sole effect is the extraction of heat from a reservoir and the performance of an equivalent amount of work.

Thus one can get

$W_1-W \leq 0.$ (1)

Since B is the reversible engine, we have
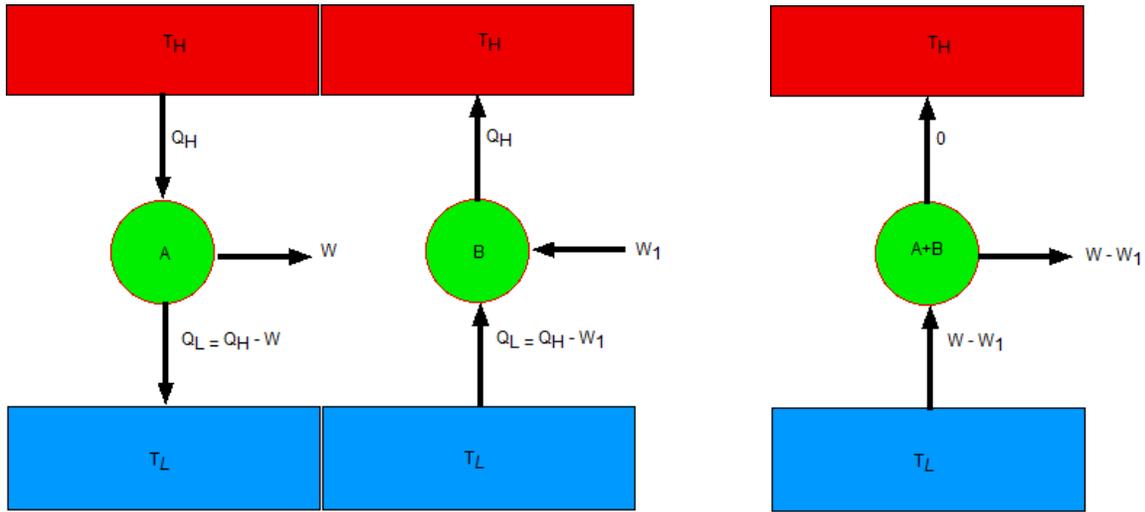
This process is prohibited because of the Kelvin's impossible engine. Hence

$$W - W_1 \leq 0. \qquad (2)$$

From Eqs.(1) and (2), one can get $W = W_1$. So if both engines are reversible, they must both do the same amount of work.

Here is the Carnot's brilliant conclusion.

If one engine is reversible, it makes no difference how it is designed.

13 Carnot inequality (irreversible engine)

For a reversible engine, we have
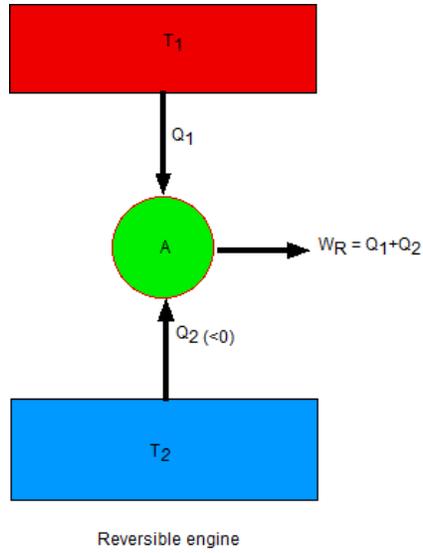
Reversible engine

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0$$

where $T_1 > T_2$, $Q_1 > 0$, and $Q_2 < 0$.

The efficiency ε_R is defined as

$$\varepsilon_R = \frac{W_R}{Q_1} = \frac{Q_1 + Q_2}{Q_1} = 1 + \frac{Q_2}{Q_1} = 1 + \frac{Q_2}{Q_1} = 1 - \frac{T_2}{T_1}$$

For an irreversible engine

Irreversible engine
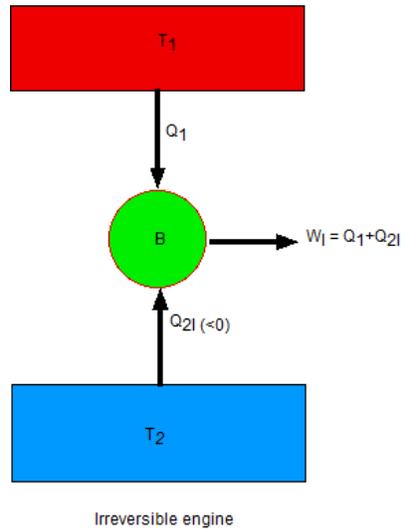
The combination of A and B gives

Reversible engine Irreversible engine   Kelvin impossible engii
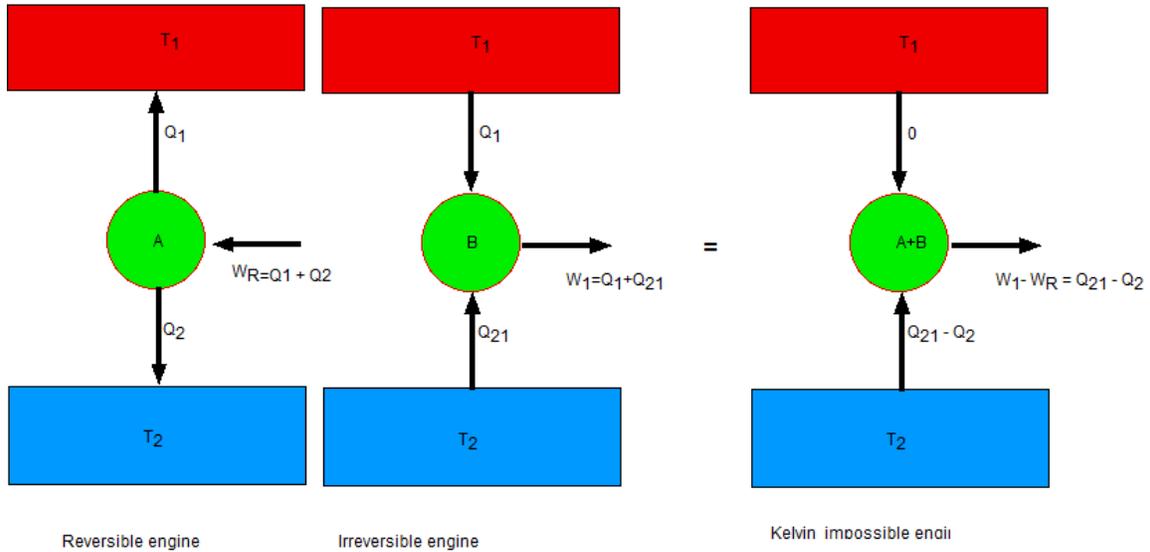
Then we have

$$W_1 < W_R$$

for a fixed Q_1 from the high temperature reservoir. The efficiency ε_1 is given by

$$\varepsilon_1 = \frac{W_1}{Q_1} < \frac{W_R}{Q_1} = \varepsilon_R = 1 - \frac{T_2}{T_1}$$

Since $W_I = Q_1 + Q_{21}$ ($Q_{21}<0$), we get

$$\frac{Q_1 + Q_{21}}{Q_1} < 1 - \frac{T_2}{T_1} \qquad \text{or} \qquad \frac{Q_{21}}{Q_1} < -\frac{T_2}{T_1}$$

Finally we obtain the Carnot inequality.

$$\frac{Q_1}{T_1} + \frac{Q_{21}}{T_2} < 0,$$

or

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} < 0, \qquad \text{for irrevercible cycle (for convenience } Q_{21} = Q_2).$$

For any irreversible cycle, in general,

24

$$\oint \frac{dQ}{T} < 0$$

The integral symbol indicates the integral is over a closed path.

14 Entropy in the irreversible process (I)

We consider the cycle which include both reversible and irreversible process. One has the Clausius inequality.

$$\oint \frac{dQ}{T} < 0$$
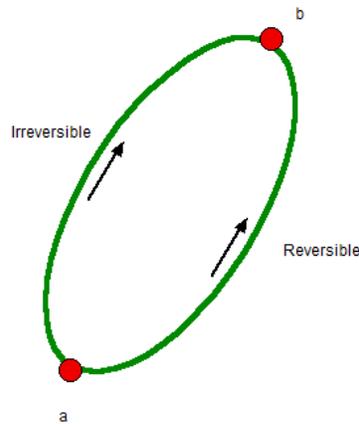
We go around the path. Then we have

$$\int_{\substack{a \to b \\ Irreversible}} \frac{dQ_{irr}}{T} + \int_{\substack{b \to a \\ Reversible}} \frac{dQ_r}{T} < 0$$

which leads to

$$\int_{\substack{a \to b \\ Irreversible}} \frac{dQ_{irr}}{T} < \int_{\substack{a \to b \\ Reversible}} \frac{dQ_r}{T} = S_b - S_a = \Delta S$$

Second law of thermodynamics

In any process in which a thermally isolated system ($\Delta Q = 0$) goes from one macrostate to another macrostate, the entropy tends to increase.

$$\int \frac{dQ_{irr}}{T} < \Delta S ,$$

25

In a small irreversible change, we hae

$$\frac{dQ_{irr}}{T} < dS$$

When the system is isolated or the system is adiabatic (no heat exchange between the system and surroundings),

$$dS > 0$$

This means that the entropy of an isolated system either remains constant or increases.

((**Note**))   Clausius impossible engine
    We consider the Clausius impossible refrigerator. The change of entropy can be evaluated as

$$\Delta S = \frac{Q}{T_H} + \frac{(-Q)}{T_L} = Q\frac{(T_L - T_H)}{T_H T_L} < 0$$

This is inconsistent with the second law of thermodynamics ($\Delta S > 0$).
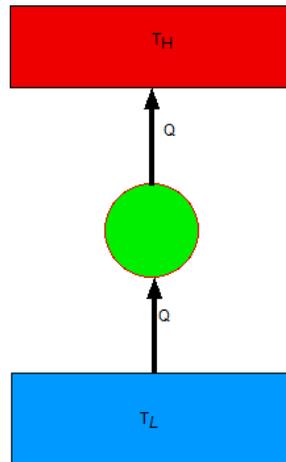
Fig.   Clausius impossible engine.

15   Entropy in the irreversible process (II)
    In order to define the entropy change ΔS for an irreversible process that takes one from an initial state i to a final state f of a system, we find a reversible process that connects states i and f. We then calculate

$$\Delta S = S_f - S_i = \int_i^f \frac{dQ_r}{T} > \int_i^f \frac{dQ_{irr}}{T} > 0$$

((Example-1))   **Contact of two systems with different temperatures**
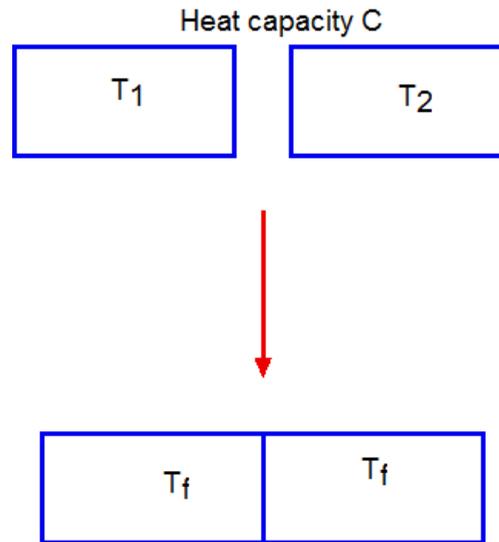
Heat capacity C

Suppose that waters (mass m) are in two containers separately. The temperatures of these containers are T_1 and T_2. The heat capacity of water per unit mass is C. We consider that these two containers are in contact. The final temperature is $T_f = (T_1+T_2)/2$ in the thermal equilibrium. The change of entropy for the container 1 is

$$\Delta S_1 = \int_{T_1}^{T_f} \frac{mCdT}{T} = mC\ln(\frac{T_f}{T_1})$$

The change of entropy for the container 2 is

$$\Delta S_2 = \int_{T_2}^{T_f} \frac{mCdT}{T} = mC\ln(\frac{T_f}{T_2})$$

The resultant change of entropy is

$$\Delta S = \Delta S_1 + \Delta S_2 = mC[\ln(\frac{T_f}{T_1}) + \ln(\frac{T_f}{T_2})]$$

or

$$\Delta S = \Delta S_1 + \Delta S_2 = mC\ln(\frac{T_f^2}{T_1 T_2}) \geq 0$$

where

$$T_f = \frac{T_1 + T_2}{2} \geq \sqrt{T_1 T_2} \qquad \text{or} \qquad \left(\frac{T_f}{T_1 T_2}\right)^2 \geq 1$$

We note that when $T_2 > T_1$, we have

$$mC(T_2 - T_f) = mC(T_f - T_1)$$

or

$$T_f = \frac{T_1 + T_2}{2}.$$

((**Example-2**))
Pure heat transfer, not involving any work, is irreversible in energy transfer, if it takes between two systems having different temperatures.
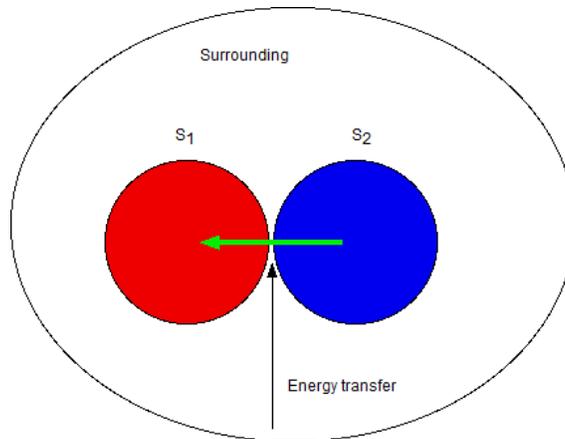
$$dE_1 = dW_1 + dQ_1 = dQ_1 = T_1 dS_1$$
$$dE_2 = dW_2 + dQ_2 = dQ_2 = T_2 dS_2$$

Here the total internal energy is constant.

$$dE_1 + dE_2 = 0 = dQ_1 + dQ_2$$

The newly created entropy,

$$dS_{total} = dS_1 + dS_2 = \frac{dQ_1}{T_1} + \frac{dQ_2}{T_2} = \frac{dQ_1}{T_1} - \frac{dQ_1}{T_2} = (\frac{T_2 - T_1}{T_1 T_2})dQ_1$$

The heat fows from high temperature to low temperature. If $dQ_1 > 0$, then $T_2 > T_1$. So that

$$dS_{total} > 0$$

16. Adiabatic free expansion (irreversible process)

System
Stopcock closed

Vacuum

Insulation
(*a*) Initial state *i*

Irreversible process

Stopcock open

(*b*) Final state *f*
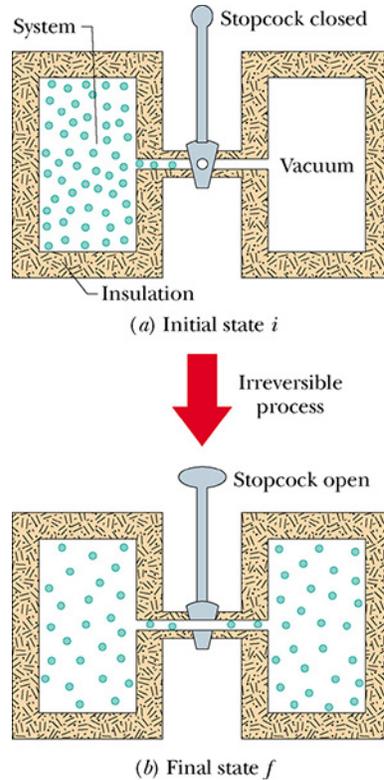
An adiabatic free expansion of an ideal gas i.e. where a greater volume suddenly becomes available to the gas is an irreversible process which proceeds through a chaotic non-equilibrium path. Nonetheless we can characterize the beginning and end points and the net values of relevant changes in energy. Since the gas expands against a vacuum it does no work and thus

$$W_{i \to f} = 0.$$

since there is no motion of the boundary (nothing to push against; there is no movable piston). Combining this with our requirement that the process is adiabatic, we have

$$E_{i \to f} = Q_{i \to f} + W_{i \to f} = 0 + 0 = 0$$

If we are dealing with an ideal gas, then the absence of a change in the internal energy implies that the temperature is the same before and after the expansion even though no temperature is defined during the irreversible process: $T_f = T_i$.

In order to calculate the entropy of this process, we need to find an equivalent reversible path that shares the same initial and final state. A simple choice is an isothermal, reversible expansion in which the gas pushes slowly against a piston. Using the equation of state for an ideal gas this implies that

$$P_i V_i = P_f V_f$$

The initial and final states a (P_i, V_i) and b (P_f, V_f) are shown on the P-V diagram. Even though the initial and final states are well defined, we do not have intermediate equilibrium states that take us from the state a (P_i, V_i) and the state b (P_f, V_f).
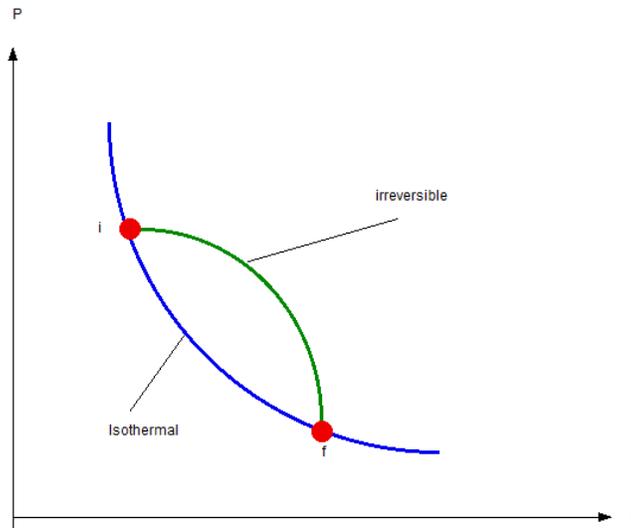
Fig.   Note that the irreversible process (green line) cannot be described in such a line in the P-V phase diagram. The isothermal process is denoted by the blue line.

We thus replace the free expansion with an isothermal expansion that connects states i and f. Then the entropy can be calculated as follows.

$$\Delta E = 0$$

$$dQ_r = -dW = PdV = \frac{RT}{V}dV \qquad \text{(reversible process)}$$

$$\Delta S = \int_{V_i}^{V_f} \frac{dQ_r}{T} = R\int_{V_i}^{V_f} \frac{dV}{V} = R\ln(\frac{V_f}{V_i})$$

Since $V_f > V_i$, ΔS is positive. This indicates that both the entropy and the disorder of the gas increase as a result of the irreversible adiabatic expansion.

17.　　The entropy for the adiabatic free expansion (microscopic staes)

Entropy can be treated from a microscopic viewpoint through statistical analysis of molecular motions. We consider a microscopic model to examine the free expansion of an ideal gas. The gas molecules are represented as particles moving randomly. Suppose that the gas is initially confined to the volume V_i. When the membrane is removed, the molecules eventually are distributed throughout the greater volume V_f of the entire container. For a given uniform distribution of gas in the volume, there are a large number of equivalent microstates, and the entropy of the gas can be related to the number of microstates corresponding to a given macrostate.
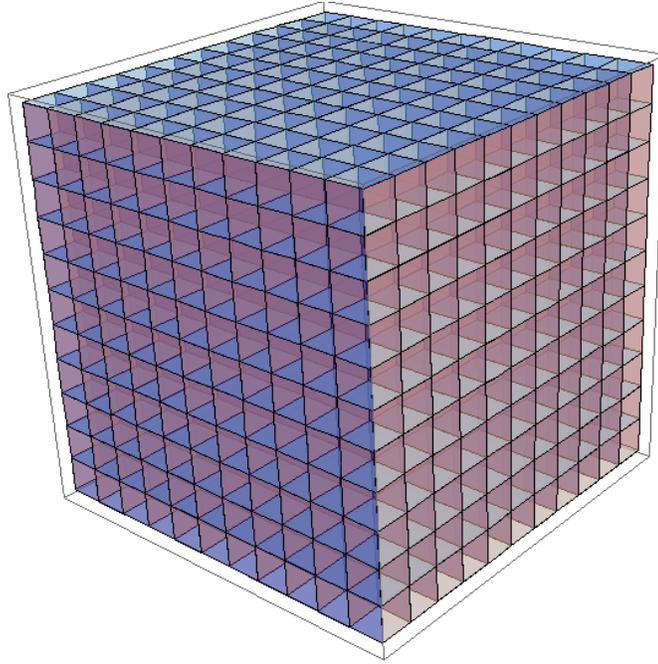
Fig.　　The volume of the system in the initial state is V_i (the macrostate). The volume of cell (the microstate) is V_m. The number of cells (sites) is given by the ratio V_i/V_m.

We count the number of microstates by considering the variety of molecular locations available to the molecules. We assume that each molecule occupies some microscopic volume V_m. The total number of possible locations of a single molecule in a macroscopic initial volume V_i is the ratio

$$w_i = \frac{V_i}{V_m},$$

which is a very large number. The number w_i represents the number of the microstates, or the number of available sites. We assume that the probability of a molecule occupying any of these sites are equal.

Neglecting the very small probability of having two molecules occupy the same site, each molecule may go into any of the w_i sites, and so the number of ways of locating N molecules in the volume becomes

$$W_i = w_i{}^N = \left(\frac{V_i}{V_m}\right)^N .$$

Similarly, when the volume is increased to V_f, the number of ways of locating N molecules increases to

$$W_f = w_f{}^N = \left(\frac{V_f}{V_m}\right)^N .$$

Then the change of entropy is obtained as

$$
\begin{aligned}
\Delta S &= S_f - S_i \\
&= k_B \ln W_f - k_B \ln W_i \\
&= k_B \ln\left(\frac{V_f}{V_m}\right)^N - k_B \ln\left(\frac{V_i}{V_m}\right)^N \\
&= Nk_B[\ln(V_f) - \ln(V_m)] - Nk_B[\ln(V_i) - \ln(V_m)] \\
&= Nk_B[\ln(V_f) - \ln(V_i)] \\
&= Nk_B \ln(\frac{V_f}{V_i})
\end{aligned}
$$

When $N = N_A$, we have

$$\Delta S = N_A k_B \ln(\frac{V_f}{V_i}) = R \ln(\frac{V_f}{V_i})$$

We note that the entropy S is related to the number of microstates for a given macrostate as

$$S = k_B \ln W .$$

The more microstates there are that correspond to a given macrostate, the greater the entropy of that macrostate. There are many more microstates associated with disordered macrostates than with ordered macrostates. Therefore,it is concluded that the entropy is a measure of disorder. Although our discussion used the specific example of the free

expansion of an ideal gas, a more rigorous development of the statistical interpretation of entropy would lead us to the same conclusion.

18.   Example:calculation of the entropy in the reversible process
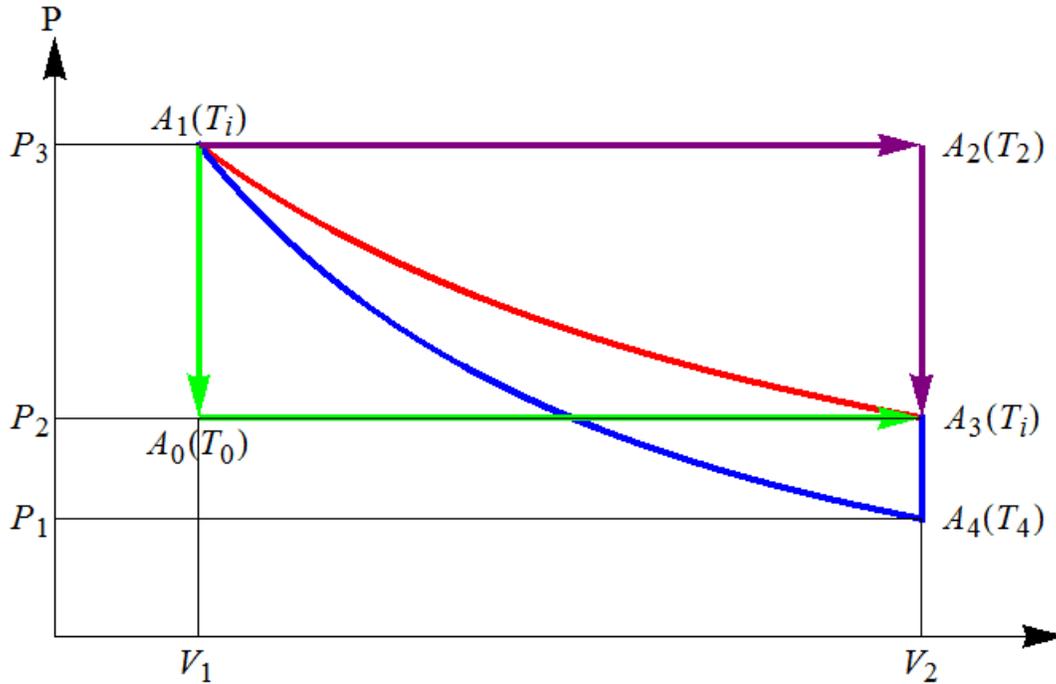
Fig.   Four paths (in the *P-V* phase diagram) used for the calculation of the change in entropy. $A_1 \rightarrow A_3$ (isothermal, denoted by red). $A_1 \rightarrow A_4 \rightarrow A_3$ (partly adiabatic, denoted by blue). $A_1 \rightarrow A_0 \rightarrow A_3$ (denoted by green). $A_1 \rightarrow A_2 \rightarrow A_3$ (denoted by purple).

As is shown, the change in the entropy is defined for the reversible process. Here we calculate the entropy along the four paths, where the path starts from the point A_1 and reaches the point A_3 in the *P-V* diagram as shown above. It is shown that the change of entropy is independent of the path chosen.

(a)   Path-1 (isothermal process): $A_1 \rightarrow A_3$ (denoted by red line)

$$PV = RT_i, \qquad \Delta E = 0, \qquad \Delta Q = -\Delta W = P\Delta V$$

Then the entropy change is

$$\Delta S = \int_{V_1}^{V_2} \frac{PdV}{T} = R\int_{V_1}^{V_2} \frac{dV}{V} = R\ln(\frac{V_2}{V_1}). \tag{1}$$

(b) **Path-2 (adiabatic process):** $A_1 \rightarrow A_4 \rightarrow A_3$ **(denoted by blue line)**

Path: $A_1 \rightarrow A_4$: (adiabatic process)

$$\Delta Q = 0, \qquad \Delta S_1 = 0,$$

which means that the change of entropy is zero.

Path: $A_4 \rightarrow A_3$ (constant volume)

$$PV = RT_i, \qquad \Delta E = \Delta Q = C_V \Delta T,$$

Then the change of entropy is

$$\Delta S_2 = C_V \int_{T_4}^{T_i} \frac{dt}{T} = C_V \ln(\frac{T_i}{T_4}) = C_V (\gamma - 1) \ln\left(\frac{V_2}{V_1}\right) = R \ln\left(\frac{V_2}{V_1}\right).$$

where

$$T_i V_1^{\gamma-1} = T_4 V_2^{\gamma-1}, \qquad \text{or} \qquad \frac{T_i}{T_4} = \left(\frac{V_2}{V_1}\right)^{\gamma-1}$$

Then we have

$$\Delta S = \Delta S_1 + \Delta S_2 = R \ln\left(\frac{V_2}{V_1}\right). \tag{2}$$

(c) **Path-3:** $\qquad A_1 \rightarrow A_0 \rightarrow A_3$ **(denoted by green line)**

Path: $A_1 \rightarrow A_0$

$$\Delta Q = C_V \Delta T,$$

$$\Delta S_1 = C_V \int_{T_i}^{T_0} \frac{dT}{T} = C_V \ln\left(\frac{T_0}{T_i}\right).$$

Path: $A_0 \rightarrow A_3$

$$\Delta Q = C_P \Delta T,$$

$$\Delta S_2 = C_P \int_{T_0}^{T_i} \frac{dT}{T} = C_P \ln\left(\frac{T_i}{T_0}\right).$$

Then we have

$$\Delta S = \Delta S_1 + \Delta S_2$$

$$= C_P \ln\left(\frac{T_i}{T_0}\right) + C_V \ln\left(\frac{T_0}{T_i}\right)$$

$$= (R + C_V) \ln\left(\frac{T_i}{T_0}\right) + C_V \ln\left(\frac{T_0}{T_i}\right)$$

$$= R \ln\left(\frac{T_i}{T_0}\right)$$

or

$$\Delta S = R \ln(\frac{V_2}{V_1}), \qquad\qquad (3)$$

where

$$P_2 V_1 = RT_0. \qquad P_2 V_2 = RT_i,$$

or

$$\frac{T_i}{T_0} = \frac{V_2}{V_1}.$$

(d)　　Path-4: $A_1 \to A_2 \to A_3$ (denoted by purple line)

Path:　$A_1 \to A_2$

$$\Delta Q = C_P \Delta T,$$

$$\Delta S_1 = C_P \int_{T_i}^{T_2} \frac{dT}{T} = C_P \ln\left(\frac{T_2}{T_i}\right).$$

Path:　$A_2 \to A_3$

$$\Delta Q = C_V \Delta T,$$

$$\Delta S_1 = C_V \int_{T_2}^{T_i} \frac{dT}{T} = C_V \ln\left(\frac{T_i}{T_2}\right).$$

Then we have

$$\Delta S = \Delta S_1 + \Delta S_2$$

$$= C_P \ln\left(\frac{T_2}{T_i}\right) + C_V \ln\left(\frac{T_i}{T_2}\right)$$

$$= (R + C_V) \ln\left(\frac{T_2}{T_i}\right) + C_V \ln\left(\frac{T_i}{T_2}\right)$$

$$= R \ln\left(\frac{T_2}{T_i}\right)$$

or

$$\Delta S = R \ln(\frac{V_2}{V_1}), \tag{4}$$

since

$$P_3 V_2 = RT_2. \qquad P_2 V_1 = RT_i$$

or

$$\frac{T_2}{T_i} = \frac{V_2}{V_1}.$$

((Conclusion))
For any reversible cycle, in general, we have

$$\oint \frac{dQ_r}{T} = \Delta S = 0$$

19   Entropy for the ideal gas during the reversible process

We now consider the reversible process from the initial state (P_i, V_i, T_i) to the final state (P_f, V_f, T_f).

$$P_i V_i = RT_i$$
$$P_f V_f = RT_f$$

36

If a system absorbs an infinitesimal amount of heat dQ during a reversible process, the entropy change of the system is equal to

$$dS = \frac{dQ}{T}$$

Consider one of the expression for dQ of an ideal gas.

$$dE = dQ - PdV$$
$$dE = C_V dT$$
$$dQ = C_V dT + PdV$$

Dividing by T

$$dS = \frac{dQ}{T} = C_V \frac{dT}{T} + \frac{P}{T} dV$$

Since

$$PV = RT \text{ , for ideal gas,}$$

we have

$$\Delta S = \int_{T_i}^{T_f} C_V \frac{dT}{T} + \int_{V_i}^{V_f} \frac{R}{V} dV$$

$$= C_V \ln \frac{T_f}{T_i} + R \ln \frac{V_f}{V_i}$$

$$= C_V \ln \frac{T_f}{T_i} + (C_p - C_V) \ln \frac{V_f}{V_i}$$

$$= C_V [\ln \frac{T_f}{T_i} + (\gamma - 1) \ln \frac{V_f}{V_i}]$$

The change in entropy depends only on the properties of the initial and final states. It does not depend on how the system changes from the initial to the final state.

In general, for n mole ($n = N/N_A$)

$$S = nC_V \ln T + nR \ln V + const$$

$$= \frac{N}{N_A} C_V \ln T + \frac{N}{N_A} R \ln V + const$$

where

$$C_V = \frac{3R}{2} = \frac{3N_A k_B}{2}$$
$$R = N_A k_B$$

Then we have

$$S = Nk_B(\frac{3}{2}\ln T + \ln V) + const$$
$$= Nk_B \ln(T^{3/2}V) + const$$
$$= Nk_B \ln(T^{\frac{1}{\gamma-1}}V) + const$$
$$= Nk_B \frac{1}{\gamma-1}\ln(TV^{\gamma-1}) + const$$

where

$$\gamma = \frac{C_P}{C_V} = \frac{5/2}{3/2} = \frac{5}{3}$$
$$\gamma - 1 = \frac{2}{3}$$

In the adiabatic process (S = constant), we have

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

or

$$PV^{\gamma} = const$$

The physical meaning of this equation for S will be discussed in Chapter 20S.

We also note that

$$\frac{\partial S}{\partial V} = \frac{P}{T} = Nk_B \frac{1}{V},$$

leading to the Boyle's law.

20   Condition for equilibrium
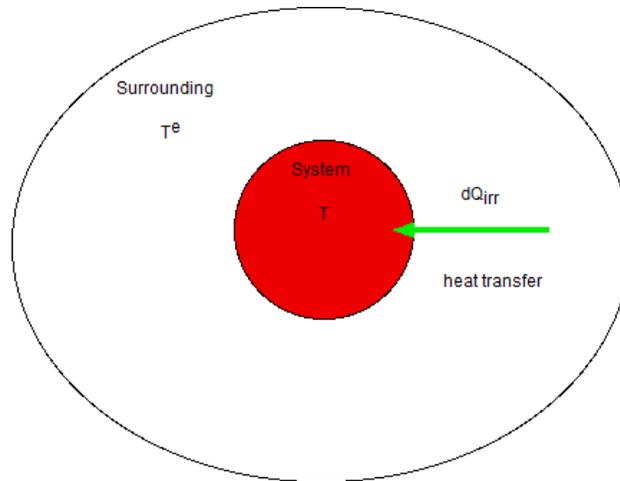
During the infinitesimal irreversible process,

$$T^{(e)} = T$$

$$\frac{dQ_{irr}}{T^{(e)}} = \frac{dQ_{irr}}{T} < dS$$

where dQ_{irr} is the heat moving from the surrounding (temperature $T^{(e)}$) to the system (temperature T). For convenience here we use $dQ_{irr} = dQ$.

The first law of the thermodynamics can be written in the usual form

$$dE = dQ + dW$$

And the inequality becomes

$$dQ = dE - dW < TdS$$
$$dE + PdV - TdS < 0$$

This inequality holds during any infinitesimal portion and, therefore, during all infinitesimal portions of irreducible process.

During the irreversible process by imposing the condition that two of the thermodynamic co-ordinates remain constant, then the inequality can be reduced to a simpler form.

(a)   If V and E are constant.

$$dS > 0.$$

which means that the entropy of a system at constant E and V increases during an irreversible process, approaching a maximum at the final state of equilibrium.

39

(b)   If *T* and *V* are constant, the inequality reduces to

$$d(E - TS) < 0$$
$$dF < 0$$

expressing the result that the Helmholtz function ($F = E - ST$) of a system at constant *T* and *V* decreases during an irreversible process and becomes a minimum at the final equilibrium.

(c)   If *T* and *P* are constant, the inequality reduces to

$$d(E + PV - TS) < 0$$
$$dG < 0$$

expressing the result that the Gibbs function ($G = F + PV$) of a system at constant *T* and *P* decreases during an irreversible process and becomes a minimum at the final equilibrium state.
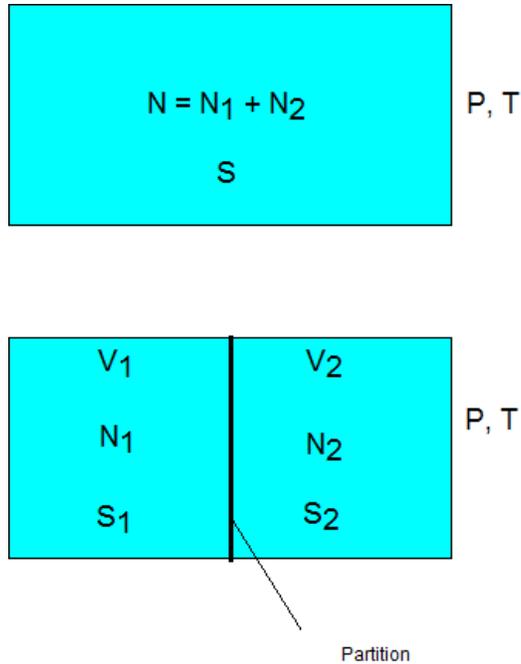
21   Intensive and extensive parameters (definitions)

Intensive variable
    P (pressure)
    T (temperature)
    μ (chemical potential)

Extensive variable
    V (volume)
    C (heat capacity)
    E (Internal energy)
    Q (heat)
    S (entropy)
    F (free energy)
    N (number of particles)

Partition

The macroscopic parameter specifying the macro-state of a homogeneous system can be classified into two types.

Let y denotes such a parameter. Consider that the system is divided into two parts by introducing a partition, and denoted by y_1 and y_2, the values of this parameter for the two subsystems.

Then two cases can arise

(1) One has $y_1 + y_2 = y$, in which the parameter y is said to be *extensive*.
(2) One has $y_1 = y_2 = y$, in which the parameter y is said to be *intensive*.

In simple terms, one can say that an extensive parameter get doubled if the size of the system is doubled, while an intensive parameter remains unchanged.

The mass (M) and the volume (V) of a system are extensive parameters. The density ρ of a system is an intensive parameter: $\rho = M / V$.

Indeed, it is clear that the ratio of any two extensive parameters is an intensive parameter.

The mean pressure (P) of a system is an intensive parameter, since both parts of a system, after subdivision, will have the same pressure as before. Similarly, the temperature T of a system is an intensive parameter. The internal energy E of a system is an extensive quantity. The total energy of the system is the same after subdivision as it was before: $E = E_1 + E_2$. The entropy S is an extensive quantity, because the heat Q is an extensive quantity. The heat capacity C is an extensive quantity.

$$T = \left(\frac{\partial E}{\partial S} \right)_V \qquad T\,(\text{intensive}),\ E\,(\text{extensive}),\ S\,(\text{extensive}).$$

$$P = -\left(\frac{\partial E}{\partial V} \right)_S \qquad P\,(\text{intensive}),\ E\,(\text{extensive}),\ V\,(\text{extensive}).$$

$$P = -\left(\frac{\partial F}{\partial V}\right)_T \qquad P \text{ (intensive)}, F \text{ (extensive)}, V \text{ (extensive)}.$$

$$S = -\left(\frac{\partial F}{\partial T}\right)_V \qquad S \text{ (extensive)}, F \text{ (extensive)}, T \text{ (intensive)}.$$

22.   Selected problems

22.1

Problem 20-22* (SP-20)   (10-th edition)**

An insulated Thermos contains 130 g of water at 80.0°C. You put in a 12.0 g ice at 0°C to form a system of ice +original water. (a) What is the equilibrium temperature of the system? What are the entropy changes of the water that was originally the ice cube (b) as it melts and (c) as it warms to the equilibrium temperature? (d) What is the entropy change of the original water as it cools to the equilibrium temperature? (e) What is the net entropy change of the ice + original water system as it reaches the equilibrium temperature.

((**Solution**))
$L_f = 333 \times 10^3$ J/kg = 333 J/g
$L_v = 2256 \times 10^3$ J/kg = 2256 J/g
$C_{water} = 4180$ J/kg.K = 4.180 J/g.K
$C_{ice} = 2220$ J/kg.K = 2.22 J/g.K
$M = 0.130$ kg water at 353 K
$m = 0.012$.kg ice cube at 273 K.

(a)   Equilibrium temperature

$$\Delta Q_1 = m[L_F + C_{water}(T_e - 273)]$$
$$\Delta Q_2 = MC_{water}(353 - T_e)$$

From the condition that $\Delta Q_1 = \Delta Q_2$, we have

$$T_e = 339.5 \text{ K}.$$

(b)

$$m\frac{L_F}{273} = 14.637 J / K$$

(c)

$$mC_{water} \ln(\frac{T_e}{273}) = 10.936 J / K$$

Then

$$\Delta S_{ice} = m[\frac{L_F}{273} + C_{water} \ln(\frac{T_e}{273})] = 25.57 J / K$$

(d)

$$\Delta S_{water} = MC_{water} \ln(\frac{T_e}{353})] = -21.18 J / K$$

(e)

$$\Delta S_{net} = \Delta S_{ice} + \Delta S_{water} = 4.395 J / K$$

22.2

Problem 20-20* (SP-20)**   **(10-th edition)**

Expand 1.00 mol of an monatomic gas initially at 5.00 kPa and 600 K from initial volume V_1 = 1.00 m³ to final volume V_f = 2.00 m³. At any instant during the expansion, the pressure P and volume V of the gas are related by

$$P = 5.00 \exp[(V_i - V) / a]$$

With P in kPa, V_i and V_f in m³, and a = 1.00 m³. What are the final (a) pressure and (b) temperature of the gas? (c) How much work is done by the gas during the expansion? (b) What is ΔS for the expansion? (Hint: use two simple reversible processes to find ΔS).

((**Solution**))
R = 8.314472 J/mol K
n =1 mol
monatomic gas
C_V = 3R/2
$P(V)$ =5 exp[(V_i-V)/a] kPa
a = 1.0 m³.
T_i = 600 K
P_i = 5 kPa
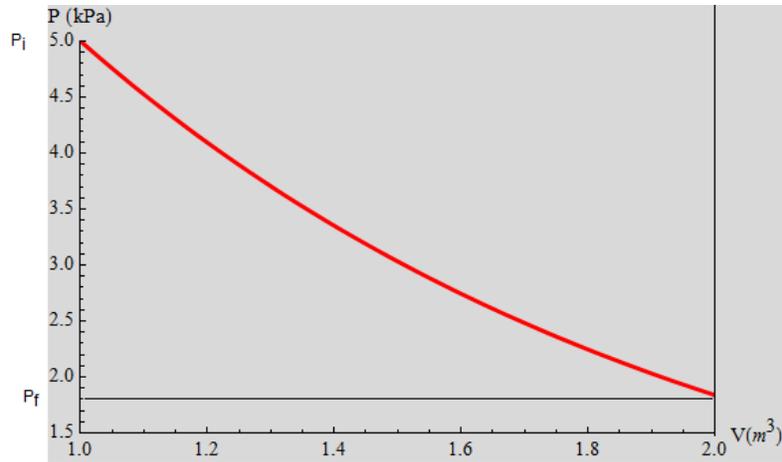
(a)

$$P_f = P(V_f = 2) = 5/e = 1.8394 \text{ kPa}$$

(b)

$$P_f V_f = RT_f$$

$$T_f = \frac{P_f V_f}{R} = \frac{1.84 \times 10^3 \times 2.0}{8.314472} = 442.6K$$

(c) The work done on the system is

$$\Delta W = -\int_{V_i}^{V_f} P dV = -5 \int_{V_i}^{V_f} \exp[\frac{V_i - V}{a}] dV$$

$$= 5a[\exp(\frac{V_i - V}{a})]_{V_i}^{V_f}$$

$$= -5a[1 - \exp(\frac{V_i - V_f}{a})] = -3.16J$$

The work done by the system is 3.16 J

(d)

$$dS = \frac{1}{T} dE + \frac{P}{T} = C_V \frac{dT}{T} + R \frac{dV}{V}$$

Then we have

$$S = \frac{3}{2} R \ln(\frac{T_f}{T_i}) + R \ln(\frac{V_f}{V_i}) = 0.237R = 1.97 J/K$$

Problem 20-35* (SP-20)**   **(10-th edition)**

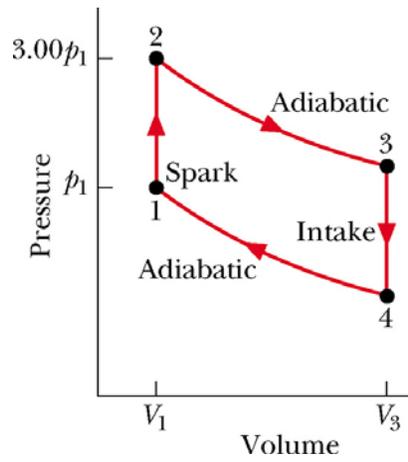The cicle in Fig. represents the operation of a gasoline internal combustion engine. Volume $V_3 = 4.00\ V_1$. Assuming the gasoline-air intake mixture is an ideal gas with $\gamma = 1.30$. What are the ratios (a) T_2/T_1, (b) T_3/T_1, (c) T_4/T_1, (d) P_3/P_1, and (e) P_4/P_1? (f) What is the engine efficiency?

((**Solution**))
$\gamma = 1.30$
State-1 (P_1, V_1, T_1)
State-2 $(P_2 = 3P_1, V_2 = V_1, T_2)$
State-3 $(P_3, V_3 = 4V_1, T_3)$
State-4 $(P_4, V_4 = 4V_1, T_4)$

(a)

$$\frac{P_2 V_2}{T_2} = \frac{P_1 V_1}{T_1}$$

$$\frac{3P_1 V_1}{T_2} = \frac{P_1 V_1}{T_1},$$

$$\boxed{\frac{T_2}{T_1} = \frac{3P_1 V_1}{P_1 V_1} = 3}$$

(b)   The path 2-3 is adiabatic; $TV^{\gamma-1} = $ constant

$$T_2 V_2^{\gamma-1} = T_3 V_3^{\gamma-1}$$

$$T_2 V_1^{\gamma-1} = T_3 (4V_1)^{\gamma-1}$$

$$\frac{T_3}{T_2} = \frac{V_1^{\gamma-1}}{(4V_1)^{\gamma-1}} = \frac{1}{4^{\gamma-1}} = \frac{1}{4^{0.3}} = 0.66$$

or

$$T_3 = 0.66T_2 = 0.66 \times 3T_1 = 1.98T_1$$

(c)   The path 4-1 is adiabatic; $TV^{\gamma-1} = $ constant

$$T_4 V_4^{\gamma-1} = T_1 V_1^{\gamma-1}$$

$$\frac{T_4}{T_1} = (\frac{V_1}{V_4})^{\gamma-1} = (\frac{1}{4})^{\gamma-1} = 0.66$$

$$\boxed{T_4 = 0.66T_1}$$

(d)

$$\frac{P_3 V_3}{T_3} = \frac{P_1 V_1}{T_1}$$

$$\frac{P_3}{P_1} = \frac{V_1}{V_3}\frac{T_3}{T_1} = \frac{1}{4} \times 2 = \frac{1}{2} \, ,$$

$$\boxed{\frac{P_3}{P_1} = \frac{1}{2}}$$

(e)

$$\frac{P_4 V_4}{T_4} = \frac{P_1 V_1}{T_1}$$

$$\frac{P_4}{P_1} = \frac{V_1}{V_4}\frac{T_4}{T_1} = \frac{1}{4} \times 0.66 = 0.165 \, ,$$

$$\boxed{\frac{P_4}{P_1} = 0.165}$$

(f)

The path 2-3 is adiabatic.

$$W_{23} = \frac{1}{\gamma-1}(P_3 V_3 - P_2 V_2) = -3.4nRT_1$$

The path 4-1 is adiabatic.

$$W_{41} = \frac{1}{\gamma-1}(P_1 V_1 - P_4 V_4) = 1.13nRT_1$$

The path 1-2 is isobaric.

$$Q_{12} = nC_V(T_2 - T_1) = \frac{n}{\gamma-1}(RT_2 - RT_1) = \frac{1}{\gamma-1}(P_2 V_2 - P_1 V_1) = 6.67RT_1$$

$$W_{12} = 0$$

The path 3-4 is isobaric.

$$W_{34} = 0$$

The total work W

$$W = W_{12} + W_{23} + W_{34} + W_{41} = -2.27nRT_1$$

46

The engine efficiency ε is

$$\varepsilon = \frac{|W|}{Q_{12}} = 0.34$$

23.   Hint of SP-20 and HW20

23.1

Problem 20-11 (SP-20)   (10-th edition)

   In an experiment, 200 g of aluminum (with a specific heat of 900 J/kg K) at 100°C is mixed with 50.0 g of water at 20°C, with the mixture thermally isolated. (a) What is the equilibrium temperature? What are the entropy changes of (b) the aluminum, (c) the water, and (d) the aluminum-water system?

m_{Al}=0.2 kg, C_{Al} = 900 J/kg K, T_{iAl} = 100 °C = 373 K
m_{water} = 0.05 kg, C_{water}=4180 J/kg K, T_{iwater} = 20 °C = 293 K

Hint:

$$S_{Al} = m_{Al}C_{Al}\int_{T_s}^{330}\frac{1}{T}dT$$

___

23.2

Problem 20-18 (SP-20)   (10-th edition)

   A 2.0 mol sample of an ideal monatomic gas undergoes the reversible process shown in Fig. The scale of the vertical axis is set by T_s = 400 K and the scale of the horizontal axis is set by S_s = 20.0 J/K. (a) How much energy is absorbed as heat by the gas? (b) What is the change in the internal energy of the gas? (c) How much work is done by the gas?
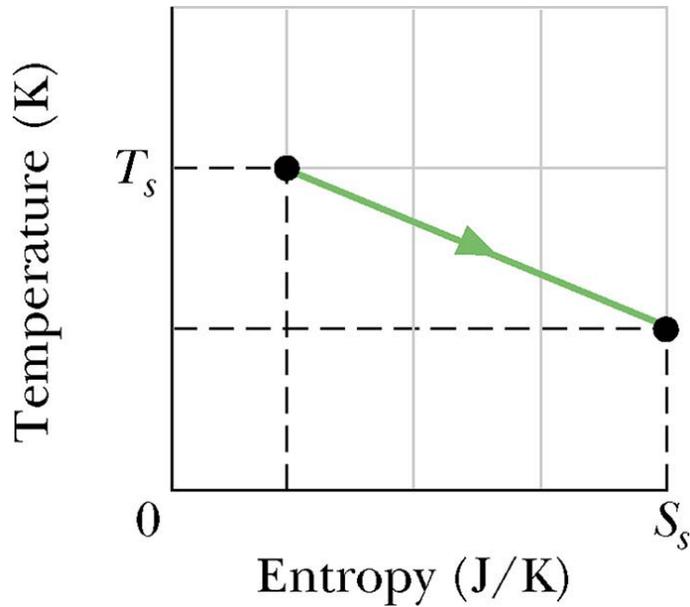
$S_s = 20$ J/K, $\quad T_s = 400$ K.

$C_V = \dfrac{3}{2} R$, $\quad R = 8.314472$ J/mol K, $\quad n = 2.0$

(a)
$$\Delta Q = \int dQ = \int T dS$$

(b)
$$\Delta E = n C_V \Delta T$$

23.3

Problem 20-16** (SP-20)   **(10-th edition)**

An 8.0 g ice at -10°C is put into a Thermos flask containing 100 cm^3 of water at 20°C. By how much has the entropy of the cube-water system changed when equilibrium is reached? The specific heat of ice is 2220 J/kg K.

$C_{ice} = 2220$ J/kg K, $\qquad C_{water} = 4180$ J/kg K
$L_F = 333 \times 10^3$ J/kg
$m_{ice} = 0.008$ kg (ice cube), $\qquad M_{water} = 100$ cm$^3 = 0.10$ kg (water)

Change of entropy:

$$\Delta S_{ice} = m_{ice} C_{ice} \int_{263}^{273} \frac{1}{T} dT + \frac{m_{ice} L_F}{273} + m_{ice} C_{water} \int_{273}^{T_s} \frac{1}{T} dT$$

48

23.4

Problem 20-30** (HW-20)   **(10-th edition)**

A 500 W Carnot engine operates between constant-temperature reservoirs at 100°C and 60.0°C. What is the rate at which energy is (a) taken in by the engine as heat and (b) exhausted by the engine as heat?
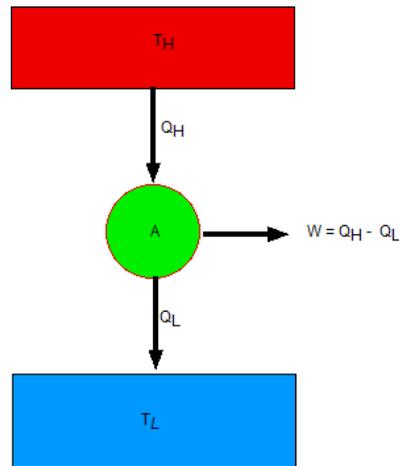
$W = Q_H - Q_L$=500 W (we assume that W is defined as the work done by the gas).
$T_H = 373$ K, $T_L = 333$ K

Carnot cycle:

$$\frac{Q_H}{T_H} = \frac{Q_L}{T_L}$$

23.5

Problem 20-34** (SP-20)   **(10-th edition)**

An ideal gas (1.0 mol) is the working substance in an engine that operates on the cycle shown in Fig. Processes BC and DA are reversible and adiabatic. (a) Is the gas monatomic, diatomic, or polyatomic? (b) What is the engine efficiency?
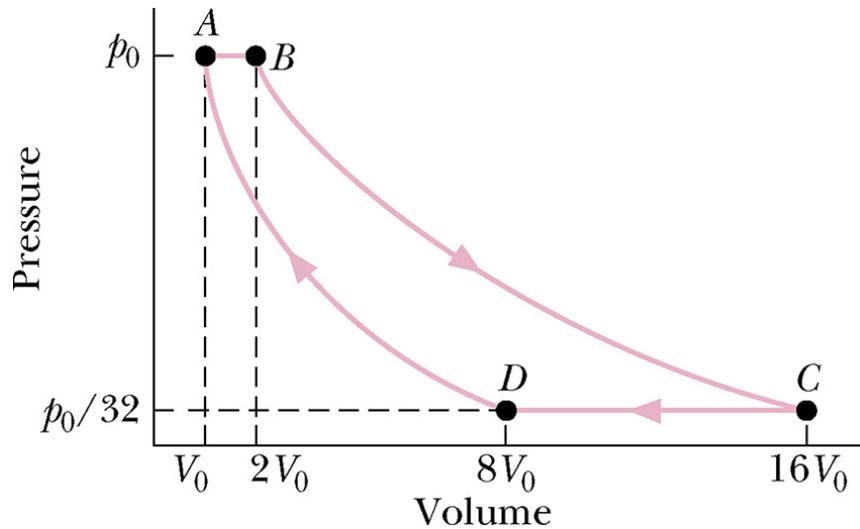
$n = 1$ mol.

$P_A = P_0,$ $\quad V_A = V_0$
$P_B = P_0,$ $\quad P_B = 2V_0$
$P_C = P_0/32$ $\quad P_C = 16V_0$
$P_C = P_0/32$ $\quad P_C = 8V_0$

(a) The path BC is adiabatic.

$$P_B V_B{}^\gamma = P_C V_C{}^\gamma$$

(b)

$$\Delta Q_{AB} = C_P(T_B - T_A)$$

$$\Delta W_{BC} = \frac{1}{\gamma - 1}(P_C V_C - P_B V_B)$$

The engine efficiency ε is defined as

$$\varepsilon = \frac{|W_{tot}|}{Q_{AB}}$$

23.6

Problem 20-62 (HW-20) $\qquad\qquad$ **(10-th edition)**

Suppose 2.00 mol of a diatomic gas is taken reversibly around the cycle shown in the *T-S* diagram of Fig., where $S_1 = 6.00$ J/K and $S_2 = 8.00$ J/K. The molecules do not rotate or oscillate. What is the energy transferred as heat Q for (a) path $1 \to 2$, (b) path $2 \to 3$, and (c) the full cycle? (d) What is the work W for the isothermal process? The volume V_1 in state 1 is 0.200 m³. What is the volume in (e) state 2 and (f) state 3? What is the

change ΔE_{int} for (g) path $1 \rightarrow 2$, (h) path $2 \rightarrow 3$, and (i) the full cycle? (Hint: (h) can be done with one or two lines of calculation using Section 19-8 or with a page of calculation using section 19-11.) (j) What is the work W for the adiabatic process?
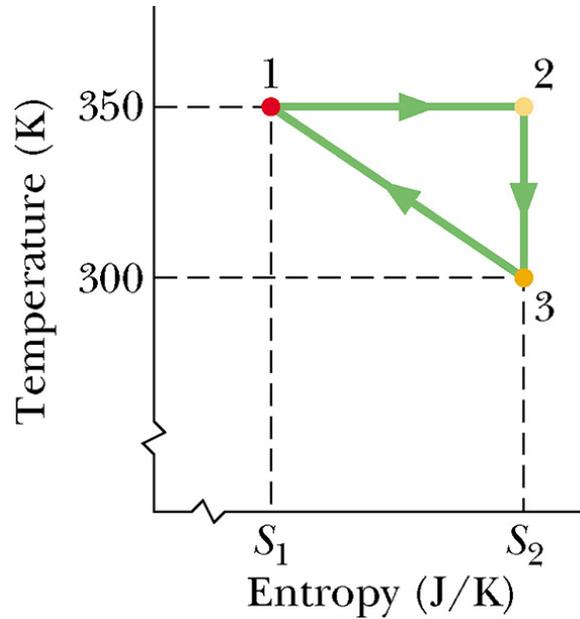
diatomic gas, $n = 2$

$$C_V = \frac{5}{2}R, \qquad C_P = \frac{7}{2}R, \qquad \gamma = \frac{C_P}{C_V} = 1.40$$

$S_1 = 6.0$ J/K, $\qquad$ $S_2 = 8.0$ J/K
$T_1 = 350$ K, $\qquad$ $T_3 = 300$ K
$V_1 = 0.2$ m^3.

(a) $\qquad \Delta Q_{12} = T_1 \Delta S = T_1(S_2 - S_1)$
(b) $\qquad \Delta Q_{23} = 0$
(d) $\qquad \Delta E_{12} = 0$
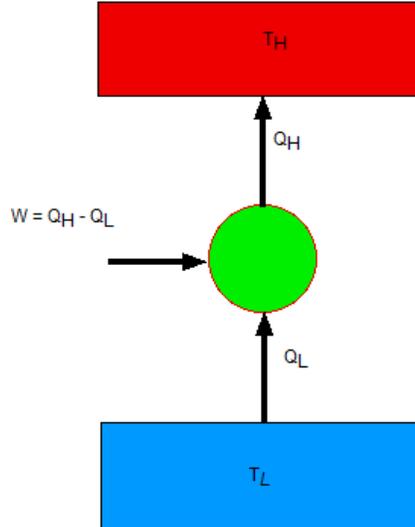
24. Link

Carnot engine (Wikipedia)
http://en.wikipedia.org/wiki/Carnot_heat_engine

Entropy (Wikipedia)
http://en.wikipedia.org/wiki/Entropy

APPENDIX-I

Refregerator

Performance of Refrigerator
Coefficeint of performance (COP) K

$$K = \frac{Q_L}{|W|}$$

((Note))
Efficiencies of real engine ε

$$\varepsilon = \frac{|W|}{Q_H}$$

APPENDIX-II
Empirical temperature and absolute temperature

   Our fundamental theorem shows us that the ratio Q_L/Q_H has the same value for all reversible engines that operate between the same empirical temperature t_H and t_L; that is, this ratio is independent of the special properties of the engine, provided it is reversible. It depends only on the empirical temperatures t_H and t_L. We may therefore write:

$$\frac{Q_L}{Q_H} = F(t_H, t_L),$$

where $F(t_H, t_L)$ is a universal function of the two temperatures t_H and t_L.

   We shall now prove that the function $F(t_H, t_L)$ has the following property:

52

$$F(t_H, t_L) = \frac{F(t_H, t_0)}{F(t_L, t_0)},$$
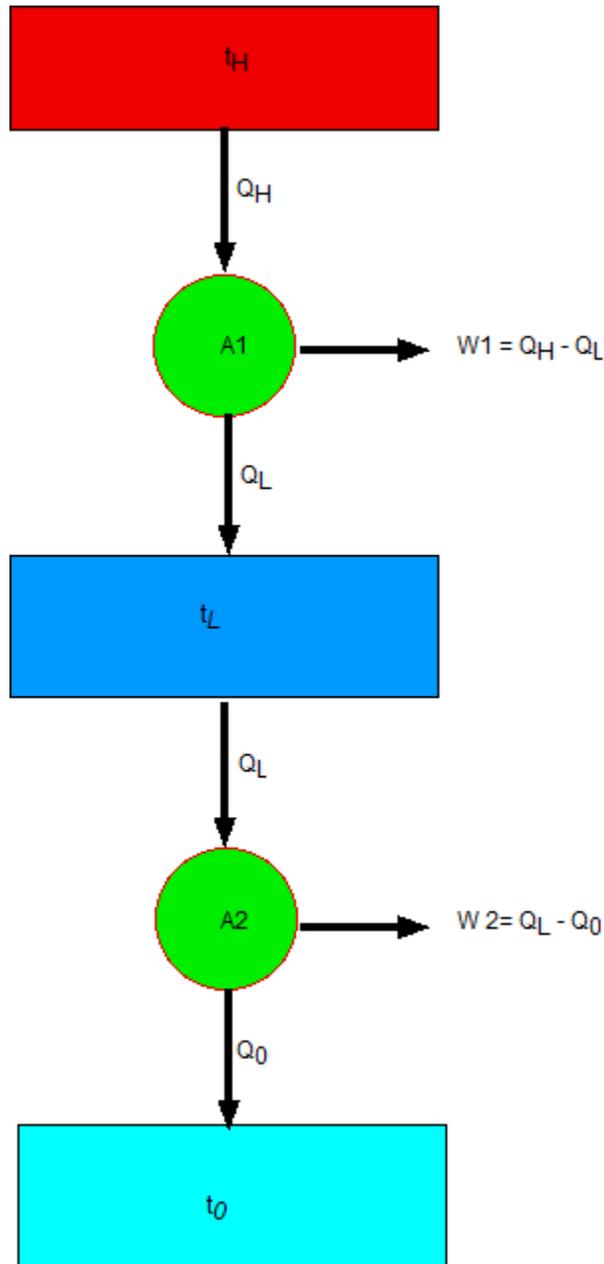
where t_0 is arbitrary.

Fig.1 $t_0 < t_L$. A series connection of the reversible cyclic engines A_1 and A_2. A_1 and A_2 work between the temperatures t_H and t_L, and t_L and t_0, respectively. If A_1 absorbs an amount of heat Q_H at t_H and gives up an amount of heat Q_L at t_L during a cycle.

If A_2 absorbs an amount of heat Q_L at t_L and gives up an amount of heat Q_0 at t_0 (Tomonaga).
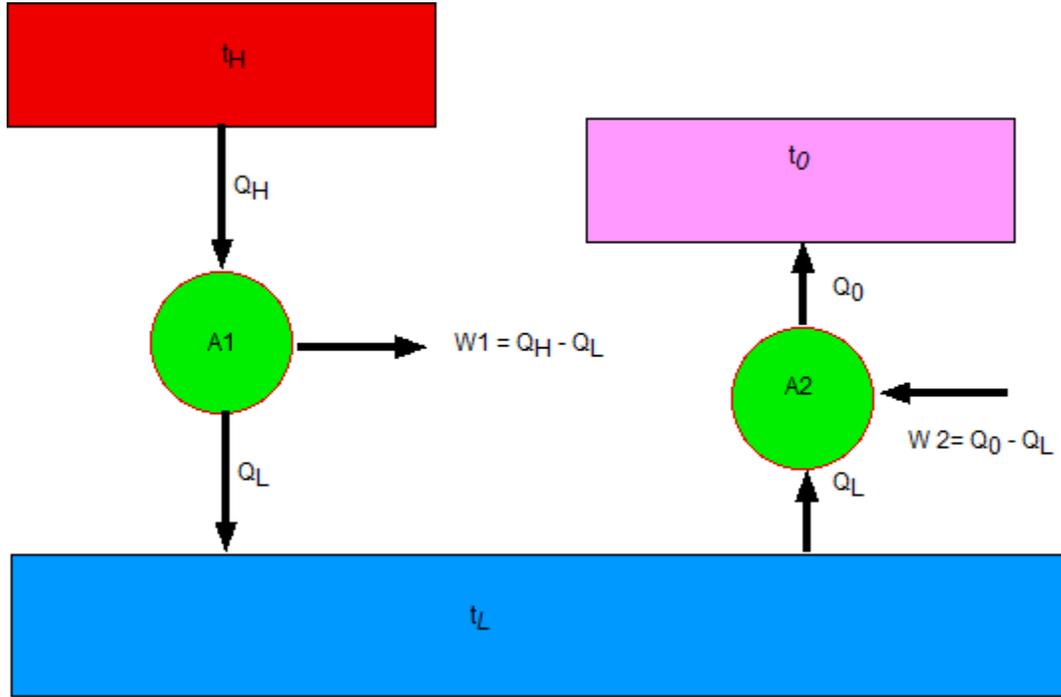
Fig.2 $t_0>t_L$. A_1 and A_2 are two reversible cyclic engines which work between the temperatures t_H and t_L, and t_L and t_0, respectively. If A_1 absorbs an amount of heat Q_H at t_H and gives up an amount of heat Q_L at t_L during a cycle. If A_2 absorbs an amount of heat Q_L at t_L and gives up an amount of heat Q_0 at t_0 (Fermi).

We consider a process consisting of series connection of the reversible engine A_1 and the reversible engine A_2 as shown in Fig.1 and Fig.2. For the engine A_2, we have the relation

$$\frac{Q_0}{Q_L} = F(t_L,t_0).$$

Similarly for the engine A_1 ($t_H>t_L$), we have

$$\frac{Q_L}{Q_H} = F(t_H,t_L).$$

Then we get

$$F(t_H,t_0) = \frac{Q_0}{Q_H} = \frac{Q_0}{Q_L}\frac{Q_L}{Q_H} = F(t_L,t_0)F(t_H,t_L),$$

or

$$F(t_H, t_L) = \frac{F(t_H, t_0)}{F(t_L, t_0)} .$$

Here we note that t_0 is arbitrary. Note that $t_0 < t_L$ (in Fig.1) and $t_0 > t_L$ (Fig.2). We choose $t_0 \to \bar{t}_0$. We may keep it constant in all our equations. It follows that the function $f(t)$ can be defined as

$$f(t) = \frac{1}{F(t, \bar{t}_0)} .$$

So we have

$$F(t_H, t_L) = \frac{f(t_L)}{f(t_H)} .$$

We place

$$\theta(t) = \alpha f(t) ,$$

where α is an arbitrary constant. Using this equation, we get

$$\frac{Q_L}{Q_H} = \frac{\theta(t_L)}{\theta(t_H)} .$$

θ is regarded as a new temperature. Note that $\theta(t)$ increases with increasing an empirical temperature. $\theta(t)$ expresses the relation between the empirical temperature and the new temperature (the <mark>absolute temperature</mark>). Note that $\theta(t)$ is not uniquely determined. $\theta(t)$ is indeterminate to the extent of an arbitrary multiplicative constant factor α.

$$\frac{Q_L}{Q_H} = \frac{T_L}{T_H} \qquad \text{(Carnot cycle)}$$

The efficiency is given by

$$\varepsilon = 1 - \frac{T_L}{T_H} .$$

The efficiency becomes 1 at $T_L = 0$ K.

((**Comment by S.Tomonaga**)) S. Tomonaga, What is physics? (Iwanami, 1979).
   "I do not know who gave a proof for the universal function. When I borrowed a book of Clausius from Riken, this proof was written on the book by pencil, next to the proof

55

given by Clausius. This book was bought from Carl Runge in Germany by Riken. The proof was written in German. So I think that the proof might be given by Runge."

((**Comment by M.S.**)) I found similar proof in the book of Enrico Fermi (Thermodynamics, 1936).

REFERENCES
E. Fermi, Thermodynamics (Dover Publication, 1936). p.39-41
S. Tomonaga, What is physics? Iwanami (1979, in Japanese).

Sin-Itiro Tomonaga

    March 31, 1906 – July 8, 1979) was a Japanese physicist, influential in the development of quantum electrodynamics, work for which he was jointly awarded the Nobel Prize in Physics in 1965 along with Richard Feynman and Julian Schwinger.
http://en.wikipedia.org/wiki/Sin-Itiro_Tomonaga

Enrico Fermi;

    29 September 1901– 28 November 1954) was an Italian-American physicist, best known for his work on Chicago Pile-1 (the first nuclear reactor), and for his contributions to the development of quantum theory, nuclear and particle physics, and statistical mechanics. He is one of the men referred to as the "father of the atomic bomb".[4] Fermi held several patents related to the use of nuclear power, and was awarded the 1938 Nobel Prize in Physics for his work on induced radioactivity by neutron bombardment and the discovery of transuranic elements. He was widely regarded as one of the very few physicists to excel both theoretically and experimentally.
http://en.wikipedia.org/wiki/Enrico_Fermi

APPENDIX-III
1.   **Born diagram**
(N. Hashitsume, Introduction to Thermal and Statistical Mechanics, Iwanami, 1980, in Japanese)

    In thermodynamics, we often use the following four thermodynamic potentials, E, F, G, and H. The diagram (called the Born's diagram) was introduced by Born (Max). In order to memorize this diagram, we give interpretation for the letters. The sun (S; entropy) pours lights on the trees (T; temperature). The water falls from the peak (P; pressure) of mountain into the valley (V; volume). We draw a square with four vertices noted by S, T, P, and V. . The light propagates from the point S to the point T. The water flows from the point P to the point V. These two arrows are denoted by the vectors given by $\overrightarrow{ST}$ (the direction of light flow) and $\overrightarrow{PV}$ (the direction of water flow). These vectors are perpendicular to each other. The four sides of the square are denoted by E, F, G, and H in a clockwise direction. Note that the side H (H: heaven) is between two vertices S (sun) and P (peak).
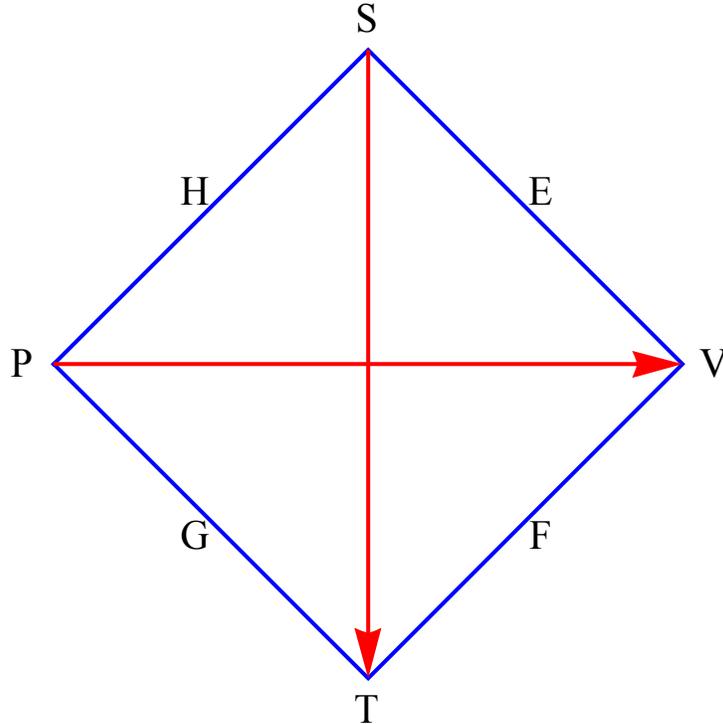
Fig.   Born diagram. *S*: entropy. *T*: temperature. *P*: pressure. *V*: volume. *H*: heaven (between S and P). *E*→*F*→*G*→*H* (clockwise). The water flow from *P* (peak) to *V* (valley). The sun light from *S* (sun) to *T* (tree).

(i)   The natural variables of the internal energy *E* is *S* and *V*.

$$dE = TdS - PdV$$

The sign before *T* is determined as plus from the direction of the vector $\overrightarrow{ST}$ ($\overrightarrow{ST}$: the direction of light). The sign before *P* is determined as minus from the direction of the vector $\overrightarrow{VP} = -\overrightarrow{PV}$ ($\overrightarrow{PV}$; the direction of water flow).

(ii)   The natural variables of the Helmholtz energy *F* is *V* and *T*.

$$dF = -SdT - PdV$$

The sign before *S* is determined as minus from the direction of the vector $\overrightarrow{TS} = -\overrightarrow{ST}$ ($\overrightarrow{ST}$: the direction of light). The sign before *P* is determined as minus from the direction of the vector $\overrightarrow{VP} = -\overrightarrow{PV}$ ($\overrightarrow{PV}$; the direction of water flow).

(iii)   The natural variables of the Gibbs energy G is P and T.

$$dG = VdP - SdT$$

The sign before S is determined as <mark>minus</mark> from the direction of the vector $\overrightarrow{TS} = -\overrightarrow{ST}$ ($\overrightarrow{ST}$: the direction of light). The sign before V is determined as <mark>plus</mark> from the direction of the vector $\overrightarrow{PV}$ ($\overrightarrow{PV}$; the direction of water flow).

(iv)   The natural variables of the enthalpy H is S and P.

$$dH = TdS + VdP .$$

The sign before T is determined as <mark>minus</mark> from the direction of the vector $\overrightarrow{ST}$ ($\overrightarrow{ST}$: the direction of light). The sign before V is determined as <mark>plus</mark> from the direction of the vector $\overrightarrow{PV}$ ($\overrightarrow{PV}$; the direction of water flow).

Maxwell's relation

(i)   The internal energy $E = E(S,V)$

For an infinitesimal reversible process

$$dE = TdS - PdV$$

showing that

$$T = \left(\frac{\partial E}{\partial S}\right)_V \quad \text{and} \quad P = -\left(\frac{\partial E}{\partial V}\right)_S$$

The Maxwell's relation;

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

(ii) The enthalpy $H = H(S,P)$ is defined as

$$H = E + PV$$

For an infinitesimal reversible process

$$\begin{aligned}dH &= dE + PdV + VdP \\ &= TdS - PdV + PdV + VdP \\ &= TdS + VdP\end{aligned}$$

showing that

$$T = \left(\frac{\partial H}{\partial S}\right)_P \quad \text{and} \quad V = \left(\frac{\partial H}{\partial P}\right)_S.$$

The Maxwell's relation:

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$

(iii)   The Helmholtz free energy $F = F(T,V)$ is defined as

$$F = E - ST \quad \text{or} \quad E = F + ST$$

For an infinitesimal reversible process

$$\begin{aligned} dF &= dE - SdT - TdS \\ &= TdS - PdV - SdT - TdS \\ &= -PdV - SdT \end{aligned}$$

showing that

$$P = -\left(\frac{\partial F}{\partial V}\right)_T \quad \text{and} \quad S = -\left(\frac{\partial F}{\partial T}\right)_V$$

The Maxwell's relation:

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

(iv)   The Gibbs free energy $G = G(T,P)$ is defined as

$$G = H - ST = (E + PV) - ST = F + PV$$
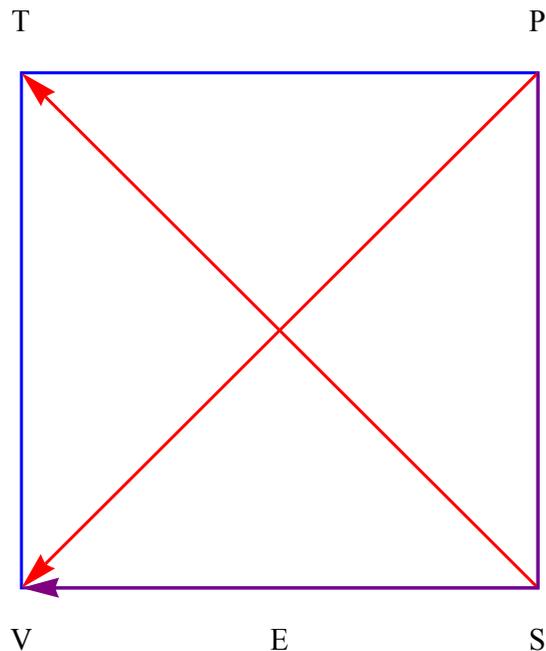
Then we have

$$dG = VdP - SdT$$

showing that

$$S = -\left(\frac{\partial G}{\partial T}\right)_P \quad \text{and} \quad V = \left(\frac{\partial G}{\partial P}\right)_T$$

(1)   The Maxwell's equation:

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

Here we consider the Maxwell's relation $\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$

For $\left(\frac{\partial P}{\partial S}\right)_V$, in the Born diagram, we draw the lines along the vectors $\overrightarrow{PS}$ and $\overrightarrow{SV}$. The resulting vector is $\overrightarrow{PV} = \overrightarrow{PS} + \overrightarrow{SV}$ (the direction of water flow)
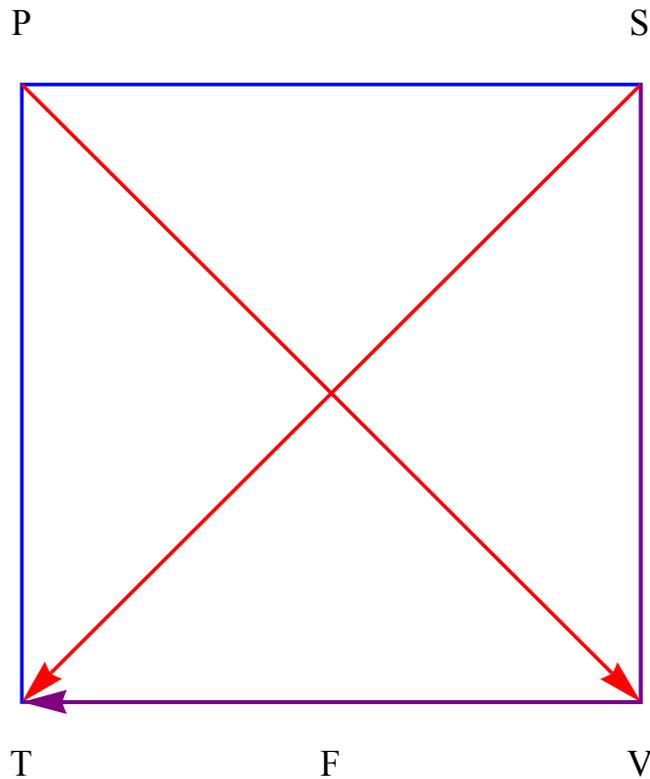

For $\left(\frac{\partial T}{\partial V}\right)_S$, in the Born diagram, we draw the lines along the vectors $\overrightarrow{TV}$ and $\overrightarrow{VS}$. The resulting vector is $\overrightarrow{TS} = \overrightarrow{TV} + \overrightarrow{VS} = -\overrightarrow{ST}$ (anti-parallel to the propagating direction of light). Then we have the negative sign in front of $\left(\frac{\partial P}{\partial S}\right)_V$ such that

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

(ii)   Maxwell's relation $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$

Here we consider the Maxwell's relation $\left(\dfrac{\partial S}{\partial V}\right)_T = \left(\dfrac{\partial P}{\partial T}\right)_V$

For $\left(\dfrac{\partial S}{\partial V}\right)_T$, in the Born diagram, we draw the lines along the vectors $\overrightarrow{SV}$ and $\overrightarrow{VT}$. The resulting vector is $\overrightarrow{ST} = \overrightarrow{SV} + \overrightarrow{VT}$ (the direction of sun light)

P   S

T   F   V

For $\left(\dfrac{\partial P}{\partial T}\right)_V$, in the Born diagram, we draw the lines along the vectors $\overrightarrow{PT}$ and $\overrightarrow{TV}$. The resulting vector is $\overrightarrow{PV} = \overrightarrow{PT} + \overrightarrow{TV}$ (the direction of water flow). Then we have the positive sign in front of $\left(\dfrac{\partial P}{\partial T}\right)_V$ such that

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$